A Study on Purge Efficiency in Purge and Trap Analysis of VOCs in Water

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A Purge and Trap Concentrator has been used to analyze various volatile organic compounds in water, operating several parameters affecting the extraction efficiencies of these compounds. The object of the present study was to observe the purge efficiencies of 40 volatile organic compounds (VOCs) in water, according to the change of parameters (purge time, dry purge time, sample temperature), and to determine the optimum condition of analysis of VOCs. The Purge and Trap Concentrator was interfaced with a narrow capillary connected to a gas chromatography mass spectrometer. At this condition, the detection limits of VOCs were in the range of 0.1-0.5 μg/L.

Keywords : Volatile organic compounds (VOCs), Purge and trap, Purge efficiency, Indirect coupling.

Introduction

As contamination of the environment grows more serious, methods for analyzing trace volatile organic compounds in water have become necessary, especially for these more specific concentration methods. Over the years, the Purge and Trap concentration method, first introduced by Bellar and Lichenberg,[1] has become widely used for extracting VOCs from various matrixes (solid,[2-6] water,[7-17] other liquids[18,19] and air.[20,21]). Recently, several papers on VOCs analysis using Solid Phase Microextraction have been reported.[22-24] The Purge and Trap process comprises three steps : purging, adsorption and desorption-trap baking.

First, the VOCs in water are purged with He gas, they are adsorbed into the trap (Tenax/charcoal/silica gel) then quickly heated at high temperature and desorbed.

Desorbed VOCs are transferred to the gas chromatograph, and, at this moment, the GC automatically starts. Because desorption time directly affects the chromatogram, desorption must be done at high temperature for a short time to obtain sharp peaks. Drying the trap is necessary, to limit the amount of moisture can be adsorbed into the trap. Two methods are available for studies using gas chromatograph/mass selective detector and Purge and Trap. In the first method, the column of gas chromatography is directly connected to the Purge and Trap interface, and whole desorbed VOCs from the Purge and Trap are injected into the GC.

In this method, we obtained good sensitivity of the compounds because of high injection volumes, accomplished by using a widebore column, such as VOCOL (0.53 mm I.D), which increases the gas flow of desorption and which also decreases the desorption time. But, this one has bad resolu-

tion, and it also requires a large mass spectrometer.

The second method uses a narrow capillary to connect the GC/MSD and Purge and Trap.[25] Desorption occurs over a short time period with large desorption gas flow, and analyses is done with split injection mode, so only a fraction of desorbed compound is injected into the GC column. This allows the use of the narrow column (0.2 mm I.D) as well as general GC. Also, this method produces good resolution in the chromatogram. During the Purge and Trap concentration, optimization of operation parameters are required to achieve maximum sensitivity and purge efficiency.[26] Many studies have been carried out on VOCs analysis that uses the Purge and Trap and the GC/MSD and purge efficiency of VOCs, however, they have been limited to certain compounds.[27-34] In the present study, optimum conditions are examined while analyzing, simultaneously, more than 40 VOCs in water by changing the operation parameters (purge time, dry purge time, sample temperature etc.), using Purge and Trap and GC/MSD with modified indirect coupling.

The objectives of the present study were to analyze 40 VOCs, simultaneously, and find the common optimum condition for effective efficiencies.

Experimental Section

Reagents and Chemicals. Blank water was prepared from the third distilled water filtered through Milli-Q and Milli-RO system from Waters. All reagents were purchased from Supelco (Bellefonte, USA); they include: VOC Standard Mix. #1, #2, #3, #4, and #5 and Internal Standard (ISTD Mix.: fluorobenzene and *o*-dichlorobenzene-d₄). Each concentration of the compounds is 2000 μg/mL.

Stock Solution. Stock solution was prepared in methanol at a concentration of 10 μg/mL with all the VOC Mix.(#1-#5). The standard solution was sealed and refrigerated at 4

°C until use.

Internal Standard Solution. ISTD mixture solution was prepared in methanol at a concentration of 50 μg/mL.

