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Polyaniline-polypyrrole coating for solid phase microextraction

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Abstract: A procedure for direct electrochemical deposition of polyaniline-polypyrrole blend coating on the surface of stainless steel wire was suggested. Incorporation of polyaniline and polypyrrole into the blend coating was confirmed by infrared spectroscopy. Key parameters (pyrrole, aniline, dopant and sulphuric acid concentrations and deposition potential) influencing the coating's mechanical stability and surface homogeneity were optimised and thermostability of the coating was investigated. A possibility to apply the coating as a new fibre for solid phase microextraction was demonstrated. The coating showed better selectivity toward aromatic, hydrophobic compounds.

Keywords: Solid phase microextraction, polyaniline, polypyrrole, gas chromatography

1 Introduction

During the last decade, solid phase microextraction (SPME) suggested by J. Pawliszyn in 1989 [1] has gained a widespread acceptance in gas chromatographic analysis as a valuable method of simultaneous sampling, preconcentration, matrix removal, and sample introduction techniques. SPME has been employed for forensic, environmental, food, and pharmaceutical samples [2, 3] and the number of publications concerning SPME is still growing. Typically, a fused silica fibre, which is coated with a thin layer of polymeric stationary phase or polymeric phase with dispersed solid adsorbent, is used to extract analytes from water, soil and gaseous samples. 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

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resin, and stable flex DVB – CAR – PDMS [4]. 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 SPME fibres with a long life and relatively low cost are highly desired. In recent years, investigations have been directed to the development of fibres based on coated metal wires.

One approach is to fix a sorbent layer using a physical deposition of a sorbent [5–9]. Another approach is an electrochemical preparation of coatings. Promising electrochemically prepared coatings are conductive polymers such as polypyrrole (PPY), polyaniline (PANI) and their derivatives as the extraction phases. Due to their electrical conductivity, electroactivity, environmental stability, chemical stability and corrosion inhibition, both PANI and PPY are widely used in rechargeable batteries, electrochromic displays, ion-exchangers, pH sensors, gas sensors, and primers for corrosion protection of steel and aluminium [10, 11]. Recently the first attempts have been made to apply the polymers as coatings for solid phase microextraction fibres. Polymer film is directly electrodeposited on the metal wire. By controlling the electropolymerisation conditions, such as applied potential, monomer concentration, changing dopant ions or by using substituted monomers, the electrodeposition is easily controlled, and is flexible [12].

PPY and its derivatives have been one of the most widely used classes of conducting polymers, since pyrrole and some of its derivatives are commercially available, and stable polymer films can be conveniently prepared on various substrate materials from organic or aqueous media by electrochemical or chemical methods [13, 14]. Run on sentence, awkward. Since PPY is formed in its oxidized form carrying positive charges, the counter ions are incorporated into the film. The counter ions provide a convenient way to introduce functional groups into the films and thus to modify film extraction properties [15]. Due to the inherent multifunctional properties of PPY, primarily $\pi - \pi$ interactions, base acid interactions and interactions from polar groups and hydrogen bonding, PPY coating can be used for SPME of a large range of analytes. For example, in [12] dodecylsulfate-doped PPY was suggested for headspace SPME of polycyclic aromatic hydrocarbons. PPY modified with tetrasulfonated nickel phthalocyanine was successfully applied for the extraction of BTEX [16]. Pawliszyn and co-workers showed that possible targets for the extraction of PPY and its derivative coatings are polar and non-polar aromatic compounds, polar and ionic drugs, inorganic and organic anions, and organometalic compounds [13–15, 17].

The other conducting polymer, PANI, has also been used for SPME. PANI coatings were applied for SPME of phenols [18] and anatoxin [19], PANI doped with polyethylene glycol and PDMS was proposed to extraction and consequent HPLC determination of phenols [20]. PANI coated on the stainless steel wire was suggested for detection of aromatic amines [21] and for trace levels of phthalates in environmental water samples [22]. It was concluded that PANI fibre in comparison with commercial silica fused SPME fibres has the advantages of higher physical stability and chemical inertness, and facile and inexpensive preparation. Moreover, PANI films are stable in different pH solutions so provide the ability to manipulate the extraction efficiency by choosing a suitable pH according to the acid-base equilibrium of the analytes.

