Preparation and characterization of polydimethylsiloxane/poly(vinylalcohol) coated solid phase microextraction fibers using sol–gel technology

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Abstract

The applicability of a composite composed of polydimethylsiloxane (PDMS) and poly(vinyl alcohol) (PDMS/PVA) as coating sorbent for SPME fibers is demonstrated here. Fused silica (FS) fibers were coated with PDMS/PVA composite through a sol–gel process, using methyltrimethoxysilane as reticulating agent. The chemical and physical properties of the sol–gel PDMS/PVA composite were determined by infrared spectroscopy and thermogravimetric analysis. Electron scanning microscopy of the prepared fibers, showed that the coating obtained was highly microporous, having a thickness of approximately 5 μm. The fibers were tested for the headspace extraction of several organic compounds (*o*-xylene, naphthalene, ethyl caprate, *p*-chlorotoluene and PCB) prior to gas chromatographic analysis. The extractive capacity of the PDMS/PVA coating was found to be superior to that of pure conventional PDMS fibers.
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1. Introduction

The basis of solid phase microextraction (SPME) is the sorption of analytes from solid or liquid samples or their headspace onto a thin (100 μm) film of a sorbent deposited over a fused silica (FS) fiber. After equilibration between sample and the sorbent film, an amount of analyte ideally proportional to its concentration in the sample is extracted. The extracted mass also depends on the affinity between the analyte and the coating material, the volume of sorbent (i.e., the length and thickness of the film) and other operational parameters such as extraction temperature and (for aqueous samples) the ionic strength [1]. Evidently, the nature of the sorbent is a key parameter relating to the thermodynamics and kinetics of the extraction process: selection of an adequate material can allow selective extraction of analytes of interest in complex samples, and a proper film thickness will ensure satisfactory extraction efficiency with an appropriate extraction time [2]. In the early days of SPME, only polymeric coatings, such as polydimethylsiloxane (PDMS),

polyacrylate (PA) and polyimide—as well as nude fused silica fibers—were employed, always in homemade devices [3]. Presently, most of the SPME applications are based on commercial, ready-to-use fibers, which are available with several different coatings (either pure polymers such as PA and PDMS or dispersions of solid adsorvents as Carboxen 1005 or divinylbenzene in polymeric matrixes) and film thicknesses [4].

However, the variety of different SPME sorbents available in the market is still limited, which restricts the range of selectivity achievable with these commercial materials. For this reason, the study of new sorbents for SPME, as well as techniques of fiber preparation, is an interesting research topic. Some of the proposals in this field are related to materials similar to those obtainable as commercial fibers. For example, Liu et al. [5,6] described the preparation of SPME fibers by immobilizing C_8-, C_{18}- and phenyl-bonded silica particles ($d_p = 5$ μm) onto stainless steel microwires using an epoxy adhesive, and applied these devices with good results to the determination of BTEX and PAH. After evaporating THF solutions of cellulose acetate mixed with PVC over silver wires, Farajzadeh and Hatami [7] made fibers coated with 15 μm highly porous sorbent films, which were successfully used in the chromatographic determination of

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n-alkanes in aqueous samples. Fibers with pure adsorptive coatings have also been prepared, Mangani and Cenciarini [8] described the manufacture of SPME fibers coated with carbon black and their application to analysis of volatile compounds in air and water.

