CHEMIJA. 2010. Vol. 21. No. 1. P. 48–53

Hollow fibre liquid phase microextraction of volatile aromatic hydrocarbons

Edita Pusvaškienė,

Nadežda Spirova,

Aleksandra Prichodko,

Vida Vičkačkaitė*

Department of Analytical and Environmental Chemistry, Vilnius University, Naugarduko 24, LT-03225 Vilnius, Lithuania

Hollow fibre liquid phase microextraction (HFLPME) was explored for benzene, toluene, ethylbenzene and *o*-xylene sampling and preconcentration.

The investigation covered the effects of extraction solvent type, extraction time and ionic strength of the sample solution. Dibutyl phthalate : *n*-octanol (1 : 1) mixture containing *n*-octane as the internal standard was used as an extracting solvent. The calibration curves were from 0.36, 0.10, 0.23 and 0.27 μg l^{-1} up to 50 μg ml^{-1} for benzene, toluene, ethylbenzene and *o*-xylene, respectively, the correlation coefficients being 0.997–0.998, enrichment factors from 112 for benzene to 260 for *o*-xylene and the detection limits 0.22, 0.06, 0.14 and 0.16 μg l^{-1} for benzene toluene, ethylbenzene and *o*-xylene, respectively. The repeatability of the results was acceptable with relative standard deviations up to 11.4%. A possibility to apply the proposed techniques for determination of aromatic hydrocarbons in tap water and snow was demonstrated.

Key words: liquid phase microextraction, gas chromatography, BTEX

INTRODUCTION

Volatile aromatic hydrocarbons are widely spread in the environment. Benzene, toluene, ethylbenzene and xylenes (BTEX) are used as solvents and as precursors for many plastics. They are found in oil and oil products and are released into the environment from petroleum refining industries [1]. Major sources of these compounds in the environment are fuel and oil spills. They also get into the atmosphere mainly via the production and combustion of gasoline, as emissions from motor vehicles and solvents [2]. Rain and snow fall contribute to the deposition of BTEX from the atmosphere by washing out particle-bound contaminants and sorbing the vapour [3]. BTEX seriously affect human health. Short-term effects include headache, fatigue, nervous system disorders, immune system depression, anaemia; long-term effects are chromosome aberrations, cancer, spasms, genotoxicity, damage to the liver, kidney, eyes and central nervous system [1]. Thus, for BTEX control in all fields of interest, precise and accurate analytical techniques are necessary. Gas chromatography is commonly used to detect BTEX. However, low concentrations of BTEX necessitate a preconcentration step, and determination of BTEX in complex matrices requires a selective extraction of the analytes.

* Corresponding author. E-mail: vida.vickackaite@chf.vu.lt

The traditional approaches in sample preparation are liquid–liquid extraction and solid-phase extraction. However, these extraction techniques have several significant drawbacks: they are labour-intensive, time-consuming, require large volumes of expensive, toxic, high-purity organic solvents.

Because of the disadvantages of conventional extraction techniques, microextraction techniques gain a growing interest. The miniaturised version of solid-phase extraction is determined as solid-phase microextraction (SPME) and that of liquid–liquid extraction as liquid phase microextraction (LPME).

There are many publications on SPME of BTEX applying commercially available SPME fibres (mainly polydimethylsiloxane coated) [4, 5], as well as home-made fibres such as NiTi alloy coated with ZrO_2 [6], amino ethyl-functionalized nanoporous silica [7], carbon nanotubes [8], silicone glue coated stainless steel wire [9].

The main LPME methodologies are single drop microextraction (SDME), dispersive microextraction and microextraction using immiscible liquid films.

In the simplest version of SDME, a microdrop of the solvent is suspended from the tip of a conventional microsyringe and immersed in a sample solution [10] or exposed to the headspace of the sample [11]. However, using direct SDME,

the droplet may be lost from the needle tip of the syringe during extraction, particularly when samples are stirred vigorously. SDME was applied for BTEX extraction using 1-octanol as an extracting solvent [12].

