

Short communication

Preparation of polyaniline coating on a stainless-steel wire using electroplating and its application to the determination of six aromatic amines using headspace solid-phase microextraction

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Abstract

A novel polyaniline (PANI) coating was prepared on a stainless-steel wire for solid-phase microextraction by electroplating method. For better mechanical strength, the stainless-steel wire was used instead of the fused silica fiber. The electroplating method had advantages of ease of preparation and simple equipments. The PANI fiber was evaluated by analyzing six aromatic amines (aniline, *N,N*-dimethylaniline, *m*-methylaniline, 2,4-dimethylaniline, 2-chloroaniline, 3,4-dichloroaniline) in water. After the analytical procedure was optimized, the linearity was from 4.8 to $2.75 \times 10^4 \mu\text{g L}^{-1}$ and the detection limits was from 0.019 to $1.06 \mu\text{g L}^{-1}$. Relative standard deviations were found to be 2.02–6.00%. Good recoveries were obtained when wastewater samples were analyzed.

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Keywords: Metallic wires; Electroplating; Fiber preparation; Polyaniline; Aromatic amines; Solid-phase microextraction

1. Introduction

Since solid-phase microextraction (SPME) was developed by Pawliszyn and his coworkers in the last decade [1,2]. It has become an attractive alternative to common sampling techniques and gained a widespread acceptance in many areas [3].

To date, several commercial and custom-made SPME fibers have been used in the extraction of trace amount of organic pollutants from different matrixes. Some of these coating materials, such as poly(dimethylsiloxane) (PDMS) [4–9], have been widely used for non-polar and less polar compounds. Other materials like polyacrylate (PA) [10–12], poly(dimethylsiloxane)–divinylbenzene (PDMS/DVB) [13], carbowax–divinylbenzene (CW/DVB) [14,15], carbowax–TR (template resin–DVB with uniform

pore sizes) [16], carboxen–PDMS [17,18], graphite [19], activated charcoal [20], Nafion [21], polymeric fullerene [22], C8-coating [23], molecularly imprinted polymers [24] were also developed to extract special compounds.

Silica fibers are fragile and must be handled with great care. So, more robust SPME fibers with a long life and relative low cost are highly desired. Along this line, Lee and co-workers [25,26] fixed bonded silica particles on metal bars using high-temperature-resistant adhesive. Djozan et al. [27,28] prepared modified copper wire and anodized aluminum wire as SPME fibers. By an electrochemical method, polypyrrole (PPY) and poly-*N*-phenylpyrrole (PPPY) were coated on the surface of metal wires to extract anions and volatile organics by Pawliszyn and co-workers [29–32]. Preparation of conducting polymers coating on metal wires by electrochemical or chemical method is very attractive and will broaden the application of SPME.

According to the principle of “like dissolves like”, the polar compounds are more likely to be extracted by polar coatings. So, the polyaniline coating is expected to efficiently

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extract compounds, such as aniline and its substituted derivatives, which are generally considered as environmental pollutants because of their toxicity and carcinogenicity [33]. In the present study, a new polyaniline (PANI) coated stainless-steel wires fiber was developed. The performance of PANI fiber was evaluated by the determination of six aromatic amines in aqueous samples using headspace SPME process coupled with GC–FID.

2. Experimental

2.1. Reagents

Standard solutions of aniline (A) (99.8%), *N,N*-dimethylaniline (NNDA) (99%), *m*-methylaniline (MA) (99%), 2,4-dimethylaniline (DMA) (99%), 2-chloroaniline (CA) (+98%), 3,4-dichloroaniline (DCA) (98%) were purchased from Acros Organics (NJ, USA). The HPLC grade acetonitrile used as solvent was also obtained from Acros Organics. Stock solutions of aromatic amines (2 mg mL⁻¹) were prepared using acetonitrile as solvent. Working solutions were obtained by gradually diluting the stock solution using de-ionized water before measurement. All the solutions were stored at 4 °C in the dark. Glassware was washed by liquid detergent and then rinsed with tap water three times with de-ionized water, to prevent the polar analytes from being absorbed onto the glass wall.