Apart from fibers recovered with conventional sorbents, there are also several papers describing alternate materials radically different from those commercially available, as well as different strategies for their preparation. Yuan et al. [9] chemically immobilized theophylline antibody over FS fibers previously treated with 3-aminopropyltriethoxysilane and glutaraldehyde, obtaining immunoaffinity-based SPME fibers; these fibers were successfully employed to extract theophylline from human serum with very high selectivity. Another class of SPME fibers suited for biological applications was proposed by Mullett and Pawliszyn [10], which showed the applicability of fibers coated with films of restricted access materials (RAM) to perform selective extraction of benzodiazepine drugs from human urine without clogging of the fiber by proteins and other similar heavy components of the matrix. The electrochemical generation of sorbent films of electroconductive polymers (e.g., polypyrrole) directly over Pt wires was described by Wu et al. [11], who employed the these metal-based SPME fibers in chromatographic determination of ionic analytes. However, an increasingly widespread approach for the development of new materials for SPME is based on sol–gel chemistry [12]. The generic sol–gel synthetic route [13] involves the controlled catalyzed hydrolysis of metal alkoxides, which generates mixtures of tri- and tetrahydroxycompounds. Simultaneously, these hydroxylated products can take part in condensation chain reactions, generating colloidal suspensions of reticulated polymeric aggregates in the reaction solvent—a sol phase. In the case of precursors, such as methyltrimethoxysilane, tetramethoxysilane or tetraethoxysilane, these aggregates are polysilicates. Hydroxylated organic species (e.g., modified polymers) can take part on the polycondensation processes, being incorporated into the polysilicate aggregates with generation of hybrid inorganic/organic materials. Under proper conditions, the polycondensation process can lead to polymeric networks with macroscopic size, with pores where the original solvent is trapped (a gel); elimination of the entrapped solvent gives a xerogel. The sol–gel technology has been used to prepare a wide variety of new materials for analytical applications, such as stationary phases for capillary chromatographic columns [14] and for capillary electrochromatography [15], immunosorbents for SPE [16] and optical sensors [17]. Its use for preparation of SPME fibers was introduced by Chong et al. [18], who used hydroxy-PDMS and methyltrimethoxysilane to coat silica fibers with PDMS. Although the sorbent film obtained was thinner than those of equivalent commercial fibers—therefore allowing faster extractions—it was highly porous, providing higher relative extraction efficiencies. The surface of the fused silica fibers was previously activated and therefore had a high density of

surface –OH groups. Since these surface hydroxyls can take part in the polycondensation process, the sol–gel PDMS film was chemically bonded to the fiber, and the resulting fibers had enhanced thermal stability compared to regular fibers with non-bonded coatings.

In this work, a novel SPME fiber, coated with a composite of PDMS and poly(vinyl alcohol), $[CH_2\text{-}CHOH]_n$ (PVA)—was prepared using a sol–gel procedure and evaluated for application to determinations by GC. PVA can be incorporated in sol–gel networks via the usual polycondensation processes and acts as a strong cross-linking agent [19]; PVA/PDMS composites already have been used in some analytical applications, such as in optodes [20]. However, their use as a sorbent, and especially as a coating for SPME fibers, was not described up to this moment.

2. Experimental

2.1. Chemicals and materials

Optical fibers (140 μm core) were obtained from ABC-Xtal (Campinas, São Paulo, Brazil). The sol–gel materials were hydroxylated polydimethylsiloxane – PDMS-OH (Aldrich, St. Louis, MO), methyltrimethoxysilane—MTMS, and trimethylmethoxysilane—TMMS (Fluka, Buchs, Switzerland), analytical grade poly(vinyl alcohol)—PVA (Carlo Erba, Milan, Italy) and trifluoroacetic acid—TFA (Acros, Geel, Belgium). Commercial 30 μm PDMS fibers fitted to the appropriate holder (Supelco Inc., Bellefont, PA) were also used. For preliminary fiber evaluation, 400 μg L^{-1} aqueous solutions of *o*-xylene, *p*-chlorotoluene, naphthalene and ethyl caprate (Aldrich) were employed. The assessment of extraction capacity of PDMS/PVA fiber was made using aqueous samples of the following polychlorinated biphenyls (PCB): 2,4,4′-trichlorobiphenyl (IUPAC congener #28); 2,2′,5,5′- (#52), 2,4,4′,5- (#74) and 3,3′,4,4′-tetrachlorobiphenyl (#77); 2,2′,4,4′,5- (#99), 2,2′,4,5,5′- (#101), 2,3,3′,4,4′- (#105), 2,3′,4,4′,5- (#118) and 3,3′,4,4′,5-pentachlorobiphenyl (#126); 2,2′,3,3′,4,4′- (#128), 2,2′,3,4,4′,5′- (#138), 2,2′,4,4′,5,5′- (#153) and 2,3,3′,4,4′,5-hexachlorobiphenyl (#156); 2,2′,3,3′,5,6,6'- (#179) and 2,2′,3,4,4′,5,5′-heptachlorobiphenyl (#180). The PCB solutions were prepared from methanolic stock solutions made from individual standards (99.0 % purity or more) supplied by AccuStandard (New Haven, CT). The extractions were performed in Teflon/silicone septa-capped 16 mL glass vials (Pierce, Rockford, IL).

