Printed in the Republic of Korea
ANALYTICAL SCIENCE & TECHNOLOGY
Vol. 25 No. 1, 39-49, 2012
http://dx.doi.org/10.5806/AST.2012.25.1.039

Simultaneous determination of 37 volatile organic compounds at ng/L concentration level in surface water by HS-SPME-GC/MS

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(Received September 22, 2011; Revised December 14, 2011; Accepted December 16, 2011)

HS-SPME-GC/MS에 의한 지표수에서 ng/L 농도 수준의 37개 휘발성유기화합물의 동시 분석

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(2011. 9. 22. 접수, 2011. 12. 14. 수정, 2011. 12. 16. 승인)

Abstract: A method to detect 37 volatile organic compounds (VOCs) in surface water was described based on headspace solid-phase micro extraction and gas chromatography-mass spectrometry. VOCs in water were vaporized for 30 min at 40 °C in a headspace vial and adsorbed on 85 μm carboxen-polydimethylsiloxane. Under the established condition, the lowest quantification limit was 4.1-96 ng/L by using 4.0 mL water sample, and the relative standard deviation was less than 15% at concentrations of 0.05 and 0.50 μg/L. The detection limits meet lower concentration than 1/10 of the water quality criteria for VOCs established by the US EPA or Germany. The LOQ is a sensitivity which the monitoring for the establishing water quality criteria requires. When the proposed method was used to analyze the target compounds in sixteen surface water samples and total 16 VOCs were detected in surface water samples collected from Gum-River. Maximum concentrations of VOCs detected were not exceeded the EPA or Germany guidelines in any of the samples.

요 약: HS-SPME GC-MS에 의한 지표수 중에 37개 휘발성유기물질을 동시에 분석하는 방법을 개발하였다. 이 방법은 물 중 휘발성유기물질을 헤드스페이스 vial에서 40 °C에서 30분간 가열 85 μm carboxen-polydimethylsiloxane에 흡착시키는 방법이다. 4.0 mL의 물 시료를 사용하여 확립한 조건하에서 정량한계는 4.1-96 ng/L의 범위를 나타냈고 이러한 검출한계는 US EPA 또는 독일에서 확립한 준거치의 1/10 이하 값을 만족시켰으며 0.05 μg/L와 0.50 μg/L의 농도에서 정밀도는 15% 이내를 보

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였다. 이 정량한계는 준거치를 결정하기 위한 조사연구에서 요구하는 최소 감도이다. 확립한 방법을 사용하여 금강물 16개 시료를 분석한 결과 16개 휘발성유기화합물이 검출되었으며 측정값은 US EPA 또는 독일에서 확립한 준거치 이하의 값을 보였다.

Key words: volatile organic compounds, surface water, headspace solid-phase micro extraction, gas chromatography-mass spectrometry

1. Introduction

Volatile organic compounds (VOCs) are organic chemicals that have a high vapor pressure at room-temperature conditions. According to the European Union,[1] VOC is any organic compound having an initial boiling point less than or equal to 250 measured at a standard atmospheric pressure of 101.3 kPa. VOCs are common contaminants found in surface water. The most commonly known VOCs are halogenated volatile organic compounds (HVOCs), chlorinated short-chain hydrocarbons (CHCs) and monocyclic aromatic hydrocarbons. They are currently used in a wide variety of industries as degreasers, solvents or chemical intermediates, and are also part of gasoline and fuels. Many VOCs are dangerous to human health or cause harm to the environment.

Many methods for the detection of VOCs in water have been reported, such as gas chromatography[2-7] and gas chromatography mass spectrometry (GC-MS).[8-27] The most effective way for determination of VOCs is by using GC-MS due to its higher confirmatory potential. Sample preparation may largely influence the sensitivity and accuracy of measurements due to the physico-chemical properties of VOCs. Several sample introduction modules were coupled to GC-MS to improve the measurement quality, such as purge and trap (P&T),[8-10] static headspace,[11-13] direct aqueous injection[14] or solid-phase microextraction (SPME).[15-27] SPME is an attractive and advantageous sample preparation method in environmental analysis due to somehow fast and simple sample preparation procedure. Using SPME, the extraction of VOCs from the sample can be done by direct immersion (DI) or by exposing the fiber to the headspace (HS) of the sample. Headspace is discriminatory in nature since only the VOCs in the injection vials can be transferred to the GC system while non-volatile interference will remain in the headspace injection vials. Although DI-SPME is the more widely used technique for semivolatile compounds, HS-SPME is more appropriate for VOCs, especially when they are dirty or complex matrices.

