

Multiwalled Carbon Nanotubes as a Solid-Phase Extraction Adsorbent for the Determination of Bisphenol A, 4-*n*-Nonylphenol, and 4-*tert*-Octylphenol

Yaqi Cai, Guibin Jiang,* Jingfu Liu, and Qingxiang Zhou

Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, P.O. Box 2871, Beijing 100085, China

The adsorptive potential of multiwalled carbon nanotubes (MWNTs) for solid-phase extraction of bisphenol A, 4-*n*-nonylphenol, and 4-*tert*-octylphenol was investigated for the first time. The three analytes are quantitatively adsorbed on a MWNTs-packed cartridge, then the analytes retained on the cartridge are quantitatively desorbed with suitable amounts of methanol. Finally, the analytes in the methanol eluate are determined by high performance liquid chromatography-fluorometric detection. Parameters influencing the extraction efficiency, such as volume of the sample solutions, pH of the sample, and the eluent volume, were examined. Comparative studies showed that MWNTs were superior to C₁₈ for the extraction of the more polar analyte bisphenol A and at least as effective as C₁₈ for the extraction of 4-*n*-nonylphenol and 4-*tert*-octylphenol. Compared to XAD-2 copolymer, MWNTs exhibited a better property for the extraction of all three analytes. The developed method has been applied to determine bisphenol A, 4-*n*-nonylphenol, and 4-*tert*-octylphenol in several environmental water samples. The accuracy of the proposed method was tested by recovery measurements on spiked samples, and good recovery results (89.8–104.2%) were obtained. Detection limits of 0.083, 0.024, and 0.018 ng mL⁻¹ for bisphenol A, 4-*n*-nonylphenol, and 4-*tert*-octylphenol, respectively, were achieved under the optimized conditions.

In recent years, the release of various harmful organic chemicals into the environment has attracted great attention worldwide because of their toxicity and widespread use. Therefore, it is crucial to develop simple, rapid, and efficient methods for monitoring the environment. The most widely used methods for analyzing these harmful organic contaminants are chromatographic techniques such as GC or HPLC, but their sensitivity and selectivity are usually insufficient for direct determination of these contaminants at a very low concentration level in complex matrix environmental samples. Therefore, a sample pretreatment step prior to chromatographic analysis is usually necessary. Nowadays, because of its advantages of high recovery, short extraction time, high enrichment factor, low cost, and low consumption of organic

solvents over liquid–liquid extraction, solid-phase extraction is the most common technique for environmental water sample pretreatment.^{1–5} Various types of solid-phase extraction sorbents, including C₁₈ or C₈ silica,^{6–8} polystyrene–divinylbenzene polymers,^{6–10} and various carbonaceous sorbents^{6,7,11–13} have been used. Of these, C₁₈ silica is the most widely used, but it shows relatively low recovery for some relatively polar analytes.^{14–17}

Carbon nanotubes are a novel and interesting carbon material first found in 1991 by S. Iijima. They can be divided into single-walled carbon nanotubes (SWNTs)¹⁸ and multiwalled carbon nanotubes (MWNTs)^{19,20} according to the carbon atom layers in the wall of the nanotubes. Because of their many unique electronic, mechanical, and chemical properties, carbon nanotubes have attracted great attention in recent years.^{21–27} With the great progress in the methods of preparing carbon nanotubes, large

