ELSEVIER

Journal of Chromatography A, 934 (2001) 51–57

JOURNAL OF CHROMATOGRAPHY A

www.elsevier.com/locate/chroma

Solid-phase microextraction of monocyclic aromatic amines using novel fibers coated with crown ether

Zhaorui Zeng*, Wenli Qiu, Min Yang, Xuan Wei, Zaifu Huang, Fang Li

Department of Chemistry, Wuhan University, Wuhan, 430072, China

Received 5 April 2001; received in revised form 17 September 2001; accepted 17 September 2001

Abstract

Three solid-phase microextraction (SPME) fibers prepared by the sol–gel method, containing hydroxydibenzo-14-crown-4 (OH-DB14C4), dihydroxy-substituted saturated urushiol crown ether (DHSU14C4) and 3,5-dibutyl-unsymmetry-dibenzo-14-crown-4-dihydroxy crown ether (DBUD14C4), respectively, were evaluated for the determination of aromatic amine (aniline, *m*-toluidine, *N*,*N*-diethylaniline, *N*-ethyl-*m*-toluidine, 3,4-dimethylaniline). The sol–gel-derived hydroxy-dibenzo-14-crown-4-coated fiber has the best affinity for several aniline derivatives. Optimization was carried out for the determination of aromatic amines with SPME fibers. The linearity was from 0.11 to 29 μg/ml and detection limits varied from 0.17 to 0.98 ng/ml. Relative standard deviation ($n=5$) was found to be 3.23–6.20%. The coating proved to be very stable at high temperature (to 340°C) and in different solvents (organic and inorganic). The method was applied to the determination of aromatic amines in wastewater samples from a pharmaceutical factory.

Keywords: Solid-phase microextraction; Amines, aromatic; Crown ethers

1. Introduction

Sample pretreatment and preconcentration is generally required for the determination of trace organic pollutants. Solid-phase microextraction (SPME), as an alternative to solid-phase extraction and liquid–liquid extraction, is simple, sensitive, time-efficient and solvent-free [1]. The analytes are extracted on to the fibers from the liquid phase or the headspace above the sample, and then thermally desorbed in the injector of the gas chromatograph. In order to achieve higher selectivities for different kinds of compounds, various materials such as polydimethylsiloxane [2–5], polyacrylate [6–8], Carbowax–divinylbenzene [9,10], polyimide [11], Carbopack [12] and polypyrrole [13] have been used as the stationary phases of the fibers. However, all these stationary phases are normally deposited physically on the surface of the fused-silica rods, which may be responsible for the lower thermal and chemical stability of the fiber. Sol–gel coating technology can overcome this problem by providing efficient incorporation of organic components into the inorganic polymeric structure [14–16]. The coating porosity provided by the sol–gel method also enhances the surface area of the fibers and allows for

*Corresponding author. Fax: +86-27-8764-7617.
E-mail address: zrzeng@whu.edu.cn (Z. Zeng).

0021-9673/01/$ – see front matter
PII: S0021-9673(01)01303-6

the use of thinner coatings to achieve acceptable stationary-phase loading and sample capacity [17].

Crown ethers have been widely used as chromatographic stationary phases because of their good selectivity resulting from its cavity structure and the strong electronegative effect of heteroatoms on the crown ether ring [18–21].

The determination of aromatic amines is important because of their toxicity and carcinogenicity [22,23]. They have been analyzed by SPME with different fibers [24–27]. In the present study, three crown ethers containing hydroxyl groups were coated on to the fused-silica rods using sol–gel technology, and the fibers were investigated by extraction of aromatic amines from aqueous samples with headspace SPME.

2. Experimental

2.1. Apparatus

To mix various solution ingredients thoroughly, an Ultrasonator Model SY-1200 (Shengyuan, China) was used. A Model TGL-16C (Anting, China) centrifuge was used to separate the sol solution from the precipitate. The fused-silica rod (140 μm O.D.) with protective polyimide coating was provided by the Academy of Post and Telecommunication, Wuhan, China.

An SC-7 GC system equipped with a split injector and a flame ionization detection (FID) system was used. On-line data collection and processing was done on a Chromatopac Model SC1100 (Kangzhi, China).

A magnetic stirrer DF-101B (Leqing, China) was used for stirring the sample during extraction. A laboratory-made SPME syringe was used to transfer the extracted sample to the GC injector for analysis. The commercially available polydimethylsiloxane (PDMS, 100 μm) and Carbowax–divinylbenzene (CW–DVB, 65 μm) coated fibers for comparison were obtained from Supelco (Bellefonte, PA, USA).