Efforts to reduce the extraction time led to the development of the dispersive liquid–liquid microextraction (DLLME) method suggested in 2006 by Assadi et al. [13]. The method is based on a ternary solvent system. A mixture of water-immiscible extraction solvent dissolved in a water-miscible disperser solvent is injected rapidly into the aqueous phase. A cloudy solution is formed. It consists of fine droplets of the extraction solvent, which are dispersed into aqueous phase. Due to the considerably large surface area of the finely dispersed extraction solvent, the extraction of the analytes is achieved rapidly. Following centrifugation, the extraction solvent containing the analytes is separated and analysed by an appropriate method. DLLME is a simple to operate, rapid and inexpensive extraction method with high preconcentration factors and low sample volume requirements. There are a few publications on the DLLME of BTEX [14, 15].

Among different versions of microextraction using immiscible liquid films, hollow fibre liquid phase microextraction (HFLPME) proposed by Pedersen-Bjergaard and Rasmussen in 1999 [16] gains an increasing interest. The technique utilizes porous, hydrophobic polypropylene hollow fibre as a membrane. The fibre is impregnated with an organic phase. This new microextraction methodology is an attractive alternative to single drop microextraction because, apart from being simple and fast, it also enables clean extract formation. The low cost of the hollow fibre enables to dispose each extraction unit after a single extraction and thus to exclude cross-contamination problems from sample to sample and to avoid the need of regeneration of the extraction unit.

HFLPME has been successfully applied for the determination of drugs [17, 18], aromatic amines [19, 20], pesticides [21, 22], phthalates [23], parabens [24]. However, there is only one publication on BTEX hollow fibre LPME [25]. The authors suggest to apply 1-octanol as an extracting solvent. However, in order to control whether the hollow fibre is well-filled with the solvent, the optical properties of the solvent should ensure the solvent to be visible in the hollow fibre. 1-Octanol does not satisfy this requirement. The aim of the present study was to simplify HFLPME of BTEX by offering another efficient extraction solvent with better optical properties and to examine the proposed HFLPME system for the extraction of BTEX from aqueous solutions.

EXPERIMENTAL

Reagents

Benzene (≥99.8%), toluene (≥99.9%), ethylbenzene (≥99.5%), *o*-xylene (≥99%), *n*-octanol (≥98%) and carbon tetrachloride (≥99.5%) were purchased from Merck. Dibutyl phthalate (DBP) (99%) was purchased from Alfa Aesar. (98%) *n*-Octane (C_8H_{18}) (98%) and acetone (≥99.9%) were purchased from Sigma-Aldrich. NaCl (analytical grade) was purchased from "Reachim" (Ukraine).

A standard stock solution containing 1 mg ml^{-1} of benzene, toluene, ethylbenzene and *o*-xylene was prepared in acetone. The stock solution was stored refrigerated at +4 °C. Working standard solutions were prepared daily by diluting the stock standard solution with distilled water to the required concentrations.

Tap water from laboratory and snow were collected in 100 ml amber glass vials which were completely filled with no headspace and closed with a metallic cap. The samples were refrigerated at 4 °C and analyzed within 12 h of sampling without any pretreatment.

Hollow-fibre liquid phase microextraction

For HFLPME, 10 ml of a sample was placed into a 12 ml vial containing a magnetic stirring bar. HPLPME was carried out using an Accurel Q 3/2 polypropylene hollow fibre membrane (Membrana, Wuppertal, Germany) with a 200 μm wall thickness, 0.2 μm pore size and 600 μm internal diameter. The hollow fibre was cut into pierces 2 cm long. One end of each pierce was heat-sealed using soldering iron. The effective internal volume of the pierce of the hollow fibre was approximately 5 μl. Each pierce was used only once. Before use, the hollow fibres had been sonicated in acetone for 10 min, then removed from acetone and allowed to dry at room temperature.

