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Simultaneous determination of ultra-trace phenols, polycyclic aromatic hydrocarbons and pesticides in surface water by gas chromatography-mass spectrometry

Young Joon Lee, Jun Bae Lee, Seon Haw Hong, Jin-Aa Oh[1] and Ho-Sang Shin[2,★]

Geum River Environment Research Center, National Institute of Environmental Research, Korea
[1]Department of Environmental Education,
[2]Department of Environmental Science Kongju National University, Kongju, Chung-Nam Do, Korea
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지표수에서 GC-MS에 의한 극미량 페놀류, 다환방향족탄화수소류와 농약류의 동시 분석법

이영준 · 이준배 · 홍선화 · 오진아[1] · 신호상[2,★]

국립환경과학원 금강물환경연구소, [1]공주대학교 환경과학과, [2]공주대학교 환경교육과
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Abstract: A gas chromatography-mass spectrometric (GC-MS) method was developed for determining 17 hazard compounds containing phenols, polycyclic aromatic hydrocarbons and pesticides in surface water. A 1.0 L surface water sample was placed in a separatory funnel and saturated with NaCl, and the solution was extracted with 40 mL of methylene chloride. Under the established condition, the lowest quantification limit was 1.0-10 ng/L and the relative standard deviations were less than 22%. The method was used to analyze 70 surface water samples collected from 35 regions in Gum-River. The samples revealed the compounds concentrations in the range of 1.1-26,604 ng/L. Maximum concentrations of compounds detected were not exceeded guidelines established in other countries. The developed method may be valuable for monitoring hazards in water.

요 약: 지표수 중에 GC-MS에 의한 페놀, 다환방향족탄화수소 및 농약류를 포함한 17 개 유해화합물을 동시에 분석하는 방법을 개발하였다. 1.0 L의 물 시료를 분액깔대기 안에 넣고 NaCl로 포화시킨 다음 40 mL methylene chloride로 추출하였다. 이 방법은 1.0-10 ng/L 범위의 정량한계를 보였고 22% 이내의 정밀도를 보였다. 확립한 방법을 사용하여 35 지역의 금강 물 70 개 시료를 분석한 결과 유해화합물이 1.1-26,604 ng/L의 농도범위로 검출되었으며 측정값은 외국에서 확립한 준거치를 초과하는 값은 없었다. 이 측정방법은 지표수에서 유해화합물에 대한 국가모니터링사업에 사용할 때 효율적인 것으로 판단된다.

Key words: phenols, polycyclic aromatic hydrocarbons, pesticides, gas chromatography-mass spectrometry, surface water

★ Corresponding author
Phone : +82-(0)41-850-8811 Fax : +82-(0)41-850-8811
E-mail : hshin@kongju.ac.kr

1. Introduction

Hazard organic compounds comprise many priority pollutants such as phenols, polycyclic aromatic hydrocarbons (PAHs) and pesticides which are toxic and ubiquitous. PAHs are persistent organic pollutants with well-known carcinogenic and mutagenic effects in humans and wildlife.[1] Pesticides are substances that play a crucial role in pest management; however, it is important to remember that all pesticides should also be considered active poisons. The environmental aspects of these compounds became increasingly important in recent years in Korea and then these have been included on priority pollutant candidates list for human health. In Korea, in order to review water quality criteria (WQC), it may be necessary enough monitoring. The monitoring requires a sensitive and simultaneous analytical method with more low detection limit than the national analytical methods.[2,3]

Many analytical procedures have been proposed for the determination of μg/L levels of phenols in water. Primary techniques currently used for the analysis of analytes in water include liquid-liquid extraction (LLE),[4-7] solid-phase extraction (SPE),[8-16] stir bar sorptive extraction (SBSE)[17] or phase-transfer catalytic extraction[18] combined with high performance liquid chromatography (HPLC),[4,5,8-12] gas chromatography (GC)[13,14] and gas chromatography-mass spectrometry (GC-MS).[6,7,14-18] Major techniques used for the analysis of PAHs in water include LLE,[19,20] SPE,[21-25] SBSE[26] or membrane extraction[27] combined with HPLC,[19-23,26,27] and GC-MS.[24,25] Analytical procedures have been proposed for the determination of trace levels of pesticides in water. Several techniques used for the analysis of pesticides in water include LLE,[28] SPE,[29-31] or direct injection[32] combined with liquid chromatography/tandem mass spectrometry (LC-MS/MS),[28,29,31,32] and GC.[30] Particularly, LC-MS/MS has been utilized widely for the identification and quantitation of pesticides in a variety of water matrices. But these methods need an expensive instrument and have given no solution for the simultaneous determination of ng/L levels of phenols, PAHs and pesticides in water.

