Solid phase microextraction of alcohols from aqueous solutions: comparison of headspace and direct extraction

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Headspace solid phase microextraction and direct solid phase microextraction techniques for the determination of methanol, ethanol, n-propanol. i-propanol, n-butanol, i-butanol, n-pentanol and i-pentanol in aqueous solutions are suggested and compared. Solid phase microextraction was performed with a fiber coated with a 70 μm film of Carbowax/divinylbenzene. Optimal extraction conditions were: the extraction was carried out for 20 min at 40 °C or at room temperature, the solutions were stirred at 800 or 400 rpm for headspace solid phase microextraction and for direct solid phase microextraction, respectively. Desorption of the analytes was carried out for 30 s at 230 °C. The precision, linearity, detection limits were determined. The techniques could be applied for the analysis of wine.

Key words: headspace solid phase microextraction, direct solid phase microextraction, gas chromatography, alcohols, aqueous solutions

INTRODUCTION

A big part of currently employed sample preparation techniques is based on solid phase extraction based on trapping of analytes present in the sample by an adsorbent material and on subsequent desorption. Classical desorption is extraction with an organic solvent. However, this approach results in a poor sensitivity in the case if only part of the extract is used for further analysis or in an elevated sample preparation time in the case of the extract concentration after desorption [1]. Moreover, solvent desorption requires high purity and consequently expensive, in many cases toxic organic solvents.

As an alternative to liquid desorption, thermal desorption is used. It can be coupled rather conveniently to gas chromatography and the carrier gas is used for thermal desorption [2].

Pawliszyn and co-workers proposed a miniaturised solid phase microextraction technique – solid phase microextraction (SPME) [3, 4]. Coupled with gas chromatography it requires no solvents, is experimentally simpler than the other extraction techniques. This technique uses a fused fiber coated with a thin layer of a selective coating to extract organic compounds from air, water or soil samples. Analytes are adsorbed onto the fiber. The fiber is transferred to the injection port of the gas chromatograph, where thermal desorption and transfer of the analytes onto the GC column take place. The commonly used fibre coatings are polymeric materials such as polydimethylsiloxane (PDMS) that are above their glass transition point at the temperatures employed and so behave similarly to organic solvents [2, 5]. As sorbents have a lower analyte capacity than typical adsorbents, the fibers coated with polymer sorbents suffer from the lack of sensitivity. This is especially noticeable for polar analytes, which have a greater affinity to the water matrix. To improve the capacity of SPME fibers, new SPME coatings containing adsorbents have recently been introduced. These include materials such as PDMS copolymers with divinylbenzene and Carbowax (polyethylene glycol) and physical mixtures of PDMS with adsorbents such as Carboxen (carbon molecular sieves) [2, 6].

Initially SPME was suggested for sampling directly in the aqueous phase [7, 8]. Then SPME was extended to compounds present in the headspace of the sample [9–11]. This approach often is faster because of the shorter analytes equilibration time between gaseous phase and the fiber coating. Also, the use of headspace SPME helps to avoid interferences of high molecular weight molecules and to ac-

complish sampling not only from the liquid but also from the solid and gaseous matrices.

To our knowledge, the literature contains very little information about SPME of alcohols for the extraction using either polyacrylate [12, 13] or polydimethylsiloxane [13] fiber.

On the other hand, new fiber coatings recommended for polar analytes should be more sensitive for alcohols extraction.

The purpose of the current work was to investigate and to compare headspace SPME and direct SPME for alcohol extraction using the recently proposed Carbowax/divinylbenzene coated fiber. This coating consists of porous particles of divinylbenzene imbedded in partially crosslinked polymer of Carbowax.

EXPERIMENTAL

Reagents

Methanol, ethanol, n-propanol, i-propanol, n-butanol, i-butanol, n-pentanol, i-pentanol and NaCl were of analytical grade and were used without further purification. A standard stock solution of methanol, ethanol, n-propanol, i-propanol, n-butanol, i-butanol, n-pentanol and i-pentanol was prepared by weighting of 0.75–0.80 mg 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.

