Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Chromatography A, 1005 (2003) 1–12
JOURNAL OF CHROMATOGRAPHY A
www.elsevier.com/locate/chroma

# Novel benzo-15-crown-5 sol–gel coating for solid-phase microextraction

Danhua Wang, Jun Xing, Jiagang Peng, Caiying Wu*
*College of Chemistry and Molecular Science, Wuhan University, Wuhan 430072, China*

Received 24 December 2002; received in revised form 5 May 2003; accepted 13 May 2003

**Abstract**

A novel dihydroxy-terminated benzo-15-crown-5 was synthesized and applied to prepare a solid-phase microextraction (SPME) fiber coating with sol–gel technology. The optimization of the sol–gel process was studied. The coating method with sol–gel was improved and completed in one run, which economized materials and allowed easier control of the fiber thickness. The repeatability of coating fiber to fiber was better than 4.94% (RSD). The surface of the fiber coating was well-distributed and an electron microscopy experiment suggested a porous structure for crown ether coating, providing high surface areas and allowing for high extraction efficiency. The coating has a high thermal stability (350 °C), long lifetime and can stand solvent (organic and inorganic) rinsing due to the chemical binding between the coating and the fiber surface. Non-polar benzene, toluene, ethylbenzene, xylenes, chlorobenzenes, polar phenolic compounds and arylamines were used to evaluate the character of the fiber coating by headspace SPME–gas chromatography technology. For phenols, the linear concentrations ranged from 5 to 1000 μg/l, the detection limits were between 0.05 and 1 μg/l, and the RSD was less than 5%. The addition of benzo-crown ether not only increases the thermal stability of the fiber coating, but also enhances the selectivity of the fiber coating. Compared with commercially available SPME fibers poly(dimethylsiloxane) and polyacrylate, the new phases showed better selectivity and sensitivity towards non-polar and polar aromatic compounds.


*Keywords:* Solid-phase microextraction; Sol–gel; Headspace analysis; Crown ethers; Volatile organic compounds; Phenols; Arylamines

## 1. Introduction

Since the solid-phase microextraction (SPME) technique was introduced by Berladi and Pawliszyn [1] in 1989, the application and study of SPME developed quickly in this decade. SPME uses polymer-coated fibers to extract analytes from aqueous or gaseous samples. Then, the fiber is inserted directly into the injector of a gas chromatography (GC) system, and the extracted analytes are thermally desorbed and analyzed. It can integrate the extraction, preconcentration, and sample introduction into one step. This convenient and solvent-free extraction method is also sensitive, inexpensive and portable. It is easily utilized with GC or liquid chromatography (LC), and other techniques [2–4]. This method has been successfully applied to analyze many compli-

*Corresponding author. Fax: +86-278-764-7617.
*E-mail address:* cywu@whu.edu.cn (C. Wu).

0021-9673/03/$ – see front matter 
doi:10.1016/S0021-9673(03)00884-7

cated samples, such as soil [5], foods [6], blood [7], urine [8] and other biological samples.

Up to now, only seven kinds of SPME coating are commercially available. Polydimethylsiloxane (PDMS), PDMS–divinylbenzene (DVB), polyacrylate (PA), Carboxen–PDMS, Carbowax (CW)–DVB, Carbowax–templated resin, and StableFlex DVB–Carboxen–PDMS. PDMS is a non-polar phase, which extracts non-polar anlytes, such as benzene compounds [9], polychlorinated biphenyls (PCBs) [10] and low-ring polycyclic aromatic hydrocarbons (PAHs) [11] very well. The PA fiber is mainly for polar compounds, like phenols [12], organophosphorous pesticides [13] and nitrogen-containing herbicides [14]. The CW–DVB fiber is more strongly polar, but its maximum temperature is only 265 °C which limits its application range.

Sol–gel chemistry can provide efficient incorporation of organic components into inorganic polymeric structures in solution under extraordinarily mild thermal conditions [15]. Major inherent advantages of sol–gel technology are: (a) low costs, (b) high thermal stability, (c) porous structure and (d) strong adhesion of the coating to the substrate due to chemical bonding. Therefore, the sol–gel technique is very suitable for SPME coating [16–19].

Crown ethers have a cavity structure, medium polarity and strong electronegative effect of heteroatoms on the crown ether ring. They have been widely used as chromatographic stationary phases for their strong directional force and good selectivity [20]. Benzo-crown ether polysiloxane extends the operating temperature from 75 to 305 °C [21] and possesses unique selectivity for phenolic compounds [22]. Zeng [17] has published an article about SPME coating with sol–gel-derived hydroxydibenzo-crown ether (OH-DB14C4), but the linear range of phenols is very narrow. This is possibly due to the fact that OH-DB14C4 has a small crown ether ring which yields low polarity [22,23] and the concentration of OH-DB14C4 in the coating is too low. In this paper, we synthesized a new dihydroxy-terminated benzo-15-crown-5 (DOH-B15C5), which had stronger polarity than OH-DB14C4 because of the bigger crown ether ring and had lower steric hindrance for hydroxy. The novel DOH-B15C5 SPME fiber exhibits a high sample capacity and good selectivity for both polar and non-polar aromatic compounds.

## 2. Experimental

### 2.1. Instrumentation

The SPME holder for manual sampling is obtained from Supelco (Bellefonte, PA, USA). Three commercially available SPME fibers: PDMS (100 μm and 30 μm) and PA (85 μm) are used for comparison with the prepared DOH-B15C5 fibers. The separations were carried out in a Wenling 9790GC system equipped with a flame ionization detection (FID) system (Zhejiang, China) and a Shimadzu Chromatopac Model C-R3A data processor. A 30 m×0.25 mm I.D., 0.25 μm Supelcowax-10 capillary column was used for benzene, toluene, ethylbenzene and xylenes (BTEX) compounds. For phenols, chlorobenzenes, and arylamines, a 30 m× 0.25 mm I.D., 0.25 μm HP-5 coating fused-silica capillary column was employed. Nitrogen was used as the carrier gas at a linear velocity of 15–16 cm/s. The GC injector was conducted in the splitless mode. The temperatures of injector and detector were maintained in the ranges of 250–300 °C and 300 °C, respectively. To analyze the BTEX compounds, the GC system was programmed to hold at 40 °C for 5 min, then heated at 20 °C/min to 130 °C, for 1 min. To analyze the phenols, the oven temperature was maintained at 80 °C for 2 min after injection, then programmed at 4 °C/min to 130 °C, then 15 °C/min to 250 °C, which was held for 5 min.