Instrumentation. A Hewlett-Packard model 5890 series gas chromatograph directly interfaced with a HP 5970 mass selective detector was used. For the data analysis. an HP 59940 MS chemstation connected to an HP 7946 disc drive was used. The extraction and concentration of the water sample were on a Tekmar LSC 3000 sample concentrator and ALS 2016. The purge and trap was connected with the GC by inserting a capillary (about 20 cm length) between the GC injection port and the purge and trap module. All chromatograms were obtained in the selective ion monitoring (SIM) mode. An HP fused-silica capillary column (50 m length × 0.2 mm I.D., cross-linked 5% phenylmethylsilicone, film thickness 0.33 μm) was coupled to the ion source. The carrier gas was helium at a flow-rate of 0.48 mL/min and the split ratio was 100 : 1. The temperatures were 200 °C for the injector, 250 °C for the detector; initial column temperature: 35 °C, initial time: 5 min, increased to 55 °C (1.5 °C/min), to 130 °C (5 °C/min) and to 200 °C (10 °C/min). The constant values of the Purge and Trap were purge flow: 40 mL/min (35 °C, 99.9999% He); dry purge flow: 20 mL/min (99.9999% He); sample volume: 5 mL; desorption temperature: 225 °C (trapping temperature: 225 °C); desorption time: 1 min; and cold trap temperature: -150 °C.

Analytical Procedure. To 5 mL sample of blank water in 5 mL syringe. 5 μL of STD stock solution (10 μg/mL) and 1 μL of ISTD solution (50 μg/mL) were spiked and then placed into a 5 ml sparger. The mixture was concentrated in the Purge and Trap and injected into the GC/MSD system.

The conditions of the GC/MSD are shown in Table 1.

Purge efficiency according to the change of purge time: Purge efficiencies were examined at purge times of 5 min, 8 min. 11 min. 13 min and 15 min at room temperature of sample temperature and 5 min of dry purge time.

Purge efficiency according to the change of sample temperature: Purge efficiencies were observed for sample temperatures of 20 °C, 30 °C. 40 °C, 50 °C and 60 °C at 11 min of purge time and 5 min of dry purge time.

Purge efficiency according to the change of dry purge time: Purge efficiencies were observed for dry purge times of 3. 5 and 7 min at 11 min of purge time and 60 °C of sample temperature.

Results and Discussion

The total ion chromatogram of VOCs obtained from the above experiment is shown in Figure 1. Retentions and characteristic mass fragment ions of each compound are in Table 2.

Purge Time Effect. The volume of VOCs purged from the sample matrix is dependent on the purge volume. The purge volume can be estimated by multiplying purge flow rate and purge time, therefore. the purged volume of VOCs at constant flow rate (40 mL/min) is set by the purge time. In the present paper. the volume of purged VOCs is related to purge efficiency.

Purge efficiencies of each compound in Table 4. are the percentile value relative to the maximum value among the variable conditions.

The purge efficiencies of VOCs for each purge time at

Table 1. GC/MS operating parameters

Column	Ultra-2 (Cross-linked 5% phenylmethylsilicon, 50 m × 0.2 mm I.D. × 0.33 um film thickness)
Carrier gas	He at 0.48 mL/min.
Split ratio	1/100
Injection port temp.	200 °C
Transfer line temp.	250 °C

Oven temp. program

Initial temp. (°C)	Initial time (min)	Rate (°C/min)	Final temp. (°C)	Final time (min)
35	5	1.5	55	0
		5.0	130	0
		10.0	200	0

SIM mode (Solvent delay: 3.0 min)

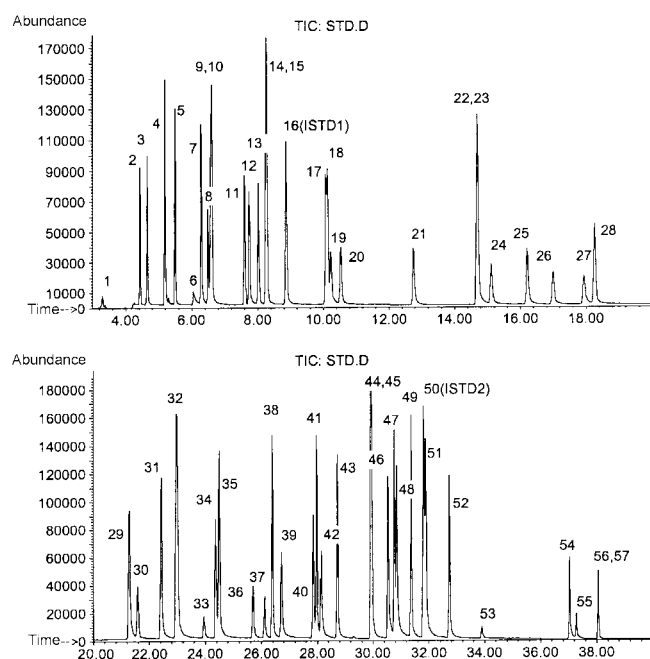| Group	Start time (min.)	Selected ions (m/z)
1	3.0	62, 64
2	4.2	61, 96, 84, 49, 63, 67, 43, 72, 77, 79, 130, 128, 83, 85, 62
3	7.1	97, 99, 62, 64, 75, 110, 78, 77, 117, 119, 96, 63, 130, 132, 174, 93, 83, 85
4	12.0	75, 77, 91, 92, 97, 83, 76, 78, 127, 129, 107, 109, 166, 164
5	20.5	112, 114, 131, 133, 91, 106, 173, 171, 104, 78, 83, 85, 75, 77, 105, 120, 156, 126
6	28.0	105, 120, 119, 91, 146, 148, 134, 152, 150, 157, 75, 111, 155
7	36.0	180, 182, 145, 128, 64, 225, 223, 227

Run time	40.33 min.

