Direct Screening of Water Samples for Benzene Hydrocarbon Compounds by Headspace Liquid-Phase Microextraction–Gas Chromatography

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Abstract

The applicability of headspace liquid-phase microextraction and gas chromatography is evaluated for the expeditious and reliable screening of tap and drinking water samples for selected volatile organic compounds (viz., benzene, toluene, ethylbenzene, and xylene isomers, BTEX). The method uses 3.5 µL of *n*-hexadecane as extraction solvent, 10 min extraction time with stirring at 1250 rpm, at 20°C and 0.38 g/mL salt addition. The enrichment factors of this method are from 135 to 213. Limits of detection are in the range of 4.1–23.5 ng/L. The relative standard deviations at 0.05, 50, 200, and 400 µg/L of spiking levels are in the range of 0.61%–4.01%. Recoveries of six BTEX from drinking water at these spiking levels are between 95.4% and 104.4%.

Introduction

Aromatic hydrocarbons are ubiquitous environmental contaminants arising from a variety of sources, including fossil fuel combustion, oil spills, and some industrial processes (1). Benzene, toluene, ethylbenzene, *m*-, *p*-, and *o*-xylene (BTEX) are important industrial chemicals, the contamination sources of which in water include the massive use of petroleum and its derivatives, and that of solvents. The BTEX content in a standard gasoline blend is approximately 18% (w/w); benzene, which is the most toxic compound in BTEX, accounts for 11% of the total BTEX fraction in gasoline (26% toluene, 11% ethylbenzene, and 52% total xylenes) (2). The US Environmental Protection Agency has included BTEX compounds on the list of National Primary Drinking Water Standards (3) and established a maximum contaminant level (MCL) of 5.0 µg/L for benzene and values over the range 0.7–10.0 mg/L for the other BTEX (4). Also, the European Union has included benzene in the list of 33 priority pollutants in waters (5,6), and established an MCL of 1.0 µg/L for benzene in drinking water (7).

Sensitive, accurate analytical methods have been developed to detect volatile organic compound concentrations below the maximum permitted levels. Techniques such as purge-and-trap (8,9), membrane extraction (10), stir bar sorptive extraction (11), and solid-phase microextraction (SPME) (12) are excellent analytical techniques that are successfully employed to achieve this goal; however, they each require a specialized apparatus with some type of solid or polymeric sorbent to collect the analyte (13). For example, the main drawbacks of SPME are that its fibers are expensive and have a limited lifetime, as they tend to degrade with increased usage. The partial loss of stationary phase results in peaks that may co-elute with the target analytes, thus affecting precision (14). In addition, when SPME is coupled to gas chromatography (GC), sample carry-over between runs has been reported for some analytes and is hard to be eliminated even at elevated temperatures (15,16).

A recent advance in organic compound analysis is the use of liquid-phase microextraction (LPME). In this technique, developed by Cantwell and co-workers (17), the analytes are distributed between the bulk aqueous phase and a microdrop of organic solvent, suspended directly at the tip of a microsyringe needle that is either immersed or placed in the headspace (HS) of a stirred aqueous sample solution. After a certain time, when sufficient amounts of analytes are transferred into the organic extractor, the microdrop is retracted into the microsyringe, and subsequently part or all of the organic solvent is injected into the chromatographic system (18). An important additional feature of LPME is the integration of extraction and injection in a microsyringe, making it possible to employ this miniaturized medium for extraction and an injection device for the GC (19–22). It is fast, inexpensive, and, due to the need for small volumes of solvent, there is minimal exposure to toxic organic solvents. Moreover, because of a wide choice of polar extraction solvents, headspace LPME seems to be even a more attractive technique. In this technique, which has gained increasing attention (23–25), the extracting solvents need not even be water immiscible, as in direct LPME from aqueous solutions (26). A variety of LPME methods, including static and dynamic HS (27), inside needle capillary adsorption trap (28), and automated HS-LPME (29) have been reported for the preconcentration of BTEX from different samples. Theis et al. (13) studied the kinetic (mass

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transfer) phenomena in HSME. They used 1-octanol as a solvent and BTEX as model compounds. They proved that mass transfer either in aqueous phase or a microdrop could be the rate determination step for the process. However, the authors reported neither the optimization of the experimental procedure for BTEX extraction, nor any real sample analyses. Mohammadi and Alizadeh (30) investigated the applicability of dynamic HS organic solvent film microextraction to the determination of BTEX in aqueous matrices. They studied the effect of several factors on the method performance; however, a relatively sophisticated computer driven laboratory-made stirring motor was used to repetitively pull and push the plunger within the glass barrel of the microsyringe.

