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Preparation and applications of polypyrrole films in solid-phase microextraction

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Abstract

Polypyrrole (PPY) and poly-*N*-phenylpyrrole (PPPY) films were prepared and applied for solid-phase microextraction (SPME). The extraction properties of the new films to volatile organic compounds were examined using an SPME device coupled with GC–flame ionization detection. A PPY-coated capillary was applied for in-tube SPME to evaluate its extraction efficiency towards less volatile compounds and ionic species. The porous surface structures of the films, revealed by scanning electron microscopy, provided high surface areas and allowed for high extraction efficiency. Compared with commercial SPME stationary phases, the new phases showed better selectivity and sensitivity toward polar, aromatic, basic and anionic compounds, due to their inherent multifunctional properties. In addition, PPY and PPPY films showed different selectivity to various groups of compounds studied, indicating that the selectivity of the films could be modified by introducing a new functional group (phenyl in PPPY) into the polymer. For in-tube SPME, the PPY-coated capillary showed superior extraction efficiency to commercial capillaries for a variety of compounds, demonstrating its potential applications for a wide range of analytes when coupled with HPLC. The sensitivity and selectivity of the films for SPME could be tuned by changing the film thickness. These results are in line with both the theoretical expectations and the results obtained by other methods, which indicate not only that PPY films can be used as new stationary phases for SPME, but also that SPME method may provide an alternative tool for studying materials like polypyrrole.

Keywords: Solid-phase microextraction; Polypyrrole films; Polyphenylpyrrole films; Volatile organic compounds; Polynuclear aromatic hydrocarbons; Beta-Blockers; Amines; Organoarsenic compounds; Alcohols

1. Introduction

Since its introduction, solid-phase microextraction (SPME) has become a popular sampling method for a variety of volatile and semi-volatile compounds due to its simple, solvent-less, reliable, and flexible properties. Reviews and books on the method development and applications have been published [1–6]. In most cases, however, the compounds that can be successfully analyzed are either non-polar or of medium polarity. Polar compounds such as phenols [7–9] and fatty acids [10] can be determined by either converting them to less polar, non-ionized forms by pH adjustment or derivatizing them to non-polar species. Only a few reports have been found in literature on direct SPME of ionic species [11–13]. In all of these studies, custom-made ionic coatings were used rather than commercial fibers. Up to now, the most successful applications of SPME are for analyses of volatile and semi-volatile organic compounds by coupling SPME with gas chromatography (GC). Little work has been carried out on less

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volatile or thermally labile compounds that are best separated by high-performance liquid chromatography (HPLC), even though SPME can be coupled to HPLC [14–16] and liquid chromatography–mass spectrometry (LC–MS) relatively easily [17,18]. These compounds include most pharmaceutical products, peptides, nucleic acids, proteins, some pesticides, organometallic compounds and ionic species. One of the main difficulties limiting the wide application of SPME–LC is the absence of suitable SPME stationary phases that not only has high extraction efficiency for the analytes but is also stable in solutions of various matrices. One of our goals is to develop new polymeric phases for SPME to extend its applications.

There has been growing interest in conducting polymers due to their multifunctional properties and potential applications, including ion exchangers, energy-storage materials, corrosion-resistant coatings, catalysts, and materials for separation, chemical sensors, actuators and the so-called ''electronic nose'' [19–48]. Among various conducting polymers studied, polypyrrole (PPY) and its derivatives have been one of the most widely used classes of conducting polymers for the past decades, 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 [38–40].

Our interests are to use PPY and its derivatives as films or coatings for SPME. PPY is expected to show different extraction efficiencies towards compounds with different functional groups. For example, it should extract aromatic compounds through the π–π interactions, especially for polycyclic aromatic hydrocarbons (PAHs). It should show better extraction efficiency for polar aromatic compounds due to the additional interactions of the polar functional groups. It should extract anionic species due to its anion exchange property. It should show different extraction selectivity to acid and base compounds due to its acid–base property and it should extract compounds that can form hydrogen bonds such as alcohols. These theoretical expectations have been confirmed by different analytical methods including chromatographic methods [19–26], electrochemical methods [32–42] and surface analytical methods [47,48].

In this work, PPY and poly-*N*-phenylpyrrole (PPPY) films were prepared on the surface of metal (Pt, Au, or stainless steel) wires by electrochemical polymerization. The coated wires were used with an SPME device [49] coupled with GC–flame ionization detection (FID) to examine their extraction properties to volatile organic compounds. The PPY film was also prepared on the inner surface of a fused-silica capillary by a chemical method to examine its performance for in-tube SPME of less volatile compounds and ionic species. Compared with commercial SPME stationary phases, the new phases showed better selectivity toward polar, aromatic and basic compounds, and anionic species, due to their inherent multifunctional properties. In addition, PPY and PPPY films demonstrated remarkably different selectivity to various groups of compounds studied, indicating that the selectivity of the film toward analytes could be modified by introducing a new functional group (phenyl in PPPY) into the polymer. The PPY-coated capillary was successfully applied for the automated in-tube SPME of various compounds when coupled on-line with HPLC.

2. Experimental

2.1. Reagents

Pyrrole (98%) (Aldrich) was distilled before use. *N*-Phenylpyrrole (99%) (Aldrich) and tetrabutylammonium perchlorate (TBAP) (electrochemical grade; Fluka, Buchs, Switzerland) were used as received. Ferric perchlorate [$Fe(ClO_4)_3 \cdot 6H_2O$] and perchloric acid (70%) were purchased from BDH (Toronto, Canada). All nine β-blockers were purchased from Sigma (St. Louis, MO, USA), including acebutolol hydrochloride, alprenolol hydrochloride, labetalol hydrochloride, metoprolol tartrate, nadolol, oxprenolol hydrochloride, pindolol, (*S*)-(−)-propranolol hydrochloride and timolol maleate. These drugs were dissolved in methanol to make stock solutions at concentrations of 1 mg/ml. The solutions were stored at 4°C and used after dilution with water to the required concentration. The six aromatic amines, 2-amino-3-methyl-3*H*-imidazo[4,5-*f*]quinoline (IQ), 2-amino-3,4-dimethylimidazo[4,5-*f*]quinoline (MeIQ), 2-amino-3,7,8-trimethylimidazo[4,5-*f*]quinoxaline (7,8-DiMeIQx), 2-amino-9*H*-pyrido[2,3-*b*]in-

dole (AαC), 2-amino-6-methyldipyrido[1,2-*a*:3′2′-*d*]imidazole (Glu-P-1) and 2-amino-1-methyl-6-phenylimidazo[4,5-*b*]pyridine (PhIP), were kindly provided by Professor H. Kataoka, Okayama University, Japan. Each amine was dissolved in methanol to make stock solutions at concentrations of 0.3 mg/ml and used after appropriate dilutions. A PAH standard containing 16 components (2000 μg/ml each in methylene chloride–benzene, 50:50) was obtained from Supelco (Bellefonte, PA, USA), diluted to 20 μg/ml with CH_2Cl_2–benzene (50:50), then to 2 μg/ml with acetonitrile, and finally to the working concentrations with water. Arsenic compounds studied include sodium methylarsonate (MMAs; Chemical Service, West Chester, PA, USA), dimethylarsinic acid (DMAs, sodium salt; Sigma), arsenobetaine (AsB), and arsenocholine (AsC). AsB and AsC were synthesized using a literature method [50]. A standard solution (1 mg/ml) of each arsenic compound was prepared in pure water, from which the chromatographic standard (mix) was prepared and diluted gradually with water when necessary. Other chemicals were obtained from Aldrich (Canada). Standard solution (1 mg/ml) for each non-polar aromatic compound, such as benzene, toluene, and naphthalene, and polar aromatic compound, such as phenol, dimethyl phthalate (DMP) and diethyl phthalate (DEP), was prepared in methanol. A mixture of these aromatic compounds was prepared in acetonitrile, which contained 10 μg/ml each of DMP, DEP and naphthalene, 20 μg/ml of phenol, 50 μg/ml of benzene and 50 μg/ml of toluene. The mixture was finally spiked into water for extraction experiments. All solvents used were of analytical-reagent grade or HPLC grade. Water was obtained from a Barnstead/Thermodyne NANO-pure ultrapure water system (Dubuque, IA, USA). The structures for some of the compounds studied are listed in Fig. 1 (structures for β-blockers and PAHs can be found in the literature [18,51]). The commercial SPME device and fibers were obtained from Supelco.

