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Solid phase microextraction fibers for alcohol determination

Auksė Tankevičiūtė, Dalia Panavaitė, Rolandas Kazlauskas, Vida Vičkačkaitė*

Department of Analytical and Environmental Chemistry, Vilnius University, Naugarduko 24, LT-2006 Vilnius, Lithuania.

The headspace solid phase microextraction (SPME) and direct solid phase microextraction techniques for the determination of methanol, ethanol, n-propanol, i-propanol, n-butanol, i-butanol, n-pentanol, i-pentanol are suggested and compared. Solid phase microextraction was performed with a fiber coated with a 100 μm film of polydimethylsiloxane. Optimal extraction conditions were: the extraction was carried out at room temperature or at 30 °C for direct and headspace SPME, respectively, extraction time in both cases was 20 min, the solutions were stirred at 200 rpm. Desorption of the analytes was carried out for 30 s at 240 °C. Considering lower detection limits achieved by headspace SPME, this technique was preferred to direct SPME.

The results obtained for polydimethylsiloxane-coated fiber were compared with those available in the literature for Carbowax–divinylbenzene, polyacrylate and Carboxen–polydimethylsiloxane coated fibers.

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

INTRODUCTION

Solid phase microextraction (SPME) is a relatively new method for extraction of organic analytes from different matrices and is a solventless, rapid, inexpensive and portable alternative to traditonal extraction methods. First it was described by Pawliszyn and co-workers in 1989 [1]. In the SPME procedure, a small diameter fiber coated with a stationary phase is placed in an aqueous or gaseous sample. The analytes partition into the stationary phase, the fiber is removed from the sample and inserted into the injector of a gas chromatograph where the analytes are thermally desorbed and analysed.

Initially, Arthur and Pawliszyn [2] used polyimide-coated fibers. Further polydimethylsiloxane (PDMS) [3, 4] and polyacrylate (PA) [5] coatings were proposed. They are homogeneous pure polymer coatings suitable for general applications. The most popular coating to date is PDMS. It is a very rugged liquid coating which is able to withstand high injector temperatures. PDMS is a nonpolar phase, however, it also can be applied successfully to polar compounds [6].

Ultimately, in addition to liquid polymeric coatings, other more specialised materials have been developed. They are mixed phases that consist of porous particles imbedded in a polymer phase. At present, mixed phases available are: PDMS–divinylbenzene (DVB), PDMS–Carboxen (CAR) (carbon molecular sieves), Carbowax (CW) (polyethylene glycol)-DVB and DVB-CAR-PDMS [7]. Mixed coatings have complementary properties compared to PDMS and PA. They have a lower mechanical stability than homogeneous polymer phases, but are highly selective. Since the majority of interactions are determined by the adsorption process on porous particles, they are more suitable for more volatile species. On the other hand, the main disadvantages of solid sorbents compared to liquids are associated with a smaller linear dynamic range and displacement effect [6].

Since the coating predetermines method selectivity, it is important to use an appropriate coating for a given application.

Lower alcohols are volatile organic compounds that play an important role in the organoleptic characterization of food and drink. They often are present in low concentrations, and therefore the extraction and concentration of volatile alcohols is one of the important areas of analysis. Surprisingly, the literature contains very little information about the SPME of lower alcohols. Recently in our laboratory a possibility to apply CW-DVB coated fiber has been examined. We concluded that the fiber can be successfully applied using headspace SPME as well as direct SPME [8]. Another heterogeneous polymer

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

phase [9], CAR-PDMS was applied for determination of some alcohols in vinegar. Also, to our knowledge, there are few articles on SPME using the both commercially available homogeneous pure polymer coatings PA [10–12] and PDMS [11, 13]. However, despite the fact that PDMS coatings are the most popular ones, there are very few data on their application for headspace SPME and there are no data on direct SPME of alcohols.

Considering the absence of sufficient data on SPME of lower alcohols, the aim of the present study was to optimise direct SPME and headspace SPME using PDMS-coated fiber, to compare the results obtained with CW-DVB and PA coated fibers and to suggest a proper coating and extraction mode for SPME of alcohols.