The main purpose of the present study is to re-evaluate the HS-LPME–GC method for the determination of BTEX in water samples, and to investigate the feasibility and limitations of this technique. The method is inexpensive, precise, and applicable to the determination of trace levels of BTEX (ng/mL).

Experimental

Chemicals

Methanol, 1-octanol, mesitylene, *n*-decane, undecane, *n*-dodecane, cyclohexane (Merck, Darmstadt, Germany), benzyl alcohol, benzene, toluene, ethylbenzene, xylene isomers (Fluka, Buchs, Switzerland), and *n*-hexadecane (Aldrich, Milwaukee, WI) were all of reagent grade and used as received. Sodium chloride (Merck) was of the highest purity available and used without any further purification.

Apparatus

Chromatographic analysis

Analysis of BTEX was performed on a Thermo Onix GC (New York, NY), model PyeUnicam Pro+, equipped with a flame ionization detector (FID). The GC was fitted with a Petrocol capillary column (50 m × 0.20 mm i.d., 0.25 µm phase thickness) from Supelco (Milwaukee, WI). The following temperature program was employed: 45°C for 4.5 min; 30°C/min to 80ºC, held for 5 min; then 60ºC/min to 15ºC, held for 3.5 min; finally, 100°C/min to 250°C, held for 13 min. The injector temperature was 250°C, and all injections were made in the splitless mode. The detector temperature was set at 300ºC. Helium (99.999%, Sabalan Gas Co., Tehran, Iran) was used as carrier gas with a constant flow of 1.2 mL/min.

HS-LPME

The HS-LPME device is illustrated in one of our previous works (26). HS-LPME was carried out in conventional 11-mL sample vials with screw tops/silicone septa (Chromacol, Trumbull, CT). A conventional 10-µL microsyringe (Hamilton, Texas) designed for GC was adopted. The absence of air bubbles was ensured by washing the syringe several times with organic solvent. The precision of the method was improved by positioning the needle in an aqueous sample at a fixed length with stands and clamps. After each extraction, the syringe was washed several times with extractant containing internal standard.

The extraction consisted of the following steps: (*i*) One microliter of organic solvent was withdrawn into the microsyringe. (*ii*) The microsyringe needle was passed through the HS sample vial septum and the needle was kept suspended over the liquid sample. (*iii*) The plunger was pressed so that the extracting organic phase was suspended very close to the surface of the sample, and held for 10 min. (*iv*) After extraction, the plunger was withdrawn and the microdrop was retracted into the microsyringe. The syringe was then removed from the top of the sample vial. Finally, the syringe needle was removed from the vial and the BTEX-enriched organic solvent was injected into the GC for analysis. The same process was repeated at least 3 times. During extraction, the samples were stirred using a MR Hei-Tec stirrer purchased from Heidolph (Kelheim, Germany) with a Teflon-coated magnetic stir bar.

Standard and spiking solutions

Stock standard solutions (5000 mg/L) were separately prepared in methyl alcohol by accurately transferring the proper amount of the analyte into 10-mL volumetric flasks and diluting to volume. Intermediate mix standard solutions were prepared by diluting the stock standard solutions in methanol. Stock and intermediate standard solutions of the internal standard, methyl cyclohexane, were prepared in the same way as when extracting solvents. The final concentration of internal standard was kept at 0.2%. Water samples were spiked at a concentration of 10–500 µg/L with standard solutions of analytes and were used for the extraction experiments. To avoid the loss of analytes, stock and intermediate solutions were stored in a refrigerator. Working solutions were prepared freshly every day by sequentially diluting the intermediate solutions.