2.2. Preparation of PPY films

PPY films could be prepared electrochemically using a three-electrode system [27]. A metal (Pt, Au, or stainless steel) wire was used as a working electrode and a platinum wire wound into cylindrical shape was utilized as a counter electrode. An Ag/AgCl electrode was employed as a reference electrode. The PPY or PPPY film was directly prepared on the surface of the working electrode from a 0.1 *M* tetrabutylammonium perchlorate–acetonitrile solution containing 0.1 *M* corresponding monomer. A constant deposition potential (0.9 V for PPY and 1.2 V for PPPY) was applied using a potentiostat (Model RDE2; Pine Instrument, Grove City, PA, USA) [27]. The metal wire coated with PPY or PPPY film was dried under N_2 and then preheated at 100°C for 20 min, and finally conditioned at 180~200°C in a GC injection port under helium protection for an hour before they were used for SPME experiments.

For in-tube SPME, PPY film was prepared on the inner surface of a fused-silica capillary (60 cm×0.25 mm I.D.) by a chemical polymerization method. In brief, the film was prepared by first passing the monomer solution (pyrrole in 50%, v/v, isopropanol) and then the oxidant solution (0.2 *M* ferric perchlorate in 0.4 *M* perchloric acid) through the capillary column with the aid of N_2. The above procedure was referred to as one PPY coating cycle, which could be repeated several times to increase the film thickness. The capillary was cleaned with acetone before it was coated. During polymerization, the color of the capillary changed gradually from yellow to black, indicating the formation of PPY film on the inner surface of the capillary. The PPY-coated capillary was then washed with methanol or acetone and dried by purging with N_2. Finally, it was coupled to HPLC, conditioned with mobile phase before use. Different silica capillaries were tested for the possibility of preparing PPY film on their inner surfaces, including untreated silica tubing and treated GC pre-columns (polar, intermediate, and non-polar). Although PPY film could be easily formed by chemical polymerization, the film could only be coated firmly on the inner surface of a polar treated GC capillary. Therefore, there may be certain chemical interactions between the polar poly(ethylene glycol) surface and the PPY film. This hypothesis was supported by our recent study [52] in which it was found that PPY could be coated much easily on the inner surface of Omegawax or Supelwax GC capillary columns which has the same polar inner face as the polar treated pre-column.

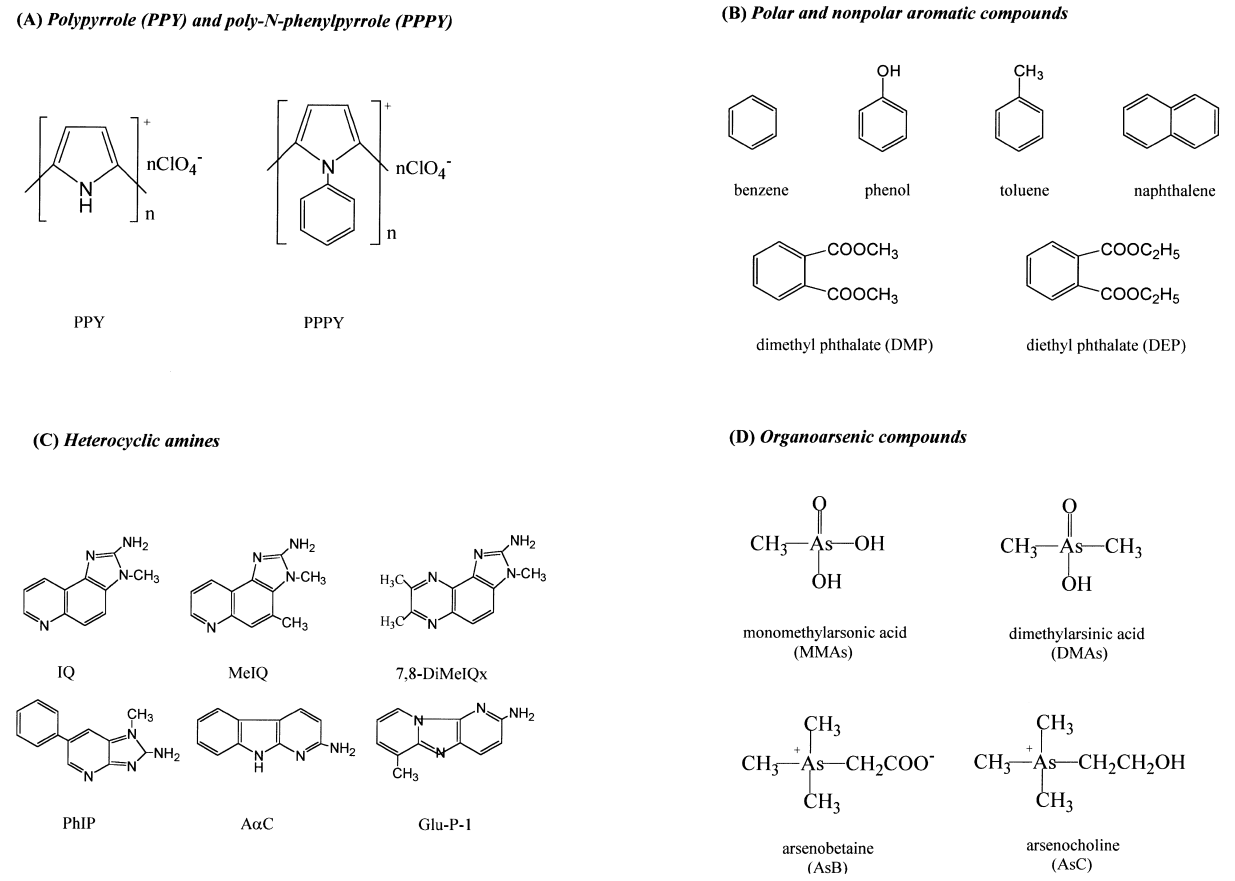

Fig. 1. Structures of polypyrrole (PPY), poly-*N*-phenylpyrrole (PPPY) and some of the compounds studied.

2.3. Scanning electron microscopy (SEM)

The scanning electron micrographs of the polymer films were obtained using a Hitachi S-570 scanning electron microscope (15 kV accelerating potential).

2.4. SPME of volatile organic compounds

As described previously [7], a modified syringe assembly was used as an SPME device, the metal wire coated with PPY or PPPY was inserted into the needle of a Hamilton syringe and attached to the plunger. The commercial SPME device and a used fiber assembly could also be utilized by replacing the fiber with a polymer-coated metal wire [49]. Gas samples were prepared by injecting 5 or 10 μl each of the volatile organic compounds into the silanized 1-l gas standard bulbs (Supelco, Mississauga, Canada) and then allowing them to stand in ambient temperature for an hour or longer to reach full evaporation and equilibration. Extraction processes were performed by standard headspace SPME procedure [1–6]. In this study, all SPME extractions were performed at room temperature. A 20-min period was found suitable for extraction and 2 min for desorption (at 200°C).

