**VILNIUS UNIVERSITY**

Edita Pusvaškienė

# DEVELOPMENT, INVESTIGATION AND APPLICATION OF NEW MIKROEXTRACTION SYSTEMS FOR THE DETERMINATION OF VOLATILE AROMATIC HYDROCARBONS

Summary of doctoral dissertation

Physical sciences, chemistry (03 P)

**Vilnius, 2010**

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The dissertation is available at the library of Vilnius University and the library of Institute of Chemistry.

**VILNIAUS UNIVERSITETAS**

Edita Pusvaškienė

# NAUJŲ MIKROEKSTRAKCIJOS SISTEMŲ KŪRIMAS, TYRIMAS IR TAIKYMAS LAKIŲ AROMATINIŲ ANGLIAVANDENILIŲ NUSTATYMUI

Daktaro disertacija

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**Vilnius, 2010**

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# INTRODUCTION

Volatile organic compounds such as benzene, toluene, ethylbenzene and xylene (BTEX) are an important group of natural and anthropogenic organic compounds. BTEX seriously affect human health. Thus, for BTEX control, precise and accurate analytical techniques are necessary.

In order to clean and concentrate the analytes, sample preparation step is commonly involved in an analytical procedure. Traditional sample preparation techniques such as liquid-liquid extraction and solid phase extraction are time-consuming and use large amounts of toxic organic solvents, which may be dangerous to human health and to the environment. Because of these disadvantages, developing of new, fast, inexpensive, environmentally friendly and easy to use microextraction techniques has been gaining a growing interest.

Solid phase microextraction (SPME) is a miniaturised version of traditional solid phase extraction. It was introduced in 1989 and in 1995 was commercialized. However, the process of the preparation of commercial SPME fibres requires expensive equipment, which accounts for the relatively high price of the fibres. Moreover, fused silica fibres are fragile and extra care must be taken during use. Therefore, more robust SPME fibres with a long life and low cost are highly desired.

In 1996 the first attempts to miniaturise liquid – liquid extraction were made. Since now various modes of liquid – liquid microextraction were suggested: single drop microextraction, dispersion liquid – liquid microextraction (DLLME), hollow fibre liquid phase microextraction (HFLPME). All these extraction methods require small amounts of extraction solvent. However, these microextraction methods are rather new, so there are no liquid-liquid microextraction techniques for volatile aromatic hydrocarbons.

**The aim of the work was** to investigate possibilities of solid phase microextraction and various liquid – liquid microextraction methods for rapid and efficient determination of volatile aromatic hydrocarbons, to develop and apply microextraction techniques for water sample analysis.

**The main tasks** set to achieve the aim were as follows**:**

1. To develop a new SPME system using carbon nanotubes as fibre coating onto a stainless steel rod. To investigate possibilities of the system to extract volatile aromatic hydrocarbons. Using suggested SPME system, to develop SPME techniques for volatile aromatic hydrocarbons and apply it for water sample analysis.
2. To investigate possibilities of hollow fibre liquid phase microextraction to extract volatile aromatic hydrocarbons. To develop hollow fibre liquid phase microextraction technique for volatile aromatic hydrocarbons and apply it for water sample analysis.
3. To investigate possibilities of liquid phase microextraction based on the solidification of a floating drop to extract volatile aromatic hydrocarbons. To develop liquid phase microextraction based on the solidification of a floating drop technique for volatile aromatic hydrocarbons and apply it for water sample analysis.
4. To investigate possibilities of dispersion-solidification liquid–liquid microextraction to extract volatile aromatic hydrocarbons. To develop dispersion-solidification liquid–liquid microextraction technique for volatile aromatic hydrocarbons and apply it for water sample analysis.
5. To compare and evaluate prepared microextraction techniques of volatile aromatic hydrocarbons.

**Statements for defence:**

1. Carbon nanotubes can be used as a sorbent for volatile aromatic hydrocarbons extraction.
2. Microextraction methods of volatile aromatic hydrocarbons are rapid, cheap, simple and efficient.
3. Selection of microextraction method depends on sample matrix.
4. Microextraction methods of volatile aromatic hydrocarbons are suitable for real objects analysis.

## 2. EXPERIMENTAL

Gas chromatography was carried out in a Varian 3400 (Palo Alto, CA, USA) gas chromatograph equipped with a flame ionisation detector coupled with integrator SP4290 (Spectra-Physics San Jose**,** CA**,** USA). For a chromatographic separation were used or two connected fused silica capillary columns – HP-5 (5 % Ph Me Silicone) (10 m × 0.53 mm, 2.65 μm in film thickness) and HP-17 (croslinked 50 % Ph Me Silicone) (10 m × 0.53 mm, 2.0 μm in film thickness) or a Equity$^{TM}$-5 fused silica capillary column (30 m × 0.53 mm, 1.5 μm film thickness) supplied by Supelco (Bellefonte, PA, USA). For sample injection 10 μL microsyringe (Hamilton, Reno, NV, USA) was used.

The SPME device was modified from a commercial SPME device (Supelco Bellefonte, PA, USA). The septum-piercing needle was removed and replaced with a larger one. Stainless steel plunger needle (600 μm o.d.) was used as a support for a coating. The end of the plunger needle (2 cm length) was polished in the way to get a groove. The plunger needle was mounted inside the external needle, cleaned with acetone in an ultrasonic bath for 10 min and dried at room temperature. A thin layer of epoxy glue was spread on the groove surface of the plunger needle and a carbon nanotube powder was gently pressed to the glue. The coated fibre was dried at room temperature in the vertical position for 2 h and then conditioned under nitrogen in an injection port of a gas chromatograph at 300$^{o}$C for 1 h.

HFLPME 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 2 cm length pierces. 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 were 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. 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.

## 3. RESULTS AND DISCUSSION

### 3.1. Solid phase microextraction of volatile aromatic hydrocarbons using carbon nanotube coating

**SPME system preparation**

One of the main problems in the preparation of SPME fibres is the mechanical stability of coatings. Since coatings as a role are fixed on the plunger needle inserted into the septum piercing needle, there is a direct contact between the coating and the inner walls of the outer needle and hence the coating little by little smears. The loss of the coating has a negative influence on the coatings extraction capacity and the repeatability of the results. We suggested different construction of the SPME fibre and incorporated the sorbent into a groove formed onto the plunger needle (Fig. 1). This construction prevents the contact of the sorbent particles with the outer needle and thus the mechanical damage of the coating is avoided.

The surface of the coating was examined by scanning electron microscopy. A groove of the plunger needle coated with carbon nanotubes powder is evidenced in the photography (Fig. 2).

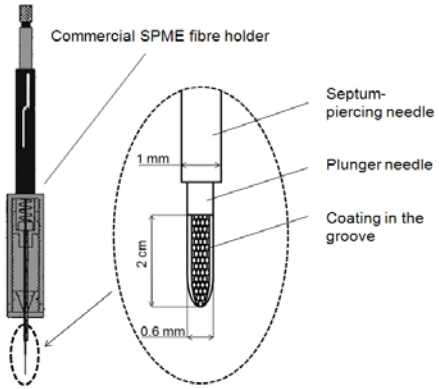


Fig. 1. SPME device scheme.