The monitoring for the establishing water quality criteria generally requires lower detection limit than 1/10 value of the water quality criteria for VOCs established by the US EPA or other advanced nations. A sensitive method is needed, which meets the above conditions.

The present study aimed to develop a HS-SPME GC-MS method to detect of 37 VOCs in surface water and to apply the method to real sample analysis. This paper focuses on the validation of sample preparation and detection methodology.

2. Materials and Methods

2.1. Materials

All organic solvents used were HPLC grade. Sodium chloride, VOC standards (methyl chloride, methyl bromide, acrolein, 1,1-dichloroethylene, 1,2-trans-dichloroethylene, 1,1,1-trichloroethane, 1,1-dichloroethane, benzene, acrylonitrile, cis-1,2-dichloroethylene, TCE, PCE, chloroform, toluene, 1,2-dichloropropane, 1,2-dichloroethane, Ethylbenzene, m-xylene, p-xylene, o-xylene, dichlorobromomethane, epichlorohydrin, chlorobenzene, styrene, 1,1,2-trichloroethane, chlorodibromomethane, N-butylbenzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene, broboform, 1,3-dichloropropylene, 1,1,2,2-tetrabromoethane, 1,2-dichlorobenzene, hexachlorobutadiene, 1,2,4-trichlorobenzene, 1,2-dibromo-3-chloropropane, naphthalene), fluorobenzene and d4-1,2-dichlorobenzene as internal standards were obtained from Sigma-

Aldrich (St. Louis, MO, USA). Commercially available SPME fibers (100 μm polydimethylsiloxane (PDMS), 65 μm polydimethylsiloxane-divinylbenzene (PDMS-DVB), 85 μm polyacrylate (PA), and 85 μm carboxen-polydimethylsiloxane (CAR-PDMS) fused-silica fibers) were purchased from Supelco (Bellefonte, PA, USA).

2.2. Apparatus

The analytical instruments used were an Agilent 6890 A gas chromatograph with a split/splitless injector (Agilent Technologies, Santa Clara, CA, USA) and Agilent 5973 N mass spectrometer (Agilent Technologies, Santa Clara, CA, USA). Combipal Autosampler (Agilent Technologies, Santa Clara, CA, USA), which allows automated HS-SPME injections, were used. The ion source was operated in the electron ionization mode (EI; 70 eV). Full-scan mass spectra (m/z 30-400) were recorded for analyte identification. An HP-InnoWax capillary column (60 m × 0.25 mm I.D. × 0.25 μm film thickness) was used. Samples were injected in the splitless mode. The flow rate of helium as a carrier gas was 1.0 mL/min. The injector temperature was set at 210 °C. The oven temperature programs were set as follows. The initial temperature of 35 °C was held for 3 min and then increased to the final temperature of 220 °C at 8 °C/min. The ions selected by SIM were as shown in *Table* 1.

2.3. SPME fibers

CAR-PDMS fused-silica fiber was evaluated for the VOCs detection. The fiber was initially conditioned according to the instructions of the manufacturer to remove contaminants and to stabilize the solid-phase. Conditioning was carried out in an extra split/splitless port with helium carrier gas prior to each adsorption.

2.4. Extraction/derivatization procedures

Surface water samples were collected from 16 basins in the Gum River without headspace in 40 mL VOC bottles containing 1 drop of 2 M HCl. The sampling sites were selected to uniformly represent all streams of the River. A volume of 4 mL sample of water were placed in a 10 mL vial. 40 μL of d4-1,2-dichlorobenzene (0.01 mg/L) as the internal standards and 0.5 g of sodium chloride were add to the sample, and vial was sealed with a septum lined cap.

The extraction was performed with a 85 μm carboxen-polydimethylsiloxane (CAR/PDMS) fiber and using magnetic stirring at 600 rpm. The fiber was conditioned prior to the first use with the temperature and conditioning recommendations described by the manufacturer. Before extraction, the vial was pre-heated for 5 min at 50 °C; then, the fiber was placed into the headspace of the vial and extraction was carried out for 30 min at 40 °C. After the sorption process, the SPME fiber was immediately desorbed at 280 °C for 5 min on the GC injection port.

2.5. Calibration and quantification

Calibration curves were established by adding standard solutions and internal standard solutions in a control water (a surface water). Sodium chloride (0.5 g) were added to the solutions. The corresponding concentrations of the standards were in the range of 0.01-5.0 μg/L. The ions selected for quantification were as in Table 1. The ratios of the VOC peak areas to the peak area of internal standard (fluorobenzene for analytes below retention time 15.6 min or d4-1,2-dichlorobenzene for analytes above retention time 18.1 min) were used to quantify the compound .