2.2. Reagents

Hydroxy-terminated silicone oil (OH-TSO) was purchased from the Chengdu Center for Applied Research of Silicone, China. 3-(2-Cyclooxypropoxyl)-propyltrimethoxysilane (KH-560), tetraethoxysilane (TEOS) and poly(methylhydrosiloxane) (PMHS) were obtained from the Chemical Plant of Wuhan University. Hydroxy-terminated-dibenzo-14-crown-4 (OH-DB14C4) was synthesized by a previously reported method [28]. Dihydroxy-substituted saturated urushiol crown ether (DHSU14C4) and 3,5-dibutyl-unsymmetry-dibenzo-14-crown-4-dihydroxy crown ether (DBUD14C4) were obtained from the Department of Environment Science, Wuhan University, China.

Aniline (A), *m*-toluidine (MT), *N*,*N*-diethylaniline (NNDEA), *N*-ethyl-*m*-toluidine (NEMT) and 3,4-dimethylaniline (3,4DMA) were purchased from Shanghai Organic Reagent Plant, Shanghai, China.

2.3. GC conditions

The capillary column used was a sol–gel-derived hydroxydibenzo-14-crown-4 (OH-DB14C4) (10 m× 0.25 mm I.D., 0.25 μm film thickness) [21]. Nitrogen was used as the carrier gas at a linear velocity of 12–15 cm/s, split ratio is 80:1. Temperatures were maintained at 260°C for the injection port, 240°C for the detector and 140°C for the column.

2.4. Preparation of standard solution

A standard solution was prepared by transferring 10 mg of each compound in a volumetric flask and diluting with acetonitrite to 10 ml at room temperature.

2.5. Solid-phase microextraction procedure

To prevent the polar analytes from being extracted on to the glass wall, the amber vials were acid washed and silanized prior to the experiments. For all analyses, a 20-μl aliquot of the standard solution and 10 ml of pH 13 NaOH solution saturated with NaCl were mixed in a 15-ml amber vial to give an aqueous solution of 2 μg/ml aromatic amines. The vials were enclosed with the caps wrapped with PTFE sealing tape after a magnet was added. During magnetic stirring, the fiber was immersed into the headspace for a period of time and then placed into

the injection of gas chromatography for thermal desorption for 7 min.

2.6. Fiber preparation

Prior to sol–gel coating, the optical fiber was dipped in acetone for 3 h to remove the protective polyimide layer, in a 1 *M* NaOH solution for 1 h to expose the maximum number of silanol groups on the surface, cleaned with water and dipped in 0.1 *M* of HCl for 30 min to neutralize the excessive NaOH, cleaned again, and dried.

OH-DB14C4 (8 mg), 90 mg OH-TSO, 10 mg PMHS, 100 μl TEOS, and 50 μl KH-560 were dissolved in 100 μl of methylene chloride. A 100-μl aliquot of TFA containing 5% water was sequentially added to the resulting solution with ultrasonic agitation for 5 min and centrifuged at 12 000 rpm for another 5 min. A sol–gel coating was formed on the outer surface of the fused-silica rod end (1 cm), after the fibers were dipped vertically into the sol–gel solution for 30 min. For each fiber, this coating process was repeated several times using a freshly prepared sol solution until the desired thickness of the coating was obtained. The fibers were placed in a desiccator for 12 h at room temperature and then conditioned at 250–350°C in nitrogen for 3 h in the GC injection port. The final thickness of the fiber was 65 μm.

Other fibers of the crown ether preparation were identical with that of the sol–gel-derived OH-DB14C4/OH-TSO-coated fiber except that the mass of DHSU14C4 and DBUD14C4 were 10 mg, and the final thickness 70 μm. The sol–gel-derived OH-DB14C4-coated fiber with no OH-TSO added and the sol–gel-derived OH-TSO-coated fiber with no OH-DB14C4 added were also prepared, and the thicknesses of these fibers were 65 and 67 μm, respectively.

2.7. IR experiment

IR spectra of the stationary phases rinsed with methylene chloride were used. For measuring the IR spectrum, the coatings of the fiber were ground and blended with potassium bromide.

3. Results and discussion

In sol–gel chemistry, a gel can be formed by the simultaneous hydrolysis and polycondensation of an organometallic precursor followed by aging and drying under ambient atmosphere [29]. Characterized by the interactions of hydroxyl groups in all steps, crown ether containing hydroxyl groups can be chemically bonded with other components by ring-opening polymerization with KH-560. Three hydroxy-terminated crown ethers, OH-DB14C4 (Fig. 1A), DHSU14C4 (Fig. 1B), and DBUD14C4 (Fig. 1C) were used.

