

Ultrathin phenyl-functionalized solid phase microextraction fiber coating developed by sol–gel deposition

Manuel Azenha^{*}, Catarina Malheiro, A. Fernando Silva

CIQ-UP, Department of Chemistry, Faculty of Science, University of Porto, Rua do Campo Alegre 687, 4169-007 Porto, Portugal

Received 9 December 2004; received in revised form 29 January 2005; accepted 8 February 2005

Abstract

A new sol–gel application for the development of SPME fibers is described. Phenyltrimethoxysilane (PTMOS) and methyltrimethoxysilane (MTMOS) were the sol–gel precursors used at different proportions, together with different water contents, catalyst and reaction time. It was observed that obtaining a good film quality was determinant for a good extracting fiber performance. The film thickness ranged 0.2–1 μm and could not be increased by multi-coating processes. Apparently, a dense, non-porous microstructure was obtained. These coatings exhibited a strong hydrophobic character, as shown by the capability of extraction of long chain and apolar aromatic compounds, which, was comparable to that of the 100 μm polydimethylsiloxane (PDMS) and 65 μm carbowax–divinylbenzene (CW–DVB). The developed fiber has shown high thermal (350 °C) and organic solvent stability (ethanol, toluene and dichloromethane), thus bearing adequate characteristics to be associated to GC and potentialities that may also envisage suitability for HPLC. The new fibers may be useful for the microextraction of non-polar compounds, although at trace levels and in simple matrixes only, due to the susceptibility to competition.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Solid-phase microextraction; Sol–gel; Coating; Fiber; Thin film; Phenyl; Factorial analysis

1. Introduction

Solid phase microextraction is a sampling and sample preparation technique developed over ten years ago by Pawliszyn [1]. SPME provides many advantages over conventional sample preparation methods by integrating sample extraction, concentration, and introduction into a single step. The approach utilizes a small amount of extraction phase dispersed on/inside a solid support such as a fiber. The nature of the extraction phase determines the selectivity towards different compound classes. The non-polar polydimethylsiloxane (PDMS) phase was the first polymer being used for SPME, while, more recently, polar phases such as polyacrylate (PA) and carbowax–divinylbenzene (CW–DVB) represented a breakthrough in the extraction of polar compounds with low affinity for the PDMS phase. However, these fibers present important drawbacks such as their relatively low

recommended operating temperature (generally in the range 200–270 °C), and their instability in organic solvents (greatly restricting the use with HPLC). The lack of proper chemical bonding of the stationary phase coating with the fiber surface, and the relatively high thickness of the conventional fibers seem to be responsible for this drawback [2].

Sol–gel coating technology has shown to be able to overcome these problems. Sol–gel chemistry provides an efficient way of incorporating organic components into inorganic polymeric structures in solutions, under mild conditions. Such polymeric structures can easily be applied as surface coatings, bearing strong adhesion to the substrate due to chemical bonding [3]. Abdul Malik and co-workers [2] chemically attached a hydroxyl-terminated PDMS coating to the surface of a fused silica fiber, showing for the first time that the sol–gel approach can be effectively used to create bonded SPME phases. The sol–gel coated PDMS fibers were stable to >320 °C, allowing for the efficient desorption of less-volatile analytes. The thinner ($\sim 10 \mu\text{m}$) coating and a porous microstructure provided efficient extraction

^{*} Corresponding author. Tel.: +351 22 6082928; fax: +351 22 6082959.
E-mail address: mazenha@fc.up.pt (M. Azenha).

rates from solution. The stability of sol–gel coated fibers in strong organic solvents as well as strongly acidic and basic solutions was shown by Gbatu et al. [4] who developed octyl-functionalized fibers for SPME–HPLC determination of organometals. Other sol–gel SPME coatings, exhibiting different selectivities, e.g. crown ether [5], polyethylene glycol [6], hydroxyfullerene [7] and polyphenylmethylsiloxane [8] coatings, have been recently reported.

In general, the sol–gel mixtures employed in these works comprise a monomeric alkoxy silane precursor and a properly functionalized polymer. However, the octyl-functionalized fibers, referred above, were obtained solely from monomeric alkoxy silanes (methyltrimethoxysilane, MTMOS, and *n*-octyltriethoxysilane, C8-TEOS). MTMOS was chosen (instead of the commonly used tetramethoxysilane or tetraethoxysilane) as the sol–gel precursor to minimize cracking and shrinkage problems encountered during the sol–gel drying step, while C8-TEOS was used as functional monomer. The present work describes a new sol–gel application for the development of phenyl-functionalized SPME fibers, using this same approach. As expected, the result was a significantly different coating as compared to the previously described polyphenylmethylsiloxane coating [8]. An ultrathin (<1 μm thick) phenyl-functionalized coating showing a good extracting capability was achieved. Special focus was directed to the description of the optimization of the sol–gel bath, the film quality and microstructure, as well as the extracting performance of the obtained fibers.

2. Reagents and materials

MTMOS, PTMOS, tridecane and 2-octanone were obtained from Sigma-Aldrich, benzene, toluene, ethylbenzene, benzaldehyde and acetophenone from Merck (Whitehouse Station, NJ) and dimethylphenol from Fluka (Buchs, Switzerland). Before use, all plastic- and glassware was decontaminated overnight in 20% nitric acid and thoroughly washed with MilliQ quality (Millipore, Billerica, MA) deionised water.

2.1. Sol–gel mixtures

Different sol–gel mixture compositions were prepared in PCR tubes. The mixtures included the precursors (MTMOS, PTMOS), water, methanol (co-solvent) and one of the following catalysts: HCl, HF or NaOH. A first set of mixtures, envisaging a complete 2^4 (=16) factorial analysis of the parameters influencing the sol–gel process was prepared. The studied parameters and respective levels chosen were: MTMOS:PTMOS molar ratio (2:1 and 1:1), water: (MTMOS + PTMOS) molar ratio (2:1 and 3:1), time of reaction (3 and 48 h) and type of catalysis (acidic, HCl 0.007 M final concentration, and alkaline, NaOH 7×10^{-6} M final concentration). Methanol was always added in the molar

ratio 2:1 relatively to water. The final volume of the mixture was planned so as to allow the desired immersion of the fiber (1 cm) and to leave a safe distance between the fiber tip and the tube bottom. The hydrolysis/condensation occurred at room temperature, stirred at 400 rpm in a vortex stirrer. Finally the mixtures were filtered (0.2 μm pore size) into new PCR tubes before further use.