2.2. Apparatus

An Agilent HP-6890N GC system (Agilent Technologies, DE, USA) equipped with a split injector and a flame ionization detection (FID) system was used, on-line data collection and processing were done on a HP Chemstation (Agilent Technologies, DE, USA). The GC capillary column (SP-2250, 30 m × 20 μm × 0.32 mm) was purchased from Supelco (Bellefonte, PA, USA). For good resolution of all six aromatic amines, the oven temperature was initially held at 50 °C, programmed at 50 °C min⁻¹ to the temperature of 100 °C, held for 3 min, then programmed at 5 °C min⁻¹ to the last temperature of 150 °C for 1 min. The injector and detector temperature were set at 250 and 280 °C, respectively. High purity nitrogen (99.99%) was used as the carrier gas and column head pressure was kept at 11.26 psi. Hydrogen and air were maintained at flow rates of 30 and 300 mL min⁻¹, respectively. Nitrogen (99.99%) was used as make-up gas at a flow rate of 30 mL min⁻¹. A SPME holder was purchased from Supelco (Bellefonte, PA, USA). A magnetic stirrer with heater (Huifeng Electrical Instrument Factory, Shanghai, China) was used to stir and heat the sample during the optimization of extraction procedure.

2.3. Preparation of SPME fiber

The diameter of the steel wire was 80 μm, measured by electronical microscope (Olympus Model BX41TF, Olympus

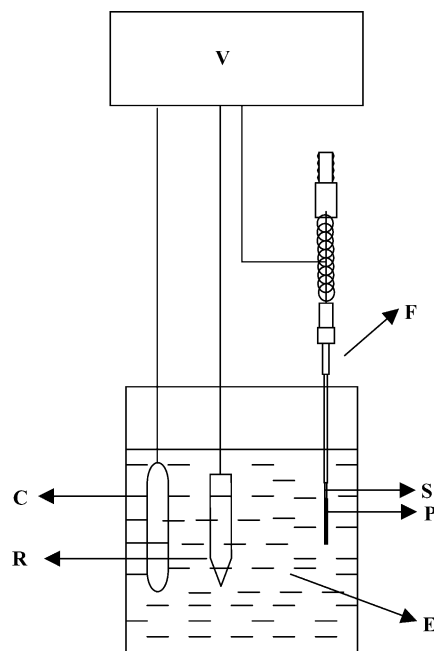


Fig. 1. The schematic diagram of electroplating of PANI (C: counter electrode, R: reference electrode, E: electrolyte, S: stainless wire, P: polyaniline coating, F: SPME fiber, also work electrode, V: electrochemstation, or potentiostat).

Corporation, Tokyo, Japan) and then polished by abrasive paper. For good repetition of coating, a CHI Electrochemstation (CHI Instru, TX, USA) was used to control the electroplate process (Fig. 1). Electrochemical polymerization was performed by a three-electrode system. The polished stainless-steel wire was used as the working electrode and the platinum electrode was utilized as the counter electrode. A calomel electrode was employed as the reference electrode. The electrolyte was composed of 0.5 mol L⁻¹ H₂SO₄ solution containing 0.025 mol L⁻¹ aniline monomer (redistilled before use). A constant deposition potential (0.8 V) was controlled by CHI chemstation. The electroplate process was repeated three times and controlled for 4 h each time. A black polymer film was formed on the surface. It was subsequently washed with de-ionized water, then with methanol or acetone for 3 min and dried under nitrogen protection at room temperature. Finally, it was conditioned at 250 °C for 30 min in the GC injector before use.

2.4. SEM and IR experiment

The surface texture of fiber types was studied by JEOL scanning electron microscopic (SEM) photography (JSM-6700F, Japan). The IR (Bruker, EQ55, Germany) experiment was carried out to confirm the formation of phenyl–*N*–phenyl bond as a result of electrochemical polymerization.