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

3. Results and Discussion

3.1. Condition of SPME fibers

Four SPME fibers (PDMS, PDMS-DVB, PA and CAR-PDMS) were evaluated to select a suitable fiber for detecting the VOCs. The adsorption efficiencies on the SPME fibers were evaluated by comparing the areas of the VOC peaks. The highest efficiency was obtained using 85 μm carboxen-polydimethyl-siloxane (CAR-PDMS) among the four fibers, and

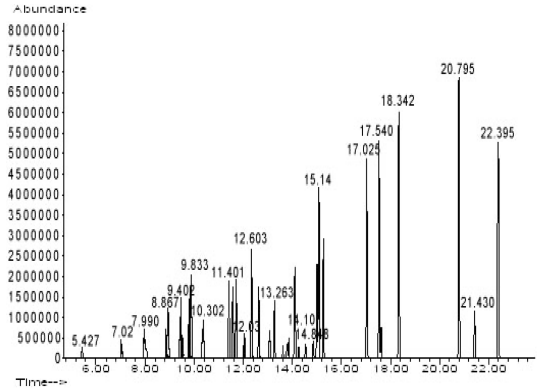

Fig. 1. GC-MS chromatogram from spiked water sample (methyl chloride 5.101 min, methyl bromide 5.212 min, acrolein 5.319 min, 1,1-dichloroethylene 5.427 min, 1,2-trans-dichloroethylene 7.02 min, 1,1,1-trichloroethane 7.09, 1,1-dichloroethane 7.078 min, benzene 7.990 min, acrylonitrile 8.021 min, cis-1,2-dichloroethylene 8.867 min, TCE 8.893 min, PCE 9.422 min, chloroform 9.402 min, toluene 9.833 min, 1,2-dichloropropane 9.873 min, 1,2-dichloroethane 10.302 min, ethylbenzene 11.401 min, m-xylene 11.564 min, p-xylene 11.721 min, o-xylene 12.630 min, dichlorobromomethane 12.03 min, epichlorohydrin 12.138 min, chlorobenzene 13.263 min, styrene 14.10 min, 1,1,2-trichloroethane 14.126 min, chlorodibromomethane 14.848 min, N-butylbenzene 15.14 min, 1,3-dichlorobenzene 17.025 min, 1,4-dichlo-robenzene 17.540 min, broboform 17.527 min, 1,3-dichloropropylene 17.630 min, 1,1,2,2,-tetrabromoethane 17.673 min, 1,2-dichlorobenzene 18.336 min, hexachlorobutadiene 18.342 min, 1,2,4-trichlorobenzene 20.795 min, 1,2-dibromo-3-chloropropane 21.430 min, naphthalene 22.395 min).

CAR-PDMS was selected as a fiber suitable for detecting VOCs. The adsorption efficiencies on the PDMS-DVB, the PDMS and the PA were 90, 85 and 37% compared to that of CAR-PDMS. The heating temperature and time of VOCs were 30 min at 40, which were somewhat modified values of the conditions established by Park or Ezquerro.[28,29]

3.2. Chromatography

The optimum conditions were applied to the analysis of the VOCs. *Fig.* 1 shows a GC-MS chromatogram of the VOCs. For the GC separation of all VOCs, the use of a semi-polar stationary phase (InnoWax) was found to be efficient. VOCs 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.

Table 1. The quantification ions and qualification ions of VOCs

Compounds	Quantification ion	Qualification ions
Methyl chloride	50	52
Methyl bromide	94	96
1,1-Dichloroethylene	61	96, 98
1,2-trans-Dichloroethylene	61	96, 98
1,1,1-Trichloroethane	97	99, 61
1,1-Dichloroethane	63	65
Benzene	78	77
cis-1,2-Dichloroethylene	61	96, 98
Trichloroethylene	130	132, 95
Tetrachloroethylene	166	164, 129
Chloroform	83	85
Toluene	91	92
1,2-Dichloropropane	63	62, 76
1,2-Dichloroethane	62	64, 49
Ethylbenzene	91	106, 92
m-Xylene	91	106, 105
p-Xylene	91	106, 105
o-Xylene	91	106, 105
Dichlorobromomethane	83	85, 129
Chlorobenzene	112	114, 77
Styrene	104	103, 78
1,1,2-Trichloroethane	97	83, 61
Chlorodibromomethane	129	127, 131
N-Butylbenzene	91	92, 134
1,3-Dichlorobenzene	146	148, 111
1,4-Dichlorobenzene	146	148, 111
Bromoform	173	171, 175
1,3-Dichloropropylene	75	77, 110
1,1,2,2,-Tetrabromoethane	266	264, 185
1,2-Dichlorobenzene	146	148, 111
Hexachlorobutadiene	225	227, 223
1,2,4-Trichlorobenzene	180	182, 145
1,2-Dibromo-3-chloropropane	157	155, 75
Naphthalene	128	127, 102
Acrylonitrile	53	52, 51
Acrolein	56	55
Epichlorohyrin	57	49

