Highly porous solid-phase microextraction fiber coating based on poly(ethylene glycol)-modified ormosils synthesized by sol–gel technology

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Abstract

The preparation and characteristics of solid-phase microextraction (SPME) fibers coated with Carbowax 20M ormosil (organically modified silica) are described here. Raw fused silica fibers were coated with Carbowax 20M-modified silica using sol–gel process. Scanning electron micrographs of fibers revealed a highly porous, sponge-like coating with an average thickness of (8 ± 1) μm. The sol–gel Carbowax fibers were compared to commercial fibers coated with 100 μm polydimethylsiloxane (PDMS) and 65 μm Carbowax–divinylbenzene (DVB). Shorter equilibrium times were possible with the sol–gel Carbowax fiber: for headspace extraction of the test analytes, they ranged from less than 3 min for benzene to 15 min for *o*-xylene. Extraction efficiencies of the sol–gel Carbowax fiber were superior to those of conventional fibers: for *o*-xylene, the extracted masses were 230 and 540% of that obtained with 100 μm PDMS and 65 μm Carbowax–DVB fibers, respectively.
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1. Introduction

The operational principle of solid-phase microextraction (SPME) is the sorption of species from solid or liquid samples over films of a sorbent deposited over fused silica fibers. Under proper conditions, an equilibration between sample and the sorbent is reached and the quantity of extracted analyte depends on its concentration in the sample and on its affinity towards the coating material, as well as the dimensions of the SPME device (length and thickness of the sorbent film) and some operational parameters (as extraction temperature and ionic strength of aqueous samples [1]). The equilibrium and speed of the extraction process are related to physico-chemical characteristics of the sorbent: choice of proper materials potentially allows selective isolation of the target analytes in complicated samples, and sorbent films with suitable thickness can warrant good extraction efficiencies with reduced equilibrium times [2]. In the first applications of SPME, lab-made devices based exclusively on pure polymeric sorbents (polydimethylsiloxane (PDMS), polyacrylate (PA) and polyimide) were used [3]; nowadays, commercial fibers available with several different coatings (polymers as PA and PDMS or dispersions of adsorbents as Carboxen or divinylbenzene (DVB) in polymers matrixes) are prevalent [4]. Most of these commercial fibers present restrictions to their use in high temperatures and their coatings are not stable towards direct exposure to organic solvents. Also, in the present the number of different available sorbents is still restricted, which limits the extent of selectivity obtainable using these commercial fibers. Therefore, the development of new SPME sorbents and fiber preparation techniques is an attractive study topic.

The sol–gel chemistry offers a relatively simple route for the synthesis of new materials by incorporation of organic compounds in inorganic polymeric structures which can be deposited as thin films over several types of surfaces [5,6], such as fused silica fibers for the production of SPME devices. Sol–gel synthesis are based on the hydrolysis and simultaneous condensation of metal alkoxides [7], producing

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sols of reticulated polymer aggregates (in the case of alkoxi-silane precursors, of polysilicates). Hydroxyorganic compounds can be merged with the polysilicate aggregates producing organically modified silicas (ormosils); further extension of the polymerization process lead to macroscopic gels of ormosils. If the process is carried out in the presence of activated fused silica, an ormosil film may be chemically bound to the surface by reaction with available hydroxyl groups. The main advantages of the sol–gel routes are their simplicity and use of relatively inexpensive materials. Also, depending on the nature of the substituents the coatings are chemically bound, and therefore are strongly adhered to the surface [8], which is a desirable characteristic of a SPME coating. Also, sol–gel SPME fiber coatings usually are highly porous, having larger surface areas and extractive capacities than conventional polymeric phases [9]. Therefore, the preparation of new SPME fibers coated with varied materials by sol–gel procedures, first described by Chong et al. [10], who used hydroxyl-PDMS and methyltrimethoxysilane to coat silica fibers with PDMS, is becoming increasingly popular. The different SPME coatings produced by sol–gel routes include ormosils based on poly(vinylalcohol) [11], hydroxyfullerene [12], *n*-octylsiloxane [13], crow ethers [14] and calixarenes [15,16].