2.5. GC separation conditions

All the GC analyses were carried out using an SPB-1 column (Supelco), 30 m×0.25 mm, 1 μm in film thickness, equipped with a 1 m deactivated fused-silica pre-column. A Varian 3400 CX gas chromatograph equipped with septum programmable

injector (SPI) and a flame ionization detector was used. Separation conditions employed for the compounds reported in this paper were: column temperature program 40°C (2 min), 20°C/min to 140°C, and stay at 140°C for 2 min; injector SPI, 200°C; detection: FID, 250°C. Helium was used as carrier gas (helium pressure: 20 p.s.i.; 1 p.s.i.=6894.76 Pa) and the GC data were acquired with a Varian Star system. The analyses of polar compounds (alcohols) in non-polar matrices (hexane or gasoline) were carried out according to a literature method [53].

2.6. In-tube solid-phase microextraction

In-tube SPME and the technique of coupling automated in-tube SPME with HPLC were described previously [15,18,58,60]. A schematic diagram of the in-tube SPME–HPLC system is illustrated in Fig. 2 of Ref. [58]. Briefly, a PPY-coated capillary (60 cm long) or one of the commercial capillaries was used as the in-tube SPME device, and placed between the sample injection loop and injection needle of the autosampler. The total internal volume of each capillary was around 30 μl. The autosampler was programmed to control the extraction, desorption and injection processes. Detailed descriptions on the operation processes of automated in-tube SPME can be found in the literature [15,18,58]. In order to compare the extraction efficiencies of different capillary stationary phases, a PPY-coated capillary and the following commercial capillaries (from Supelco) were examined under the same conditions. Omegawax 250 (0.25 μm film thickness, 0.25 mm I.D.), SPB-1 (0.25 μm film thickness, 0.25 mm I.D.), SPB-5 (0.25 μm film thickness, 0.25 mm I.D.), and a retention gap capillary (a polar silica tubing, 0.25 mm I.D., which was also used as host capillary to make the PPY-coated capillary).

2.7. LC separation and detection

The HPLC system used was a Model 1100 series LC instrument coupled with a UV detector and an atmospheric pressure (AP) electrospray ionization (ESI) mass spectrometer (Agilent Technologies, Palo Alto, CA, USA). The separation and mass detection of β-blockers were carried out by the methods developed previously [58]. The conditions for separation and detection of other compounds are described below.

2.7.1. Polar and non-polar aromatics

The aromatic compounds tested include benzene, toluene, phenol, naphthalene, DMP and DEP. Separation of these compounds was performed using a Hypersil BDS C_{18} column (5.0 cm×2.1 mm I.D., 3 μm particle size) from Agilent Technologies under room temperature. The mobile phase consisted of acetonitrile–water (40:60) with a flow-rate of 0.2 ml/min (isocratic elution). A UV detector, set at 200 nm, was used for the first 7 min, and then changed to 219 nm for the rest of the run (see Fig. 7, below).

2.7.2. Polycyclic aromatic hydrocarbons

For the separation of 16 PAHs, a Supelcosil LC-PAH column (5 cm×4.6 mm, 3 μm particle size) with a Supelguard LC-18 guard cartridge (both from Supelco) was used at ambient temperature. Mobile phase: initially, acetonitrile–water (50:50) was kept for 1 min, then the concentration of acetonitrile (CH_3CN) was increased linearly and reached 95% at 15 min and held at this ratio for the rest of the run. Flow-rate was kept at 0.8 ml/min. UV detection was performed using a wavelength program to optimize the signal intensities (see Fig. 8, below).

2.7.3. Aromatic amines

The separation of six amines was performed using a Hypersil BDS C_{18} column (5.0 cm×2.1 mm I.D., 3 μm particle size) from Agilent Technologies under room temperature. The mobile phase consisted of acetonitrile–methanol–water–acetic acid (15:15:70:1, pH 4) with a flow-rate of 0.2 ml/min. ESI-MS detection conditions: nebulizer gas, N_2 (40 p.s.i.); drying gas, N_2 (10 l/min, 350°C); fragmentor voltage, 90 V; ionization mode, positive; mass scan range, 100–300 amu; selected ion monitoring (SIM), m/z 199 (IQ), 213 (MeIQ), 228 (7,8-DiMeIQx), 225 (PhIP), 184 (AαC), and 198 (Glu-P-1).

2.7.4. Organoarsenic compounds

An anionic-exchange column Supelcosil LC-SAX1 (25 cm×4.6 mm I.D., 5 μm particle size) from Supelco was used for the separation of organoarsenic compounds at room temperature. Mobile phase was 50 m*M* ammonium acetate solution

(containing 0.1% trifluoroacetic acid and 30% methanol), with a flow-rate of 0.5 ml/min. ESI-MS detection conditions: nebulizer gas, N_2 (40 p.s.i.); drying gas, N_2 (10 l/min, 350°C); fragmentor voltage, 50 V; ionization mode, positive; mass scan range, 100–300 amu; SIM, m/z 165 (AsC), 179 (AsB), 141 (MMAs), and 139 (DMAs).

3. Results and discussion

3.1. Polymer film preparation and SEM studies

Pyrrole and some of its derivatives can be polymerized easily with oxidation reactions by either an electrochemical method or a chemical method. The advantages of electrochemical method are that it can be controlled easily by a cyclic voltammetry or by a constant potential method, and it is more flexible, because polymers with different functional groups can be formed easily by changing counter ions or using substituted pyrrole monomers under controlled electrochemical conditions. For example, PPY or PPPY film could be easily coated on a metal wire by a constant potential method. However, the substrate used must be conductive to form polymer film. Chemical polymerization method is capable of producing polymers on a large scale, but its flexibility is limited by the oxidizing reagents used and the reaction conditions. For instance, the PPY film was coated on the inner surface of a silica capillary easily and quickly by reacting pyrrole monomer with oxidizing reagent $Fe(ClO_4)_3$. However, under the same conditions, PPPY film could hardly be formed on the inner surface of the capillary probably due to the higher oxidation potential required for PPPY formation (1.2 V for PPPY, 0.9 V for PPY). Another advantage of the electrochemical method is that the polymer film can be coated directly on the metal wires (such as stainless steel) which have better mechanical strength than silica fiber. Since silica fibers are fragile, caution must be taken to prevent them from breaking during stirring and injection. More importantly, conducting polymer-coated metal wires can be used to develop an electrochemically modulated SPME device and technique, which utilize the unique property of conducting polymers, as described in a recent report [13].

The surface characteristics of the polymer films were investigated by SEM. As shown in Fig. 2, the PPY- and PPPY-coated surfaces possess different porous structures. The porous inner surface of a PPY-coated capillary can also be observed as presented in Fig. 3. The SEM images of the host capillary were included in Fig. 3 for comparison. The porous structures should significantly increase the effective surface areas of the films, and therefore higher extraction efficiency can be expected compared with non-porous films. In addition, the extraction efficiency and selectivity of the film for SPME will increase when the film thickness increases due to the increase of specific surface areas (results will be shown later). The enhanced extraction efficiency of porous SPME coatings relative to non-porous SPME coatings has been demonstrated by the recent studies on porous SPME coatings [54,55] and sol–gel SPME coatings [56]. The difference in morphology between PPY and PPPY as shown in Fig. 2 may partially account for their different SPME properties (see next section). Previous studies also showed that the differences in morphology had a significant effect on the response of the polypyrrole-based sensors to different vapors [27].