2.5. Experimental procedure

The new PANI fiber was used to extract six aromatic amines using headspace SPME technique for evaluating

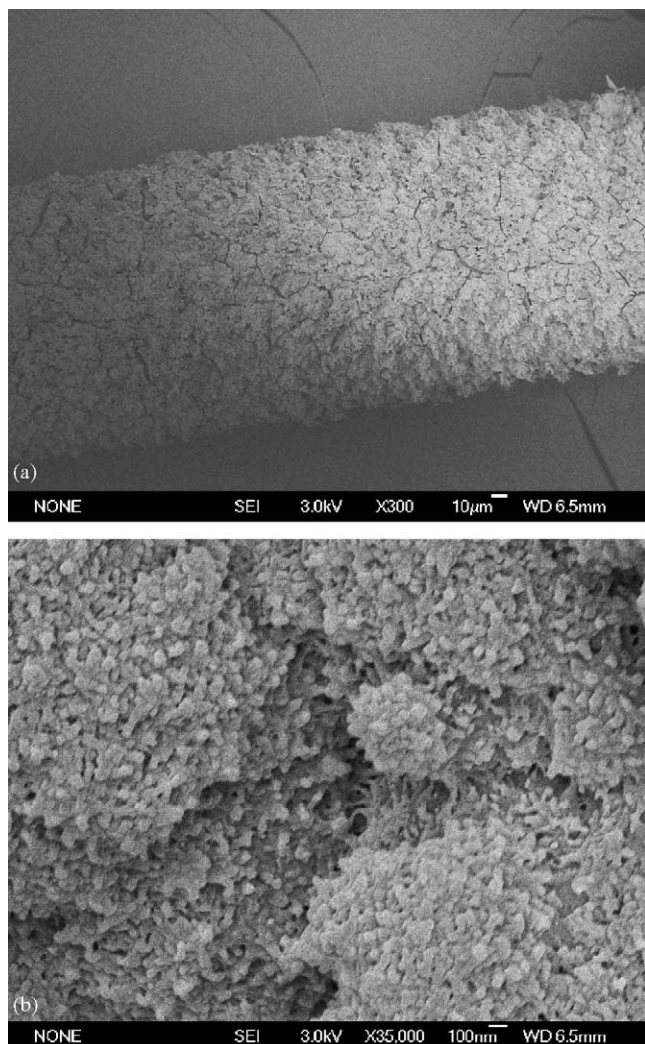


Fig. 2. The SEM photography of the PANI fiber: (a) the panorama of the fiber and (b) the amplified part of the fiber.

its performance. Briefly, 10 mL water solution containing $2 \mu\text{g mL}^{-1}$ of aromatic amines was extracted by the headspace exposed fiber in a sealed 150 mL conical flask under stirring. After extraction, the fiber was transferred to the GC port for analytes desorption and further analysis. Several key factors, including extraction time, desorption time, extraction temperature and desorption temperature, NaCl concentration and pH value of the aqueous samples, were optimized. The fiber was conditioned at 250°C for 10 min to remove the carryover on the fiber between each two extraction.

3. Result and discussion

3.1. Fiber properties

Fig. 2 is the SEM photography of the PANI fiber surface. It is obvious that the surface is rough and apertures with

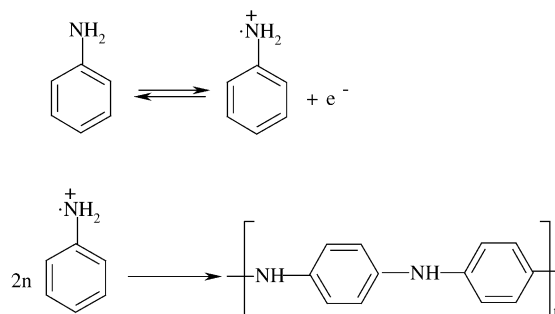


Fig. 3. The mechanism of the oxidative polymerization of polyaniline.

different depth exist. The coating thickness is about $50 \mu\text{m}$. Apparently, this special rough surface of the fiber greatly increased the total contact area with the analytes. Fig. 3 shows the mechanism of the oxidative polymerization of polyaniline. Normally aniline has two absorption bands for N–H vibration in $3500\text{--}3200 \text{ cm}^{-1}$. After the aniline is polymerized, N–H vibration only showed one absorb band at 3433 cm^{-1} (Fig. 4). The IR spectrum shows that the phenyl–N–phenyl bond formed during the electrochemical polymerization.

