Simultaneous Analysis of Volatile Organic Compounds in Water Using Purge and Trap Gas-Chromatography–Mass-Spectrometry

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Introduction

The analysis conditions for purge and trap (P&T) gas-chromatograph–mass-spectrometer (GC-MS) are specified in US EPA Method 524.2 for volatile organic compounds (VOC) analysis in drinking water. A trap tube packed with carbon is used in this method. As a result, reducing the amount of water introduced into the GC-MS during desorption is effective for performing stable analysis. In this application note, we report on the simultaneous analysis of 83 VOC components using the PT7000 system, which is a purge and trap concentration introduction system equipped with a high-performance MCS.

GCMS - QP2020 NX | PT7000 Purge and Trap | AS7100 Vial Autosampler

Method

The purge and trap system included PT7000 and vial autosampler AS7100, which have been used for highly sensitive analysis of mold odor substances. GC–MS used the GCMS-QP2020 NX (Shimadzu Corporation). The MCS of the PT7000 was subjected to a highly inert treatment to reduce the influence of VOC adsorption, and achieve efficient and stable water removal. For VOC analysis, the GC capillary column used was a moderately polar column TC-VMS (0.25 mm I.D. × 30 m df = 1.4 µm). The desorb time was reduced from 4 to 2 min, as recommended by EPA Method 524.2. Tables 1 and 2 show the detailed analytical conditions, including other parameters. In addition to Restek's Calibration Mix # 4, # 5, # 7A, # 7B, and # 8A, the VOC standard solution was made by dissolving three components of Tokyo Kasei Industry's bromomethane, dichlorodifluoromethane, and trichlorofluoromethane in methanol, mixing them, and preparing 100 ppm as a mixed standard stock solution of 83 components. The calibration curve standard solutions were prepared in 40 mL vials by adding the mixed standard stock solution to the water sample in increments of 0.5 to 10 ppb, respectively. Fluorobenzene was used as an internal standard, and *p*-bromofluorobenzene and 1,2-dichlorobenzene-d_4 were used as surrogates. They were mixed so that their concentrations after addition in water were 5 ppb, respectively, and they were placed in an internal bottle, and 2 µL per 5 mL of the sample was automatically added using the vial autosampler function.

Table 1 P&T Method Conditions

Standby		**Bake**	
Valve oven temp.	150 ℃	**Bake time**	8 min
Transfer line temp.	150 ℃	**Bake temp.**	260 ℃
Mount temp.	60 ℃	**MCS bake temp.**	260 ℃
Purge ready temp.	35 ℃	**Bake flow rate**	80 mL/min
MCS temp.	40 ℃	**Bake sparger time**	10 min
Standby flow rate	40 mL/min	**After bake time**	2 min
B.O.T temp.	150 ℃	**After bake flow rate**	200 mL/min
Purge MCS temp.	40 ℃	**Autosampler**	
Dry purge MCS temp.	40 ℃	**Sampling time**	0.2 min
Purge		**I.S. addition**	ON
Prepurge time	0 min	**Fill I.S. time**	0.2 min
Prepurge flow rate	0 mL/min	**Transfer time**	0.25 min
Sample temp.	60 ℃	**Loop wash time**	0.25 min
Preheat time	0.01 min	**Loop purge time**	0.25 min
Purge time	11 min	**Rinse frequency**	3
Purge temp.	0 ℃	**Bake fill time**	0.2 min
Purge flow rate	40 mL/min	**Bake transfer time**	0.25 min
Dry purge time	1 min	**Bake drain time**	0.25 min
Dry purge temp.	20 ℃	**Bake drain flow rate**	100 mL/min
Dry purge flow rate	40 mL/min	**Note**	
Desorb		**Sparger**	5 mL
GC start	Start of desorb	**Trap**	Vocarb 3000
Desorb Preheat temp.	250 ℃	**Sample loop**	5 mL
Drain	ON	**Chiller Tray**	ON
Desorb time	2 min	**Purge Gas**	Nitrogen
Desorb temp.	250 ℃		
Desorb flow rate	40 mL/min		