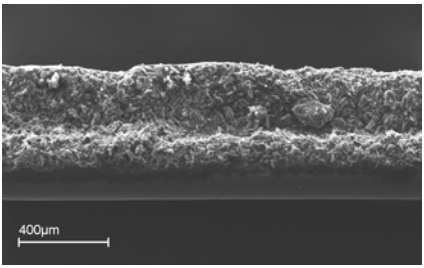


Fig. 2. Scanning electron microscope photography of SPME fibre coated with carbon nanotubes.

**SPME coating properties**

The thermal stability of the coating was evaluated and it was determined that the coating can be operated without any damage up to 280°C.

In order to examine coating selectivity, the fibre was tested for different classes of compounds. For this reason the fibre was held for 30 minutes in the aqueous solution containing 10 mg $L^{-1}$ of 2-butanone, *n*-butanol, *n*-butyl acetate, *o*-xylene, phenol, and methyl benzoate. The peak areas were compared with those obtained after direct syringe injection (1 µL) of the same solution. As seen in Fig.3, the fibre selectivity increases in the sequence *n*-butanol < 2-butanone < phenol < *n*-butyl acetate < methyl benzoate < *o*-xylene. The correlation of the extraction efficiency with the octanol-water partition coefficients can be observed. The compounds having higher log $K_{ow}$ values possess more affinities towards the coating indicating that hydrophobic interactions. The sorption of compounds containing an aromatic ring (*o*-xylene and methyl benzoate) is the strongest probably because of the π-π interaction between the carbon nanotube walls and the aromatic ring. On the other hand, the coating poorly extracts polar phenol.

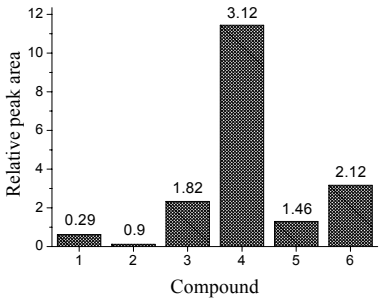


Fig.3. Coating selectivity study: (1) 2-butanone, (2) *n*-butanol, (3) *n*-butyl acetate, (4) *o*-xylene, (5) phenol, (6) methyl benzoate. $K_{ow}$ data are presented over the respective bars. Concentrations of the analytes are 10 mg $L^{-1}$. Direct SPME for 30 min. Peak areas normalised to the peak areas achieved after 1 µl syringe injection of the solution with the same analyte concentration.

Since the carbon nanotube coating layer was not uniform (was thicker in the middle of the groove and thinner at the edges) the extraction of the less volatile compounds could be problematic because of their low sorption/desorption from the thicker coating layer and could cause peak tailing because of the differences in the coatings thickness. On the other hand, volatile compounds as a role need only few seconds to be desorbed even from a thick sorbent layer so the proposed SPME system is expected to show good preconcentration for volatile compounds. As the selectivity investigations showed the best coatings affinity to aromatic hydrocarbons, the further work the SPME system was investigated for the extraction of aromatic hydrocarbons.

**Optimisation of SPME parameters**

Desorption investigations were accomplished after direct SPME of benzene, toluene, ethylbenzene and *o*-xylene. As it was shown above, the coating can be operated without any damage up to the 280$^{o}$C temperature so, for the further experiments this desorption temperature was selected. Desorption time from 10 to 180 s was investigated. A standard solution containing 10 mg $L^{-1}$ of each analyte was used. Direct SPME was held for 15 min using 600 rpm stirring rate of the solution. The carry-over was measured with one blank injection following the initial desorption. The results showed that at the desorption temperature of 280$^{o}$C all the analytes were quantitatively desorbed from the fibre coating after 2 min and no carry over effect was observed in blank injections. Therefore in the further work 2 min desorption time was used.

Direct and headspace SPME modes were investigated and compared. The effect of main extraction parameters, such as sampling temperature, extraction time and salt concentration in the sample were studied.

Sample agitation is an important kinetic parameter. Stirring of the sample solution reduces the time required to reach the equilibrium and extraction time by enhancing the diffusion of the analytes towards the fibre. We used a vigorous agitation of the aqueous sample (600 rpm) that, on the other hand, did not result in suck and spatter formation that could impair the contact of the solution with the fibre surface.

Direct SPME was carried out at room temperature since at elevated temperatures coating/water distribution constants of the analytes decrease and hence resulting in the decrease in the extraction efficiency. For headspace SPME the extraction temperature

has a double impact. Higher temperatures lead to higher vapour pressure of the analytes and hence their concentrations in headspace increase. On the other hand**,** partition coefficients of the analytes between fibre coating and headspace decrease with the temperature. Thus the temperature for optimum extraction efficiency was determined experimentally.

The effect of temperature was studied in the range of 20 - 70$^{o}$C by exposing SPME fibre in the headspace of the solution containing 10 mg L$^{-1}$ of each analyte for 15 min. As can be seen in Fig. 4, the extraction ability increases, with increasing temperature, up to 60-70$^{o}$C, due to the increasing distribution constant of analytes between the aqueous phase and headspace. However, for most of the aromatic hydrocarbons studied a slight decrease in adsorption capacity was observed when temperature further increased up to 70$^{o}$C. For further experiments 60$^{o}$C temperature was adopted.

The extraction time for both direct and headspace SPME was studied in the range 5-30 min. Fig. 5 shows the extraction time profiles for the studied BTEX obtained by direct SPME. As expected, at the beginning the extraction efficiency increased with extraction time. All the studied analytes reached equilibrium after about 20 min. The same extraction time was observed also in the case of headspace SPME (results not shown).

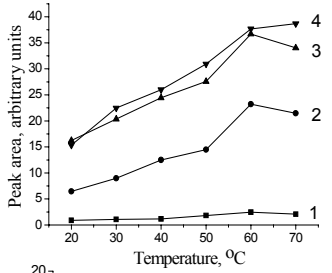


Fig. 4. Effect of extraction temperature on the peak area of (1) benzene, (2) toluene, (3) ethylbenzene and (4) *o*-xylene. Concentrations of the analytes are 10 mg L$^{-1}$. Headspace SPME for 15 min at room temperature; desorbtion at 280$^{o}$C for 2 min.

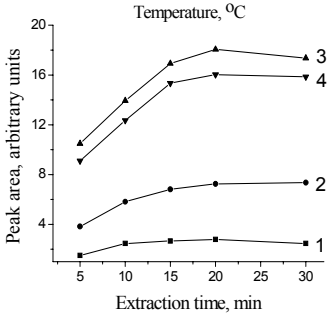


Fig. 5. Effect of extraction time on the on the peak area of (1) benzene, (2) toluene, (3) ethylbenzene and (4) *o*-xylene. Concentrations of the analytes are 10 mg L$^{-1}$. Direct SPME at room temperature; desorption at 280ºC for 2 min.

The addition of salt to the aqueous sample solution generally causes a decrease in solubility of the organic compounds in the water, and this has been widely used to enhance the extraction of analytes. The extraction was performed in the presence of different concentrations of NaCl (from saltless up to saturation). The results showed that using both headspace (Fig. 6) and direct SPME the extraction efficiency gradually increases with increasing concentration of NaCl and the maximum signal was achieved when the solution was saturated by NaCl. 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 analytes. Consequently, analytes are favoured to move to the fibre (direct SPME) or to the headspace and then to the fibre (headspace SPME). In further experiments, 0.4 g $mL^{-1}$ of NaCl was added to the samples.