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 weighing of 0.76–0.82 g of each analyte. The stock solution was stored refrigerated at +4 °C. The working standard solutions were prepared daily by diluting the stock standard solution with distilled water to the required concentrations.

Instrumentation

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

SPME was performed with a 100 μm film of PDMS on a fiber housed in its manual holder (Supelco Bellefonte, PA, USA). New fibers were conditioned under a nitrogen stream at 250 °C for 30 minutes.

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

The initial step in the development of the method using SPME with a PDMS-coated fiber was the determining of desorption conditions.

In contrast to desorption with an organic solvent employed in the classical solid phase extraction, for SPME coupled to gas chromatography thermal desorption is used. It requires no high purity and thus expensive, in many cases toxic organic solvents, is experimentally simpler than the desorption with organic solvent and results in high sensitivity due to the fact that all the extract is used for further analysis.

The optimisation of thermal desorption has an important influence on accuracy and sensitivity. Two desorption parameters – desorption temperature and desorption time – were optimised.

The diffusion coefficient of the analytes in the coating increases and the gas / coating distribution constant rapidly decreases with temperature increase [6]. On the other hand, volatile analytes are readily removed from the coating at relatively low temperatures. To determine an optimal desorption temperature for the alcohols examined, the injector temperature range from 200 to 280 °C (recommended operating temperature range for the PDMS fiber) was investigated. A test was performed exposing the fiber for 15 min to the standard alcohol solution, followed by thermal desorption inside the GC injector for 2 min.

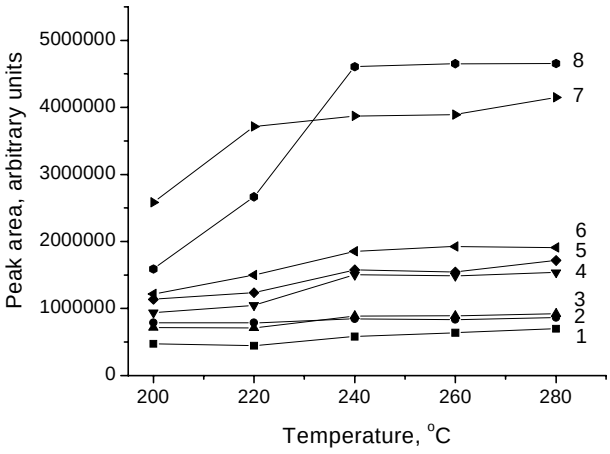

Fig. 1. Effect of desorption temperature on the peak area of *1* – methanol (511 mg/l^{-1}), *2* – ethanol (489 mg/l^{-1}), *3* – i-propanol (474 mg/l^{-1}), *4* – n-propanol (475 mg/l^{-1}), *5* – i-butanol (478 mg/l^{-1}), *6* – n-butanol (475 mg/l^{-1}), *7* – i-pentanol (481 mg/l^{-1}) and *8* – n-pentanol (490 mg/l^{-1}). The fiber was exposed for 15 min to the standard alcohol solution and desorbed for 2 min

As shown in Fig. 1, above 240 °C there was no significant change in alcohol desorption efficiency. For the further experiments, the lowest possible desorption temperature (240 °C) was selected, because high temperatures can shorten the coatings lifetime and result in the bleeding of a polymer, causing difficulties in separation and quantification.

At 240 °C the effect of desorption time on desorption efficiency was studied. The theoretical desorption times at elevated temperatures are very short, so desorption times from 3 s to 60 s were investigated. Figure 2 demonstrates that at a 30 s desorption time the highest desorption efficiency was achieved. So in the further work the desorption time 30 s therefore was used.

