Gas chromatographic determination of alcohols using microextraction with xylene drop

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Liquid phase microextraction of alcohols from aqueous solutions was studied. The analytes examined were methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-methyl-1-propanol, 1-pentanol, 3-methyl-1-butanol. A hydrophobic o-xylene drop containing internal standard octane was used as extracting solvent. The effectiveness of microextraction was investigated injecting the extracting drop with absorbed analytes into the gas chromatograph.

Extraction time, extracting drop volume, stirring rate, ionic strength of the solutions were optimised. The method suggested was evaluated in terms of repeatability, detection limits and linear response range. The optimised technique was applied to the analysis of beer and vine alcohols.

Key words: liquid phase microextraction, gas chromatography, alcohols

INTRODUCTION

Liquid–liquid extraction is among the oldest of the preconcentration and matrix isolation techniques in analytical chemistry. However, conventional liquid–liquid extraction uses large amounts of solvents that are often hazardous, and is time-consuming to perform. To overcome these disadvantages, new techniques such as flow injection extraction, solid-phase extraction, solid-phase microextraction (SPME), liquid phase microextraction (LPME) have been developed [1]. Liquid-phase microextraction is a fairly new method of sample preparation. Jeannot and Cantwell proposed this simple technique in which a microdrop of toluene was suspended on the tip of Teflon rod [2]. Then the authors simplified this method and the microdrop was suspended on microsyringe tip immersed in the stirred aqueous sample solution [3]. The extraction drop remains on the tip of the syringe for a set extraction time after which the drop is withdrawn from the solution into the syringe. In this case all the contents of the syringe is then injected directly into a GC system without any additional steps of preconcentration or purification. LPME requires very small volumes of expensive, toxic, high-purity organic solvents, is fast and those are significant advantages over the most commonly used liquid-liquid extraction and solid-phase extraction techniques. Comparison of SPME and LPME showed that the two techniques are comparable in terms of precision, sensitivity and analysis time [2]. SPME has the advantage that there is no solvent peak in the gas chromatogram. On the other hand, the SPME device time is limited as the solid-phase materials degrade with usage. Desorption of the analyte from the fiber in the GC injector is slower than conventional solvent evaporation and sometimes leads to analyte peak tailing. In some cases, especially in the case of the analytes of low volatility, a memory effect can take place. LPME overcomes those problems. Moreover, LPME can be performed with the simplest of devices, a conventional microsyringe, whereas the equipment employed in SPME is more elaborated and expensive. In addition, although the variety of commercially available SPME fibers is constantly increasing, the choice of solvents for liquid microextraction is much broader.

In the last few years LPME has been reported to be applied for determination of a wide variety of organic materials [1, 2, 4–8], but there were no data on the LPME of alcohols. In our laboratory a possibility of headspace LPME of some alcohols was investigated [9]. In this study, an investigation of liquid phase microextraction of alcohols directly from the solution is described.

EXPERIMENTAL

Chemicals

Methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-methyl-1-propanol, 1-pentanol, 3-methyl-1-bu-

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tanol, butyl acetate, toluene, octane, o-xylene and NaCl were of analytical-reagent grade and were used without further purification. A standard stock solution of methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-methyl-1-propanol, 1-pentanol and 3-methyl-1-butanol was prepared by weighing 0.75–0.85 g of each analyte. The stock solution was stored refrigerated at +4 °C. Standard solutions were prepared daily by diluting the standard stock solution in distilled water to desirable concentrations.

The extracting organic phase was o-xylene containing a known concentration of octane.

Instrumentation

Single drop microextraction was performed in a 13 ml volume vial closed with a silicone rubber septum placed in the cap. The vial was stirred on a magnetic stirrer (MLW RH3, Germany).

Single drop microextraction was performed with a commercially available 10 µl microsyringe (Hamilton Microliter 700 series syringe). During extraction the syringe was fixed above the extraction vial so that the needle passed the septum and the needle tip was immersed about 1 cm in the solution. Then a drop of the extracting solvent was suspended from the needle tip. After the extraction is finished, the drop is retracted back into the needle and injected directly into the GC.

