Talanta 97 (2012) 432–437

Contents lists available at SciVerse ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Use of flat-sheet membrane extraction with a sorbent interface for solvent-free determination of BTEX in water

Hekap Kim*, Seyoung Kim, Soohyung Lee

Department of Environmental Science, College of Natural Sciences, Kangwon National University, 192-1 Hyoja 2-dong, Chuncheon, Kangwon-do 200-701, Republic of Korea

ARTICLE INFO

Article history:
Received 6 March 2012
Received in revised form
27 April 2012
Accepted 30 April 2012
Available online 14 May 2012

Keywords:
Flat-sheet membrane extraction
Silicone membrane
Sorbent interface
Volatile organic compounds

ABSTRACT

An analytical method for solvent-free determination of benzene, toluene, ethylbenzene, and xylenes (BTEX) in water using flat-sheet membrane extraction with a sorbent interface (MESI) coupled to GC–MS was established by optimizing the flow rates of the donor (20 ml water) and acceptor (helium) phases and extraction temperature. BTEX compounds permeated through a nonporous silicone membrane and evaporated into the acceptor phase were purged into a cryofocusing trap (−30 °C) with helium gas. Enriched compounds were thermally desorbed into a capillary gas chromatograph and detected with a mass spectrometer. The optimum flow rates of the donor and acceptor phases were set at 1.5 and 55 ml min^{-1}, respectively, and the temperature of the membrane extraction module was maintained within the 28–30 °C range. The method as established showed low method detection limits (MDLs: ~0.1 μg l^{-1}) and highly linear calibration curves ($r^2 > 0.998$) for all of the four compounds. High repeatability (relative standard deviation < ~5%) and a reasonably high extraction recovery (62–78%), after a single pass of the sample through the extraction module, also were established. Further, the method's high compatibility with the purge and trap (P&T) method indicates its applicability to field measurement. Other advantages include rapidity, simplicity, and a ready extendibility to automated on-line monitoring.

1. Introduction

Benzene, toluene, ethylbenzene, and xylenes (BTEX) are volatile organic compounds (VOCs) that can cause adverse health effects such as chromosome aberrations, cancer, and damage to the liver, kidneys, eyes, and central nervous system [1]. These compounds are formed from the combustion of wood and fuels, industrial paints, degreasing agents, aerosols, and solvents.

Conventional analytical methods for determination of VOCs (including BTEX) in water require, prior to chromatographic separation and detection, discrete sample preparation steps including extraction, purification, and enrichment [2]. Liquid–liquid extraction (LLE), solid-phase extraction (SPE), purge and trap (P&T), and headspace extraction [3–5] are the most commonly employed methods, but are costly, time-consuming, and often lead to loss of analytes during sample preparation.

Other solvent-free methods, for example solid-phase microextraction (SPME) [6], stir bar sorptive extraction (SBSE) [7], and membrane extraction (ME) [2,8], recently have been developed, and many attempts have been made to establish them for the purposes of environmental analyses.

The application of ME technology to VOC analysis using a flat-sheet membrane (FSME) has a relatively long history that dates to the 1980s. Both passive [9,10] and active [11–15] sampling methods have been applied. Practical applications to environmental measurement or monitoring have proved elusive however, probably due to the long analytical time incurred by long sampling times (1 h to several days) for passive sampling, low enrichment factors for a limited volume of samples, or the unsatisfactory linearity of calibration curves.

In efforts to overcome these shortcomings, hollow-fiber membrane extraction (HFME) has been attempted for VOC analysis since the 1990s [16–18]. This method has an advantage over FSME in that it can generate a larger surface area for contact with water, resulting in higher extraction efficiency and shorter extraction times. However, HFME modules normally cannot be repeatedly used: hollow-fiber membranes, lacking mechanical durability, need to be replaced after a single or several uses. Alternatively, for the addition of mechanical strength, an SPME hollow-fiber-coated copper wire was prepared and used in combination with headspace sampling [19]. Hauser et al. [20] used both ME methods in combination with stirring of aqueous samples, and optimized extraction temperature, stirring speed, and salt-addition extraction conditions for quantifications as low as the 0.1 μg l^{-1} level. However, these methods require mechanical agitation of aqueous samples for efficient contact with the matrix or for evaporation of analytes into the headspace, mostly by employing magnetic stirring. Application of membrane extraction to VOC analysis using both FSME and HFME was recently reviewed [21].