Results and Discussion

Selection of the extracting solvent

Organic liquids for LPME should be of appropriate solvent volatility, selectivity, and viscosity. The former criterion is important in order not to lose the organic phase during extraction, while the other criteria are important in order to obtain high extraction recoveries. Based on these considerations, and with focus on "green" organic liquids, it was decided to test several solvents differing in polarity and water solubility, screened on the basis of the principle of "like dissolves like". The final choice of solvent was based on extraction efficiency, rate of drop evaporation, and excellent gas chromatographic behavior. Solvent selection was performed by extraction of the spiked water sample (5.0 mL at 1 mg/L) with the organic solvent drop (1 µL). Two series of experiments were performed. In the first experiment, de-ionized water was spiked with the desired analytes and extracted with single solvents, such as 1-octanol, benzyl alcohol, mesitylene, *n*-decane, undecane, *n*-dodecane, and *n*-hexadecane. In the second set, extraction was done with 3 different mixtures of the undecane and *n*-dodecane solvents (which were shown to have better extracting capability after *n*-hexadecane) in ratios of 2:1, 1:1, and 1:2 v/v. Spiked water samples were extracted at room temperature (25°C) for 10 min with stirring at 400 rpm.

Averages of the ratios of the peak areas of the analytes versus the internal standard for each solvent system are shown in Figure 1. As is evident from the figure, higher extraction efficiencies were achieved with *n*-hexadecane. On the basis of this, $C_{16}H_{36}$ was chosen as the extracting solvent in further experiments. It should be noted that 1-octanol and mesitylene have some overlaps with the analytes' peaks, and hence their results are not included in the figure.

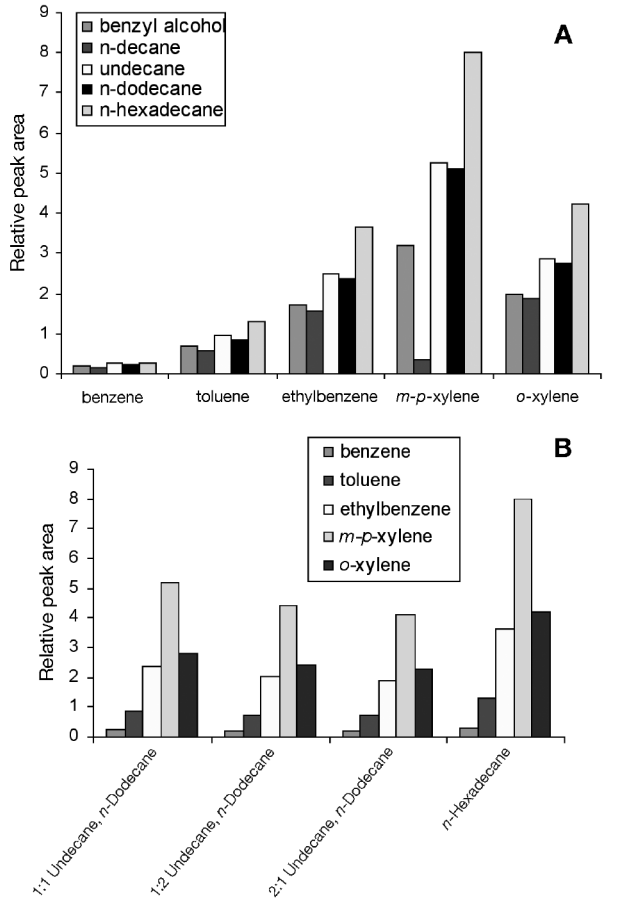

Figure 1. Extraction efficiency of organic solvents: single solvents (A) and three different mixtures of undecane and *n*-dodecane (B).

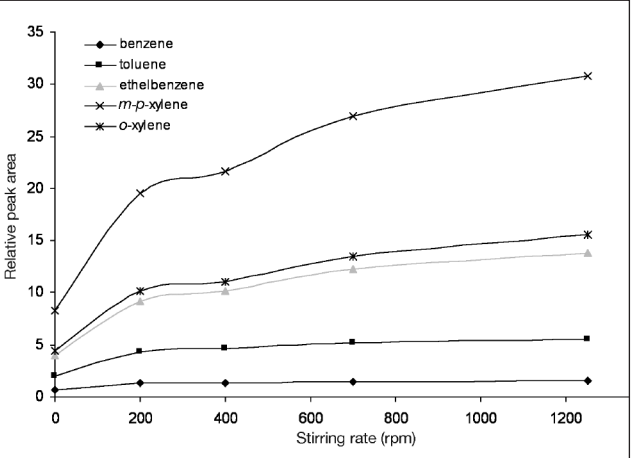

Figure 2. The effect of the rate of stirring on BTEX extraction.