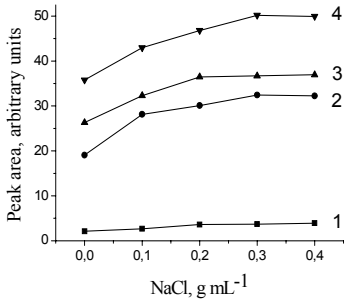


Fig. 6. Effect of NaCl content on the peak area of (1) benzene, (2) toluene, (3) ethylbenzene and (4) *o*-xylene. Concentrations of the analytes are 10 mg $L^{-1}$. Headspace SPME for 20 min at 60°C; desorbtion at 280°C for 2 min.

**Analytical performance**

The quality parameters of the SPME methods such as linearity, limits of detection, repeatability were measured under the optimised conditions. For both headspace and direct SPME the calibration graphs were linear up to 100 mg $L^{-1}$ and the correlation coefficients for all the analytes were satisfactory ($R^2 > 0.996$). The limits of detection, defined as three times of base-line noise, for both direct and headspace SPME modes are similar and are presented in Table 1. The repeatabilities of the both SPME modes were determined by five repetitions analysis of two different concentrations of the analytes under optimum conditions (Table 1).

**Table 1.** BTEX detection limits and result repeatabilities

| Analyte | Detection limit, µg $L^{-1}$ | | RSD, % (n=5) | | | |
|---|---|---|---|---|---|---|
| | Direct SPME | Headspace SPME | Direct SPME | | Headspace SPME | |
| | | | 10 µg $L^{-1}$ | 1 mg $L^{-1}$ | 10 µg $L^{-1}$ | 1 mg $L^{-1}$ |
| Benzene | 0.39 | 0.38 | 11.0 | 7.7 | 11.4 | 6.8 |
| Toluene | 0.14 | 0.10 | 12.4 | 7.1 | 12.0 | 8.2 |
| Ethylbenzene | 0.11 | 0.16 | 11.6 | 6.1 | 12.9 | 5.9 |
| *o*-Xylene | 0.09 | 0.27 | 12.5 | 9.9 | 13.3 | 9.1 |

**Sample analysis**

A possibility to use the fibre for real sample analysis was demonstrated applying it to the determination of the studied compounds in petrol station waste water. In order to eliminate the extraction of low volatility components headspace SPME was used. In addition, headspace SPME was preferred since it gave slightly lower detection limits. Fig. 7 illustrates chromatograms of the petrol station waste water after treatment without (a) and with addition of standard solution of BTEX (b).

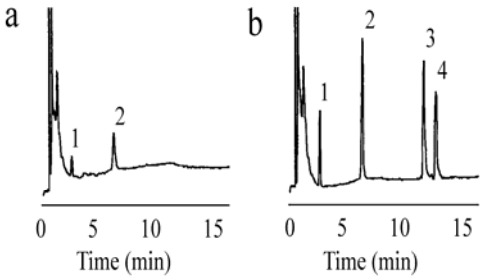


Fig. 7. Chromatograms of the petrol station waste water after treatment without (a) and with addition of standard solution of BTEX (b). (1) benzene, (2) toluene, (3) ethylbenzene and (4) *o*-xylene. Concentrations of the analytes are 10 mg $L^{-1}$.

Before treatment the concentrations of benzene, toluene, ethylbenzene and o-xylene were respectively 4.8, 4.64, 1.39 and 1.92 µg $L^{-1}$. After treatment the concentration of aromatic hydrocarbons resulted very low and only benzene (0.86 µg $L^{-1}$) and toluene (0.67 µg $L^{-1}$) were detected. The concentrations of the other two analytes were under the detection limit.

### 3.2. Hollow-fibre liquid phase microextraction of volatile aromatic hydrocarbons

Hollow-fibre liquid phase microextraction utilizes porous, hydrophobic polypropylene hollow fibre as a membrane. The fibre is impregnated with an organic phase. This microextraction methodology is simple, fast, enables clean extract formation. 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.

**Optimisation of extraction conditions**

For efficient performance of HFLPME, several parameters that influence the extraction efficiency were studied and optimized. Those parameters were the nature of the extraction solvent, the extraction time and 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 the polypropylene hollow fibre and to be separated from the analyte peaks in the chromatogram.

Until now only one article was published on HFLPME of BTEX where *n*-octanol was proposed as an extraction solvent. However, refractive index of *n*-octanol (1.43) is quite different from that of polypropylene (1.49) and thus polypropylene hollow fibre immersed in *n*-octanol is not transparent. Because of this, 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, besides that, 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. In the case of $CCl_4$, after 30 min extraction the hollow fibre did not contain the extraction solvent any more. Probably, because of a significant solubility (800 mg $L^{-1}$) and of a high volatility (boiling point 76.2$^{o}$C) $CCl_4$ dissolved in the aqueous solution and evaporated through an open end of a 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. 8 extraction efficiencies of different solvents are demonstrated. The extraction efficiencies using n-octanol and DBP were similar. In addition, differently

from n-octanol, DBP refractive index (1.51) is quite similar to that of polypropylene. Thus, after the immersion of the hollow fibre into DBP, 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 ($1.33\times10^{-2}$ Pa s), thus for DBP it takes 30-35 min to penetrate polypropylene pores and to fill the hollow fibre. In order to accelerate hollow fibre filling process, n-octanol : DBP mixtures in ratios 1:1, 1:2 and 2:1 were tested for the extraction. Extraction efficiencies of all those mixtures were similar, however DBP : n-octanol (1:2) was hardly visible in the hollow fibre. 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, a mixture of DBP : n-octanol (1:1) was chosen as an extracting solvent for the further work.

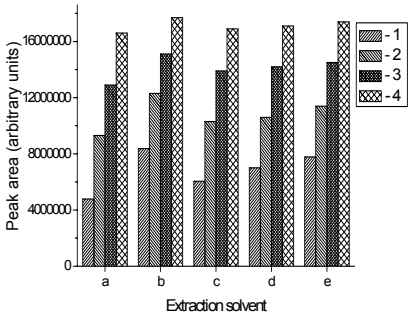


**Fig.8.** Effect of HFLPME solvent on the peak area of (1) benzene, (2) toluene, (3) ethylbenzene and (4) *o*-xylene. Concentration of each analyte is 10 μg $mL^{-1}$. Extraction solvents: (a) *n*-octanol, (b) DBP, (c) DBP : *n*-octanol (1:2), (d) DBP : *n*-octanol (1:1), (e) DBP : *n*-octanol (2:1). Extraction time 30 min. Solution stirring rate 800 rpm.

*n*-Heptane, *n*-octane and *n*-nonane were tested as internal standards. *n*-Octane was the best one 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 peak area of analyte to that of *n*-octane. *n*-Octane concentration in the extraction solvent was 100 μg $mL^{-1}$.

Extraction time was evaluated between 10 and 60 min. According to the curves presented in Fig. 9, for all the analytes except benzene the equilibrium was not reached even after the extraction time of 60 min.

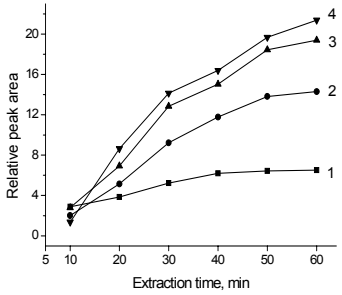


**Fig. 9**. Effect of extraction time on the peak area of (1) benzene, (2) toluene, (3) ethylbenzene and (4) *o*-xylene. Extraction solvent DBP : *n*-octanol (1:1). Extraction time 30 min. Solution stirring rate 800 rpm. Peak areas normalised to the corresponding peak areas using *n*-octane.