* Corresponding author. Tel.: +82 33 250 8577; fax: +82 33 251 3991.
E-mail addresses: kimh@kangwon.ac.kr, hekapkim@hotmail.com (H. Kim).

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http://dx.doi.org/10.1016/j.talanta.2012.04.058

FSME, however, remains a promising technology in that the extraction efficiency and enrichment factors can be improved by varying some operating parameters such as the flow rates of the water sample (donor phase) and/or stripping gas (acceptor phase), and extraction temperature. Additionally, the extraction module, typically composed of stainless steel and a flat-sheet membrane, can be used for a relatively long time, the membrane being located between two halves of a solid support and mechanically strong. In addition, the flat-sheet membrane is cheap and readily available on the market. Enrichment of analytes prior to chromatographic separation and detection, moreover, can be elevated by repeated sample extractions through the extraction module [22].

Various membrane materials have been tested for their applicability to the analysis of hydrophobic VOCs such as BTEX. Nonporous polymeric membranes, for example, silicone rubber [15,23] and silicone polycarbonate copolymer [5,10,12,13] were found to be appropriate. A donor phase flow rate through the extraction module of 5 or 10 ml min^{-1} was arbitrarily chosen; other flow rates for improvement of extraction efficiency were not fully investigated. Pervaporation (permeation and vaporization) of analytes can be increased by varying the flow rates of the donor and acceptor phases. A sorbent interface is usually located between the extraction module and the gas chromatographic system (the so-named membrane extraction with a sorbent interface, or MESI) in order to enrich VOCs transferred from the extraction module [11–13,24]. Analytes are then thermally desorbed and transferred to the gas chromatographic system for quantitative determination.

The present study aimed to establish a method for determination of BTEX in water using a flat-sheet MESI coupled to GC–MS, specifically by optimizing the flow rates of the donor and acceptor phases, along with the extraction temperature. A single pass of the donor phase through the extraction module, using the established method, resulted in sufficiently high extraction recovery and reproducibility for low-ppb-level analysis.

2. Materials and methods

2.1. Reagents and materials

Five standard compounds (benzene, toluene, ethylbenzene, *o*-xylene, and *p*-xylene) and fluorobenzene (internal standard) were purchased from Supelco (Bellefonte, PA). Methanol was purchased from Burdick & Jackson (Morristown, NJ). Standard water samples, which were used for method validation tests, were prepared in methanol and included the five standard compounds noted above. A nonporous silicone membrane (83 μm thick, TI-8075) was purchased from Taejin Chemical (Gimpo, Gyeonggi-do, Korea) and used for the extraction of the compounds. Tenax-TA (60/80 mesh, Supelco) was packed in the cryofocusing trap for enrichment of the BTEX transferred from the extraction module.

2.2. Description of overall system

The extraction module (Fig. 1-A) employed in all of the tests was based on the design introduced in our previous study [22]. The body of the module, composed of stainless steel, incorporates donor and acceptor channels separated by a silicone membrane. The volume of the groove in the half-cell is 1.2 ml, and the surface area of the groove in contact with either the donor or the acceptor is 8.15 cm^2.

The overall analytical system is comprised of the three components shown in Fig. 1-B: (a) sampling and extraction; (b) focusing and desorption; and (c) separation and detection. The extraction module is connected to the thermal desorber (KnR, Seongnam, Gyeonggi-do, Korea), where cryogenic focusing (−30 °C) and thermal desorption (300 °C) of analytes are carried out. The desorbed analytes are then conveyed through a column of the GC and detected by the MS (7890 A GC/5975C MS: Agilent Technologies, Inc., Santa Clara CA).

