Analysis of Volatile Organic Compounds by Purge-and-Trap Gas Chromatography/Mass Selective Detection

Application

Environmental

Author

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Abstract

Purge-and-trap sample concentration followed by gas chromatography with mass spectral detection is the most widely used technique for the analysis of volatile compounds in water. Using 5-mL water samples, most target compounds can be quantitated at 0.5 µg/L or lower. Analysis of 25-mL samples provides even greater sensitivity. Agilent Technologies' Purge-and-Trap/Gas Chromatography/Mass Spectral Detection system is recognized worldwide for its reliability, sensitivity and ease of use. Agilent also provides specialized environmental software, consumables, and gas chromatography columns for volatiles analysis. When combined with Agilent's service and support, laboratories have everything required to produce high-quality, reliable results.

Introduction

Without careful monitoring, many chemical by-products of modern industrial production can be released into the environment, often contaminating ground and surface water bodies upon which we all depend. In many parts of the world, public drinking water is chlorinated to kill disease-causing bacteria. Some byproducts of this process, such as the halogenated methanes, are unhealthy at high concentrations. Therefore, chlorinated drinking water must be routinely monitored for these compounds and others to ensure public safety.

Numerous analytical techniques have been developed over the last 25 years to analyze for volatile organic compounds (VOCs) in ground and surface water, wastewater, and drinking water. Today, the most widely used analytical technique in the world for VOC analysis is purge-and-trap (P&T) sample concentration combined with gas chromatography and mass selective detection (GC/MSD).

Purge-and-trap has been adopted so widely because of its ability to remove and concentrate most or all of the VOCs in water samples. When combined with the Agilent Technologies GC/MSD, the system can be used to quantitate VOCs at concentrations as low as 0.1 µg/L (ppb). The Agilent GC/MSD has become the standard system in most environmental laboratories worldwide because it offers unmatched sensitivity, selectivity, stability, and ease-of-use. This paper illustrates use of P&T/GC/MSD as a universal technique for the analysis of VOCs in water samples.

Experimental

Table 1 lists the instrumentation and some of the conditions that were used for the analysis of VOCs in water samples. The exact conditions need to be optimized for the kind of samples that are to be analyzed. Agilent Technologies provides the necessary instrumentation, supplies and services to help ensure that laboratories adopting this technology can successfully analyze their samples.

Table 1. P&T/GC/MSD Instrumentation

Gas chromatograph/mass spectrometer	Agilent GC/MSD
Environmental analysis software	Agilent EnviroQuant ChemStation software
Column	20-m × 0.18-mm × 1.0-µm J&W DB-VRX
GC Inlet	Split/Splitless operated in the split mode
Carrier gas	Helium
Purge-and-trap concentrator	Tekmar-Dohrmann
Trap	Vocarb 3000
Purge-and-trap automatic sampler	Tekmar-Dohrmann
Water sample size	5 or 25 mL (5-mL samples used for this work)

Standard solutions containing 60 common VOCs dissolved in methanol were purchased from AccuStandard, Inc. (New Haven, CT USA).

Results and Discussion

P&T sample concentration involves bubbling helium gas through a water sample (usually 5 mL or 25 mL) for several minutes. As the helium bubbles through the sample it sweeps dissolved VOCs out of the water and into a trap that contains one or more adsorbents. During purging, the trap is held at 35 °C allowing the VOCs to be adsorbed on the packing material. After a suitable purging time (typically 11 minutes), the trap is heated to desorb the VOCs which are swept with the helium carrier gas into the GC/MSD.

Figure 1 shows a chromatogram obtained by P&T/GC/MSD analysis of a 5-mL water sample containing 60 different VOCs, each at a concentration of 5 µg/L. The compounds are identified in Table 2.