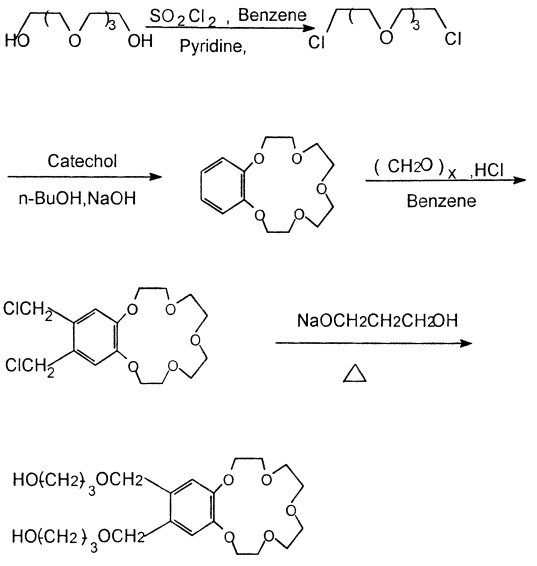
### 2.2. Reagents

Hydroxy-terminated silicone oil (OH-TSO, molecular mass average 3500), tetraethoxysilane (TEOS), and poly(methylhydrosiloxane) (PMHS) were obtained from the Chemical Plant of Wuhan University. Trifluoroacetic acid (TFA) was purchased from Aldrich (Allentown, PA, USA). All solvents used in this study were of analytical-reagent grade. Four kinds of stock solution were prepared. Solutions of BTEX compounds, chlorobenzenes (chlorobenzene, *o*-chlorotoluene, *p*-chlorotoluene, *m*-dichlorobenzene, *o*-dichlorobenzene, *p*-dichlorobenzene), arylamines (*o*-toluidine, *p*-chloroaniliane, *p*-cresidine, 4-chloro-*o*-toluidine, 2,4-diaminetoluene, 2,4-diaminoanisole, 2-amino-4-nitrotoluene, 4-aminodiphenyl, 4,4′-oxydianiline, benzidine, 4,4′-diamino-

diphenylmethane, *o*-aminoazotoluene, 3,3′-dimethyl-4,4′-diaminodiphenylmethane, 3,3′-dimethylbenzidine, 4,4′-thiodianiline, 3,3′-dichorobenzidine, 4,4′-methylene-bis(2-chloraniline), 3,3′-dimethoxybenzidine) and phenols (*m*-cresol, 2,6-dimethylphenol, *o*-nitrophenol, 2,4-dimethylphenol, 3,5-dimethylphenol, 2,4-dichlorophenol, *p*-chlorophenol, 2,4,6-trichlorophenol) were prepared by dissolving 10 mg of each compound in a 10-ml volumetric flask diluted with methanol at room temperature. Stock and working standards were stored at 4 °C in the refrigerator. The aqueous solutions were prepared daily by diluting standard solution with deionized water to give the corresponding solution for extraction. All amber vials, magnetic spin bars, and volumetric flasks were silanized with dichlorodimethylsilane prior to the experiments.

### 2.3. Synthesis of dihydroxy-terminated benzo-15-crown-5

The reaction scheme for the synthesis of the crown ethers is shown below.




4,5-Dihydroxy (propyl) methloxide-benzo-15-crown-5

The benzo-15-crown-5 was synthesized according to Ref. [24].

The structure of DOH-B15C5 was identified by nuclear magnetic resonance (NMR), mass spectrometry (MS) and IR:

$^{1}$H-NMR ($C^{2}HCl_3$, tetramethylsilane, ppm): 6.84 (s, 2 aromatic H), 4.44 (s, 4 benzylic H), 3.70–4.10 (m, 20 ethylenic H), 3.57 (m, 4 hydroxymethyl H), 1.78 (m, 4 methene H), 3.05 (s, 2 hydroxy H).

MS (*m*/*z*) ($M^+$): 444.

IR spectrum: 3354 $cm^{-1}$ (O–H), 2926 $cm^{-1}$ (Ar–H), 2870 $cm^{-1}$ (C–H), 1518 $cm^{-1}$ (C–C of Ar), 1250 $cm^{-1}$ (C–O).

### 2.4. Preparation of SPME fiber

Before coating the sol–gel stationary phase, the protective polyimide layer was removed from the fiber by dipping it into acetone for several hours. Then the fiber was dipped in 1 *M* NaOH solutions for 1 h to expose the maximum number of silanol groups on the surface of the fiber, cleaned with water, and then placed in 0.1 *M* HCl solutions for 20 min to neutralize the excess NaOH, cleaned again and dried.

The sol solution was prepared at 25 °C as follows: 20 mg of DOH-B15C5 was dissolved in 200 μl methylene chloride, 90 mg of OH-TSO, 10 mg of PMHS, and 100 μl of TEOS were added and mixed thoroughly. An 80-μl volume of TFA containing 5% water was added to the resulting solution with ultrasonic agitation for 4 min. The mixture was centrifuged at 13 000 rpm for 6 min. The white precipitate at the bottom of the tube was removed and the clear sol solution was used for fiber coating.

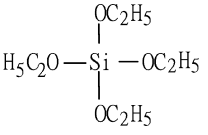
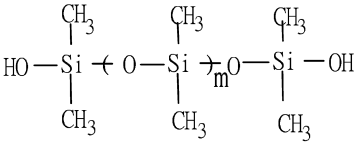
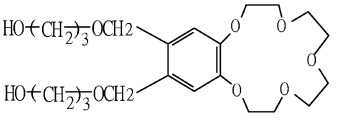
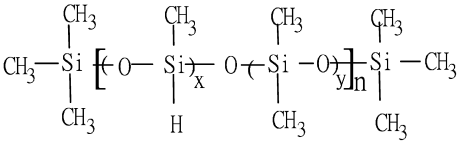
The treated fiber was dipped vertically into the sol solution and held for 5 min, during which a sol–gel coating was formed on the bare outer surface of the fiber end. For each fiber, this coating process was repeated several times each time for 2 min in the same sol solution until the thickness of the coating wanted was obtained. The fiber was removed and placed in a desiccator at room temperature for 24 h, then conditioned at 200–350 °C under nitrogen for 6 h in the GC injection port with gradually rising temperature. After removal from the injector, the fiber was cooled to room temperature and soaked in water and methylene chloride for 1 h, respectively, to clean the fiber. After drying, the fiber was con-

ditioned at 300–350 °C under nitrogen for 2 h. The final thickness of the fiber was 67 μm. The thickness of coated fiber was measured by microscope. The thickness of coated fiber was the semidiameter of the coated fiber minus the semidiameter of the bare fiber. Using the same method, different concentrations of DOH-B15C5 and different thickness (0–100 μm) SPME fibers were obtained. The blank fiber only has no crown ether. The length of each coated fiber is 1 cm.