2.3. Membrane extraction

Twenty (20) ml aqueous standard solutions were analyzed in all of the tests. Because extraction efficiency varies with temperature [11,25], the extraction module was placed in a container that was maintained between 28 and 30 °C. The flow rates of the acceptor (He gas) and donor (water) phases were optimized for efficient extraction by running 5 μg l^{-1} standard solutions. Four different flow rates (45, 50, 55, and 60 ml min^{-1}) of the acceptor phase were tested while the flow rate of the donor phase was set at 2 ml min^{-1}. After the optimum flow rate of the acceptor phase was established, three different flow rates (1, 1.5, and 2 ml min^{-1}) of the donor phase were evaluated. These donor-phase flow rates were precisely controlled by means of a diaphragm pump (STEPDOS® 08, KNF, Switzerland). Upon completion of the initial extraction, the focused

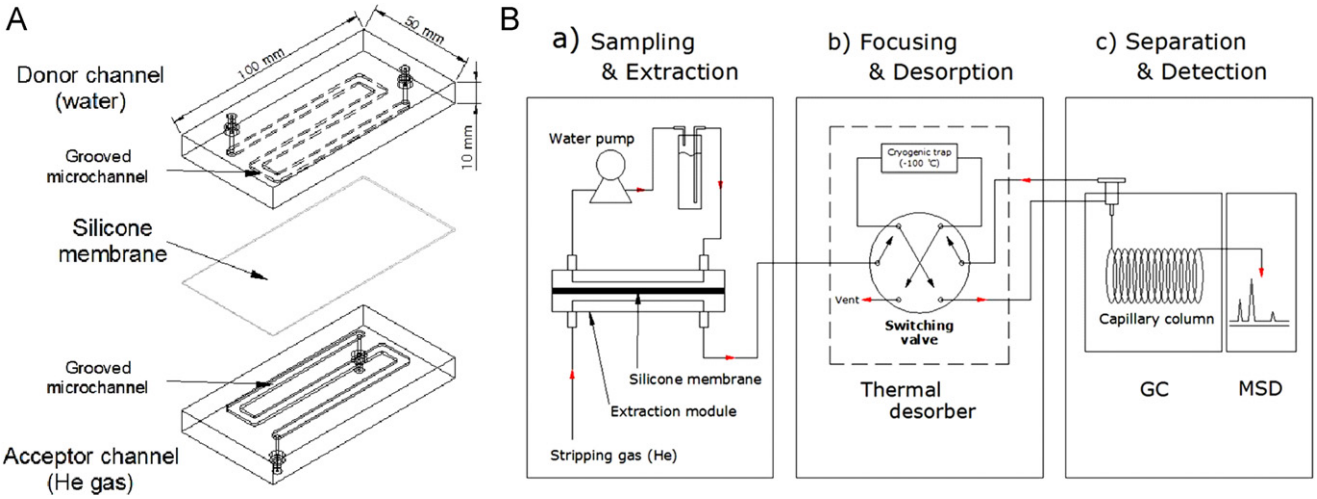

Fig. 1. Schematic diagram of the tested flat-sheet membrane extraction module (A) and the three-component analytical system (B): (a) sampling and extraction, (b) focusing and desorption, (c) separation and detection.

analyte was analyzed using GC–MS. The drained aqueous solution was then returned to the sample container for further extraction and analysis. This operating cycle was repeated five more times (for a total of 6 runs).

2.4. Analytical conditions

The cryofocusing trap containing 30 mg of Tenax® was cooled to −30 °C to enrich the analytes. For subsequent thermal desorption, the trap was heated to 300 °C at a rate of 4.5 °C s^{-1} and maintained at that temperature for 10 min. The desorbed analytes were then injected into the GC–MS at a split ratio of 20:1 while the injector temperature was maintained at 200 °C. The analytical column used was an HP-5 (30 m length × 0.25 mm i.d. × 0.5 μm film thickness; Hewlett Packard, Palo Alto, CA). The oven temperature was programmed as follows: remaining at 45 °C for 1 min; increasing to 100 °C at 7 °C min^{-1}; increasing to 250 °C at 30 °C min^{-1} and remaining at that temperature for 10 min. The temperatures of the MS ion source and transfer line were 230 and 280 °C, respectively. Quantitative determination of each analyte (*m*/*z* 77 and 78 for benzene; 77 and 91 for toluene; and 77, 91 and 106 for ethylbenzene and the xylenes) was conducted in the selective ion monitoring (SIM) mode.