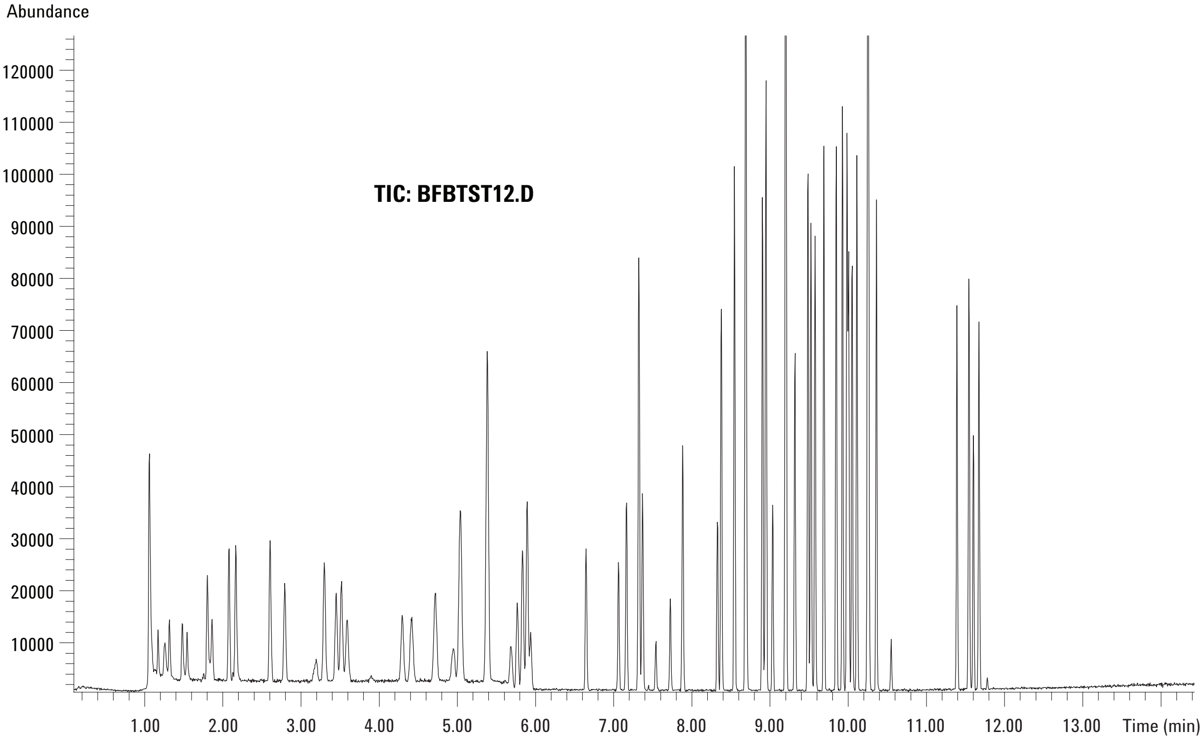

Figure 1. Chromatogram of the volatile organic compounds listed in Table 2. A 5-mL water sample containing each analyte at the 5-µg/L level was analyzed using the P&T/GC/MS system listed in Table 1. The internal standard and two surrogate compounds were present at 10 ppb and are designated in Table 2.

Table 2 Calibration Regression Coefficient r^2 Values

Number	Name	RT (min)	Quant Ion
1	Dichlorodifluoromethane	1.17	85
2	Chloromethane	1.25	50
3	Vinyl chloride	1.31	62
4	Bromomethane	1.48	94
5	Chloroethane	1.54	64
6	Trichlorofluoromethane	1.80	101
7	**1,1-Dichloroethene**	2.08	96
8	Methylene chloride	2.16	84
9	trans-1,2-Dichloroethene	2.60	96
10	1,1-Dichloroethane	2.79	63
11	cis-1,2-dichloroethene	3.30	96
12	Bromochloromethane	3.45	128
13	**Chloroform**	3.51	83
14	2,2-Dichloropropane	3.59	77
15	**1,2-Dichloroethane**	4.29	62
16	**1,1,1-Trichloroethane**	4.42	97
17	1,1-Dichloropropene	4.47	75
18	**Carbon tetrachloride**	4.95	117
19	**Benzene**	5.04	78
20	Fluorobenzene (Internal Standard)	5.38	96
21	Dibromomethane	5.76	93
22	1,2-Dichloropropane	5.83	63
23	Trichloroethene	5.89	95
24	Bromodichloromethane	5.94	83
25	cis-1,3-Dichloropropene	6.65	75
26	trans-1,3-Dichloropropene	7.06	75
27	**1,1,2-Trichloroethane**	7.16	83
28	Toluene	7.32	92
29	1,3-Dichloropropane	7.37	76
30	Dibromochloromethane	7.54	129
31	1,2-Dibromoethane	7.72	107
32	**Tetrachloroethene**	7.88	166
33	1,1,1,2-Tetrachloroethane	8.33	131
34	Chlorobenzene	8.38	112
35	Ethyl benzene	8.55	91
36	m&p-Xylene	8.69	106
37	**Bromoform**	8.70	173
38	Styrene	8.90	104
39	**1,1,2,2-Tetrachloroethane**	8.94	83
40	o-Xylene	8.95	106
41	1,2,3-Trichloropropane	9.03	75
42	Isopropylbenzene	9.20	105
43	4-Bromofluorobenzene (Surrogate)	9.20	95
44	Bromobenzene	9.32	156
45	n-Propylbenzene	9.49	91
46	2-Chlorotoluene	9.52	91
47	4-Chlorotoluene	9.58	91
48	1,3,5-Trimethylbenzene	9.69	105
49	t-Butylbenzene	9.85	119
50	1,2,4-Trimethylbenzene	9.93	105
51	s-Butylbenzene	9.98	105
52	1,3-Dichlorobenzene	10.00	146
53	1,4-Dichlorobenzene	10.05	146
54	4-Isopropyltoluene	10.11	119
55	1,2-Dichlorobenzene-d4 (Surrogate)	10.25	152
56	1,2-Dichlorobenzene	10.26	146
57	**1,4-Dichlorobenzene**	10.36	146
58	n-Butylbenzene	10.36	91
59	1,2-Dibromo-3-chloropropane	10.55	75
60	1,2,4-Trichlorobenzene	11.39	180
61	Naphthalene	11.54	128
62	Hexachlorobutadiene	11.61	225
63	1,2,3-Trichlorobenzene	11.67	180