### 2.5. Headspace (HS) extraction procedure

The sample vial containing a magnetic spin bar was sealed with a septum to prevent sample evaporation. The vial was placed in a heating bath for a given time before the SPME sampling to reach thermal equilibrium. Exposing the coated fiber end to the gas phase performed the extraction. The gas volume is 10 ml in the 25-ml vial. After the extraction, the fiber was withdrawn into the needle

Table 1
Names, functions, molecular masses and chemical structures of the coating solution ingredients for sol–gel SPME fibers

| Ingredient | Function | Molecular mass | Chemical structure |
|---|---|---|---|
| Tetraethoxysilane | Sol-gel precursor | 208 |  |
| Hydroxy-treminated poly(dimethylsiloxane) | Coating stationary phase | 3500 |  |
| Dihydroxy-treminated benzo-15-crown-5 | Coating stationary phase | 444 |  |
| Poly(methylhydrosiloxane) | Deactivation reagent | ~1000 |  |
| Trifluoroacetic acid (5% water) | Acid catalyst | 114 | $CF_3COOH$ |

and removed from the sample matrix. The fiber was then immediately inserted into the heated GC injector port.

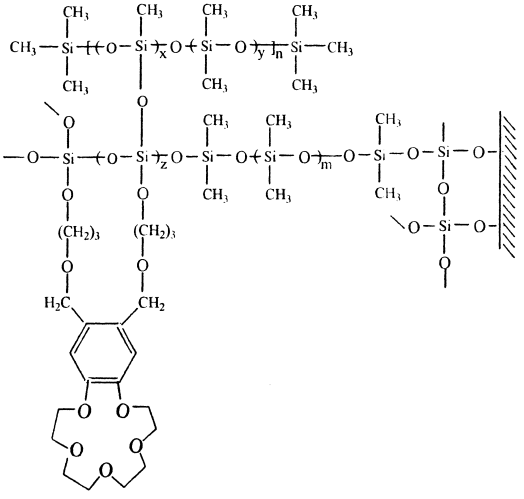
## 3. Results and discussion

### 3.1. Optimization of the sol–gel process

An important operation for SPME fiber coating technology is the creation of a uniform and stable stationary phase coating at the fiber end. In the sol–gel approach, two major sets of reaction take place during sol–gel processing: (1) hydrolysis of the precursor and (2) polycondensation of the hydrolyzed products and other hydroxy-terminated active compounds in the sol–gel system. These reactions are catalyzed by acids or bases and lead to the formation of a polymeric network, the polymeric network can also react with the silanol groups on the fused-silica fiber surface [15], forming a stable surface-bonded polymeric coating. It is known [25,26] that the sol–gel coating process may undergo cracking and shrinkage during the gel-drying step, especially for thick films. In this study, through optimization of the sol–gel process involve altering precursors, changing the molecular mass of OH-TSO, varying the content of DOH-B15C5, changing the drying time and conditioning method of sol–gel coating, a uniform and stable DOH-B15C5 coated fiber can be achieved.

The main aim of our optimization was to acquire a uniform sol solution state and prolong the time of sol solution, so as to coat different thickness SPME fibers. The precursor of methyltrimethoxysilane and more than 5000 molecular mass OH-TSO were used in our study, respectively, but they could not form uniform sol solution state. Table 1 shows our optimization materials and the optimization proportion of constituents is in Section 2.4. The sol–gel course is a dynamic process, so the coating process should be completed within 20 min under solution conditions. With stabilized temperature and concentration of ingredients, the thickness of the fiber can controlled repeated times with one sol solution. This method economized materials and reduced cost, and at the same time overcame the need for fresh sol solution for each coating time. DOH-B15C5 molecules in the sol–gel network are selectors for compounds with conjugate π electric system, cavity structure and medium polar character. So, the mass of DOH-B15C5 added to the sol–gel solution can affect the selectivity of the coating. In this study, optimization of the mass of DOH-B15C5 in the sol–gel solution was done by preparing fibers from sol–gel solutions containing DOH-B15C5 at 0, 10 and 20 mg, in which the concentration of crown ether in the coated fiber is 0, 4.8 and 9.1%, respectively.

There are five major reaction processes that occur during the sol–gel formation [27]: (1) catalytic hydrolysis of the alkoxide precursor, (2) polycondensation of the hydrolyzed products into a three-dimensional sol–gel network, (3) chemical bonding of hydroxy-terminated silicone oil and DOH-B15C5 to the evolving sol–gel network, (4) chemical anchoring of the evolving sol–gel polymer to the surface of the fiber, and (5) deactivation of surface-bonded sol–gel coating. The structure of the coated fiber is represented as follows:



The comparison of coating repeatability was also studied. To evaluate the repeatability of the coating method, three different fibers were coated under the same conditions. The concentration of crown ether in the coated fiber was 9.1%. The thickness of each fiber is 65, 67, 69 μm, respectively. The length of all the fibers is 1 cm. Table 2 is the comparison of the mass absorbed using three different fibers for three phenols. Although the thicknesses of the fiber are slightly different, the direct comparisons of mass

Table 2
The repeatability of different coated crown ether fibers[a]

| Fiber | The mass absorbed of coating (peak area) | | |
|---|---|---|---|
| | 2,6-Dimethylphenol | 2,4-Dichlorophenol | 2,4,6-Trichlorophenol |
| 65 μm | 5001 | 10 323 | 23 890 |
| 67 μm | 5037 | 10 845 | 24 170 |
| 69 μm | 5210 | 11 234 | 26 134 |
| RSD (%) | 2.20 | 4.23 | 4.94 |

[a] Conditions: analyte concentrations in the sample, 0.1 μg/ml phenols; extraction time, 40 min; extraction temperature, 40 °C; desorption time, 2 min; the aqueous saturated with NaCl and acidified to pH 1 with HCl.

absorbed have little changes. The RSD is less than 4.94%, which has acceptable repeatability.

### 3.2. Scanning electron microscopy (SEM) studies

Figs. 1 and 2 show the micrographs of the 55 μm the DOH-B15C5 fiber obtained by SEM. This fiber contains 4.8% DOH-B15C5. As can be seen from the figures, the coating possesses a porous structure and the surface of the fiber is very well-distributed. A high surface area will be able to provide large stationary phase loading and high extraction capacity.

