Solid-phase microextraction of parabens by polyaniline–polypyrrole coating

Vilma Čiuvašovaitė,

Edita Adomavičiūtė and

Vida Vičkačkaitė

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

A solid-phase microextraction fibre based on the electrochemically deposited polyaniline–polypyrrole coating has been suggested for the extraction and consequent gas chromatographic determination of parabens. The parameters affecting the extraction of analytes, such as extraction time, salt addition, desorption temperature and time, have been investigated. Optimized direct extraction was carried out at room temperature for 30 min in the presence of 0.4 g mL^{-1} of NaCl in the sample solution. Desorption of the analytes was carried out at 280 °C for 15 min. Precision, linearity and detection limits were determined. The coating was applied for the determination of parabens in cosmetics.

Key words: solid phase microextraction, polyaniline–polypyrrole coating, gas chromatography, parabens

INTRODUCTION

Parabens are esters of p-hydroxybenzoic acid (Fig. 1). Due to their bactericidal and fungicidal properties they are used as preservatives for pharmaceutical preparations, cosmetics and as food additives [1]. Some parabens are found naturally in vegetal sources [2]. Parabens exhibit differences in their antimicrobial activities and, therefore, optimal effectiveness is obtained by a combination of parabens. For example, methylparaben and propylparaben are often used together due to the observed synergetic effects [3]. For many years parabens have been considered among the preservatives with low toxicity. However, some years ago it was declared that some paraben preservatives were estrogenic and so could affect the endocrine system of humans and probably cause breast cancer [4, 5]. Due to their wide use and resistance to antimicrobial degradation, parabens also get into the environment and can affect wildlife. However, little work has been done to quantify their distribution and fate in the environment. Because of those reasons, fast, inexpensive and reliable analytical methods for paraben determination are highly required.
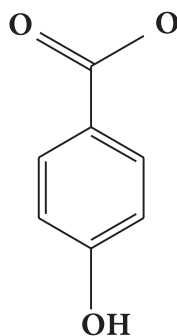
One of the most common methods for paraben analysis is gas chromatography [4]. Since the concentration of parabens in the environment is rather low and cosmetics present rather complex matrices for the analysis, it is necessary to apply a pre-concentration or isolation step prior to the chromatographic analysis. Those purposes can be achieved by solid phase microextraction (SPME). It was proposed by Pawliszyn and co-workers [6] and is a simple, solventless and rather inexpensive method. When coupled with GC, SPME can integrate sampling, extraction, preconcentration and sample introduction into a single step.

Up to now, several kinds of SPME coatings are commercially available: polydimethylsiloxane (PDMS), PDMS–divinyl benzene (DVB), polyacrylate, carboxen CAR–PDMS, carbowax (CW)–DVB, CW–templated resin, and stable flex DVB–CAR–PDMS [7]. SPME has been employed in numerous applications for forensic, environmental, food and pharmaceutical samples [8], but to our knowledge, there are only two works on SPME of parabens [1, 9]. J. K Lokhnauth and H. Snow [1] examined five commercial fibres and concluded that the best extraction efficiency was reached with DVB/CAR/PDMS fibre. Also in [9] five fibres were tested and a fibre coated with PA was chosen for the paraben extraction. However, commercial SPME fibres are rather expensive. Furthermore, they utilize a silica fibre as an extraction phase support and because of that are fragile and must be handled with a great care. So, more robust long-life SPME fibres of a relatively low cost are highly desired. In recent years, investigations have been directed to the development of fibres based on coated metal wires.

One of the approaches is to fix a sorbent layer using a physical deposition of a sorbent [10–14]. Another approach is electrochemical preparation of coatings. Among them a promising alternative is the use of conductive polymers, such as polypyrrole (PPY), polyaniline (PANI) and their derivatives as the extraction

Fig. 1. Structure of parabens. R = CH$_3$ for methylparaben, R = C$_2$H$_5$ for ethylparaben, R = C$_3$H$_7$ for propylparaben

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

phases [15–19]. PPY and its derivatives is one of the most widely used classes of conducting polymers, since pyrrole and some of its derivatives are commercially available, and their stable polymer films can be conveniently prepared on various substrate materials from organic or aqueous media by electrochemical or chemical methods [20, 21]. Coatings of PPY and its derivatives were used for SPME of polycyclic aromatic hydrocarbons [17], BTEX [16], polar and ionic drugs, inorganic and organic anions, and organometalic compounds [15, 21, 22].