Figure 1. Purge and Trap-GC/MSD chromatogram of 5 mL of VOCs (10 ppb) spiked water sample. Peak identity: same as Table 2.

constant sample temperature and dry purge time (room temperature and 5 min respectively) were observed. There are several tendencies for purge efficiency. The typical tendencies of each compound are shown in Figure 2. They are classified in five groups. Purge efficiency decreases as purge time increases-Group 1. first decreases and then increases purge efficiency-Group 2. purge efficiency increases as purge time increases-Group 3. first increases and then decreases purge efficiency-Group 4 and independent to purge time-Group 5. The relationship between purge efficiency and boiling points of each VOCs are shown in Figure 3.

Compounds in Group 1 or Group 2 have very low boiling points or high volatility and their retention times are within 20 min. Compounds of low boiling point (below 90 °C), were purged efficiently from the water, although the purge time was short. Compounds of high volatility were extracted from the water sample and trapped effectively for a short time, demonstrating high purge efficiency. As purge time became longer. adsorbed analytes were desorbed simutaneously by purge flow gas. The phenomena suggests that adsorption-desorption equilibrium between VOCs and the trap is not successful for long purge times. Therefore. purge efficiency decreases as purge time is increased.

In contrast, the compounds in Group 3 and Group 4 have

Table 2. Retentions and characteristic mass fragment ions of volatile organic compounds

Peak No.	VOCs	Retentions		Mass fragment ions (m/z)	MW
		t_R (min)	Rt_R		
1	Vinyl chloride	3.296	0.372	62 64	62.50
2	1,1-Dichloroethylene	4.443	0.501	61 96 98 63	96.95
3	Methylene chloride	4.658	0.525	49 84 86 51	84.94
4	trans-1,2-Dichloroethylene	5.198	0.586	61 96 98 63	96.94
5	1,1-Dichloroethane	5.495	0.620	63 65 83 98	98.96
6	Methyl ethyl ketone	6.046	0.682	43 44 57 72	72.10
7	cis-1,2-Dichloroethylene	6.298	0.710	61 96 98 63	96.95
8	2,2-Dichloropropane	6.494	0.732	77 41 79 97	112.99
9	Bromochloromethane	6.578	0.742	130 128 49 93	129.35
10	Chloroform	6.607	0.745	83 85 47 119	119.39
11	1,1,1-Trichloroethane	7.597	0.857	97 99 61 117	133.42
12	1,2-Dichloroethane	7.742	0.873	62 64 78 100	98.96
13	1,1-Dichloropropene	8.016	0.904	75 110 113 77	112.99
14	Benzene	8.251	0.930	78 77 52 76	78.11
15	Carbontetrachloride	8.282	0.934	119 117 121 84	153.84
16	Fluorobenzene (ISTD1)	8.868	1.000	96 70 50 75	96.10
17	1,2-Dichloropropane	10.069	1.135	63 65 61 76	112.99
18	Trichloroethylene	10.128	1.142	132 130 134 95	131.40
19	Dibromomethane	10.231	1.154	174 172 93 95	173.86
20	Bromodichloromethane	10.527	1.187	83 85 127 129	163.83
21	cis-1,3-Dichloropropene	12.743	1.437	75 77 110 112	110.98
22	trans-1,3-Dichloropropene	14.688	1.656	75 77 110 112	110.98
23	Toluene	14.689	1.656	91 92 65 51	92.13
24	1,1,2-Trichloroethane	15.117	1.705	97 99 83 61	133.42
25	1,3-Dichloropropane	16.209	1.828	76 78 41 49	112.99
26	Dibromochloromethane	16.997	1.917	127 125 79 81	208.28
27	1,2-Dibromoethane	17.935	2.022	107 109 79 81	187.88
28	Tetrachloroethylene	18.261	2.059	166 164 129 131	165.82
29	Chlorobenzene	21.282	2.400	112 114 77 50	112.56
30	1,1,1,2-Tetrachloroethane	21.577	2.433	131 131 117 119	167.86