Optimization of agitation

Agitation of the sample reduces time to reach thermodynamic equilibrium and increases extraction efficiencies. To evaluate the effect of sample stirring, water samples (spiked at 1 mg/L with analytes) were extracted in triplicate with $C_{16}H_{36}$ at 10 min time intervals with varying stirring rates (up to 1250 rpm). Stirring rates above 1250 rpm were not evaluated because they destabilized the drop. The typical results are shown in Figure 2. At 1250 rpm, a maximum amount of analyte was extracted with the fastest attainment of equilibrium. This stirring rate, therefore, was fixed for further microextractions.

Effect of temperature

It was reported that a higher temperature allowed an increase in the extraction efficiency (16); however, for volatile analytes, the extraction temperature has a double impact on HS-LPME. At a higher temperature, the diffusion coefficients in both sample and HS are higher and the extraction time may be shorter, but the partition coefficients for the analytes between the organic solvent and gaseous phase are lower (31). The temperature of the sample influences the evaporation of BTEX into the HS. It was expected

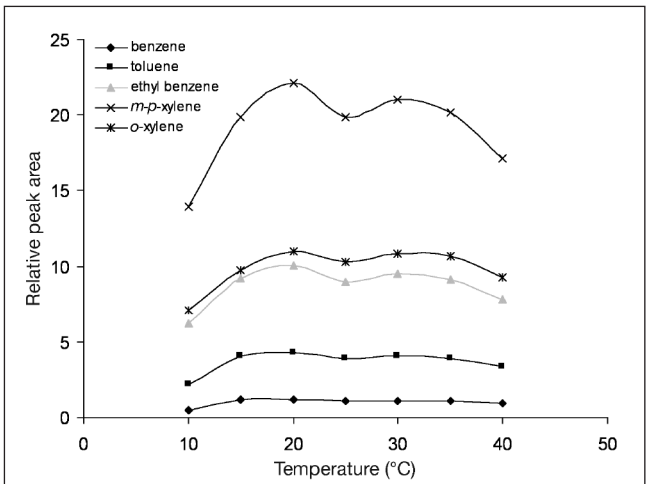

Figure 3. Extraction efficiencies obtained at various extraction temperatures.

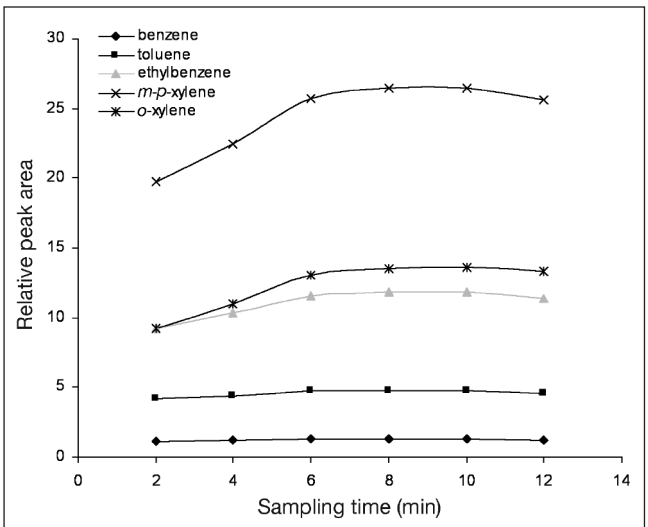

Figure 4. Effect of extraction time on the extraction of BTEX.

that an increase in sample temperature would result in improved extraction efficiency, because of the increased evaporation of the analyte and the analyte concentration in the HS. The effect of sample temperature on the extraction efficiency was studied by exposing an *n*-hexadecane-extracting drop for 10 min in the HS while changing the sample temperature from 10°C to 40°C. Figure 3 shows that the amounts of the analytes extracted into the *n*-hexadecane drop, and sensitivity of the method increases with an increase in the temperature up to 20°C. This can be explained by the fact that at higher temperatures, the vapor pressure of the analytes and their concentrations in HS increase. Above the temperature mentioned, the amount of the analytes extracted decreases, probably because the partition coefficients to the extraction phase decrease. Hence, the optimum sampling temperature for a fixed extraction time of 10 min was 20°C.