The second set of preparations followed a similar procedure and was also designed for complete factorial analysis, 2^3 (=8) in this case. The parameters and respective levels were: MTMOS:PTMOS molar ratio (4:1 and 3:1), water: (MTMOS + PTMOS) molar ratio (2:1 and 1:1), and type of catalysis (acidic, HF 0.007 M final concentration, and alkaline, NaOH 7×10^{-6} M final concentration). The time of reaction was fixed at 72 h in this set of mixtures.

2.2. Sol–gel flow-coating on glass plates

Before the deposition, the glass plates were immersed 1 h in NaOH 1 M to increase the number of surface silanol groups, and finally washed successively with HCl 0.1 M, water and methanol. Afterwards, the plates were placed in a homemade holder with an inclination of 30°. The mixtures were then simply spread along the top side of the plate and flowed down. The coatings were allowed to dry at room temperature.

2.3. Fiber preparation

Silica optical fiber (Corning Cable Systems, Hickory, NC) of diameter $125.0 \pm 2 \mu\text{m}$ with primary polyacrylate coating was used. The fiber was cut in 12 cm pieces and the primary coating was removed in a 10 cm end of the fiber by dipping in 1,2-dichloroethane. Afterwards, the uncoated end was immersed in NaOH and washed in the same manner as the glass plates. The fibers were handled very carefully using safety goggles, as they can easily break and be propelled.

2.4. Fiber assemblage and dip-coating

Prior to dip-coating the optical fiber was assembled to the parts of spared commercial devices (Supelco, Bellefont, CA) and stainless steel tubes which were obtained by extrusion of a larger section tube and cut free of chipped edges by electro-erosion. To attach the fiber to the plastic screw Araldit glue was used and left to settle 24 h before further handling.

The SPME devices assembled were then inserted in a SPME manual holder (Supelco) for the dip-coating process. The fiber came out of the needle and was vertically immersed (1 cm) inside the PCR tube containing the sol–gel mixture during 30 min at room temperature. After that period the fiber was retracted inside the needle and then conditioned 30 min at 300 °C under nitrogen in the GC injector port. In some cases triply coated fibers were prepared, and therefore,

this dip-coating process was repeated three times, using new sol–gel mixtures.

2.5. Scanning electron microscopy (SEM)

The fibers were coated with a gold vapour layer prior to analysis by SEM using a JEOL JSM-6301F (Peabody, MA) instrument with 1.3 nm resolution.

2.6. Extraction studies

Prior to the first use the fibers were conditioned for 1 h at 300 °C under nitrogen at the GC injector port. An aqueous solution daily prepared and containing 1 mg/L of each of the following solutes was used throughout the extraction studies: benzene, toluene, ethylbenzene, 2-octanone, benzaldehyde, acetophenone, dimethylphenol and tridecane. The extractions were performed inside 22 mL Supelco SPME vials (23 mm × 85 mm) filled with a solution volume of 10 mL. The vial contents were magnetically stirred at 1000 rpm by means of 12 mm × 4.5 mm magnetic stir bars (Kartell, Noviglio, Italy). The temperature and time of extraction were respectively 40 °C and 30 min. All the experiments were performed in triplicate.

Beside the sol–gel fibers, two other, 100 μm polydimethylsiloxane (PDMS) and 65 μm carbowax/divinylbenzene (CW/DVB), commercial fibers (Supelco) were also studied for comparison purposes.

2.7. Extraction kinetics

This and the following studies were carried out using the best performing sol–gel fiber only. The kinetics of extraction of benzene, toluene and ethylbenzene by this sol–gel fiber was studied and compared with the extraction kinetics by PDMS and CW/DVB fibers. A mixed solution of 0.5 mg/L in each compound was subjected to headspace extraction as described in the previous section. Varying extraction times, between 2 and 52 min, were applied.

2.8. Single-versus multi-compound extraction

The extraction of benzene (50–300 μg/L) from either standalone solutions or solutions containing also 10 mg/L ethylbenzene was carried out with the sol–gel fiber. The extraction time was 15 min, while other parameters were as described in Section 2.6.

2.9. Thermal and organic solvent stability

2.9.1. Durability

The extraction of benzene, toluene and ethylbenzene (0.15 mg/L each) was used to assess the sol–gel fiber condition after thermal and organic solvent stability tests. The fiber was subject to successively higher conditioning (for 30 min) temperature: 270, 300, 320 and 350 °C, as well as overnight

Table 1
GC–FID operation parameters

GC parameters	
Injection mode	Splitless (2 min) (fiber was left 8 additional min in the injector with the split valve on, to assure complete cleaning)
Injection port temperature	230 °C
Column flow	N ₂ , 2.5 mL/min
Temperature program	50 °C (2 min) + 10 °C/min up to 180 °C (15 min)
FID parameters	
H ₂ flow	30 mL/min
Auxiliary gas (N ₂) flow	30 mL/min
O ₂ enriched air flow	400 mL/min
Temperature	270 °C

exposure to methanol, toluene and dichloromethane and then its condition was assessed.

A study of the coating damage over 150 cycles of thermal and solvent usage followed. A cycle comprised 5 min immersion in methanol followed by 2 min at 320 °C in the injector liner. The fiber condition was verified every 30 cycles.

The same extracting conditions described in the previous section were applied.

2.10. Gas-chromatography determinations

The GC determinations were performed on a Hewlett Packard, 5890 Series II instrument equipped with a split/splitless injector, a VOCOL capillary column (60 m length, 0.32 mm internal diameter, 1.8 μm film thickness) from Supelco and a flame ionization detector (FID). The instrumental parameters used are listed in Table 1. The amounts of compounds extracted by the different fibers were determined against calibration by direct injection of 0.1 μL of a 1 g/L mixed solution in methanol (at least two replicates in the course of each work session).

