

Solvent-free determination of BTEX in water using repetitive membrane extraction followed by GC-MS

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반복적인 막 추출과 GC-MS를 이용한 물 중 BTEX의 분석

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Abstract: An analytical method for solvent-free determination of benzene, toluene, ethylbenzene, and xylenes (BTEX) in water using repetitive membrane extractions coupled to cryofocusing and GC-MS was derived. BTEX compounds that permeated through a nonporous silicone membrane from the aqueous phase and evaporated into the acceptor phase were purged into a cryofocusing trap (-100 °C) with helium gas. The BTEX compounds, thus enriched in the trap, were thermally desorbed into a capillary column GC and detected using an MS. The flow rate of the donor phase (30 mL water) was set at 10 mL/min, and membrane extractions, accomplished by returning the water drained from the extraction module to the sample container, were repeated three times at 20 ± 2 °C. Although recoveries (%) were variable, from the highest for benzene (approximately 80%) to the lowest for ethylbenzene and xylenes (3.5-10%), the method showed satisfactory precision (RSD 2.2-10%) with good-linearity calibration curves (r^2 0.9976-0.9997 in 1-100 µg/L range) for all of the compounds. The method detection limits (MDLs) ranged from 0.16 to 1.8 µg/L. The results showed the method's advantages such as short analysis time and overall simplicity without solvent compared to the conventional techniques.

요 약: 용매를 사용하지 않고 반복적으로 막 추출한 후 저온농축과 GC-MS로 물 중 BTEX를 분석하는 방법을 시도하였다. 물로부터 비공성막의 silicone 막을 투과한 BTEX를 He 기체를 통해 -100 °C의 저온 농축장치로 보낸 후 열 탈착과 GC-MS로 분석하였다. 물 시료(30 mL)는 10 mL/min로 흘려주었고, 한 번 추출된 시료는 다시 되돌려서 두 번 더 추출하였다. Benzene에 대한 회수율은 가장 높아 약 80%인 반면에, ethylbenzene과 xylenes에 대한 회수율은 3.5-10%로 낮은 편이었다. 그렇지만, RSD는 모두 10% 미만 이었고 검량선의 직선성(r^2)도 0.9976-0.9997로 높은 편이었으며, 방법검출한계도 1.8 µg/L 이었다. 이 방법은 짧은 추출 시간, 용매의 미사용 및 분석의 편의성의 장점을 갖고 있다.

Key words : BTEX, cryofocusing, GC-MS, repetitive membrane extractions, nonporous silicone membrane

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1. Introduction

Volatile organic compounds (VOCs) in water can have adverse effects in both humans and the environment. Conventional quantitative analyses of VOCs require discrete sample preparation steps including extraction, purification, and enrichment, prior to chromatographic separation and detection.¹ Liquid-liquid extraction (LLE), solid-phase extraction (SPE), purge and trap, and headspace extraction²⁻⁴ have been commonly used. These methods, however, are costly and time-consuming, and often lead to loss of analytes during sample preparation. Recently developed solvent-free alternative techniques are solid-phase microextraction (SPME),⁵ stir bar sorptive extraction (SBSE),⁶ and membrane extraction (ME),^{1,7} of which many environmental applications have been attempted.

ME technology, for example, has been applied to VOC analysis using flat-sheet membrane extraction (FSME) since the 1980s. Both passive^{8,9} and active¹⁰⁻¹³ sampling methods have been tested. However, the methods have not yet been practically applied to environmental measurement or monitoring, probably due to the long analysis time necessitated by the long sampling duration (1 hour to several days) for passive sampling⁴, the low-enrichment factors for low-volume samples, or the unsatisfactory linearity of calibration curves.¹²

Hollow-fiber membrane extraction (HFME), studied and trialed since the 1990s, represents an attempt to tackle FSME's drawbacks.¹⁴⁻¹⁶ HFME, compared with FSME, can generate a larger water-contact surface area, affording higher extraction recovery and shortening the extraction time. Still, HFME modules have been widely used either: those are not sufficiently durable over repeated applications, and to be replaced after several or even a single use.