The unsealed end of the fibre was connected to a 0.7 cm diameter syringe needle inserted into the silicone rubber septum placed in the extraction vial cap. For several minutes the hollow fibre was immersed into the receiving phase (DBP : *n*-octanol (1 : 1) containing an internal standard *n*-octane). The receiving phase impregnated its walls and penetrated inside the hollow fibre filling it completely. Then the fibre was withdrawn from the receiving phase, washed with distilled water in order to eliminate the excess of the receiving phase, and immersed into the sample solution. The sample vial was placed on a magnetic stirrer. After the extraction, the vial cap together with the needle and the hollow fibre was removed from the vial, 1 μl of the extract was withdrawn into a 10 μl microsyringe and injected into the GC system.

GC analysis

Extracted analytes were detected using gas chromatography. Gas chromatography was carried out in a Varian 3400 (Palo Alto, CA, USA) gas chromatograph equipped with a flame ionisation detector coupled with an SP4290 integrator (Spectra-Physics San Jose, CA, USA) and an Equity™-5 fused silica capillary column (30 m × 0.53 mm, 1.5 μm film thickness) supplied by Supelco (Bellefonte, PA, USA). A splitless injection mode was used. The injector temperature was 280 °C, and the detector temperature 300 °C. The oven temperature was initially set at 40 °C for 2 min, then gradually ramped to 70 °C (3 °C min^{-1}), to 290 °C (50 °C min^{-1}) and kept for

12 min. The following gas flow rates were used: carrier gas (nitrogen) 10, make-up gas (nitrogen) 20, hydrogen 30 and air 300 ml min^{-1}. One millilitre of the extract was injected for GC analysis.

RESULTS AND DISCUSSION

Optimization of extraction conditions

To ensure the efficient performance of the extraction, several parameters that influence the extraction efficiency were studied and optimized. Those parameters were the nature of the extraction solvent, the extraction time, and the ionic strength of the solution.

An extraction solvent had to meet some main requirements: to extract the analytes quite well, to be able to penetrate into the pores of a polypropylene hollow fibre and to be separated from the analyte peaks in the chromatogram.

In [25], *n*-octanol was proposed as an extraction solvent for BTEX. However, the refractive index of *n*-octanol (1.43) is quite different from that of polypropylene (1.49), and thus the polypropylene hollow fibre immersed in *n*-octanol is not transparent. Therefore, using *n*-octanol as an extraction solvent it is not possible to control the fibre filling quality. Our purpose was to find another extraction solvent that demonstrates good extraction properties and is visible in the hollow fibre.

We examined BTEX extraction efficiencies using *n*-octanol, carbon tetrachloride, DBP and some mixtures of *n*-octanol : DBP as an extraction solvent. HFLPME was carried for 30 min from 10 mL of aqueous solutions with BTEX concentrations of 10 μg ml^{-1}.

In the case of CCl_4, after 30 min of extraction the hollow fibre did not contain the extraction solvent any more. Probably because of a significant solubility (800 mg l^{-1}) and high volatility (boiling point 76.2 °C) CCl_4 dissolved in the aqueous solution and evaporated through the open end of the syringe needle. *n*-Octanol and DBF are less soluble and less volatile, and thus after 30 min extraction the hollow fibre contained the solvent for a subsequent GC analysis.

In Fig. 1, the extraction efficiency of different solvents is demonstrated. The extraction efficiency using *n*-octanol and DBP was similar. In addition, differently from *n*-octanol, the DBP refractive index (1.51) is quite similar to that of polypropylene. Thus, after immersing the hollow fibre into DBP, the walls of the hollow fibre became transparent and the level of the solvent in the capillary could be easily observed. On the other hand, DBP viscosity is rather high (1.33×10^{-2} Pa s), thus, for DBP it takes 30–35 min to penetrate polypropylene pores and to fill the hollow fibre.