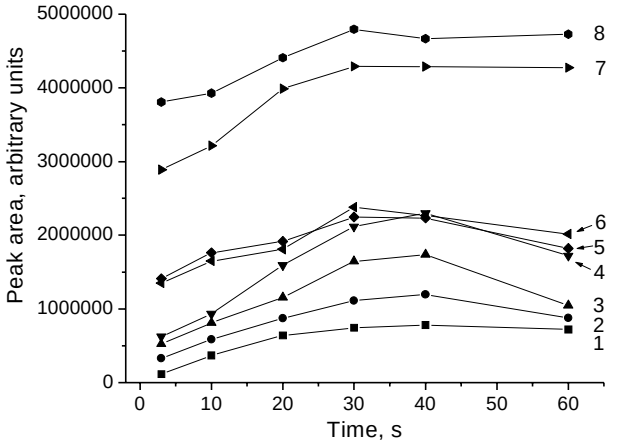

Fig. 2. Effect of desorption time on the peak area of *1* – methanol (511 mg/l^{-1}), *2* – ethanol (489 mg/l^{-1}), *3* – i-propanol (474 mg/l^{-1}), *4* – n-propanol (475 mg/l^{-1}), *5* – i-butanol (478 mg/l^{-1}), *6* – n-butanol (475 mg/l^{-1}), *7* – i-pentanol (481 mg/l^{-1}) and *8* – n-pentanol (490 mg/l^{-1}). The fiber was exposed for 15 min to the standard alcohol solution and desorbed at 240 °C

Direct SPME conditions

In order to examine the extraction conditions, the fiber was immersed directly into the sample solution and the analytes were transferred directly from the sample matrix to the extracting phase. The stirring rate of the solution, extraction time and the ionic strength of the solution were examined. 10 ml of standard solution of alcohols was used for the experiments.

In the case of direct SPME, an efficient agitation of a sample is extremely important in order to reduce the effect caused by the "depletion zone". This zone is formed close to the fiber as a result of fluid shielding and small diffusion coefficients of analytes in liquid matrices [6]. Standard sample solutions were continuously agitated for 15 min up to 600 rpm. Above 200 rpm the peak areas were constant, therefore this stirring rate was used in the further experiments.

The sampling time was examined exposing the fiber to the solution stirred at 200 rpm for up to 30 min. Figure 3a shows the sorption time profile achieved by measuring the peak area for selected analytes while increasing the extraction time. The time at which the peak area becomes constant was considered the equilibration time. After 20 min there was little variation in peak areas and therefore the 20 min extraction time was selected for subsequent studies.

Addition of salt to the aqueous samples usually increases the fiber / matrix distribution constant of neutral organic molecules and hence increases also the amount extracted. In [14] three types of salts, NaCl, Na_2SO_4 and $MgSO_4$, were tested for ionic strength influence on ester extraction efficiency, and sodium chloride was recognised to originate the highest peak areas. Hence, in our work the ionic strength of the solution was modified by addition of NaCl, and a study of the influence of sodium chloride concentration in the solution on the extraction was performed. To 10 ml of the standard