Both HFME and FSME recently have been evaluated in a review of membrane extraction for VOC analysis.¹⁷ FSME, despite its disadvantages relative to HFME, remains a promising technology in that its extraction recovery and enrichment factors can be improved by optimizing operation parameters such as sample flow rate, stripping gas flow rate, and extraction

temperature. Additionally, FSME's extraction module, consisting usually of two stainless steel or acrylic plastic plates with a flat-sheet membrane in between, can be used repetitively. Moreover, the flat-sheet membrane is cheap and readily available on the market. Enrichment of analytes can be elevated prior to chromatographic analysis by repetitive extraction from the aqueous phase using the extraction module.

Among the various membrane materials tested for their applicability to the study of hydrophobic VOCs, nonporous polymeric membranes composed of silicone rubber^{13,18} and silicone polycarbonate copolymer^{4,9,11,12} have proved to be appropriate for benzene, toluene, ethylbenzene, and xylenes (BTEX) and halogenated hydrocarbon analysis. The flow rate through the extraction module in the donor phase was set at either 5 or 10 mL/min. Pervaporation (permeation of analytes through one side of a membrane and evaporation into the other side) depends on the membrane's concentration gradient, and extraction recovery is determined by Fick's first law of diffusion. Therefore, pervaporation can be increased by varying the flow rate of the stripping gas. The sorbent interface usually is located between the extraction module and the GC system and maintained at an ambient temperature in order to enrich VOCs transferred from the extraction module.^{10-12,19} Analytes are thermally desorbed and quantitatively determined by the GC system.

In this study, a method for quantitative determination of BTEX in water was attempted employing FSME coupled to cryofocusing (-100 °C) and GC-MS. Repetitive extractions were performed by continually, after each extraction, turning the donor phase back to the sample container. Analytes were directly enriched onto the cryogenic trap without any adsorbent trap between the extraction module and the GC.

2. Experimental

2.1. Reagents and materials

Five BTEX compounds (benzene, toluene, ethylbenzene, *o*- and *p*-xylenes) were purchased from Supelco (Bellefonte, PA), and methanol was acquired

from Burdick & Jackson (Morristown, NJ). Aqueous standard solutions were prepared in methanol for method validation, and included the above BTEX compounds. Nonporous silicone membrane (83 μm thickness, TI-8075) was purchased from Taejin Chemical (Gimpo, Gyeonggi-do, Korea) and used for extraction of BTEX compounds. To enrich BTEX compounds pervaporated from the extraction module, Tenax-TA (35/65 mesh; Alltech, Deerfield, IL) was used in the cold trap.

2.2. Description of overall system

Two types of extraction module (designated types I and II) were developed and tested (Fig. 1). The body of each module, composed of stainless steel, incorporated donor and acceptor channels separated by a silicone membrane (Fig. 1). The volumes of the grooves in the half-cells of extraction modules I and II were 0.2 and 1.2 mL, respectively, and the surface areas of the grooves in contact with either the donor or the acceptor phase were 2.51 and 8.15 cm^2 , respectively.

The overall analytical system was comprised of three compartments (see Fig. 2): a) sampling and extraction; b) focusing and desorption; c) separation and detection. The extraction module was connected to the thermal desorber (KnR, Seongnam, Gyeonggi-do, Korea), where cryogenic focusing ($-100\text{ }^\circ\text{C}$) and thermal desorption ($300\text{ }^\circ\text{C}$) of analytes were carried out. The desorbed analytes were then conveyed through a column of the GC by helium gas, and

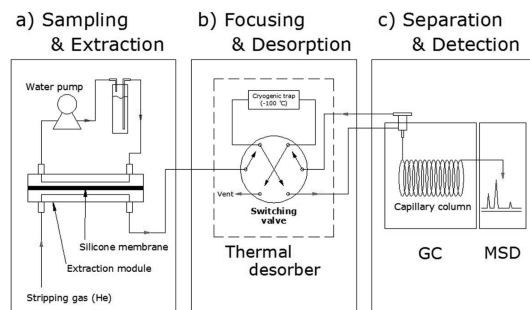


Fig. 2. Schematic diagram of three-part analytical system: a) sampling & extraction; b) focusing & desorption; c) separation & detection.

detected by the MS (7890A GC/5975C MS; Agilent Technologies, Inc., Santa Clara CA).