### 3.3. Characterizations of the DOH-B15C5 fiber

The maximum operation temperatures of different fibers after they were conditioned for 1 h at 250, 300, 320, and 350 °C were studied. Under microscopy, the 100 μm blank sol–gel fiber at 300 °C had a slight cracking phenomenon, the 30 μm blank sol–gel fiber at 320 °C had the same cracking phenomenon, but the 80 μm 10 mg and 70 μm 20 mg crown ether fibers had not even at 350 °C.

Fig. 3 further illustrates the thermal stability of the 34 μm 10 mg DOH-B15C5 fiber. The extraction quantities were not significantly affected after the fiber was conditioned for 1 h at 250, 280, 300, 320

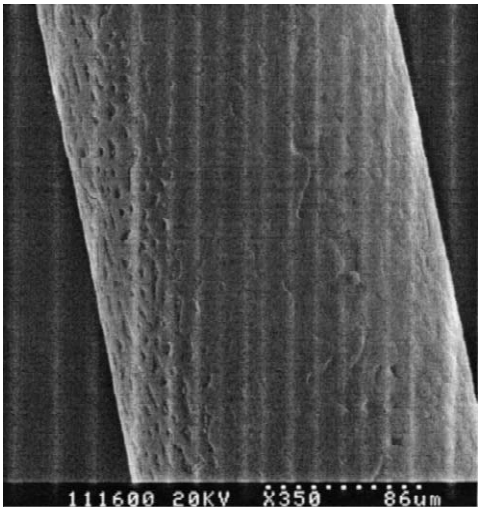



Fig. 1. Scanning electron micrograph of the DOH-B15C5 fiber at 350-fold magnification.

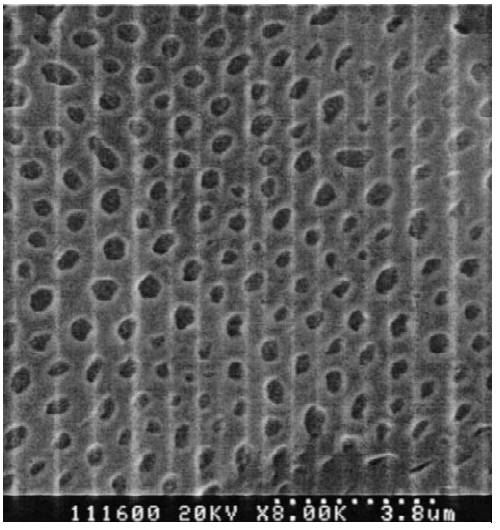



Fig. 2. Scanning electron micrograph of the DOH-B15C5 fiber at 8000-fold magnification.

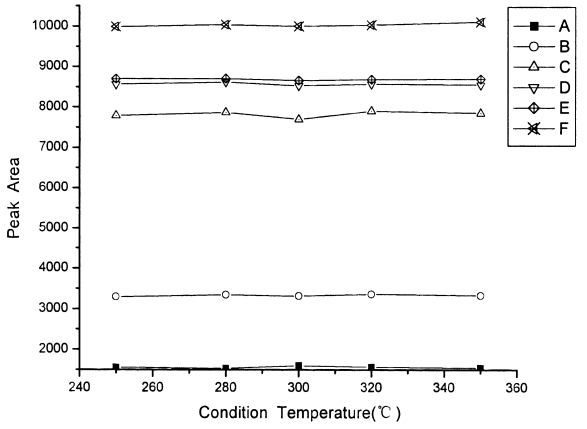



Fig. 3. The condition temperature profile of the 34 μm 10 mg DOH-B15C5 fiber for 10 μg/l BTEX compounds. Conditions: extraction temperature, 30 °C; extraction time, 2 min (stirring and saturated with NaCl); desorption time, 1 min. A = Benzene; B = toluene; C = ethylbenzene; D = *p*-xylene; E = *m*-xylene; F = *o*-xylene.

and 350 °C. This shows the high thermal stability of the fiber, even over 350 °C, but the maximum temperature of 100 μm PDMS is 280 °C. Such a high operating temperature is due to the strong adhesion of the coating to the substrate through chemical bonging. The high thermal stability of the DOH-B15C5 fiber also allows one to eliminate the sample carryover problem. Obviously, with the addition of benzo-crown ether, the thermal stability of the fiber coating was increased.

The solvent stability of the 67 μm 20 mg DOH-B15C5 fiber was studied (see Table 3). Table 3 illustrates that the extraction ability for three phenols had no obvious decrease after dipping in methylene chloride for 0, 1, 2, 4 h, respectively, the RSDs were less than 2.25%.

The life span of the 67 μm 20 mg DOH-B15C5 fiber was also evaluated (see Table 4). The fiber was used more than 150 times at 300 °C, the RSD was less than 3.83%, it was still stable and reusable (the commercial fiber can only be used for 50–100 times). Under microscopy, the surface of the coating is smooth and has no cracking phenomenon. Such a long life span and solvent stability are benefits from the strong chemical bonding between the sol–gel-generated organic–inorganic composite coating and the silica fiber surface.

### 3.4. Analysis of BTEX compounds

BTEX compounds are volatile organic compounds (VOCs) of great social and environmental significance, because they are hazardous to the human nervous system even at parts-per-billion concentrations. Benzene is classified as a human carcinogen and is a risk factor for leukemia and lymphomas

Table 3
Influence of solvent (methylene chloride) on the 67 μm 20 mg DOH-B15C5 fiber[a]

| Phenol | The mass absorbed of coating (peak area) | | | | |
|---|---|---|---|---|---|
| | 0 h | 1 h | 2 h | 4 h | RSD (%) |
| 2,6-Dimethylphenol | 5017 | 5002 | 5073 | 5134 | 1.19 |
| 2,4-Dichlorophenol | 11 102 | 10 682 | 10 987 | 11 214 | 2.09 |
| 2,4,6-Trichlorophenol | 24 145 | 22 981 | 24 078 | 23 752 | 2.25 |

[a] Conditions as in Table 2.

Table 4
Lifetime of the 67 μm 20 mg DOH-B15C5 fiber at 300 °C[a]

| Phenol | The mass absorbed of coating (peak area) | | | | |
|---|---|---|---|---|---|
| | 0 | 50th | 100th | 150th | RSD (%) |
| 2,6-Dimethylphenol | 5217 | 5059 | 5001 | 4975 | 2.14 |
| 2,4-Dichlorophenol | 11 762 | 11 247 | 11 023 | 10 987 | 3.17 |
| 2,4,6-Trichlorophenol | 25 147 | 24 561 | 24 279 | 22 954 | 3.83 |

[a] Conditions as in Table 2.