Instrumentation

SPME was carried out in a 13 ml vial closed with a silicone rubber septum placed in the cap. The vial was placed in a water-jacketed vessel on a magnetic stirrer (RH3, MLV, Germany) and kept at a desirable temperature with a circulating water-bath (UH, MLW, Germany).

SPME was performed with a 70 μm thick Carbowax™/DVB StableFlex™ fiber housed in its manual holder (Supelco Bellefonte, PA, USA). New fibers were conditioned under a nitrogen stream at a temperature of 260 °C for 30 min.

Gas chromatography was carried out in a Chrom 5 (Czech Republic) gas chromatograph equipped with a flame ionisation detector coupled with an integrator. A glass column 2.5 m long and 3 mm i.d. packed with Separon SDA (150 μm) was employed. The following gas flow rates were used: nitrogen 45, hydrogen 30 and air 300 ml min^{-1}. The temperature of the injector and of the detector was 220 °C, the temperature of the column was 160 °C.

RESULTS AND DISCUSSION

Desorption conditions

To determine the optimal desorption temperature, the injector temperature from 200 to 250 °C (optimal temperature range for the fibre used) was examined. The fiber was immersed into 5 ml of standard alcohol solution for 15 min at room temperature and then thermally desorbed for 2 min. As one can see in Fig. 1, above 230 °C the desorption did not increase any more. So for the further work

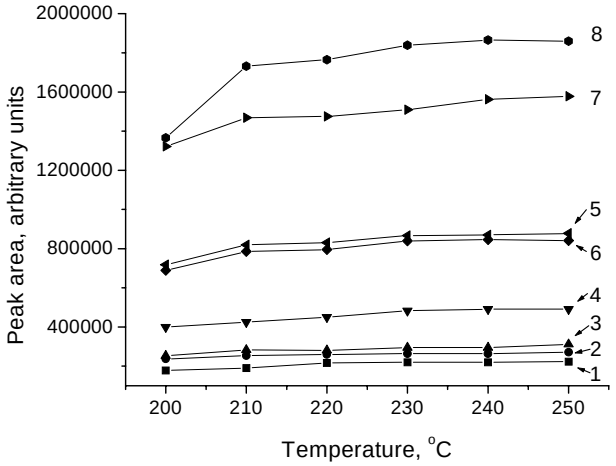

Fig. 1. The effect of desorption temperature on the peak area of 1 – methanol (493 μg/ml^{-1}), 2 – ethanol (488 μg/ml^{-1}), 3 – i-propanol (507 μg/ml^{-1}), 4 – n-propanol (492 μg/ml^{-1}), 5 – i-butanol (483 μg/ml^{-1}), 6 – n-butanol (498 μg/ml^{-1}), 7 – i-pentanol (499 μg/ml^{-1}) and 8 – n-pentanol (520 μg/ml^{-1}). The fiber was exposed for 15 min to headspace at room temperature and desorbed for 2 min

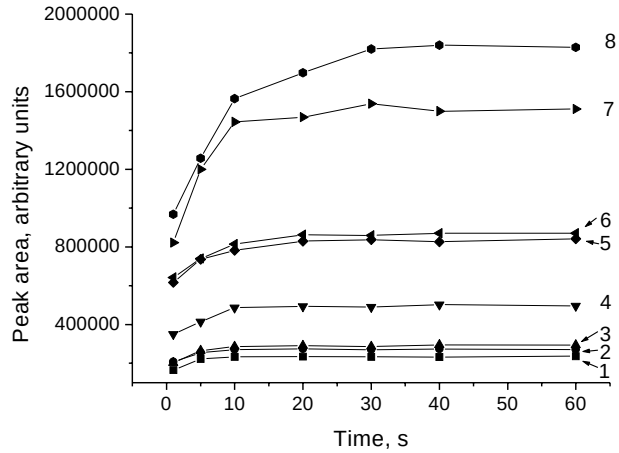

Fig. 2. The effect of desorption time on the peak area of 1 – methanol (493 μg/ml^{-1}), 2 – ethanol (488 μg/ml^{-1}), 3 – i-propanol (507 μg/ml^{-1}), 4 – n-propanol (492 μg/ml^{-1}), 5 – i-butanol (483 μg/ml^{-1}), 6 – n-butanol (498 μg/ml^{-1}), 7 – i-pentanol (499 μg/ml^{-1}) and 8 – n-pentanol (520 μg/ml^{-1}). The fiber was exposed for 15 min to headspace at room temperature and desorbed at 230 °C

a temperature of 230 °C was chosen. Higher temperatures were avoided in order to minimise the thermal bleed of the fiber coating.