In order to accelerate the hollow fibre filling process, *n*-octanol : DBP mixtures in the ratios 1 : 1, 1 : 2 and 2 : 1 were tested for the extraction. The extraction efficiency of all these mixtures was similar; however, DBP : *n*-octanol (1 : 2) was hardly visible in the hollow fibre. The optical properties of the other two mixtures were good. In addition, due to the lower viscosity, the mixture DBP : *n*-octanol (1 : 1) filled the space inside the hollow fibre in 2–3 min, while in the case of DBP : *n*-octanol (2 : 1) about 10 min were required. So, the DBP : *n*-octanol (1 : 1) mixture was chosen as an extracting solvent for the further work.

In order to correct variable injection volumes, an internal standard was required. For this purpose, *n*-heptane, *n*-octane and *n*-nonane were tested. *n*-Octane was the best because it was eluted between the analytes, and its peak was well separated from the analyte peaks. An analytical signal was taken as the ratio of the peak area of the analyte to that of *n*-octane.

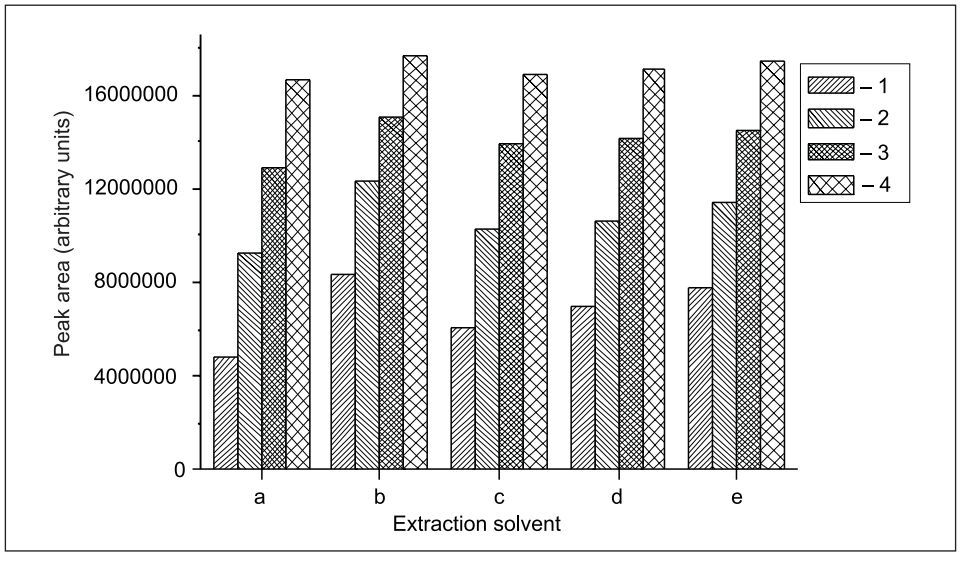

Fig. 1. Effect of HFLPME solvent on the peak area of (1) benzene, (2) toluene, (3) ethylbenzene and (4) *o*-xylene. Concentration of each analyte is 10 μg ml^{-1}. Extraction solvents: (a) *n*-octanol, (b) DBP, (c) DBP : *n*-octanol (1:2), (d) DBP : *n*-octanol (1 : 1), (e) DBP : *n*-octanol (2 : 1). Extraction time 30 min. Solution stirring rate 800 rpm