[28]. Therefore it is important to determine their concentration in the water. The 34 μm 10 mg sol–gel crown ether fiber was used to analyse BTEX compounds.

Fig. 4 is the chromatogram of BTEX compounds using the Supelcowax-10 capillary column. The six BTEX compounds could be well separated.

The extraction temperature profile is shown in Fig. 5. We can see that with increase of extraction temperature, the extraction quantities of all BTEX compounds tended to decrease. For efficiently controlling the stable temperature, we selected 30 °C as the extraction temperature for BTEX compounds.

Fig. 6 shows the extraction time profile of the DOH-B15C5 fiber for 10 μg/l BTEX compounds under agitated and saturated with salt sampling conditions at 30 °C temperature. The results indicate that the equilibration time is very short, approximately 90 s for all six BTEX compounds. Under the same conditions, the commercial 100 μm PDMS fiber needed several minutes to reach equilibration. The porous structure helps faster mass transfer during extraction, so the equilibration time is shorter. For the same advantage, the desorption time is very short. For all BTEX compounds, the desorption process can be completed within 60 s at 280 °C. Such a short extraction and desorption equilibration times result in a short analysis time.

According to above experiments, the analytical conditions for BTEX compounds with HS-SPME–GC are 2 min of extraction at 30 °C, 1 min desorption at 280 °C, the aqueous solution saturated with NaCl and constant stirring at 85% of maximum. Fig. 7 is the direct comparisons of different fibers under optimum conditions. From Fig. 7, we can see clearly that the sequence of extraction quantities is 34 μm 10 mg DOH-B15C5 > 30 μm blank > 30 μm PDMS. With the increase of crown ether, the extraction quantities are greatly enhanced. This could be explained by the fact that the phenyl in DOH-B15C5

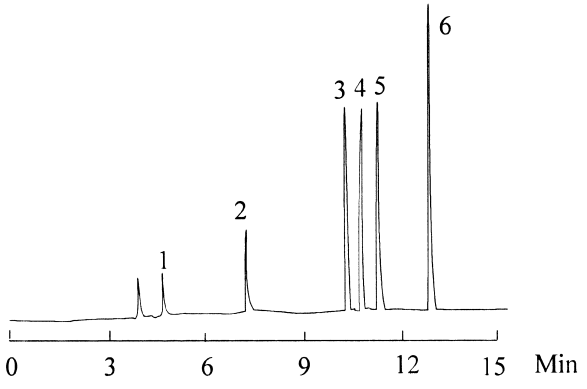



Fig. 4. The chromatogram of 10 μg/l BTEX compounds using the 34 μm 10 mg DOH-B15C5 fiber and HS-SPME–GC system. Conditions: extraction temperature, 30 °C; extraction time, 2 min (stirring and saturated with NaCl); desorption time, 1 min. 1 = Benzene; 2 = toluene; 3 = ethylbenzene; 4 = *p*-xylene; 5 = *m*-xylene; 6 = *o*-xylene.

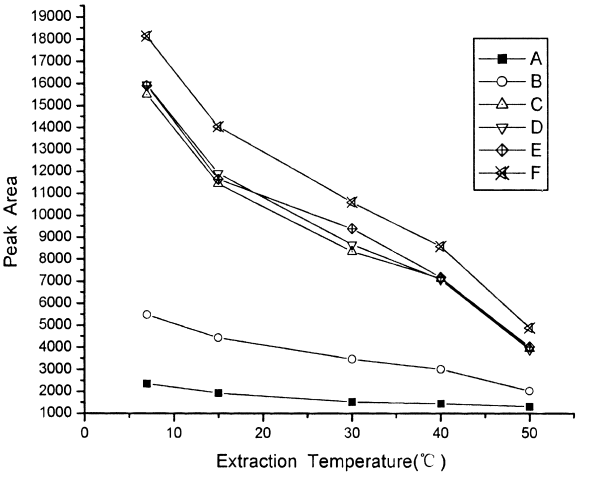



Fig. 5. The extraction temperature profile of the 34 μm 10 mg DOH-B15C5 fiber for 10 μg/l BTEX compounds. Conditions: extraction time, 2 min (stirring and saturated with NaCl); desorption time, 1 min. A = Benzene; B = toluene; C = ethylbenzene; D = *p*-xylene; E = *m*-xylene; F = *o*-xylene.

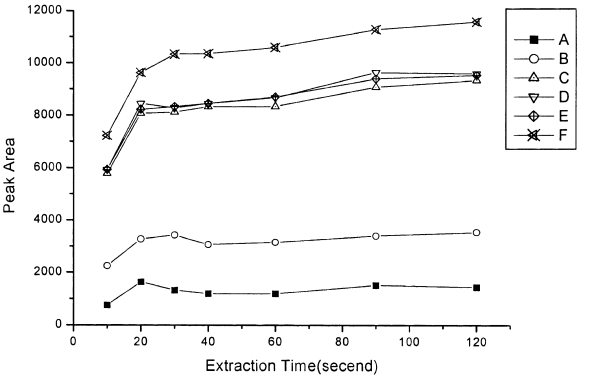



Fig. 6. The extraction time profile of the 34 μm 10 mg DOH-B15C5 fiber for 10 μg/l BTEX compounds. Conditions: extraction temperature, 30 °C; other conditions as in Fig. 5. A = Benzene; B = toluene; C = ethylbenzene; D = *p*-xylene; E = *m*-xylene; F = *o*-xylene.

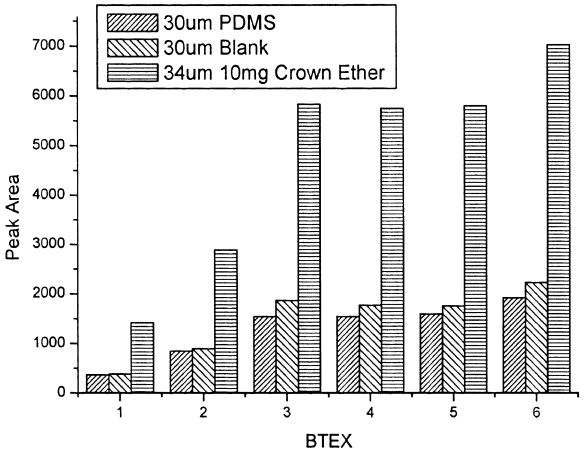



Fig. 7. The comparisons of extraction quantities using three different fibers for 10 μg/l BTEX compounds. Conditions as in Fig. 5. 1 = Benzene; 2 = toluene; 3 = ethylbenzene; 4 = *p*-xylene; 5 = *m*-xylene; 6 = *o*-xylene.

enhances π–π interaction with BTEX compounds, but PDMS does not.