Table 2 GC - MS Method Conditions

GC-MS	GCMS - QP2020 NX (Shimadzu Corporation)
Column	TC-VMS 0.25 mmI.D. x 30 m , df = 1.40 µm (GL Sciences Inc.)
Split ratio	1:40
Oven Temp.	40 ℃(hold 2.5 min) – 7 ℃/min – 70 ℃ - 25 ℃/min – 240 ℃ (1 min)
Carrier gas	He, 180 kPa
Scan range	35 – 300 amu

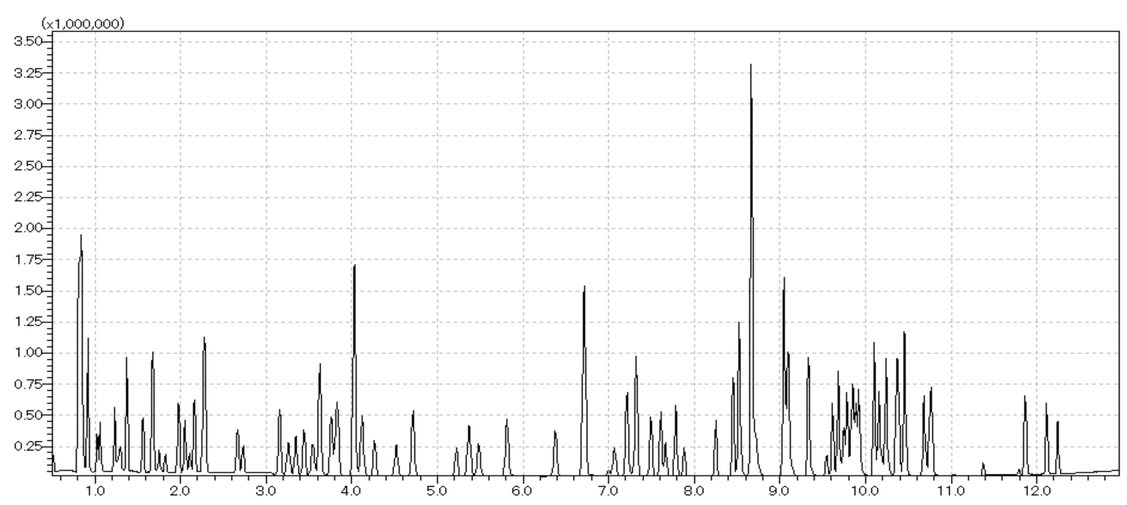

Fig.1 Total Ion Current Chromatogram (TICC)

Results and Conclusion

Fig. 1 depicts the total ion current chromatogram (TICC) obtained under the aforementioned analytical conditions. In 83 VOCs, excellent separation was demonstrated. The RSDs of the internal standard and surrogate were both less than 5%. Table 3 displays the retention time, calibration curve, and percent RSD at 0.5 ppb for each compound. As specified by the method, the percent RSD for all components were less than 20% (except Iodomethane) . In fact, for most components, except 8 components, they were less than 10 %. The linearity, MDL, and accuracy results were also satisfactory.
The PT7000 system and GCMS - QP2020 NX combined analysis produced good results for VOC analysis in water and was applicable to EPA Method 524.