3.3. Validation of the assay

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 HS-SPME

Table 2. The detection limits of VOCs in water and water quality criteria suggested by USEPA and other advanced nations

Compounds	Unit	LOD	LOQ	WQC	WQC/10
Methyl chloride	μg/L	2.1	6.9		3.0
Methyl bromide	μg/L	1.9	6.2		4.7
1,1-Dichloroethylene	μg/L	0.0024	0.0078	5.7×10^{-2}	5.7×10^{-3}
1,2-trans-Dichloroethylene	μg/L	0.0021	0.0065	7.0×10^{2}	7.0×10^{1}
1,1,1-Trichloroethane	μg/L	0.0013	0.0041	2.0×10^{2}	2.0×10^{1}
1,1-Dichloroethane	μg/L	0.0064	0.0210	5.7×10^{-1}	5.7×10^{-2}
Benzene	μg/L	0.0087	0.0280	2.2	0.22
cis-1,2-Dichloroethylene	μg/L	0.0056	0.0180	70	7.0
Trichloroethylene (TCE)	μg/L	0.0061	0.0190	2.5	0.25
Tetrachloroethylene (PCE)	μg/L	0.0057	0.0180	0.63	0.063
Chloroform	μg/L	0.0057	0.0180	5.7	0.57
Toluene	μg/L	0.0129	0.0410	6.8×10^{3}	6.8×10^{2}
1,2-Dichloropropane	μg/L	0.0044	0.0140	5.0×10^{-1}	5.0×10^{-2}
1,2-Dichloroethane	μg/L	0.0033	0.0100	3.8×10^{-1}	3.8×10^{-2}
Ethylbenzene	μg/L	0.0193	0.0610	3.1*	0.31*
m-Xylene	μg/L	0.0205	0.0650	2.0*	0.2*
p-Xylene	μg/L	0.0155	0.0490	2.0*	0.2*
o-Xylene	μg/L	0.0302	0.0960	2.0*	0.2*
Dichlorobromometane	μg/L	0.0063	0.0200	0.55	0.055
Chlorobenzene	μg/L	0.0041	0.0130	1.3×10^{2}	1.3×10^{1}
Styrene	μg/L	0.0028	0.0090	100	10
1,1,2-Trichloroethane	μg/L	0.0036	0.0110	0.6	0.06
Chlorodibromomethane	μg/L	0.0050	0.0160	0.4	0.04
N-Butylbenzene	μg/L	0.0018	0.0057	-	-
1,3-Dichlorobenzene	μg/L	0.0022	0.0070	3.2×10^{2}	3.2×10^{1}
1,4-Dichlorobenzene	μg/L	0.0046	0.0150	6.14*	0.64*
Bromoform	μg/L	0.0060	0.0190	4.3	0.43
1,1,2,2-Tetrabromoethane	μg/L	0.0027	0.0087	-	-
Hexachlorobutadiene	μg/L	0.0022	0.0070	0.44	0.044
1,2,4-Trichlorobenzene	μg/L	0.0023	0.0075	8.73*	0.873*
1,2-Dibromo-3-chloropropane	μg/L	0.0015	0.0047	0.2	0.02
Naphthalene	μg/L	0.0020	0.0064	100	10
1,3-Dichloropropylene	μg/L	0.0017	0.0054	10	1.0
1,2-Dichlorobenzene	μg/L	0.0020	0.0062	2.7×10^{3}	2.7×10^{2}
Acrylonitrile	μg/L	0.0010	0.0040	4.0×10^{-2}	0.0051
Acrolein	μg/L	0.9440	3.0070	1.90×10^{2}	19.0
Epichlorohydrin	μg/L	0.0500	0.1600		3.0

*Suggested by Germany

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

The US Environmental Protection Agency[30] has established water quality criteria for human health for VOCs between 0.057 μg/L and 6800 μg/L as shown in *Table* 2. In Korea, water quality criteria (WQC) for VOCs have not yet been established excepts for benzene and toluene, 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