2.5. Method validation

Seven-point linear calibration curves were drawn for the individual BTEX compounds (in the 0.5–25 μg l^{-1} concentration range) after the peak area for each compound was normalized by that for fluorobenzene as the internal standard (10 μg l^{-1} in water).

The method detection limits (MDLs) were determined with reference to seven replicated measurements, according to the US EPA method [26]. The analytical reproducibility of the established method was evaluated after calculating the RSDs (%) of the seven replicated measurements for two concentrations (5 and 20 μg l^{-1}). The extraction recovery (%) for each analyte was tested at the 5 μg l^{-1} level.

To determine how much of each compound remains in the silicone membrane after a single run (memory effect), He alone was flown through the extraction module without the donor phase. This test was carried out at three concentrations: 2, 10, and 20 μg l^{-1}.

2.6. Comparison with P&T method

The current method was compared with the P&T method developed by the US EPA [27]. For this purpose, seven-point linear calibration curves were drawn using the P&T method over the same range as the membrane extraction method. Tests for recovery and reproducibility were carried out and MDLs were determined.

2.7. Application to field samples

For validation of the developed method for field applicability, five lake-water samples were collected in 40 ml amber glass vials (without headspace) from five locations in Euam Lake (Chuncheon, Korea). Twenty milliliters of each sample was analyzed for BTEX using following both the established MESI method and the P&T method. The results obtained by the two methods were compared for compatibility.

3. Results and discussion

In the present study, flat-sheet membrane extraction was coupled to a GC–MS through cryofocusing and thermal desorption. Although the extraction efficiency of the analytes increased with temperature, 28–30 °C was determined to be the optimum in this system, as higher temperatures (35, 40, and 45 °C) increased the pressure inside the extraction module (due probably to water evaporation), thereby interfering with the flow of the acceptor phase from certain time points (11, 9, and 6 min for 35, 40, 45 °C, respectively).

The salt effect on extraction recovery also was studied, using 0, 5, 10, and 20% (w/v) NaCl solution. A test showed that the extraction efficiency decreased with increased salt concentrations for all of the compounds. Similar results were obtained for dichloromethane and toluene [17], and BTEX [28] in previous studies, where hollow fiber membrane extraction was applied. This salting-in effect can be attributed to the change in the physical properties of the extraction membrane in the interface of aqueous and gaseous phases [28], giving rise to the reduction in