Figure 1 and Table 2 show several places where the target compounds are not fully resolved in the chromatogram. Because different ions are used for quantitation, the overlapping peaks are no problem, as shown in Figure 2. In Figure 2a, a portion of the total ion chromatogram (TIC) has been enlarged showing peaks that overlap. As seen in Figure 2b, the extracted ion chromatograms used for quantitation of these compounds have peaks that are fully resolved. The GC/MSD system uses a combination of chromatography and ion selectivity to resolve all of the peaks, providing faster analyses with quantitation that is precise and accurate.

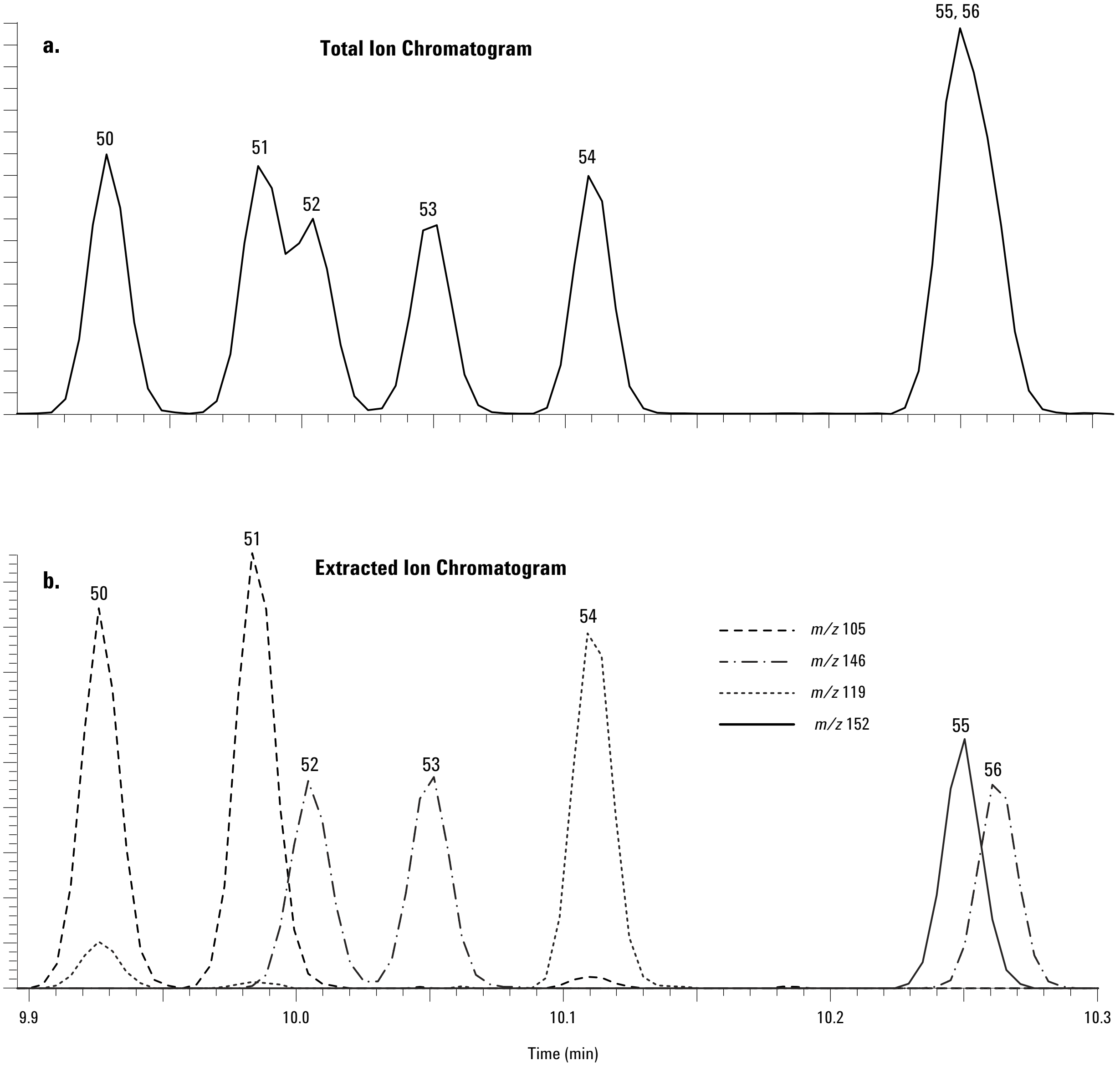

Figure 2. a) A portion of the total ion chromatogram in figure 1. The peaks are identified in Table 2. s-Butylbenzene (51) and 1,3-dichlorobenzene (52) are partially resolved while 1,2-dichlorobenzene (56) and its deuterated analog (55) (used as a surrogate) are unresolved. b) The extracted ions used for quantifying these compounds show peaks that are fully resolved.

Figure 3 shows calibration curves for chloroform (0.5 to 100 µg/L) and 1,2-dichloroethane (0.5 to 250 µg/L) that were generated by purging 5-mL spiked water samples. The Agilent MSD typically displays good linearity over four orders of magnitude. However, the region of linearity is compound dependent, i.e., not all compounds are linear over the same calibration range. Laboratories are usually able to generate linear calibration curves over two orders of magnitude for a large number of analytes, such as those listed in Table 2.

