

## Trace level analysis of 25 semi-volatile organic compounds in surface water by gas chromatography-mass spectrometry

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## 지표수에서 GC/MS에 의한 25개 준휘발성유기화합물의 극미량 분석

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**Abstract:** A gas chromatography-mass spectrometric (GC-MS) method was developed for determining 25 semi-volatile organic compounds in water. A 1.0 L water sample was placed in a separatory funnel and saturated with NaCl, and the solution was extracted two times with 40 mL of methylene chloride. Under the established condition, the linear quantification range was 0.02-800 ng/L and the relative standard deviation was less than 15%. The method was used to analyze 16 surface water samples collected from various regions in Gum-River. The samples revealed SVOC concentrations in the range of 0.02-96.8 ng/L. Maximum concentrations of VOCs detected were not exceeded the EPA or Germany guidelines in any of the samples. The developed method may be valuable for monitoring SVOCs in water.

**요 약:** 지표수 중에 GC-MS에 의한 25개 준휘발성유기물질을 동시에 분석하는 방법을 개발하였다. 1.0 L의 물 시료를 분액깔대기 안에 넣고 NaCl로 포화시킨 다음 40 mL methylene chloride로 두 번 추출하였다. 이 방법은 0.01-800 ng/L 범위의 직선성을 보였고 15% 이내의 정밀도를 보였다. 확립한 방법을 사용하여 금강물 16개 시료를 분석한 결과 준휘발성유기화합물이 0.02-96.8 ng/L의 농도범위로 검출되었으며 측정값은 US EPA 또는 독일에서 확립한 준거치 이하의 값을 보였다. 이 측정방법은 지표수에서 SVOCs 대한 국가모니터링사업에 사용할 때 효율적인 것으로 판단된다.

**Key words:** semi-volatile organic compounds, gas chromatography-mass spectrometry, surface water

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## 1. Introduction

Semi-volatile organic compounds (SVOCs) comprise many priority pollutants such as polycyclic aromatic hydrocarbons (PAHs) and organochlorine pesticides (OCPs) which are toxic, persistent and ubiquitous. These SVOCs may pose a threat to terrestrial and aquatic ecosystems, and human health once released into the environment. Atmospheric transport is the primary distribution pathway, moving these pollutants from atmospheric emission sources via deposition to terrestrial and aquatic ecosystems. These organic compounds can be found far from any source in different environmental media such as waters, soils, biota or even ice-cores.<sup>1,2</sup> In order to assess potential risks of these pollutants for the natural environment and human health, data on their atmospheric occurrence are needed from all regions of the globe. Methods that accurately obtain these pollutants concentrations are therefore of great importance.

Many analytical procedures have been proposed for the determination of ng/L levels of SVOCs in water. Primary techniques currently used for the analysis of SVOCs in water include liquid-liquid extraction (LLE),<sup>3-5</sup> solid-phase extraction (SPE)<sup>6-8</sup> or membrane extraction<sup>9</sup> combined with high performance liquid chromatography (HPLC),<sup>4</sup> gas chromatography (GC)<sup>5,8</sup> and gas chromatography-mass spectrometry (GC/MS).<sup>3,6,7,9</sup> Particularly, SPE-GC-MS has been utilized widely for the identification and quantitation of SVOCs in a variety of water matrices. But these methods need a long time for loading and eluting for the determination of pg/L levels of SVOCs in water. Recently, a specific method for SVOCs analysis was developed relying on headspace solid phase microextraction (SPME),<sup>10,11</sup> but these methods have not sensitivity enough to detect pg/L levels of SVOCs in water.

This paper describes a LLE procedure to detect pg/L levels of SVOCs in water combined with analysis by gas chromatography-mass spectrometry-selected ion monitoring (GC-MS-SIM). This paper focuses on the validation of sample preparation and detection methodology. The developed method was

used to determine SVOCs in surface water samples.