2.11. Bulk sol–gel film production for surface area determination and Fourier transform infrared (FTIR) spectroscopy analysis

A relatively large amount (~2 g) of film material was necessary for these experiments. Therefore, a different procedure, rather than optical fiber dip-coating, was used in order to obtain bulk quantities of the film material. Ten times higher volumes of the sol–gel mixtures were prepared as described above and were spread in plastic round plates (15 cm diameter) and left to dry for 24 h at room temperature. The thin film obtained was then crushed and part of it was sent for outsource nitrogen adsorption analysis (Faculty of Engineering, University of Porto), while the remaining was used, in nujol, for the FTIR analysis, performed with a Perkin–Elmer (Boston, MA) Spectrum RX I instrument.

2.12. Data treatment

2.12.1. Normalization

Because the extraction capability of the different fibers was evaluated with several different compounds at the same time, and there was the need to express in a single parameter the fiber's performance, the following procedure was adopted:

- The amount of each extracted compound was normalized to $Q_{\text{norm}} = Q/Q_{\text{max}}$, where Q is the amount of the compound extracted by a certain fiber and Q_{max} is the highest amount of that compound obtained within the whole set of fibers.
- The normalized global extraction capability of a fiber was then calculated as:

$$Q_{\text{norm}}(\text{fiber } i) = Q_{\text{norm}}(\text{compound 1}) \\ + Q_{\text{norm}}(\text{compound 2}) + \dots$$

- different $Q_{\text{norm}}(\text{fiber } i)$ values were calculated considering either the 8 compounds altogether, or, depending on the purpose, just the following subsets: aromatic compounds, aliphatic compounds, apolar compounds, polar compounds.

2.12.2. Factorial analysis

The factorial analysis was performed by resorting to the Yates algorithm [9] which allows a simple way of computing the effects of the factors, as well as their interactions. The error associated to the values of the effects and interactions was calculated, for a level of confidence 99.7%, as $6(\sigma^2/N)^{1/2}$, where N stands for the total number of observations and σ^2 is the mean variance observed in the replicates (3) within the different experiments. The effects and interaction were considered significant when their magnitude was higher than the associated error.

3. Results and discussion

3.1. Choice of sol–gel mixture variables and their respective levels

A first set of sol–gel mixtures, designed for a 2^4 factorial analysis, was tested by flow-coating on glass plates, for a quick screening of the film quality that could be expected in the glass fibers. The initial choice of the factors studied and their respective levels (see the experimental section) was made accordingly to previously reported sol–gel work [4] using similar precursors. All the coatings obtained on the glass plates were opaque, highly irregular, with small adherence to the glass. These observations were also confirmed by dip-coating deposition on glass fiber, for a few limited cases. These unsatisfactory results prompted for the choice of different levels of the factors. That task was facilitated by the observation that: the coatings obtained after longer reaction

Table 2

Experimental parameters used to produce the different sol–gel fibers and microextraction normalized results obtained

Sol–gel mixture	H ₂ O:MOS	MTMOS:PTMOS	Catalyst	Response (Q_{norm})
1	2:1	4:1	HF	2.15
2	1:1	4:1	HF	0.85
3	2:1	3:1	HF	5.39
4	1:1	3:1	HF	0.94
5	2:1	4:1	NaOH	7.57
6	1:1	4:1	NaOH	0.76
7	2:1	3:1	NaOH	4.76
8	1:1	3:1	NaOH	1.80

Assigned + and – levels: H₂O:MOS: (+) 1:1; (–) 2:1.

MTMOS:PTMOS: (+) 3:1; (–) 4:1 catalyst: (+) NaOH; (–) HF.

time, alkaline catalysis, lower water contents and lower PTMOS contents were clearly less irregular and opaque relative to their counterparts. The final set of sol–gel mixtures reflects these observations and the experiments performed under the factorial design are listed in Table 2. The time of reaction was set to 72 h and withdrawn from the factorial analysis, thus meaning that a final 2^3 complete factorial analysis was performed.

The new mixtures were also tested in the flow coating of glass plates and in this case more or less transparent, homogeneous films were obtained. Therefore, the work proceeded to the dip-coating of glass fibers using this set of mixtures.

3.2. Extraction performance of the sol–gel coated fibers

The eight fibers prepared by dip-coating in the sol–gel mixtures, presented in Table 2, were used for the microextraction of a set of organic compounds comprising different chemical characters: polar, non-polar, aromatic and aliphatic. The normalized results of the extraction are presented in the same table and they refer to the situation where all the eight compounds were taken into account. When only subsets (polar, non-polar, aromatic, aliphatic) of compounds, were considered, similar profiles of response within the eight fibers were obtained (data not shown), thus suggesting that the differences in the sol–gel mixture reflected in the extraction performance in the same manner for all the compounds, regardless of their chemical character. In fact, observing Fig. 1, which shows the percentage of extracted compounds by the eight different fibers, a general trend can be found: the increasing order of extracted compounds by any of the fibers was benzaldehyde–acetophenone–dimethylphenol < benzene < toluene < ethylbenzene–octanone < tridecane. This trend clearly indicates, as expected, highly hydrophobic fiber coatings bearing affinity for long chain and aromatic compounds.