3.2. Optimization of experimental procedure

Repeatability and sensitivity of the SPME method highly depends on the status of an analyte distribution between the headspace and the polymeric phase. All of these experimental procedures were repeated twice. Figs. 5–8 show the average values of two replicates and error bars indicating the range of the two data points. And because the shapes of all chromatograms are good and very symmetrical, we use the peak height as the y-axis.

The extraction time affects the achievement of the equilibrium and was studied. Ten milliliters of standard water solutions ($20 \mu\text{g mL}^{-1}$) were extracted at room temperature ($\sim 15^\circ\text{C}$) under stirring for a series of the exposure time from 5 to 120 min. The peak heights of each compound were plotted with the corresponding extraction time (Fig. 5). The peak

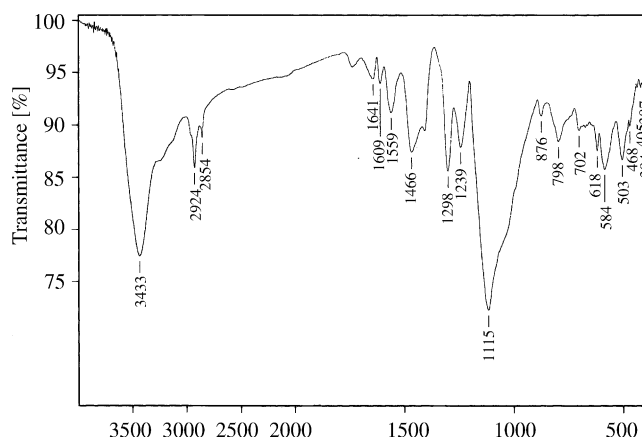


Fig. 4. The IR spectrum of the coating on the PANI fiber.

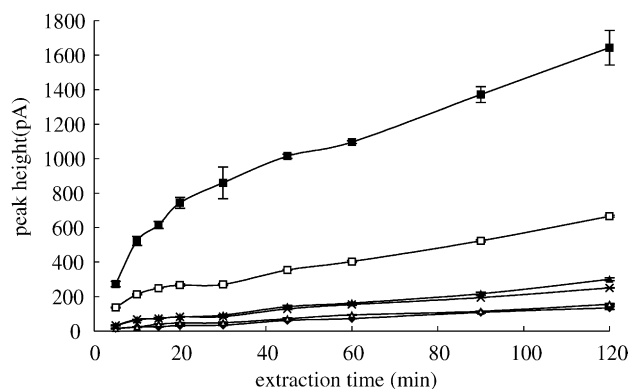


Fig. 5. The effect of the extraction time: (◆) aniline; (■) *N,N*-dimethylaniline; (△) *m*-methylaniline; (×) 2,4-dimethylaniline; (▲) 2-chloroaniline; (□) 3,4-dichloroaniline.

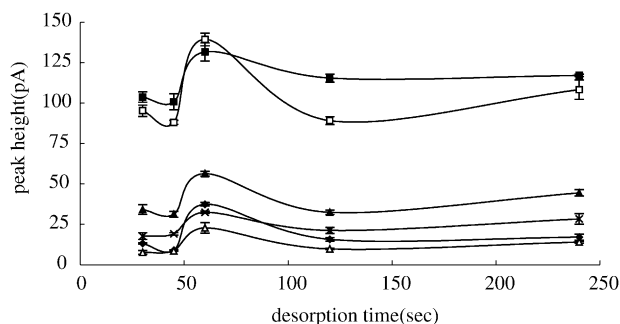


Fig. 6. The effect of desorption time: (◆) aniline; (■) *N,N*-dimethylaniline; (△) *m*-methylaniline; (×) 2,4-dimethylaniline; (▲) 2-chloroaniline; (□) 3,4-dichloroaniline.

heights increased with the length of the extraction time. However, this increase was quite small except for the first 15 min in the case of *N,N*-dimethylaniline. For routine rapid analysis, a 20 min extraction was sufficient if constant operation conditions were maintained.