## 2. Experimental

### 2.1. Chemicals and reagents

2,4-Dimethyl phenol, 4-chloro phenol, dichlorvos, 3-methyl-4-chlorophenol, dimethyl phthalate, 2,6-dinitro toluene, 2,4-dinitrophenol, 4-nitrophenol, 2,4-dinitrotoluene, diethyl phthalate, 2-methyl-4,6-dinitrophenol, hexachlorobenzene, dinoseb, heptachlor, di-n-butyl phthalate, chlorpyrifos, heptachlor epoxide A, heptachlor epoxide B, endosulfan I, endosulfan II, dieldrin, butyl benzyl phthalate, bis(2-ethyl hexyl)adipate, metoxychlor and di-n-octyl phthalate were purchased from Aldrich (USA). Analytical grade sodium chloride, methylene chloride, acetone and methanol were from J. T. Baker (USA). Water was purified by milli-Q equipment (Millipore Corp., Milford, MA, USA).

### 2.2. Water sampling

Surface water samples were collected from 22 basins in the Gum River in 1.0 L glass bottles containing 2 drop of 2 M HCl. The sampling sites were selected to uniformly represent all streams of the River. Sampling was performed seasonally, at the winter (on February 2011), at the spring (on May 2011) and at the summer (on August 2011) at 22 sites. Glass bottles were carefully filled just to overflowing, without passing air bubbles through sample.

### 2.3. Extraction procedure

Extraction method of this study was used by modifying EPA method 610.<sup>12</sup> In a 1.0 L separating funnel, 1.0 L of water-sample was placed. 25  $\mu$ L of phenanthrene-d10 internal standard solution (1 mg/L in methanol) were added to the solution, and the sample was extracted two times with 40 mL of methylene chloride by mechanical shaking for 5 min. The total organic phase was evaporated in vacuum rotary evaporator and to approximately 0.1  $\mu$ L under a stream of nitrogen gas and then transferred into a V-shape auto sampler vial. 2  $\mu$ L sample of the solution was injected into the GC system.

#### 2.4. Gas chromatography-mass spectrometry

The gas chromatograph used was an Agilent 7890 A with a split/splitless injector (Agilent Technologies, Santa Clara, CA, USA). The analytical column was a 60 m HP-5MS column (cross-linked 5% phenylmethylsilicon, 0.25 mm I.D.  $\times$  0.25  $\mu$ m F.T). The flow rate of helium as a carrier gas was 1.0 mL/min. The injector temperature was set at 310 °C. The oven temperature program began at 80 °C (held for 5 min), raised to 180 °C at 10 °C/min (held for 10 min), and rose to 300 °C at 10 °C/min (held for 15 min). All mass spectra were obtained with an Agilent 5975 B instrument (Agilent Technologies, Santa Clara, CA, USA). The ion source was operated in the electron ionization mode (EI; 70 eV, 230 °C). Full-scan mass spectra ( $m/z$  45-800) were recorded for the identification of analytes at a high concentration. Confirmation of trace chemicals was completed by three MS characteristic ions, and the ratio of the three MS

characteristic ions and the GC-retention time matched the known standard compound. The ions selected in this study were as shown in *Table 1*.

#### 2.5. Calibration and quantification

Calibration curves for SVOC were established by extraction after adding 1.0, 5.0, 10, 50 and 100 ng of the standard and 25 ng of the internal standard (phenanthrene-d10) to 1.0 L of water. The ratios of the peak area of the standard to that of the internal standard were used in the quantification of the compounds.

The lowest limit of detection (LOD) and limit of quantification (LOQ) were determined as the lowest concentration of the standard solution resulting in a signal-to-noise ratio of 3:1 and 10:1.