Limits of detection (LODs), linearity and precision were studied (see Table 5). For all BTEX compounds, the LODs are between 0.01 and 0.05 μg/l. The linearity range of the compounds was 0.5 to 1000 μg/l. For the solution containing 10 μg/l of each of the BTEX compounds, the RSD was below 4%. These results show that the DOH-B15C5 fiber used in this study has a high extraction efficiency for non-polar BTEX compounds.

### *3.5. Analysis of phenols*

Phenolic compounds are a group of organic pollutants present in the environment as a result of various processes such as industrial, biogeochemical and as pesticide degradation products [29]. A number of phenolic compounds have been included in the legislation, so the analytical determination of phenol and its derivatives is very necessary. These compounds show a high polarity, and the 85 μm PA SPME fiber was available for the extraction of phenols [12]. The phenols have low Henry's law constant values. Most of the phenols could be forced into the headspace by decreasing their solubility in the aqueous phase through saturating with sodium chloride and acidifying to pH 1 with concentrated acid [12], to maintain the neutral form.

For this study, a standard 25-ml headspace vial with 15 ml of 0.1 mol/l HCl saturated with 5.6 g of NaCl was used. All samples were constantly stirred at 85% of the maximum stirring rate of the stirrer. The 67 μm 20 mg DOH-B15C5 fiber was used to analysis of phenolic compounds.

Extraction temperature has a double impact: at higher temperature, the extraction time is shorter; but the adsorbed quantities of compounds decrease. So, there is an optimal extraction temperature at which one can get ideal adsorbed quantities and rapid equilibrium time. From Fig. 8, we can see 40 °C is the optimum extraction temperature for phenols.

Fig. 9 shows the extraction time profile of the sol–gel CE fiber for 0.1 μg/ml phenols at 40 °C. It takes 40 min for all phenolic compounds except 2,4,6-trichlorophneol to reach equilibrium. The 2,4,6-trichlorophneol needs 60 min to reach equilibrium. The profile of desorption time for 0.1 μg/ml phenols at 300 °C in the injector was studied. A time of 2 min is necessary for all phenols.

From the above experiments, the analytical conditions for phenols with HS-SPME–GC are 40 min of extraction at 40 °C, 2 min of desorption at 300 °C,

Table 5
Limits of detection (LODs), linear ranges, correlation coefficients, and precisions for the analysis of BTEX compounds with HS-SPME–GC using the DOH-B15C5 fiber

| Compound | LOD[a] (μg/l) | Linear range (μg/l) | Correlation coefficient | RSD (%, $n=6$), 10 μg/l |
|---|---|---|---|---|
| Benzene | 0.05 | 0.5–$10^3$ | 0.9978 | 4.1 |
| Toluene | 0.02 | 0.2–$10^3$ | 0.9983 | 2.1 |
| Ethylbenzene | 0.01 | 0.1–$10^3$ | 0.9986 | 3.2 |
| *p*-Xylene | 0.01 | 0.1–$10^3$ | 0.9987 | 3.5 |
| *m*-Xylene | 0.01 | 0.1–$10^3$ | 0.9990 | 2.4 |
| *o*-Xylene | 0.01 | 0.1–$10^3$ | 0.9989 | 2.5 |

[a] Limit of detection (signal-to-noise = 3).

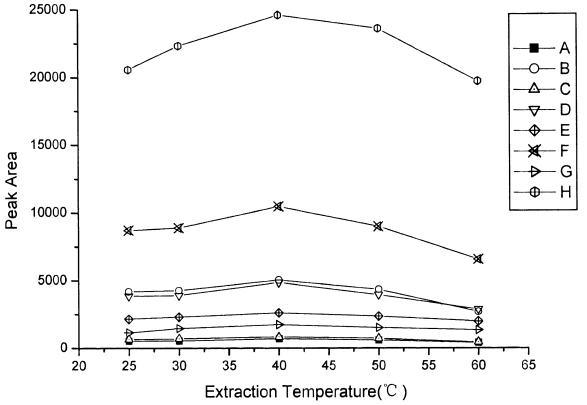



Fig. 8. The extraction temperature profile of the 67 μm 20 mg DOH-B15C5 fiber for 0.1 μg/ml phenols. Conditions: extraction time, 40 min; desorption time, 2 min. A = *m*-Cresol; B = 2,6-dimethylphenol; C = *o*-nitrophenol; D = 2,4-dimethylphenol; E = 3,5-dimethylphenol; F = 2,4-dichlorophenol; G = *p*-chlorophenol; H = 2,4,6-trichlorophenol.

the aqueous solution saturated with NaCl and acidified to pH 1 with HCl, and constant stirring at 85% maximum.

Fig. 10 shows the direct comparisons of different fibers under optimum conditions. The sequence of extraction quantities is 67 μm 20 mg DOH-B15C5 > 85 μm PA > 100 μm blank > 100 μm PDMS. The data in Fig. 10 show that the PDMS fiber was not suitable for all of the polar analytes studied. Although the sol–gel blank fiber is better than the PDMS fiber, the extraction quantities for phenols are

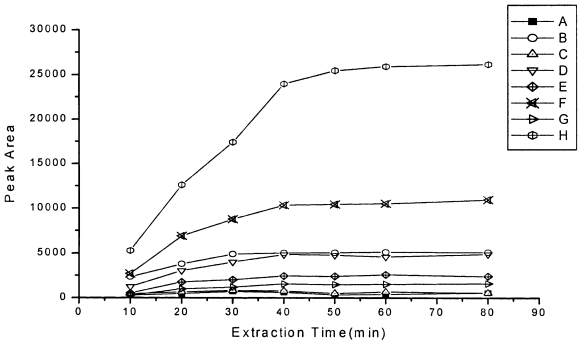



Fig. 9. The extraction time profile of the 67 μm 20 mg DOH-B15C5 fiber for 0.1 μg/ml phenols at 40 °C. Conditions as in Fig. 8. A = *m*-Cresol; B = 2,6-dimethylphenol; C = *o*-nitrophenol; D = 2,4-dimethylphenol; E = 3,5-dimethylphenol; F = 2,4-dichlorophenol; G = *p*-chlorophenol; H = 2,4,6-trichlorophenol.