Extraction time

LPME is a process dependent on equilibrium rather than exhaustive extraction. In most LPME applications, the efficiency of extraction increased with the extraction time. The extraction of the seven analytes into the organic drop was carried out at 2, 4, 6, 8, 10, and 12 min (Figure 4). The amount of BTEX extracted by HS-LPME increased when exposure time was increased from 2 to 12 min. Although equilibrium could not be attained within this interval, 10 min was chosen as the sampling time for subsequent experiments, because a long extraction time may result in organic drop vaporization, and consequently lead to poor sensitivity and precision.

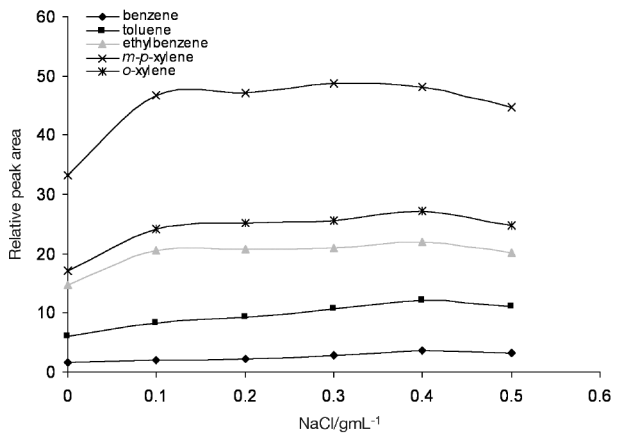

Figure 5. Effect of ionic strength on the extraction of BTEX.

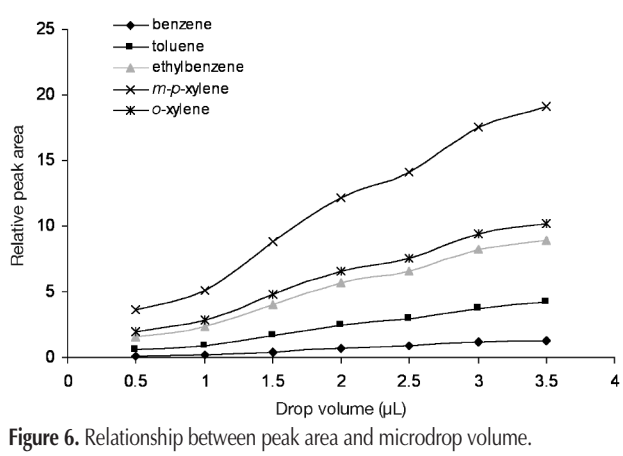

Figure 6. Relationship between peak area and microdrop volume.

Optimization of salt addition on extraction

It was of interest to examine the influence of salt addition on the efficiency of extraction. For this purpose, the ionic strength of solutions was modified by addition of sodium chloride. In order to investigate the effect of ionic strength, a series of spiked samples with various concentrations of NaCl (0–10%) were prepared by adding of calculated weight of NaCl into a 5 mL volume of sample solution. Plots of relative peak area versus ionic

Table I. Linearity Data, LOD (ng/L), and Enrichment Factors (EF) of HS-LPME of BTEX in GC–FID System

Compound	Linear range (µg/L)	Correlation coefficient	LOD (ng/L)	EF (%)
Benzene	10–500	0.9996	23.48	135
Toluene	10–500	0.9989	11.10	197
Ethylbenzene	10–500	0.9993	9.26	188
m-, *p*-Xylene	10–500	0.9995	4.10	185
o-Xylene	10–500	0.9992	7.00	213

Table II. Relative Recoveries and Precision of HS-LPME in Three Water Samples Spiked with BTEX.

		Precision (RSD%)		Relative recoveries (%)	
Analyte	Concentration added (mg/L)	Tap Water	Drinking Water	Tap Water	Drinking Water
Benzene					
	5.0×10^{-4}	3.58	3.96	96.27	95.18
	0.05	2.97	3.67	102.12	99.20
	0.20	0.85	0.61	101.60	97.60
	0.40	3.13	2.03	103.18	101.10
Toluene					
	5.0×10^{-4}	3.88	3.75	97.32	98.53
	0.05	3.02	3.68	104.27	102.05
	0.20	0.85	0.63	103.81	98.69
	0.40	3.12	2.00	104.39	102.83
Ethylbenzene					
	5.0×10^{-4}	3.65	4.01	98.00	96.24
	0.05	3.02	3.63	102.75	99.18
	0.20	0.84	0.63	101.90	97.70
	0.40	3.12	2.00	103.62	100.90
***m*-, *p*-Xylene**					
	5.0×10^{-4}	3.72	3.69	95.38	96.89
	0.05	3.02	3.63	98.68	97.50
	0.20	0.85	0.63	98.50	96.96
	0.40	3.12	1.99	98.71	98.00
***o*-Xylene**					
	5.0×10^{-4}	3.44	3.77	95.64	97.00
	0.05	3.02	3.63	98.80	98.61
	0.20	0.85	0.63	98.73	97.00
	0.40	3.12	1.99	101.15	98.68