2.2. PDMS/PVA fiber preparation

Pieces (∼2 cm) of optical fiber were soaked in concentrated sulfuric acid for 3 h to remove the original polymeric layer and to expose the fused silica (FS) core. The FS pieces were then rinsed with distilled water and dipped into 1 mol L^{-1} NaOH for 1 h to activate surface silanol

groups. The basic solution was removed and the fibers were exposed to $0.1\,mol\,L^{-1}$ HCl for 30 min. The activated FS pieces were then rinsed with distilled water, dried at $120\,^{\circ}C$ and stored for no more than 12 h in a desiccator before use. The PDMS/PVA sol was prepared vortexing a mixture of $600\,\mu L$ of MTMS, 300 mg of PDMS-OH, 80 mg of PVA and $400\,\mu L$ of 95% aqueous TFA for 2 min in a silanized glass tube. Activated FS pieces were dipped into the PDMS/PVA sol for 1 h up to a depth of 1 cm. The coating process was repeated three times each with a freshly prepared PDMS/PVA sol. The coated fibers were end-capped in a 20% (v/v) methanolic solution of TMMS for 1 min. The lab-made finished fibers were mounted on used, discarded commercial (Supelco) SPME assemblies, after careful removal of the original (deteriorated) fiber. Prior to use, the PDMS/PVA fibers were conditioned in the injector of a GC (2 h at $100\,^{\circ}C$ and then 6 h at $280\,^{\circ}C$) under $1\,mL\,min^{-1}$ of He. The remaining sol from fiber coating processes was allowed to gel, ground, washed with distilled water and methanol, and conditioned under the same conditions as the fibers. The resulting xerogel was submitted to TGA and IR analysis.

2.3. Characterization of the sol–gel PDMS/PVA fibers

Thermogravimetric analysis of the PDMS/PVA composite was performed under inert atmosphere (N_2) in a 2050 Thermogravimetric Analyzer (TA Instruments, New Castle, DE), over the temperature range of 30–$1000\,^{\circ}C$ (heating rate of $10\,^{\circ}C\,min^{-1}$). The infrared absorption spectrum of the material between 400 and $4000\,cm^{-1}$ was obtained in a Bomem MB-102 FTIR spectrometer (ABB, St-Laurent, Canada). Morphological evaluation of the coatings was performed by scanning electron micrography with a T-300 microscope (JEOL, Tokyo, Japan).

2.4. Gas chromatography

In the preliminary evaluation of the PDMS/PVA fibers, a HP-6850 GC-FID (Agilent Technologies, Wilmington, DE) equipped with a split/splitless injector (operated in the splitless mode throughout the work) and a $30\,m \times 0.32\,mm \times 0.25\,\mu m$ HP-1 capillary column was used; helium ($1.0\,mL\,min^{-1}$) was the carrier gas. The injector and detector temperatures were 250 and $280\,^{\circ}C$, respectively, and the column oven was programmed from 50 to $200\,^{\circ}C$ at $20\,^{\circ}C\,min^{-1}$ with an isothermal final plateau of 2 min. Other experiments were performed in a AutoSystem XL GC-ECD (Perkin Elmer, Norwalk, CT) fitted with a similar column and using helium ($1.3\,mL\,min^{-1}$) as carrier gas. The injector and detector temperatures were, respectively, 280 and $320\,^{\circ}C$. The column oven temperature was programmed as follows: from 140 to $190\,^{\circ}C$ at $10\,^{\circ}C\,min^{-1}$, held 5 min, up to 220 at $5\,^{\circ}C\,min^{-1}$, held for 5 min, up to 240 at $5\,^{\circ}C\,min^{-1}$ and held for 5 min.