At 230 °C the effect of desorption time on desorption efficiency was studied. Desorption times from 1 s to 1 min were investigated. For most of the analytes 10 s desorbtion time was sufficient (Fig. 2). For n-pentanol, and i-pentanol that have higher boiling points the desorption time is longer, nevertheless a 30 s desorption time is completely sufficient. Thus, in the further work a 30 s desorption time was used.

Headspace SPME conditions

To optimise headspace SPME conditions, 5 ml of standard alcohol solution was placed into the extracting vial, the SPME fiber was fixed in the headspace above the solution, and the stirring rate of the solution, extraction temperature, extraction time and ionic strength of the solution were examined.

An equilibrium between the aqueous and vapour phases can be achieved more rapidly by stirring the aqueous sample. In our experiments water samples were continuously agitated for 15 min at 100–800 rpm with a magnetic stir bar on a stir plate. The maximum peak areas were obtained at 800 rpm, so this stirring rate was chosen for the further work. Higher stirring rates were not used because of the spattering, which could have a negative effect on the reproducibility of the sorption conditions.

The effect of sorption temperature was studied by exposing the SPME fiber for 15 min at to a temperature of 20–50 °C. The extraction curves show that the amount of the analytes adsorbed increased up to 35–40 °C (Fig. 3). This can be explained by the fact that at higher temperatures the vapour pressure of the analytes and hence their concentrations in the headspace increase. Above the temperatures mentioned, the amount of the analytes extracted decreases, probably because desorption of the analytes from the SPME fiber coating increases more rapidly than the concentration of the analytes in the headspace. So the optimum extraction temperature was determined to be 40 °C.

For optimum repeatability of the analysis it is necessary to choose a time in which an equilibrium between the fiber and the headspace and between the headspace and the sample is reached. The equilibrium time was examined by exposing the fiber to the headspace for different periods of time at 40 °C. One can see in Fig. 4a that a 20-min extraction time is sufficient to reach the equilibrium.

Addition of salt often improves the extraction of analytes in SPME [6]. To modify the ionic strength, we added NaCl, which is commonly used for this purpose. To 5 ml of the standard alcohol solution

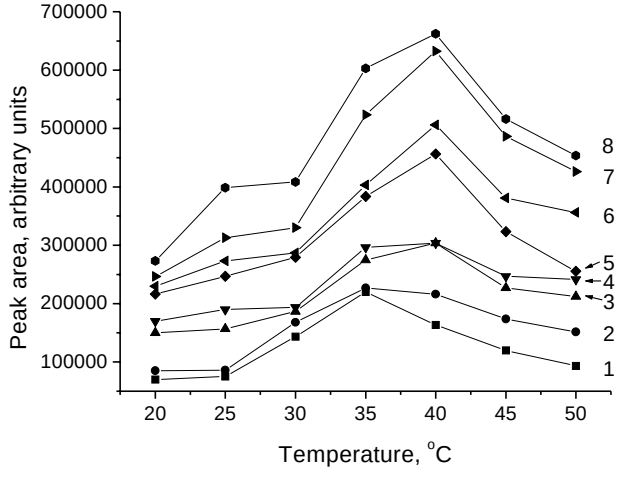

Fig. 3. The effect of extraction temperature on the peak area of 1 – methanol (493 μg/ml^{-1}), 2 – ethanol (488 μg/ml^{-1}), 3 – i-propanol (507 μg/ml^{-1}), 4 – n-propanol (492 μg/ml^{-1}), 5 – i-butanol (483 μg/ml^{-1}), 6 – n-butanol (498 μg/ml^{-1}), 7 – i-pentanol (499 μg/ml^{-1}) and 8 – n-pentanol (520 μg/ml^{-1}). The fiber was exposed to headspace for 15 min and desorbed at 230 °C for 30 s