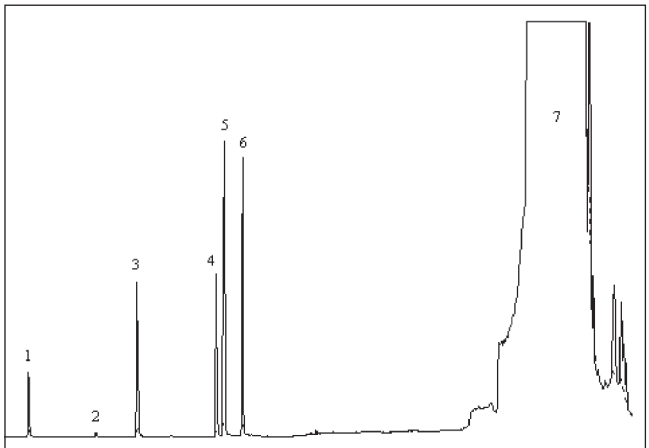

Figure 7. GC–FID chromatograms for tap water sample. Benzene, 1; methylcyclohexan (internal standard), 2; toluene, 3; ethylbenzene, 4; *m*-, *p*-xylene, 5; *o*-xylene, 6; *n*-hexadecane (solvent), 7.

strength are shown in Figure 5. According to the curves, it is clear that the addition of ionic strength enhances the transport of the analytes to the extracting drop, especially for xylene isomers. This can be explained by the fact that water molecules form hydration spheres around the salt ions. These hydration spheres reduce the concentration of available water to dissolve analyte molecules; hence, it was expected that this would drive additional analytes into the extraction phase. However, at NaCl concentrations above 0.4 g/mL, the extraction efficiency did not change any further. This can be explained by the fact that the solubility of NaCl at 20°C is < 0.4 g/mL. Based on this consideration, all remaining extraction experiments were performed at saturated salt conditions.

Solvent drop volume

The rise of the analytes' extraction with increasing drop size has been observed by several workers (32–35). To increase the sensitivity of the HS-LPME method, the solvent drop volume was optimized. For this purpose, extractions were performed from spiked water solutions containing 1 µg/L of the analytes by increasing the drop volume from 0.5 to 3.5 µL. As expected, peak areas of BTEX increased with drop volume (data in Figure 6). However, using high drop volumes of organic solvent can result in the loss of the organic drop. Thus, a 3.5 µL drop volume was used for further experiments in order to avoid these losses.

Quantitative analysis

Under optimal extraction conditions, enrichment factor, the linearity, and limits of detection were determined. As shown in Table I, the six BTEX could be preconcentrated up to 213-fold. By plotting peak areas versus concentrations of analytes in the sample solution, calibration curves were obtained, which showed that coefficients of correlation (*r*) were all above 0.9989. The limits of detection (LODs at S/N = 3) ranged from 4.1 to 23.48 ng/L.

Recoveries from natural water samples

The feasibility of using this method for BTEX screening in tap and drinking water samples was then tested at spiked concentration levels of 0.05, 50, 200, and 400 µg/L (no target analytes could be detected in the sample). The optimized extraction protocol was applied to these samples and the recoveries were calculated as the ratio of the concentrations found in natural and deionized water samples, spiked with the same amount of analytes. For each sample, at each concentration, the extraction was repeated six times. Relative recoveries and precision were calculated and are listed in Table II. As can been seen, acceptable recoveries (95.38–104.39%) were obtained for all analytes in the tested water samples and the relative standard deviations (RSD) were lower than 4.01% for all the six analytes. The higher recoveries that were observed for the analytes in tap water samples may be due to the higher content of organic matter and the presence of suspended solids in these types of water samples. A chromatogram of analytes after solvent microextraction in a spiked river water sample (1 µg/L) with a 3.5 µL drop of *n*-hexadecane is shown in Figure 7.