2.3. Membrane extraction

Thirty mL aqueous standard solutions were analyzed in all of the tests. Because extraction recovery is affected by temperature,^{10,20} the laboratory air temperature was maintained at $20 \pm 2\text{ }^\circ\text{C}$. Two different extraction modules were compared in duplicate for extraction recovery, specifically by running 50 $\mu\text{g/L}$ standard solutions. The flow rate of the donor phase (water) was set at 10 mL/min according to the protocol established in previous studies,^{12,13} whereas that of the acceptor phase (helium gas) was set at 20 mL/min. For evaluation of each extraction module, aqueous standard solutions with two different concentrations of each BTEX compound, that is, 100 and 140 $\mu\text{g/L}$, were examined to determine the optimum number of repetitive extractions. Upon completion of the initial extraction, the focused analyte was analyzed using the GC-MS. The drained aqueous solution, for the purposes of the following extraction and analysis, was then returned to the sample container. This operating cycle was repeated five times, total six cycles.

2.4. Analytical conditions

The cryofocusing trap, containing 30 mg of Tenax[®], was cooled to $-100\text{ }^\circ\text{C}$ to enrich the analytes. Preparatory to thermal desorption of the analytes, the trap was heated to $300\text{ }^\circ\text{C}$ at a rate of $4.5\text{ }^\circ\text{C/s}$ and maintained

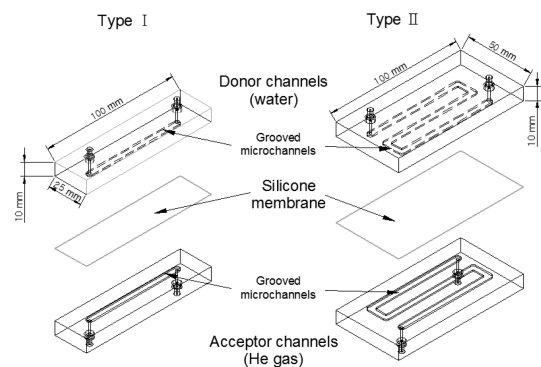


Fig. 1. Schematic diagrams of two tested flat-sheet membrane extraction modules (types I and II).

at that temperature for 10 min. The desorbed analytes were injected into the GC-MS at a split ratio of 20:1. The temperature of the injector was maintained at 250 °C. The analytical column used was a capillary HP-5 (30 m length \times 0.25 mm i.d. \times 0.5 μ m film thickness; Hewlett Packard, Palo Alto, CA). The oven temperature was programmed as follows: remain at 35 °C for 1 min; increase to 250 °C at 7 °C/min; hold at 250 °C for 10 min. The temperatures of the MS ion source and transfer line were 230 and 280 °C, respectively, and quantitative determination of each analyte (m/z 77 and 78 for benzene, 77 and 91 for toluene, 77, 91 and 106 for ethylbenzene, and 77, 91 and 106 for both *o*- and *p*-xylenes) was conducted in the selected ion monitoring (SIM) mode.

2.5 Method validation

Using the average values of the duplicated measurements for each concentration (concentration range: 1-100 μ g/L), eight-point linear calibration curves were drawn for the individual BTEX compounds. Three concentration levels (10, 50, and 80 μ g/L) were utilized to determine the validity of the calibration curves for quantitative analysis. Method detection limits (MDLs) were determined with reference to seven replicated measurements, following the U.S. EPA method.²¹ The analytical reproducibility of the established method was evaluated after calculating the RSDs (%) of the seven replicated measurements for two concentrations (10 and 40 μ g/L). The extraction recovery (%) for each analyte was tested at three levels (5, 40, and 80 μ g/L). Both the freshly prepared aqueous standard solutions and the drained aqueous solutions collected after three repetitive extractions (the selected optimum number of extractions) were analyzed using the purge and trap method for each level,²² and the chromatographic responses obtained from the GC-MS runs were compared to calculate the extraction recovery.