3.2. Gas phase extraction of volatile organic compounds

Several groups of volatile organic compounds with different functional groups were chosen to examine the extraction properties of the PPY and PPPY films. Compared with commercial SPME fibers, the new films showed better selectivity toward polar compounds [49]. For example, the new films had better selectivity to methanol or ethylamine relative to the less polar benzene and toluene compounds, while commercial fibers responded more sensitively to the less polar aromatic compounds [49]. It is not surprising that polypyrrole and its derivatives are sensitive to methanol, ammonia, and other polar gaseous compounds given their structures are concerned, such as their hydrogen bonding ability. These results are in line with those studies on gas sensors and electronic nose [27,45,57].

More importantly, PPY and PPPY showed significantly different extraction properties to the compounds studied due to their differences in chemical

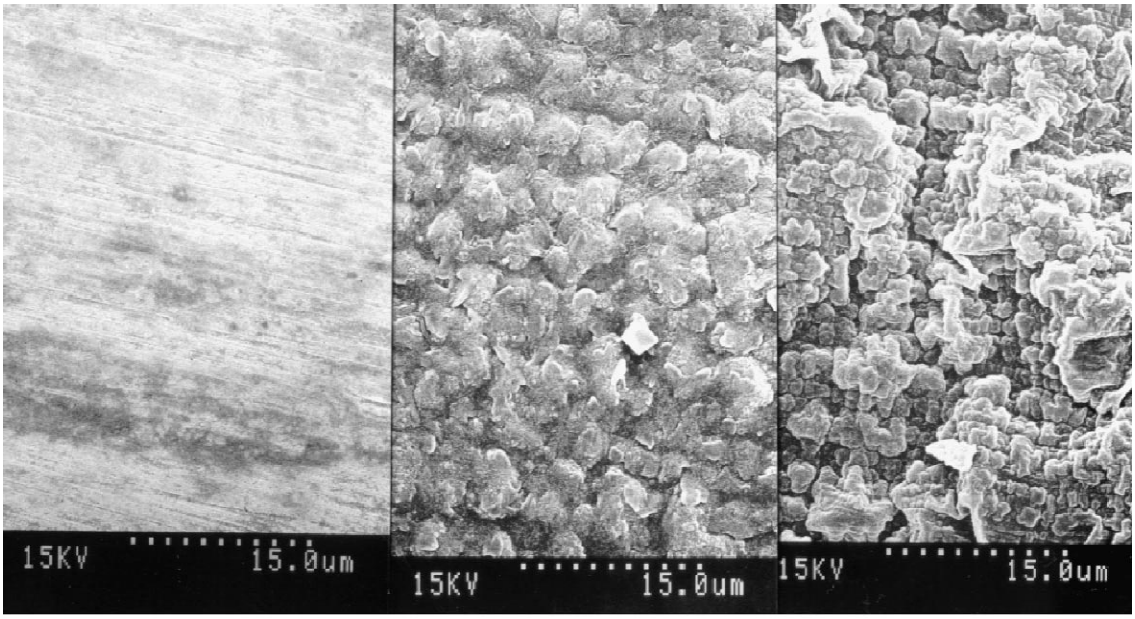

Fig. 2. Scanning electron micrographs of (A) metal (stainless steel) wire surface, (B) PPY-coated metal wire surface and (C) PPPY-coated metal wire surface.

structures and surface properties. For example, as shown in Fig. 4, both PPY and PPPY gave high response to methanol, but PPPY responded to the aromatic compounds more sensitively than PPY because of the phenyl group incorporated into PPPY. The same phenomenon was also observed in a previous study on potentiometric gas sensors based on PPY and its co-polymer with nitrotoluenes [57]. These results demonstrate that the selectivity of the films (molecular/analyte recognition) can be modified by introduction of additional functional groups to the polymer. In addition, an interesting discovery was found when performing SPME for a mixture, which contained the same amount (mass) of each of the *n*-alcohols and their isomers. As shown in Fig. 5A, with the increase of carbon numbers or boiling points of the aliphatic alcohol, a nearly linear increase in signal intensity was observed when using the PDMS [poly(dimethylsiloxane)] fiber for SPME. This result is easy to understand because the PDMS fiber has the same chemical composite as the GC column used in this study. Both contain the non-polar liquid poly(dimethylsiloxane) stationary phase, which retain or extract analytes by absorption based on hydrophobic interaction. For a homologous series of compounds, there exists a linear relationship between the number of carbons (or boiling points) and their retention power on this stationary phase (linear retention index). However, a remarkably different response pattern was obtained when performing SPME with PPPY film for the same sample mixture under the same conditions. PPPY extracted *n*-alcohols more selectively than their isomers (Fig. 5B). This is possibly due to the steric hindrance of phenyl group in PPPY on hydrogen bonding, since the main interactions between alcohol and PPPY include not only the hydrophobic interaction but also hydrogen bonding. Another important feature of the new films is that they showed the smallest responses to non-polar aliphatic hydrocarbons such as hexane (see Fig. 4). Therefore, it is possible to use them to extract polar compounds from non-polar matrices (e.g., extraction of alcohols from hexane as illustrated in Fig. 6).

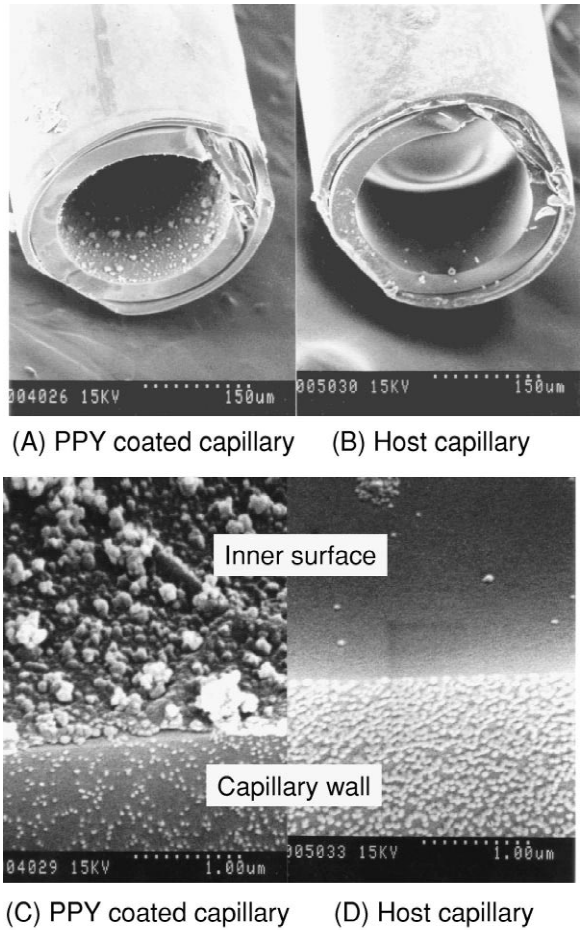

Fig. 3. Scanning electron micrographs of the PPY-coated capillary [(A) cross-sectional view, (C) enlarged inner surface view] and the host silica capillary [(B) cross-sectional view, (D) enlarged inner surface view].