However, it is possible to work at non-equilibrium state if constant extraction conditions are maintained. For further work 40 min extraction time was chosen as it was sufficiently long to reach 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 solubility of the organic compounds in the water, and this has been widely used to enhance the extraction of analytes. In our work the extraction was performed in the presence of different concentrations of NaCl (from saltless up to saturation). The results presented in Fig. 10 demonstrate that the extraction efficiency initially increases with increasing concentration of NaCl and the maximum signal is achieved at the concentration of 0.2 g $mL^{-1}$. On the basis of the results obtained, in further experiments 0.2 g $mL^{-1}$ of NaCl was added to the samples.

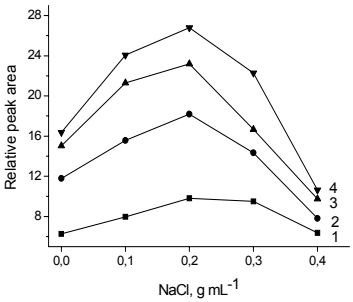


**Fig. 10.** Effect of NaCl content on the peak area of (1) benzene, (2) toluene, (3) ethylbenzene and (4) *o*-xylene. Extraction solvent DBP : *n*-octanol (1:1). Extraction time 40 min. Solution stirring rate 800 rpm. Peak areas normalised to the corresponding peak areas using *n*-octane.

**Analytical performance**

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

For the enrichment factor calculation, three replicate extractions were performed at the optimal conditions from the aqueous solution, containing 10 μg $mL^{-1}$ of each analyte. The enrichment factors are presented in Table 2. The calibration curves were drawn with three replicate direct injections of the extracts obtained after applying 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. Correlation coefficients were 0.997 - 0.998. For detection limits calculation, three replicate extractions were performed. Detection limits defined as three times of base-line noise are presented in Table 2. The repeatabilities were determined by five repetitions analysis for two concentrations of BTEX. Relative standard deviations (RSDs) were calculated and are summarized in Table 2. These data show that repeatability of the methods is satisfactory.

**Table 2.** Enrichment factors, detection limits and repeatabilities

| Analyte | Enrichment factor | Detection limit, μg $L^{-1}$ | RSD % (n = 5) | |
|---|---|---|---|---|
| | | | 1 mg $L^{-1}$ | 10 mg $L^{-1}$ |
| 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 |

**Sample analysis**

The method was applied to real water and snow samples. Tap water from 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 small quantity of BTEX (Fig. 11).

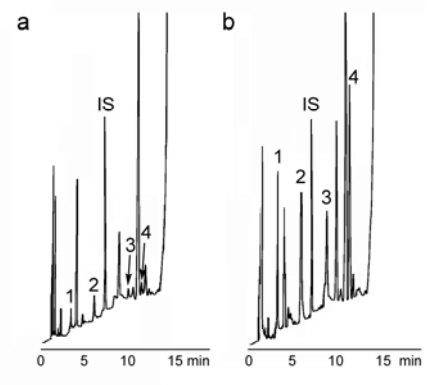


**Fig. 11.** Chromatograms of the snow (a) and of the snow spiked with BTEX containing 5 μg $L^{-1}$ of each analyte (b) obtained after HFLPME: (1) benzene, (2) toluene, IS - internal standard *n*-octane (100 μg $mL^{-1}$), (3) ethylbenzene and (4) *o*-xylene. Extraction solvent DBP : *n*-octanol (1:1). Extraction time 40 min. Solution stirring rate 800 rpm. NaCl concentration 0.2 g $mL^{-1}$.

Concentrations of BTEX were calculated using standard addition method and were determined to be 0.44, 0.21, 0.28 and 0.35 μg $L^{-1}$ for benzene, toluene, ethylbenzene and *o*-xylene, respectively.

### 3.3. Volatile aromatic hydrocarbons liquid phase microextraction based on the solidification of a floating drop

In liquid phase microextraction based on solidification of a floating organic drop (LPME-SFO) an extracting solvent must have a melting point which is near to room temperature. A droplet of the extracting solvent is floated on the surface of aqueous solution containing target analytes and solution is stirred for a required time. Afterwards, the sample vial is cooled by inserting it into an ice bath. After solidification the floating organic drop is transferred into a small conical vial where it melts quickly at room temperature and an aliquot of the solvent is taken for the analysis. Solidification of a floating organic drop facilitates the process of extract collection as the extract after solidification can easily be separated from the aqueous solution.

**Optimisation of extraction conditions**

Seven potential extraction solvents: *n*-hexadecane, *n*-heptadecane, 1-chlorooctadecane, 1-undecanol, 1-dodecanol, 2-dodecanol and cyclohexanol were examined using LPME-SFO method. For LPME-SFO method 40 μL of extraction

solvent were placed on the surface of an aqueous solution containing 10 μg $mL^{-1}$ of BTEX and extraction was held for 30 min. Cyclohexanol was rejected immediately since it was quite soluble (water solubility 36 g $L^{-1}$) and did not form a separate phase in the aqueous solution. The other six extraction solvents were slightly soluble (1-chlorooctadecane 30 mg $L^{-1}$) or practically insoluble (*n*-hexadecane, *n*-heptadecane, 1-undecanol, 1-dodecanol, 2-dodecanol) in water. The worst extraction efficiency demonstrated nonpolar solvents *n*-hexadecane and *n*-heptadecane (Fig. 12), *n*-heptadecane being even less efficient than n-hexadecane. The difference in the extraction efficiency of

*n*-hexadecane and *n*-heptadecane can probably be explained by the fact that the extraction temperature (19°C) was below the melting point of *n*-heptadecane and thus during the extraction the solvent was in the solid state. The same extraction behaviour was observed for 1-dodecanol and 2-dodecanol. Despite the similarity of the isomer properties, 2-dodecanol demonstrated better extraction efficiency due to its liquid state during the extraction.

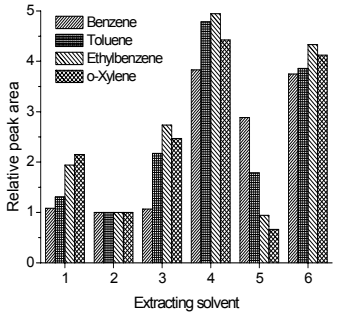


**Fig.12.** Effect of LPME-SFO solvent on the peak areas of BTEX. Concentration of each analyte is 10 μg $mL^{-1}$. Extraction time 30 min, solution stirring rate 400 rpm, extraction solvent volume 40 μL. Extraction solvents: (1) *n*-hexadecane, (2) *n*-heptadecane, (3) 1-chlorooctadecane, (4) 1-undecanol, (5) 1-dodecanol, (6) 2-dodecanol. Peak areas normalised to the corresponding peak areas using *n*-heptadecane.

1-Undecanol showed the highest extraction efficiency. In addition, 1-undecanol demonstrated good chromatographic behaviour as its boiling point was lower than that of the other four solvents but its chromatographic peak was easily distinguished from the analyte peaks. For the reasons mentioned, 1-undecanol was selected as an extraction solvent.