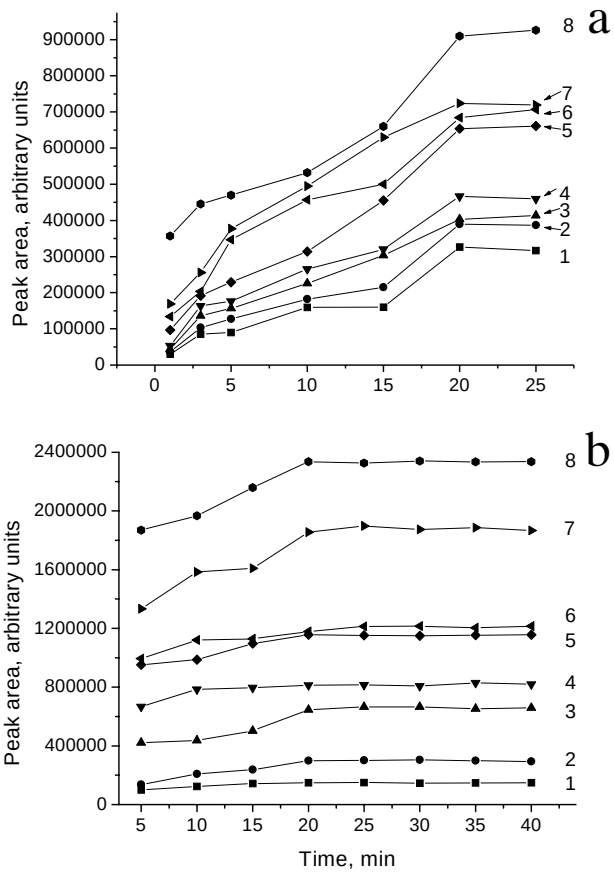

Fig. 4. The effect of extraction time on the peak area of 1 – methanol (493 μg/ml^{-1}), 2 – ethanol (488 μg/ml^{-1}), 3 – i-propanol (507 μg/ml^{-1}), 4 – n-propanol (492 μg/ml^{-1}), 5 – i-butanol (483 μg/ml^{-1}), 6 – n-butanol (498 μg/ml^{-1}), 7 – i-pentanol (499 μg/ml^{-1}) and 8 – n-pentanol (520 μg/ml^{-1}). a – headspace SPME at 40 °C, b – direct SPME at room temperature. Desorption at 230 °C for 30 s