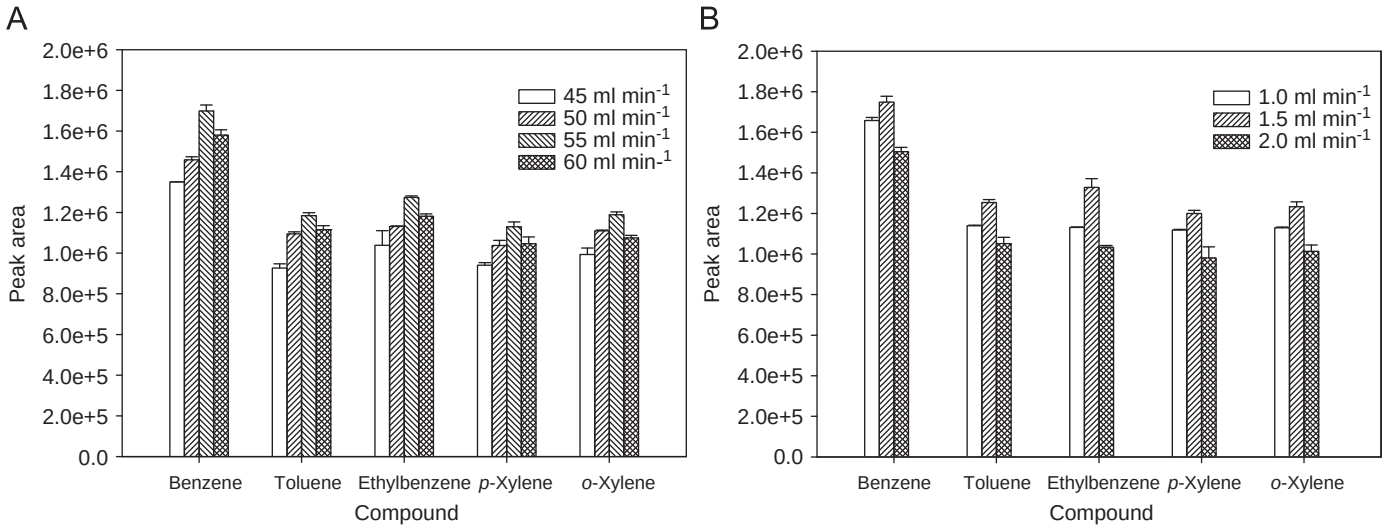

Fig. 2. (A) Optimization of the flow rate of the acceptor phase using 5 μg l^{-1} aqueous standard when the flow rate of the donor phase was 2 ml min^{-1} (n=2). The flow rate of 55 ml min^{-1} showed the highest peak area. (B) Optimization of the flow rate of the donor phase using 5 μg l^{-1} aqueous standard when the flow rate of the acceptor phase was 55 ml min^{-1} (n=2). The flow rate of 1.5 ml min^{-1} showed the highest peak area.

the diffusion rates of the analytes. Thus, no salt was added in further tests.

3.1. Optimum flow rates of donor and acceptor phases

Fig. 2-A shows the variations of the peak areas with varying flow rates of the acceptor phase at a fixed flow rate of the donor phase (2 ml min^{-1}). It is apparent that 55 ml min^{-1} is the optimum condition for the tested system. At this flow rate, the flow rates of the donor phase were compared at three levels, and 1.5 ml min^{-1} was found to show the highest response among the three conditions (Fig. 2-B). Accordingly, the flow rates of the donor and acceptor phases were set at 1.5 and 55 ml min^{-1}, respectively.

In our previous study, the flow rates of the donor and acceptor phases were set at 10 and 20 ml min^{-1}, respectively, without establishing any other conditions [22]. Under these conditions, the recoveries, ranging from 54–78% for all of the compounds, were reasonably satisfactory. This result represents a great improvement over the authors' previous study, which obtained poor results for ethylbenzene and the xylenes (~4–11%). Extraction recovery was greatly improved by lowering the flow rates of the donor phase.

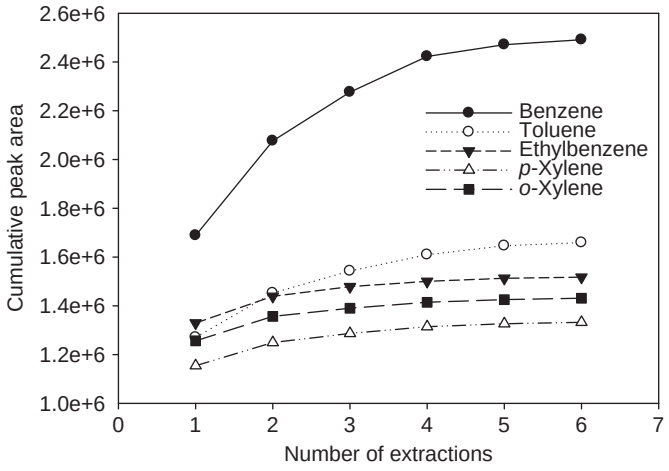

Fig. 3. Plot of cumulative peak areas versus the number of extractions for respective compounds.

3.2. Optimum number of extractions

Using the set flow rates of the donor and acceptor phases, a standard solution (5 μg l^{-1}) was repetitively analyzed by returning the analyzed sample to the sample container. Thereafter, cumulative peak areas after successive runs were calculated and plotted against the number of extractions (Fig. 3). Although the peak areas for individual compounds increased logarithmically with the extraction number, only a single extraction was chosen for further tests, owing to the fact that a single extraction alone gave rise to a satisfactory recovery, and repetitive extractions, furthermore, require significant analysis time (14 min for each extraction) and tedious work.

3.3. Method validation

3.3.1. Calibration curves

Seven-point calibration curves using the flat-sheet MESI method are drawn in Fig. 4-A. As is clear, the coefficients of determination (r^2) for benzene, toluene, ethylbenzene, *p*-xylene, and *o*-xylene were highly linear, ranging from 0.9987 to 0.9996. Calibration curves for the P&T method also were prepared for comparison with the flat-sheet MESI method, and were found to be highly linear in the same concentration ranges, with r^2 values from 0.9979 to 0.9993 (Fig. 4-B).