2.5. Extraction time profiles for the PDMS/PVA fiber

The peak area versus extraction time profiles for *o*-xylene, *p*-chlorotoluene, naphthalene and ethyl caprate were determined using headspace extractions of these compounds. Aliquots of 5.0 mL of $400\,\mu g\,L^{-1}$ aqueous solutions of these compounds were enclosed in 16 mL vials, stirred at 1200 rpm and the PDMS/PVA fiber exposed to the vial headspace for periods up to 60 min. The extracted analytes were desorbed, separated and detected by GC-FID. Although preliminary studies showed no visible carry-over for desorption times as low as 60 s, for practical reasons the fiber was kept in the injector for the duration of the run.

2.6. Sample capacity of the PDMS/PVA fibers

Headspace extractions of PCB from aqueous samples was employed to determine the sample capacity of the PDMS/PVA fiber. Triplicate headspace extractions of 5.0 mL of samples with $1.16\,\mu g\,L^{-1}$ of each tested PCB, enclosed in 16 mL vials and stirred at 1200 rpm, were performed. The extraction time was 40 min, and the separation and detection was done by GC-ECD.

3. Results and discussion

The infrared absorption spectra of the PDMS/PVA sol–gel composite is shown in Figure 1; the corresponding spectra of conventional sol–gel PDMS prepared according to Chong et al. [18] is also shown for comparison purposes. The broad absorption band at $3400\,cm^{-1}$ corresponds to the axial stretching of O–H bonds, and it was attributed to residual hydroxyl groups not eliminated after the end-capping treatment; with minor intensity, this band is also present on the regular PDMS. Other absorption peaks match both those of
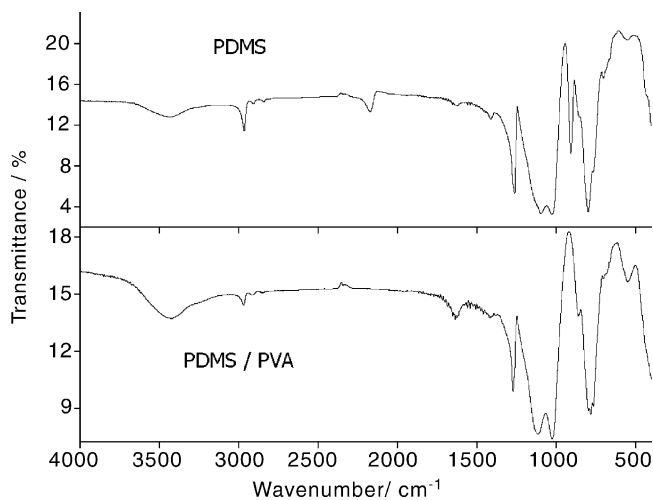

Fig. 1. Infrared absorption spectra of the sol–gel PDMS/PVA composite and of conventional sol–gel PDMS.

sol–gel PDMS, as well as thos of conventional PDMS gum of the literature [21]: 2970 cm^{-1} (stretching of C–H bonds on methyl groups) and 1026, 1128 and 1273 cm^{-1} (stretching of Si–O bonds). Some peaks present on the sol–gel PDMS (2174 and 909 cm^{-1}) and not found on the PDMS/PVA spectrum were attributted to Si–H bounds from polymethyl-hydrosilane, used in the preparation of the former according the mentioned original procedure. The broad absorption peak around 1640 cm^{-1} found on PDMS/PVA can be at-tributed to the stretching of alkenic and vinylic C=C bonds, possibly formed by loss of water from PVA chains incorpo-rated in the polymer framework (in pure PVA, dehydration takes place at temperatures as low as 190 °C [22]). However, the presence of the hydroxyl absorption band suggests that the dehydration of the PVA chains may was not have been complete in the conditions used.