So, at this point the question of understanding what was causing the large differences on the extraction capabilities of the fibers arose. From the exposed above, the different sol–gel

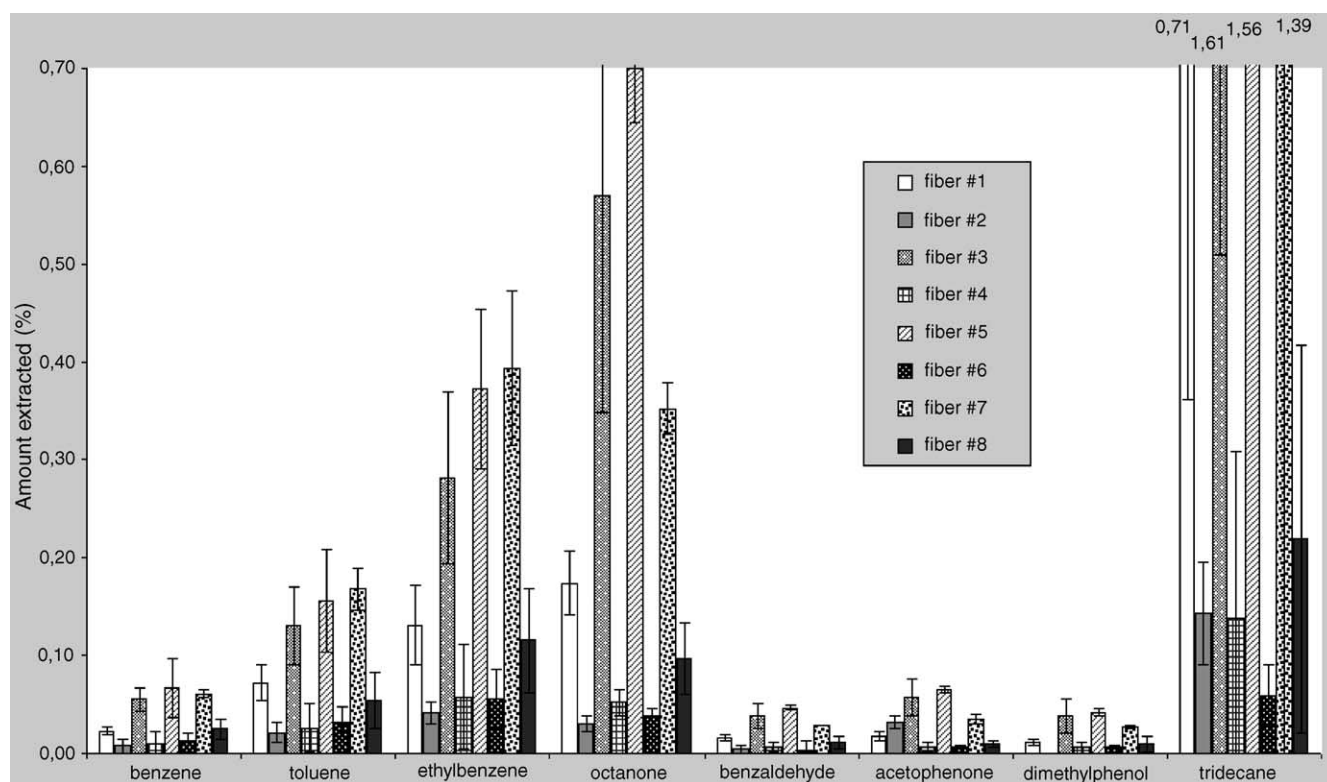


Fig. 1. Extracting performance observed with the eight different sol-gel fibers. Experimental conditions: headspace extraction at 40 °C during 20 min. Error bars are the confidence intervals ($P=0.05$, $n=3$).

mixtures employed in the production of the fibers seemed to result in chemically similar coatings. Perhaps the differences observed could be due to different physical microstructures or simply due to different extracting phase volume. Some information on this issue was obtained by SEM inspection and by nitrogen adsorption analysis.

3.3. Microstructure of the sol-gel coatings

The SEM analysis revealed the formation of very thin films whose presence was also confirmed by X-ray analysis that showed the inclusion of carbon on the surface composition. The FTIR absorption spectrum obtained for the bulk polymer (Fig. 2) shows a broad peak around 1630 cm^{-1} which can be attributed to the stretching of C=C bonds, thus pointing to the presence of phenyl groups. The other absorption peaks match those expected for a PDMS polymer (see [10] for example, and Fig. 2).

The film thickness ranged $0.2\text{--}1\text{ }\mu\text{m}$ and was estimated from SEM images. The process of successive coatings (three in this case) was found not to be advantageous because the second and third coatings did not adhere quite effectively as the first coating. The difference probably resides in the fact that the first coating is covalently bound to the substrate through condensation of silica surface silanols with the hydroxyl-terminated points of the sol-gel network, while the subsequent coatings face now a hydrophobic substrate lacking the abundance of surface silanol groups. Additionally, it

was observed that the triply coated fibers had the same extraction capability as the fibers with one coating. These results contrast with those reported of successively obtained sol-gel multi-coatings e.g. [2,5], based, however, on sol-gel mixture compositions that were quite different than those used in the present work.

The SEM images give the impression of a dense, non-porous structure for all the coatings. However, the SEM technique does not possess enough resolution to show clearly both micro- and mesopores, since they fall in the $2\text{--}500\text{ \AA}$ range. For that reason, bulk quantity films ($\sim 2\text{ g}$) were produced in large plastic plates and their surface area determined by nitrogen adsorption analysis. The values of surface area obtained were below $10\text{ m}^2/\text{g}$, thus corroborating the non-porous appearance shown by SEM observation.

The main difference observed among the different fibers was, in fact, the film quality in terms of substrate coverage. Some fibers presented severe microscopic irregularity (Fig. 3A,B), corresponding to lower substrate coverage, while other fibers (Fig. 3C) presented a homogeneous film formation with full coverage of the substrate. Merging the data of extraction performance with the film quality observations, the following general correlation could be formulated: better quality films (full substrate coverage, which means higher amount of extracting material) resulted in better extraction performance. Indeed, the film illustrated in Fig. 3C was obtained from the sol-gel mixture #5 which presented the best extraction performance.