Table 3. The standard curves and linearities of VOCs in water

Compounds	Unit	Conc. range	Calibration curves	R^2
Methyl chloride	μg/L	5~100	Y=0.0706x+0.0057	0.9993
Methyl bromide	μg/L	5~100	Y=0.9214x+0.0012	0.9966
1,1-Dichloroethylene	μg/L	0.01~0.5	Y=0.0587x+0.0003	0.9970
1,2-trans-Dichloroethylene	μg/L	0.01~0.5	Y=0.0401x+0.0007	0.9955
1,1,1-Trichloroethane	μg/L	0.01~0.5	Y=0.4843x+0.0005	0.9982
1,1-Dichloroethane	μg/L	0.02~0.5	Y=0.046x+0.0006	0.9961
Benzene	μg/L	0.03~0.5	Y=1.0081x-0.0005	0.9977
cis-1,2-Dichloroethylene	μg/L	0.02~0.5	Y=0.1196x-0.0013	0.9979
Trichloroethylene (TCE)	μg/L	0.02~5	Y=0.2043x+0.0171	0.9988
Tetrachloroethylene (PCE)	μg/L	0.02~0.5	Y=1.1521x+0.0067	0.9998
Chloroform	μg/L	0.02~5	Y=0.1987x+0.005	0.9998
Toluene	μg/L	0.05~5	Y=3.9107x+0.2091	0.9994
1,2-Dichloropropane	μg/L	0.01~1	Y=0.6268x+0.0285	0.9951
1,2-Dichloroethane	μg/L	0.01~0.5	Y=0.1302x+0.0017	0.9970
Ethylbenzene	μg/L	0.1~2.0	Y=8.5411x+0.0105	0.9988
m-Xylene	μg/L	0.1~1.0	Y=5.9696x-0.0417	0.9968
p-Xylene	μg/L	0.1~1.0	Y=7.6735x+0.1281	0.9952
o-Xylene	μg/L	0.1~1.0	Y=8.6218x-0.0785	0.9971
Dichlorobromometane	μg/L	0.01~1.0	Y=0.2925x+0.0034	0.9976
Chlorobenzene	μg/L	0.01~0.5	Y=3.4967x+0.0482	0.9990
Styrene	μg/L	0.01~0.5	Y=3.9683x+0.0101	0.9995
1,1,2-Trichloroethane	μg/L	0.01~0.5	Y=0.6902x-0.0023	0.9996
Chlorodibromomethane	μg/L	0.01~0.5	Y=0.3149x-0.0032	0.9966
N-Butylbenzene	μg/L	0.01~0.5	Y=14.037x+0.0692	0.9975
1,3-Dichlorobenzene	μg/L	0.01~0.5	Y=4.3976x+0.0127	0.9990
1,4-Dichlorobenzene	μg/L	0.01~0.5	Y=4.4176x+0.0202	0.9969
Bromoform	μg/L	0.01~0.5	Y=0.0122x+0.0001	0.9913
1,2-Dichlorobenzene	μg/L	0.01~0.5	Y=4.427x+0.0419	0.9958
Hexachlorobutadiene	μg/L	0.01~0.5	Y=1.9288x+0.0169	0.9962
1,2,4-Trichlorobenzene	μg/L	0.01~0.5	Y=3.6679x+0.0192	0.9972
1,2-Dibromo-3-chloropropane	μg/L	0.01~0.5	Y=0.0092x-0.0001	0.9973
Naphthalene	μg/L	0.01~0.5	Y=10.199x+0.1213	0.9977
1,3-Dichloropropylene	μg/L	0.01~0.5	Y=0.196x-0.00004	0.9985
1,1,2,2-Tetrabromoethane	μg/L	0.01~0.5	Y=0.5046x+0.0088	0.9971
Acrylonitrile	μg/L	0.005~0.0.1	Y=1.9415x+0.0019	0.9989
Acrolein	μg/L	5~100	Y=0.3402x-0.0004	0.9981
Epichlorohydrin	μg/L	0.1~5	Y=0.1468x+0.0012	0.9995

1/10 WQC). The LOQs of all VOCs in this study meet lower concentration than 1/10 of the water quality criteria for VOCs established by the US EPA or Germany as shown in *Table* 2.

Examination of the typical standard curve by computing a regression line of the peak area ratios of VOCs to internal standard on the concentration using a least-squares fit demonstrated a linear relationship with correlation coefficient of above 0.99. The line of best fits for VOCs are as in *Table* 3.

The precision and accuracy of the assay were very good, as shown in *Table* 4. For five independent determinations at the concentration range of 0.05-0.5 μg/L, the relative standard deviation was less than 15%.