Gas chromatography was carried out in a Chrom 5 (Czech Republic) gas chromatograph equipped with a flame ionisation detector coupled with integrator. A glass column 2.5 m long and 3 mm i.d. packed with Separon SDA (150 µm) was employed. The following gas chromatographic conditions were used: flow rate of nitrogen 45 ml min^{-1}, hydrogen 30 ml min^{-1}, air 300 ml min^{-1}. The temperature of the injector and of the detector was 190 °C. The column temperature was programmed: kept at 160 °C for 22 min, then increased to 180 °C at a rate of 20 °C min^{-1} and kept at 180 °C for 18 min.

RESULTS AND DISCUSSION

An extracting solvent used for LPME from aqueous solutions must be insoluble or very slightly soluble in water and to solve well the analytes of interest. Moreover, in the case of LPME followed by GC, the peak of the extracting solvent must be separated from the analytes peaks in the chromatogram. In our previous work [9], for the extraction of alcohols by headspace LPME ethylene glycol has been applied. However, ethylene glycol is soluble in water and so cannot be applied for direct extraction from water solutions. To overcome this problem, in this work instead of hydrophilic ethylene glycol we applied hydrophobic o-xylene. To correct variable injection volumes, octane was used as an internal standard. An analytical signal was taken as the peak area ratio of analyte to octane. A chromatogram of standard alcohol solution after extraction with a drop of o-xylene containing octane as internal standard is presented in Fig. 1.

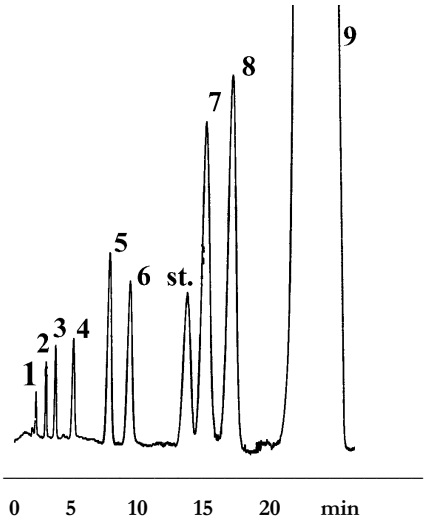

Fig. 1. Chromatogram of a standard alcohol solution. *1* – methanol, *2* – ethanol, *3* – 2-propanol, *4* – 1-propanol, *5* – 2-methyl-1-propanol, *6* – 1-butanol, *7* – 3-methyl-1-butanol, *8* – 1-pentanol, *9* – o-xylene, st – octane

Extracting drop volume and stirring rate

An equilibrium between the aqueous and organic phases can be achieved more rapidly by agitation of aqueous sample. On the other hand, fast stirring rates can

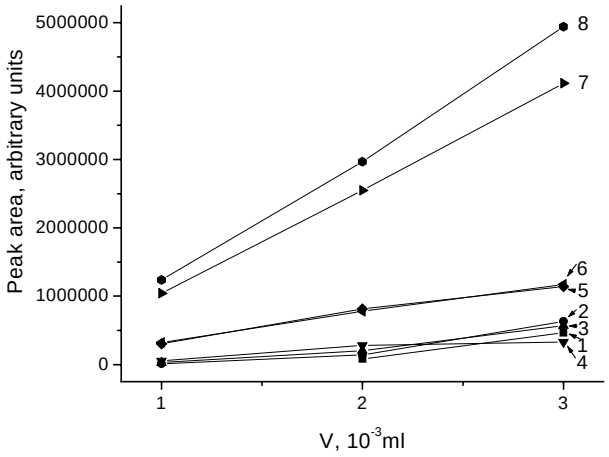

Fig. 2. Effect of stirring rate and extracting drop volume on peak areas. *1* – methanol, *2* – ethanol, *3* – 2-propanol, *4* – 1-propanol, *5* – 2-methyl-1-propanol, *6* – 1-butanol, *7* – 3-methyl-1-butanol, *8* – 1-pentanol. The o-xylene drop was exposed to the headspace of 5 ml of aqueous solution for 15 min. In the case of 1 µl drop the solution was stirred at 300 rmp, 2 µl – 200 rmp, 3 µl – 100 rmp