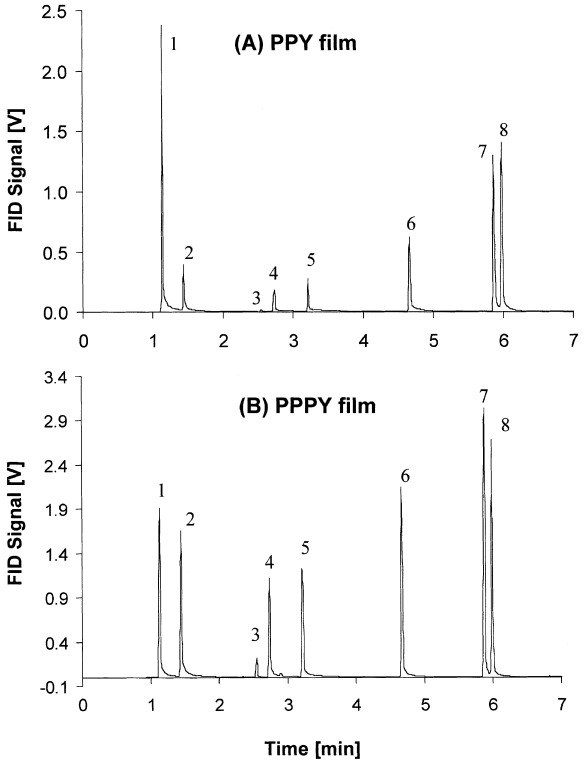

Fig. 4. Gas chromatograms for a mixture of volatile organic compounds obtained by SPME–GC–FID with (A) PPY- and (B) PPPY-coated wires as SPME devices. 1: Methanol, 2: acetone, 3: hexane, 4: tetrahydrofuran (THF), 5: benzene, 6: toluene, 7: ethylbenzene, and 8: *p*-xylene.

3.3. In-tube solid-phase microextraction

For in-tube SPME, several parameters were optimized to achieve the best extraction efficiency. These parameters include capillary length, stationary phases, extraction time profile, sample matrix and pH. The results obtained from the studies of capillary length effect and extraction time profile are similar to those of previous studies [15,18,58], therefore they will not be discussed in detail. In this study, all the results were obtained using a 60 cm long capillary with 15 draw/eject cycles (30 μl for each cycle at a flow-rate of 100 μl/min). The effects of sample matrix and pH on the extraction were examined using several buffer solutions with pH 1.5–11.5. The results showed that higher extraction efficiency was obtained at a high pH buffer solution (Tris–HCl, pH 8.5) for basic compounds such as β-blockers and aromatic amines. However, for non-polar PAHs and arsenic compounds, sample matrix and pH did not have significant effect on their extraction efficiency. Therefore, Tris–HCl buffer at pH 8.5 was used for β-blockers and amines, water was used for other compounds in this work.

The extracted analytes could be desorbed from the capillary with mobile phases by simply switching the six-port valve to the INJECT position. The desorbed analytes were easily transported to the LC column with mobile phase flow. The entire in-tube SPME extraction and desorption processes was accomplished automatically within 15 min, and no signifi-

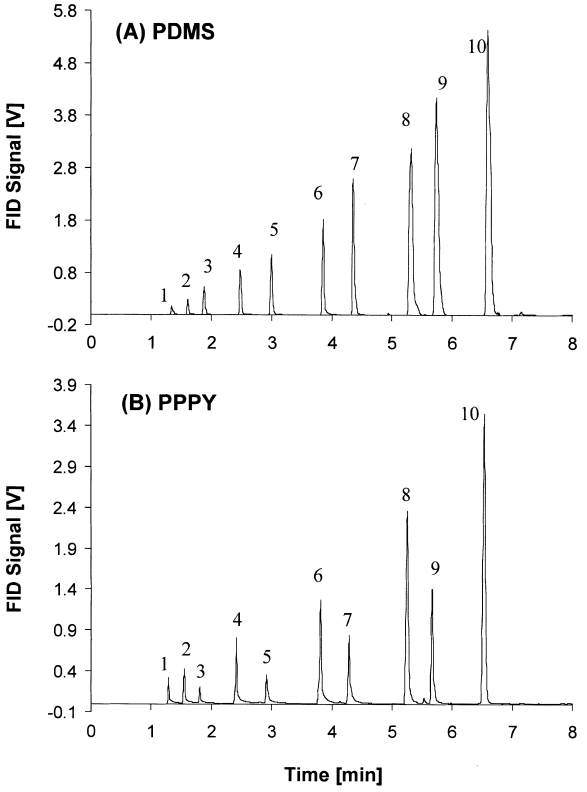

Fig. 5. Gas chromatograms for a mixture of 10 alcohols obtained by SPME–GC–FID with (A) PDMS (30 μm thickness), and (B) PPPY film. 1: Methanol, 2: ethanol, 3: 2-propanol, 4: 1-propanol, 5: 2-butanol, 6: 1-butanol, 7: 2-pentanol, 8: 1-pentanol, 9: 2-hexanol, 10: 1-hexanol.

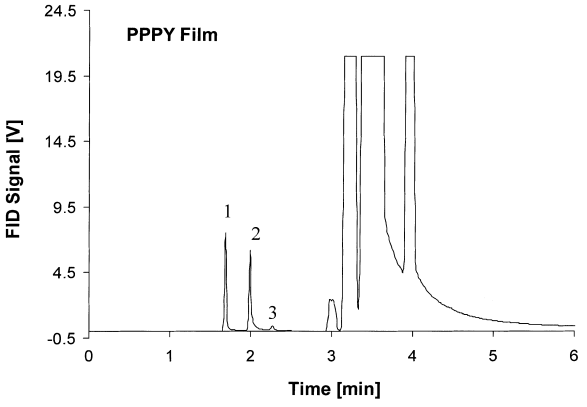

Fig. 6. SPME–GC analysis of 40 μg/ml methanol (1), ethanol (2), and 2-propanol (3) in hexane using PPPY film.

cant carryover of analytes was observed. Under the above conditions, different capillary coatings were evaluated for their extraction efficiencies to the groups of compounds, based on the amount of analyte extracted:

$$n_A = FA = (m/A_d)A \quad (1)$$

where n_A is the amount (mass) of analyte extracted by SPME, F is the detector response factor which can be calculated by comparing the amount of analyte (m) injected and the area counts (A_d) obtained by liquid injection ($F = m/A_d$), A is the response (area counts) obtained by SPME. The results are discussed below.

3.3.1. Polar and non-polar aromatic compounds

Since polypyrrole contains a conjugated π structure, it is expected that it will extract aromatics easily through π–π and hydrophobic interactions and these interactions will increase accordingly with the increase of aromatic rings, such as for PAHs. These expectations were approved by the results obtained in this study as shown in Fig. 7 and Table 1. For non-polar aromatics, the coating had stronger extraction efficiency toward naphthalene (peak 6) than benzene (peak 3) and toluene (peak 5). In addition, PPY extracted more efficiently for the polar aromatics such as DMP (peak 2) and DEP (peak 4) than for the non-polar aromatics such as benzene (peak 3) and toluene (peak 5). The high selectivity of PPY for polar aromatics is due to the additional interactions between the polar components of the polymer and analytes. However, it did not extract phenol strongly, likely due to the weak interaction between the polymer and the weak acidic molecules [22]. These results are also consistent with those of earlier studies [19–23] on using PPY-coated stationary phases for HPLC analyses of the similar compounds.

Compared with other coatings tested under the same conditions, as shown in Table 1, the PPY-coated capillary demonstrated the best extraction efficiency for the compounds studied due to its multifunctional property and the high surface areas of the porous structure. SPB-1 and SPB-5 contain non-polar capillary coatings, they showed (as expected) better selectivity to non-polar compounds such as benzene, toluene, and naphthalene.