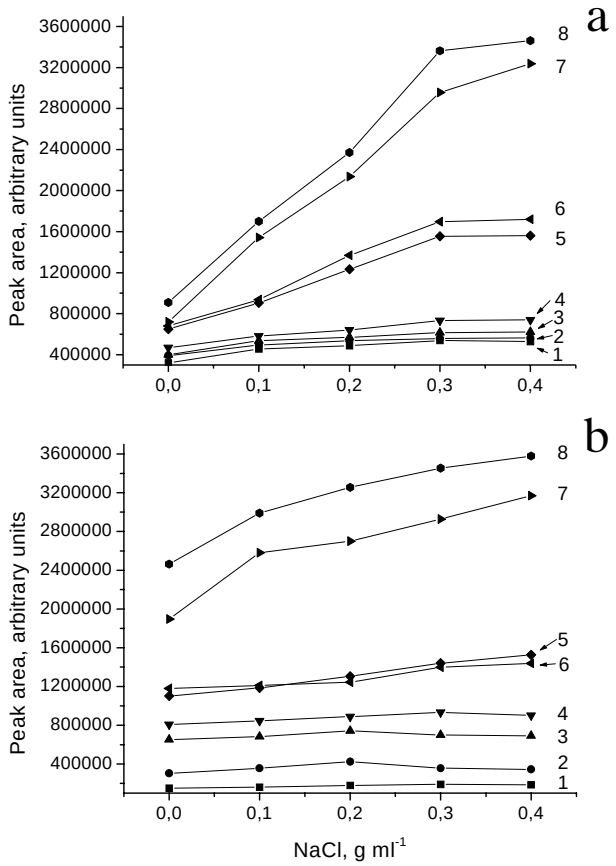

Fig. 5. The effect of NaCl content on the peak area of 1 – methanol (493 μg/ml^{-1}), 2 – ethanol (488 μg/ml^{-1}), 3 – i-propanol (507 μg/ml^{-1}), 4 – n-propanol (492 μg/ml^{-1}), 5 – i-butanol (483 μg/ml^{-1}), 6 – n-butanol (498 μg/ml^{-1}), 7 – i-pentanol (499 μg/ml^{-1}) and 8 – n-pentanol (520 μg/ml^{-1}). a – headspace SPME at 40 °C, b – direct SPME at room temperature. Desorption at 230 °C for 30 s

up to 2 g of NaCl were added. There was no sense to add more salt, because at 0.4 g ml^{-1} saturated salt conditions were reached. The curves presented in Fig. 5a show that addition of NaCl enhances the extraction efficiency. In further work 0.4 g ml^{-1} of NaCl was added.

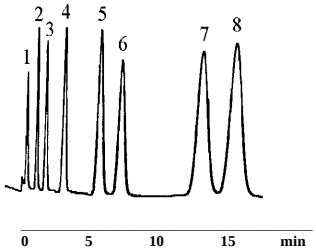

Fig. 6. The chromatogram of standard solution of alcohols: 1 – methanol (493 μg/ml^{-1}), 2 – ethanol (488 μg/ml^{-1}), 3 – i-propanol (507 μg/ml^{-1}), 4 – n-propanol (492 μg/ml^{-1}), 5 – i-butanol (483 μg/ml^{-1}), 6 – n-butanol (498 μg/ml^{-1}), 7 – i-pentanol (499 μg/ml^{-1}) and 8 – n-pentanol (520 μg/ml^{-1}). The fiber was exposed to headspaceat at 40 °C for 20 min and desorbed at 230 °C for 30 s

A chromatogram of standard solution of alcohols obtained after the headspace SPME at optimised conditions is presented in Fig. 6.

Direct SPME conditions

In direct SPME an extracting fiber must be immersed completely into the sample solution, so instead of 5 ml 10 ml of standard solution was used for the experiments. As in the case of headspace SPME, the stirring rate of the solution, extraction time and the ionic strength of the solution were examined. Extraction at the elevated temperatures was not studied, because there was no need to transfer the analytes into the headspace. Moreover, with an increase of the temperature the efficiency of the extraction should decrease, because the partition coefficients of the extracting phase decrease.

For stirring rate studies, water samples were continuously agitated for 15 min at 100–800 rpm. Above 400 rpm the peak areas did not change any more, so this stirring rate was chosen for the further work.

Extraction time was examined exposing the fiber to the solution stirred at 400 rpm for 5–40 min. One can see in Fig. 4b that a 20 min extraction time is sufficient to reach an equilibrium between the solution and the fiber.

Examining the influence of ionic strength, to 10 ml of a standard alcohol solution up to 4 g of NaCl (up to 0.4 g ml^{-1}) was added. Addition of NaCl enhanced the extraction efficiency (Fig. 5b). Thus, as in the case of headspace SPME, for further work 0.4 g ml^{-1} of NaCl were used.

Comparison of headspace and direct SPME

The quality parameters of the SPME methods such as linearity, repeatability and limits of detection (LOD) were calculated under the optimized conditions described above. For both methods studied, the linear ranges for metanol and ethanol were within 0.1 mg ml^{-1} and for the other alcohols within 0.05 mg ml^{-1}. The correlation coefficients of the linear calibration graphs were 0.996–0.999 (n = 6). Limits of detection were defined as the concentration of the analyte that produced a peak three times higher that the baseline noise. Both methods gave LOD of the same order (Table 1). More volatile analytes had a bit smaller LOD in the headspace and those with a higher boiling point had smaller LOD in the case of direct SPME.