result in dislodgment of the organic drop from the needle tip. In our experiments water samples were continuously agitated at room temperature at different stirring rates with a magnetic stir bar using 1, 2 and 3 µl volume o-xylene drops. As was expected, the smaller drop was used the bigger stirring rate could be applied without damage to the drop. One, 2 and 3 µl drops remained fixed to the needle for 30 min at stirring rates 400, 200 and 100 rmp, respectively. Significantly larger analyte peak areas were obtained in the case of 3 µl o-xylene drop (Fig. 2), this solvent volume at a stirring rate 100 rpm was chosen for further work.

Sampling time

Solvent microextraction is not an exhaustive extraction method and analytes are partitioned between the bulk aqueous phase and the organic microdrop [6]. The total amount of the analytes transferred in the drop reaches its maximum when equilibrium between the two immiscible phases is established. As can be seen in Fig. 3, the analytes studied in our case reached equilibrium in 10–15 min. So for the further work a 15 min sampling time was chosen.

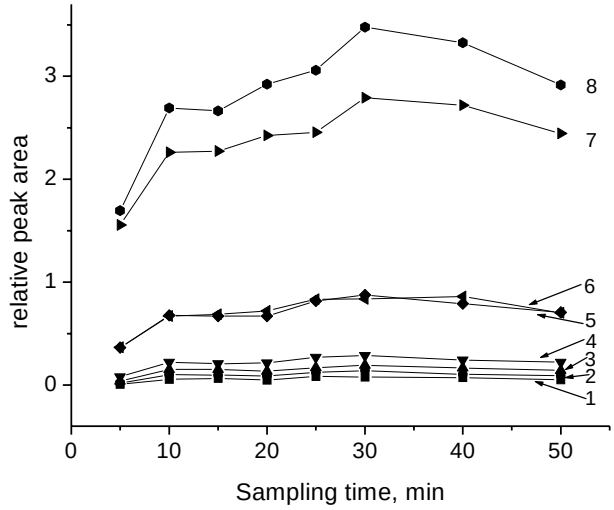

Fig. 3. Effect of sampling time on the relative peak areas of *1* – methanol, *2* – ethanol, *3* – 2-propanol, *4* – 1-propanol, *5* – 2-methyl-1-propanol, *6* – 1-butanol, *7* – 3-methyl-1-butanol, *8* – 1-pentanol. A 3 µl o-xylene drop was exposed to the headspace of 5 ml of aqueous solution at a stirring rate 100 rpm

Ionic strength of solution

Data on the influence of ionic strenghth on the extraction efficiency are contradictory. Some authors state that with the increase of ionic strenghth the extraction efficiency decreases [5, 6], the others [10], on the contrary, maintain that it increases. So we had to examine this dependence for the case of the alcohols studied.

The ionic strength of solution was modified by addition of NaCl, which is commonly used for this purpose. To 5 ml of water solution from 0.1 to 0.4 g ml^{-1} of NaCl was added. The plot of relative peak areas *vs*. the amount of NaCl added is shown in Fig. 4. It is evident that the addition of NaCl promotes the transport of the analytes to the extracting drop. The influence of NaCl can be probably explained by the fact that water molecules form hydration spheres around the ionic salt molecules. These hydration spheres reduce the concentration of water available to dissolve analyte molecules; thus it is expected this will drive additional analytes into the extraction phase [10]. However, at NaCl quantities above 0.3 g ml^{-1} the extracting efficiency didn't change any more, because in fact the saturation of the solution with NaCl was reached and so the ionic strength did non change any more. For the further work saturated salt conditions with NaCl concentration of 0.4 g ml^{-1} were chosen.