- (1) Lin, C. K. *Trends Anal. Chem.* **1988**, 7, 340.
- (2) Moors, M.; Massart, D. L.; McDowall, R. D. *Pure Appl. Chem.* **1994**, 66, 27.
- (3) Thurmn, E. M.; Mills, M. S. *Solid-Phase Extraction: Principles and Practice*; Wiley: New York, 1988.
- (4) Terada, K. *Anal. Sci.* **1991**, 7, 187.
- (5) Barceló, D.; Hennion, M. C. *Anal. Chim. Acta* **1995**, 318, 1.
- (6) Simpson, N. J. K. *Solid-Phase Extraction: Principles, Techniques, and Applications*; Basel: Marcel Dekker: New York, 2000.
- (7) Fritz, J. S. *Analytical Solid-Phase Extraction*; Wiley-VCH: New York, 1999.
- (8) Pocurull, E.; Marcé, R. M.; Borrull, F. *Chromatographia* **1995**, 41, 521.
- (9) Brouwer, E. R.; Brinkman, U. A. Th. *J. Chromatogr., A* **1994**, 678, 521.
- (10) Przyjazny, A. *J. Chromatogr.* **1985**, 346, 61.
- (11) Rodriguez, I.; Turnes, M. I.; Mejuto, M. C.; Cela, R. *J. Chromatogr., A* **1996**, 721, 297.
- (12) Rodriguez, I.; Turnes, M. I.; Mejuto, M. C.; Cela, R. *J. Chromatogr., A* **1997**, 786, 285.
- (13) Bacaloni, A.; Goretti, G.; Lagana, A.; Petronio, B. M.; Rotatori, M. *Anal. Chem.* **1980**, 52, 2033.
- (14) Hennion, M.-C.; Coquart, V. *J. Chromatogr.* **1993**, 642, 211.
- (15) Di Corcia, A.; Marchetti, M. *Anal. Chem.* **1991**, 63, 580.
- (16) D'Ascenzo, G.; Gentili, A.; Marchese, S.; Marino, A.; Perret, D. *Chromatographia* **1998**, 48, 497.
- (17) Crescenzi, C.; Di Corcia, A.; Guerriero, E.; Samperi, R. *Environ. Sci. Technol.* **1997**, 31, 479.
- (18) Iijima, S. *Nature (London)* **1991**, 354, 56–58.
- (19) Iijima, S.; Ichihashi, T. *Nature (London)* **1993**, 363, 603–605.
- (20) Bethune, D. S.; Kiang, C. H.; de Vries, M. S.; Gorman, G.; Savoy, R.; Vazquez, J.; Beyers, R. *Nature (London)* **1993**, 363, 605–607.
- (21) Ebbensen, T. W. *Phys. Today* **1996**, 49, 26.
- (22) Amelinckx, S.; Zhang, X. B.; Bernaerts, D.; Zhang, X. F.; Ivanov, V.; Nagy, J. B. *Science* **1994**, 265, 635–639.
- (23) Inoue, S.; Ichikuni, N.; Suzuki, T.; Uematsu, T.; Kaneko, K. *J. Phys. Chem. B* **1998**, 102, 4689–4692.

* Corresponding author. Fax: 8610-62849179. E-mail: gbjiang@mail.rcees.ac.cn.

efforts have been devoted to their fields of application, such as hydrogen storage,^{28,29} quantum nanowires,³⁰ catalyst supports,^{31,32} and chemical sensors,^{33,34} etc. From the report by Long,³⁵ we can learn that MWNTs have very strong adsorption to dioxin, and they can be expected to be an ideal sorbent for dioxin removal. According to the report of Davis,³⁶ the internal surface of the carbon nanotubes interacts strongly with the enzyme proteins, and the carbon nanotubes appear to act as a benign host to encapsulate protein molecules in their internal tube cavity. The strong interaction between carbon nanotubes and dioxin or other molecules may be attributed to the unique structure and electronic properties of carbon nanotubes. The hexagonal arrays of carbon atoms in graphene sheets of carbon nanotubes' surface have a strong interaction with the two benzene rings of dioxin. In recent years, Miguel Valcárcel and co-workers have explored the analytical potential of C₆₀ fullerene, a carbon nanotubes-related structure, as a solid-phase adsorbent for chelates or ion pairs of metal ions, organic compounds, and organometallic compounds from aqueous solutions.^{37–40} Their experimental results have shown that this carbon nanotubes-related structure, C₆₀ fullerene, is a superior adsorbent for the solid-phase extraction of chelates or ion pairs of metal ions and organometallic compounds.

All of the facts mentioned above reveal to us that carbon nanotubes maybe have great analytical potential as an effective solid-phase extraction adsorbent for some suitable compounds. However, to the best of our knowledge, so far, there have been no reports on this topic. In the present paper, the applicability of MWNTs as packing adsorbents for solid-phase extraction was investigated by using three endocrine disruptors, bisphenol, 4-*n*-nonylphenol, and 4-*tert*-octylphenol, as model compounds. The three analytes were extracted by a MWNTs-packed cartridge. Then the cartridge was washed with 10% methanol aqueous solution, and the three analytes attracted on MWNTs were eluted

with a suitable amount of methanol. Finally, the eluate was analyzed by high performance liquid chromatography.