In addition to the above mentioned modes to control conducting polymer properties (applied potential, monomer concentration, changing dopant ions or by using substituted monomers), blend coatings have been suggested. Iroh and Rajagopalan studied electrochemical synthesis of polyaniline-polypyrrole blend coatings on carbon fibres and found that thermal stability of the blend coatings lies between the homopolymeric PANI and PPY coatings [23]. However, to our knowledge blend PANI-PPY coatings have not been applied for SPME.

It would be of great interest to combine mechanical properties and extraction ability of PANI and PPY, so in this work we propose the electrochemically prepared PANI-PPY blend coating on the surface of stainless steel wire and its application as a new fibre for SPME.

2 Experimental

2.1 Reagents

Pyrrole (98%), aniline (99%), 2-butanone (99.5%), n-butanol (98%), n-pentanol (99%), n-hexanol (98%), benzyl alcohol (99%), n-butyl acetate (99%), o-xylene (98%), phenol (99.5%), methyl benzoate (99%), poly(sodium 4-styrenesulfonate) (PSS) (MW 70000 and 1000000) were purchased from “Aldrich”. Pyrrole and aniline were distilled before use.

A standard stock solution containing 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 10^{-2} mol L^{-1} of n-butanol, n-pentanol, n-hexanol and benzyl alcohol was prepared in distilled water. The standard stock solutions were stored refrigerated at 4 °C. Working standard solutions were prepared daily by diluting the stock standard solution with distilled water to the required concentrations.

2.2 Instrumentation

SPME was carried out in 13 ml vial closed with a silicone rubber septum containing cap. The vial was positioned on a magnetic stirrer (RH3, MLV, Germany).

Homemade SPME fibre was housed in a 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 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). Injector temperature was 260 °C, detector temperature was 200 °C. The oven temperature program was initially set at 50 °C for 2 min, then gradually ramped to 100 °C (5 °C/min), 200 °C (2 °C/min) and held for 5 min. Following gas flow rates were used: carrier (nitrogen) 10, make-up gas 20, hydrogen 30 and air 300 ml $\min^{-1}$.

The surface of the fibres was studied by multimode scanning probe microscope (Digital Instruments, USA).

The Fourier transform infrared (FTIR) spectra were obtained by using Perkin-Elmer Spectrum BX FTIR spectrometer. The coatings were ground and mixed with IR grade potassium bromide powder. Homogeneous pellets were obtained by subsequent pressing of the mixture.

2.3 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. Stainless steel plunger needle (300 μ o.d.) was used as a support for a 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.

Polymer films were prepared electrochemically using a three electrode system. The stainless steel plunger needle was used as a working electrode, reference electrode was Ag/AgCl, counter electrode was a platinum wire. All the polymeric films were prepared at ambient temperature from aqueous solutions with desirable pyrrole, aniline, PSS and H_2SO_4 concentrations by applying a constant deposition potential of $0.4 - 0.7$ V for 2 h. The electric charge consumed for the polymer electrodeposition was $0.2 - 1.2$ C. The coated fibre was dried at room temperature for 2 h and then conditioned under nitrogen in an injection port of a gas chromatograph at 280 °C for 1 h.

3 Results and discussion

In [19] 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 °C [18]. This temperature is rather low and restricts the use of high injection temperature that is required for efficient desorption of less-volatile analytes. On the other hand, dodecylsulfate-doped PPY is thermally stable up to 300 °C [12]. Thus, it is of great interest to combine the porosity of PANI with the thermal stability of PPY in order to prepare a thermally stable coating with the extracting characteristics of PPY and PANI films. We made an attempt to reach the scope by co-deposition of PANI and PPY.