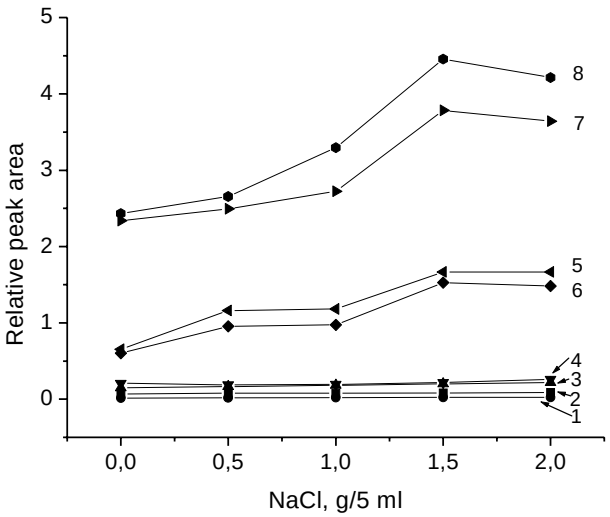

Fig. 4. Effect of NaCl addition on the relative peak areas of *1* – methanol, *2* – ethanol, *3* – 2-propanol, *4* – 1-propanol, *5* – 2-methyl-1-propanol, *6* – 1-butanol, *7* – 3-methyl-1-butanol, *8* – 1-pentanol. A 3 µl o-xylene drop was exposed to the headspace of 5 ml of aqueous solution for 15 min at a stirring rate 100 rpm

Precision, linearity and detection limits

The linear response range was examined on 5 ml of aqueous solutions of alcohols. Two grams of NaCl was added to the extraction vial before analysis and the extracting vial was placed on the magnetic stirrer and stirred at 100 rpm. Sampling with 3 µl of o-xylene drop containing internal standard octane was carried out for 15 min. The linear ranges for all the alcohols investigated were within 1 mg ml^{-1}. The correlation coefficients of the linear calibration graphs for all the

Table 1. **Detection limits of GC determination of alcohols in standard aqueous solutions after LPME with o-xylene drop**

Compound	Detection limit, μg ml^{-1}
Methanol	43.6
Ethanol	20.1
2-propanol	10.7
1-propanol	6.8
2-methyl-1-propanol	2.1
1-butanol	2.8
3-methyl-1-butanol	1.0
1-pentanol	1.1

analytes except methanol and ethanol were 0.980–0.999 (n = 8), for methanol the coefficient was 0.940 (n = 5) and for ethanol 0.983 (n = 6). One can see from Table 1 that the limits of analytes differed significantly. The lower solubility of the analyte, the lower its detection limit.

Repeatabilities were calculated between five concurrent measurements for standard solutions with two different concentrations of analytes (Table 2). The RSD values (except methanol and ethanol) did not exceed 7%. For methanol and ethanol the repeatabilities were worse than for the other analytes, possibly because the examined concentrations of methanol and ethanol were close to their detection limits.

Table 2. **Repeatability of GC determination of alcohols in standard aqueous solutions after LPME with o-xylene drop (n = 5)**

Compound	Concentration, μg ml^{-1}	Repeatability, %
Methanol	194	13
	48.4	27
Ethanol	196	5.7
	49.0	22
2-propanol	190	3.8
	47.5	6.8
1-propanol	193	2.2
	48.2	4.9
2-methyl-1-propanol	190	3.6
	47.4	2.8
1-butanol	191	4.2
	47.8	3.9
3-methyl-1-butanol	193	5.4
	48.1	2.8
1-pentanol	189	5.5
	47.2	3.1