Table 2. Continued

Peak No.	VOCs	Retentions		Mass fragment ions (m/z)	MW
		t_R (min)	Rt_R		
31	Ethylbenzene	22.420	0.705	91 106 78 65	106.16
32	*m,p*-Xylene	22.974	0.722	91 106 77 51	106.17
33	Bromoform	23.951	0.753	173 175 79 81	252.77
34	Styrene	24.360	0.766	104 103 78 51	104.16
35	*o*-Xylene	24.491	0.770	91 106 77 65	106.17
36	1,1,2,2-Tetrachloroethane	25.693	0.808	83 85 168 166	167.86
37	1,2,3-Trichloropropane	26.110	0.821	75 77 110 112	148.44
38	Isopropylbenzene	26.380	0.830	105 120 77 51	120.19
39	Bromobenzene	26.713	0.840	77 156 158 51	157.02
40	2-Chlorotoluene	27.853	0.876	91 126 89 63	126.58
41	*n*-Propylbenzene	27.972	0.879	91 120 78 65	120.19
42	4-Chlorotoluene	28.140	0.885	91 126 89 63	126.58
43	1,3,5-Trimethylbenzene	28.716	0.903	105 120 91 77	120.19
44	*tert*-Butylbenzene	29.919	0.940	119 91 134 77	134.21
45	1,2,4-Trimethylbenzene	29.957	0.942	105 120 77 63	120.19
46	*m*-Dichlorobenzene	30.540	0.960	146 148 111 75	147.01
47	*sec*-Butylbenzene	30.759	0.967	105 134 77 79	134.21
48	*p*-Dichlorobenzene	30.847	0.970	146 148 111 75	147.01
49	*p*-Isopropyltoluene	31.373	0.986	119 134 117 65	134.21
50	1,2-Dichlorobenzene-d₄ (ISTD2)	31.813	1.000	150 152 115 78	151.01
51	*o*-Dichlorobenzene	31.885	1.002	146 148 111 75	147.01
52	*n*-Butylbenzene	32.734	1.029	91 93 134 105	134.21
53	1,2-Dibromo-3-chloropropane	33.912	1.066	157 155 75 77	236.36
54	1,2,4-Trichlorobenzene	37.041	1.164	182 180 145 109	181.46
55	Naphthalene	37.278	1.172	128 129 102 64	262.70
56	1,2,3-Trichlorobenzene	38.047	1.196	182 180 145 109	128.16
57	Hexachlorobutadiene	38.064	1.196	225 227 223 260	262.70

Table 3. Compounds in each group

Group	Compound
Group 1(7)	*trans*-1,3-Dichloropropene, Toluene, 1,1,1-Trichloroethane, *cis*-1,3-Dichloropropene, *m,p*-Xylene, *o*-Xylene
Group 2 (11)	1,2-Dichloroethane, methylene chloride, 1,1-Dichloroethylene, *trans*-1,2-Dichloroethylene, 1,1-Dichloroethane, Chloroform, Benzene, Carbontetrachloride, 1,2-Dichloropropane, Trichlroethylene, Dichlorobromomethane
Group 3 (2)	Bromoform, 1,1,2,2-Tetrachloroethane
Group 4 (13)	Isopropylbenzene, *tert*-butylbenzene, *sec*-Butylbenzene, Bromobenzene, 2-Chlorotoluene, 1,3-Dichlorobenzene, *n*-Propylbenzene, 1,3,5-Trimethylbenzene, 1,2,4-Trimethylbenzene, 1,4-Dichlorobenzene, *p*-Isopropyltoluene, 1,2-Dichlorobenzene, *n*-Butylbenzene
Group 5 (5)	Dibromochloromethane, Ethylbenzene, 1,1,2-Trichloroethane, Chlorobenzene, Styrene

parenthesis is the number of compounds

low volatility or high boiling points, detected by GC/MSD after 20 min. Because they take a long time to extract from the water and desorb to the trap, purge efficiency becomes greater as purge time is increased, especially for the compounds above the boiling point (over 140 °C).

In Group 5, the purge efficiencies of almost all compounds are less than 70%. They have boiling points of 100-130 °C, which is a medium value and is not affected by the purge time.

As can be seen, the VOCs that have boiling points less than 140 °C show a decrease in purge efficiency with an increase in purge time. For VOCs within boiling points above over 140 °C, the opposite trends occurred.

Sample Temperature Effect. Purge efficiency was observed for change in the sample temperatures (20 °C, 30 °C, 40 °C, 50 °C and 60 °C) at constant purge time and dry purge time (11 min and 5 min). The typical curve of each compound is shown in Figure 4.