Desorption time determines how fast an analyte is completely released to GC system. This can not only seriously improve the sensitivity of the analytical method, but also decrease the carryover. This parameter was thus studied by

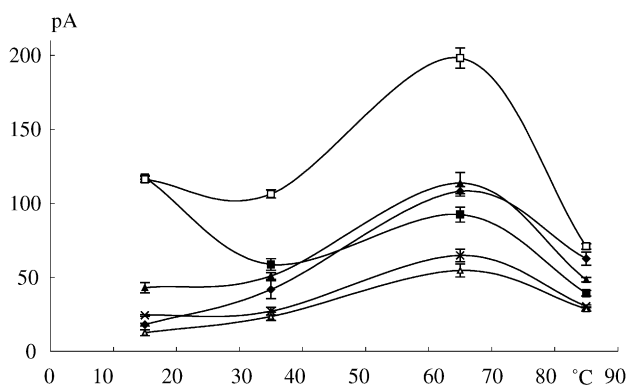


Fig. 7. The effect of extraction temperature: (◆) aniline; (■) *N,N*-dimethylaniline; (△) *m*-methylaniline; (×) 2,4-dimethylaniline; (▲) 2-chloroaniline; (□) 3,4-dichloroaniline.

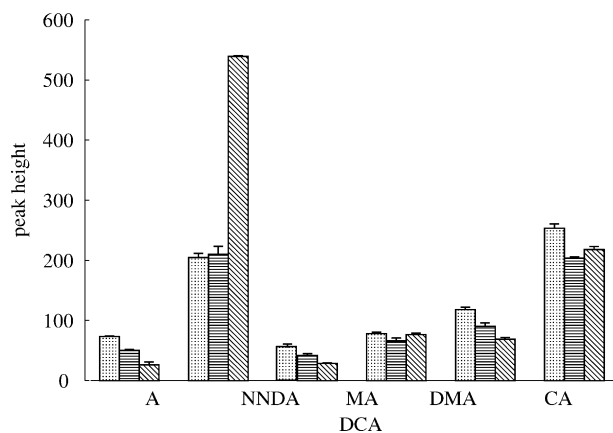


Fig. 8. The effect of salt and pH. (Dotted bars) No salt and no base; (horizontal bars) addition of base but no salt; (rhombic bars) addition of salt but no base.

a similar experimental procedure as described above. This time, a lower analyte concentration ($2 \mu\text{g mL}^{-1}$) was used in view of the good sensitivity of the method. The tested desorption time was in the range from 30 s to 10 min (360 s). Fig. 6 shows the peak height profiles of analytes with the varying desorption time. All peak heights firstly rose significantly with the increase of desorption time and the highest values were obtained at 1 min. Then it decreased gradually and approached a plateau, where the exhaustive desorption was reached. The desorption time was finally chosen as 1 min.

The extraction temperature is also a very important parameter because it can affect the rate and equilibrium of extraction. The tested temperature varied from 15 to 85°C as shown in Fig. 7. The maximum peak heights were obtained at 65°C . Room temperature was adopted to ensure a stable and simple operation without decreasing the sensitivity of the method seriously. As for the desorption temperature, it was found that the desorption of aromatic amines was exhaustive at above 250°C . And even after the fiber desorbed in the injector at 280°C , there was no decline in the extraction capability. The GC port temperature was controlled at 250°C for the analysis.