Application

The developed method was applied for the analysis of beer "Švyturys Ekstra" and white vine "Sophia Chardonnay" (Bulgaria). To 5 ml of analyzed drink 2 g of NaCl was added and the mixture was stirred at 100 rpm and sampling with 3 μl of o-xylene drop containing an internal standard, octane, was carried out for 15 min. The first trials showed that extraction from beer is much more complicated than from the distilled water matrix. When stirred, beer forms froth and it is necessary to wait 20–30 min until the froth disappears. Moreover, even after that, differently from the standard solutions, the drop of o-xylene did not remain fixed on the needle tip. It can probably be caused by a big quantity of organic materials present in beer. The drop remained stable only after a 100-fold dilution of the beer. However, in this case the concentrations of all the analytes except ethanol were too low to be detected. Using the standard addition method, we determined that the ethanol concentration was 51 mg ml^{-1}. A chromatogram of beer is presented in Fig. 5.

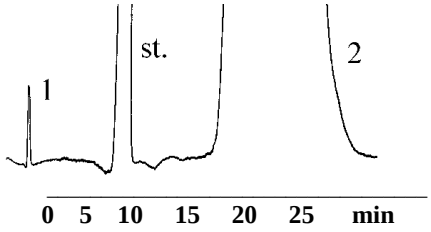

Fig. 5. Chromatogram of 100-fold diluted beer after LPME with o-xylene drop. *1* – ethanol, *2* – o-xylene, *st* – octane. A 3 μl o-xylene drop was exposed to the headspace of 5 ml of aqueous solution for 15 min at a stirring rate 100 rpm

In the case of undiluted white vine, the drop of o-xylene did not remain fixed on the needle tip, either, but just a 10-fold dilution was sufficient to eliminate this problem. As one can see in Fig. 6, besides ethanol the vine examined contained also 2-methyl-1-propanol (184 μg ml^{-1}) and 2-methyl-1-bu-

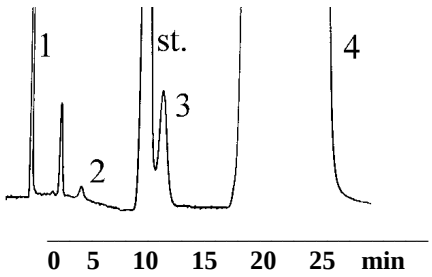

Fig. 6. Chromatogram of 10-fold deluted vine after LPME with o-xylene drop. *1* – ethanol, *2* – 2-methyl-1-propanol, *3* – 3-methyl-1-butanol, *4* – o-xylene, *st* – octane. A 3 μl o-xylene drop was exposed to the headspace of 5 ml of aqueous solution for 15 min at a stirring rate 100 rpm.

tanol (1500 μg ml^{-1}). The concentration of ethanol was determined after a 400-fold dilution of vine and was 115 mg ml^{-1}.

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DUJŲ CHROMATOGRAFINIS ALKOHOLIŲ NUSTATYMAS, NAUDOJANT MIKROEKSTRAKCIJĄ KSILENO LAŠU

S a n t r a u k a

Tirta skystos fazės alkoholių mikroekstrakcija iš vandeninių tirpalų. Buvo tirtos šios analitės: metanolis, etanolis, 1-propanolis, 2-propanolis, 1-butanolis, 2-metil-1-propanolis, 1-pentanolis, 3-metil-1-butanolis. Ekstrahuojantis tirpiklis – o-ksileno lašas, turintis vidinio standarto oktano. Mikroekstrakcijos efektyvumas tirtas leidžiant ekstrahuojantį lašą su absorbuotomis analitėmis į dujų chromatografą. Buvo optimizuotas ekstrahuojančio lašo tūris, tirpalo maišymo greitis, ekstrakcijos trukmė, tirpalo joninė jėga.

Įvertintas pasiūlyto metodo pasikartojamumas, analičių aptikimo ribos, tiesinis koncentracijų intervalas. Optimizuotas metodas buvo pritaikytas alaus ir vyno alkoholiams nustatyti.