As for poly(ethyleneglycol)s (PEG) as sol–gel organomodifiers, the only report of its use in SPME devices is from Wang et al. [17], who described the preparation and application of fibers coated with Superox-4—a high-temperature alternative for conventional PEG-based chromatographic stationary phases, with average molar mass of $4,000,000\,\mathrm{g\,mol^{-1}}$ [18]. The following reactions were proposed for the production of this ormosil:corresponding to the hydrolysis of the MTMS precursor (Eq. (1)), generation of polysilicates by condensation of the silanols (Eq. (2)) and incorporation of PEG chains in the polysilicate aggregates (Eq. (3)).

The application of the PEG congener known as Carbowax 20M (which has an average molar mass ranging from 14,000 to $16,000\,\mathrm{g\,mol^{-1}}$) instead of polymer with higher average molecular masses such as the above employed can be also of interest. Its maximum useful temperature is lower than that of heavier congeners such as Superox-4 ($225\,^{\circ}\mathrm{C}$ versus $275\,^{\circ}\mathrm{C}$, when employed as GC stationary phase [19]). However, for a long time, this material has been the most popular PEG-based GC stationary phase and techniques for stabilization of Carbowax 20M films over different surfaces have been extensively studied [20,21]. Therefore, in this paper we describe the preparation and characterization of SPME fibers based on a Carbowax 20M ormosil.

2. Experimental

2.1. Chemicals and materials

Optical fibers ($128\,\mu\mathrm{m}$ core) were used as support (ABC-Xtal, Campinas, São Paulo, Brazil). The sol–gel materi-als were methyltrimethoxysilane (MTMS), and trimethyl-methoxysilane (TMMS, Fluka, Buchs, Switzerland), tri-fluoroacetic acid (TFA, Acros, Geel, Belgium) and Carbowax 20M (Analabs, North Haven, CT, USA). For comparison purposes, commercial $100\,\mu\mathrm{m}$ PDMS and $65\,\mu\mathrm{m}$ Carbowax–DVB fibers fitted to the appropriate holder (Supelco Inc., Bellefont, PA) were employed. During the analytical evaluation of the fiber, aqueous test samples containing $400\,\mu\mathrm{g\,L^{-1}}$ of benzene, toluene, ethylbenzene and *o*-xylene (BTEX) diluted from methanolic stock solutions (Fluka) were employed. The extractions were performed in Teflon/silicone septa-capped $7\,\mathrm{ml}$ glass vials (Supelco).

2.2. Preparation of sol–gel Carbowax 20M fibers

Two centimetre pieces of optical fiber were dipped in sulfuric acid for $3\,\mathrm{h}$ to remove the original protective layer. The fused silica (FS) pieces obtained were rinsed with distilled water and soaked in $1\,\mathrm{mol\,L^{-1}}$ NaOH for $1\,\mathrm{h}$ for surface activation. The excess base was removed exposing the fibers to $0.1\,\mathrm{mol\,L^{-1}}$ HCl solution for $1/2\,\mathrm{h}$, and the activated raw fibers were subsequently flushed with distilled water, dried at $120\,^{\circ}\mathrm{C}$ and stored in a dissicator before use for no more than $12\,\mathrm{h}$. The Carbowax 20M ormosil sol phase was prepared mixing $400\,\mu\mathrm{L}$ of MTMS, $800\,\mathrm{mg}$ of Carbowax 20M and $0.5\,\mathrm{ml}$ of 95% aqueous TFA (catalyst) in a silanized glass tube. For the surface coating, the raw activated FS fibers were dipped vertically in this sol solution up to a depth of $1\,\mathrm{cm}$, for $1\,\mathrm{h}$. Multiple Carbowax 20M-ormosil were deposed repeating the procedure five times, each with a freshly prepared sol. The processed fibers were mounted on used commercial (Supelco) SPME assemblies, after careful removal of the original, worn-out fiber. The remaining sol from fiber coating processes was allowed to gel, ground, washed with distilled water and methanol, dried overnight at $110\,^{\circ}\mathrm{C}$ and submitted to TGA and IR analysis. The fibers were conditioned in the injector of a GC at $230\,^{\circ}\mathrm{C}$ and under $1\,\mathrm{ml\,min^{-1}}$ of He for periods of time up to $60\,\mathrm{h}$.