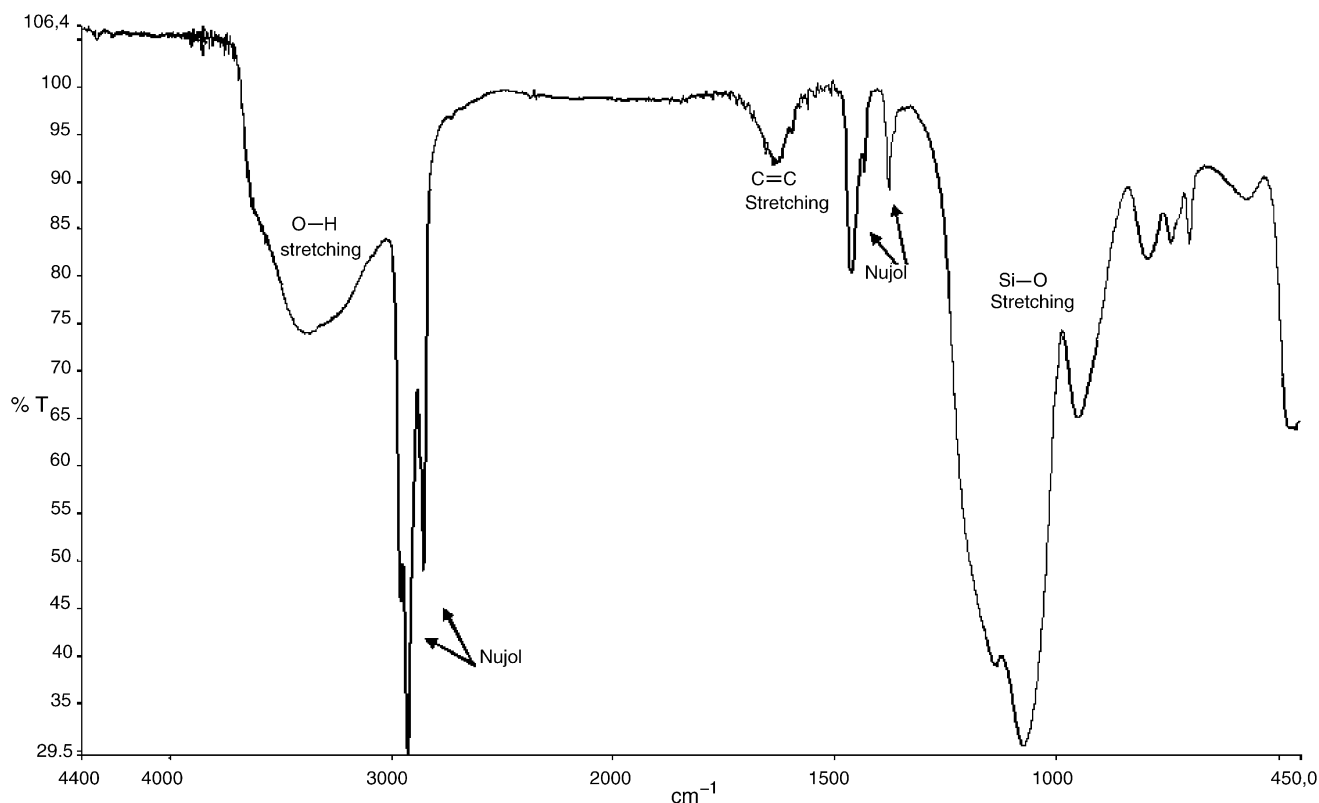


Fig. 2. FTIR absorption spectrum of the phenyl-functionalized sol-gel polymer.

Therefore, the results presented so far, indicate that the film quality (governed by the corresponding sol-gel mixture composition) was the key item ruling the final observed extracting performance. The factorial experimental design selected for this study allowed some insight into the relative importance of the varying parameters of the sol-gel mixture with the view of obtaining good quality films.

3.4. Effects of the parameters of sol-gel mixture on the extracting capability

The factorial analysis allowed the determination of the most influent parameters and their interactions, with respect to the achievement of the best performing fibers. The results are presented in Table 3.

Table 3
Results of the factorial analysis

Effect	Effect magnitude	Associated error ($\alpha = 99\%$)
Average	3.0	0.25
<i>a</i>	-3.9	
<i>b</i>	0.39	
<i>ab</i> Interaction	0.17	
<i>c</i>	1.4	
<i>ac</i> Interaction	-1.0	
<i>bc</i> Interaction	-1.3	
<i>abc</i> Interaction	1.8	

a: H₂O:MOS; *b*: MTMOS:PTMOS and *c*: catalyst.

The most influential effect, -3.9, was observed for the H₂O:MOS ratio, which means that changing this parameter from the + level (1:1) to the - level (2:1) was the most important contribution to obtain higher responses. The effect of the catalyst, 1.4, came next in terms of importance. The positive sign means that the + level (NaOH) favoured higher responses. The effect of the MTMOS:PTMOS ratio had only a small influence (effect magnitude: 0.39) comparing to the other two parameters.

In the formation of sol-gel films, the processes of aggregation, gelation and drying occur in a few minutes. In that short period, the competition between evaporation, favouring film compactness, and additional condensation, favouring film stiffness, greatly influences the final structure. The process of network growth prior to film deposition also allows controlling the microstructure of the film. While highly branched systems are less prone to capillary stress and therefore, to collapse, the weakly branched systems are interpenetrable causing a dense packing that often leads to film breakage [3]. In the system under study the obtainment of non-cracked films was favoured essentially by the alkaline catalysis, which favours branching [11], and by a H₂O:MOS ratio of 2:1 in comparison to 1:1. The interpretation of the effect of this last parameter is not straightforward. In fact, while high water content is favourable to a fast and extensive hydrolysis, it is, in turn, unfavourable to the condensation step, as water is one of the condensation products. Perhaps