2.6. Application to field samples

For validation of the developed method's applicability, four lake-water samples (designated A, B, C, and D) were collected in 40 mL amber glass vials (without

headspace) from four locations in Euam Lake (Chuncheon, Korea). Thirty (30) milliliters of each sample was analyzed for the five analytes using the GC-MS (SIM mode) following the established method.

3. Results and Discussion

3.1. Selection of membrane module

As shown in *Fig. 3*, the type II module showed a 1.6- to 2.2-fold higher response than the type I module. This difference arose from the fact that the type II module has a 3.2-fold higher groove-surface area (8.15 cm²) than the type I module (2.51 cm²). The deviation from direct extraction-recovery-to-surface-area proportionality, meanwhile, might have resulted from other relevant factors such as the specific donor and acceptor flow rates in the respective modules. The type II module, accordingly, was selected for the subsequent tests.

3.2. Optimum number of extractions

After selection of the membrane module, the optimum number of repetitive extractions of BTEX compounds from the same sample was determined so as to attain the highest possible VOC enrichment factors. The cumulative GC peak area up to the sixth run, for each compound, is indicated in *Fig. 4*. The four compounds other than benzene nearly plateaued

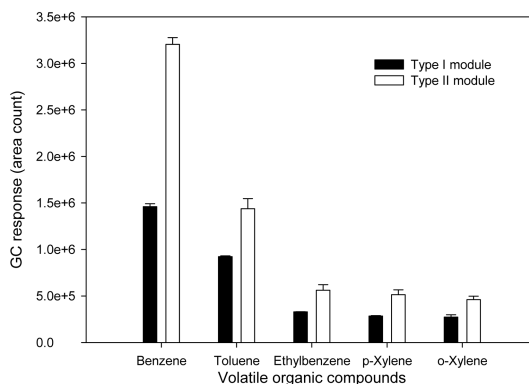


Fig. 3. Comparison of average GC responses for two extraction modules. The error bars indicate the standard deviations of the duplicated measurements. The type II module showed 1.6- to 2.2-fold higher responses than the type I module.

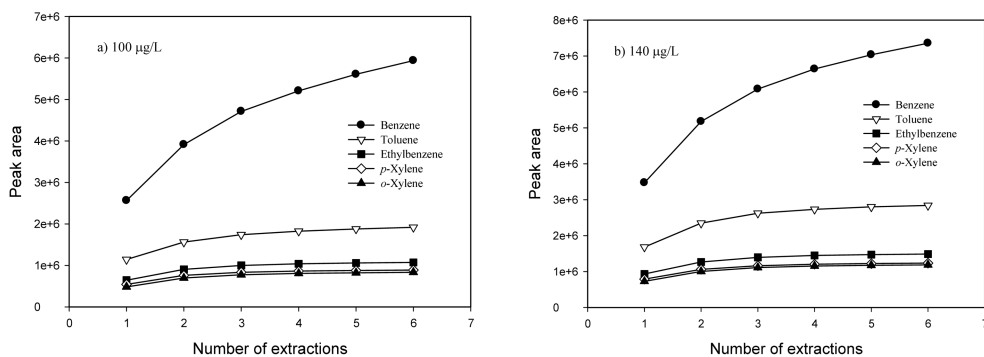


Fig. 4. Determination of optimum number of repetitive extractions according to plots of cumulative peak area vs. extraction number. Three cycles of extractions were chosen, based on the analysis time and recovery.

at the third run, whereas benzene showed a continuously increasing cumulative area even after the third run. The cumulative area for benzene from the first run to the third accounted for approximately 80% of the total peak area, whereas those for the others accounted for 91-94%. Therefore, for sample analysis purposes, and considering both analysis time and efficiency, the number of repetitive extractions, each accomplished

by circulating the drained aqueous sample back through the extraction module, was set at 3.