This paper describes a LLE procedure to detect ng/L levels of phenols, PAHs and pesticides in water combined with analysis by GC-MS. This paper focuses on the validation of sample preparation and detection methodology. The developed method was used to determine phenols, PAHs and pesticides in surface water samples.

2. Experimental

2.1. Chemicals and reagents

Phenol, 2,4-dimethyl phenol, 2,4,5-trichlorophenol, bromoxynil, captan, chlorothalonil, demeton-O, demeton-S, dimethoate, diuron, ethyl paranitrophenyl phenylphosphorothioate (EPN), furfural, hexazinone, linuron, 2-chloronaphthalene, acenaphthene, fluoranthene, fluorine 2,4,6-tribromophenol, 1-fluoronaphthalene, and terphenyl-d14 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 in 1.0 L glass bottles containing 2 drop of 2 M HCl. Glass bottles were carefully filled just to overflowing, without passing air bubbles through sample. Surface water samples were collected from thirty-five basins in the Gum River, which contain thirteen surface water samples near industry area. The sampling sites were selected to uniformly represent all streams of the River and the sampling time was in June and August 2012.

2.3. Extraction procedure

In a 1.0 L separating funnel, 1.0 L of surface water-sample was placed. 25 μL of phenanthrene-d10 as an internal standard solution (1 mg/L in methanol), 2,4,6-tribromophenol, 1-fluoronaphthalene, and terphenyl-d14 as surrogates (each 1 mg/L in methanol) were added to the solution. The solution 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 mL under a stream of nitrogen gas, and then transferred into a V-shape auto sampler vial. 2 mL sample of the solution was injected into the GC system.

2.4. GC-MS

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% phenyl-methylsilicon, 0.25 mm I.D.×0.25 μm 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 raised to 310 °C at 10 °C/min (held for 15 min). All mass spectra were obtained with an Agilent 5975 B instruments (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 shown in *Table* 1.

Table 1. The quantification and qualification ions of analytes

Compounds	Quantification ions, m/z	Qualification ion, m/z
Furfural	96	95, 67
Phenol	94	66, 65
Diuron	187	189, 124
2,4,5-Trichlorophenol	196	198, 200
2-Chloronaphthalene	162	127, 164
Acenaphthene	153	154, 152
Fluorene	166	165, 163
Demeton-O	88	89, 171
Bromoxynil	277	275, 279
Demeton-S	88	60, 170
Dimethoate	87	93, 125
Chlorothalonil	266	264, 268
Linuron	61	187, 248
Fluoranthene	202	200, 203
Captan	79	149, 77
Hexazinone	171	83, 71
EPN	157	185, 141

2.5. Calibration and quantification

Calibration curves for the analytes 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 (phenamthrene-d10) to 1.0 L of surface water, which undetected analytes. 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 of the analytes. *Fig.* 1 and *Fig.* 2 show GC-MS chromatograms of the analytes. For the GC separation of the analytes, the use of a nonpolar stationary phase was found to be efficient. The analytes showed sharp peaks, and the compound was quantified as integration of peak area. The retention times of analyte standards and internal standards are shown in *Fig.* 1 and 2. No extraneous peak was observed in the chromatograms near the retention times of the 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 limit of detection (LOD) and limit of quantification (LOQ) in this study were shown in *Table* 2. The LOD and LOQ were defined by 3.14 times and 10.0 times respectively, the standard deviation for replicate determination (n=7) from samples spiked at the concentration of 1.0-10.0 ng/L in surface water. The combination of a high yield and the high sensitivity of the analytes by GC-MS (SIM) permit the sensitive detection of the analytes.