2.3. Physical, chemical and morphological characterization of the Carbowax 20M sol–gel SPME coating

Thermogravimetric analysis of the Carbowax 20M ormosil was performed under inert atmosphere (N_2) in a 2050 Thermogravimetric Analyzer (TA Instruments, New Castle, DE), over the temperature range of 30–$1000\,^{\circ}\mathrm{C}$ (heating rate of $10\,^{\circ}\mathrm{C\,min^{-1}}$). The infrared absorption spectrum of the material in KBr pellets and between 400 and $4000\,\mathrm{cm^{-1}}$ was obtained in a Bomem MB-102 FTIR spectrometer (ABB, St. Laurent, Canada). Visual evaluation of the coatings was performed by scanning electron micrography with a JSM 6360-LV microscope (JEOL, Tokyo, Japan).

2.4. Analytical performance of the Carbowax 20M sol–gel SPME fibers

An AutoSystem XL GC–FID (Perkin-Elmer, Norwalk, CT) with a split/splitless injector (operated in split-less mode in all runs), fitted with a HP-5 column ($L = 30 \, \text{m} \times d_c = 0.32 \, \text{mm} \times d_f = 0.25 \, \mu\text{m}$) and using helium ($1.0 \, \text{ml min}^{-1}$) as carrier gas, was employed through all work. The injector and detector were kept at 230 °C and the column oven programmed as follows: 2 min at 40 °C, then heat up to 110 °C at 7 °C min^{-1}, and from 110 to 130 °C at 20 °C min^{-1}. For all experiments, the fibers were exposed for periods of time from 5 to 45 min to the headspace of 3.0 ml aliquots of the aqueous test sample magnetically stirred at 1200 rpm. The extracted analytes were immediately desorbed, separated and detected by GC–FID; the desorption time was varied from 5 to 60 s. As comparison, 30 min headspace extractions of the same samples with 100 μm PDMS and 65 μm Carbowax–DVB commercial fibers were also performed.

3. Results and discussion

The IR spectra of the sol–gel Carbowax 20M ormosil (not shown here) displays bands at $-3430 \, \text{cm}^{-1}$ (axial stretching of O–H bonds on hydroxyl groups from PEG chains and unreacted silanol terminations in the polysilicate reticulates [22]); 1036, 1157 and 1273 cm^{-1} (Si–O bond stretching); 2915 and 2881 cm^{-1} (methyl C–H stretching); 1455 cm^{-1} (C–H bending); 1351 cm^{-1} (C–O stretching); 1110 cm^{-1} (asymmetric Si–O–C stretching) and 1782 cm^{-1} (carbonyl C=O stretching, which can be produced by thermal dehydration of terminal –OH groups in PEG chains after the drying of the material [23]). These spectral features are consistent with the chemical structure of the material expected from the reactions shown in Eq. (1)–(3).