EXPERIMENTAL SECTION

Apparatus and Reagents. All reagents were of analytical reagent grade, and purified water from a Milli-Q system was used throughout the experiments. 4-*n*-Nonylphenol and 4-*tert*-octylphenol were obtained from Tokyo Kasei Kogyo Co. LTD, Japan, and bisphenol A was obtained from Acros Organics (NJ). Standard stock solutions (1000 µg/mL) containing these compounds were prepared by dissolving an appropriate amount of these compounds in methanol. Working solutions were prepared daily by an appropriate dilution of the stock solutions with water. LC-grade methanol and acetonitrile were purchased from Scharlance Chemie SA, Barcelona, Spain. Sodium hydroxide and hydrochloric acid were guarantee grade reagents (Beijing Chemicals Corporation, Beijing, China). An Agilent ZORBAX SPE C₁₈ (EC) cartridge (0.5 g, 6 mL, polypropylene) was purchased from Agilent Corporation, USA. XAD-2 resin (20–60 mesh) was purchased from Rohm and Haas (Philadelphia, PA). MWNTs with an average external diameter of 30–60 nm were kindly provided by Tsinghua-Nafine Nano-Powder Commercialization Engineering Center, Chemical Engineering Department of Tsinghua University, Beijing, China, and they were examined using JEOL FEG-SEM (JSM-6301F) scanning electron microscopes with a resolution (SEI) of 1.5 nm. The N₂ adsorption isotherm at 77 K was gravimetrically determined using a NOVA 1200 surface area analyzer after preevacuation of the nanotube samples at 373 K and 1 mPa for 8 h. The specific surface area of MWNTs was determined from the linear portion of the BET plots ($P/P_0 = 0.04–0.25$).

The HPLC equipment used included an Agilent 1100 series IsoPump, an Agilent 1100 series FLD detector and a Rheodyne 7225i injector. The separations were performed on an Agilent Zorbax Eclipse XDB-C₈ column (150 × 4.6 mm; particle size, 5 µm). The mobile phase was a mixture of acetonitrile and water (75:25, v/v), and 1 mL/min was selected as the flow rate of the mobile phase. The fluorescence detector settings were as follows: 220-nm excitation, 315-nm emission. A personal computer equipped with an Agilent ChemStation program for LC systems was used to acquire and process chromatographic data. Peak area was used as the analytical measurement.

Solid-Phase Extraction Cartridge. A MWNTs-packed cartridge was prepared by modifying an Agilent ZORBAX SPE C₁₈ (EC) cartridge (0.5 g, 6 mL, polypropylene). The C₁₈ packing of the cartridge was evacuated, then 0.5 g of MWNTs was packed into the cartridge. The 20-µm polypropylene upper and lower frits remained at each end of the cartridge to hold the MWNTs packing in place. Then the outlet tip of the cartridge was connected to a model SHZ-3 (III) vacuum pump (Yuhua Instrument Co., Ltd., Zhengzhou, Henan), and the inlet end of the cartridge was connected to a PTFE suction tube whose other end was inserted into sample solution. Prior to use, the entire solid-phase extraction assembly was carefully washed with sufficient methanol.

Procedure. Prior to a preconcentration step, the MWNTs-packed cartridge was preconditioned by washing it with 5 mL of methanol and was activated with 5 mL of water. The pH of samples was adjusted to about neutral value with 1 mol/L of sodium hydroxide or hydrochloric acid solution. Then a known volume of purified water or sample water spiked with three analytes was

- (24) Ren, Z. F.; Huang, Z. P.; Xu, J. W.; Wang, J. H.; Bush, P.; Siegal, M. P.; Provencio, P. N. *Science* **1998**, *282*, 1105–1107.
- (25) Chen, J.; Hamon, M. A.; Hu, H.; Chen, Y.; Rao, A. M.; Eklund, P. C.; Haddon, R. C. *Science* **1998**, *282*, 95–98.
- (26) Park, C.; Baker, R. T. K. *J. Phys. Chem. B* **1998**, *102*, 5168–5177.
- (27) Wong, S. S.; Joselevich, E.; Wooley, A. T.; Cheung, C. L.; Lieber, C. M. *Nature (London)* **1998**, *394*, 52–55.
- (28) Dillon, A. C.; Jones, K. M.; Bekkedahl, T. A.; Kiang, C. H.; Bethune, D. S.; Heben, M. J. *Nature (London)* **1997**, *386*, 377–379.
- (29) Liu, C.; Fan, Y. Y.; Liu, M.; Cong, H. T.; Cheng, H. M.; Dresselhaus, M. S. *Science* **1999**, *286*, 1127–1129.
- (30) Tans, S. J.; Devoret, M. H.; Dai, H.; Thess, A.; Smalley, R. E.; Geerligs, L. J.; Dekker, C. *Nature (London)* **1997**, *386*, 474–477.
- (31) Planeix, J. M.; Coustel, N.; Coq, B.; Brotons, V.; Kumbhar, P. S.; Dutartre, R.; Geneste, P.; Bernier, P.; Ajayan, P. M. *J. Am. Chem. Soc.* **1994**, *116*, 7935–7936.
- (32) Chen, G.; Lakshmi, B. B.; Fisher, E. R.; Martin, C. R. *Nature (London)* **1998**, *393*, 346–349.
- (33) Kong, J.; Franklin, N. R.; Zhou, C.; Chapline, M. G.; Peng, S.; Cho, K.; Dai, H. *Science* **2000**, *287*, 622–625.
- (34) Luo, H. X.; Shi, Z. J.; Li, N. Q.; Gu, Z. N.; Zhuang, Q. K. *Anal. Chem.* **2001**, *73*, 915–920.
- (35) Long, R. Q.; Yang, R. T. *J. Am. Chem. Soc.* **2001**, *123*, 2058–2059.
- (36) Davis, J. J.; Green, M. L. H.; Hill, H. A. O.; Keung, Y. C.; Sadler, P. J.; Sloan, J.; Xavier, A. V.; Tsang, S. C. *Inorg. Chim. Acta* **1998**, *272*, 261–266.
- (37) Petit de Peña, Y.; Gallego, M.; Valcárcel, M. *Anal. Chem.* **1995**, *67*, 2524–2529.
- (38) Ballesteros, E.; Gallego, M.; Valcárcel, M. *J. Chromatogr.* **2000**, *869*, 101–110.
- (39) Baena, J. R.; Gallego, M.; Valcárcel, M. *Analyst* **2000**, *125*, 1495–1499.
- (40) Baena, J. R.; Gallego, M.; Valcárcel, M. *Anal. Chem.* **2002**, *74*, 1519–1524.