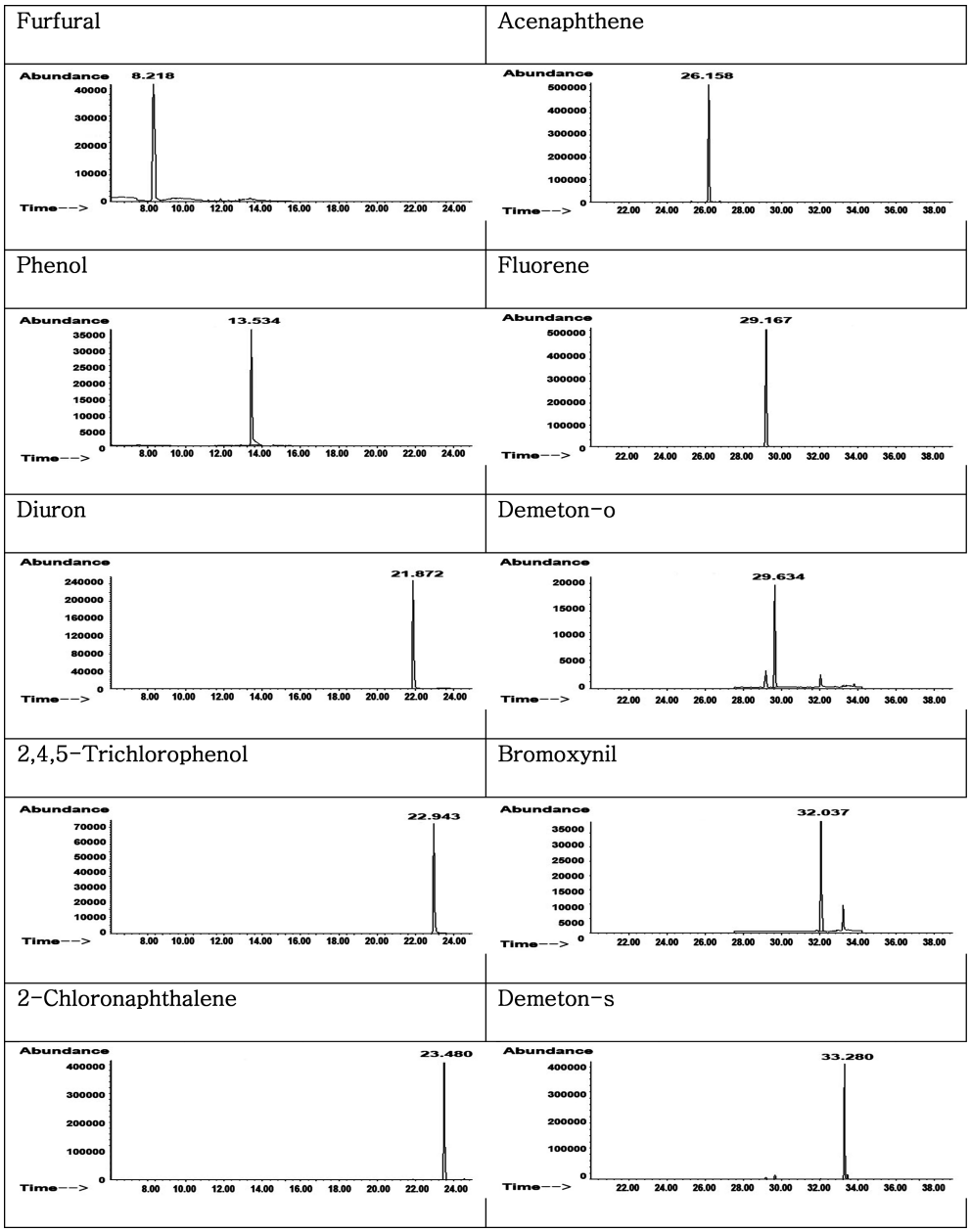

Fig. 1. GC-MS chromatogram of the extract from water sample spiked in the concentration of 1.0-200.0 ng/L (furfural: 8.218 min, phenol: 13.534 min, diuron: 21.872 min, 2,4,5-trichlorophenol: 22.943 min, 2-chloronaphthalene: 23.480 min, acenaphthene: 26.158 min, fluorene: 29.167, demeton-O: 29.634 min, bromoxynil: 32.037min, demeton-S: 33.280 min).

In Korea, water quality criteria (WQC) for the analytes have not yet been established, but they may be necessary to review water quality criteria after enough monitoring and risk assessment. 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 analytes in this study meet 0.1 times lower concentration than the water quality