The thermal stability of the sol–gel PDMS/PVA coating can be assessed from Figure 2, which shows its TGA curve with superimposed second derivative, to assist the location of transition temperatures. For comparison, the equivalent data obtained with pure sol–gel PDMS prepared accord-ing to the original procedure of Chong et al. [18] is also shown. In contrast to pure PDMS, the PDMS/PVA compos-ite is more stable at higher temperatures. The first impor-
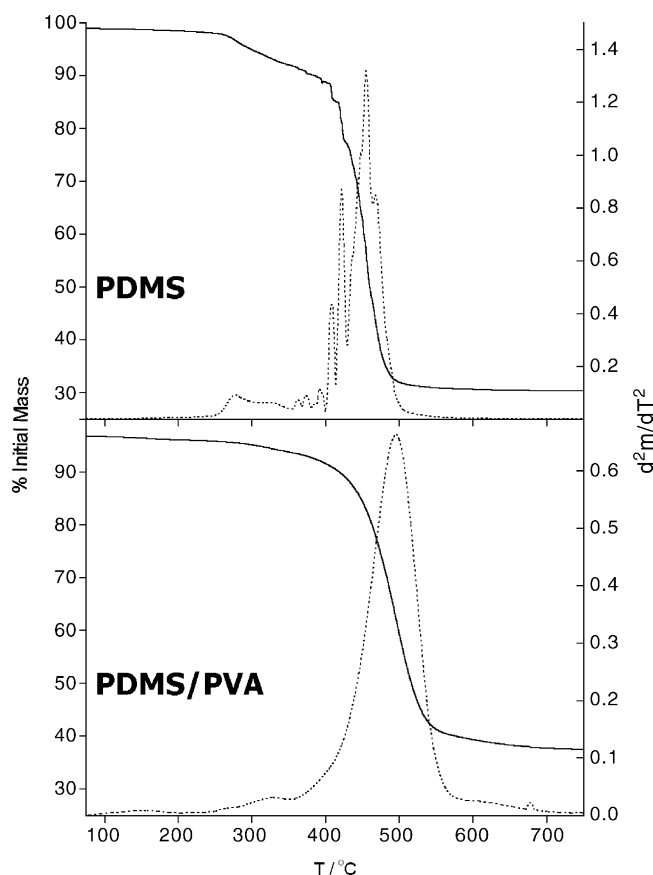
tant mass loss occurs for pure sol–gel PDMS at 276 °C; for the PDMS/PVA, only a slightly degradation happens at this temperature. Between 275 °C and 350 °C, 5.0% of the pure sol–gel PDMS is lost, while for the sol–gel PDMS/PVA only 1.8% of the total mass is lost in the same temperature range. The improved thermal stability of the PDMS/PVA material can be attributed to the additional cross-linkage promoted by the presence of PVA in the reaction mixture. Enhanced thermal stability is an extremely desirable feature of a SPME material, resulting in fibers with extended working temper-ature ranges, as well as chromatograms with cleaner base-lines since the amount of bleeding from the fiber coating during thermal desorption is also reduced.

Another aspect of the TGA curves to be considered is the fraction of the material remaining after complete ther-mal decomposition, which can be regarded as consisting es-sentially as pure SiO$_2$. For the sol–gel PDMS/PVA, at after 750 °C the residual was 36% of the starting mass, and for pure sol–gel PDMS it was 30%. A possible reason for this comparatively higher silica content would be a fast reaction rate for the cross-linking process between the PVA and the silanol agglomerates (formed by hydrolysis and condensa-tion of the MTMS precursor). If this cross-linking is faster than the condensation between the silanol agglomerates and the PDMS-OH, the resulting final material would have a higher silica content, being more "inorganic" in character.

The morphology of the PDMS/PVA fibers can be assessed from Fig. 3, which shows scanning electron micrographies of the fibers under different magnifications. The average thickness of the PDMS/PVA layer was estimated as being ~5 μm, which is considerably thinner than most conven-tional SPME fibers (100 μm for PDMS and 85 μm for poly-acrylate). As the diameter of the FS core is 140 μm and the coating length is of 10 mm, the volume of extracting phase on the lab-made PDMS/PVA fibers is 0.046 mm^3, consider-ably less than that of conventional fibers (e.g., 0.132 mm^3 and 0.612 mm^3 for 30 μm and 100 μm PDMS, respectively [23]). The pore structure of the PDMS/PVA coating can be seen in Fig. 3B and C. With 2K magnification, the sur-face of the PDMS/PVA coating seems to be compact and non-porous; however, the 20 K magnification picture shows a high density of small pores with apparent diameters up to 100 nm.