The repeatability of the methods was calculated for two different concentrations by analysing five replicate samples. Relative standard deviations (RSDs) are listed in Table 2. Headspace SPME showed a better repeatability (except for methanol and ethanol). In most cases RSDs were higher for a lower analyte concentration.

The techniques were tested for analysis of white wine "Pinot bianco" (Italy). A chromatogram of the wine obtained after headspace SPME (Fig. 7) shows that all the analytes except n-pentanol are present in the wine. Peaks of the same six analytes are observed also in the case of direct SPME. However, for quantitative analysis the matrix effect should be considered. This requests additional investigation, which is in progress.

Table 1. **Limits of detection for headspace SPME and direct SPME of alcohols**

Compound	LOD, μg ml^{-1}	
	Headspace SPME	Direct SPME
Methanol	10.5	17.3
Ethanol	7.61	13.7
n-Propanol	4.01	6.93
i-Propanol	4.74	8.89
n-Butanol	2.59	1.67
i-Butanol	2.06	1.89
n-Pentanol	1.23	0.82
i-Pentanol	1.38	0.94

Table 2. **Repeatabilities for headspace SPME and direct SPME of alcohols (n = 5, P = 0.95)**

Compound	Concentration, μg ml^{-1}	RSD, % (n = 5)	
		Headspace SPME	Direct SPME
Methanol	493	14	14
	61.6	20	14
Ethanol	488	9.6	7.4
	60.9	8.5	7.5
n-Propanol	492	5.7	9.9
	61.5	7.0	11
i-Propanol	507	7.0	10
	63.3	8.9	11
n-Butanol	498	3.7	9.9
	62.3	6.3	9.7
i-Butanol	483	3.2	9.8
	60.4	6.8	9.8
n-Pentanol	520	2.6	10
	65	3.9	9.2
i-Pentanol	499	3.1	10
	62.4	4.4	11

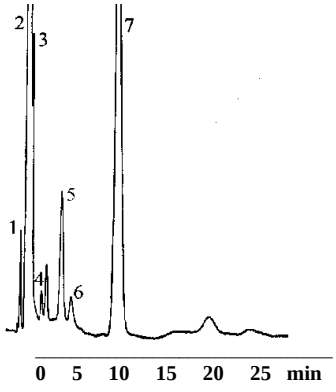

Fig. 7. The chromatogram of white wine "Pinot bianco": 1 – methanol, 2 – ethanol, 3 – i-propanol, 4 – n-propanol, 5 – i-butanol, 6 – n-butanol, 7 – i-pentanol. The fiber was exposed to headspaceat at 40 °C for 20 min and desorbed at 230 °C for 30 s

Received 25 August 2003
Accepted 25 October 2003

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ALKOHOLIŲ KIETAFAZĖ MIKROEKSTRAKCIJA IŠ VANDENINIŲ TIRPALŲ: EKSTRAKCIJOS IŠ VIRŠERDVĖS IR TIESIOGINĖS EKSTRAKCIJOS PALYGINIMAS

S a n t r a u k a

Pasiūlyti ir palyginti kietafazės mikroekstrakcijos iš viršerdvės ir tiesioginės kietafazės mikroekstrakcijos metodai metanoliui, etanoliui, n-propanoliui, i-propanoliui, n-butanoliui, i-butanoliui, n-pentanoliui ir i-pentanoliui vandeniniuose tirpaluose nustatyti. Kietafazė mikroekstrakcija atlikta strypeliu, padengtu 70 μm storio Carbowax/divinilbenzeno sluoksniu. Optimalios kietafazės mikroekstrakcijos iš viršerdvės ir tiesioginės kietafazės mikroekstrakcijos sąlygos yra atitinkamai: ekstrakcijos trukmė 20 min, ekstrakcijos temperatūra 40°C arba kambario temperatūra, tirpalo maišymo greitis 800 arba 400 apsisukimų per minutę. Analitės desorbuojamos 30 s 230°C temperatūroje. Nustatytos analičių aptikimo ribos, įvertintas rezultatų pasikartojamumas. Pasiūlytos metodikos gali būti pritaikytos vyno analizei.