Fig. 2 shows the IR spectra of pure hydroxy-dibenzo-14-crown-4 (OH-DB14C4), sol–gel-derived crown ether stationary phases (OH-DB14C4/OH-TSO) and sol–gel-derived OH-TSO stationary phase (OH-TSO). The feature identified by dibenzo crown ether: 1251.45 cm^{-1} (Ar–O–C) also appeared in OH-DB14C4/OH-TSO. However, the decrease in hydroxy group peak in OH-DB14C4 shows it has been chemically bonded with other components.

In general, the extraction efficiency declines with the number of analyses due to the high temperature

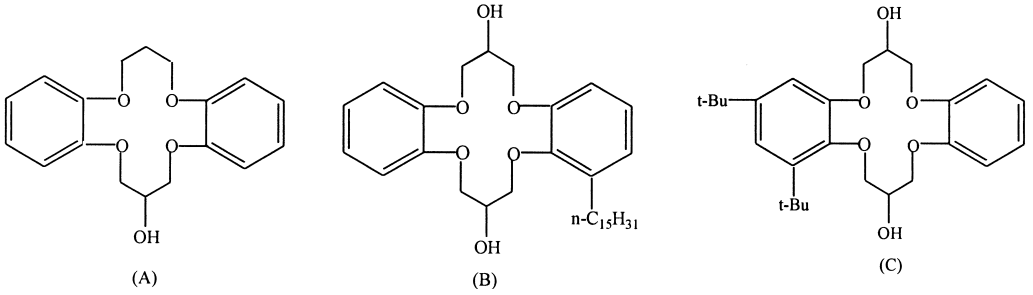

Fig. 1. Structures of (A) OH-DB14C4, (B) DHSU14C4, (C) DBUD14C4.

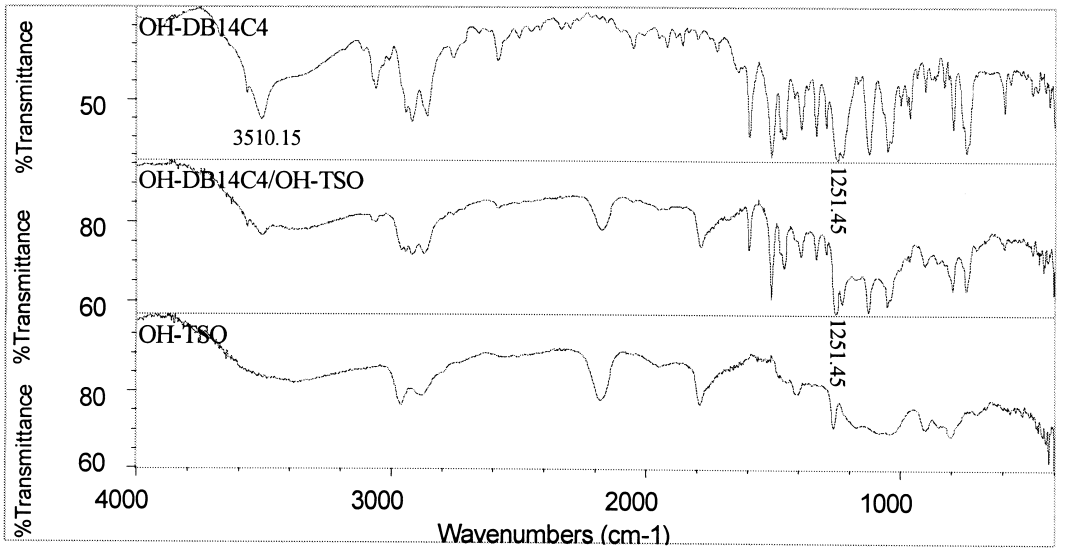

Fig. 2. IR spectra of coatings OH-DB14C4, OH-DB14C4/OH-TSO, and OH-TSO.

and solvent. As a result of sol–gel coating technology, the stronger chemical binding between the coating and the fiber surface can enhance the thermal and chemical stability of the fiber. Sol–gel-derived OH-DB14C4 fiber can withstand higher temperature to 340°C without loss of extraction efficiency and can be dipped in water for 5 h with minor loss of extraction efficiency. The average lifetime of the fiber was 150 uses.