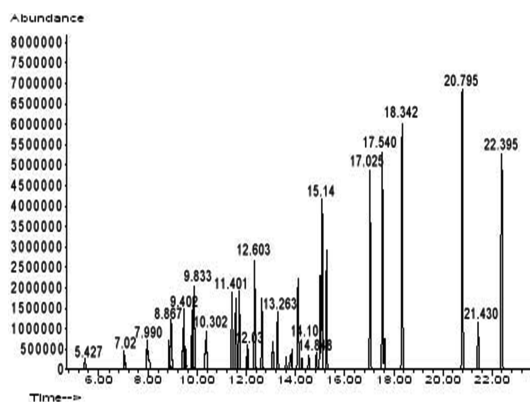
### 3. Results and Discussion

#### 3.1. Chromatography

The optimum conditions were applied to the analysis

*Table 1.* The quantification ions and qualification ions of SVOCs

Compounds	Quantification ion	Qualification ions
2,4-Dimethyl phenol	107	122, 121
4-Chloro phenol	128	65, 130
Dichlorvos	109	79, 185
3-Methyl-4-chlorophenol	107	142, 77
Dimethyl phthalate	163	77, 164
2,6-Dinitro toluene	165	89, 63
2,4-Dinitrophenol	184	154, 63
4-Nitrophenol	139	65, 109
2,4-Dinitrotoluene	165	89, 63
Diethyl phthalate	149	177, 150
2-Methyl-4,6-dinitrophenol	198	105, 121
Hexachlorobenzene	284	286, 282
Dinoseb	211	163, 147
Heptachlor	100	272, 274
Di-n-butyl phthalate	149	104, 150
Chlorpyrifos	197	199, 314
Heptachlor epoxide A	183	253, 217
Heptachlor epoxide B	353	351, 355
Endosulfan 1	241	237, 239
Endosulfan 2	241	237, 239
Dieldrin	79	81, 263
Butyl benzyl phthalate	149	91, 206
Bis(2-ethyl hexyl)adipate	129	147, 112
Metoxychlor	227	228, 212
Di-n-octyl phthalate	149	167, 279



*Fig. 1.* GC-MS chromatogram of the extract from water sample spiked in the concentration of 0.5-10.0 ng/L. (2,4-Dimethyl phenol 20.441 min, 4-Chlorophenol 21.498 min, Dichlorvos 22.749 min, 3-Methyl-4-chlorophenol 23.635 min, Dimethyl phthalate 27.808 min, 2,6-Dinitrotoluene 28.242 min, 2,4-Dinitrophenol 29.737 min, 4-Nitrophenol 30.052 min, 2,4-Dinitrotoluene 30.812 min, Diethyl phthalate 32.717 min, 2-Methyl-4,6-Dinitrophenol 33.829 min, Hexachlorobenzene 37.174 min, Dinoseb 39.109 min, Heptachlor 41.205 min, Di-n-butyl phthalate 41.700 min, Chlorpyrifos 42.356 min, Heptachlor epoxide B 43.604 min, Heptachlor epoxide A 43.727 min, Endosulfan 44.704 min, Dieldrin 45.456 min, Endosulfan 2 46.391 min, Butylbenzyl phthalate 47.147 min, Bis(2-ethyl hexyl)adipate 47.361 min, Methoxychlor 49.211 min, Di-n-octylphthalate 49.722 min

of the SVOCs. *Fig. 1* shows a GC-MS chromatogram of the SVOCs. For the GC separation of the SVOC, the use of a nonpolar stationary phase was found to be efficient. SVOCs showed sharp peaks, and the compound was quantified as integration of peak area. The retention times of VOC standards and internal standards are shown in *Fig. 1*. No extraneous peak was observed in the chromatograms near the retention times of analytes.

### 3.2. Detection limits

Limits of detection (LOD) and limits of quantification (LOQ), calculated as described in materials and methods, were estimated from this study. The method detection limit (LOD and LOQ) in this study was shown in *Table 2*. The combination of a high yield and the high sensitivity of the analytes by

GC-MS (SIM) permit the detection of SVOCs at concentrations well below those reported previously.