These r^2 values are higher than those reported by Köller et al. [15], who used an extraction module composed of four flat-sheet silicone membranes (r^2 values: 0.965 for benzene; 0.991–0.996 for toluene and the *o*,*m*-xylenes), whereas they are comparable to those (0.9954–1.000) of Hauser and Popp [18], who used hollow-fiber silicone membranes to extract BTEX compounds.

The lower slopes in the calibration curves for the P&T method can be attributed to the fact that extraction recovery for the internal standard (fluorobenzene) is higher than that for the flat-sheet MESI. Hence, the ratio of the analyte peak area to the internal standard peak area was lower with the P&T method.

3.3.2. Method detection limits (MDLs)

The MDLs for benzene, toluene, ethylbenzene, *p*-xylene, and *o*-xylene were estimated to be 0.097, 0.12, 0.12, 0.13, and 0.12 μg l^{-1}, respectively (Table 1). These values are close to those for the P&T method, which ranged from 0.082 μg l^{-1} for benzene to 0.10 μg l^{-1} for toluene (Table 1).

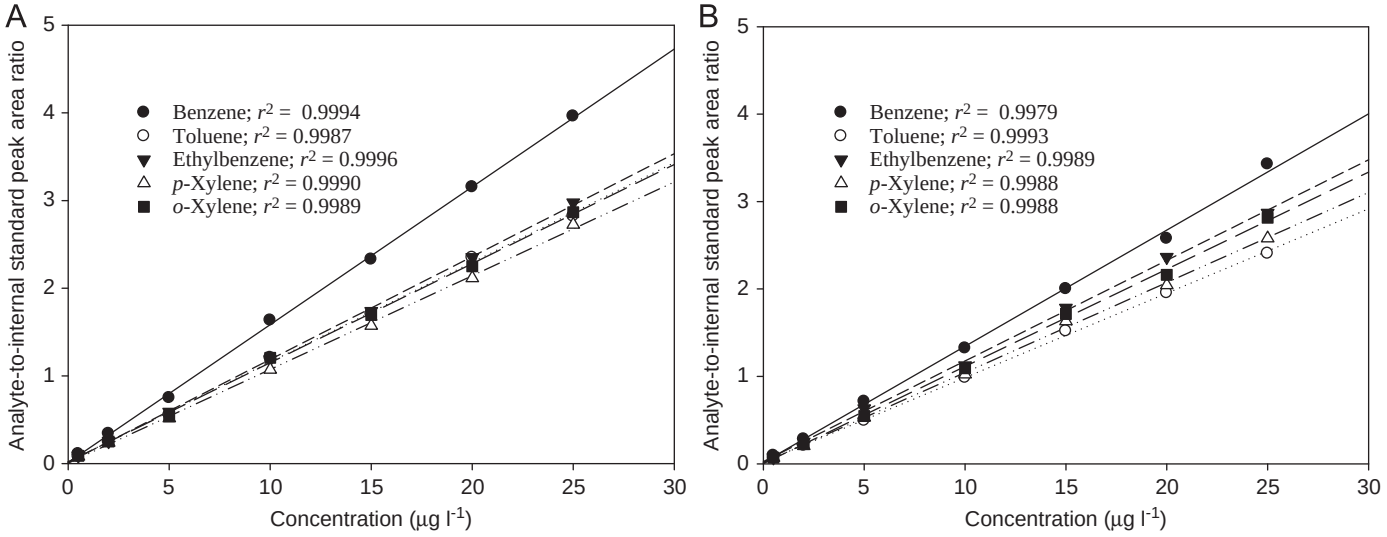

Fig. 4. Comparison of calibration curves for flat-sheet MESI (A) and P&T (B) methods.