In general, as the sample temperature rises it is presumed that the purge efficiency increases, since the distribution of VOCs in the liquid phase and gas phase is the function of the temperature.[35] Most VOCs showed increasing purge efficiency at high temperature, especially methylethylketone, which showed a sharp increase in purge efficiency.

As can be seen in the graph of the relationship between boiling point and purge efficiency (Figure 5), purge efficiency did not vary greatly with changes in the boiling points of compounds for each sample temperature. However, we
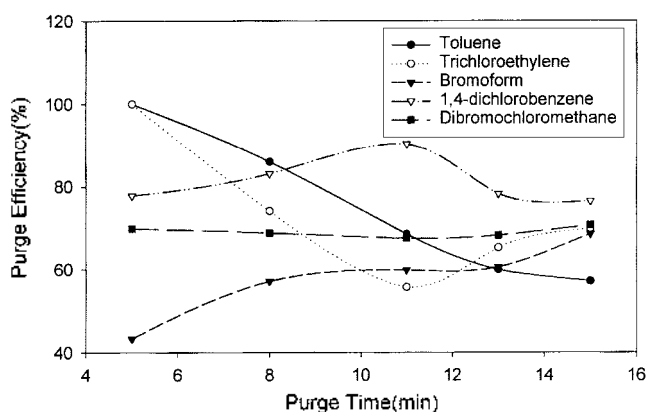
Figure 2. Purge efficiencies of VOCs according to change of purge time at sample temp/drypurge time (room temperature/5 min.).

found that the purge efficiencies of almost all VOCs increased at higher temperatures.

Dry Purge Time Effect. At the purge time of 11 min. sample temperature 60 °C. we observed the efficiency of VOCs at dry purge time of 3. 5 and 7 min. (The typical compound for each condition is shown in Figure 6)

Dry purge step is used to eliminate adsorbed water in the trap from the purge step. Most VOCs demonstrates the highest purge efficiency at 5 min, and the increasing order of purge efficiency was 5 min > 3 min > 7 min. The low purge efficiency at 7 min of dry purge time shows that VOC desorption occurs simultaneous with the elimination of moisture in the long dry purge step. Therefore, purge efficiency decreases if the dry purge time is too long. And also, purge efficiency decreased at 3 min of dry purge time, this suggests that trapped water elimination is not sufficient. with the residue of water in the trap prohibiting effective desorption of

VOCs. Figure 7. Shows a diagram of purge efficiency and the standard deviation (SD) at 5 min of dry purge time.

The Optimum Condition. From the result of experiments that varied the purge time. dry purge time and sample temperature the optimum condition for effective efficiency of simultaneous analysis of VOCs is: purge time at 11 min. sample temperature at 60 °C and dry purge time at 5 min. As for sample temperature and dry purge time. almost all VOCs showed the best purge efficiency at the same condition (60 °C, 5 min). But for purge time, the results differed for their boiling points and molecular weights. So we observed purge efficiency according to the change of purge time (5 min. 11 min. 13 min and 15 min) at constant sample temperature and dry purge time (60 °C. 5 min). For the VOCs that have low boiling points or high volatility. the purge efficiency decreased as the purge time increased. (11 min → 13 min → 15
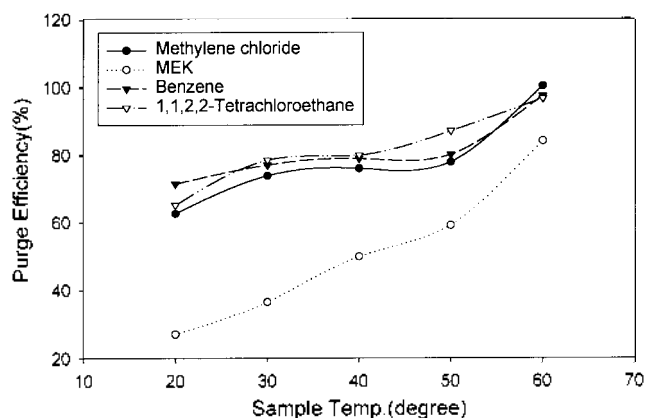