Fig. 4 shows the peak area versus extraction time pro-files for headspace extractions of *o*-xylene, *p*-chlorotoluene, naphthalene and ethyl caprate with the PDMS/PVA fiber. Equilibration is extremely fast, being reached in less than 1 min; for ethyl caprate, the equilibrium time estimated from the profile is less than 15 min. Short equilibration times such as those observed here are characteristic of sol–gel coated fibers [18]. Since the coatings provided by the sol–gel pro-cess are thinner, saturation with the extracted analytes takes less time than with conventional fibers, coated with compact and relatively thicker films of sorbents.

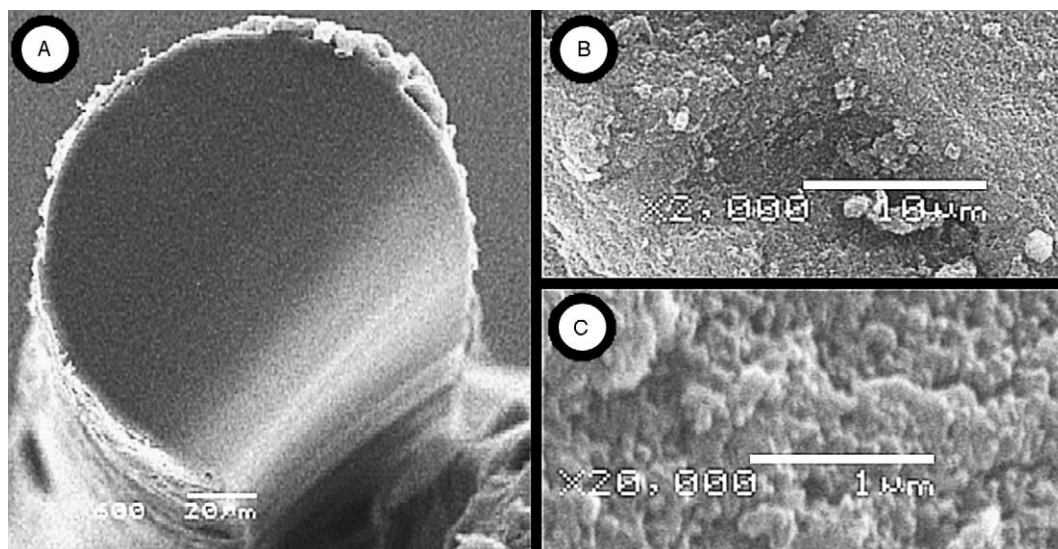Fig. 5 compares the peak areas obtained in headspace ex-tractions of PCB with the PDMS/PVA fiber and with a con-

Fig. 2. TGA curves (continuous lines) and second derivative of TGA curves (dotted lines) for the sol–gel PDMS/PVA composite (bottom) and for pure sol–gel PDMS (top).

Fig. 3. Scanning electron micrographies of a PDMS/PVA fiber: A: axial view, 600-fold magnification; B: surface of the fiber coating, 2K magnification and C: the same, 20K magnification.

ventional 30 μm PDMS fiber; typical chromatograms are shown in Fig. 6. It should be noticed that it was not possible to resolve PCB #105 and #153; therefore the areas reported here for these analytes are the sum for both species. This figure illustrates the exceptional sample loading capacity of the PDMS/PVA coated fiber, when compared to the commercially available material: the masses extracted with both fibers are similar, even considering the thinner coating of the sol–gel PDMS/PVA fiber (the volume of sorbent available on the lab-made fiber is ∼1/3 of the amount on a conventional 30 μm PDMS fiber). It is possible to obtain fibers with thicker sorbent films and higher absolute extractive capacity increasing the number of consecutive sol–gel coating cycles. The precision (as R.S.D. of the peak areas) obtained with the sol–gel PDMS/PVA ranged from 3.4 to