In headspace SPME, analytes extracted by the polymeric coating are related to the overall equilibrium of the analytes in the three-phase system: a polymeric, a headspace, and an aqueous solution. In general, the amounts of the analytes extracted by the polymeric coatings of fibers in headspace SPME are dependent on several factors such as the selectivity of the coating, the extraction time, the extraction temperature, pH value and the ionic strength of the matrix.

The amount of an analyte should not affect its distribution ratios among the three phases when equilibrium is achieved. Fig. 3 shows that the extraction time for reaching equilibrium between all the aromatic amines is only 40 min, a time considerably shorter than that required for conventional techniques because of the faster mass transfer of analytes in the gel structure.

Fig. 4 represents the extraction temperature profiles for the aromatic amines in the mixture. It is shown that the extraction ability of the fiber increased with temperatures lower than 55°C, but decreases significantly above 55°C. Extraction ability is mainly controlled by two factors, distribution velocity and partition coefficient. The distribution velocity, which helps analytes to enter the gas phase and solid-phase coating, increases with increased temperature. Extraction is an exothermic process and

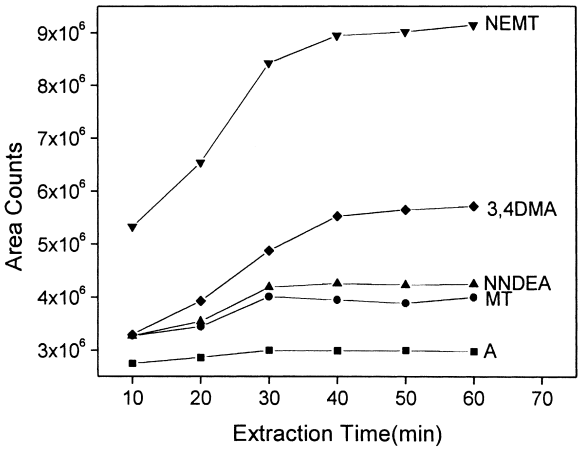

Fig. 3. Effect of extraction time on the signal intensity of aromatic amines. Extraction temperature, 20°C (room temperature); desorption time: 5 min; pH 7; constant stirring.

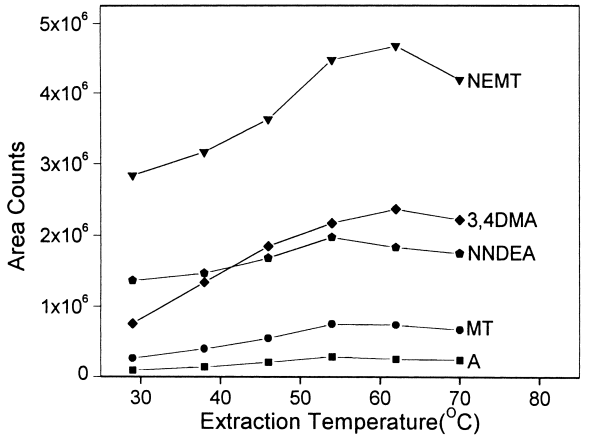

Fig. 4. Influence of extraction temperature on the signal intensity of aromatic amines. Extraction time: 40 min; desorption time: 5 min; pH 7; constant stirring.

the partition coefficient, which determines the ratio of analytes extracted, is inversely related to temperature. The first factor is dominant in the range below 55°C, while the second factor becomes dominant above 55°C.

Adding salt to the matrix and/or adjusting pH values of the matrix can decrease the solubility of the analytes in water and increase their extraction efficiencies [6]. In this experiment, more aromatic anilines can be extracted at higher pH (pH 13).

In Fig. 5, a comparison is given of the extraction efficiencies of sol–gel-derived OH-DB14C4/OH-TSO-, DHSU14C4/OH-TSO-, DBUD14C4/OH-TSO-, OH-TSO- and OH-DB14C4-coated fibers. Sol–gel-derived OH-DB14C4 fiber, which has no OH-TSO in the coating, has the lowest extraction efficiencies, because OH-TSO lengthens the chain of the network leading to a larger porous structure and increased surface area of the fiber and helps the stationary phase spread on the glass surface uniformly. Therefore, it keeps the coating from shrinking during the formation of gel and from cracking on the surface of the fiber. On the other hand, all the crown ether-coated fibers containing OH-TSO have higher extraction efficiencies compared with OH-TSO-coated fibers due to higher selectivity of the crown ethers for polar compounds. Among the three crown ether fibers, extraction efficiencies decreased with increasing number of alkyl groups (*n*-pentadecyl, *tert.*-butyl) on the crown ether ring attributed to the decreased polarity of the fibers and the increased steric hindrance.