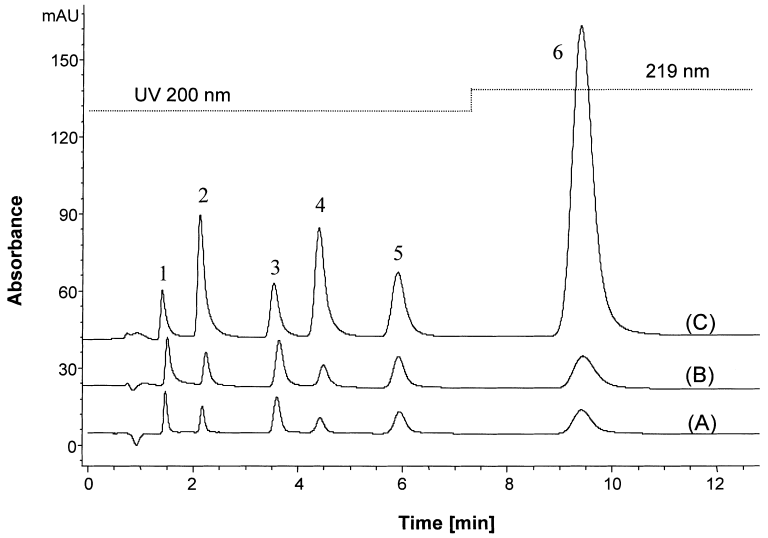

Fig. 7. HPLC–UV chromatograms of polar and non-polar aromatic compounds by (A) standard injection (10 μl), (B) non-coated host silica capillary in-tube SPME and (C) PPY-coated capillary in-tube SPME. Peak identification and concentration: (1) phenol (400 ng/ml), (2) DMP (200 ng/ml), (3) benzene (1000 ng/ml), (4) DEP (200 ng/ml), (5) toluene (1000 ng/ml), and (6) naphthalene (200 ng/ml).

Omegawax did not show good extraction efficiency for the compounds studied, but it did show slightly higher extraction selectivity to DMP and DEP relative to benzene and toluene due to its polar property.

One of the advantages of using a PPY-coated capillary for in-tube SPME over commercial capillaries is that the extraction efficiency and selectivity can be easily manipulated by controlling the thickness of the film. For example, the extraction efficiency increased gradually with the increase of coating thickness (i.e., the number of PPY coating cycles) as shown in Table 2. Meanwhile, the selectivity of the film for polar aromatic compounds (DEP and DMP), and polycyclic aromatics (naphthalene) relative to benzene were also increased.

To examine the compatibility of PPY in-tube SPME with solvent gradient conditions and to further evaluate the extraction ability of PPY for polycyclic aromatics, a mixture of 16 PAHs was analyzed by standard injection and in-tube SPME. As shown in

Table 1
Extraction properties of the in-tube SPME with different capillaries for the polar and non-polar aromatic compounds[a]

Compound	F[b]	Amount of analyte extracted (ng)[c]					Extraction yield (%)[d]					Selectivity factor ($\alpha_{A/benzene}$)[e]				
		Host	SPB-1	SPB-5	Omeg	PPY	Host	SPB-1	SPB-5	Omeg	PPY	Host	SPB-1	SPB-5	Omeg	PPY
Phenol	0.059	3.6	3.9	1.0	3.9	7.2	1.8	1.9	0.5	2.0	3.6	0.8	0.9	0.1	0.9	1.2
DMP	0.048	3.0	1.9	0.8	3.6	13.9	3.0	1.9	0.8	3.6	13.9	1.4	0.9	0.2	1.6	4.5
Benzene	0.138	10.9	10.3	18.1	11.1	15.5	2.2	2.1	3.6	2.2	3.1	1.0	1.0	1.0	1.0	1.0
DEP	0.039	2.6	1.7	1.5	3.5	13.8	2.6	1.7	1.5	3.5	13.8	1.2	0.8	0.4	1.6	4.4
Toluene	0.124	10.8	10.0	32.7	11.6	32.2	2.2	2.0	6.5	2.3	6.4	1.0	1.0	1.8	1.0	2.1
Naphthalene	0.013	2.6	3.8	10.3	9.4	18.8	2.6	3.8	10.3	9.4	18.8	1.2	1.8	2.8	4.2	6.0

[a] Analyte concentrations in the sample: phenol (200 ng/ml), DMP (100 ng/ml), benzene (500 ng/ml), DEP (100 ng/ml), toluene (500 ng/ml), naphthalene (100 ng/ml).
[b] A 10-μl sample was injected by standard liquid injection to obtain F (detector response factor for each analyte, see Eq. (1)).
[c] A 1-ml sample was used for in-tube SPME, the amount of analyte extracted (n_A) was calculated by Eq. (1).
[d] The extraction yields (%) are the percentages of extracted amount of analytes per initial amounts of analytes in a 1-ml sample solution.
[e] Selectivity factors were calculated by comparing the extraction yield of an analyte relative to that of benzene.

Table 2
Effect of PPY film thickness on extraction efficiencies for the polar and non-polar aromatic compounds[a]

Compound	Amount of analyte extracted (ng)					Extraction yield (%)					Selectivity factor ($\alpha_{A/benzene}$)				
	0-PPY	1-PPY	2-PPY	3-PPY	4-PPY	0-PPY	1-PPY	2-PPY	3-PPY	4-PPY	0-PPY	1-PPY	2-PPY	3-PPY	4-PPY
Phenol	3.6	4.9	5.7	6.6	7.2	1.8	2.5	2.9	3.3	3.6	0.8	1.1	1.1	1.1	1.2
DMP	3.0	5.3	8.7	11.6	13.9	3.0	5.3	8.7	11.6	13.9	1.4	2.4	3.4	3.9	4.5
Benzene	10.9	11.3	12.7	15.0	15.5	2.2	2.3	2.5	3.0	3.1	1.0	1.0	1.0	1.0	1.0
DEP	2.6	6.1	9.2	11.9	14.4	2.6	6.1	9.2	11.9	14.4	1.2	2.7	3.6	4.0	4.4
Toluene	10.8	13.9	19.3	26.5	32.2	2.2	2.8	3.9	5.3	6.4	1.0	1.2	1.5	1.8	2.1
Naphthalene	2.6	5.8	9.3	13.4	18.8	2.6	5.8	9.3	13.4	18.8	1.2	2.6	3.7	4.5	6.0

[a] The coating thickness of PPY increases from 0-PPY (coating cycle, without coating) to 4-PPY (coating cycles). Detector response factor (F) and other conditions (and notes) as in Table 1.

Fig. 8, the retention times of PAHs by standard injection agree well with those by in-tube SPME, which illustrates that SPME sampling does not affect the retention of the analytes under solvent gradient conditions. Compared with other coatings studied, PPY demonstrated again the highest extraction efficiency for the PAHs studied (Table 3). In addition, the extraction efficiency increased with the increase of molecule size due to the increased π–π and hydrophobic interactions. However, for PAHs larger than benzo[*b*]fluoranthene, the hydrophobic interactions became dominant and a slight decrease in extraction efficiency was observed. These trends were also found in a previous study on SPME of PAHs [55]. Due to the high extraction ability of PPY, the PPY-coated capillary in-tube SPME–HPLC method could be applied to detect low concentration of PAHs (up to 0.5 ng/ml), which was not detectable using standard injection method (detection limit, DL = 10 ng/ml).