3.1 Optimum coating composition

As the stability and robustness of the coating are important in practical application of SPME, the coating quality was evaluated on the basis of the surface homogeneity and on the mechanical adhesion of the film.

The first parameter examined was the ratio of pyrrole and aniline used. Electrolytes with following aniline:pyrrole (mol L^{-1}) compositions were prepared: 0.1 : 0.1; 0.05 : 0.15; 0.15 : 0.05. As can be seen from the photos presented in Figure 1, the morphology of the coatings is affected by the molar concentration of monomer. For the deposition of the first two coatings, approximately the same electric charge (about 0.8 C) was consumed. Nevertheless, the coating deposited from the first electrolyte was rather smooth meanwhile the second coating resulted inhomogeneous and mechanically unstable. Contrarily, for the deposition of the coating from the solution containing 0.15 : 0.05 mol L^{-1} of aniline:pyrrole the charge consumed was rather small (0.2 C) suggesting that the coating was rather thin or its density was rather low. Anyway, the coating was inhomogeneous and easily detached from the support. Thus further investigations were accomplished using 0.1 : 0.1 mol L^{-1} aniline:pyrrole concentrations.

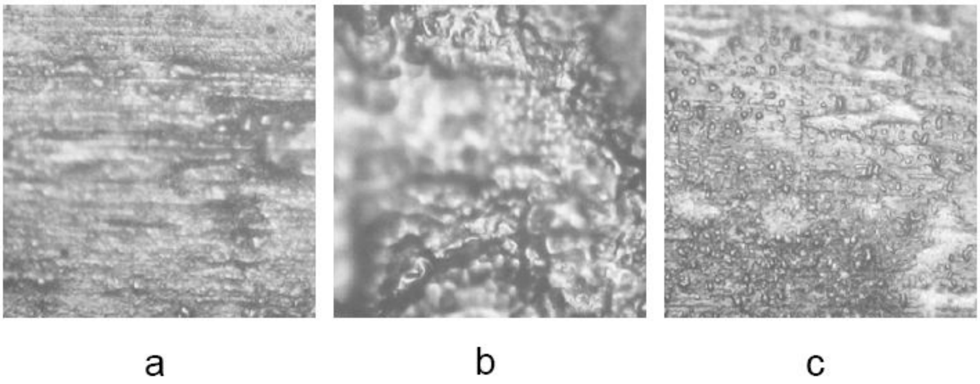

Fig. 1 Multimode scanning probe microscope images (magnification 200) of PANI-PPY coatings. Concentrations of aniline:pyrrole (mol L^{-1}) : (a) 0.1:0.1; (b) 0.05:0.15; (c) 0.15:0.05.

It is known that the physical properties of PPY films are influenced by the counter ions used. J. Wu and J. Pawliszyn showed that thermal stability and mechanical properties of the films could be improved when large aromatic counter ions were incorporated into the films and that a more stable PPY coating was produced using poly(sodium 4-styrenesulfonate) (PSS) as the counter ions during polymerisation [15]. Moreover, large counter ion should enlarge coatings selectivity for hydrophobic compounds. In our work a counter ion PSS of 700000 and 1000000 average molecular weight at the concentration of 4 g L^{-1} was used. More uniform coating was obtained from the electrolyte containing $1,000,000$ average molecular weight PSS(Figure 2). The coatings were obtained from electrolytes containing 1 and 4 g L^{-1} of PSS (MW 1000000). The coating deposited from the electrolyte with bigger PSS quantity was more homogeneous and mechanically stable.