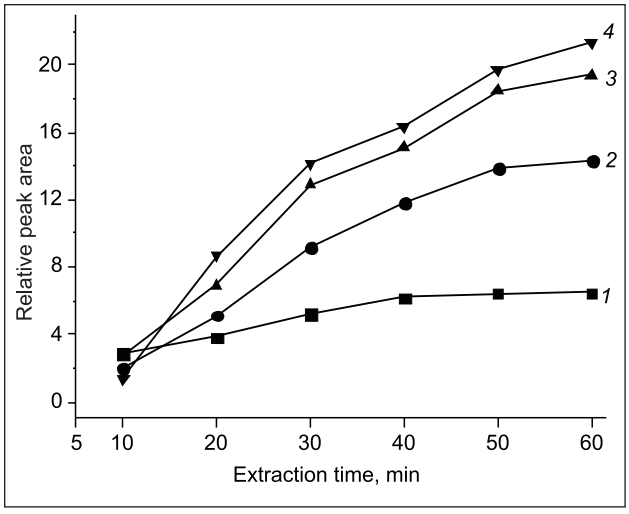

Fig. 2. Effect of extraction time on the peak area of (*1*) benzene, (*2*) toluene, (*3*) ethylbenzene and (*4*) *o*-xylene. Extraction solvent DBP : *n*-octanol (1 : 1). For other extraction conditions, see Fig. 1. Peak areas are normalised to the corresponding peak areas using *n*-octane

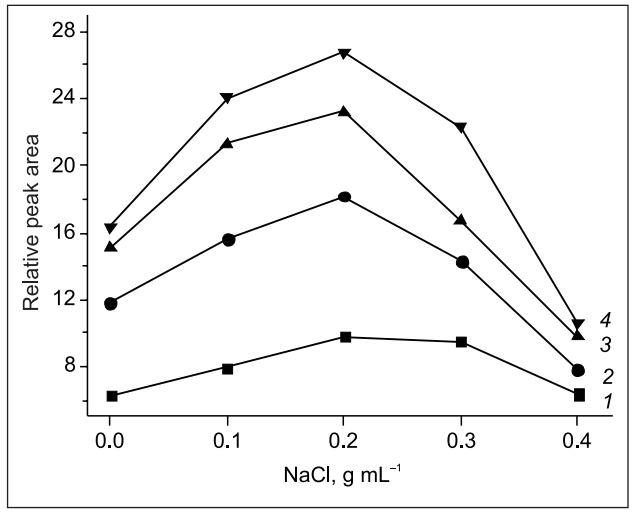

Fig. 3. Effect of NaCl content on the peak area of (*1*) benzene, (*2*) toluene, (*3*) ethylbenzene and (*4*) *o*-xylene. Extraction time 40 min. For other extraction conditions, see Fig. 2

The concentration of *n*-octane in the extraction solvent was 100 μg ml^{-1}.

One of the advantages of HFLPME is the possibility to apply high stirring rates (since the receiving phase is protected by the hollow fibre) and thus to reduce the time required to reach the equilibrium of the analytes between the aqueous and the receiving phases. In this work, we applied the 800 rpm stirring rate.

Extraction time was evaluated between 10 and 60 min. The maximum extraction efficiency would be achieved when an equilibrium between the two immiscible phases is established. According to the curves presented in Fig. 2, for all the analytes except benzene, the equilibrium was not reached even after the extraction time of 60 min. However, it is possible to work in the non-equilibrium state if constant extraction conditions are maintained. For the further work, 40 min was chosen as the extraction time, because it is sufficiently long to reach a high extraction efficiency and, on the other hand, corresponds to time required for GC analysis (29.4 min).

The addition of a salt to the aqueous sample solution generally causes a decrease in the solubility of the organic compounds in the water, and this has been widely used to enhance the extraction of the analytes. In our work, extraction was performed in the presence of different NaCl concentrations (from saltless up to saturation).

The results presented in Fig. 3 demonstrate that the extraction efficiency initially increases with increasing the concentration of NaCl, and the maximum signal is achieved at a concentration of 0.2 g ml^{-1}. The increase in the extraction extent can be explained by the engagement of water molecules in the hydration spheres around the ionic salt and hence in the reduction of the water concentration available to dissolve