3.3.2. β-Blockers and aromatic amines

In order to examine the potential application of PPY-coated capillary in-tube SPME–LC for the analysis of drugs and pharmaceutical products, two groups of basic compounds (β-blockers and aromatic

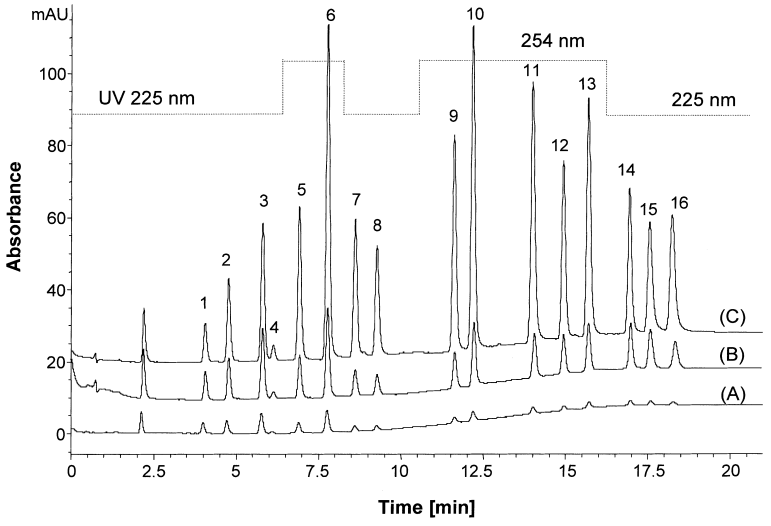

Fig. 8. Separation of a PAH mixture (an aqueous solution containing 100 ng/ml of each component) with solvent gradient by (A) standard injection (10 μl), (B) non-coated host silica capillary in-tube SPME and (C) PPY-coated capillary in-tube SPME. Peak identification: (1) naphthalene, (2) acenaphthylene, (3) acenaphthene, (4) fluorene, (5) phenanthrene, (6) anthracene, (7) fluoranthene, (8) pyrene, (9) benzo[*a*]anthracene, (10) chrysene, (11) benzo[*b*]fluoranthene, (12) benzo[*k*]fluoranthene, (13) benzo[*a*]pyrene, (14) dibenzo[*a*,*h*]anthracene, (15) benzo[*ghi*]perylene, and (16) indeno[1,2,3-*cd*]pyrene.

Table 3
Comparison of the extraction efficiencies for polycyclic aromatic hydrocarbons (PAHs) by different capillary coatings

Compound	Detector response[a], F	Amount of analyte extracted (ng) or extraction yield (%)[b]				
		Host	Omeg	SPB-1	SPB-5	PPY
Naphthalene	0.058	0.9	1.7	1.9	3.0	5.9
Acenaphthylene	0.046	0.6	1.8	2.5	3.7	7.6
Acenaphthene	0.027	0.7	1.8	4.1	4.6	6.7
Fluorene	0.213	1.2	2.1	3.8	6.3	8.1
Phenanthrene	0.050	0.8	2.5	4.4	5.4	11.1
Anthracene	0.024	0.8	2.6	4.9	7.3	11.8
Fluoranthene	0.090	1.0	3.2	5.8	10.3	17.5
Pyrene	0.115	1.1	3.1	6.1	12.0	18.0
Benz[*a*]anthracene	0.082	1.5	4.8	6.1	9.9	20.7
Chrysene	0.052	1.4	4.4	5.2	9.2	18.7
Benzo[*b*]fluoranthene	0.072	1.9	6.3	6.4	8.6	23.3
Benzo[*k*]fluoranthene	0.107	1.5	5.8	5.7	8.4	15.7
Benzo[*a*]pyrene	0.079	1.8	6.0	6.0	8.8	18.7
Dibenz[*a,h*]anthracene	0.098	1.4	4.9	2.9	6.1	10.7
Benzo[*ghi*]perylene	0.099	1.6	5.2	3.1	6.7	10.8
Indeno[1,2,3-*cd*]pyrene	0.088	1.9	7.3	6.3	8.8	16.0

[a] Detector response factors (F) were obtained by injecting 10 μl of 1 μg/ml sample solution (10 ng of each PAH was injected).
[b] A 1-ml sample (100 ng/ml of each PAH) was used for in-tube SPME, the amount of analyte extracted (n_A) was calculated by Eq. (1). The extraction yield (%) = $100n_A/M$, M is the initial amount of each analyte in the 1-ml sample solution. Since the concentration of each analyte is 100 ng/ml, M = 100 ng.

amines) were tested. It was shown that the acid property of PPY was stronger than its base property [24,25], therefore it is expected that PPY could extract these basic compounds efficiently.

As shown in Table 4, under the same extraction and desorption conditions, PPY showed superior extraction efficiency for most of the β-blockers as compared to other coatings tested. This PPY-coated capillary in-tube SPME–HPLC–MS method was successfully applied for analysis of β-blockers in biological samples [58]. Higher extraction efficiency was also obtained for amines by PPY coating compared with commercial coatings as shown in Table 5. The high extraction ability of PPY to these compounds is due to the increased interactions between polymer and analytes, such as base–acid,

Table 4
Comparison of the extraction efficiencies for β-blockers obtained by in-tube SPME with different capillary coatings

Compound	Detector response[a], F ($\cdot 10^{-5}$)	Amount of analyte extracted (ng) or extraction yield (%)[b]				
		Host	SPB-1	SPB-5	Omeg	PPY
Nadolol	0.74	1.8	1.9	1.6	2.0	5.6
Pindolol	0.60	2.5	2.5	2.7	13.9	14.0
Acebutolol	0.71	3.2	2.1	2.6	9.7	17.1
Timolol	0.85	3.7	3.8	3.3	4.8	11.9
Metoprolol	0.32	2.9	3.4	3.4	4.6	13.8
Oxprenolol	0.69	3.1	2.9	3.3	10.2	16.4
Labetalol	2.33	3.4	3.8	2.3	16.5	18.9
Propranolol	0.86	2.9	4.1	7.6	21.1	16.6
Alprenolol	0.71	2.8	6.1	9.3	14.5	15.6

[a] Detector response factors (F) were obtained by injecting a 10-μl of 100 ng/ml sample solution (1 ng of each analyte was injected).
[b] A 1-ml sample (100 ng/ml of each analyte) was used for in-tube SPME, the amount of analyte extracted (n_A) was calculated by Eq. (1). The extraction yield (%) = $100n_A/M$, M is the initial amount of each analyte in the 1-ml sample solution. Since the concentration of each analyte is 100 ng/ml, M = 100 ng.

Table 5
Comparison of the extraction efficiencies for the aromatic amines by in-tube SPME with different capillaries

Compound	m/z (M+1)	Detector response[a], F ($\cdot 10^{-5}$)	Amount of analyte extracted (ng)[b] or extraction yield (%)[c]				
			Host	SPB-1	SPB-5	Omeg	PPY
IQ	199	0.16	1.3	2.1	2.0	3.3	11.4
MeIQ	213	0.25	2.3	2.3	2.4	5.6	12.8
7,8-DiMeIQx	228	0.18	2.2	2.4	2.3	4.4	13.9
PhIP	225	0.27	2.0	1.9	2.2	5.9	16.1
AαC	184	0.76	2.6	1.6	2.4	6.7	24.0
Glu-P-1	198	1.11	3.1	2.6	3.2	10.3	23.9

[a] Detector response factors (F) were obtained by injecting 10 μl of 100 ng/ml sample solution (each amine 10 ng was injected), thus $F=10/A_d$ (A_d is the responses of detector (area counts).
[b] A 1-ml sample solution (100 ng/ml of each analyte) was used for in-tube SPME, the amount of analyte extracted (n_A) was calculated by Eq. (1).
[c] The extraction yield (%)$=100n_A/M$, M is the total amount of each analyte in the 1 ml solution. Since the initial concentration of each analyte is 100 ng/ml, $M=100$ ng.

dipole–dipole interactions and hydrogen bonding, in addition to the π–π and hydrophobic interactions.