The US Environmental Protection Agency<sup>13</sup> has established water quality criteria for human health for SVOCs between 0.039 ng/L and  $2.7 \times 10^5$  µg/L as shown in *Table 2*. In Korea, water quality criteria (WQC) for the SVOCs have not yet been established, but they may be necessary to review water quality criteria after enough monitoring and risk assessment have been completed. Establishing water quality criteria for human health through the monitoring, requires a sensitive analytical method with more low detection limit than the water quality criteria established in other nations (generally 1/10 WQC). The LOQs of all SVOCs in this study meet 0.1 times lower concentration than the water quality criteria for VOCs established by the US EPA or Germany as shown in

*Table 2.* The detection limits of SVOCs in water and water quality criteria suggested by USEPA.

Compounds	Unit	LOD	LOQ	WQC	WQC/10
4-Chlorophenol	ng/L	0.53	1.7	-	
2,4-Dimethylphenol	ng/L	0.43	1.4	6.40E+05	6.40E+04
2,4-Dinitrophenol	µg/L	0.19	0.6	70	7.0
2-Methyl-4,6-dinitrophenol	µg/L	0.05	0.2	1.3E+01	1.3
3-Methyl -4-chlorophenol	ng/L	2.60	8.3	3.0E+06	3.0E+05
4-Nitrophenol	µg/L	0.25	0.8	60	6.0
2,4-Dinitrotoluene	ng/L	0.70	2.1	1.1E+02	1.1E+01
2,6-Dinitrotoluene	ng/L	2.59	8.2	5.0E+01	5.0
Dichlorvos	ng/L	2.54	8.1	1.2E+02*	1.2E+01*
Dinoseb	µg/L	0.05	0.2	7.0	0.7
Chlorpyrifos	ng/L	0.39	1.2	2.0E+04	2.0E+03
Dieldrin	ng/L	0.006	0.018	5.2E-02	5.2E-03
Endosulfan I	ng/L	2.83	9.0	1.1E+05	1.1E+04
Endosulfan II	ng/L	2.03	6.5	1.1E+05	1.1E+04
Heptachlor	ng/L	0.005	0.016	7.9E-02	7.9E-03
Heptachlor epoxide A	ng/L	0.004	0.012	3.9E-02	3.9E-03
Heptachlor epoxide B	ng/L	0.003	0.010	3.9E-02	3.9E-03
Hexachlorobenzene	ng/L	0.006	0.020	2.8E-01	2.8E-02
Methoxychlor	ng/L	0.47	1.48	4.91E+04*	4.91E+03*
Butyl benzyl phthalate	ng/L	2.76	8.78	1.5E+06	1.5E+05
Bis(2-ethylhexyl)adipate	ng/L	1.52	4.83	3.0E+05	3.0E+04
Diethyl phthalate	ng/L	2.37	7.56	1.7E+07	1.7E+06
Dimethyl phthalate	ng/L	3.26	10.37	2.7E+08	2.7E+07
Di-n-butyl phthalate	ng/L	3.01	9.60	2.0E+06	2.0E+05
Di-n-octyl phthalate	ng/L	5.31	16.92	1.4E+05	1.4E+04

\*suggested by Germany

Table 2.

### 3.3. Calibration curve and linearity

Examination of typical standard curve by computing a regression line of peak area ratios of SVOCs on concentration using a least-squares fit demonstrated a linear relationship with correlation coefficients of above 0.994. The line of best fits for VOCs are as described in Table 3.

### 3.4. Extraction and recovery

In spite of the conditions improvement of other alternative extraction techniques, solid-phase extraction (SPE) and liquid-liquid extraction (LLE) are still the most efficient techniques for the routinely performed analysis of SVOCs in water. SPE was initially considered to replace LLE, but problems such as reproducibility, sorption capacity and interfering impurities reduce the attractiveness of SPE. Also,

these methods need a long time for loading and eluting for the determination of pg/L levels of SVOCs in water. Therefore, LLE was performed for analysis of SVOCs in water.

Several water samples at the concentration of 0.1-50 ng/L were prepared and the relative recovery was calculated by percentage of the derivatives recovered. The recoveries of SVOCs were values between 85 and 120% as shown in Table 4.

### 3.5. Precision and accuracy

The reproducibility of the assay was very good. For five independent determinations in the concentration of 0.1-100 ng/L, the accuracy was within 100±13%, and the precision was less than 15% (Table 5).