The effect of extraction solvent volume on the analytical signal was studied in the range of 5 – 50 μL. For ethylbenzene and *o*-xylene, increase in the extraction solvent

volume lead to lower peak areas (Fig. 13), the biggest peak areas were achieved using 5 μL volume. For more volatile benzene and toluene, with the increase in extraction solvent volume peak areas initially increased and reached the maximum at 20 μL.

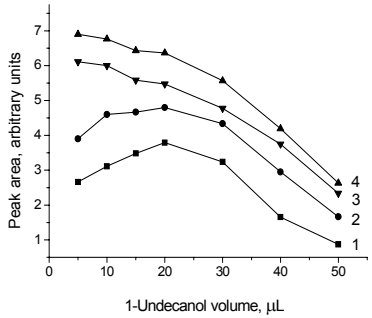


**Fig. 13**. Effect of LPME-SFO solvent volume on the peak area of (1) benzene, (2) toluene, (3) ethylbenzene and (4) *o*-xylene. Concentration of each analyte is 10 μg $mL^{-1}$. Extraction solvent 1-undecanol, extraction time 30 min, solution stirring rate 400 rpm.

Benzene is the most dangerous BTEX compound, being a recognized carcinogen. Thus it was important to prepare an extraction technique allowing determination of the lowest possible concentrations of benzene. This was the reason why we considered 20 μL as the optimal extraction solvent volume.

Extraction time was evaluated between 10 and 70 min. According to the curves presented in Fig. 14, the equilibrium was reached after 60 min extraction time. So, for further work 60 min extraction time was chosen.

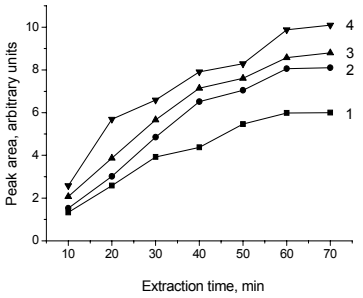


**Fig. 14.** Effect of LPME-SFO extraction time on the peak area of (1) benzene, (2) toluene, (3) ethylbenzene and (4) *o*-xylene. Concentration of each analyte is 10 μg $mL^{-1}$, 1-undecanol volume 20 μL, solution stirring rate 400 rpm.

The extraction was performed in the presence of different concentrations of NaCl (from saltless up to saturation). The results presented in Fig. 15 demonstrate that the

extraction efficiency initially increases with increasing concentration of NaCl and the maximum signal is achieved at the concentration of 0.2 g $mL^{-1}$. On the basis of the results obtained, in further experiments 0.2 g $mL^{-1}$ of NaCl was added to the samples.

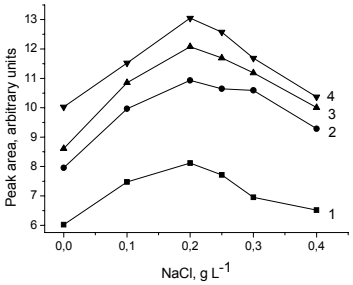


**Fig. 15.** Effect of NaCl content on the peak area of (1) benzene, (2) toluene, (3) ethylbenzene and (4) *o*-xylene. Concentration of each analyte is 10 μg $mL^{-1}$, 1-undecanol volume 20 μL, solution stirring rate 400 rpm, extraction time 60 min.

**Analytical performance**

The quality parameters of the suggested methods such as linearity, limits of detection, enrichment factors and repeatabilities were calculated under the optimized extraction conditions. However, before that, in order to improve repeatability, *n*-heptane (1 μg $mL^{-1}$) was added to the extraction solvent as an internal standard.

The calibration curves were drawn with three replicate direct injections of the extracts obtained after applying LPME-SFO procedure with 7 calibration points. The linear ranges were from 0.52, 0.33, 0.25 and 0.25 up to 10 μg $mL^{-1}$ for benzene, toluene, ethylbenzene and *o*-xylene respectively. Correlation coefficients were 0.997 - 0.998. For detection limits calculation, three replicate extractions were performed. Detection limits defined as three times of base-line noise are presented in Table 3.

**Table 3.** Detection limits of volatile aromatic hydrocarbons

| Analyte | Detection limit, μg $L^{-1}$ |
|---|---|
| Benzene | 0.31 |
| Toluene | 0.20 |
| Ethylbenzene | 0.15 |
| *o*-Xylene | 0.15 |

The enrichment factors are presented in Table 4. The lowest enrichment factor is for benzene and the highest for *o*-xylene.

**Table 4.** Volatile aromatic hydrocarbons enrichment factors and repeatabilities of the results

| Analyte | Enrichment factor | RSD % (n = 5) | |
|---|---|---|---|
| | | 1 mg $L^{-1}$ | 0,01 mg $L^{-1}$ |
| Benzene | 90 | 5.6 | 11.2 |
| Toluene | 125 | 4.6 | 10.6 |
| Ethylbenzene | 198 | 6.1 | 9.5 |
| *o*-Xylene | 264 | 7.3 | 9.9 |

Relative standard deviations (RSDs) were calculated and are summarized in Table 4. These data show that repeatability is satisfactory.

**Sample analysis**

The method was applied to real water and snow samples. Tap water from laboratory and snow collected in a parking place and in the city park were analysed immediately after sampling without any pretreatment. The results showed that tap water and snow from the city park were free of BTEX or their concentrations were below detection limits. The snow from the parking place contained small quantity of BTEX (Fig. 16). Concentrations of BTEX were calculated using standard addition method. and were determined to be 1.66, 0.90, 0.49 and 0.46 μg $L^{-1}$ for benzene, toluene, ethylbenzene and *o*-xylene, respectively.

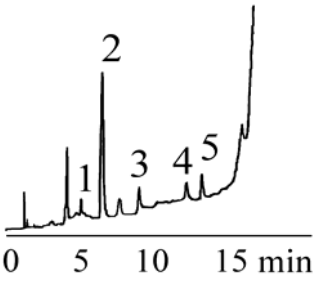


**Fig. 16.** Chromatogram of the snow from a parking place. (1) benzene, (2) internal standard *n*-heptane (1 μg $mL^{-1}$), (3) toluene, (4) ethylbenzene and (5) *o*-xylene. NaCl concentration 0.2 g $mL^{-1}$. Extraction conditions: 1-undecanol volume 20 μL, solution stirring rate 400 rpm, extraction time 60 min.

### 3.4. Dispersive liquid-liquid microextraction of volatile aromatic hydrocarbons

Dispersive liquid-liquid microextraction (DLLME) method is based on ternary component solvent system. A mixture of water-immiscible extraction solvent dissolved in a water-miscible disperser solvent is injected rapidly into aqueous sample. A cloudy solution formed consists of fine droplets of extraction solvent dispersed into aqueous phase. Due to the considerably large surface area between the extraction solvent and the aqueous sample, the extraction of the analytes is achieved quickly. Then centrifugation takes place and the extraction solvent with the analytes is sedimented and analysed by appropriate method. DLLME is simple to operate, and is an especially rapid, inexpensive extraction method with high preconcentration factors and low sample volume requirements. In the present study, DLLME method has been investigated for the determination of volatile aromatic hydrocarbons in aqueous solutions.

**Optimisation of extraction conditions**

For efficient performance of the extraction, several parameters, i.e. the nature and the volume of the extraction solvent and of the disperser solvent, the extraction time and ionic strength of the solution were studied and optimized.