No previous studies have considered repetitive extraction of VOCs such as BTEX compounds from water samples. The advantage of repetitive extraction is that it can produce, at the cost of analysis time, higher-enrichment factors. Thus, this method would be valuable for achieving lower MDLs in cases

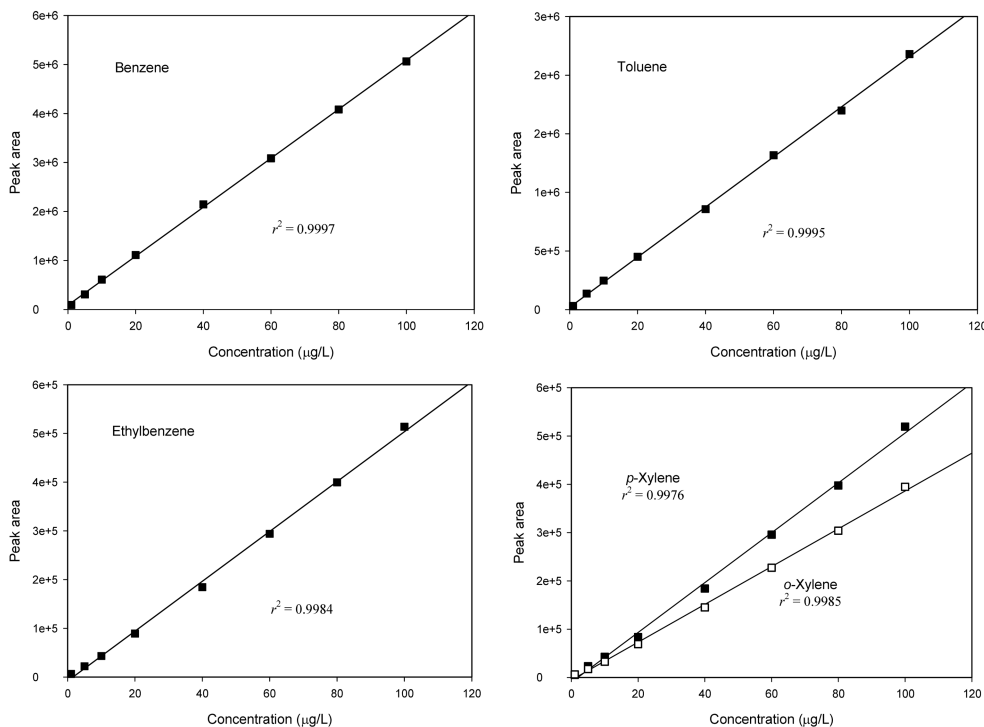


Fig. 5. Linear calibration curves for five BTEX compounds. The coefficients of determination (r^2) of the curves were all greater than 0.998.

where the sample volumes are limited. Also, this system, in conjunction with an auto sampler, can be automated with ease.

3.3. Method validation

With the three-time-consecutive extraction method incorporating the flat-sheet membrane module, eight-point calibration curves were drawn, as shown in Fig. 5. The coefficients of determination (r^2) for benzene and toluene, from the first single extraction, were 0.9957 and 0.9982, respectively. However, using the cumulated area from three repetitive extractions, these values were increased to 0.9997 for benzene and 0.9995 for toluene, indicating improvement in linearity. The values for the other compounds, by contrast, were not increased by repetitive extraction, because they showed sufficiently high calibration curve linearity (0.9984, 0.9976, and 0.9985 for ethylbenzene, *p*-xylene, and *o*-xylene, respectively).

These values are higher than those reported by Köller *et al.*,¹³ 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 *o*- and *m*-xylenes), whereas they are comparable to those of Hauser and Popp (0.9954-1.000),¹⁶ who used hollow-fiber silicone membranes to extract BTEX compounds. These results show that repetitive

extraction improves the linearity of calibration curves.