The MDLs ($\sim$0.1 $\mu g\,l^{-1}$) for the current method are much lower than those for the authors' previous method [22], which ranged from 0.2 $\mu g\,l^{-1}$ for benzene to 1.8 $\mu g\,l^{-1}$ for *o*-xylene. Notably, the MDLs for ethylbenzene and the xylenes were approximately 12-to-15-fold improved. These values, in fact, are similar to those from the FSME [15] and the HFME [18,24] methods. The established method, therefore, can effectively determine whether BTEX concentrations in drinking water comply with the US EPA's maximum contaminant levels (MCLs), which are 5, 1000, 700, and 10000 $\mu g\,l^{-1}$ for benzene, toluene, ethylbenzene, and the total xylenes, respectively.

3.3.3. Accuracy, precision, and memory effect

For the level (5 $\mu g\,l^{-1}$) tested, the current method showed, for all of the BTEX compounds, reasonable recoveries ranging between 62 and 78%. These values are lower than those ($>$90%) for the P&T method, but nonetheless are relatively high, considering that only a single pass of a water sample through the extraction module was made. Higher extraction recovery can be achieved through repeated extractions [22]. When two and three successive extractions were applied, the recoveries were improved, ranging from 66 (*m,p*-xylenes) to 89% (toluene) and from 68 (*m,p*-xylenes) to 95% (toluene), respectively. Despite the improvement of the cumulative recoveries, particularly for toluene and benzene, a single extraction was enough for common BTEX analysis, and thus was chosen for field application. Hence, by simply optimizing the flow rates of the donor and acceptor phases, recovery could be greatly increased.

The analytical reproducibility of the current method was very high for the 5 and 20 $\mu g\,l^{-1}$ levels, with RSD values ranging from 3.4 to 5.5%; these are comparable to those for the P&T method (3.5–5.4%), and are great improvements compared with the authors' previously reported results (2.2–10%) [22].

The memory effects for all of the BTEX compounds were very low, ranging from 0.04 to 0.13%, indicating that the carryover of these compounds from the immediately previous run was negligible. This probably resulted from the significantly longer time

Table 1
Comparison of method detection limits (MDLs), extraction recoveries, reproducibility, and sample preparation time for benzene, toluene, ethylbenzene, and xylenes (BTEX) between flat-sheet membrane extraction with a sorbent interface (MESI) and purge and trap (P&T) methods.

Compound	MDLs ($\mu g\,l^{-1}$)		Extraction recovery (%)		Reproducibility (RSD%)			Sample preparation time (min)	
	MESI	P&T	MESI	P&T	Conc. ($\mu g\,l^{-1}$)	MESI	P&T	MESI	P&T
Benzene	0.097	0.082	64.8	93.7	5	4.1	4.4	14[a]	21[b]
					20	3.4	4.0		
Toluene	0.12	0.10	77.9	92.6	5	3.7	4.6		
					20	4.6	3.5		
Ethylbenzene	0.12	0.090	63.5	91.6	5	4.1	5.0		
					20	4.9	4.1		
p-Xylene	0.13	0.098	62.1	90.9	5	4.5	5.4		
					20	3.7	4.2		
o-Xylene	0.12	0.094	67.5	91.5	5	5.5	4.5		
					20	4.1	4.8		

[a] Time needed for membrane extraction prior to the enrichment of the analytes in the cryofocusing trap.
[b] Sum of time needed for gas sparging of a sample with helium gas (11 min), dry purging for the removal of water from the sorbent trap (6 min), and thermal desorption into the cryofocusing trap (4 min).