17.0%, which is within the same order of magnitude as obtained here with the 30 μm PDMS fiber (R.S.D. between 1.8 and 16.1%) and adequate for routine analytical applications. As for selectivity, when compared to regular PDMS, the sol–gel PDMS/PVA seems to have a higher affinity for the heavier, more retained PCB: for the congeners #28 (t_R = 7.4 min) and #52 (t_R = 8.2 min) the extracted amounts with PDMS/PVA are 84% and 85%, respectively, of those extracted with the 30 μm PDMS, where for the congeners #125 (t_R = 17.7 min), #156 (t_R = 19.0 min) and #180 (t_R = 20.1 min) these fractions are 180, 171 and 177% of those with 30 μm PDMS.

To assess the reproducibility of the coating procedure with the sol–gel PDMS/PVA composite, batches of fibers were prepared on different dates, one month apart, and applied to
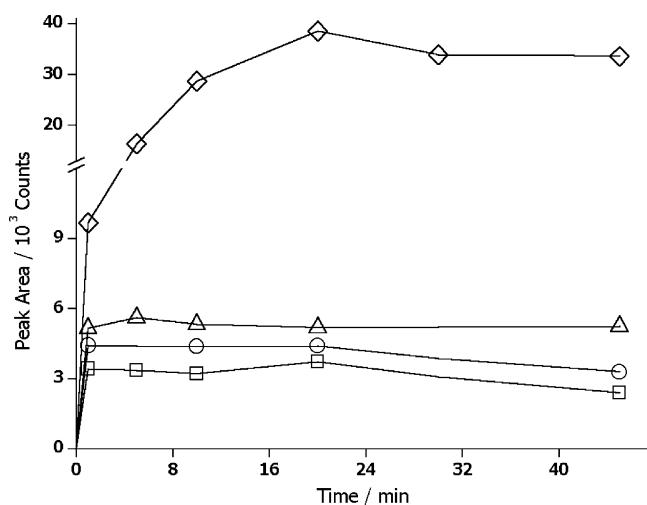

Fig. 4. PDMS/PVA headspace extraction time profiles for o-xylene (□), p-chlorotoluene (○), naphthalene (△) and ethyl caprate (◇).
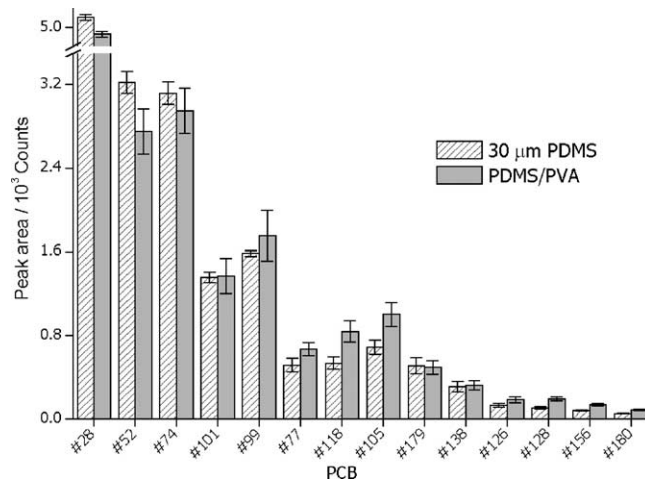

Fig. 5. Peak areas of PCB (identified by their IUPAC congener numbers) after headspace extraction from a 1.16 μg L^{-1} aqueous solution with the sol–gel PDMS/PVA fiber and with a commercial 30 μm PDMS fiber.