Conclusion

In the present work, an HS-LPME method was developed and applied to extract BTEX hydrocarbons from aqueous solutions. Several parameters of the extraction procedure were studied and optimized (such as types of extracting solvent, extraction temperature, extraction time, microdrop volume, and ionic strength). Using methyl cyclohexane as the internal standard, the method was successfully applied to the analysis of BTEX in tap and drinking water samples.

Compared to other microextraction methods, HS-LPME provides a satisfactory precision (ranging from 0.61 to 4.01%) and was similar to the values obtained previously for SPME, static HS, and HS-SPME (36,37). It yields lower detection limits for the tested analytes in water samples (varied between 4.1–23.5 ng/L), compared to 0.08–0.6 ng/mL obtained by HS-SPME for BTEX determination in aqueous samples (37). The method shows good linearity over the concentration range 10–500 µg/L. HS-LPME has also numerous advantages, such as: simplicity, low cost, ease of operation, high sensitivity, no possibility of sample carry-over, extremely low consumption of toxic solvents, and short analysis time. However, this technique requires more elaborate manual operations because of drop loss and dislodgment.

References

1. R.J. Woodhead, R.J. Law, and P. Matthiessen. Polycyclic aromatic hydrocarbons in surface sediments around england and wales, and their possible biological significance. *Mar. Pollut. Bull.* **38:** 773–790 (1999).
2. L.M.L. Nollet. *Handbook of Water Analysis.* Marcel Dekker, New York, NY 2001, Chapter 33.
3. http://www.epa.gov/safewater/consumer/mcl.pdf, 4 Jan 2006.
4. http://toxics.usgs.gov/definitions/btex.html, 4 Jan 2006.
5. Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 concerning the quality of bathing water. *Off. J. Eur. Commun.* **327** (2002).
6. Decision 2455/2001/EC of the European Parliament and of the Council of 20 November 2001 on dangerous substances in water. *Off. J. Eur. Commun.* **331** (2001).
7. Directive 98/83/EC of the Council of 3 November 1998 on the