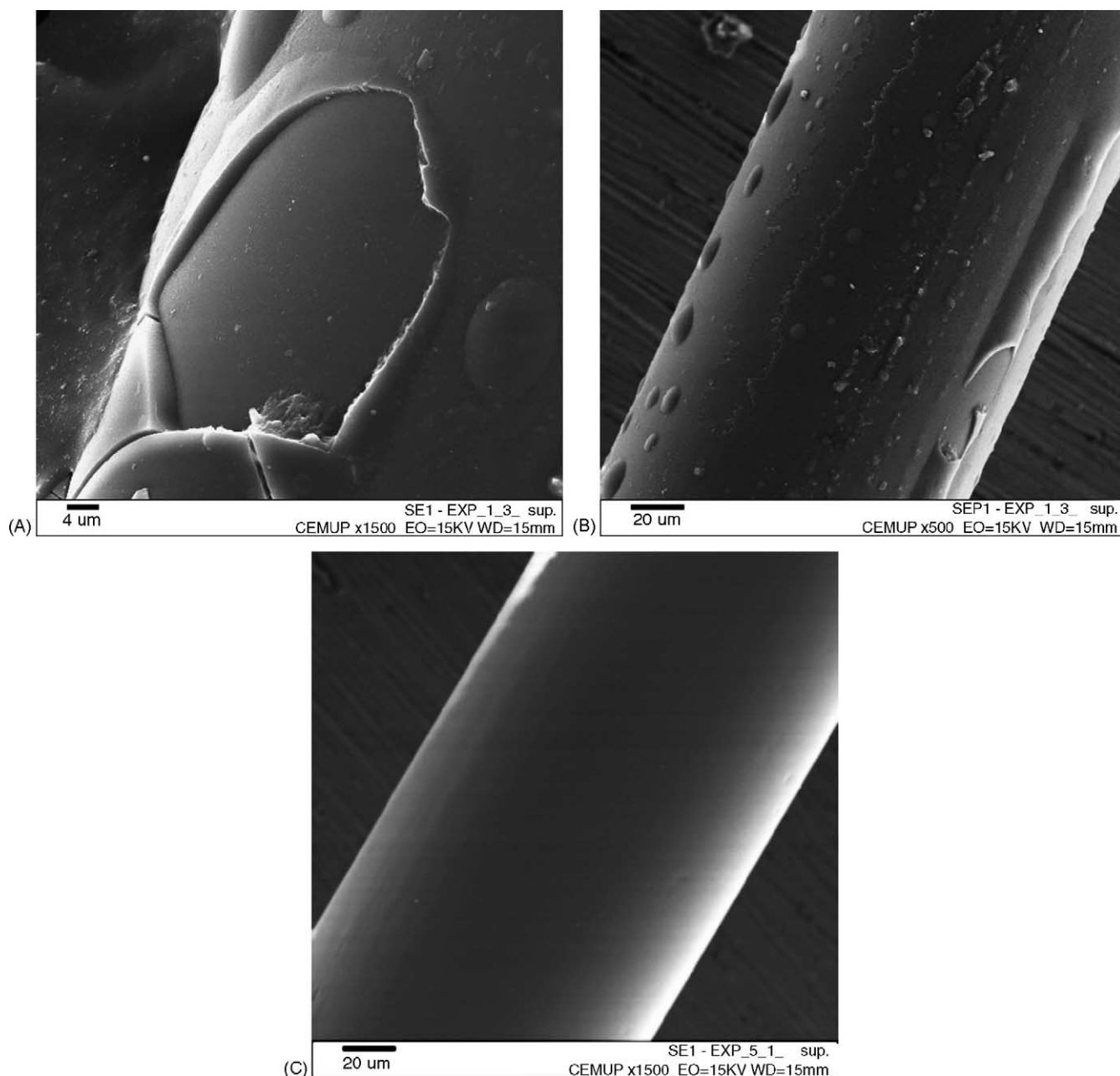


Fig. 3. SEM longitudinal top view of three different sol-gel coated fibers.

the 2:1 ratio corresponds to a compromise condition in this system (the results with the 2:1 ratio were also better than those with the ratio 3:1, although obtained with a different set of parameter levels – initial 2^4 factorial).

The calculated effect magnitudes are the average effect of a certain parameter when considering the whole set of experiences altogether. It means that the effect of changing the level of a parameter may not be the same in every situation. The effect of a parameter may be dependent on the actual levels of the other parameters, and, in this case, the parameters are said to interact. These interactions can be estimated by the factorial analysis and were included in Table 3. Three

significant interactions were found: two double interactions ($\text{H}_2\text{O}:\text{MOS}/\text{catalyst}$ and $\text{MTMOS}:\text{PTMOS}$ ratio/ catalyst) and a strong triple interaction. This fact demonstrates the complexity of the sol-gel process under study, which leads to the difficulty of predicting the effect of a parameter change, thus making its optimization a complicated task.

3.5. Sol-gel coated fibers versus commercial PDMS and CW/DVB fibers

For comparison purposes, the extraction performance of two commercial fibers, 100 μm PDMS and 65 μm CW/DVB

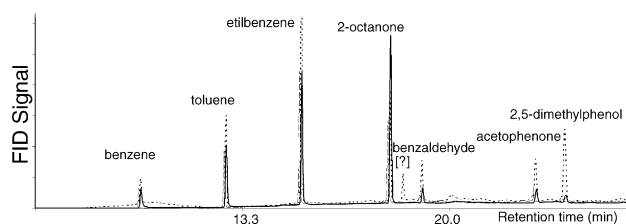


Fig. 4. Headspace-SPME GC-FID chromatograms obtained for the sol-gel (—), PDMS (---) and CW-DVB (...) fibers. Experimental conditions: extraction at 40 °C during 20 min; see Table 1 for GC-FID operating parameters.

was evaluated under the same conditions used to test the different sol-gel fibers. The results of that comparison are shown in the chromatogram in Fig. 4 (only the best-performing sol-gel fiber, prepared from the sol-gel mixture #5, was considered in this case). At the experimental conditions used, the sol-gel fiber #5 extracted similar or slightly higher amounts of compounds than the PDMS fiber. On the other hand, the extraction of polar and aromatic compounds with the sol-gel fiber was lower than with the CW/DVB fiber, while the extraction of compounds with long aliphatic chain (octanone and tridecane) was higher with the sol-gel fiber.

The higher extraction of polar and aromatic compounds with the CW/DVB fiber is not surprising due to the polar/aromatic character conferred by the polyethyleneglycol phase and divinylbenzene particles, respectively. Unexpected was the fact that a <math><1\ \mu\text{m}</math> thick fiber was extracting similarly to a 100 μm thick fiber, both bearing an apolar character. Possible explanations could reside in kinetics and extraction mechanism (adsorption versus absorption) differences.