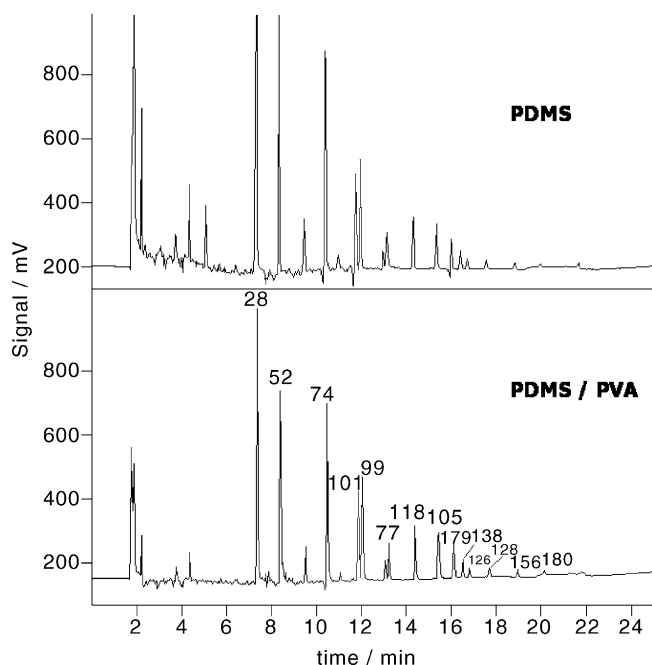Fig. 6. GC-ECD chromatograms for headspace extractions of $1.16\,\mu g\,L^{-1}$ PCB mixture using the sol–gel PDMS/PVA fiber (bottom) and a $30\,\mu m$ PDMS fiber (top). PCB peaks identified by the corresponding IUPAC congener number.

headspace extractions of a $1.16\,\mu g\,L^{-1}$ PCB aqueous sample. The results are shown in Fig. 7. It can be seen that the extractive properties of the two tested specimens are quite similar, despite being homemade materials; in fact, except for #28, the difference between the average areas obtained for each PCB with both fibers can be considered, with 95% confidence, as statistically equivalent. It should be noted that one of the specimens tested here had already been employed for ca. 150 extractions before this experiment, whereas the other was a newly coated fiber.
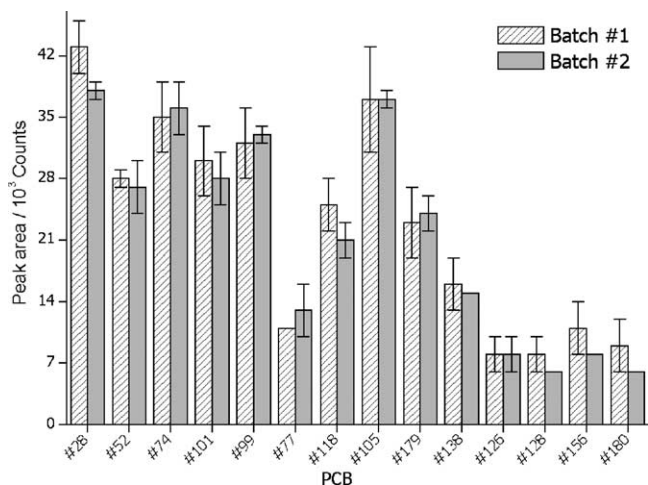

Fig. 7. Peak areas of PCB (identified by their IUPAC congener numbers) after headspace extraction from a $1.16\,\mu g\,L^{-1}$ aqueous solution with sol–gel PDMS/PVA fibers from different preparation batches.

4. Conclusions

The PDMS/PVA composite proposed here as a material for SPME fiber coating can be an attractive alternative for several applications. It can be synthesized in situ by a simple, straightforward sol–gel polycondensation route. Compared to the commercial conventional SPME fibers, the thinner and highly microporous coating produced by this sol–gel process gave faster extractions and showed potentially higher analyte loadings. In relation to similar siloxane-based SPME coatings prepared by sol–gel processes, the additional cross-linking provided by the poly(vinyl alcohol) seems to improve the thermal stability of the material. Also, it provides a sorbent with slightly different chemical properties (e.g., with unsaturated polymeric chains), which reflected also on minute differences on the extraction efficiencies of the test compounds (such as the PCB) when compared to pure PDMS fibers. Further studies are being carried out, to a complet assessment of the selectivity of this new coating. Finally, the simplicity of the sol–gel coating procedure provides excellent batch-to-batch reproducibility of the lab-made fibers. The sol–gel PDMS/PVA fiber is currently being employed in applications where fibers with high thermal stability are desirable, such as quantitation of sub-$\mu g\,L^{-1}$ levels of pesticides on plant infusions by GC-ECD and on direct SPME-MS coupling [24].

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