### 3.6. Water analysis

We used the proposed method to analyze the target SVOCs in twenty-two surface water samples. Total

Table 3. The standard curves and linearity of SVOCs in water

Compounds	Unit	Conc. range	Calibration curves	R <sup>2</sup>
2,4-Dimethyl phenol	ng/L	1100	Y=0.006x-0.001	0.997
4-Chloro phenol	ng/L	1100	Y=0.003x+0.006	0.996
Dichlorvos	ng/L	5100	Y=0.012x-0.009	0.999
3-Methyl-4-chlorophenol	ng/L	5100	Y=0.005x+0.003	0.995
Dimethyl phthalate	ng/L	10500	Y=0.027x+0.121	0.999
2,6-Dinitro toluene	ng/L	1100	Y=0.005x+0.016	0.997
2,4-Dinitrophenol	µg/L	0.110	Y=0.126x-0.010	0.999
4-Nitrophenol	µg/L	0.110	Y=0.812x-0.038	0.997
2,4-Dinitrotoluene	ng/L	1100	Y=0.004x-0.008	0.997
Diethyl phthalate	ng/L	10500	Y=0.025x+0.314	0.996
2-Methyl-4,6-dinitrophenol	µg/L	0.110	Y=1.801x-0.031	0.996
Hexachlorobenzene	ng/L	0.011	Y=0.016x+0.000	0.994
Dinoseb	µg/L	0.110	Y=5.263x-0.299	0.999
Heptachlor	ng/L	0.0510	Y=0.003x+0.008	0.997
Di-n-butyl phthalate	ng/L	10500	Y=0.050x+0.263	0.996
Chlorpyrifos	ng/L	1100	Y=0.002x+0.007	0.998
Heptachlor epoxide A	ng/L	0.0510	Y=0.002x-0.010	0.994
Heptachlor epoxide B	ng/L	0.0510	Y=0.050x+0.016	1.000
Endosulfan 1	ng/L	10100	Y=0.001x+0.001	0.996
Endosulfan 2	ng/L	10100	Y=0.001x-0.000	0.994
Dieldrin	ng/L	0.0510	Y=0.005x+0.013	0.998
Butyl benzyl phthalate	ng/L	10500	Y=0.018x+0.068	0.998
Bis(2-ethyl hexyl)adipate	ng/L	10500	Y=0.016x-0.071	0.998
Metoxychlor	ng/L	1100	Y=0.014x+0.001	0.997
Di-n-octyl phthalate	ng/L	10500	Y=0.089x+2.499	0.999

Table 4. Recovery test results for the analysis of SVOCs in water ( $n=5$ )