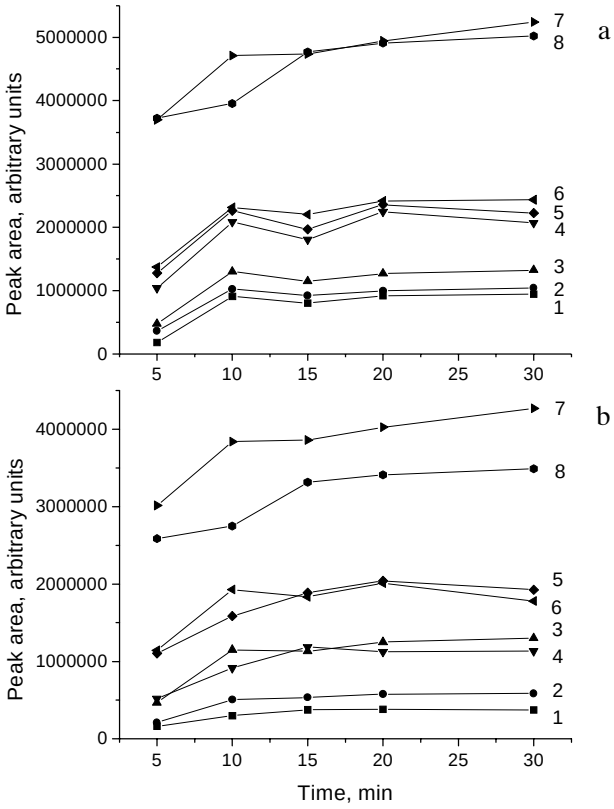

Fig. 3. Effect of extraction time on the peak area of *1* – methanol (511 mg/l^{-1}), *2* – ethanol (489 mg/l^{-1}), *3* – i-propanol (474 mg/l^{-1}), *4* – n-propanol (475 mg/l^{-1}), *5* – i-butanol (478 mg/l^{-1}), *6* – n-butanol (475 mg/l^{-1}), *7* – i-pentanol (481 mg/l^{-1}) and *8* – n-pentanol (490 mg/l^{-1}). a – direct SPME at room temperature, b – headspace SPME at 60 °C. Desorption at 240 °C for 30 s

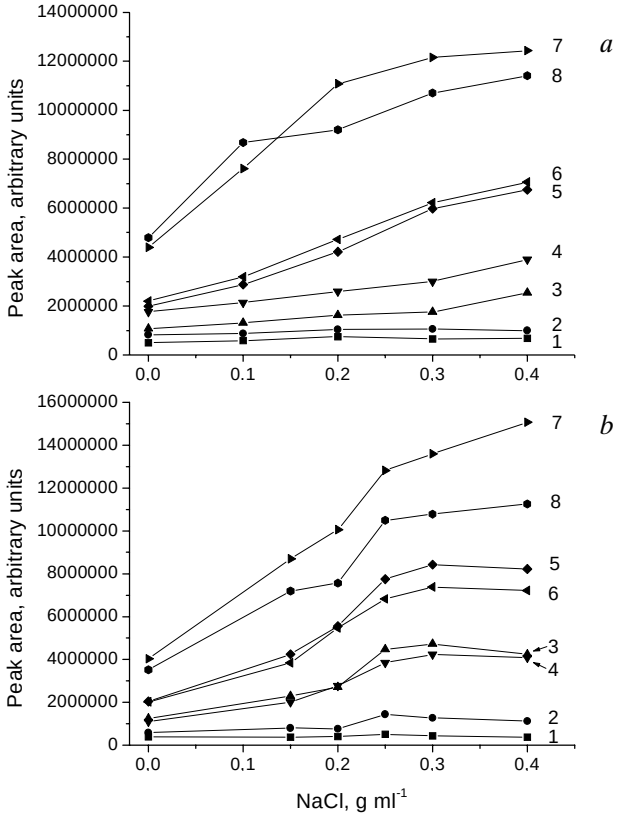

Fig. 4. Effect of NaCl content on the peak area of *1* – methanol (511 mg/l^{-1}), *2* – ethanol (489 mg/l^{-1}), *3* – i-propanol (474 mg/l^{-1}), *4* – n-propanol (475 mg/l^{-1}), *5* – i-butanol (478 mg/l^{-1}), *6* – n-butanol (475 mg/l^{-1}), *7* – i-pentanol (481 mg/l^{-1}) and *8* – n-pentanol (490 mg/l^{-1}). *a* – direct SPME at room temperature, *b* – headspace SPME at 60 °C Desorption at 240 °C for 30 s

alcohol solution up to 4 g (0.4 g ml^{-1}) NaCl was added (Fig. 4a). The addition of NaCl enhances extraction efficiency, possibly because the water molecules form hydration spheres around the salt ions. These hydration spheres reduce the concentration of water available to dissolve analyte molecules, hence it is expected that this will drive additional analytes into the extraction phase [15]. However, at NaCl concentrations above 0.4 g ml^{-1} the extraction efficiency did not change any further. This can be explained by the fact that the saturated salt conditions were reached. Therefore for further work 0.4 g ml^{-1} of NaCl were used.

Headspace SPME conditions

For the optimisation of headspace SPME, 5 ml of standard alcohol solution was placed into the extracting vial. A PDMS fiber was fixed in the headspace above the solution. The stirring rate, extraction temperature, extraction time and ionic strength of the solution were examined.