The MDLs for benzene, toluene, ethylbenzene, *p*-xylene, and *o*-xylene were estimated to be 0.2, 0.4, 1.4, 1.3, and 1.8 $\mu\text{g/L}$, respectively (Table 1). For three different levels (5, 40, and 80 $\mu\text{g/L}$), benzene showed relatively high extraction recoveries ranging between 76.1 and 83.3%. Toluene showed the next-highest extraction recoveries, which ranged from 48.0 to 64.3%. In contrast, ethylbenzene and xylenes showed poor extraction recoveries (3.15-10.7%). Such lower recoveries for ethylbenzene and xylenes may be explained by Graham's law of diffusion, according to which high-molecular-weight VOCs such as ethylbenzene and xylenes diffuse through a membrane at lower rates than low-molecular-weight benzene and toluene. It is suggested that lowering the flow rate of the donor phase, which results in a longer duration of analyte membrane diffusion, would help to solve this problem. Relevant succeeding experiments are currently ongoing in the authors' laboratory. Preliminary results are promising but more testing is required prior to the final selection of optimum conditions.

The analytical reproducibility for the 10 and 40 $\mu\text{g/L}$ levels was relatively satisfactory, ranging from 2.2 to 10% RSD. An external calibration check using three different levels (10, 50, and 80 $\mu\text{g/L}$) showed that the concentrations measured with the calibration

Table 1. MDLs, recoveries, and RSDs for five compounds (n = 7)

Compound	MDL ($\mu\text{g/L}$)	Average recovery (%)			RSD (%)	
		5 $\mu\text{g/L}$	40 $\mu\text{g/L}$	80 $\mu\text{g/L}$	10 $\mu\text{g/L}$	40 $\mu\text{g/L}$
Benzene	0.2	83	85	76	2.2	6.1
Toluene	0.4	63	64	48	5.5	9.4
Ethylbenzene	1.4	9.8	5.1	3.8	8.3	7.8
<i>p</i> -Xylene	1.3	11	4.3	3.8	9.2	9.5
<i>o</i> -Xylene	1.8	5.0	3.7	3.2	7.0	10

Table 2. Comparison between spiked and measured concentrations ($\mu\text{g/L}$)

Benzene		Toluene		Ethylbenzene		<i>p</i> -Xylene		<i>o</i> -Xylene	
Spiked	Measured	Spiked	Measured	Spiked	Measured	Spiked	Measured	Spiked	Measured
10.0	10.5	10.0	11.2	10.0	9.6	10.0	11.5	10.0	9.8
50.0	50.8	50.0	52.7	50.0	47.2	50.0	52.7	50.0	51.4
80.0	82.3	80.0	79.0	80.0	82.1	80.0	79.5	80.0	83.1

curves were within a 5.6% deviation from the spiked (known) concentrations (Table 2), proving that this method is useful for measuring BTEX compounds, though extraction recoveries for ethylbenzene and xylenes are low.

For determination of BTEX compounds, the purge and trap method coupled to GC-MS is the most commonly used, and has been reported to yield reliable results for all compounds (MDLs 0.010 to 0.024 $\mu\text{g/L}$; RSDs 2.7 to 9.6%; recoveries 86.9 to 100%).²² However, this method requires the difficult step of removing moisture from adsorbents with helium gas, due to the fact that water moisture is trapped in adsorbents during sample preparation. Insufficient trap-drying can lead to shutdown of GC-MS and loss of samples. Membrane extraction, contrastingly, has the advantage over the purge and trap method in that it does not require this step, simply because it entails the use of a nonporous hydrophobic membrane, through which water molecules cannot permeate. In fact, in the course of the present experimentation (> 100 runs), no

problems arose with the GC-MS.