3.6. Extraction kinetics

The kinetics of extraction of benzene, toluene and ethylbenzene with the sol-gel #5, CW/DVB and PDMS fibers were recorded and are presented in Fig. 5. The profiles of extraction with the sol-gel and PDMS fibers are similar, the extraction rate decaying smoothly until the equilibrium is established and a plateau on the extracted amount being reached after 20–30 min. In the case of ethylbenzene, a clearly faster extraction rate was found for the PDMS fiber, while for the two other tested compounds none appreciable difference was observed. Therefore, the formerly presented good performance of the sol-gel fiber relatively to the PDMS fiber could not be explained by a faster extraction with the sol-gel fiber.

3.7. Extraction mechanism

Independently of the nature of the coating, analyte molecules get attached to its surface. Whether they migrate to the bulk of the coating or remain on its surface depends on the diffusion coefficient of an analyte in the coating. When the diffusion coefficients are high (close to those in organic

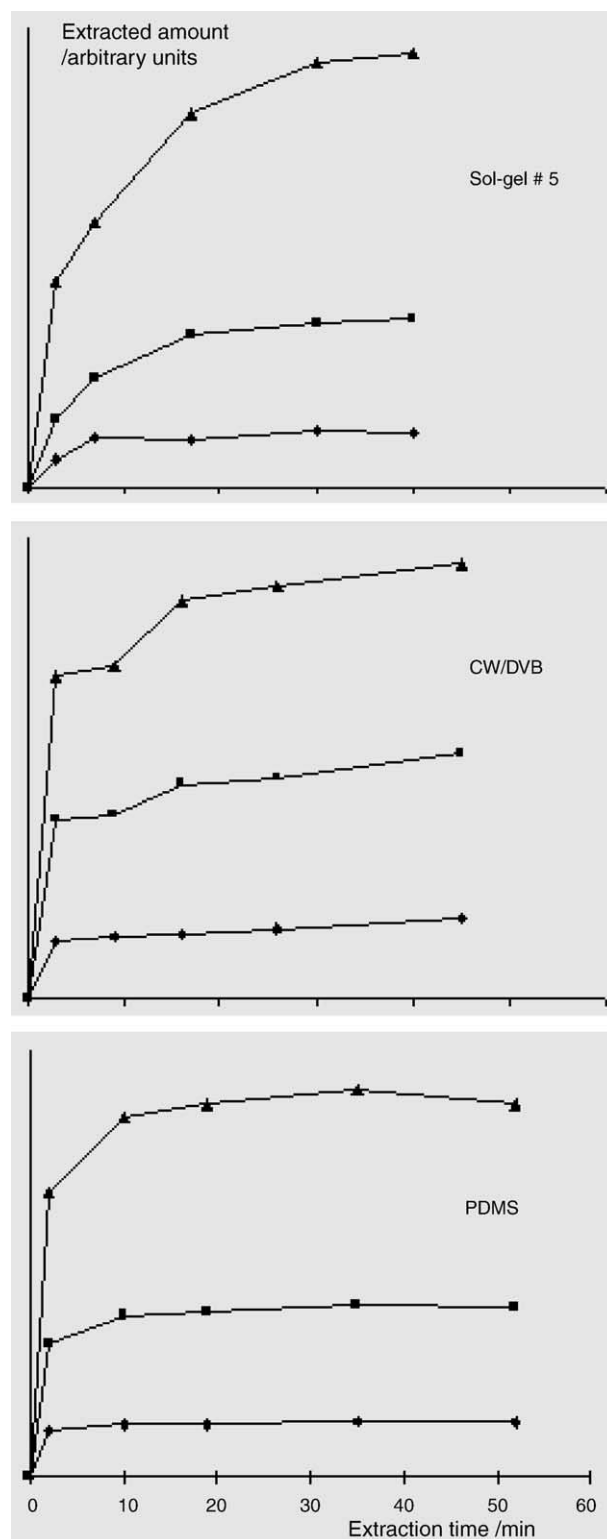


Fig. 5. Time profiles of the extraction from a mixture of benzene, toluene and ethylbenzene, using the sol-gel, PDMS and CW-DVB fibers. Experimental conditions: headspace extraction at 40 °C. (◆) Benzene, (■) toluene and (▲) ethylbenzene.

solvents) the coating extracts primarily via absorption (liquid behaviour). This is the case of the PDMS coating. On the other hand, when the diffusion coefficients are so small that within the time frame of SPME analysis, essentially all the molecules remain on the surface of the coating, the extraction occurs via adsorption [12]. Coatings extracting via absorption exhibit a very high linear range which is not affected by multi-compound competition. On the contrary, the limited surface adsorption sites on the adsorbing coatings result in a diminished linear range and the extraction of a compound, under certain conditions, may suffer competition from other compounds.

The studies of sol-gel coatings described in the literature do not provide any objective data on its primary mechanism, although one might hypothesize that in the cases where the sol-gel system consisted of a sol-gel precursor and an appropriately functionalized polymer, one of the consequences of using the polymer is limited cross-linking, which helps the coating maintain liquid-like properties. However, porous coatings are claimed by some authors, e.g. [2], which present SEM images showing sponge-like coatings that may point to high branching or crosslinking, resulting in the evanescence of liquid-like properties. This subject seems worthy of future study. It was decided to perform a simple experiment that could provide some insight onto the primary extraction mechanism of the sol-gel fiber, based on linear range and competition information. The single extraction of benzene (at 50–300 $\mu\text{g/L}$) versus the extraction of benzene in the presence of ethylbenzene (at 10 mg/L) was studied, the results being shown in Fig. 6. The extraction of benzene was found to be significantly diminished by the simultaneous extraction of ethylbenzene, thus being affected by competition. Moreover, the linear response was limited to approximately 100 $\mu\text{g/L}$ in both cases. The information collected points to adsorption as the primary mechanism of extraction by this coating. Hence, the possible explanation for the good performance of the sol-gel fiber hypothesised in this study, its possible liquid behaviour, appears to be unlikely.