3.4. River sample analysis

Table 4. Intra-day laboratory precision and accuracy results for the analysis of VOCs in water (n=5)

Compounds	Spiked Conc. (μg/L)	Calculated Conc. Mean ± SD (μg/L)	Accuracy (%)	Precision (%)
Methyl chloride	10	10.22±0.751	102.2	7.4
	50	49.83±3.400	99.6	6.8
Methyl bromide	10	10.39±0.928	103.6	8.9
	50	49.98±1.671	96.9	3.4
1,1-Dichloroethylene	0.05	0.046±0.003	92	8.6
	0.5	0.453±0.028	90	6.3
1,2-trans-Dichloroethylene	0.05	0.048±0.003	96	6.0
	0.5	0.468±0.028	94	6.3
1,1,1-Trichloroethane	0.05	0.049±0.004	97	7.6
	0.5	0.495±0.022	99	4.4
1,1-Dichloroethane	0.05	0.051±0.005	101.2	10.4
	0.5	0.500±0.040	100	8.1
Benzene	0.1	0.096±0.007	96	7.6
	0.5	0.479±0.013	96	2.8
cis-1,2-Dichloroethylene	0.05	0.050±0.0026	101	5.3
	0.5	0.468±0.036	94	7.9
TCE	0.05	0.055±0.0047	112	8.5
	0.5	0.485±0.020	97	4.2
PCE	0.05	0.049±0.004	98	7.6
	0.5	0.479±0.019	96	4.1
Toluene	0.1	0.093±0.013	94	13.7
	0.5	0.532±0.023	106	4.5
Ethylbenzene	0.1	0.104±0.010	104	9.8
	0.5	0.470±0.032	94	6.9
m-Xylene	0.1	0.105±0.008	105	8.1
	0.5	0.523±0.040	104	7.6
p-Xylene	0.1	0.108±0.010	108	9.7
	0.5	0.507±0.011	102	2.2
o-Xylene	0.1	0.088±0.009	88	10.2
	0.5	0.477±0.018	95	3.9
Chloroform	0.05	0.048±0.001	97	2.3
	0.5	0.481±0.016	96	3.3
1,2-Dichloropropane	0.05	0.048±0.001	97	2.4
	0.5	0.500±0.034	100	6.8
1,2-Dichloroethane	0.05	0.048±0.004	96	9.2
	0.5	0.484±0.018	98	3.8
Dichlorobromometanee	0.05	0.044±0.004	88	9.6
	0.5	0.475±0.031	95	6.7

We used the proposed method to analyze the target VOCs in sixteen surface water samples. No interfering peak was observed in the chromatograms near the retention times of analytes due to discriminatory nature of SPME. Total 16 VOCs were detected in surface water samples collected from Gum River in

Table 4. Continued

Compounds	Spiked Conc. (μg/L)	Calculated Conc. Mean ± SD (μg/L)	Accuracy (%)	Precision (%)
1,3-Dichloropropylene	0.05	0.048±0.003	97	7.0
	0.5	0.510±0.034	102	6.7
Chlorobenzene	0.05	0.053±0.004	106	8.2
	0.5	0.518±0.010	104	2.0
Styrene	0.05	0.055±0.008	112	14.5
	0.5	0.511±0.041	102	8.1
1,1,2-Trichloroethane	0.05	0.054±0.003	107	5.8
	0.5	0.500±0.039	100	8.0
Chlorodibromomethane	0.05	0.046±0.004	93	9.3
	0.5	0.482±0.021	96	4.4
N-Butyl benzene	0.05	0.055±0.0078	110	14.2
	0.5	0.493±0.011	98	2.2
1,3-Dichlorobenzene	0.05	0.056±0.006	112	10.8
	0.5	0.528±0.024	105.7	4.6
1,4-Dichlorobenzene	0.05	0.056±0.006	113	11.4
	0.5	0.526±0.025	105.4	4.9
Bromoform	0.05	0.055±0.005	111	9.3
	0.5	0.483±0.029	96	6.1
1,1,2,2-Tetrabromoethane	0.05	0.056±0.004	112	6.8
	0.5	0.498±0.023	99	4.8
1,2-Dichlorobenzene	0.05	0.046±0.003	93	7.7
	0.5	0.494±0.019	98	4.0
Hexachlorobutadiene	0.05	0.049±0.005	98	10.6
	0.5	0.492±0.013	98	2.7
1,2,4-Trichlorobenzene	0.05	0.044±0.004	89	9.5
	0.5	0.477±0.010	95	2.2
1,2-Dibromo-3-chloropropane	0.05	0.045±0.004	90	9.3
	0.5	0.049±0.011	98	2.4
Naphthalene	0.05	0.051±0.001	102	5.3
	0.5	0.519±0.018	104	6.6
Acrylonitrile	0.025	0.024±0.002	96	5.1
	0.1	0.0984±0.009	98.4	8.7
Acrolein	10	9.193±0.386	91.9	4.2
	50	48.7±3.11	97.6	6.4
Epichlorohydrin	10	9.475±0.371	94.8	3.9
	50	51.024±3.723	102.0	7.3