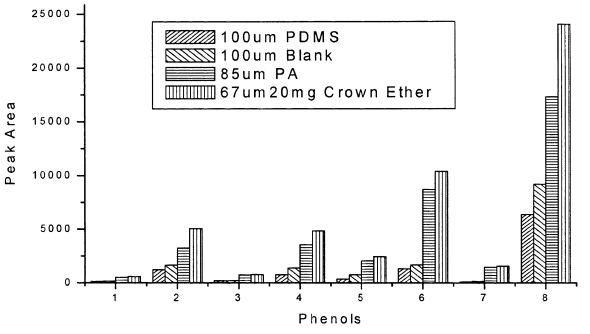



Fig. 10. The comparisons of extraction quantities using four different fibers for 0.1 μg/ml phenols compounds under optimum conditions. 1 = *m*-Cresol; 2 = 2,6-dimethylphenol; 3 = *o*-nitrophenol; 4 = 2,4-dimethylphenol; 5 = 3,5-dimethylphenol; 6 = 2,4-dichlorophenol; 7 = *p*-chlorophenol; 8 = 2,4,6-trichlorophenol.

still less. With the increase of DOH-B15C5, the extraction quantities increase much high, even exceed the PA fiber. There are some reasons for this good function: the three-dimensional network in the coating provides a higher surface area and sample

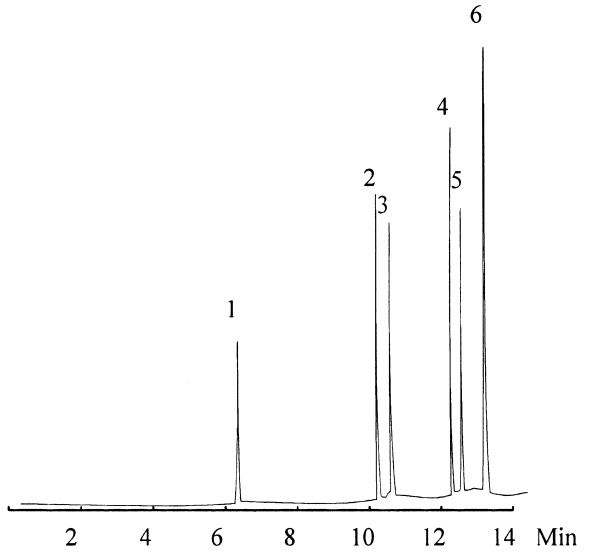



Fig. 11. SPME–GC–FID analysis of 0.01 μg/ml chlorobenzenes using the 67 μm 20 mg DOH-B15C fiber. Conditions: 50 °C for 5 min, then programmed at 5 °C/min to 90 °C, finally at 20 °C/min to 200 °C for 3 min; injection temperature, 250 °C; FID, 280 °C; extraction temperature, 30 °C; extraction time, 30 min (stirring and saturated with NaCl); desorption time at splitless mode, 2 min. 1, Chlorobenzene; 2, *o*-chlorotoluene; 3, *p*-chlorotoluene; 4, *m*-dichlorobenzene; 5, *o*-dichlorobenzene; 6, *p*-dichlorobenzene.

Table 6
Limits of detection (LODs), linear ranges, correlation coefficients, and precisions for the analysis of phenols with HS-SPME–GC using the DOH-B15C5 fiber

| Compound | LOD[a] (μg/l) | Linear range (μg/l) | Correlation coefficient | RSD (%, $n=6$), 0.1 mg/l |
|---|---|---|---|---|
| *m*-Cresol | 1 | 5–$10^3$ | 0.9991 | 3.4 |
| 2,6-Dimethylphenol | 0.25 | 1–$10^3$ | 0.9994 | 2.1 |
| *o*-Nitrophenol | 0.8 | 5–$10^3$ | 0.9992 | 4.1 |
| 2,4-Dimethylphenol | 0.25 | 1–$10^3$ | 0.9997 | 3.4 |
| 3,5-Dimethylphenol | 0.5 | 1–$10^3$ | 0.9992 | 4.2 |
| 2,4-Dichlorophenol | 0.1 | 0.5–$10^3$ | 0.9998 | 4.0 |
| *p*-Chlorophenol | 0.5 | 1–$10^3$ | 0.9994 | 3.1 |
| 2,4,6-Trichlorophenol | 0.05 | 0.1–$10^3$ | 0.9999 | 4.7 |

[a] Limit of detection (signal-to-noise = 3).

capacity, the crown ether increases hydrogen-bonding forces to phenolic compounds and the polarity of the coating, and the high thermal desorption temperature overcomes the sample carryover problem.

LODs, linearity and precision were also studied (see Table 6). For these phenols, LODs are between 0.05 and 1 μg/l. The linearity range of the compounds was 5–1000 μg/l. These results are better than the literature data [17,29–31]. The RSDs were less than 5%, which shows acceptable precision.

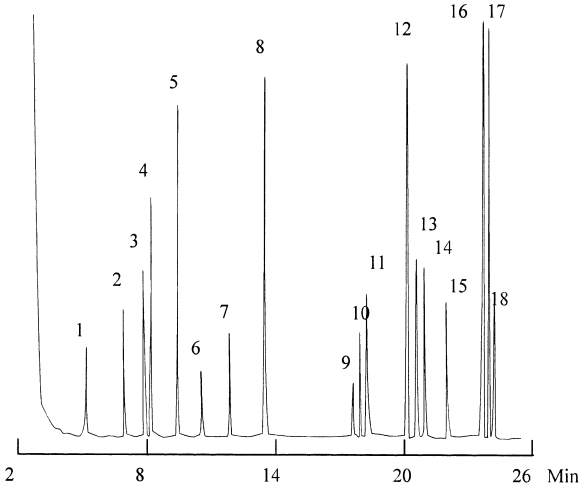



Fig. 12. SPME–GC–FID analysis of 1 μg/ml carcinogenic arylamines using the 67 μm 20 mg DOH-B15C5 fiber. Conditions: 60 °C for 1 min, programmed at 10 °C/min to 190 °C, then at 3 °C/min to 250 °C, finally at 10 °C/min to 260 °C for 8 min; injection temperature, 250 °C; FID, 290 °C; extraction temperature, 30 °C; extraction time, 30 min (stirring and no salt); desorption time at splitless mode, 2 min. 1, *o*-Toluidine; 2, *p*-chloroaniliane; 3, *p*-cresidine; 4, 4-chloro-*o*-toluidine; 5, 2,4-diaminetoluene; 6, 2,4-diaminoanisole; 7, 2-amino-4-nitrotoluene; 8, 4-aminodiphenyl; 9, 4,4′-oxydianiline; 10, benzidine; 11, 4,4′-diaminodiphenylmethane; 12, *o*-aminoazotoluene; 13, 3,3′-dimethyl-4,4′-diaminodiphenylmethane; 14, 3,3′-dimethylbenzidine; 15, 4,4′-thiodianiline; 16, 3,3′-dichorobenzidine; 17, 4,4′-methylene-bis(2-chloraniline); 18, 3,3′-dimethoxybenzidine.