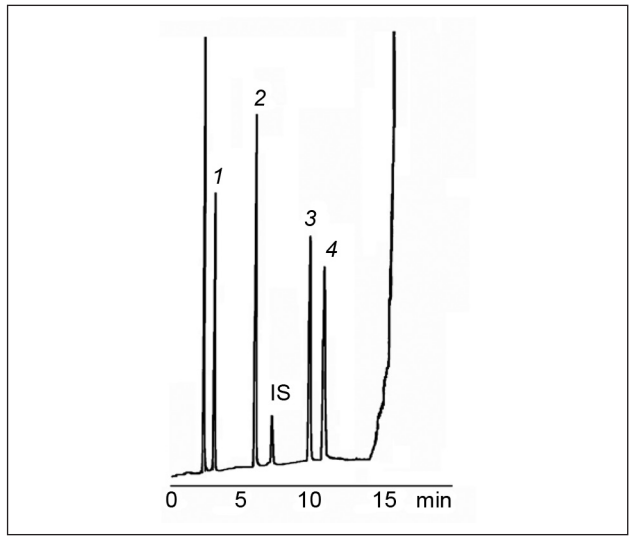

Fig. 4. Chromatogram of the standard solution of (*1*) benzene, (*2*) toluene, (*3*) ethylbenzene and (*4*) *o*-xylene obtained after HFLPME. IS – internal standard *n*-octane (100 μg ml^{-1}). NaCl concentration 0.2 g ml^{-1}. For other extraction conditions, see Fig. 3. For GC conditions, see Experimental

the analytes. Consequently, the analytes are favoured to move to the extraction solvent. At the further increase of the concentration of NaCl, the extraction efficiency decreased, probably because dissolved NaCl has changed the physical properties of the extraction film in the interface of the aqueous and organic phases and thus the diffusion of the analytes into the organic phase was reduced. On the basis of these results, in the further experiments 0.2 g ml^{-1} of NaCl was added to the samples.

A chromatogram of the extract of the standard solution of BTEX obtained at optimized extraction conditions is presented in Fig. 4.

Table. **Enrichment factors, detection limits and repeatabilities**

Analyte	Enrichment factor	Detection limit, μg l^{-1}	RSD, % (n = 5)	
			1 μg ml^{-1}	10 μg ml^{-1}
Benzene	112	0.22	11.4	6.6
Toluene	208	0.06	9.9	6.5
Ethylbenzene	252	0.14	8.8	8.8
o-Xylene	260	0.16	9.4	7.4

Validation of the method

The quality parameters of the suggested methods, such as linearity, limits of detection, enrichment factors and repeatabilities, were calculated under optimized extraction conditions.

To calculate the enrichment factor, three replicate extractions were performed in the optimal conditions from the aqueous solution containing 10 μg ml^{-1} of each analyte. The enrichment factor was calculated as the ratio of the final analyte concentration in the extraction solution and its concentration in the original solution. The actual concentration of each extracted analyte was calculated from the calibration curves. The enrichment factors are presented in Table. The calibration curves were drawn with three replicate direct injections of the extracts obtained after applying the HFLPME procedure with 12 calibration points. The linear ranges were from 0.36, 0.10, 0.23 and 0.27 up to 50 μg ml^{-1} for benzene, toluene, ethylbenzene and *o*-xylene, respectively. The correlation coefficients were 0.997–0.998. To calculate the detection limits, three replicate extractions were performed. The detection limits, defined as three times of the base-line noise, are presented in Table.

The repeatability was determined by the analysis of five repetitions for two BTEX concentrations. Relative standard deviations (RSDs) were calculated and summarized (Table). These data show that the repeatability of the method is satisfactory.

Application

The method was applied to real water and snow samples. Tap water from the laboratory and snow collected in a parking place were analysed immediately after sampling without any pretreatment.

The results showed that tap water was free of BTEX. The snow from the parking place contained a small quantity of BTEX (Fig. 5). The concentrations of BTEX were calculated using the standard addition method and found to be 0.44, 0.21, 0.28 and 0.35 μg l^{-1} for benzene, toluene, ethylbenzene and *o*-xylene, respectively.