There are no special requirements for PPY deposition media, but polymerisation of aniline should be carried out in strong acidic solution [24]. As a rule, sulphuric acid is used to produce PANI. We employed electrolytes with 0.05, 0.1 and 0.25 mol L^{-1} of sulphuric acid. The most smooth and adherent coating was obtained from the electrolyte

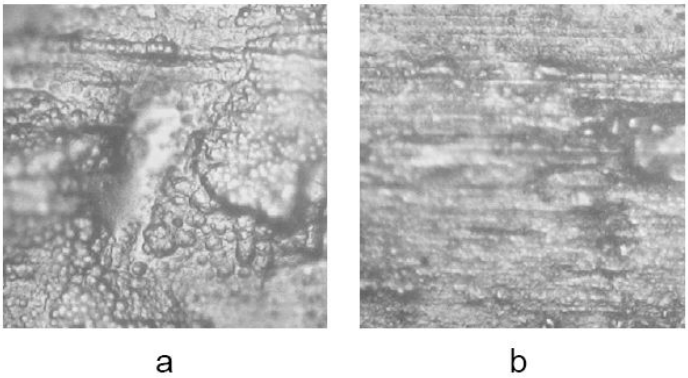

Fig. 2 Multimode scanning probe microscope images of PANI-PPY coatings using PSS of (a) 70000 and (b) 1000000 molecular weight. Electrolyte composition: aniline 0.1 mol L^{-1}, pyrrole 0.1 mol L^{-1}, PSS 4 g L^{-1}, H_2SO_4 0.25 mol L^{-1}

with the biggest H_2SO_4 concentration. Moreover, at lower H_2SO_4 concentrations in order to deposit the coating we had to apply higher deposition potential (0.7 V instead of 0.5 V used for the other depositions).

At last, 4 different types of coatings were prepared applying different deposition potentials from solution of the same composition (aniline 0.1 mol L^{-1}, pyrrole 0.1 mol L^{-1}, PSS 4 g L^{-1}, H_2SO_4 0.25 mol L^{-1}). At low deposition potentials deposit structure was uniform, clumsy/awkward meanwhile increased deposition potentials resulted in uneven surfaces Figure 3.

Considering all the investigations mentioned above, the optimum coating conditions were chosen: aniline 0.1 mol L^{-1}, pyrrole, 0.1 mol L^{-1}, PSS (MW 1000000) 4 g L^{-1}, H_2SO_4 0.25 mol L^{-1}, deposition potential 0.4 V.

3.2 FTIR studies

Figure 4 shows the comparison of the infrared spectrum of the PANI-PPY coating with the spectra of PANI and PPY coatings. Polyaniline coating shows characteristic peaks at 1615 cm^{-1} (due to C=N stretching), 1558 cm^{-1} (due to C-N stretching) and 1301 cm^{-1} (due to N-H deformation). Polypyrrole coating shows characteristic peaks at 1558, 1042, 964 and 783 cm^{-1}. Those peaks are due to C-N stretching and pyrrole ring vibrations. The presence of those peaks in the infrared spectrum of the composite coating confirms the incorporation of PANI and PPY into the coating. The additional peaks (at 1186 and 1103 cm^{-1}) present in the spectrum of PANI-PPY coating appear due to the presence of the dopant PSS.

3.3 Thermal stability

Coating/gas distribution constants of the adsorbed analytes rapidly decrease with injection temperature increase allowing an efficient desorption of analytes. On the other hand,