The thermal properties of the sol–gel Carbowax 20M coating can be assessed from Fig. 1, which shows its TGA curve; the second derivative of this plot was added to the figure to help its interpretation. Three thermal events are visible: the first starts at ∼50 °C and peaks near 108 °C (mass loss of 39.7% of the original material). It was attributed to the release of water and other low molar mass reaction products sorbed or entrapped inside the pore structure of the polymer not released from the gel during its drying on conventional oven after its preparation, as well as the completion of the loss of terminal hydroxyl in the Carbowax 20M chains. Around 230–250 °C, there is a diminutive mass loss only perceivable in the second derivative curve. These temperatures are close to that widely appointed as the limit of thermal stability of Carbowax 20M [24], and therefore this occurrence was attributed to loss or degradation of unbound molecules of this species. The main mass loss step happens between 375 and 413 °C, corresponding to a loss of 48.6% of the initial mass; no other thermal episode was visible after this temperature,
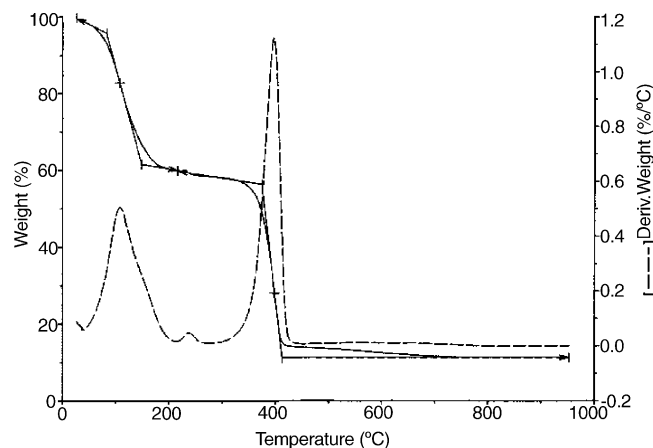

Fig. 1. TGA curves (continuous line) and its second derivative of TGA curves (dotted line) for the sol–gel Carbowax 20M ormosil.

and the residue (possibly pure SiO$_2$) represents 11.8% of the starting material. As the two initial thermal episodes were likely to be merely the elimination of extraneous substances retained by the material after its preparation (which, in the fiber, will be eliminated after its initial conditioning) or completion of dehydration of Carbowax 20M, the last event was considered as characteristic of the thermal degradation of the Carbowax 20M ormosil and can be assigned to its maximum practicable temperature.

Fig. 2 shows micrographs of a fiber coated with five layers of sol–gel Carbowax 20M ormosil. The most remarkable feature of the coating is its highly porous, sponge-like aspect; indeed, it appears to consist in an agglomerate of microspheres with up to ∼2 μm diameter. The average thickness of the sol–gel Carbowax 20M coating, measured comparing micrographies of the five-layered fibers and raw FS rods was estimated as being $8 \pm 1 \, \mu\text{m}$.

There are several reports on the literature regarding the effects of PEG in the morphology of silica-based materials produced by sol–gel chemistry, apart from its chemical
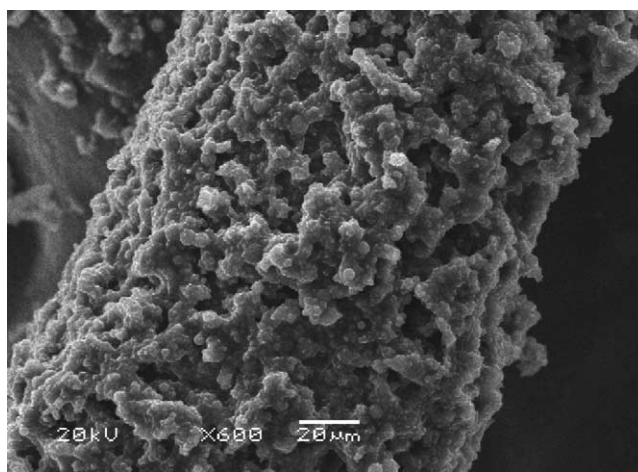