the concentration range and frequency as following: 1,1,1-Trichloroethane (0.01-0.02 μg/L, 19%), benzene (0.06-0.13 μg/L, 100%), TCE (0.02-0.17 μg/L, 25%), PCE (0.02-0.03 μg/L, 13%), chloroform (0.03-1.04 μg/L, 75%), toluene (0.10-0.18 μg/L, 100%), 1,2-dichloropropane (0.06 μg/L, 6%), 1,2-dichloroethane (0.09 μg/L, 6%), ethylbenzene (0.12-1.07 μg/L, 100%), m-xylene (0.12-0.26 μg/L, 100%), p-xylene (0.22-0.34 μg/L, 100%), o-xylene (0.19-0.37 μg/L, 100%), dichlorobromometane (0.02-0.28 μg/L, 50%), styrene

Table 5. Analytical results of VOCs in real sample (unit: μg/L)

Compounds\Sample	1	2	3	4	5	6	7	8
Methyl chloride	ND	ND	ND	ND	ND	ND	ND	ND
Methyl bromide	ND	ND	ND	ND	ND	ND	ND	ND
1,1-Dichloroethylene	ND	ND	ND	ND	ND	ND	ND	ND
1,2-trans-Dichloroethylene	ND	ND	ND	ND	ND	ND	ND	ND
1,1,1-Trichloroethane	ND	0.01	0.02	ND	0.02	ND	ND	ND
1,1-Dichloroethane	ND	ND	ND	ND	ND	ND	ND	ND
Benzene	0.09	0.07	0.06	0.07	0.07	0.07	0.06	0.09
cis-1,2-Dichloroethylene	ND	ND	ND	ND	ND	ND	ND	ND
Trichloroethylene (TCE)	ND	0.17	ND	0.06	0.02	ND	ND	ND
Tetrachloroethylene (PCE)	ND	ND	ND	0.02	0.03	ND	ND	ND
Chloroform	ND	0.61	0.13	0.21	0.14	0.36	1.04	ND
Toluene	0.14	0.18	0.12	0.10	0.10	0.11	0.12	0.10
1,2-Dichloropropane	ND	0.06	ND	ND	ND	ND	ND	ND
1,2-Dichloroethane	ND	ND	ND	ND	ND	0.09	ND	ND
Ethylbenzene	0.12	0.15	0.13	0.14	0.15	0.13	0.12	0.12
m-Xylene	0.15	0.16	0.15	0.15	0.26	0.14	0.14	0.14
p-Xylene	0.25	0.29	0.26	0.27	0.34	0.25	0.26	0.25
o-Xylene	0.21	0.26	0.21	0.25	0.37	0.21	0.21	0.21
Dichlorobromometane	ND	0.11	0.02	0.03	0.03	0.06	0.28	ND
Chlorobenzene	ND	ND	ND	ND	ND	ND	ND	ND
Styrene	ND	0.02	ND	ND	ND	ND	ND	ND
1,1,2-Trichloroethane	ND	ND	ND	ND	ND	ND	ND	ND
Chlorodibromomethane	ND	0.04	0.02	ND	0.04	0.05	0.14	ND
N-Butylbenzene	ND	ND	ND	ND	ND	ND	ND	ND
1,3-Dichlorobenzene	ND	ND	ND	ND	ND	ND	ND	ND
1,4-Dichlorobenzene	ND	ND	ND	ND	ND	ND	ND	ND
Bromoform	ND	ND	ND	ND	ND	ND	ND	ND
1,2-Dichlorobenzene	ND	ND	ND	ND	ND	ND	ND	ND
Hexachlorobutadiene	ND	ND	ND	ND	ND	ND	ND	ND
1,2,4-Trichlorobenzene	ND	ND	ND	ND	ND	ND	ND	ND
1,2-Dibromo-3-chloropropane	ND	ND	ND	ND	ND	ND	ND	ND
Naphthalene	ND	ND	ND	ND	ND	ND	ND	ND
1,3-Dichloropropylene	ND	ND	ND	ND	ND	ND	ND	ND
1,1,2,2-Tetrabromoethane	ND	ND	ND	ND	ND	ND	ND	ND
Acrylonitrile	ND	ND	ND	ND	ND	ND	ND	ND
Acrolein	ND	ND	ND	ND	ND	ND	ND	ND
Epichlorohydrin	ND	ND	ND	ND	ND	ND	ND	ND

(0.01-0.02 μg/L, 19%), chlorodibromomethane (0.02-0.14 μg/L, 63%) and naphthalene (0.01 μg/L, 6%). The results of VOCs are as in *Table* 5.