An extraction solvent should satisfy several requirements: it should demonstrate a good extraction capability of the compounds of interest; it should have a higher density than water; its solubility in water should be low. In addition, in the case of subsequent gas chromatographic analysis, the solvent should demonstrate good gas chromatography behaviour and it should be soluble in the disperser reagent.

In order to select an extraction solvent, 40 µL of extraction solvent was mixed with 500 µL of acetone and the solution obtained was rapidly injected into the aqueous solution containing 1 µg $mL^{-1}$ of BTEX. The mixture was centrifuged for 2 min. and the sedimented phase was injected into GC for the analysis. Several potential extraction solvents - carbon tetrachloride, chloroform, chlorobenzene, bromobenzene and 1,2-dichlorobenzene - were examined.

Dichloromethane and chloroform were rejected immediately as they resulted too water soluble (13 and 8 g $L^{-1}$, respectively) and did not form a separate phase in the aqueous solution. Retention time of chlorobenzene was very close to that of benzene.

Moreover, as the solvent peak was very broad, it also interfered with toluene determination. Bromobenzene and dichlorobenzene were not suitable for BTEX extraction because of the presence of significant quantity of benzene in the solvents. Thus carbon tetrachloride was the only solvent suitable for DLLME of BTEX. However, even in the case of carbon tetrachloride small concentrations of benzene could not be determined as carbon tetrachloride retention time was also close to that of benzene. Thus for our further work three analytes – toluene, ethylbenzene and *o*-xylene – were selected.

The effect of extraction solvent volume on the analytical signal was studied in the range of 10 – 50 μL. For all the analytes increase in the extraction solvent volume led to lower peak areas (Fig. 17). However, 10 μL of carbon tetrachloride resulted in too small and difficult to handle volume of the sedimented phase. Thus 15 μL of carbon tetrachloride was determined to be the optimal extraction solvent volume.

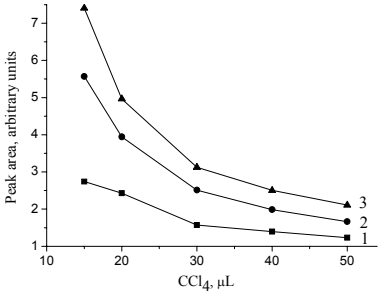


**Fig.17**. Effect of DLLME solvent volume on the peak area of (1) toluene, (2) ethylbenzene and (3) *o*-xylene. Concentration of each analyte is 1 μg $mL^{-1}$, acetone volume 500 μL, centrifugation 2 min.

The main selection criterion of disperser solvent for DLLME is its miscibility with extraction solvent and aqueous phase. As the disperser solvent must be miscible with the organic phase and with the aqueous phase, the choice of it is rather limited. Referring to the literature and considering low toxicity and cost, acetone was selected as disperser solvent for our work.

Different acetone volumes (0.1 – 1.5 mL) were used maintaining constant quantity of the extraction solvent carbon tetrachloride (15 μL). With the increase in acetone volume, peak areas initially increased because at low acetone volume the cloudy state was not stable and probably this caused incomplete extraction. On the other hand, with the further increase in acetone volume, analyte peak areas began to decrease (Fig. 18).

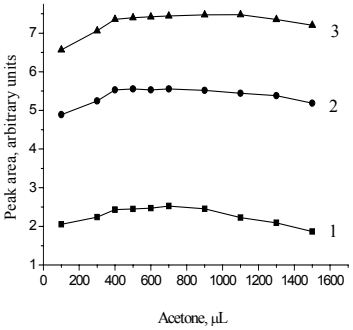


**Fig.18.** Effect of DLLME disperser solvent volume on the peak area of (1) toluene, (2) ethylbenzene and (3) *o*-xylene. Concentration of each analyte is 1 µg $mL^{-1}$, carbon tetrachloride volume 15 µL, centrifugation 2 min.

Probably because of a significant quantity of acetone in the aqueous phase, the partition of the analytes between the extraction solvent and the aqueous phase decreased. Hence, 0.4 - 0.9 mL acetone volume was the optimum. In order to have a convenient 0.5 mL acetone – $CCl_4$ mixture volume for the injection and considering that the optimum $CCl_4$ volume is 15 µL, 0.485 mL of acetone volume was selected for the further work.

For DLLME extraction time is defined as the time between injection of mixture of disperser solvent and extraction solvent and centrifuge step. DLLME extraction time up to 30 min was investigated. Peak area variations at different extraction time were not significant. Evidently, the surface area between the aqueous and organic phase was large, and 20 – 30 seconds (that take place between the injection and the beginning of the centrifugation) were sufficient for the extraction.

In order to examine salt influence on DLLME of the analytes of interest, the extraction was performed in the presence of different concentrations of NaCl (from saltless up to saturation). The results presented in Fig. 19 demonstrate that the extraction efficiency decreases with increasing concentration of NaCl probably because dissolved NaCl may have changed the physical properties of Nernst diffusion film of the droplets and thus impeded the extraction. Moreover, addition of big quantities of salt was inacceptable as after the injection of extraction-disperser solvent mixture the saturation of the aqueous solution with the salt is reached. Thus, after centrifugation the sedimented phase contains not only the extraction solvent but also the salt. Assuming this, in further experiments no salt was added to the samples.

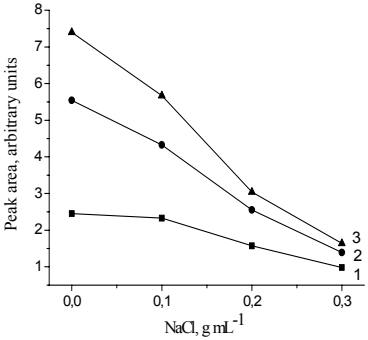


**Fig.19.** Effect of NaCl content on the peak area of (1) toluene, (2) ethylbenzene and (3) *o*-xylene. Concentration of each analyte is 1 μg $mL^{-1}$, carbon tetrachloride volume 15 μL, acetone volume 485 μL, centrifugation 2 min.

**Analytical performance**

The quality parameters of the suggested method such as linearity, limits of detection, enrichment factors and repeatabilities were calculated under the optimized extraction conditions. However, before that, in order to improve repeatability, *n*-octane (1 μg $mL^{-1}$) was added to the extraction solvent as an internal standard.

The calibration curves were drawn with three replicate direct injections with 10 calibration points. The linear ranges for all the analytes were up to 2 mg $mL^{-1}$. Correlation coefficients were 0.998 - 0.999. Limits of detection, enrichment factors and repeatabilities are presented in Table 5.

**Table 5.** Volatile aromatic hydrocarbons enrichment factors, detection limits and repeatabilities

| Analyte | Enrichment factor | Detection limit, μg $L^{-1}$ | RSD, % (n = 5) | |
|---|---|---|---|---|
| | | | 1 μg $mL^{-1}$ | 0.1 μg $mL^{-1}$ |
| Toluene | 144 | 0.4 | 5.0 | 8.5 |
| Ethylbenzene | 224 | 0.35 | 9.6 | 9.6 |
| *o*-Xylene | 239 | 0.33 | 7.5 | 11.7 |

The enrichment factors are similar for ethylbenzene and *o*-xylene and a bit lower for toluene. This can be explained by higher toluene water solubility.