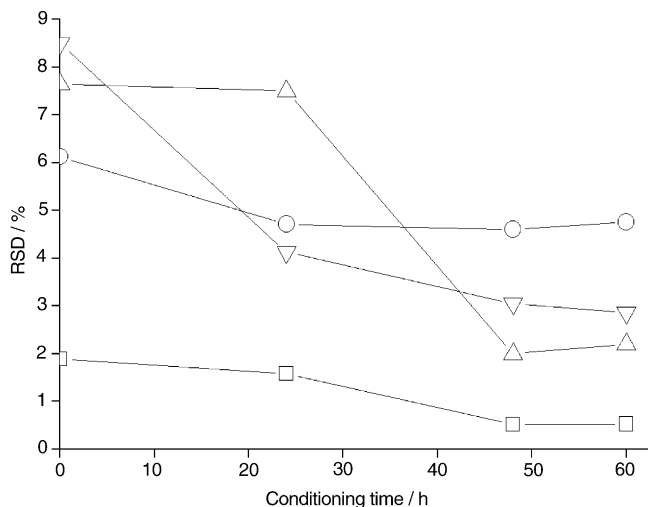Fig. 2. Electron scanning micrography (600× magnification) of a sol–gel Carbowax 20M ormosil fiber.

Fig. 3. Precision of areas (as R.S.D. % of triplicate extractions) of BTEX peaks as function of fiber conditioning time. Analytes: benzene (□); toluene (○); ethylbenzene (△); and *o*-xylene (▽).
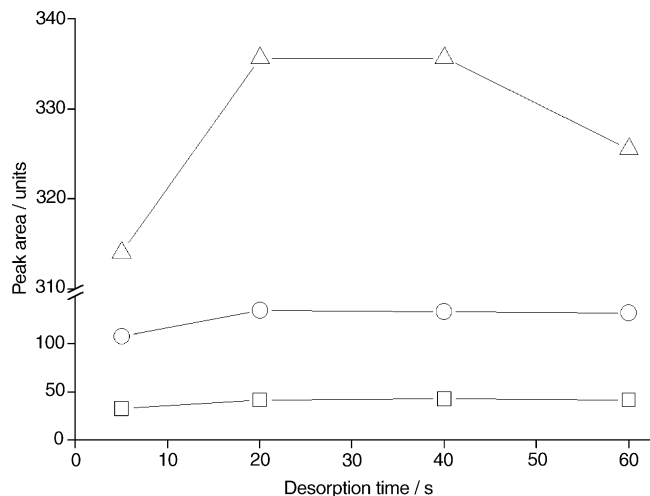

Fig. 4. Peak areas for the test analytes as function of desorption time. Analytes: benzene (□); toluene (○); and ethylbenzene (△) (the curve for *o*-xylene is similar to that of ethylbenzene and was omitted for clarity).

incorporation to formed species. For example, porosity of sol–gel silica can be controlled by the concentration of PEG on the reaction media [25], and were attributed to the effects of this species on the viscosity of the sol phases and activity of water in the reaction media, rather than the chemical incorporation of the PEG to the ormosil itself. In special, the formation of microspheres similar to those apparently present in the coating of these fibers is characteristic of sol–gel silica produced in presence of PEG [23,26]. Visual comparison of this sol–gel Carbowax 20M-coated fiber with the previously reported sol–gel Superox-4 analogue [17] shows that its surface is much more porous than the later, which is an extremely desirable property for a SPME coating. Besides, the observation of the mass loss around 108 °C in the thermogram of the material can be related to the structure of the ormosil: reaction sub-products and solvents can be retained inside the silica microspheres, which can demand more severe conditions than those here adopted for the washing and drying of the gel to be released. After the above observations, special attention was paid to the conditioning of the fibers before use. Fig. 3 shows the R.S.D. of triplicate HS extractions from BTEX test samples using fibers conditioned for periods up to 60 h. It can be seen that the precision of the measured peak areas improves with the conditioning time up to 50 h, specially for the heavier test analytes—e.g. for *o*-xylene, the R.S.D. for the replicates goes from 8.5% (non-conditioned fiber) to 2.9%. This increase on the precision of the measurements was associated to the thermal stabilization of the coating. Considering these observations, the conditioning of new fibers was defined as 50 h at 230 °C (Fig. 4).