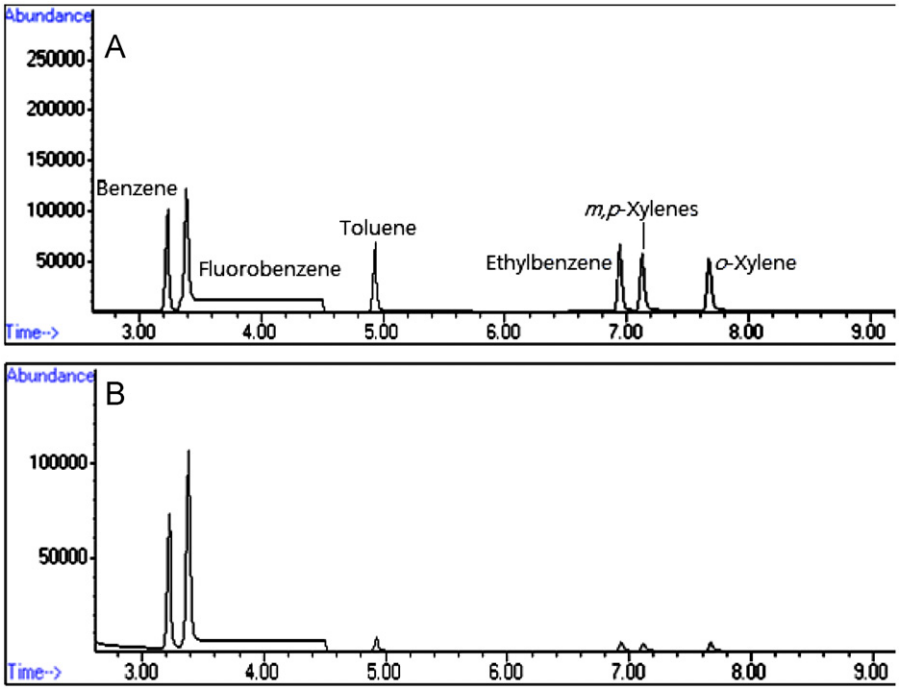

Fig. 5. Chromatograms for an aqueous 5 $\mu g\,l^{-1}$ standard solution (A) and a water sample (B).

Table 2
Concentrations ($\mu g\,l^{-1}$) of BTEX in field samples and relative percent differences (RPD, %) between flat-sheet MESI and P&T methods.

Sample ID	Benzene			Toluene			Ethylbenzene			*p*-Xylene			*o*-Xylene		
	MESI	P &T	RPD	MESI	P &T	RPD	MESI	P &T	RPD	MESI	P &T	RPD	MESI	P &T	RPD
A	4.38	4.45	1.56	0.975	1.02	4.02	0.675	0.659	2.41	0.531	0.556	4.57	0.569	0.590	3.70
B	1.26	1.33	5.92	0.979	1.02	4.24	0.756	0.796	5.10	0.692	0.712	2.88	0.687	0.705	2.68

(14 min) required for purging the analytes in the acceptor phase using a relatively high He flow rate (55 ml min^{-1}).

3.4. Application to field samples

Fig. 5-A shows a gas chromatogram for an aqueous standard solution containing 5 $\mu g\,l^{-1}$ of each of the five compounds. Fig. 5-B shows a chromatogram for lake-water sample A. Among the five samples, only two samples (A and B) showed BTEX concentrations above the MDLs (Table 2). The samples were also analyzed by the P&T method, after which the concentrations measured with the two methods were compared (Table 2) by calculating the relative percent differences (RPDs) between the values. Although the BTEX concentrations were low, the RPDs, ranging from 1.6 to 5.9%, were low for all of the compounds. This is additional confirmation that the current method, offering the advantages of simplicity and rapidity, can be used as an effective alternative to the P&T method. Furthermore, this system can be easily automated for the purposes of both laboratory measurement and field monitoring of BTEX in water. A few fully automated on-line monitoring devices already have been developed by KnR (a firm working in cooperation with the authors), and are scheduled for installation at surface-water monitoring stations in Korea.

4. Conclusions

An analytical method for determination of BTEX in water using flat-sheet nonporous silicone membrane extraction coupled to GC–MS was established. The optimum temperature range for extraction was 28–30 °C. The flow rates of the donor and acceptor phases in the extraction module were important parameters for extraction efficiency; 1.5 and 55 ml min^{-1}, respectively, were found to be optimum. The method showed relatively high accuracy (recovery: 62–78%) and precision (RSD < 5%) for a single extraction, as well as a utility for quantification at low $\mu g\,l^{-1}$ levels (MDL 0.1 $\mu g\,l^{-1}$). Comparison of the current method with the P&T method using both lab and field sample tests showed good consistency between them. The extraction module was highly durable and could be used, repeatedly, more than 100 times. Moreover, in runs under the established conditions, permeation of water through the membrane was not a problem. In summary, this method can be extensively applied to both automated continuous on-line field monitoring and automated laboratory measurement of BTEX.

Acknowledgment

This study was supported by the Center for Aquatic Ecosystem Restoration (CAER) of the Ministry of Environment (MOE, Republic of Korea)'s Eco-STAR Project.

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