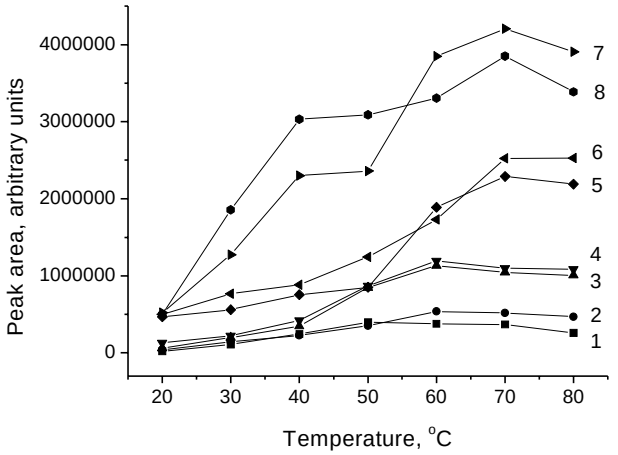

Fig. 5. Effect of extraction temperature on the peak area of *1* – methanol (511 mg/l^{-1}), *2* – ethanol (489 mg/l^{-1}), *3* – i-propanol (474 mg/l^{-1}), *4* – n-propanol (475 mg/l^{-1}), *5* – i-butanol (478 mg/l^{-1}), *6* – n-butanol (475 mg/l^{-1}), *7* – i-pentanol (481 mg/l^{-1}) and *8* – n-pentanol (490 mg/l^{-1}). The fiber was exposed to headspace for 20 min and desorbed at 240 °C for 30 s

An equilibrium between the aqueous and the vapour phases can be achieved more rapidly by stirring the aqueous sample. In our experiments water samples were continuously agitated at room temperature at different stirring rates with a magnetic stir bar on a stir plate. Up to 600 rpm stirring rates were used. Higher stirring rates were avoided because of the spattering, which may cause a negative effect on the reproducibility of the sorption conditions. The peak areas of all the analytes increase with increasing the stirring rate up to 200 rpm. Hence in further work a stirring rate of 200 rpm was chosen.

An increase in extraction temperature causes a transfer of the analytes to the headspace. So, differently to direct SPME, headspace SPME requires optimisation of the sample temperature during the sorption process. Optimisation of the sorption temperature was studied by exposing the SPME fiber in the headspace for 15 min at a sample stirring rate of 200 rpm. A sample temperature range 20–80 °C was examined and the dependence of the peak area on the temperature of the sample was studied. As one can see in Fig. 5, the peak areas increase with the temperature up to 60 °C for the analytes with a lower boiling point and up to 70 °C for less volatile analytes. In order not to exceed the boiling point of the most volatile methanol (65.4 °C), 60 °C was selected as the optimum temperature.

The equilibrium time was examined by exposing the fiber to the headspace for different periods of time at 60 °C. Twenty minutes of extraction time was found sufficient to reach the equilibrium (Fig. 3, *b*).

Also, a study of the influence of ionic strength on the extraction was performed. As in the case of direct SPME, the ionic strength of the solution was modified by addition of NaCl. The concentration of NaCl was chosen within 0–0.4 g ml^{-1}. The plot of the peak area *vs*. the amount of NaCl added at the optimal solution temperature of 60 °C and stirring rate of 200 rpm. is shown in Fig. 4b.

Table. **Limits of detection (mg l^{-1}) for headspace SPME and direct SPME of alcohols**

Compound	PDMS		CW-DVB [8]		PA [12]	CAR-PDMS [9]
	Direct	Headspace	Direct	Headspace	Headspace	Headspace
Methanol	25.4	17.0	17.3	10.5		
Ethanol	19.5	15.4	13.7	7.61		
n-Propanol	13.9	9.81	6.93	4.01	4.4	
i-Propanol	11.5	8.88	8.89	4.74		
n-Butanol	7.22	12.7	1.67	2.59	6.9	
i-Butanol	6.84	10.4	1.89	2.06	6.0	0.853
n-Pentanol	4.36	7.41	0.82	1.23		
i-Pentanol	3.21	7.22	0.94	1.38	5.4	0.223

As in the case of direct SPME, addition of NaCl promotes the transport of the components to the fiber. The biggest peak areas were obtained at 0.4 g ml^{-1} NaCl concentration, so this salt concentration was considered optimal.