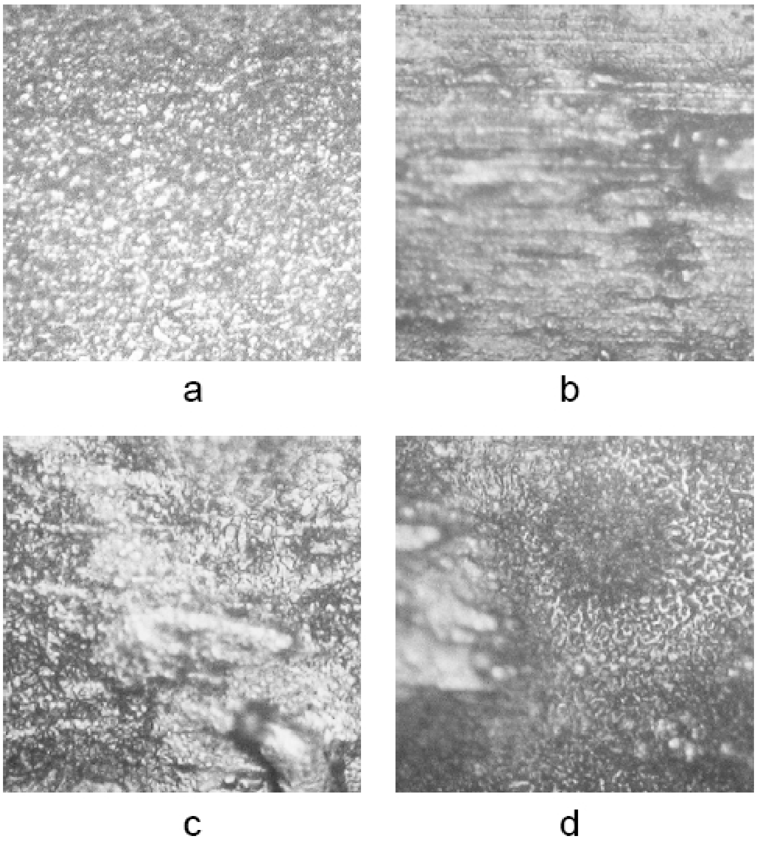

Fig. 3 Multimode scanning probe microscope images of PANI-PPY coatings obtained at deposition potential (V): (a) 0.4; (b) 0.5; (c) 0.6; (d) 0.7. Electrolyte composition: aniline 0.1 mol L^{-1}, pyrrole 0.1 mol L^{-1}, PSS (1000000) 4 g L^{-1}, H_2SO_4 0.25 mol L^{-1}.

desorption temperature is limited by coatings thermal stability. Therefore, the thermal stability of the coating was evaluated. Figure 5 shows the blank chromatograms at 260, 270 and 280 °C temperature. It is evident that the coating can be operated without any damage at 260 °C. However, when it was exposed to 270 °C, some artifacts were increased and they increased even more at 280 °C injector temperature.

3.4 Coating selectivity

In order to examine the 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^{-3} mol L^{-1} of 2-butanone, n-butanol, n-butyl acetate, o-xylene, phenol, benzyl alcohol and methyl benzoate. As seen in Figure 6, the fibre selectivity increases in the sequence 2-butanone < n-butanol < n-butyl acetate < phenol < benzyl alcohol < methyl benzoate < o-xylene. More efficient extraction of aromatic compounds can be explained by $\pi - \pi$ interaction, because both of the coating composites contain a conjugated π structure. It was expected that the coating should extract alcohols because of hydrogen bonds for-