CONCLUSIONS

The paper describes the use of HFLPME for BTEX sampling and preconcentration. The proposed method provides for high enrichment factors, is sufficiently reproducible and linear over a broad concentration range, environmentally friendly. Only about 5 microlitres of the extracting solvent are used for the extraction. The technique is compatible with the GC. The detection limits obtained by HFLPME are of the same order as those obtained using SPME [8, 9, 26] and DLLME [14, 15]. Additionally, hollow fibre enables an excellent sample clean-up, thus the sample does not need additional filtration or centrifugation. Due to its simplicity, extremely low consumption of hazardous organic solvents and low cost, the method is a promising technique for BTEX analysis in aqueous matrices.

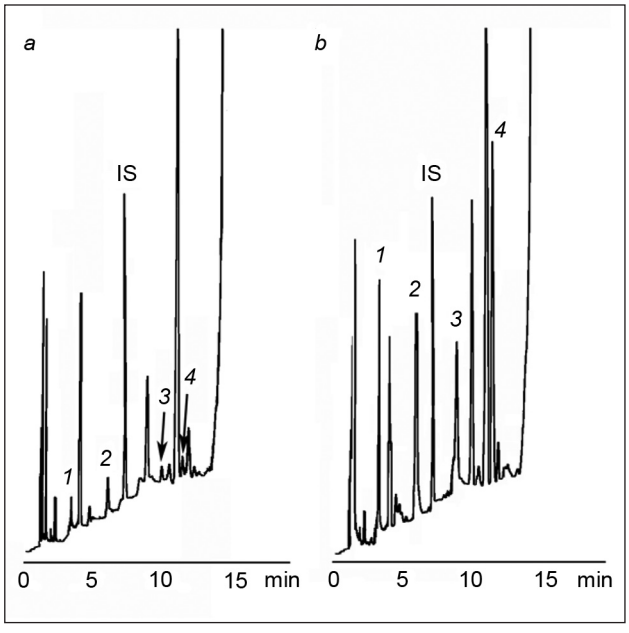

Fig. 5. Chromatograms of the snow (*a*) and of the snow spiked with BTEX containing 5 μg l^{-1} of each analyte (*b*) obtained after HFLPME: (*1*) benzene, (*2*) toluene, IS – internal standard *n*-octane (100 μg ml^{-1}), (*3*) ethylbenzene and (*4*) *o*-xylene. NaCl concentration 0.2 g ml^{-1}. For other extraction conditions, see Fig. 3. For GC conditions, see Experimental

ACKNOWLEDGEMENT

This work has been supported by the Lithuanian State Science and Studies Foundation.

Received 8 January 2010
Accepted 25 January 2010

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Edita Pusvaškienė, Nadežda Spirova, Aleksandra Prichodko, Vida Vičkačkaitė

LAKIŲ AROMATINIŲ ANGLIAVANDENILIŲ SKYSTAFAZĖ MIKROEKSTRAKCIJA KAPILIARE

S a n t r a u k a

Tirta benzeno, tolueno, etilbenzeno ir *o*-ksileno skystafazė mikroekstrakcija kapiliare. Nustatyta ekstrahento prigimties, ekstrakcijos trukmės ir tirpalo joninės jėgos įtaka ekstrakcijos efektyvumui. Ekstrahentu pasirinktas dibutilftalato : *n*-oktanolio (1 : 1) mišinys, vidiniu standartu – *n*-oktanas. Kalibracinės kreivės benzenui, toluenui, etilbenzenui ir *o*-ksilenui tiesinės nuo 0,36, 0,10, 0,23 ir 0,27 μg l^{-1} iki 50 μg ml^{-1} analičių koncentracijos, koreliacijos koeficientai 0,997–0,998, sukoncentravimo laipsnis nuo 112 (benzeno) iki 260 (*o*-ksileno), aptikimo ribos 0,22 μg ml^{-1} (benzeno), 0,06 μg l^{-1} (tolueno), 0,14 μg l^{-1} (etilbenzeno) ir 0,16 μg l^{-1} (*o*-ksileno), santykiniai standartiniai nuokrypiai ne didesni kaip 11,4 %. Parodyta galimybė pritaikyti metodą lakiems aromatiniams angliavandeniliams nustatyti geriamo vandens ir sniego mėginiuose.