Figs. 5 and 6 show extraction and desorption profiles for headspace extractions of the test sample with the sol–gel Carbowax 20M fiber. It can be seen that both the extraction equilibration and desorption are extremely rapid: for benzene and ethylbenzene, equilibration is reached respectively in less

than 3 min and less than 10 min. As for the desorption, under the conditions here employed all species are completely desorbed after 20 s of the fiber being introduced in the GC injector. Fast mass transference to and from the fiber coating such as those observed here are typical of fibers coated with sol–gel ormosils [10,11], due to the combination of reduced coating thickness and high porosity provided by this process. Therefore, both saturation of the coating with the analytes and their thermal desorption are faster when compared to fibers coated with thick compact polymeric films. Fig. 5 shows the extraction time profiles for extraction of BTEX test sample. It can be seen that the equilibration is extremely fast: less than 1 min for benzene and ∼10 min for ethylbenzene. This is typical of sol–gel SPME fibers [11] and is a consequence of the thinner coatings provided by this fiber preparation technique.
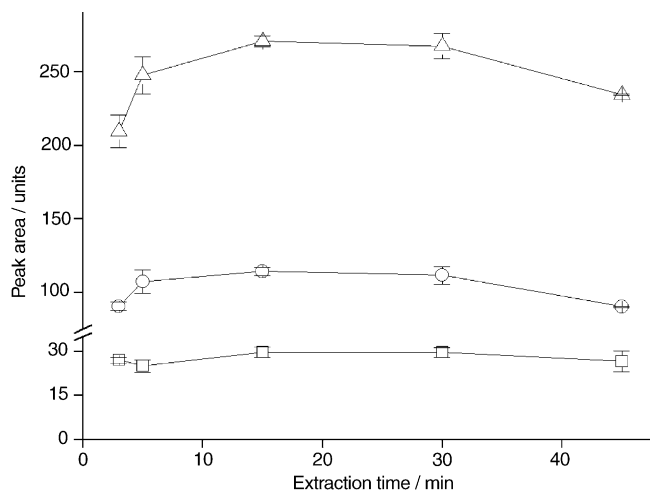

Fig. 5. Extraction time profiles for the test analytes: benzene (□); toluene (○) and ethylbenzene (△) (the curve for *o*-xylene is similar to that of ethylbenzene and was omitted for clarity).
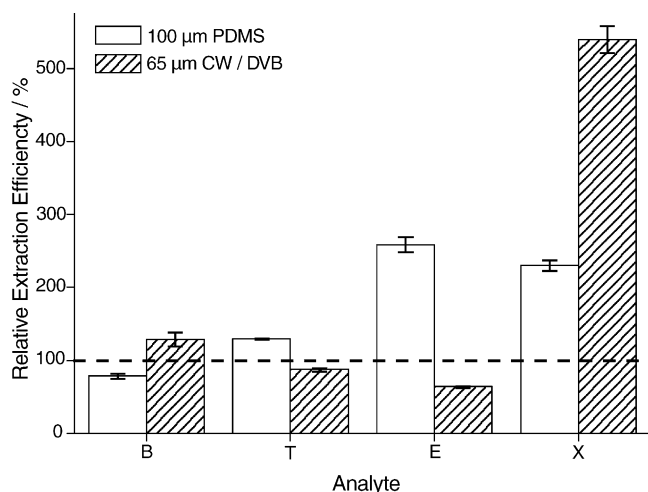
Fig. 6. Relative extraction efficiencies for $100\,\mu m$ PDMS and $65\,\mu m$ Carbowax-DVB fibers compared to sol–gel Carbowax 20M fiber.