**Sample analysis**

The method was applied to water samples analysis. Osmosis cleaned tap water (AB "Vilniaus degtinė") petrol station waste water and waste water cleaned from dye residue

("UAB Baltik vairas") were analysed without any pretreatment. The osmosis cleaned water did not contain the analytes of interest even if it was polluted with unidentified compounds (Fig. 20a). Petrol station waste water was rather polluted (Fig. 20b) and contained also the analytes of interest. Concentrations of the analytes were calculated using standard addition method and were determined to be 0.25, 0.20 and 0.16 for toluene, ethylbenzene and *o*-xylene, respectively. Unfortunately, the method was inappropriate for the extraction of "UAB Baltik vairas" waste water as after injection the mixture of extraction-disperser solvents solid sediments formed. Thus, after centrifugation the extraction phase was mixed with solid particles and it was impossible to collect an extraction solvent with the analytes.

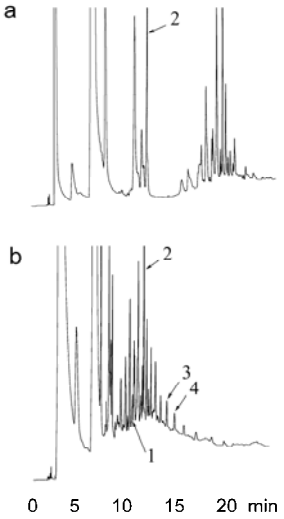


**Fig.20.** Chromatograms osmosis cleaned water (a) and petrol station waste water: (1) toluene, (2) internal standard *n*-octane (1 µg $mL^{-1}$), (3) ethylbenzene and (4) *o*-xylene. Carbon tetrachloride volume 15 µL, acetone volume 485 µL, centrifugation 2 min.

### 3.5. Dispersion-solidification liquid-liquid microextraction of volatile aromatic hydrocarbons

A possibility to combine two liquid phase microextraction methods – DLLME and solidification of a floating drop – was investigated. By this modification we expected to extend the applicability of DLLME method for volatile compounds and to overcome some problematic points of DLLME such as the use of toxic halogenated extraction

solvents and the necessity to filter samples containing solid particles. While we progressed with our work, Leong et al. published an article concerning combination of DLLME and solidification of a floating drop for extraction of some halogenated organic compounds and termed the method as DLLME-SFO.

**Optimisation of extraction conditions**

In 3.3 for LPME-SFO of volatile aromatic hydrocarbons 1-undecanol has been selected as an extraction solvent. As 1-undecanol is also soluble in acetone, acetonitrile and methanol normally used as disperser reagents in DLLME, it was selected as a potential extraction solvent also for DLLME-SFO method. As in the case of LPME-SFO, 20 µL 1-undecanol was used for the extraction.

As acetone is the most commonly used in DLLME, it was selected as disperser solvent for our work.

Different acetone volumes (0.3 – 2.0 mL) were used maintaining constant quantity of the extraction solvent 1-undecanol (20 µL). With the increase in acetone volume, peak areas initially increased because at low acetone volume the cloudy state was not stable and probably this caused incomplete extraction. On the other hand, with the further increase in acetone volume, analyte peak areas began to decrease. Probably because of a significant quantity of acetone in the aqueous phase, the partition of the analytes between the extraction solvent and the aqueous phase decreased. When acetone volume exceeded 2 mL, because of the solubility of the extraction solvent in water-acetone mixture, the volume of the organic phase became too small for the injection into GC. Hence, 0.4-0.8 mL acetone volume was the optimum. In order to have a convenient 0.5 mL acetone - 1-undecanol mixture volume for the injection and considering that the optimum 1-undecanol volume is 20 µL, 0.48 mL of acetone volume was selected for the further work.

DLLME-SFO extraction time up to 30 min was investigated. Peak area variations at different extraction time were not significant. Evidently, the surface area between the aqueous and organic phase was large, and 20 – 30 seconds (between the injection and the beginning of the centrifugation) were sufficient for the extraction.

Addition of the salt had a favourable influence on the separation of the organic phase. When the salt was not added, even after 5 min centrifugation aqueous phase was

not transparent as contained some quantity of dispersed 1-undecanol. This can be explained by the fact that 1-undecanol density is close to aqueous phase density. With the addition of NaCl, the density of the aqueous phase increased. So when 0.2 g $mL^{-1}$ of NaCl was added, the separation of the phases was facilitated and 2 min centrifugation was sufficient for their complete separation.

**Analytical performance**

The quality parameters of the suggested methods such as linearity, limits of detection, enrichment factors and repeatabilities were calculated under the optimized extraction conditions. Before that, in order to improve repeatability, *n*-heptane (1 µg $mL^{-1}$) was added to the extraction solvent as an internal standard. The linear ranges were from 0.58, 0.27, 0.18 and 0.17 up to 10 µg $mL^{-1}$ for benzene, toluene, ethylbenzene and *o*-xylene respectively. Correlation coefficients were 0.997 - 0.998. Enrichment factors, detection limits and repeatabilities of the results are presented in Table 6.

**Table 6.** Volatile aromatic hydrocarbons enrichment factors, detection limits and repeatabilities

| Analyte | Enrichment factor | Detection limit, µg $L^{-1}$ | RSD, % (n = 5) | |
|---|---|---|---|---|
| | | | 1 mg $L^{-1}$ | 0.01 mg $L^{-1}$ |
| Benzene | 87 | 0.35 | 7.0 | 12.0 |
| Toluene | 142 | 0.16 | 7.8 | 9.9 |
| Ethylbenzene | 212 | 0.11 | 8.3 | 11.7 |
| *o*-Xylene | 290 | 0.10 | 8.0 | 11.5 |

**Sample analysis**

Tap water from laboratory and snow collected in a parking place and in the city park were analysed immediately after sampling without any pretreatment. Only the snow from the parking place contained small quantity of BTEX (Fig. 21). Concentrations of BTEX were calculated using standard addition method. and were determined to be 1.76, 0.81, 0.54 and 0.53 µg $L^{-1}$ for benzene, toluene, ethylbenzene and *o*-xylene, respectively.

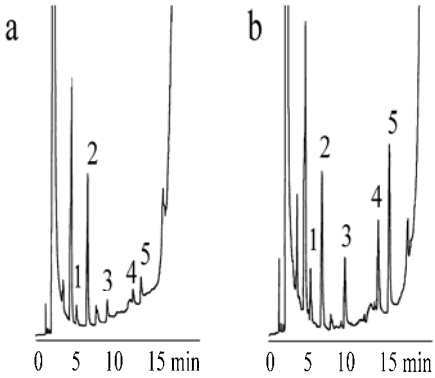


**Fig.21.** Chromatograms of the snow from the parking place (a) and of the snow spiked with BTEX containing 3 μg $L^{-1}$ of each analyte (b), obtained after DLLME-SFO : (1) benzene, (2) internal standard *n*-heptane (1 μg $mL^{-1}$), (3) toluene, (4) ethylbenzene and (5) *o*-xylene. NaCl concentration 0.2 g $mL^{-1}$.

### 3.6. Comparison of different microextraction methods of volatile aromatic hydrocarbons

In this chapter all the examined BTEX microextraction methods are compared and their advantages and shortcomings are revealed.