Compounds	Unit	Spiked Conc.	Recovery (%)	Mean Recovery $\pm$ SD (RSD%)
4-Chloro phenol	ng/L	10	106, 100, 103, 102, 121	107 $\pm$ 8.5 (8.0)
		50	96, 99, 97, 109, 100	100 $\pm$ 5.2 (5.2)
2,4-Dimethyl phenol	ng/L	10	105, 11, 142, 112, 130	120 $\pm$ 15.6 (13.0)
		50	97, 97, 101, 99, 118	102 $\pm$ 9.1 (8.9)
2,4-Dinitro phenol	$\mu$ g/L	1.0	107, 109, 114, 101, 87	103 $\pm$ 10.3 (10.0)
		5.0	109, 89, 98, 95, 96	97 $\pm$ 7.2 (7.4)
2-Methyl-4,6-dinitro phenol	$\mu$ g/L	1.0	107, 109, 122, 100, 89	105 $\pm$ 12.2 (11.6)
		5.0	109, 104, 99, 98, 108	103 $\pm$ 5.0 (4.8)
3-Methyl-4-chloro phenol	ng/L	10	105, 93, 104, 110, 109	104 $\pm$ 6.7 (6.5)
		50	74, 77, 99, 101, 77,	85 $\pm$ 13.5 (15.8)
4-Nitro phenol	$\mu$ g/L	1.0	105, 100, 106, 103, 108	104 $\pm$ 3.1 (3.0)
		5.0	105, 111, 97, 91, 99	101 $\pm$ 7.8 (7.7)
2,4-Dinitro toluene	ng/L	10	100, 112, 123, 105, 96	107 $\pm$ 10.7 (10.0)
		50	108, 110, 95, 107, 108	106 $\pm$ 5.8 (5.5)
2,6-Dinitro toluene	ng/L	10	105, 106, 104, 98, 101	103 $\pm$ 3.2 (3.1)
		50	96, 100, 95, 98, 113	100 $\pm$ 7.5 (7.5)
Dichlorvos	ng/L	10	101, 103, 118, 105, 100	105 $\pm$ 7.2 (6.9)
		50	101, 99, 103, 111, 100	103 $\pm$ 5.0 (4.9)
Dinoseb	$\mu$ g/L	1.0	106, 109, 122, 100, 89	105 $\pm$ 12.2 (11.6)
		5.0	107, 110, 98, 96, 100	103 $\pm$ 5.0 (4.8)
Chlorpyrifos	ng/L	10	102, 104, 114, 105, 109	107 $\pm$ 4.9 (4.5)
		50	96, 93, 98, 91, 81	91 $\pm$ 6.3 (6.5)
Dieldrin	ng/L	10	107, 123, 108, 103, 106	109 $\pm$ 7.9 (7.2)
		50	103, 93, 94, 111, 111	102 $\pm$ 8.7 (8.5)
Endosulfan	ng/L	10	107, 106, 115, 105, 106	108 $\pm$ 4.1 (3.8)
		50	111, 101, 99, 108, 111	106 $\pm$ 5.6 (5.2)
Endosulfan	ng/L	10	108, 106, 114, 98, 90	103 $\pm$ 9.5 (9.2)
		50	94, 90, 96, 103, 106	98 $\pm$ 6.4 (6.5)
Heptachlor	ng/L	10	110, 113, 100, 108, 94	105 $\pm$ 7.7 (7.4)
		50	113, 106, 84, 92, 115	102 $\pm$ 13.6 (13.4)
Heptachlor epoxide A	ng/L	10	98, 96, 105, 83, 96	96 $\pm$ 7.9 (8.2)
		50	109, 120, 101, 112, 107	110 $\pm$ 6.9 (6.2)
Heptachlor epoxide B	ng/L	10	106, 104, 107, 102, 105	105 $\pm$ 2.1 (2.0)
		50	107, 99, 102, 95, 99	101 $\pm$ 4.4 (4.4)
Hexachloro benzene	ng/L	0.1	94, 91, 97, 97, 101	96 $\pm$ 4.0 (4.1)
		0.5	110, 93, 97, 96, 88	97 $\pm$ 8.0 (8.3)
Methoxychlor	ng/L	10	109, 103, 97, 101, 94	101 $\pm$ 5.9 (5.9)
		50	90, 107, 99, 98, 96	98 $\pm$ 5.9 (6.0)
Butyl benzyl phthalate	ng/L	100	105, 102, 107, 98, 99	102 $\pm$ 3.9 (3.8)
		200	97, 93, 99, 97, 105	98 $\pm$ 4.7 (4.8)
Bis(2-ethylhexyl) adipate	ng/L	100	106, 99, 102, 102, 108	104 $\pm$ 3.7 (3.5)
		200	98, 97, 97, 97, 102	98 $\pm$ 2.2 (2.3)