Table 3 Calibration, Accuracy and Precision

No.	Compounds	Calibration (0.1 - 10 ppb)		MDL (n=7, 0.5 ppb)			
		R.T.	Linearity	Ave.Conc.	MDL	Accuracy	Precision
		(min)	(r^2)	(ppb)	(ppb)	(± 20 %)	(≦20 %)
1	Dichlorodifluoromethane	0.919	0.9993	0.47	0.123	94	8.7
2	Chloromethane	1.031	0.9985	0.46	0.103	91	7.5
3	Vinyl chloride	1.063	0.9997	0.48	0.138	95	9.7
4	Bromomethane	1.234	0.9999	0.41	0.211	82	17.2
5	Chloroethane	1.302	0.9997	0.46	0.130	92	9.4
6	Trichlorofluoromethane	1.376	1.0000	0.48	0.125	96	8.7
7	Ethyl ether	1.566	1.0000	0.47	0.119	94	8.5
8	1,1-Dichloroetylene	1.671	1.0000	0.47	0.134	94	9.5
9	Carbon disulfide	1.683	0.9999	0.48	0.066	96	4.6
10	Iodomethane	1.755	0.9991	0.40	0.242	79	20.4
11	Allyl chloride	1.982	0.9999	0.47	0.071	95	5.0
12	Dichloromethane	2.055	0.9997	0.48	0.089	96	6.2
13	Acetone	2.115	0.9981	0.50	0.192	101	12.7
14	*trans*-1,2-Dichloroethylene	2.167	0.9999	0.47	0.075	95	5.3
15	MTBE	2.283	0.9999	0.47	0.063	94	4.4
16	1,1-Dichloroethane	2.671	0.9999	0.47	0.097	94	6.9
17	Acrylonitrile	2.738	0.9994	0.46	0.153	93	11.0
18	*cis*-1,2-Dichloroethylene	3.165	0.9999	0.49	0.049	98	3.3
19	2,2-Dichloropropane	3.266	0.9998	0.50	0.030	101	2.0
20	Bromochloromethane	3.351	1.0000	0.49	0.050	99	3.3
21	Chloroform	3.448	0.9998	0.46	0.023	93	1.6
22	Tetrachloromethane	3.551	0.9998	0.48	0.067	96	4.7
23	Tetrahydrofuran	3.635	0.9994	0.46	0.025	92	1.8
24	2-Butanone	3.634	0.9993	0.54	0.047	108	2.9
25	1,1,1-Trichloroethane	3.631	0.9999	0.48	0.045	96	3.1
26	Methyl acrylate	3.635	0.9989	0.48	0.034	95	2.4
27	1,1-Dichloropropene	3.767	0.9997	0.48	0.026	95	1.8
28	1-Chlorobutane	3.839	0.9994	0.48	0.025	96	1.7
29	Benzene	4.034	0.9998	0.48	0.024	95	1.6
30	Propionitrile	4.115	0.9999	0.50	0.052	99	3.5
31	Methacrylonitrile	4.132	0.9992	0.46	0.056	92	4.1
32	1,2-Dichloroethane	4.273	0.9999	0.48	0.033	97	2.3
I.S.	Fluorobenzene (I.S.)	4.527	-	-	-	-	-
33	Trichloroethene	4.722	0.9999	0.48	0.039	96	2.7
34	Dibromomethane	5.230	1.0000	0.49	0.049	98	3.3
35	1,2-Dichloropropane	5.377	0.9998	0.50	0.055	100	3.7
36	Bromodichloromethane	5.490	0.9998	0.49	0.048	97	3.3
37	Methyl methacrylate	5.820	0.9981	0.46	0.076	92	5.5
38	*cis*-1,3-Dichloropropene	6.383	0.9995	0.48	0.040	96	2.8
39	Toluene	6.720	0.9993	0.47	0.042	94	3.0
40	Chloroacetonitrile	7.010	0.9851	0.53	0.147	105	9.3
41	2-Nitropropane	7.069	0.9995	0.49	0.040	97	2.8
42	1,1-Dichloropropanone	7.078	0.9997	0.46	0.060	92	4.3
43	Tetrachloroethylene	7.220	0.9998	0.49	0.028	98	1.9