Fig. 6 compares the extraction efficiencies of sol–gel-derived OH-DB14C4/OH-TSO-coated fiber with PDMS- and CW–DVB-coated fibers. According to the principle of 'like dissolves like', polar aromatic amines have higher affinities for the polar coating than that for the non-polar coating, therefore, more aromatic amines are extracted by polar CW–DVB- and sol–gel-derived OH-DB14C4/OH-TSO coatings than that by non-polar PDMS coating. At the same

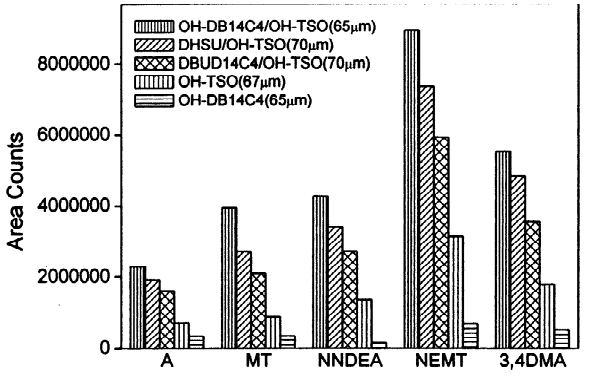

Fig. 5. Coating evaluation for the extraction of monocyclic aromatic amines with sol–gel-derived (1) OH-DB14C4/OH-TSO-, (2) DHSU14C4/OH-TSO-, (3) DBUD14C4/OH-TSO-, OH-TSO-, OH-DB14C4-coated fibers. Extraction time, 40 min; extraction temperature, 55°C; desorption time: 5 min; pH 13; constant stirring.

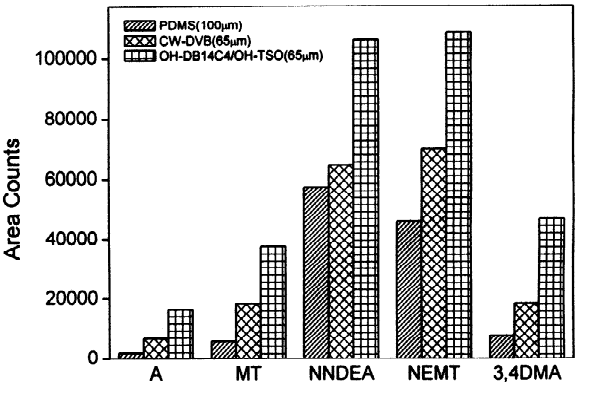

Fig. 6. Coating evaluation for the extraction of monocyclic aromatic amines with PDMS-, CW–DVB-, sol–gel-derived OH-DB14C4/OH-TSO-coated fibers. SPME–GC conditions as in Fig. 5.

Table 1
Linear ranges, detection limits and precision of anilines (n=5)

Compound	RSD (%)	LOD (ng/ml)	Linear range (μg/ml)
A	3.23	0.96	0.13–20.7
MT	6.12	0.98	0.11–25.9
NNDEL	5.20	0.23	0.14–20.1
NEML	6.20	0.17	0.16–23.3
3,4DMA	4.82	0.27	0.20–29.1

time, the three-dimensional network in the coating structure provides a higher surface area and sample capacity for sol–gel-derived OH-DB14C4/OH-TSO fiber, which exhibits higher extraction efficiencies for aromatic amines than that for CW–DVB fiber.

Table 1 summarizes the limits of detection (LODs), relative standard deviations (RSDs), and linear ranges for the extraction of aromatic amines using the sol–gel-derived OH-DB14C4/OH-TSO-coated fiber. The LODs were estimated by the concentrations of the aromatic amines that produce signals three times the background noise. It can be seen that LODs were from 0.17 to 0.98 ng/ml for all the aromatic amines. The RSD values were between 3.23 and 6.20% (n=5) for all aromatic amines examined. The linear ranges were from 0.1 to 29 μg/ml for all of the aromatic amines tested.

A wastewater sample from a pharmaceutical factory was detected and the results were found to contain 0.7 μg/ml of aniline and 0.3 μg/ml of 3,4-dimethylaniline by the SPME technique and the recoveries of an added 0.3 μg/ml of each compound were 90.4 and 86.6%, respectively.