The other conducting polymer, PANI, has been used to extract aromatic amines and phenols [19, 23], PANI doped with polyethylene glycol and PDMS extract phenols [24]. PANI fibre in comparison with commercial silica fused SPME fibres has the advantages of higher physical stability and chemical inertness, facile and inexpensive preparation. Moreover, PANI films are stable in different pH solutions, so they provide an ability to manipulate the extraction efficiency by choosing suitable pH according to the acid-base equilibrium of the analytes.

In [25] it was shown, that the porosity of PANI is more than that of PPY. Whereas porous structure increases the effective surface areas of the films, higher extraction efficiency of PANI in comparison with PPY can be expected. However, thermal stability of the PANI film was reported to be about 200 ºC [18]. This temperature is rather low and restricts the possibility to use high injection temperature that is required for an efficient desorption of less volatile analytes. On the other hand, dodecylsulfate-doped PPY is thermally stable up to 300 ºC [17]. Thus, in our previous work [26] we suggested to combine the porosity of PANI with the thermal stability of PPY by codeposition of PANI and PPY in order to prepare a thermally stable coating with the extracting characteristics of PPY and PANI films. The purpose of the present study is to examine a possibility to apply a PANI-PPY blend coating for SPME of parabens.

EXPERIMENTAL

Reagents
Methyl-4-hydroxybenzoat (methylparaben) (99%), ethyl-4-hydroxybenzoat (ethylparaben) (99%) and propyl-4-hydroxybenzoat (propylparaben) (99%), pyrrole (98%), aniline (99%), 2-butanone (99.5%), n-butanol (98%), benzyl alcohol (99%), n-butyl acetate (99%), o-xylene (98%), phenol (99.5%), methyl benzoate (99%), poly(sodium 4-styrenesulfonate) (PSS) (MW 1000000), methanol (99.9%) were purchased from "Aldrich". Pyrrole and aniline were distilled before use. Ethanol (GC grade) and NaCl (analytical grade) were purchased from "Reachim" (Ukraine).

A standard stock solution containing $1 \cdot 10^{-1}$ mol L^{-1} of 2-butanone, n-butanol, n-butyl acetate, o-xylene, phenol, benzyl alcohol and methyl benzoate was prepared in methanol.

A standard stock solution containing $1 \cdot 10^{-1}$ mol L^{-1} of methylparaben, ethylparaben and propylparaben was prepared in ethanol. The stock solutions were stored refrigerated at +4 ºC. 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 cap containing a septum. Homemade SPME fibre was housed in its manual holder (Supelco Bellefonte, PA, USA).

Gas chromatography was carried out in a Varian 3400 gas chromatograph equipped with a flame ionisation detector coupled with an integrator SP4290 (Spectra-Physics) and 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). The injector's temperature was 280 ºC, the detector's temperature was 240 ºC, the column temperature program was 50 ºC (2 min), 5 ºC min⁻¹ to 100 ºC, 2 ºC min⁻¹ to 240 and stay at 240 ºC for 5 min. The following gas flow rates were used: carrier (nitrogen) 10, make-up gas 20, hydrogen 30 and air 300 mL min⁻¹.

SPME fibre preparation
The SPME device was modified from a commercial SPME device. The septum-piercing needle was removed and replaced with a larger one. A stainless steel plunger needle (300 μ o.d.) was used as a support for the coating. The plunger needle was mounted inside the external needle, cleaned with acetone in an ultrasonic bath for 10 min and dried at room temperature.