Table 4. Continued

Compounds	Unit	Spiked Conc.	Recovery (%)	Mean Recovery $\pm$ SD (RSD%)
Diethyl phthalate	ng/L	100	104, 106, 116, 102, 98	105 $\pm$ 6.8 (6.5)
		200	100, 100, 95, 102, 103	100 $\pm$ 3.0 (3.0)
Dimethyl phthalate	ng/L	100	105, 100, 110, 97, 105	103 $\pm$ 4.9 (4.7)
		200	99, 105, 107, 98, 102	102 $\pm$ 3.7 (3.6)
Di-n-butyl phthalate	ng/L	100	108, 110, 123, 101, 123	113 $\pm$ 9.5 (8.4)
		200	101, 105, 100, 95, 106	101 $\pm$ 4.4 (4.3)
Di-n-octyl phthalate	ng/L	100	107, 108, 118, 99, 129	112 $\pm$ 11.8 (10.5)
		200	113, 117, 100, 101, 110	108 $\pm$ 7.3 (6.7)

Table 5. Intra-day laboratory precision and accuracy results for the analysis of SVOCs in water ( $n=5$ )

Compounds	unit	Spiked Conc.	Mean $\pm$ SD (RSD%)	Accuracy (%)	Precision (%)
4-Chloro phenol	ng/L	10	9.32 $\pm$ 1.15	93	11.3
		50	50.74 $\pm$ 6.23	101	12.3
2,4-Dimethylphenol	ng/L	10	9.89 $\pm$ 1.29	99	13.0
		50	48.37 $\pm$ 4.29	97	8.9
2,4-Dinitrophenol	$\mu$ g/L	1.0	1.08 $\pm$ 0.06	108	8.0
		5.0	4.94 $\pm$ 0.35	99	7.1
2-Methyl-4,6-dinitro phenol	$\mu$ g/L	1.0	0.98 $\pm$ 0.11	98	11.0
		5.0	5.41 $\pm$ 0.26	108	4.8
3-Methyl -4-chloro phenol	ng/L	10	11.11 $\pm$ 0.78	111	7.1
		50	51.58 $\pm$ 8.29	103	14.9
4-Nitro phenol	$\mu$ g/L	1.0	1.00 $\pm$ 0.03	99	2.6
		5.0	4.98 $\pm$ 0.37	99	7.5
2,4-Dinitro toluene	ng/L	10	9.98 $\pm$ 0.88	100	8.8
		50	48.12 $\pm$ 2.57	96	5.3
2,6-Dinitro toluene	ng/L	10	11.31 $\pm$ 0.35	113	3.1
		50	46.28 $\pm$ 3.47	93	7.5
Dichlorvos	ng/L	10	9.53 $\pm$ 0.66	95	6.9
		50	49.02 $\pm$ 2.39	98	4.9
Dinoseb	$\mu$ g/L	1.0	1.04 $\pm$ 0.09	104	9.0
		5.0	5.11 $\pm$ 0.30	102	6.1
Chlorpyrifos	ng/L	10	10.38 $\pm$ 0.86	104	8.3
		50	54.14 $\pm$ 4.32	108	8.0
Dieldrin	ng/L	10	9.80 $\pm$ 1.28	98	13.1
		50	50.62 $\pm$ 4.98	101	9.8
Endosulfan I	ng/L	10	9.46 $\pm$ 0.36	95	3.8
		50	52.36 $\pm$ 2.75	105	5.2
Endosulfan II	ng/L	10	9.74 $\pm$ 0.62	97	6.3
		50	52.92 $\pm$ 3.26	106	6.2
Heptachlor	ng/L	10	10.66 $\pm$ 0.80	107	7.5
		50	51.66 $\pm$ 6.93	103	13.4