44	*trans*-1,3-Dichloropropene	7.325	0.9992	0.47	0.036	94	2.5
45	4-Methyl-2-pentanone	7.330	0.9988	0.44	0.033	89	2.5
46	1,1,2-Trichloroethane	7.499	1.0000	0.49	0.056	97	3.8
47	Ethyl methacrylate	7.616	0.9975	0.44	0.070	87	5.3
48	Dibromochloromethane	7.671	0.9996	0.48	0.051	95	3.6
49	1,3-Dichloropropane	7.790	0.9998	0.47	0.037	94	2.6
50	1,2-Dibromoethane	7.887	0.9998	0.47	0.037	95	2.6
51	2-Hexanone	8.259	0.9968	0.44	0.136	89	10.2
52	Chlorobenzene	8.456	0.9998	0.47	0.048	95	3.4
53	Ethylbenzene	8.524	0.9990	0.45	0.052	91	3.8
54	1,1,1,2-Tetrachloroethane	8.538	0.9999	0.49	0.062	97	4.3
55	*m,p*-Xylene	8.672	0.9992	0.45	0.054	90	4.0
56	*o*-Xylene	9.052	0.9991	0.47	0.046	94	3.3
57	Bromoform	9.084	0.9993	0.49	0.036	99	2.4
58	Styrene	9.101	0.9979	0.42	0.058	84	4.6
59	Isopropylbenzene	9.339	0.9986	0.46	0.086	92	6.2
SURR.	*p*-Bromofluorobenzene (SURR.)	9.551	-	-	-	-	-
60	Bromobenzene	9.619	0.9972	0.52	0.058	103	3.8
61	n-Propylbenzene	9.687	0.9986	0.50	0.084	101	5.6
62	1,1,2,2-Tetrachloroethane	9.752	0.9953	0.51	0.043	103	2.8
63	2-Chlorotoluene	9.787	0.9979	0.51	0.045	102	2.9
64	1,2,3-Trichloropropane	9.840	0.9957	0.52	0.095	105	6.0
65	1,3,5-Trimethylbenzene	9.859	0.9996	0.50	0.107	100	7.2
66	*trans*-1,4-Dichloro-2-butene	9.893	0.9990	0.48	0.053	96	3.6
67	4-Chlorotoluene	9.926	0.9965	0.49	0.089	98	6.0
68	*tert*-Butylbenzene	10.103	0.9978	0.51	0.082	101	5.4
69	Pentachloroethane	10.100	0.9928	0.58	0.188	116	10.8
70	1,2,4-Trimethylbenzene	10.161	0.9992	0.49	0.103	99	7.0
71	sec-Butylbenzene	10.244	0.9990	0.50	0.083	99	5.6
72	*p*-Isopropyltoluene	10.365	0.9993	0.49	0.108	99	7.3
73	*m*-Dichlorobenzene	10.383	0.9971	0.51	0.063	103	4.1
74	*p*-Dichlorobenzene	10.457	0.9981	0.51	0.061	101	4.0
75	n-Butylbenzene	10.686	0.9991	0.49	0.070	99	4.7
76	Hexachlorethane	10.753	0.9978	0.52	0.138	103	8.9
SURR.	1,2-Dichlorobenzene-d_4 (SURR.)	10.767	-	-	-	-	-
77	1,2-Dichlorobenzene	10.774	0.9984	0.51	0.076	101	5.0
78	1,2-Dibromo-3-Chloropropane	11.381	0.9907	0.51	0.155	102	10.1
79	Nitrobenzene	11.797	0.9949	0.55	0.332	111	20.0
80	Hexachlorobutadiene	11.863	0.9957	0.53	0.047	107	3.0
81	1,2,4-Trichlorobenzene	11.880	0.9997	0.53	0.119	107	7.5
82	Naphthalene	12.120	0.9988	0.51	0.077	103	5.0
83	1,2,3-Trichlorobenzene	12.250	0.9989	0.49	0.034	98	2.4

References

METHOD 524.2. MEASUREMENT OF PURGEABLE ORGANIC COMPOUNDS IN WATER BY CAPILLARY COLUMN GAS CHROMATOGRAPHY/MASS SPECTROMETRY
Revision 4.1, Edited by J.W. Munch (1995)

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