The polymer films were prepared electrochemically using a three electrode system. The stainless steel plunger needle was used as a working electrode, Ag/AgCl was a reference electrode, a platinum wire served as a counter electrode. All the polymeric films were prepared at ambient temperature from aqueous solutions containing 0.1 mol L^{-1} pyrrole, 0.1 mol L^{-1} aniline, 4 g L^{-1} PSS and 0.25 mol L^{-1} H_2SO_4 by applying a constant deposition potential of 0.4 V. The coated fibre was dried at room temperature for 2 h and then conditioned under nitrogen in an injection port of the gas chromatograph at 300 ºC for 1 h.

RESULTS AND DISCUSSION

Coating selectivity
First of all the selectivity of the coating was examined. For this purpose, the SPME fibre was tested for different classes of compounds. The fibre was kept for 30 minutes in the aqueous solution containing $1 \cdot 10^{-3}$ mol L^{-1} of 2-butanone, n-butanol, n-butyl acetate, o-xylene, phenol, benzyl alcohol and methyl benzoate. As seen in Fig. 2, the fibre exhibits the best selectivity to the compounds with an aromatic ring. For them the selectivity increases in the following sequence: phenol < benzyl alcohol < methyl benzoate < o-xylene. A more efficient extraction of the aromatic compounds can be explained by the π –π interaction, because both PANI and PPY contain a conjugated π structure. The correlation of the extraction efficiency with the octanol–water partition coefficients can be observed. The compounds having higher log K_{ow} values (log K_{ow} 1.46, 2.12 and 3.12 for phenol, methyl benzoate and o-xylene, respectively) possess more affinities towards the coating indicating that hydrophobic interactions (mainly due to the presence of PSS in the coating) play an important role. On the other hand, the fibre extraction resulted in the decrease of *n*-butanol and 2-butanone peaks. This indicates that the selectivity of the fibre can be observed for aromatic hydrophobic hydrocarbons in the presence of short-chain alcohols and ketones. Consequently, it was expected that the coating could be successfully applied for the extraction of parabens in the matrices containing ethanol (e. g., cosmetics).
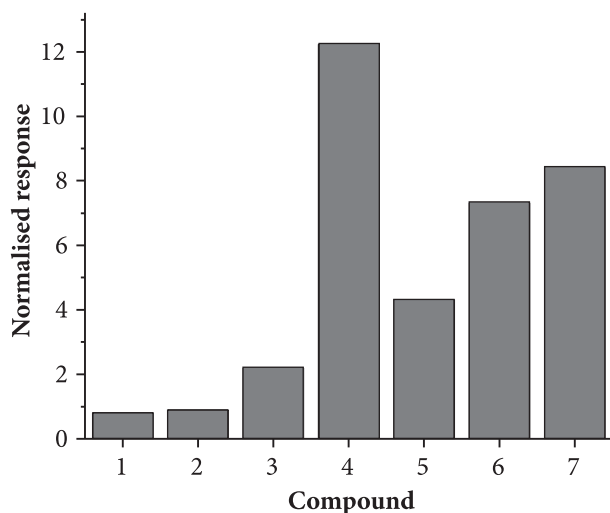
Fig. 2. Comparison of PANI-PPY coating selectivity: (1) 2-butanone, (2) n-butanol, (3) n-butyl acetate, (4) o-xylene, (5) phenol, (6) benzyl alcohol, (7) methyl benzoate. Concentrations of the analytes are $1 \cdot 10^{-3}$ mol L^{-1}. Direct extraction for 30 min. Peak areas normalised to the peak areas achieved after 1 µl syringe injection of the solution with the same analyte concentration

Paraben desorption conditions

The injection port temperature is an important factor in the fibre desorption, and gas/coating distribution constants of the adsorbed analytes rapidly decrease with an increase in the temperature. Our previous investigations showed [26] that the coating can be operated without any damage up to the 280 ºC temperature, so, this desorption temperature was selected for the further experiments.

Desorption time from 1 to 20 min was investigated. A standard solution containing $1 \cdot 10^{-3}$ mol L^{-1} of each analyte was used. Direct SPME was held for 20 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 ºC all the analytes were quantitatively desorbed from the fibre coating after 15 min and no carry-over effect was observed in the blank injections. Therefore, in the further work, a fifteen-minute desorption time was used.