Detection limits obtained by all the methods examined are rather similar. An exception is DLLME. Using this method 2 – 4 times higher detection limits were obtained probably because of the worth extraction efficiency of carbon tetrachloride, that was used as an extraction solvent. Unfortunately, a number of proper extraction solvents for traditional DLLME is quite limited and $CCl_4$ was the best available. Moreover, even at the optimized extraction conditions one of the analytes (benzene) was not detected because the peak of benzene in the chromatogram overlapped with the peak of the extraction solvent.

A bit higher detection limit of *o*-xylene was obtained using headspace SPME, as *o*-xylene is less volatile than the other 3 analytes.

Repeatability of the results is similar for all the methods examined. Slightly bigger RSDs for HFLPME could probably be explained by the formation of air bubbles on the walls of hollow fibre when a sample solution is vigorously stirred. The bubbles prevent the sample solution contact with the hollow fibre and the solvent in the hollow fibre pores. Hollow fibre surface area covered with the bubbles differs from extraction to

extraction, affecting the repeatability of the results. On the other hand, low stirring rates should improve the repeatability of the results but should enlarge the extraction time.

The fastest microextraction technique was DLLME, the microextraction itself occurred in few seconds and additional 2 minutes served for centrifugation of the sample. DLLME-SFO is slightly longer, as additional 5 min are needed for the extract solidification and then 2 min for the extract melting.

The biggest extraction time was in the case of LPME-SFO. In this case 1-undecanol was used as an extracting solvent. It is quite viscous, thus the analytes need more time to migrate into its drop.

One of the most important advantages of all the methods studied is that the methods do not use (SPME) or use very small quantities of toxic organic solvents. An additional advantage of SPME is an absence of the solvent peak in the chromatogram. In the other methods studied solvent volumes are so small that are not significant in the economic and environmental point of view. More important is a chromatographic behaviour of the solvents. It was especially evident using carbon tetrachloride (DLLME) that co-elute with benzene. The retentions of *n*-octanol and DBF (HFLPME) and 1-undecanol (LPME-SFO and DLLME-SFO) are stronger than those of the analytes. This makes a chromatographic separation of the analytes easier but, on the other hand, the chromatographic analysis becomes longer. In the case of volatile $CCl_4$ chromatographic analisis time is 19.8 min, in the case of *n*-octanol-DBF is 28.4 min, in the case of 1-undecanol is 29.8 min.

For a selection of the extraction method sample matrix should be regarded. For clean samples all the examined methods can be used (DLLME can be used for all the analytes except benzene). In the case of polluted samples headspace SPME or HFLPME is preferred.

## CONCLUSIONS

1. A new SPME method was created, where carbon nanotubes as a fibre coating was incorporated into a groove of a stainless steel rod. The thermal stability and selectivity of the coating was evaluated, the SPME system is suitable for the extraction of aromatic hydrocarbons. Both direct and headspace SPME modes parameters for volatile aromatic hydrocarbons were optimized, the quality parameters were defined: limits of detection of BTEX 0.09 – 0.39 μg $L^{-1}$, the repeatabilities ($s_r$) 5.9 – 13.3 %;

2. The possibilities of HFLPME to extract volatile aromatic hydrocarbons were studied. A mixture of DBP : *n*-octanol (1:1) was chosen as an extracting solvent. BTEX extraction parameters of HFLPME were optimized, the quality parameters were defined: enrichment factors of BTEX were 112 – 260, limits of detection 0.06 – 0.22 μg $L^{-1}$, the repeatabilities ($s_r$) 6.5– 11.4 %;

3. The possibilities of liquid phase microextraction based on the solidification of a floating drop to extract volatile aromatic hydrocarbons were studied. 1 - undecanol was selected as an extraction solvent. Extraction parameters of BTEX were optimized, the quality parameters were defined: enrichment factors of BTEX were 90 - 264, limits of detection 0.15 – 0.31 μg $L^{-1}$, the repeatabilities ($s_r$) 5.6 – 11.2 %;

4. The possibilities of DLLME to extract volatile aromatic hydrocarbons were studied. Carbon tetrachloride was selected as an extraction solvent, acetone was selected as disperser solvent. Extraction parameters of BTEX were optimized. Benzene could not be determined under the optimized extraction conditions. The quality parameters were defined: enrichment factors of volatile aromatic hydrocarbons were 144 - 239, limits of detection 0.33 – 0.40 μg $L^{-1}$, the repeatabilities ($s_r$) 5.0 – 11.7 %;

5. The possibilities of DLLME-SFO to extract volatile aromatic hydrocarbons were studied. 1 - undecanol was chosen as an extraction solvent, acetone was selected as disperser solvent. Extraction parameters of BTEX were optimized. The quality parameters were defined: enrichment factors of volatile aromatic hydrocarbons were 87 - 290, limits of detection 0.10 – 0.35 μg $L^{-1}$, the repeatabilities ($s_r$) 7.0 – 12.0 %;

6. All the examined BTEX microextraction methods (headspace SPME method using carbon nanotubes as a fibre for water sample analysis, hollow-fibre liquid phase microextraction, liquid phase microextraction based on the solidification of a

floating drop, dispersive liquid-liquid microextraction and dispersion-solidification liquid-liquid microextraction) are compared. Detection limits and repeatability of the results are similar for all the methods examined. An exception was DLLME, where higher detection limits were obtained. The fastest microextraction technique was DLLME and the biggest extraction time was in the case of LPME-SFO. One of the most important advantages of all the methods studied is that the methods do not use (SPME) or use very small quantities of organic solvents. For clean samples all the examined methods can be used, in the case of polluted samples headspace SPME or HFLPME is preferred.

7. All the prepared BTEX microextraction methods could be apply for analysis of real water and snow samples.

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## SANTRAUKA

Pasiūlyta nauja kietafazės mikroekstrakcijos sistema, kurioje nerūdijančio plieno strypelis dengtas anglies nanovamzdeliais, ištirtas jos terminis stabilumas ir atrankumas, nustatyta, kad sistema tinka lakių aromatinių angliavandenilių ekstrakcijai iš tirpalo ir iš viršerdvės.

Ištirtos keturių skysčių-skysčių mikroekstrakcijos metodų - skysčių-skysčių mikroekstrakcijos kapiliare, mikroekstrakcijos užšaldomu tirpiklio lašu, dispersinės skysčių-skysčių mikroekstrakcijos ir dispersinės skysčių-skysčių mikroekstrakcijos užšaldant ekstraktą - galimybės ekstrahuoti lakius aromatinius angliavandenilius.

Optimizuotos tirtų metodų ekstrakcijos sąlygos, nustatytos pagrindinės analizinės charakteristikos. Visų metodų rezultatų pasikartojamumas ir aptikimo ribos artimi. Išimtis – dispersinė skysčių-skysčių mikroekstrakcija, kuria gautos kiek didesnės aptikimo ribos. Greičiausi ekstrakcijos metodai - dispersinė skysčių-skysčių mikroekstrakcija ir dispersinė skysčių-skysčių mikroekstrakcija užšaldant ekstraktą, ilgiausiai trunka mikroekstrakcija užšaldomu tirpiklio lašu. Švarių mėginių ekstrakcijai tinka visi tirti metodai, užterštiems mėginiams geriau tinka kietafazė mikroekstrakcija iš viršerdvės arba skysčių-skysčių mikroekstrakcija kapiliare.

Paruoštos lakių aromatinių angliavandenilių mikroekstrakcijos metodikos pritaikytos vandens ir sniego mėginių analizei.