4. Conclusions

The three SPME fibers, OH-DB14C4/OH-TSO, DHSU14C4/OH-TSO and DBUD/OH-TSO in this work, were prepared by a sol–gel method and investigated with five aromatic amines. They exhibit high thermal stability (to 340°C) and solvent stability. The sol–gel-derived hydroxydibenzo-14-crown-4-coated fiber has the best affinity for several aromatic amine derivatives. The extraction ability shows no significant decline after it has been used 150 times. The fiber was applied to analyze wastewater samples from a pharmaceutical factory. The characteristics of the novel fibers will widen their application range.

Acknowledgements

This work was kindly supported by the Nature Science Foundation of Hubei Province (Grant No: 2000J010) and the Science Committee of Wuhan (Grant No: 996005132), Wuhan, Hubei, China.

References

[1] R.P. Belardi, J. Pawliszyn, Water Pollut. Res. J. Can. 24 (1989) 179.
[2] C.L. Arthur, L.M. Killam, K.D. Buchholz, J. Pawliszyn, J.R. Berg, Anal. Chem. 64 (1992) 1960.
[3] B. Larsen, S. Facchetti, J. Madsen, J. Agric. Food Chem. 43 (1995) 2138.
[4] R. Young, V. Lopez-Avila, W.F. Beckert, J. High Resolut. Chromatogr. 19 (1996) 247.
[5] J.Y. Horng, S.D. Huang, J. Chromatogr. A 678 (1994) 313.
[6] K.D. Buchholz, J. Pawliszyn, Anal. Chem. 66 (1994) 160.
[7] A.A. Boyd-Boland, J.B. Pawliszyn, J. Chromatogr. A 704 (1995) 163.
[8] H. Verhoeven, T. Beuerle, W. Schwab, Chromatography 46 (1997) 63.
[9] T.J. Clark, J.E. Bunch, J. Chromatogr. Sci. 35 (1997) 209.
[10] B.J. Hall, J.S. Brodbelt, J. Chromatogr. A 777 (1997) 275.
[11] C.L. Arthur, J. Pawliszyn, Anal. Chem. 62 (1990) 2145.
[12] D.W. Potter, J. Pawliszyn, Environ. Sci. Technol. 28 (1994) 298.
[13] J. Wu, J. Pawliszyn, J. Chromatogr. A 909 (2001) 37.
[14] D. Wang, S.L. Chong, A. Malik, Anal. Chem. 69 (1997) 4566.
[15] Y. Guo, L.A. Colón, Anal. Chem. 67 (1995) 2511.
[16] J.D. Hayes, A. Malik, J. Chromatogr. B 695 (1997) 3.
[17] S.L. Chong, D. Wang, J.D. Hayes, B.W. Wilhite, A. Malik, Anal. Chem. 69 (1997) 3889.
[18] Z.R. Zeng, C.Y. Wu, X.H. Fang, Z.F. Huang, Y.T. Wang, J. Chromatogr. 589 (1992) 368.
[19] Z.R. Zeng, C.Y. Wu, H. Yan, Z.F. Huang, Y.T. Wang, Chromatography 34 (1992) 85.
[20] C.Y. Wu, C.M. Wang, Z.R. Zeng, X.R. Lu, Anal. Chem. 62 (1990) 968.
[21] Z. Zeng, W. Qiu, H. Xing, Z. Huang, Anal. Sci. 8 (2000) 851.
[22] S. Laha, R.C. Luthy, Environ. Sci. Technol. 24 (1990) 363.
[23] M. Dalene, G. Skarping, J. Chromatogr. 331 (1985) 321.
[24] A. Fromberg, T. Nilsson, B.R. Larsen, L. Montanarella, S. Facchetti, J.Ø. Madsen, J. Chromatogr. A 746 (1996) 71.

[25] S.D. Huang, C.P. Cheng, Y.H. Sung, Anal. Chim. Acta 343 (1997) 101.
[26] L.S. DeBruin, P.D. Josephy, J. Pawliszyn, Anal. Chem. 70 (1998) 1986.
[27] W.H.J. Vaes, E.U. Ramos, H.J.M. Verhaar, W. Seinen, J.L.M. Hermens, Anal. Chem. 68 (1996) 4463.
[28] Y.T. Wang, J.J. Zhou, H.J. Wan, Z.S. Xie, Z.F. Huang, Chem. J. Chin. Univ. 11 (1990) 1292.
[29] J. Fricke, R. Caps, In: J.D. Mackenzie, D.R. Ulrich (Eds.), Ultrastructure Processing of Advanced Ceramics, Wiley, New York, 1988.