Paraben extraction conditions

In the case of SPME of volatile compounds, agitation is required to facilitate the equilibration between the bulk of the aqueous sample and the fibre. We used a vigorous agitation of the solution (600 rpm) that, on the other hand, did not result in a spattering that could change the properties of the fibres surface.

Direct SPME was carried out at room temperature since at elevated temperatures coating/water distribution constant of the analytes decreases, hence resulting in a decrease in the extraction efficiency. The extraction time was studied in the range of 10–60 minutes. For optimum repeatability of the analysis, equilibrium between the sample and the fibre should be reached. However, even a sixty-minute extraction time was not sufficient for reaching the equilibrium (Fig. 3). Because of that, for the further work we chose non-equilibrium conditions and established a thirty-minute extraction time constantly maintaining the extraction time precisely the same.
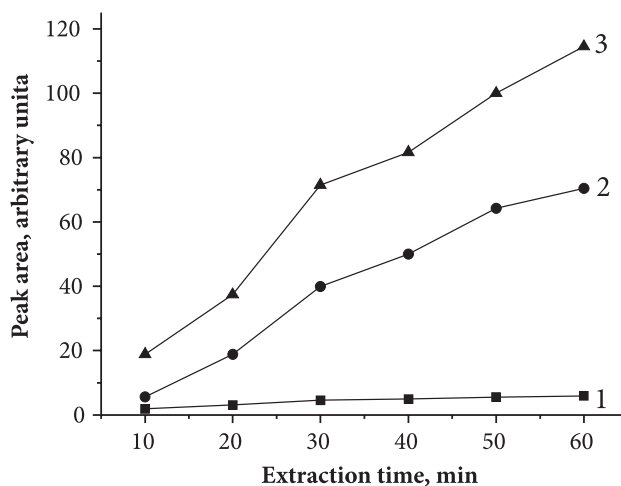

Fig. 3. Effect of extraction time on the peak area of (1) methylparaben, (2) ethylparaben and (3) propylparaben. Direct SPME at room temperature; desorption at 280 ºC for 15 min

The addition of salt to the solution could improve the sensitivity of the analytes of SPME method because of the increased ion strength in the aqueous phase and salting the analytes out of the solution into the coating. In order to increase the ionic strength we added NaCl, which is commonly used for this purpose. To the standard solution of parabens, different portions up to saturation of NaCl were added. From the curves presented in Fig. 4 it is evident that the addition of NaCl enhances the extraction efficiency. In further experiments 0.4 g mL^{-1} of NaCl was added.
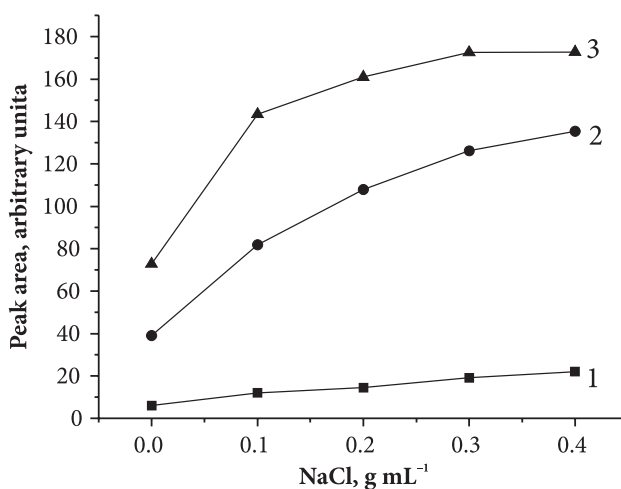

Fig. 4. Effect of NaCl content on the peak area of (1) methylparaben, (2) ethylparaben and (3) propylparaben. Direct SPME at room temperature for 30 min; desorption at 280 ºC for 15 min

The attempts to accomplish SPME from the headspace were not successful probably because of low volatility of the parabens analysed. Even at the elevated extraction temperatures (50–80 ºC) we did not succeed in reaching a preconcentration of the analytes. Moreover, the peak areas obtained after the headspace SPME were several times smaller in comparison with the peak areas obtained after the direct injection.