SPME mode and fiber selection

A comparative study between headspace and direct SPME was carried out in order to establish their efficiency.

The quality parameters of the SPME method such as linearity, repeatability and limits of detection (LOD) were calculated under the optimised conditions described above.

For direct SPME, the linear ranges for the determination of the alcohols studied were within 0.2 mg ml^{-1}. In the case of headspace SPME, the linear ranges for most of the analytes studied were wider (within 0.5 mg ml^{-1}) and only for methanol and ethanol were within 0.2 mg ml^{-1}. For all the analytes good linearities were observed, with the correlation coefficients >0.996 (n = 6). Only for methanol in the case of direct SPME the correlation coefficient was rather small, 0.971. Limits of detection were defined as the concentration of the analyte that produces a peak three times higher than the baseline noise. As shown in Table 1, the LOD (except for n-butanol and i-pentanol) is somewhat higher for direct SPME.

The repeatability of the methods was calculated for two different concentrations (approximately 400 and 50 mg l^{-1}) analysing five replicate samples. In most cases RSDs were higher at a lower analyte concentration. Acceptable repeatabilities (RSD up to 8%) were achieved only for butanols and pentanols. On the contrary, for more volatile analytes relative standard deviations were 15–30%, indicating a rather poor repeatability.

Considering the lower detection limits achieved by headspace SPME, this method should be preferred to the direct SPME of alcohols using PDMS fiber. Moreover, headspace has the advantage of avoiding contamination and increasing fiber lifetime [14].

In addition, the results obtained for PDMS coated fiber were compared with those available in the literature for SPME of alcohols using CW-DVB [8], PA [12] and CAR-PDMS [9] coated fibers. The data presented in Table show that for all the analytes studied SPME with a CW-DVB coated fiber gives lower detection limits both for headspace and direct SPME. Furthermore, the reproducibility of the method using CW-DVB fiber was significantly better (RSDs for all the analytes except methanol do not exceed 10%) than using PDMS fiber. Unfortunately, there are few data concerning PA and CAR-PDMS coated fibers; moreover, all the data are for headspace SPME. However, the available results allow to suppose that for lower alcohol extraction PA fiber is more favorable than PDMS but worse than CW-DVB fiber and that CAR-PDMS is probably the best fiber for alcohol SPME. However, for a stricter conclusion, more exhaustive results on PA and CAR-PDMS fibers are desirable.

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**Auksė Tankevičiūtė, Dalia Panavaitė,
Rolandas Kazlauskas, Vida Vičkačkaitė**

KIETAFAZĖS MIKROEKSTRAKCIJOS PLUOŠTELIAI ALKOHOLIAMS NUSTATYTI

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 100 μm storio polidimetilsiloksanu. Optimalios tiesioginės kietafazės mikroekstrakcijos ir kietafazės mikroekstrakcijos iš viršerdvės sąlygos atitinkamai yra: ekstrakcijos trukmė 20 min, ekstrakcijos temperatūra – kambario temperatūra arba 30°C, tirpalo maišymo greitis 200 apsisukimų per minutę. Analitės desorbuojamos 30 s 240°C temperatūroje. Kadangi kietafazės mikroekstrakcijos iš viršerdvės atveju gautos mažesnės analičių aptikimo ribos, šis ekstrakcijos variantas pripažintas geresniu.

Rezultatai, gauti panaudojus polidimetilsiloksanu padengtą strypelį, buvo palyginti su literatūroje aprašytais rezultatais, gautais panaudojus Carbowax-divinilbenzenu, poliakrilatu ir Carboxen-polidimetilsiloksanu padengtus strypelius.