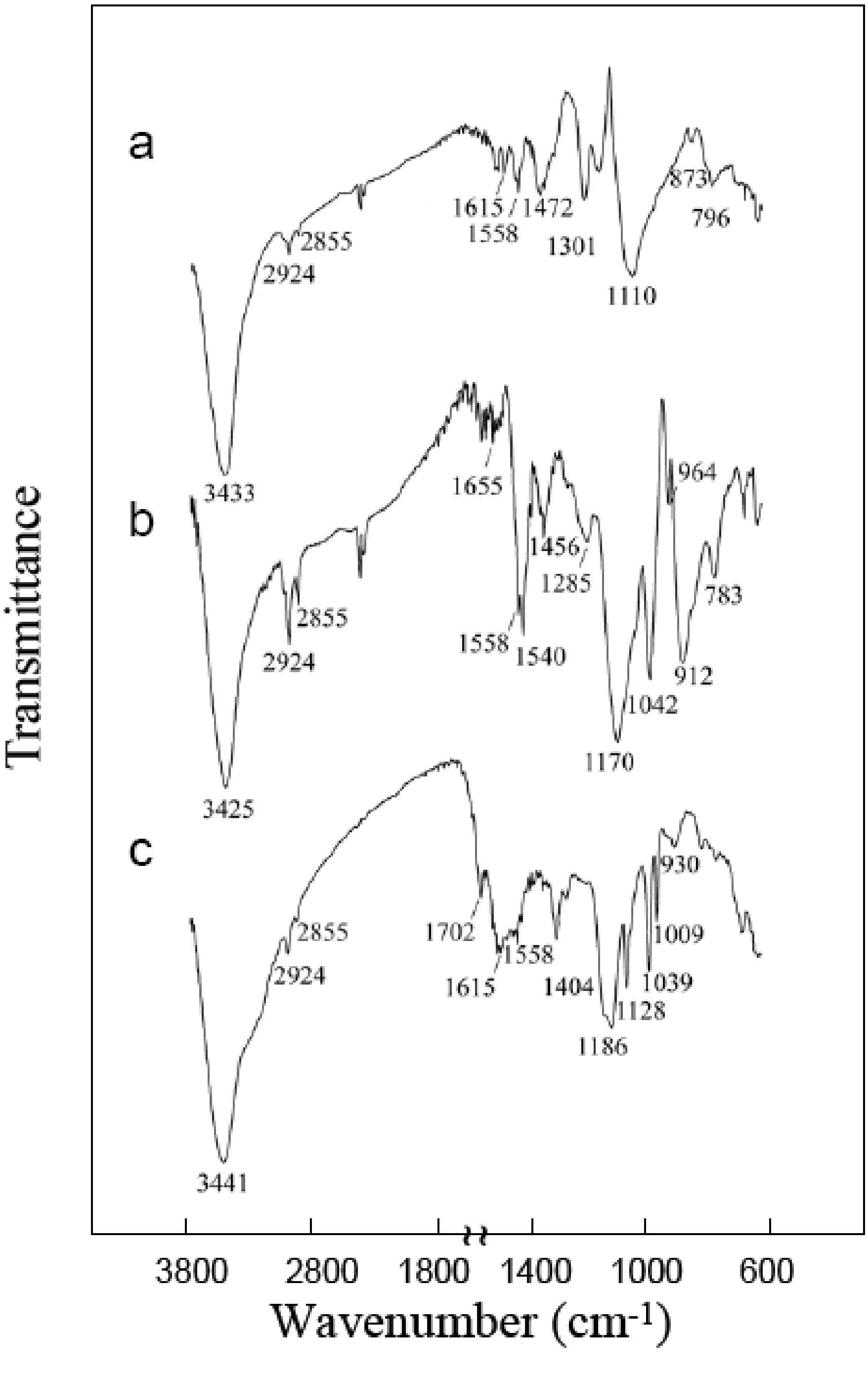

Fig. 4 IR spectra of (a) PANI, (b) PPY and (c) PANI-PPY composit coatings.

mation. However, the extraction of o-xylene was considerably increased in respect with phenol. The correlation of the extraction efficiency with the octanol-water partition coefficients can be observed. The compounds having higher $logK_{ow}$ values ($logK_{ow}$ 1.46, 2.12 and 3.12 for phenol, methyl benzoate and o-xylene respectively) possess more affinities

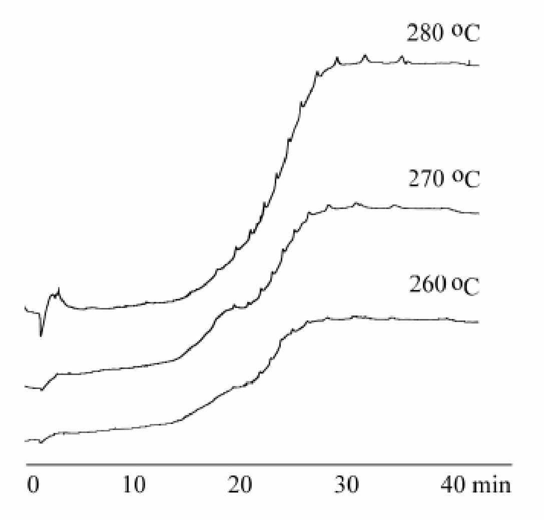

Fig. 5 Blank chromatograms for PANI-PPY coated SPME fibre desorbed at different temperatures. The oven temperature program was: 50 °C (2 min), then ramped to 200 °C (6 °C/min) and held for 20 min.