### *3.6. Analysis of chlorobenzenes and carcinogenic arylamines*

In addition, we have used our 67 μm 20 mg DOH-B15C5 fiber to analyse six chlorobenzenes and 18 carcinogenic arylamines. Fig. 11 is the chromatogram of 0.01 μg/ml chlorobenzenes for the DOH-B15C5 fiber. A 25-ml headspace vial with 15 ml deionized water and 5 g NaCl were used. The fiber was exposed in the headspace of the vial at 30 °C for 30 min. Fig. 12 is the chromatogram of 1 μg/ml arylamines. A 25-ml headspace vial with 20 ml deionized water and no salt were used. The fiber was inserted the aqueous sample at 30 °C for 30 min. The two results above further illustrate that the DOH-B15C5 fiber shows sufficient selectivity for non-polar and polar aromatic compounds.

## 4. Conclusion

The structure of the new DOH-B15C5 is very suitable for the sol–gel technique because it has less steric hindrance and a good solubility in solution state. The coating method is improved and has low cost, the new sol–gel coated DOH-B15C5 fiber exhibits high solvent stability and longer application lifetime, thermal stability (≥350 °C), improved

selectivity and sensitivity towards different aromatic compounds (non-polar or polar). The porous structure increases the speed of extraction and desorption. The high thermal stability allows the use of high-injection temperatures for efficient desorption of less-volatile analytes, so a great number of less-volatile compounds can be analyzed by SPME–GC.

## Acknowledgements

This work was supported by the National Natural Science Foundation of China and the Research Fund for the Doctoral Program of Higher Education of China.

## References

[1] R.P. Belardi, J. Pawliszyn, Water Pollut. Res. J. Can. 24 (1989) 179.
[2] S. Li, S.G. Weber, Anal. Chem. 69 (1997) 1217.
[3] Y. Hirata, J. Pawliszyn, J. Microcol. Sep. 6 (1994) 443.
[4] A.M. Sheila, H.L. Said, C.T. David, J. Chromatogr. A 829 (1998) 377.
[5] R. Baciocchi, M. Attina, G. Lombardi, M.R. Boni, J. Chromatogr. A 911 (2001) 135.
[6] X.P. Lee, T. Kumazawa, K. Sato, O. Suzuki, Chromatographia 42 (1996) 135.
[7] E. Schimming, K. Levsen, C. Kohme, W. Schurmann, Fresenius J. Anal. Chem. 363 (1999) 88.
[8] M.R. Lee, Y.C. Yeh, W.S. Hsiang, C.C. Chen, J. Chromatogr. B 707 (1998) 91.
[9] V. Ignacio, C. Carolina, J. High Resolut. Chromatogr. 19 (1996) 472.
[10] L. Maria, P. Manuel, L. Pedro, C. Rafael, Anal. Chem. 73 (2001) 5858.
[11] G. Gmeiner, C. Krassnig, E. Schmid, H. Tausch, J. Chromatogr. B 705 (1998) 132.
[12] K.D. Buchholz, J. Pawliszyn, Anal. Chem. 66 (1994) 160.
[13] S. Magdic, A. Boyd-Boland, K. Jinno, J. Pawliszyn, J. Chromatogr. A 736 (1996) 219.
[14] A. Boyd-Boland, J. Pawliszyn, J. Chromatogr. A 704 (1995) 163.
[15] S.L. Chong, D. Wang, J.D. Hayes, B.W. Wilhite, A. Malik, Anal. Chem. 69 (1997) 3889.
[16] S. Bigham, J. Medlar, A. Kabir, C. Shende, A. Alli, A. Malik, Anal. Chem. 74 (2002) 752.
[17] Z.R. Zeng, W.L. Qiu, Z.F. Huang, Anal. Chem. 73 (2001) 2429.
[18] Z.Y. Wang, C.H. Xiao, C.Y. Wu, H.M. Han, J. Chromatogr. A 893 (2000) 157.
[19] J.X. Yu, L. Dong, C.Y. Wu, L. Wu, J. Xin, J. Chromatogr. A 978 (2002) 37.
[20] C.Y. Wu, C.M. Wang, Z.R. Zeng, X.R. Lu, Anal. Chem. 62 (1990) 968.
[21] C.Y. Wu, X.C. Zhou, Z.R. Zeng, X.R. Lu, L.F. Zhang, Anal. Chem. 63 (1991) 1874.
[22] C.Y. Wu, L.S. Cai, Y.J. Wang, H.M. Han, Z.R. Zeng, Z.Y. Yu, H. Yuan, Chromatographia 37 (1993) 374.
[23] J.L. Ge, R.N. Fu, Z.F. Huang, Y.T. Wang, J. Microcol. Sep. 3 (1991) 250.
[24] C.J. Pedersen, J. Am. Chem. Soc. 89 (1967) 7017.
[25] S.S. Prakash, C.J. Brinker, A.J. Hurd, S.M. Rao, Nature 374 (1995) 439.
[26] G.W. Scherer, J. Non-Cryst. Solids 100 (1988) 77.
[27] C.J. Brinker, G.W. Scherer, Sol–Gel Science. The Physics and Chemistry of Sol–Gel Processing, Academic Press, San Diego, CA, 1990.
[28] US Environmental Protection Agency, Carcinogenic Effects of Benzene: An Update, 1998; EPA/60/P-97/001F, US Government Printing Office, Washington, DC, 1998.
[29] E. Gonzalez-Toledo, M.D. Prat, M.F. Alpendurada, J. Chromatogr. A 923 (2001) 45.
[30] L. Wennrich, P. Popp, M. Moder, Anal. Chem. 72 (2000) 546.
[31] G. Ohlenbusch, M.U. Kumke, F.H. Frimmel, Sci. Total Environ. 253 (2000) 63.