The addition of salt, usually sodium chloride (NaCl), to about a 60% saturated solution, as reported in previous paper [34], often could improve the sensitivity for some organic compounds of SPME method because of the increased ion strength in the aqueous phase and salting the analytes out of solution into the headspace phase and the fiber. The peak heights were compared between the initial solution with 2 g of NaCl (20%) and without salt. The result showed that there were no distinct changes of sensitivity for most of the test compounds (Fig. 8). The amount of aromatic amines adsorbed by the fiber should be enhanced by a high pH, since basic condition ensures that more amines are in their neutral form theoretically. Thus, the base potassium hydroxide was added to evaluate its effect. The comparison of a basic solution ($\text{pH} > 13$) and controlled solution (Fig. 8) showed that high pH value did not enhance the sensitivity. This might be

Table 1
Main parameters for the determination of six aromatic amines investigated

Compound	Linear range ($\mu\text{g mL}^{-1}$)	Detection limit ($\times 10^{-3}$) ($\mu\text{g mL}^{-1}$)	Relative standard deviation (%) ($n = 6$)
Aniline	0.069–27.5	0.69	6.00
<i>N,N</i> -Dimethylaniline	0.053–21.3	1.06	5.44
<i>m</i> -Methylaniline	0.051–20.5	1.02	2.02
2,4-Dimethylaniline	0.051–20.6	1.02	3.11
2-Chloroaniline	0.0051–20.4	0.02	4.03
3,4-Dichloroaniline	0.0048–19.4	0.019	3.01

explained by assuming that the addition of salt and base may prolong the extraction time because diffusion and adsorption of the analytes were slower than in pure water [35].

3.3. Linearity, sensitivity and precision of the developed method

Table 1 showed the limits of detection (LOD), relative standard deviations (R.S.D.) and the linearity range. The reproducibility of the method was determined by six repetitions analysis of $2 \mu\text{g mL}^{-1}$ standards spiked water samples under identical operating condition. The result showed that the PANI fiber had as good precision as that of the commercial CW/DVB fiber for the mostly analytes [34], which was reported as the most suitable fiber to extract aromatic amines [34]. For all the tested aromatic amines, the LODs were from 0.019 to $1.06 \mu\text{g L}^{-1}$ (all LODs based on $S/N = 3$), which were higher than that of the commercial CW/DVB fiber [34] by one order of magnitude. The linearity ranges were from 0.0048 to $27.5 \mu\text{g mL}^{-1}$.

3.4. Environmental sample analysis

A wastewater sample was collected at a sewage outfall of a wastewater treatment factory in Beijing. The analysis was carried out under the optimized conditions described above. The result was listed in Table 2. The concentration of aromatic amines found in the wastewater was very low and four of them were under the detection limit. The reason might be that some aromatic amines can be converted into toxic *N*-nitroso compounds through the reaction with nitrosylating agents in environment [33]. Ideal recoveries were obtained by the spiked experiment of $2 \mu\text{g}$ standards into 10 mL wastewater

Table 2
Results of six aromatic amines in a wastewater sample and the spiked recoveries ($n = 5$)

	Found ^a ($\times 10^{-3}$) ($\mu\text{g mL}^{-1}$)	Recovery (%)
Aniline	2.65	94.1 ± 6.1
<i>N,N</i> -Dimethylaniline	nd	89.9 ± 4.3
<i>m</i> -Methylaniline	nd	91.8 ± 6.1
2,4-Dimethylaniline	nd	91.3 ± 3.4
2-Chloroaniline	nd	89.3 ± 7.3
3,4-Dichloroaniline	0.72	99.6 ± 2.7

^a nd: not detected.

sample, which confirmed the reliability and feasibility of this proposed method.

4. Conclusion

A new polyaniline (PANI) fiber coated stainless metallic wires fiber was prepared by electrochemical method. The performance of the PANI fiber was evaluated by the determination of six aromatic amines and results performed nearly as good precision and sensitivity as the commercial fibers. It was successfully used for the extraction of six aromatic amines at trace levels in the environmental wastewater. The advantages of the fiber compared with the traditional fibers are the ease of preparation, good mechanical strength and low cost.