towards the coating indicating that hydrophobic interactions (mainly due to the presence of PSS in the coating) play an important role. The prevailing mechanism of interaction was verified by the extraction of four alcohols: n-butanol, n-pentanol, n-hexanol and benzyl alcohol with $logK_{ow}$, respectively 0.9, 1.4, 2.03 and 1.1. As seen in Figure 7, the extraction of aliphatic alcohols increases with the increase of carbon chain number due to the increase of hydrophobic interaction. However, benzyl alcohol was extracted more readily than the other tested alcohols, despite its lower $logK_{ow}$ than those for n-pentanol and n-hexanol. Thus $\pi - \pi$ interaction should be considered as bringing the biggest contribution to the coating extraction ability.

4 Conclusion

It was demonstrated that the PANI-PPY coating selectively extracts aromatic compounds through $\pi - \pi$ interactions and has better extraction efficiency for hydrophobic compounds. Moreover, it also extracts phenol that was slightly extracted with PPY coating as indicated in [13]. Thermal stability of the proposed coating is sufficiently high for the analysis of less-volatile compounds. The results obtained allow to expect that the coating should be promising for the extraction of parabens that are widely used as preservatives for pharmaceutical preparations, cosmetics and as food additives. The work in this direction is in progress.

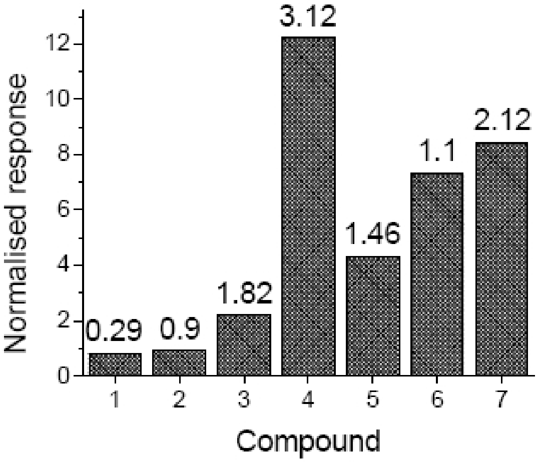

Fig. 6 Comparison of PANI-PPY coating selectivity: (1) 2-butanone, (2) n-butanol, (3) n-butyl acetate, (4) o-xylene, (5) phenol, (6) benzyl alcohol, (7) methyl benzoate. K_{ow} data are presented over the respective bars. Concentrations of the analytes 10^{-3} mol L^{-1}. Direct extraction for 30 min. Peak areas normalised to the peak areas achieved after 1 μl syringe injection of the solution with the same analyte concentration.

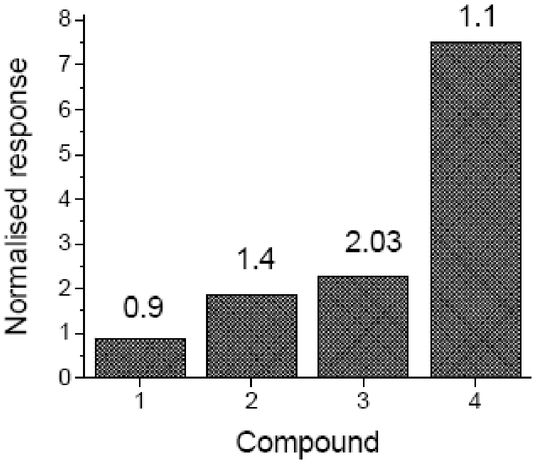

Fig. 7 Comparison of PANI-PPY coating selectivity: (1) n-butanol, (2) n-pentanol, (3) n-hexanol, (4) benzyl alcohol. K_{ow} data are presented over the respective bars. Concentrations of the analytes $2{\cdot}10^{-3}$ mol L^{-1}. Direct extraction for 30 min. Peak areas normalised to the peak areas achieved after 1 μl syringe injection of the solution with the same analyte concentration.

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