Figure 4. Purge efficiencies of VOCs according to change of sample temperature at purge time/drypurge time (11 min/5 min).
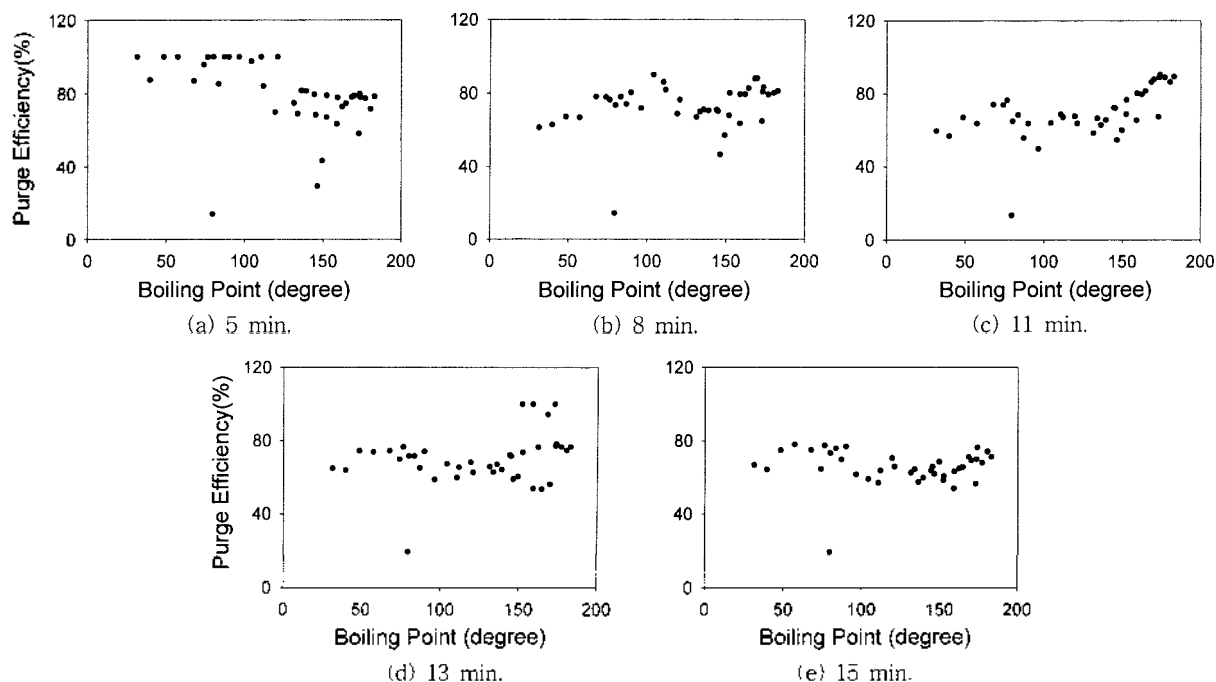

(a) 5 min.   (b) 8 min.   (c) 11 min.

(d) 13 min.   (e) 15 min.