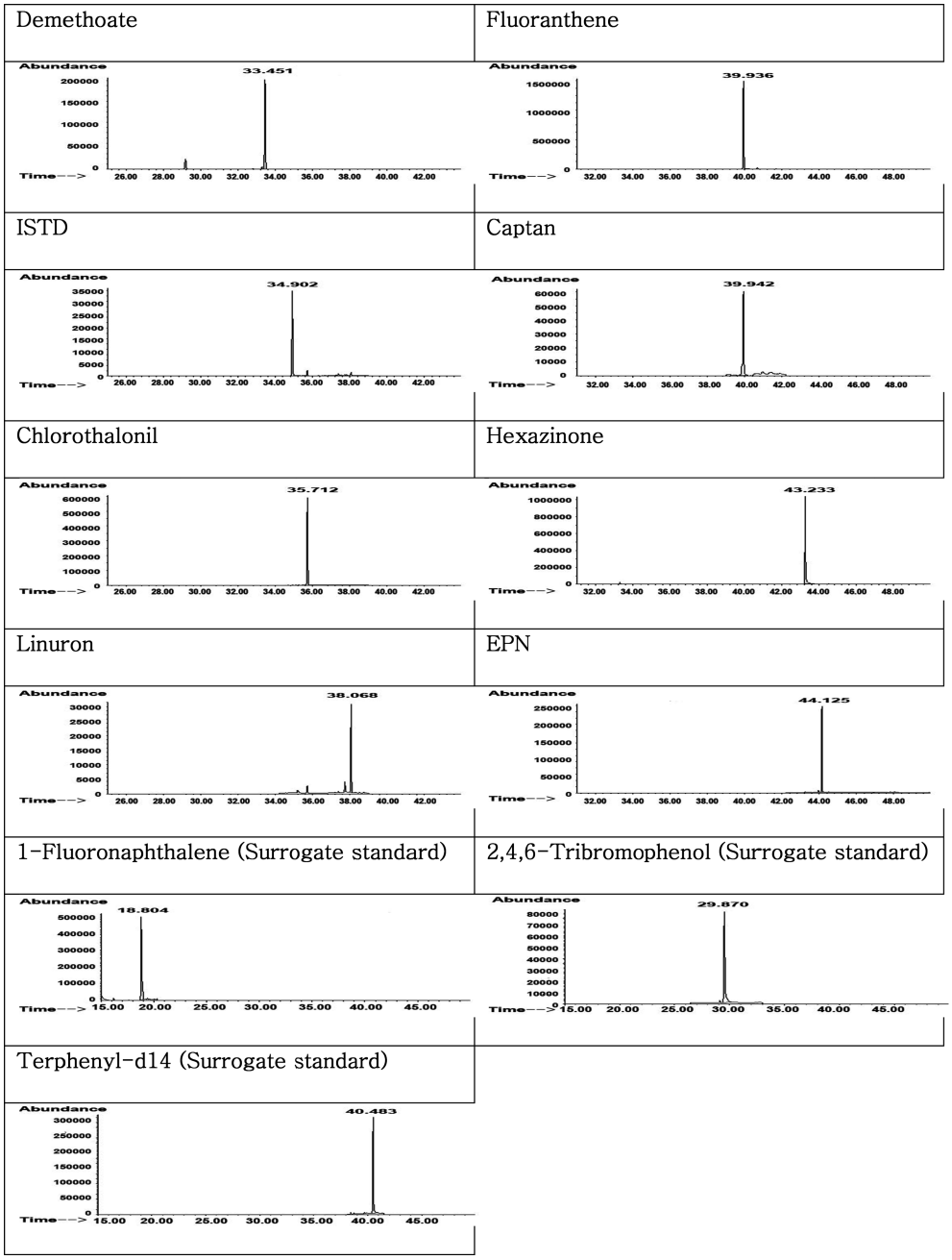

Fig. 2. GC-MS chromatogram of the extract from water sample spiked in the concentration of 1.0-200.0 ng/L (dimethoate: 33.451, ISTD: 34.902 min, chlorothalonil: 35.712 min, linuron: 38.068 min, fluoranthene: 39.936 min, captan: 39.942 min, hexazinone: 43.233 min, EPN: 44.125 min, 1-Fluoronaphthalene(SS): 18.804, 2,4,6-Tribromophenol(SS): 29.870 min, Terphenyl-d14(SS): 40.483 min).

criteria for analytes established by the other countries such as Australia, Newzealand, Germany, Netherlands, Canada and United States of America.