Some compounds such as benzene, toluene, ethylbenzene, m-xylene, p-xylene and o-xylene were detected in all samples due to originate from gasoline. Maximum concentrations of VOCs detected were not exceeded the EPA guidelines in any of the samples. Especially, VOCs detected in surface showed significantly lower than the EPA or Germany guidelines.[30]

4. Conclusion

In this paper, we present a simple and automatic method to detect VOCs in surface water samples.

Table 5. Continued

Compounds\Sample	9	10	11	12	13	14	15	16
Methyl chloride	ND	ND	ND	ND	ND	ND	ND	ND
Methyl bromide	ND	ND	ND	ND	ND	ND	ND	ND
1,1-Dichloroethylene	ND	ND	ND	ND	ND	ND	ND	ND
1,2-trans-Dichloroethylene	ND	ND	ND	ND	ND	ND	ND	ND
1,1,1-Trichloroethane	ND	ND	ND	ND	ND	ND	ND	ND
1,1-Dichloroethane	ND	ND	ND	ND	ND	ND	ND	ND
Benzene	0.08	0.013	0.08	0.10	0.07	0.07	0.10	0.09
cis-1,2-Dichloroethylene	ND	ND	ND	ND	ND	ND	ND	ND
Trichloroethylene (TCE)	ND	0.06	ND	ND	ND	ND	ND	ND
Tetrachloroethylene (PCE)	ND	ND	ND	ND	ND	ND	ND	ND
Chloroform	0.03	ND	0.09	ND	0.27	0.05	0.11	0.05
Toluene	0.11	0.15	0.10	0.13	0.10	0.10	0.13	0.10
1,2-Dichloropropane	ND	ND	ND	ND	ND	ND	ND	ND
1,2-Dichloroethane	ND	ND	ND	ND	ND	ND	ND	ND
Ethylbenzene	0.12	0.13	1.07	0.12	0.12	0.12	0.13	0.12
m-Xylene	0.15	0.15	0.12	0.14	0.14	0.13	0.15	0.13
p-Xylene	0.26	0.27	0.22	0.24	0.25	0.24	0.28	0.23
o-Xylene	0.21	0.24	0.19	0.21	0.20	0.20	0.25	0.20
Dichlorobromometane	ND	ND	0.06	ND	ND	ND	0.03	ND
Chlorobenzene	ND	ND	ND	ND	ND	ND	ND	ND
Styrene	ND	0.01	ND	ND	ND	ND	0.01	ND
1,1,2-Trichloroethane	ND	ND	ND	ND	ND	ND	ND	ND
Chlorodibromomethane	0.02	0.02	0.04	ND	ND	ND	0.03	0.02
N-Butylbenzene	ND	ND	ND	ND	ND	ND	ND	ND
1,3-Dichlorobenzene	ND	ND	ND	ND	ND	ND	ND	ND
1,4-Dichlorobenzene	ND	ND	ND	ND	ND	ND	ND	ND
Bromoform	ND	ND	ND	ND	ND	ND	ND	ND
1,2-Dichlorobenzene	ND	ND	ND	ND	ND	ND	ND	ND
Hexachlorobutadiene	ND	ND	ND	ND	ND	ND	ND	ND
1,2,4-Trichlorobenzene	ND	ND	ND	ND	ND	ND	ND	ND
1,2-Dibromo-3-chloropropane	ND	ND	ND	ND	ND	ND	ND	ND
Naphthalene	ND	ND	ND	ND	ND	ND	0.01	ND
1,3-Dichloropropylene	ND	ND	ND	ND	ND	ND	ND	ND
1,1,2,2-Tetrabromoethane	ND	ND	ND	ND	ND	ND	ND	ND
Acrylonitrile	ND	ND	ND	ND	ND	ND	ND	ND
Acrolein	ND	ND	ND	ND	ND	ND	ND	ND
Epichlorohydrin	ND	ND	ND	ND	ND	ND	ND	ND

The LOQs of VOCs were significantly lower than the EPA or Germany guidelines, and the accuracy and precision of this method were very good. The relative standard deviation was less than 15%. We used the proposed method to analyze the target VOCs in sixteen surface water samples. Total 16 VOCs were detected in surface water samples collected from Gum-River. Maximum concentrations of VOCs detected were not exceeded the EPA guidelines in any of the samples. We will further use this method to detect VOCs in surface water and perform the risk assessment of the detected compounds.

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