Figure 3. Purge efficiencies of VOCs according to boiling points of each compound at purge time (5, 8, 11, 13 and 15 min.).
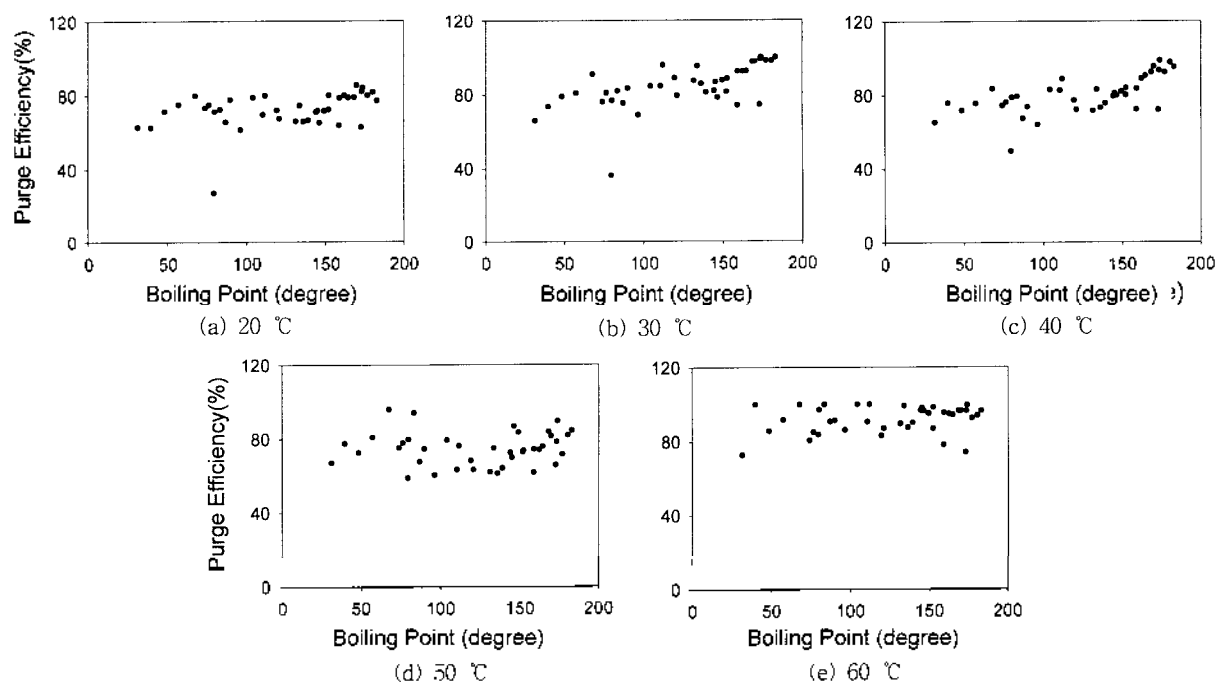
Figure 5. Purge efficiencies of VOCs according to boiling points of each compound at sample temperature (20, 30, 40, 50, 60 °C).
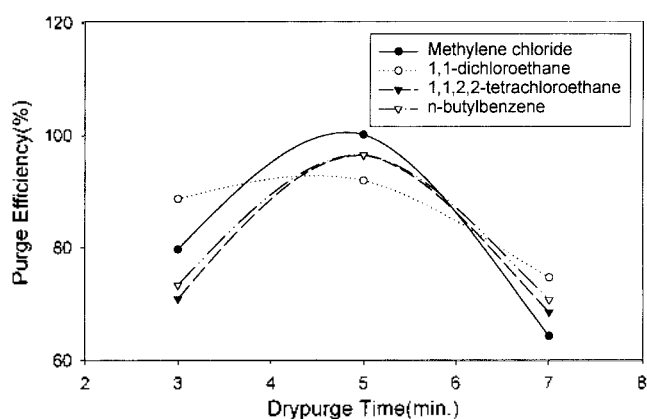

Figure 6. Purge efficiencies of VOCs according to change of dry purge times at purge time/sample temperature. (11 min/60 °C).

min) For the VOCs that have high boiling points or low volatility, the purge efficiency decreased as follows: 13 min → 11 min → 15 min. In both cases, the lowest purge efficiency

is at 15 min. This suggests that purge efficiency decreases because large amounts of moisture are absorbed in the trap, which affects adsorption/desorption of VOCs if purging lasts for a long time at high temperature (60 °C). Some differences in purge efficiency were observed at 11 min and 13 min of purge time. In case of long purge time, the moisture from the water sample was not adsorbed into the trap, but was also carried into the GC/MSD. Because of this, purge time was as short as possible. The optimum condition of simultaneous analysis of 40 VOCs is as follows: purge time at 11 min, sample temperature at 60°C and dry purge time at 5 min.

Conclusions

40 VOCs from water samples were separated using Purge and Trap and GC/MSD, and their mass spectra were obtained. The optimum condition, which satisfies commonly the maximum purge efficiency of all compounds, was determined in the present study with the simultaneous analyses of
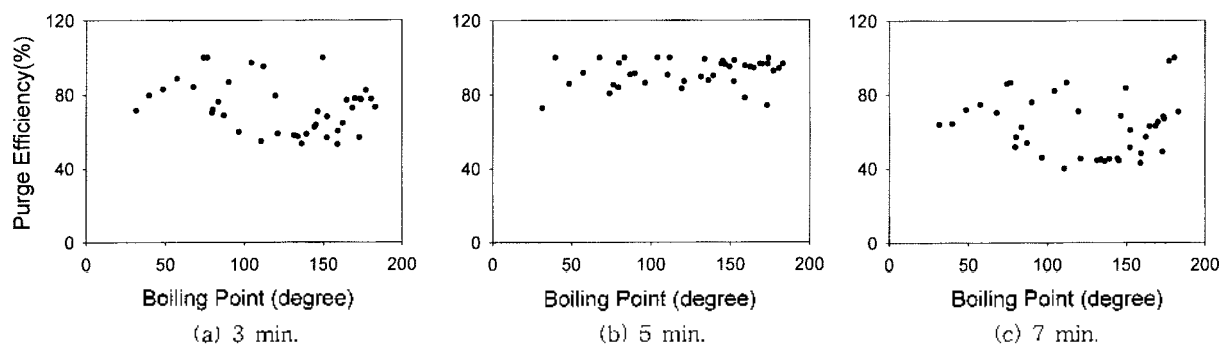

Figure 7. Purge efficiencies of VOCs according to boiling points of each compounds at dry purge time (3, 5, 7 min.)