3.3. Calibration curve and linearity

Examination of typical standard curve by computing a regression line of peak area ratios of

Table 2. The detection limits and calibration curves of analytes in water (ng/L)

Compounds	LOD	LOQ	Linear equation	r^2
Acenaphthene	0.45	1.43	y=34.49x+0.0012	0.9996
Fluoranthene	0.34	1.08	y=81.96x+0.0159	0.9988
2,4,5 Trichloro phenol	1.14	3.63	y=3.870x-0.0038	0.9996
2-Chloro naphthalene	1.23	3.90	y=42.67x-0.0999	0.9996
Diuron	1.53	4.86	y=26.42x+0.1181	0.9990
Fluorene	0.35	1.13	y=42.03x+0.0827	0.9988
Chlorothalonil	1.45	4.63	y=30.56x+0.0197	0.9991
Furfural	3.00	9.54	y=4.645x-0.0148	0.9995
Phenol	3.01	6.39	y=2.357x+0.0169	0.9982
Demeton-O	2.42	7.72	y=3.706x+0.0148	0.9993
Bromoxynil	2.29	7.30	y=0.8047x-0.0006	0.9999
Dimethoate	2.94	9.36	y=9.226x-0.0274	0.9999
Linuron	1.89	6.03	y=5.115x+0.0260	0.9997
Demeton-S	2.67	8.52	y=18.83x-0.0976	0.9998
Captan	3.07	9.79	y=4.236x-0.0077	0.9992
Hexazinone	1.78	5.66	y=39.63x-0.1792	0.9998
EPN	2.90	9.25	y=8.835x-0.1189	0.9984

Table 3. Recovery test results for the analysis of analytes in water (n=5)

Compounds	Unit	Spiked conc	Mean recovery ± SD (RSD%)
Acenaphthene	μg/L	0.01	98±16.3 (16.6)
		0.05	89±16.7 (18.7)
Fluoranthene	μg/L	0.01	105±13.1 (12.5)
		0.05	91±10.5 (11.5)
2,4,5 Trichlorophenol	μg/L	0.05	105±16.1 (15.3)
		0.25	88±12.3 (14.0)
2-Chloronaphthalene	μg/L	0.05	92±11.6 (12.60
		0.25	103±11.1 (10.8)
Diuron	μg/L	0.05	85±12.2 (14.3)
		0.25	91±17.7 (19.5)
Fluorene	μg/L	0.05	111±8.4 (7.5)
		0.25	86±12.3 (14.3)
Chlorothalonil	μg/L	0.05	100±12.9 (12.9)
		0.25	97±12.8 (13.2)
Furfural	μg/L	0.1	89±10.7 (12.0)
		0.5	95±15.4 (16.2)
Phenol	μg/L	0.1	105±10.8 (10.2)
		0.5	99±10.3 (10.4)
Demeton-O	μg/L	0.1	97±7.9 (8.2)
		0.5	82±15.0 (18.3)
Bromoxynil	μg/L	0.1	89±8.7 (9.7)
		0.5	96±12.7 (13.1)
Dimethoate	μg/L	0.1	94±18.2 (19.5)
		0.5	97±11.5 (11.9)
Liuron	μg/L	0.1	87±8.2 (9.4)
		0.5	101±10.2 (10.1)
Demeton-S	μg/L	0.1	83±8.1 (9.8)
		0.5	106±10.8 (10.2)
Captan	μg/L	0.1	112±9.1 (8.1)
		0.5	97±7.9 (8.1)
Hexazinone	μg/L	0.1	89±12.7 (14.2)
		0.5	114±11.2 (9.8)
EPN	μg/L	0.1	97±14.9 (15.4)
		0.5	113±6.9 (6.1)
1-Fluoronaphthalene (surrogate)	ng/L	25	90±14.0 (15.5)
2,4,6 Tribromophenol (surrogate)	ng/L	25	91±9.0 (9.9)
Terphenyl-d14 (surrogate)	ng/L	25	107±13.3 (12.4)

analytes on concentration using a least-squares fit demonstrated a linear relationship with correlation coefficients of above 0.998. The line of best fits for analytes are described in *Table* 2.