With the high sensitivity of the Agilent GC/MSD system, laboratories usually only need to purge 5-mL samples. However, when additional sensitivity is required, the P&T system can accommodate 25-mL samples which increases the sensitivity by a factor of 5 for most compounds.

Conclusions

Automated P&T/GC/MS is the most widely used technique for the analysis of volatile organic compounds in drinking water, waste water, factory effluent and ground water. Agilent Technologies provides the necessary instrumentation, GC columns, supplies and services required for laboratories to succeed with these analyses. Agilent's EnviroQuant software has been specifically designed for the needs of environmental laboratories.

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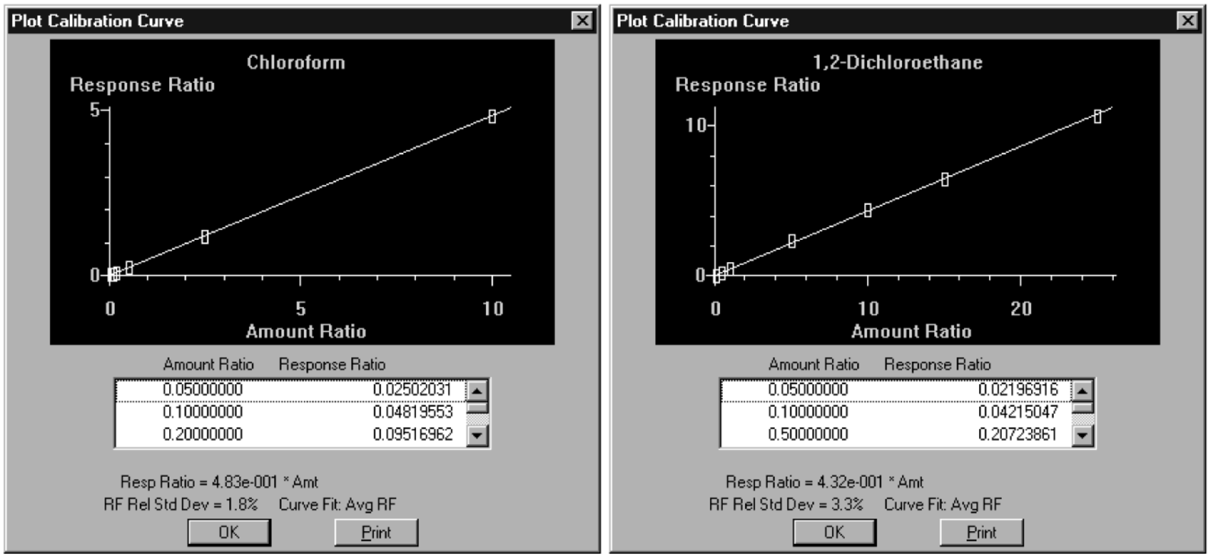

Amount Ratio	Response Ratio
0.05000000	0.02502031
0.10000000	0.04819553
0.20000000	0.09516962

Resp Ratio = 4.83e-001 * Amt
RF Rel Std Dev = 1.8%   Curve Fit: Avg RF

Amount Ratio	Response Ratio
0.05000000	0.02196916
0.10000000	0.04215047
0.50000000	0.20723861

Resp Ratio = 4.32e-001 * Amt
RF Rel Std Dev = 3.3%   Curve Fit: Avg RF

a. **b.**

Figure 3. Calibration curves for: a) chloroform (0.5-100 µg/L) and b) 1,2-dichloroethane (0.5-250 µg/L).

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