Table 4. Purge efficiencies and relative standard deviation (RSD) of VOCs at 11 min, 13 min and 15 min of purge times (sample temp./ drypurge time: 60 °C/5 min)

VOCs	11 min		13 min		15 min	
	PE (%)	RSD (%)	PE (%)	RSD (%)	PE (%)	RSD (%)
1,1-Dichloroethylene	72.7	6.4	70.3	12.4	70.0	9.1
Methylene chloride	100.0	8.0	72.9	12.4	83.1	10.1
trans-1,2-Dichloroethylene	85.8	7.7	82.4	7.2	80.1	8.0
1,1-Dichloroethane	91.8	10.5	88.0	5.5	88.8	9.8
Methyl ethyl ketone	83.8	6.5	78.7	12.2	100.0	6.2
Chloroform	100.0	8.9	92.4	2.8	98.4	6.0
1,1,1-Trichloroethane	80.6	10.8	89.1	2.9	74.5	9.9
1,2-Dichloroethane	100.0	8.9	99.5	6.6	95.3	9.9
Benzene	97.1	10.3	95.6	7.7	87.5	10.3
Carbontetrachloride	85.2	9.0	93.4	2.7	80.2	9.6
Fluorobenzene (ISTD1)	74.3	7.8	83.5	8.9	65.7	9.7
1,2-Dichloropropane	86.2	10.2	80.3	10.1	64.2	10.3
Trichloroethylene	90.8	9.0	84.2	9.0	71.5	7.9
Dichlorobromomethane	91.3	7.1	88.6	9.8	79.1	5.6
cis-1,3-Dichloropropene	100.0	8.3	90.8	8.6	81.7	7.8
trans-1,3-Dichloropropene	100.0	7.1	94.1	6.0	82.5	4.8
Toluene	90.6	4.1	88.2	8.8	74.0	6.4
1,1,2-Trichloroethane	99.1	9.0	100.0	6.1	85.7	7.6
Dibromochloromethane	83.2	6.8	100.0	4.5	83.5	10.3
Tetrachloroethylene	87.1	8.1	92.5	9.2	68.9	7.1
Chlorobenzene	89.6	7.4	100.0	6.7	72.6	9.5
Ethylbenzene	87.6	6.7	100.0	6.3	69.9	9.5
m,p-Xylene	90.1	5.1	100.0	6.2	74.1	10.0
Bromoform	95.0	6.6	100.0	14.0	92.8	6.5
Styrene	98.1	4.7	100.0	9.1	85.5	8.2
o-Xylene	96.6	4.9	100.0	8.5	82.4	9.3
1,1,2,2-Tetrachloroethane	96.3	6.9	92.7	9.6	100.0	5.7
Isopropylbenzene	98.3	6.4	100.0	8.2	84.2	7.3
Bromobenzene	87.0	3.4	87.7	8.5	82.6	6.4
2-Chlorotoluene	78.2	5.6	81.2	7.3	73.4	7.6
n-Propylbenzene	95.4	6.6	100.0	6.9	85.4	8.3
4-Chlorotoluene	94.8	6.9	100.0	7.1	87.1	8.0
1,3,5-Trimethylbenzene	94.2	8.6	100.0	7.2	85.9	8.7
tert-Butylbenzene	96.5	6.1	100.0	5.8	88.1	8.6
1,2,4-Trimethylbenzene	96.5	3.7	100.0	6.1	90.1	7.5
1,3-Dichlorobenzene	74.0	4.5	72.8	4.1	71.7	6.8
sec-Butylbenzene	96.4	8.8	100.0	6.4	87.8	11.4
1,4-Dichlorobenzene	99.9	3.8	97.2	4.9	96.8	7.8
p-Isopropyltoluene	92.5	8.3	100	7.5	85.5	10.8
o-Dichlorobenzene-d₄ (ISTD2)	84.1	9.8	91.1	3.1	79.3	15.4
1,2-Dichlorobenzene	94.0	5.5	92.5	3.4	93.8	6.1
n-Butylbenzene	96.4	4.6	95.9	8.0	84.6	11.1

40 VOCs in water.

The optimum conditions of Purge and Trap that satisfied the maximum efficiency of tens of compounds were as follows: purge time at 11 min, dry purge time at 5 min, sample temperature at 60 °C at constant purge flow (40 mL/min), constant desorption flow (20 mL/min), desorption temperature (225 °C) and desorption time (1 min). At this optimum condition, the purge efficiency of each compound is more than 70% and their RSD is within 10%. (Table 4)

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