quality of water intended for human consumption. *Off. J. Eur. Commun.* **330** (1998).
8. J. Drozd and J. Novak. Headspace gas analysis by gas chromatography. *J. Chromatogr. A* **165:** 141–165 (1979).
9. A.J. Nunez, L.F. Gonzalez, and J. Janak. Pre-concentration of headspace volatiles for trace organic analysis by gas chromatography. *J. Chromatogr. A* **300:** 127–162 (1984).
10. M.J. Yang, S. Harms, Y.Z. Luo, and J. Pawliszyn. Membrane extraction with a sorbent interface for capillary gas chromatography. *Anal. Chem.* **66:** 1339–1346 (1994).
11 M. Marczak, L. Wolska, W. Chrzanowski, and J. Namiesnik. Microanalysis of volatile organic compounds (VOCs) in water samples – methods and instruments. *Microchim. Acta* **155:** 331–348 (2006).
12. J. Pawliszyn. Solid-Phase Microextraction, Theory and Practice. John Wiley & Sons, New York, NY 1997.
13. A.L. Theis, A.J. Waldack, S.M. Hansen, and M.A. Jeannot. Headspace solvent microextraction. *Anal. Chem.* **73:** 5651–5654 (2001).
14. H. Prozen and L. Zupancic-Kralj. Solid-phase microextraction. *Trends Anal. Chem.* **18:** 272–282 (1999).
15. M. de Fatima Appandurada. Solid-phase microextraction: a promising technique for sample preparation in environmental analysis. *J. Chromatogr. A* **889:** 3–14 (2000).
16. E. Psillakis and N. Kalogerakis. Solid-phase microextraction versus single-drop microextraction for the analysis of nitroaromatic explosives in water samples. *J. Chromatogr. A* **938:** 113–120 (2001).
17. M. Ma and F.F. Cantwell. Solvent microextraction with simultaneous back-extraction for sample cleanup and preconcentration: preconcentration into a single microdrop. *Anal. Chem.* **71:** 388–393 (1999).
18. M. Kaykhaii and M. Rahmani. Headspace liquid-phase microextraction for quantitation of hexanal in potato crisps by gas chromatography. *J. Sep. Sci.* **30:** 573–578 (2007).
19. M. Khajeh, Y. Yamini, and J. Hassan. Trace analysis of chlorobenzenes in water samples using headspace solvent microextraction and gas chromatography–electron capture detection. *Talanta* **69:** 1088–1094 (2006).
20. M.A. Jeannot and F.F. Cantwell. Mass transfer characteristics of solvent extraction into a single drop at the tip of a syringe needle. *Anal. Chem.* **69:** 235–239 (1997).
21. M.A. Jeannot and F.F. Cantwell. Solvent Microextraction into a Single Drop. *Anal. Chem.* **68:** 2236–2240 (1996).
22. A. Tankeviciute, R. Kazlauskas, and V. Vickackaite. Headspace extraction of alcohols into a single drop. *Analyst* **126:** 1674–1677 (2001).
23. Y. He, A. Vargas, and Y. Kang. Headspace liquid-phase microextraction of methamphetamine and amphetamine in urine by an aqueous drop. *Anal. Chim. Acta* **589:** 225–230 (2007).
24. H. Ebrahimzadeh, Y. Yamini, F. Kamarei, and M. Khalili-Zanjani. Application of headspace solvent microextraction to the analysis of mononitrotoluenes in waste water samples. *Talanta* **72:** 193–198 (2007).
25. A.R. Fakhari, P. Salehi, R. Heydari, S. Nejad-Ebrahimi, and P.R. Haddad. Hydrodistillation-headspace solvent microextraction, a new method for analysis of the essential oil components of Lavandula angustifolia Mill. *J. Chromatogr. A.* **1098:** 14–18 (2005).
26. M. Kaykhaii, S. Nazari, and M. Chamsaz. Determination of aliphatic amines in water by gas chromatography using headspace solvent microextraction. *Talanta* **65:** 223–228 (2005).
27. J. Arab, Y. Yamini, M. Haji-Hosseini, and M. Shamsipur. Headspace solvent microextraction of trace amounts of BTX from water samples. *Chem. Anal. (Warsaw)* **49:** 129–137 (2004).
28 M.E. McComb, R.D. Oleschuk, E. Giller, and H.D. Gesser. Microextraction of volatile organic compounds using the inside needle capillary adsorption trap (INCAT) device. *Talanta* **44:** 2137–2143 (1997).
29. G. Ouyang, W. Zhao, and J. Pawliszyn. Kinetic calibration for automated headspace liquid-phase microextraction. *Anal. Chem.* **77:** 8122–8128 (2005).
30. A. Mohammadi and N. Alizadeh. Automated dynamic headspace organic solvent film microextraction for benzene, toluene, ethylbenzene and xylene renewable liquid film as a sampler by a programmable motor. *J. Chromatogr. A* **1107:** 19–28 (2006).
31. L. Zhao and H.K. Lee. Application of static liquid-phase microextraction to the analysis of organochlorine pesticides in water. *J. Chromatogr. A* **919:** 381–388 (2001).
32. M.A. Farajzadeh and A.A. Matin. Semi-micro solvent extraction as a rapid and efficient preconcentration technique for the determination of *n*-alkanes in oil contaminated water and soil samples by capillary gas chromatography. *Chromatographia* **55:** 225–229 (2002).
33. J. Chiang and S. Huang. Determination of haloethers in water with dynamic hollow fiber liquid-phase microextraction using GC-FID and GC–ECD. *Talanta* **71:** 882–886 (2007).
34. R. Batlle and C. Nerin. Application of single-drop microextraction to the determination of dialkyl phthalate esters in food simulants. *J. Chromatogr. A* **1045:** 29–35 (2004).
35. M.R. Khalili Zanjani, Y. Yamini, S. Shariati, and J.A. Jonsson. A new liquid-phase microextraction method based on solidification of floating organic drop. *Anal. Chim. Acta* **585:** 286–293 (2007).
36. Ó. Ezquerro, G. Ortiz, B. Pons, and M.T. Tena. Determination of benzene, toluene, ethylbenzene, and xylenes in soils by multiple headspace solid-phase microextraction. *J. Chromatogr. A* **1035:** 17–22 (2004).
37. J.C. Flórez Menéndez, M.L. Fernández Sánchez, J.E. Sánchez Uría, E. Fernández Martínez, and A. Sanz-Medel. Static headspace, solid-phase microextraction, and headspace solid-phase microextraction for BTEX determination in aqueous samples by gas chromatography. *Anal. Chim. Acta* **415:** 9–20 (2000).

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