The extraction efficiency of the sol–gel Carbowax 20M fiber is compared to some commercial counterparts on Fig. 6; Fig. 7 shows a typical chromatogram obtained with these fibers. To help the evaluation of the data, the areas were normalized in relation to the sol–gel fiber (relative extraction efficiency = 100 × area with commercial fiber/area with sol–gel fiber). It can be seen that for the more volatile analytes in the test mixture—benzene and toluene—the extraction efficiency of the sol–gel Carbowax 20M fiber is comparable to that of its counterparts. For the heavier species, it tends
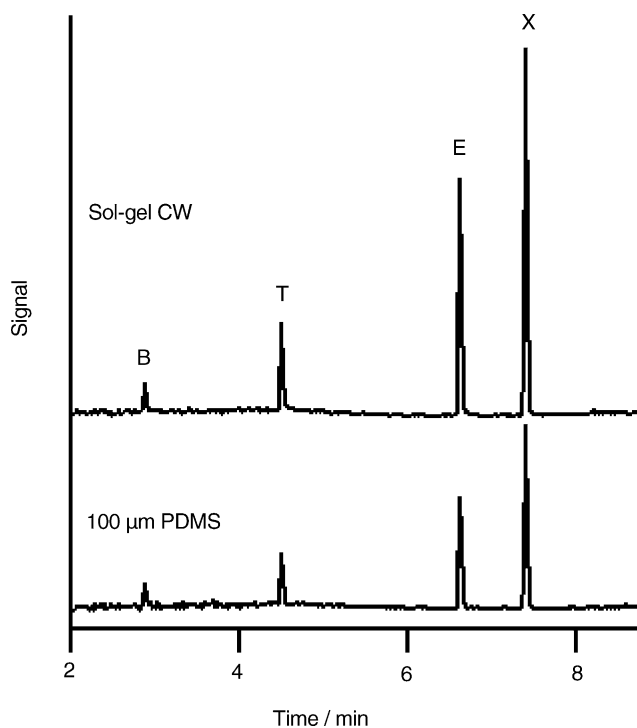

Fig. 7. GC–FID chromatograms corresponding to HS extractions of $400\,\mu m\,L^{-1}$ aqueous BTEX with $100\,\mu m$ PDMS and sol–gel Carbowax 20M fiber; same signal scale employed in both chromatograms.

to be larger, e.g. for *o*-xylene, the extracted masses for the sol–gel fiber are 230 and 540% of the masses extracted with $100\,\mu m$ PDMS and $65\,\mu m$ Carbowax–DVB fibers, respectively. These values are representative of the remarkable sample capacity of the sol–gel Carbowax 20M fiber. Computed the average thickness of the sorbent film, the apparent volume of coating on these fibers is $-0.017\,mm^3$, which is only 2.6 and 4.6% of the coating volume of the $100\,\mu m$ PDMS and $65\,\mu m$ Carbowax–DVB fibers, respectively [27]. As for the chromatograms, it can be seem that the chromatographic profile of the sol–gel Carbowax 20M fiber is similar to that of $100\,\mu m$ PDMS fiber. Also, as it can be seen from the baseline of its chromatogram, no peaks attributable to artifacts or non-reacted substituents can be discerned.

4. Conclusions

The use of Carbowax 20M as organic modifier in sol–gel coatings for SPME fibers presented here can result in fiber with interesting properties. When compared to the commercial conventional fibers—and even with other similar sol–gel coatings—Carbowax 20M ormosil films are notably porous, which is a desirable properties of a coating for SPME fiber, since it tends to provide faster equilibration and desorption with improved extraction efficiency. Since these morphological properties of sol–gel silicas prepared in the presence of PEG have been related to modifications of properties of the reactional media caused by these polymers—and not necessarily by their incorporation to the polysilicate reticulates—it seems that Carbowax 20M and related polymers have potential use as general additives to improve porosity in any sol–gel formulation for preparation of SPME coatings. As for the sol–gel Carbowax 20M ormosil coated fibers here described, further studies are being carried out to have a more complete picture of their analytical properties; they are also being currently employed in several real-life analytical applications, such as the screening of contaminants released by plastic containers for use in microwave ovens and in the monitoring of contamination of ground water by fuel leakage from gas stations.

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