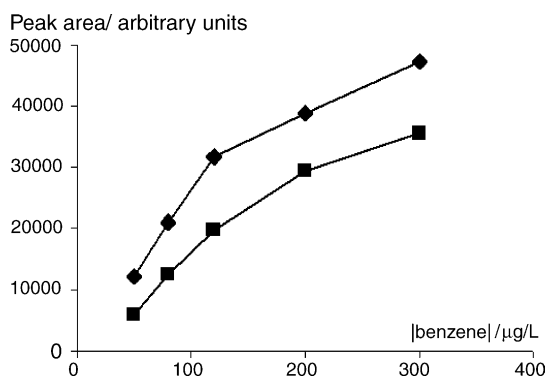


Fig. 6. Calibrations curves for benzene alone (\blacklozenge) and in the presence of 10 mg/L ethylbenzene (\blacksquare). Sol-gel fiber, headspace sampling at 40 °C during 20 min.

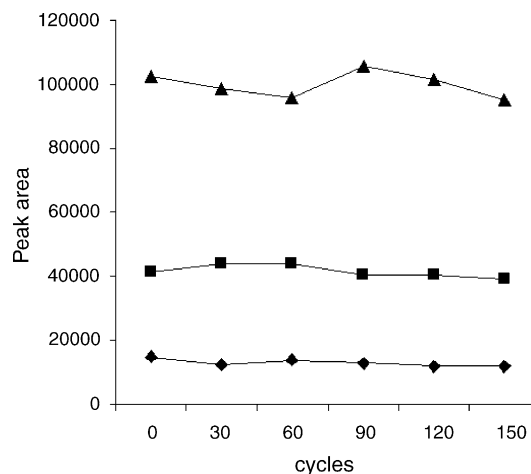


Fig. 7. Durability of the sol-gel fiber evaluated as the capability of extraction of benzene, toluene and ethylbenzene along 150 cycles of methanol and 320 °C exposure. (\blacklozenge) Benzene, (\blacksquare) toluene and (\blacktriangle) ethylbenzene.

3.8. Thermal and organic solvent stability

3.8.1. Durability

The thermal stability experiments have shown that conditioning/injecting the sol-gel fiber at up to 350 °C (maximum temperature allowed by the GC injector port septum) did not reduce the extracting capability (data not shown). It was observed that overnight exposure to ethanol, toluene and dichloromethane did also not affect the fiber's performance.

As durability is concerned, it was observed that the fiber condition was not significantly affected by 150 cycles of methanol and 320 °C exposure (Fig. 7) thus confirming its great thermal and solvent stability.

3.9. Fiber production reproducibility

The extraction of benzene, toluene and ethylbenzene using three sol-gel coated fibers prepared in different days was compared in order to evaluate the fiber production reproducibility. The between-fiber relative standard deviations obtained, 25–30%, were unsatisfactory, and are comparable to those reported by Gbatu et al. [4]. The difficulty of high fiber production reproducibility seems to be a problem even at the more controlled commercial production level, as it is not uncommon to observe significant differences from different lots of fibers.

4. Conclusions

The achievement of well formed phenyl-functionalized coatings depended upon the choice of several parameters of the sol-gel process, namely the water-to-siloxane ratio, catalyst, reaction time and PTMOS-to-MTMOS ratio. Good film quality was determinant for a good extracting fiber performance. The film thickness ranged 0.2–1 μm and could

not be increased by multi-coating processes. Apparently, a dense, non-porous microstructure was obtained. These coatings exhibited a strong hydrophobic character, as shown by the capability of extraction of long chain and apolar aromatic compounds, which, surprisingly, was comparable to that of the 100 μm PDMS and 65 μm CW–DVB, for these compounds. These results could not be explained in terms of faster sol–gel fiber kinetics or in terms of absorption as its primary extracting mechanism. The developed fiber has shown high thermal and organic solvent stability. It may be useful for the microextraction of non-polar compounds, although at trace levels and in simple matrixes only, due to the susceptibility to competition. The fiber has shown adequate characteristics to be associated to GC and potentialities that may also envisage suitability for HPLC.

Acknowledgements

The authors thank Prof. Paulo Marques for providing the optical fiber, and Prof. Jos José Luís Figueiredo for the nitrogen adsorption analysis.

References

- [1] C. Arthur, J. Pawliszyn, *Anal. Chem.* 62 (1990) 2145.
- [2] S. Chong, D. Wang, J. Hayes, B. Wilhite, A. Malik, *Anal. Chem.* 69 (1997) 3889.
- [3] C. Brinker, G. Scherer, *Sol–Gel Science. The Physics and Chemistry of Sol–Gel Processing*, Academic Press, San Diego, 1990, Chapter 13.
- [4] T. Gbatu, K. Sutton, J. Caruso, *Anal. Chim. Acta* 402 (1999) 67.
- [5] Z. Zeng, W. Qiu, M. Yang, X. Wei, Z. Huang, F. Li, *J. Chromatogr. A* 934 (2001) 51.
- [6] Z. Wang, C. Xiao, C. Wu, H. Han, *J. Chromatogr. A* 893 (2000) 157.
- [7] J. Yu, L. Dong, C. Wu, L. Wu, J. Xing, *J. Chromatogr. A* 978 (2002) 37.
- [8] L. Cai, J. Xing, L. Dong, C. Wu, *J. Chromatogr. A* 1015 (2003) 11.
- [9] F. Yates, *The design and analysis of factorial experiments*, Imperial Bureau of Soil Science, Bulletin 35, Herts, 1937.
- [10] A. Lopes, F. Augusto, *J. Chromatogr. A* 1056 (2004) 13.
- [11] J. Wright, A. Sommerdijk, *Sol–gel Materials. Chemistry and Applications*, Taylor and Francis, London, 2001, Chapter 2.
- [12] T. Gorecki, in: J. Pawliszyn (Ed.), *Applications of Solid Phase Microextraction*, Royal Society of Chemistry, Hertfordshire, 1999, Chapter 7.