Analytical performance

The quality parameters of the direct SPME method, such as linearity, repeatability and limits of detection (LOD) were calculated

under the optimised conditions described above. The repeatability of the method was determined by five repetition analysis of two different concentrations of the analytes. Relative standard deviations (RSDs) are listed in Table 1.

The limits of detection (based on S/N = 3) are presented in Table 2. They are much lower for ethylparaben and propylparaben likely due to their lower solubility in water in respect of methylparaben. The linearity ranges were within $1 \cdot 10^{-3}$ mol L^{-1}. For all the analytes, good linearities were observed with correlation coefficients ≥ 0.995 (n = 7).

Table 1. Repeatabilities of SPME of parabens (n = 5)

Analyte	Concentration, mol L^{-1}	RSD, %
Methylparaben	$5 \cdot 10^{-3}$	14.9
	$5 \cdot 10^{-4}$	19.1
Ethylparaben	$5 \cdot 10^{-3}$	14.4
	$5 \cdot 10^{-4}$	16.5
Propylparaben	$5 \cdot 10^{-3}$	12.2
	$5 \cdot 10^{-4}$	13.0

Table 2. Detection limits of parabens, mol L^{-1}

Analyte	Detection limit, mol L^{-1}
Methylparaben	$1.7 \cdot 10^{-5}$
Ethylparaben	$8.0 \cdot 10^{-7}$
Propylparaben	$7.0 \cdot 10^{-8}$

Sample analysis

A possibility to use the fibre for a real sample analysis was demonstrated by applying it to the determination of parabens in cosmetics: Nivea Visage moisturising tonic and Matt Touch (Lumene) facial tonic. Fig. 5 presents a chromatogram of the Matt Touch. The samples were diluted 10 times before the analysis and analysed under the conditions described above. Standard addition method was used for the analysis. In the Matt Touch facial tonic $2.2 \cdot 10^{-4}$, $4.5 \cdot 10^{-4}$ and $3.3 \cdot 10^{-4}$ mol L^{-1} of methylparaben, ethylparaben and propylparaben, respectively, was determined. In the Nivea Visage moisturising tonic only methylparaben at a concentration of $2 \cdot 10^{-4}$ mol L^{-1} was determined.

Fig. 5. Chromatogram of Matt Touch (Lumene) facial tonic. (1) methylparaben, (2) ethylparaben and (3) propylparaben. Direct SPME at room temperature for 30 min; desorption at 280 ºC for 15 min, NaCl 0.4 g mL⁻¹. For gas chromatographic conditions see Experimental part
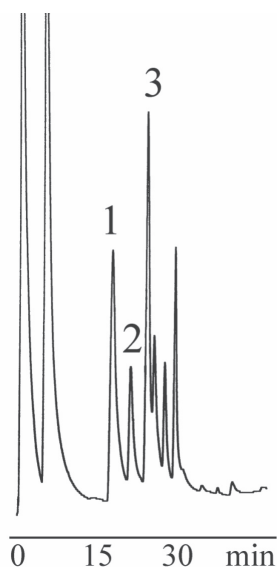
Recovery testing was carried out by spiking 50 μL $1 \cdot 10^{-1}$ mol L-1 standard BTEX mixtures to 10 mL of the diluted sample. The obtained results were compared with the known amounts of standard BTEX added to the matrix. The percent recoveries were between 93.2–106.4%.

CONCLUSIONS

The above results show that SPME using a stainless steel wire electrochemically coated with a blend PANI-PPY coating offers an attractive alternative to commercially available SPME fibres for the determination of small quantities of parabens in the matrices containing ethanol. The fibre exhibits high thermal stability, satisfactory repeatability, the construction of the fibre is very simple and easy to prepare.