3.4. Application to field samples

Fig. 6(a) shows a gas chromatogram for an aqueous standard solution containing 40 $\mu\text{g/L}$ of each of the five compounds. Fig. 6(b) shows a chromatogram for a lake sample A. For samples A, B, C, and D, benzene was found at levels of 4.5, 2.9, 2.0, and 3.5 $\mu\text{g/L}$, respectively. Toluene peaks were found in the chromatograms of three samples (A, B, and C) but just below its MDL (0.40 $\mu\text{g/L}$). However, the other three compounds were not detected in any of the samples.

In this study, 30 mL water samples were analyzed to test the field applicability of the developed method. Use of larger volumes of samples can lower the MDLs for BTEX compounds and detect them even at lower concentrations. In a subsequent pilot study, a 300 mL lake-water sample was analyzed, and all five peaks, including ethylbenzene and xylenes, which were not detected in the 30 mL water samples, were observed, indicating that an increase of sample

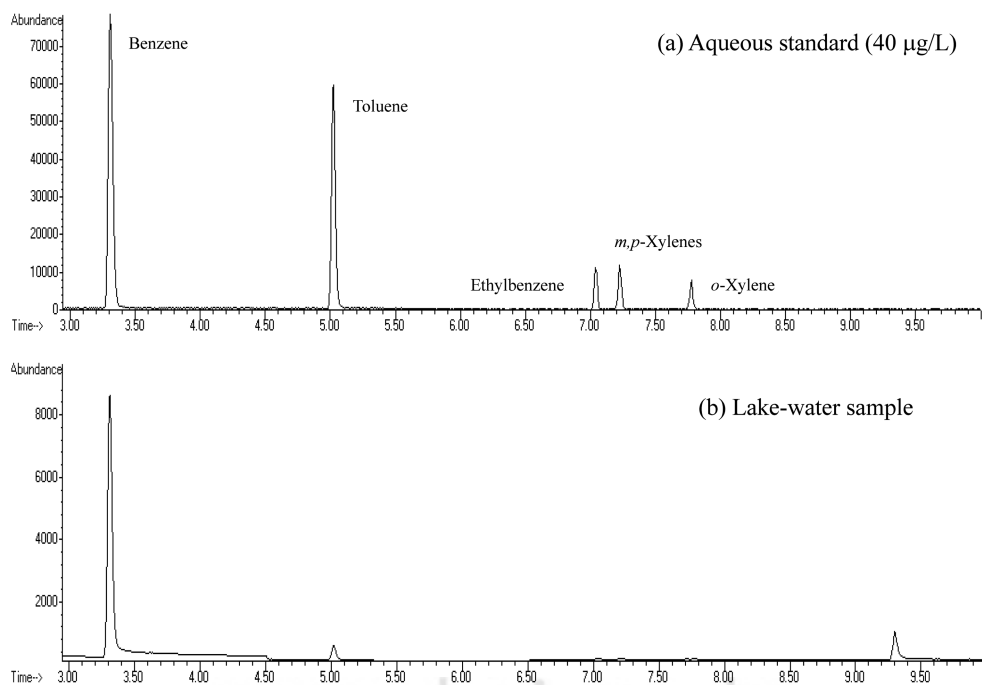


Fig. 6. Chromatograms of (a) 40 $\mu\text{g/L}$ aqueous standard solution and (b) 30 mL lake-water sample.

volume makes possible the quantitative determination of low-level BTEX compounds in water.

4. Conclusion

Using three repetitive extractions with a flat-sheet silicose membrane in conjunction with cryofocusing and GC-MS, benzene and toluene in water can be measured to levels of a few $\mu\text{g/L}$ with reliable accuracy and reproducibility. However, this method might not be suitable for determination of ethylbenzene and xylenes in water, due to their low recoveries and high MDLs, even though the calibration curves are relatively linear. In order to solve this problem, use of lower flow rates in the donor phase needs to be attempted. This system can be extensively applied to the analysis of VOCs other than BTEX compounds, such as trihalomethanes in chlorinated drinking water, after the analytical conditions are set. Additionally, the system can be automated for consecutive analysis of water samples for VOCs, both in the field and in the laboratory.

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