3.3.3. Organoarsenic compounds

Four organoarsenicals were used to examine the possibility of using PPY to extract organometallic compounds. As shown in Table 6, among all the tested capillaries, the PPY-coated capillary gave the best extraction efficiency to most of the compounds except for AsC. The main interactions between analytes and commercial capillary stationary phases are hydrophobic interactions and the interactions from polar functional groups. For the PPY-coated capillary, however, another interaction – the electrostatic interaction – between charged analytes and PPY coating should also be considered. The extraction efficiency of PPY to the four arsenic compounds followed the order of MMAs>DMAs>AsB>AsC. The difference in extraction efficiencies is mainly due to the difference in electrostatic interaction between PPY (positively charged) and the compounds, since in water solution, MMAs and DMAS are negatively charged (anions), AsB is neutral species, while AsC is positively charged (cation). These results demonstrated the selectivity of PPY to anionic compounds. The inherent anion exchange property of PPY was also used recently for extraction of inorganic anions such as arsenate, selenite, and selenate [59]. Chloride and sulfate contents in tap water were evaluated directly by coupling PPY in-tube SPME to ion chromatography (IC) [59]. The multifunctional properties of PPY film should be useful for metal speciation when coupling the PPY in-tube SPME with a suitable separation and

Table 6
Extraction properties of different capillary coatings for organoarsenic compounds by in-tube SPME[a]

Compound	F ($\times 10^{-5}$)[b]	Amount of analyte extracted (ng)[c]					Extraction yield (%)[d]					Selectivity factor ($\alpha_{A/AsC}$)[e]				
		Host	SPB-1	SPB-5	Omeg	PPY	Host	SPB-1	SPB-5	Omeg	PPY	Host	SPB-1	SPB-5	Omeg	PPY
MMAs	3.83	1.2	0.9	0.9	1.3	4.4	5.9	4.5	4.7	6.3	22.0	2.1	1.8	1.8	2.1	6.4
DMAs	1.35	1.4	1.0	1.1	1.6	3.0	7.2	5.1	5.6	7.8	15.2	2.5	2.0	2.2	2.6	4.4
AsB	0.37	0.8	0.7	0.7	0.9	1.6	4.3	3.5	3.6	4.6	8.0	1.5	1.4	1.4	1.5	2.3
AsC	0.18	0.6	0.5	0.5	0.6	0.7	2.9	2.5	2.6	3.0	3.4	1.0	1.0	1.0	1.0	1.0

[a] The sample solution contains 20 ng/ml each of the analytes.
[b] A 20-μl sample containing 0.4 ng each of the analytes was directly injected to obtain F (detector response factor for each analyte, see Eq. (1)).
[c] A 1-ml sample was used for in-tube SPME, the amount of analyte extracted (n_A) was calculated by Eq. (1).
[d] The extraction yields (%) are the percentages of extracted amount of analytes per initial amounts of analytes in a 1-ml sample solution.
[e] Selectivity factor ($\alpha_{A/AsC}$) was calculated by comparing the extraction yield of an analyte relative to that of AsC.

detection method such as LC–inductively coupled plasma (ICP) MS, since both inorganic (anionic species such as AsO_4^{3-}) and organic (such as MMAs and AsB) forms of metals can be extracted and detected.

3.4. Precision, limit of detection and linearity

The precision (RSD) obtained using PPY-coated capillary in-tube SPME varies depending on the compounds and concentrations studied. For polar and aromatic compounds, the RSD values obtained are between 0.8 to 8.3% (100 ng/ml sample). However, for anionic species, the RSDs are not as good as the above values probably due to the stronger electrostatic interaction between charged polymer and analytes [59]. In this work, by precisely controlling the film preparation conditions and performing SPME under the same conditions, the differences between fibers or capillaries were less than 10% (which are better or comparable to those found for commercial fibers or capillaries in this study). Linearity studies showed that the PPY in-tube SPME method was linear over at least two orders of magnitude for most of the compounds studied. Due to the high extraction efficiency of PPY coating, lower detection limits ($S/N=3$) could be achieved for most of the analytes, as compared with the standard injection and SPME with commercial capillaries. For example, a linear relationship was obtained for each β-blocker in the range of 1 to 200 ng/ml with correlation coefficients better than 0.9940. The RSD values for the concentrations studied were 1.2–6.3% ($n=3$). The detection limits ($S/N=3$) were less than 0.1 ng/ml for most β-blocker compounds. The PPY-coated capillary in-tube SPME method gave 10–37-times higher sensitivity than the standard injection method (10-μl injection, 100-ng/ml sample) [58].

3.5. Stability of PPY films

The stability of PPY film was comparable to those of commercial coatings tested. For in-tube SPME of polar or aromatic compounds, even after hundreds of extraction cycles (samples), no significant change in its extraction performance was observed. It is stable in the mobile phases used in HPLC in this work. More importantly, PPY film is stable in solutions having different pH values. This property of PPY provides the opportunity to manipulate the extraction efficiency by using a suitable pH buffer based on the acid–base equilibrium of the analytes in the solution. For example, Tris–HCl buffer at pH 8.5 was selected for extraction of β-blockers and aromatic amines in this work. However, highly concentrated anionic species might reduce the lifetime of the film due to the changes in the structure or morphology of the polymer during exchange of counter ions [59]. In addition, strong redox reagents could change the oxidation state of PPY films and thus the extraction properties. In a recent study, redox reagents were used to control the retention of amino acids on a PPY-coated LC column [60]. For thermal desorption of volatile compounds in GC, PPY and PPPY films were stable under helium or N_2 protection up to 200°C. However, it was shown that PPY would degrade slowly under room temperature but degrade fast at higher temperature when exposed to air or oxygen [61]. The thermal stability of PPY and some of its derivatives was studied by thermal analysis methods and it was found that great improvement in the stability could be achieved by using aromatic counter ions such as *p*-toluene sulfonate [61].

4. Conclusions

In this research, PPY and its derivative PPPY films have been prepared and applied for SPME. The high extraction ability of the new films showed in this study demonstrates the importance of developing new coating materials for SPME to extend its application range.

Due to the inherent multi-functionality and/or multi-interaction properties of pyrrole polymers (π–π, acid–base and dipole–dipole interactions, hydrogen bonding, and ion exchange), a wide range of applications can be expected when coupling this SPME method with suitable separation and detection techniques. Based on our results, possible targets for analysis are aromatic compounds (both polar and non-polar), polar and ionic drugs, inorganic and organic anions, and organometallic compounds. To increase the selectivity and sensitivity of SPME, a specific functional group can be incorporated into the

polymer as illustrated in this paper by PPPY film for aromatic compounds. The functionality of the polymer can also be modified by changing the counter ions, or by forming composites or copolymers with other materials [38–40]. Therefore, the selectivity and/or sensitivity can be further improved. Since PPY is an inherently conducting polymer, it offers the opportunity to use electrochemical potential to modulate the extraction and desorption processes, as reported recently on using poly-3-methylthiophene for SPME of inorganic arsenate [13].

Our results of using polypyrrole films for SPME are in good agreement with the results expected from the structures of the polymers and with those obtained by other methods. This demonstrates that SPME technique may provide a useful tool for studying the properties of materials like polypyrroles by using compounds with known properties, in addition to its application as a sampling method.

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