References

1. J. K. Lokhnauth and N. H. Snow, *Anal. Chem.*, 77, 5938 (2005).
2. H. P. Bais, R. Vepachedu and J. M. Vivanco, *Plant physiology and biochemistry*, **41**, 345 (2003).
3. M. Borremans, J. Van Loco, P. Roos and L. Goeyens, *Chromatographia*, **59**, 47 (2004).
4. A. M. Peek, *Anal. Bioanal. Chem.*, **386**, 907 (2006).
5. E. J. Routledge, J. Parker, J. Odum, J. Ashby and J. P. Sumpter, *Toxicol. Appl. Pharm.*, **153**, 12 (1998).
6. R. P. Belardi and J. Pawliszyn, *Water Pollut. Res. J. Canada,* **24**, 179 (1989).
7. Supelco Chromatography (2005–2006), Sigma-Aldrich Co., USA, 805 (2005).
8. J. Pawliszyn, *Solid phase microextraction. Theory and practice,* 247 p. Wiley-VCH, New York (1997).
9. P. Canosa, I. Rodriguez, E. Rubi, M. H. Bollain and R. Cela, *J. Chromatogr A*, **1124**, 3 (2006).
10. Y. Liu, Y. Shen and M.L. Lee, *Anal. Chem.*, **69**, 190 (1997).
11. Y. Liu and L. Lee, *Anal. Chem.*, **69**, 5001 (1997).
12. M. Farajzadeh and N. A. Rahmani, *Analytical Sciences*, **20**, 1359 (2004).
13. D. Panavaitė, E. Adomavičiūtė and V. Vičkačkaitė, *Chemija*, **17**, 61 (2006).
14. D. Panavaitė, A. Padarauskas and V. Vičkačkaitė, *Anal. Chim. Acta*, **571**, 45 (2006).
15. J. Wu and J. Pawliszyn, *Anal. Chim. Acta*, **520**, 257 (2004).
16. D. Djazan, M. H. Pournaghi-Azar and S. Bahar, *Chromatographia*, **59**, 595 (2004).
17. A. Mohammadi, Y. Yamini and N. Alizadeh, *J. Chromatogr. A*, **1063**, 1 (2005).
18. H. Bagheri, A. Mir and E. Babanezhad, *Anal. Chim. Acta*, **532**, 89 (2005).
19. H. Minjia, T. Chao, Z. Quanfang and J. Guibin, *J. Chromatogr. A*, **1048**, 257 (2004).
20. J. Wu and J. Pawliszyn, *J. Chromatogr A*, **909**, 37 (2001).
21. J. Wu, X. Yu, H. Lord and J. Pawliszyn, *Analyst*, **125**, 391 (2000).

22. J. Wu, W. M. Mullett and J. Pawliszyn, *Anal. Chem*., **74**, 4855 (2002).

23. T. H Ding, H. H. Lin and Ch. W. Whang, *J. Chromatogr A*, **1062**, 49 (2005).

24. M. Huang, G. Jiang and Y. Cai, *J. Sep. Sci*., **28**, 2218 (2005).

25. A. Ghassempour, N. Mashkouri Najafi, A. Mehdinia, S. Saeed Hosseiny Davarani, M. Fallahi and M. Nakhshab, *J. Chromatogr. A*, **1078**, 120 (2005).

26. V. Vičkačkaitė and V. Čiuvašovaitė, *Cent. Eur. J. Chem*. (in press).

Vilma Čiuvašovaitė, Edita Adomavičiūtė, Vida Vičkačkaitė

PARABENŲ KIETAFAZĖ MIKROEKSTRAKCIJA POLIPIROLO‒POLIANILINO DANGA

S a n t r a u k a

Parabenų dujų chromatografiniam nustatymui pasiūlytas kietafazės mikroekstrakcijos strypelis, pagamintas elektrochemiškai nusodinus ant nerūdijančios vielos pagrindo polianilino–polipirolo dangą.

Ištirti ekstrakcijos efektyvumą veikiantys parametrai (ekstrakcijos trukmė, tirpalo joninė jėga, desorbcijos temperatūra ir trukmė). Tiesioginė kietafazė mikroekstrakcija buvo atliekama 30 min kambario temperatūroje į tirpalą pridėjus 0,4 g mL^{-1} NaCl. Analitės desorbuojamos 15 min 280°C temperatūroje. Nustatyti tiesiniai koncentracijų intervalai, aptikimo ribos bei rezultatų pasikartojamumas. Danga pritaikyta nustatyti parabenus kosmetikoje.