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References

- [1] R.P. Belardi, J. Pawliszyn, *Water Pollut. Res. J. Can.* 24 (1989) 179.
- [2] C.L. Arthur, J. Pawliszyn, *Anal. Chem.* 62 (1990) 2145.
- [3] J. Pawliszyn (Ed.), *Applications of Solid Phase Microextraction*, The Royal Society of Chemistry, Cambridge, UK, 1999.
- [4] X. Yu, H. Yuan, T. Georecki, J. Pawliszyn, *Anal. Chem.* 71 (1999) 2998.
- [5] S.A. Barshick, W.H. Griest, *Anal. Chem.* 70 (1998) 3015.
- [6] B. Szostek, J.H. Aldstadt, *J. Chromatogr. A* 807 (1998) 253.
- [7] Y. Yang, D.J. Miller, S.B. Hawthorne, *J. Chromatogr. A* 800 (1998) 257.
- [8] F. Guan, K. Watanabe, A. Ishii, H. Seno, T. Kumazawa, H. Hattori, O. Suzuki, *J. Chromatogr. B* 714 (1998) 205.
- [9] X. Yu, J. Pawliszyn, *Anal. Chem.* 72 (2000) 1788.
- [10] L. Wennrich, P. Popp, M. Möder, *Anal. Chem.* 72 (2000) 546.
- [11] A.A. Boyd-Boland, J. Pawliszyn, *J. Chromatogr. A* 704 (1995) 163.
- [12] L. Pan, M. Adams, J. Pawliszyn, *Anal. Chem.* 67 (1995) 4396.
- [13] M.E. Miller, J.D. Stuart, *Anal. Chem.* 71 (1999) 23.
- [14] L.S. DeBruin, P.D. Josephy, J. Pawliszyn, *Anal. Chem.* 70 (1998) 1986.
- [15] F. Hernandez, J. Beltran, F.J. Lopez, J.V. Gaspar, *Anal. Chem.* 72 (2000) 2313.

- [16] T. Gorecki, X. Yu, J. Pawliszyn, *Analyst* 124 (1999) 643.
- [17] R. McCallum, P. Pendleton, R. Schumann, M.U. Trinh, *Analyst* 123 (1998) 2155.
- [18] P.A. Martos, J. Pawliszyn, *Anal. Chem.* 70 (1998) 2311.
- [19] C.P. Kuo, J. Shiea, *Anal. Chem.* 71 (1999) 4413.
- [20] Dj. Djozan, Y. Assadi, *Chromatographia* 45 (1997) 183.
- [21] L. Pan, J. Pawliszyn, *Anal. Chem.* 69 (1997) 196.
- [22] C.H. Xiao, Z.L. Liu, Z.Y. Wang, C.Y. Wu, H.M. Han, *Chromatographia* 52 (2000) 803.
- [23] P. Popp, A. Paschke, *Chromatographia* 49 (1999) 686.
- [24] E.H.M. Koster, C. Crescenzi, W.D. Hoedt, K. Ensing, G.J. Jong, *Anal. Chem.* 73 (2001) 3140.
- [25] Y. Liu, M.L. Lee, K.J. Hageman, Y. Yang, S.B. Hawthorne, *Anal. Chem.* 69 (1997) 5001.
- [26] Y. Liu, Y. Shen, M.L. Lee, *Anal. Chem.* 69 (1997) 190.
- [27] Dj. Djozan, Y. Assadi, G. Karim-Nezhad, *Chromatographia* 56 (2002) 611.
- [28] Dj. Djozan, Y. Assadi, S.H. Haddadi, *Anal. Chem.* 73 (2001) 4054.
- [29] J. Wu, X. Yu, H. Lord, J. Pawliszyn, *Analyst* 125 (2000) 391.
- [30] J. Wu, H.L. Lord, J. Pawliszyn, H. Kataoka, *J. Microcolumn Sep.* 12 (2000) 255.
- [31] J. Wu, J. Pawliszyn, *Anal. Chem.* 73 (2001) 55.
- [32] J. Wu, J. Pawliszyn, *J. Chromatogr. A* 909 (2001) 37.
- [33] M. Dalene, G. Skarping, *J. Chromatogr.* 331 (1985) 321.
- [34] L. Müller, E. Fattore, E. Benfenati, *J. Chromatogr. A* 791 (1997) 221.
- [35] K.D. Buchholz, J. Pawliszyn, *Environ. Sci. Technol.* 27 (1993) 2844.