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

Compounds	Unit	Spiked conc	Mean ± SD	Accuracy (%)	Precision (%)
Acenaphthene	μg/L	0.01	0.011±0.0001	110	7.9
		0.05	0.054±0.004	108	8.1
Fluoranthene	μg/L	0.01	0.011±0.0003	96	8.6
		0.05	0.047±0.008	94	18.0
2,4,5 Trichlorophenol	μg/L	0.05	0.047±0.009	94	18.9
		0.25	0.22±0.03	89	14.0
2-Chloronaphthalene	μg/L	0.05	0.046±0.007	91	15.6
		0.25	0.25±0.04	102	15.9
Diuron	μg/L	0.05	0.043±0.003	85	7.4
		0.25	0.22±0.02	90	9.5
Fluorene	μg/L	0.05	0.054±0.001	109	1.9
		0.25	0.27±0.01	108	2.9
Chlorothalonil	μg/L	0.05	0.050±0.007	99	14.6
		0.25	0.27±0.01	107	2.6
Furfural	μg/L	0.1	0.11±0.01	109	10.3
		0.5	0.50±0.07	100	13.0
Phenol	μg/L	0.1	0.10±0.02	102	16.1
		0.5	0.48±0.04	95	8.2
Demeton-O	μg/L	0.1	0.11±0.02	107	14.2
		0.5	0.52±0.09	103	17.2
Bromoxynil	μg/L	0.1	0.10±0.02	97	21.9
		0.5	0.54±0.05	108	9.7
Dimethoate	μg/L	0.1	0.11±0.02	106	14.3
		0.5	0.51±0.07	102	13.7
Liuron	μg/L	0.1	0.11±0.02	110	14.4
		0.5	0.55±0.05	111	8.6
Demeton-S	μg/L	0.1	0.10±0.01	97	13.1
		0.5	0.52±0.06	103	11.4
Captan	μg/L	0.1	0.11±0.01	107	11.4
		0.5	0.58±0.02	116	3.3
Hexazinone	μg/L	0.1	0.11±0.01	107	10.0
		0.5	0.56±0.09	113	15.1
EPN	μg/L	0.1	0.09±0.01	91	14.4
		0.5	0.51±0.05	103	9.7

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 phenols, PAHs and pesticides in water. SPE was initially considered to replace LLE, but problems such as reproducibility, sorption capacity and interfering impurities in case of simultaneous determination of the various types-analytes reduce the attractiveness of SPE. Also, these methods need a long time for loading and eluting for the determination of ng/L levels of analytes in water. Therefore, LLE was performed for analysis of analytes in water.

Several samples at the concentration of 0.01 and

0.05 μg/L were prepared and the relative recovery was calculated by percentage of the analytes recovered. As a result, the recoveries of the analytes were values between 82 and 114% as shown in *Table* 3.

3.5. Precision and accuracy

The reproducibility of the assay was very good. For five independent determinations in the concentration of 0.01 and 0.05 μg/L, the accuracy was in the range of 85-116%, and the precision was less than 22% (*Table* 4).

3.6. Water analysis

We used the proposed method to analyze the target analytes in 70 surface water samples. The concentrations of 6 hazardous compounds were detected in surface water samples collected from Gum-River: Acenaphthene (1.4-4.8 ng/L), fluoranthene (1.1-22.0 ng/L), diuron (13.0 ng/L), fluorene (1.1-173.6 ng/L), phenol (10.0-26,604 ng/L) and dimethoate (3,405.7 ng/L). 2,4,5-Trichlorophenol, 2-chloronaphthalene, chlorothalonil, furfural, demeton-O, demeton-S, bromoxynil, linuron, captan, hexazinone and EPN were not detected in all sample.

A similar study was not conducted in Korea. The concentrations of phenols, PAH_S and pesticides in environmental water were comparable to those present in other countries. Phenol was detected in the concentration range of nd-35.0 μg/L in China,[4] 12.9-15.5 μg/L in Iran,[5] and nd-20.0 μg/L in Germany.[17] PAHs were detected in the concentration range of nd-0.8 μg/L in Brazil,[20] and nd-0.03 μg/L in Taiwan.[24] Diuron was detected in the concentration of 0.6 μg/L in Spain.[29] The total concentrations of phenol in environmental water were similar to those obtained from Iran and Germany, and a little lower than those found in China. The total concentrations of PAH_S in environmental water were similar to those obtained from Brazil and a little higher than those found in Taiwan. The concentration of diuron detected in this study was 1/60 lower than that found in Spain.

The water concentration data of the analytes 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 phenols, PAHs and pesticides in surface water.

4. Conclusions

In this paper, we examined the analytical parameters critical to liquid extraction method of phenols, PAHs and pesticides from surface water and their GC-MS characteristics. The peak of the analytes showed good chromatographic properties using a non-polar column and show a sensitive response for the EI-MS (SIM). For example, the LOQ of fluoranthene was 1.08 ng/L. The method was used to analyze 35 water samples from various regions of Gum-River. The samples taken revealed analyte concentrations in the range of 1.1-2,660 ng/L. The phenol, PAHs, and diuron concentrations in surface water were similar to those obtained from Iran, German and Brazil, and very lower than those found in the China and Spain. 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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