Table 5. Continued

Compounds	unit	Spiked Conc.	Mean $\pm$ SD (RSD%)	Accuracy (%)	Precision (%)
Heptachlor epoxide A	ng/L	10	10.77 $\pm$ 0.80	108	7.4
		50	50.51 $\pm$ 3.09	101	6.1
Heptachlor epoxide B	ng/L	10	10.73 $\pm$ 0.22	107	2.0
		50	56.18 $\pm$ 2.48	112	4.4
Hexachloro benzene	ng/L	0.1	0.11 $\pm$ 0.004	108	4.1
		0.5	0.50 $\pm$ 0.04	100	8.3
Methoxychlor	ng/L	10	11.02 $\pm$ 0.75	110	6.8
		50	52.21 $\pm$ 3.24	104	6.2
Butyl benzyl phthalate	ng/L	100	108.6 $\pm$ 4.82	109	4.4
		200	200.2 $\pm$ 10.51	100	5.2
Bis(2-ethylhexyl) adipate	ng/L	100	100.2 $\pm$ 4.99	100	5.0
		200	199.5 $\pm$ 5.46	100	2.7
Diethyl phthalate	ng/L	100	101.8 $\pm$ 6.67	102	6.5
		200	209.0 $\pm$ 6.24	105	3.0
Dimethyl phthalate	ng/L	100	108.9 $\pm$ 5.51	109	5.1
		200	205.2 $\pm$ 7.62	103	3.7
Di-n-butyl phthalate	ng/L	100	107.4 $\pm$ 9.23	107	8.6
		200	194.7 $\pm$ 8.53	97	4.4
Di-n-octyl phthalate	ng/L	100	91.2 $\pm$ 9.73	91	10.7
		200	203.9 $\pm$ 13.84	102	6.8

13 SVOCs were detected in surface water samples collected from Gum-River as following : 4-Chlorophenol (47.8 ng/L), 2,4-Dimethyl phenol (1.6-25.5 ng/L), dichlorvos (27.7-63.8 ng/L), chlorpyrifos (8.4-43.4 ng/L), dieldrin (30.8 ng/L), endosulfan (9.8-18.7 ng/L), heptachlor (4.6 ng/L), heptachlor epoxide B (8.5 ng/L), hexachlorobenzene (0.02-0.14 ng/L), butyl benzyl phthalate (BBP) (8.9-36.6 ng/L), bis(2-ethylhexyl) adipate (DEHA) (11.2-24.9 ng/L), diethyl phthalate (DEP) (8.7-96.8 ng/L), dimethyl phthalate (DMP) (9.2-70.0 ng/L). Some compounds such as 2,4-dinitrophenol, 2-methyl-4,6-dinitrophenol, 3-methyl-4-chlorophenol, 4-nitrophenol, 2,4-dinitrotoluene, 2,6-dinitrotoluene, dinoseb, endosulfan II, heptachlor epoxide A, methoxychlor, di-n-butyl phthalate, di-n-octyl phthalate were not detected in all sample. Maximum concentrations of SVOCs detected were not exceeded the EPA guidelines in any of the samples.

A similar study was conducted in Nakdong-River,

in which SVOCs were not detected.<sup>14</sup> Although the data on all analytes are limited, the concentrations for DMP, DEP, BBP and DEHP in surface water have been routinely reported from other studies. The total concentrations of DMP, DEP, BBP and DEHP in surface water were comparable to those present other countries; in the Netherlands (nd-5.0  $\mu$ g/L),<sup>15</sup> in North Sea of German (nd-10.2 ng/L),<sup>16</sup> and in China (nd-57.8  $\mu$ g/L).<sup>17</sup> The total concentrations of DMP, DEP, BBP and DEHP in surface water were similar to those obtained from North Sea of German, and 1/10-1/100 lower than those found in the Netherlands and China

The water concentration data of SVOCs were studied to test the applicability of the proposed method across all the procedures. No problem was found in the result of the application of the developed method across all the procedures. This result indicates that the proposed analytical method may be valuable for monitoring SVOCs in surface water.



## 4. Conclusions

In this paper, we examined the analytical parameters critical to the SVOCs liquid extraction method and GC-MS characteristics.

The peak of the SVOCs showed good chromatographic properties using a non-polar column and show a sensitive response for the EI-MS (SIM). For example, the LOQ of hexachlorobenzene was 0.02 ng/L. The method was used to analyze 22 water samples from various regions of Gum-River. The samples taken revealed SVOC concentrations in the range of 0.02-96.8 ng/L. The phthalate concentrations in surface water were similar to those obtained from North Sea of German, and very lower than those found in the Netherlands and China. The method may be valuable for the national monitoring project of SVOC in surface water, waste water, ground water and tap water.

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