passed through the preconditioned cartridge at a flow rate of 8 mL/min. After the sample solution had passed through, the cartridge was washed with 5 mL of 10% methanol aqueous solution to remove coadsorbed matrix materials from the cartridge. Then the analytes retained on the solid-phase extraction packing were eluted with 2.5 mL of methanol. Finally, 50 μ L of methanol eluate was injected into the HPLC system for determination. By using the methanol standard solutions of the three analytes, the external calibration curve can be acquired, then the concentration of the three analytes in the eluate can also be acquired. Finally, the recoveries of the three analytes at different conditions can be obtained by comparing the concentrations of three analytes in the eluate with the spiked concentration levels.

Recommended Procedure for Water Sample Analysis. A tap water sample was collected from a water tap in our laboratory. River water samples were collected from the section of Beijing in the Yongding River valley. A wastewater sample was collected at a discharge gate of effluent of the biggest municipal wastewater treatment plant in Beijing, the Gaobidian wastewater treatment plant. A seawater sample was collected from the Bering and Chukchi Sea by the Chinese polar research vessel Xuelong during the First Chinese Arctic Research Expedition from July to September 1999. The collected water samples were filtered through a Millipore cellulose membrane with pore size 0.45 μ m immediately after sampling and were maintained in glass containers, then stored at a temperature of 4 $^{\circ}$ C. The pH of the samples was adjusted to about neutral value with 1 mol/L of sodium hydroxide or hydrochloric acid solution. Then, following the experimental procedure recommended above, these water samples could be preconcentrated, separated and determined.

RESULTS AND DISCUSSION

Physical Characterization of MWNTs. The SEM image of the MWNTs at high magnification is shown in Figure 1. From Figure 1, many MWNTs with general outer diameters of 30–60 nm can be observed. Other nanotubes with diameters beyond the above range also exist. Because many nanotubes twist together and both of their ends are not visible at the same time, the length of nanotubes cannot be measured. The specific surface area of multiwalled carbon nanotubes was determined from the linear portion of the BET plots ($P/P_0 = 0.04\text{--}0.25$): 131.74 m²/g.

Evaluation of MWNTs as Solid-Phase Extraction Sorbents. To evaluate the analytical potential of MWNTs as Solid-Phase Extraction adsorbents, bisphenol A, 4-*n*-nonylphenol, and 4-*tert*-octylphenol were adopted as model compounds. The effects of different parameters, such as the sample volume, the eluent volume, and the pH of sample solution, on the recoveries were carefully investigated.

To obtain reliable and reproducible analytical results and a high concentration factor, it is very important to get satisfactory recoveries for all the compounds studied in as large a volume of sample solutions as possible. So it is necessary to obtain the breakthrough volumes in the solid-phase extraction. To determine the breakthrough volumes, different volumes of purified water at pH 5–8 were spiked with the three analytes at 20 ng/mL concentration levels. Following the experimental procedure, the recoveries of the three analytes at different volumes were obtained. The effects of sample volumes on the recoveries of the three analytes are shown in Figure 2. From Figure 2, we know that

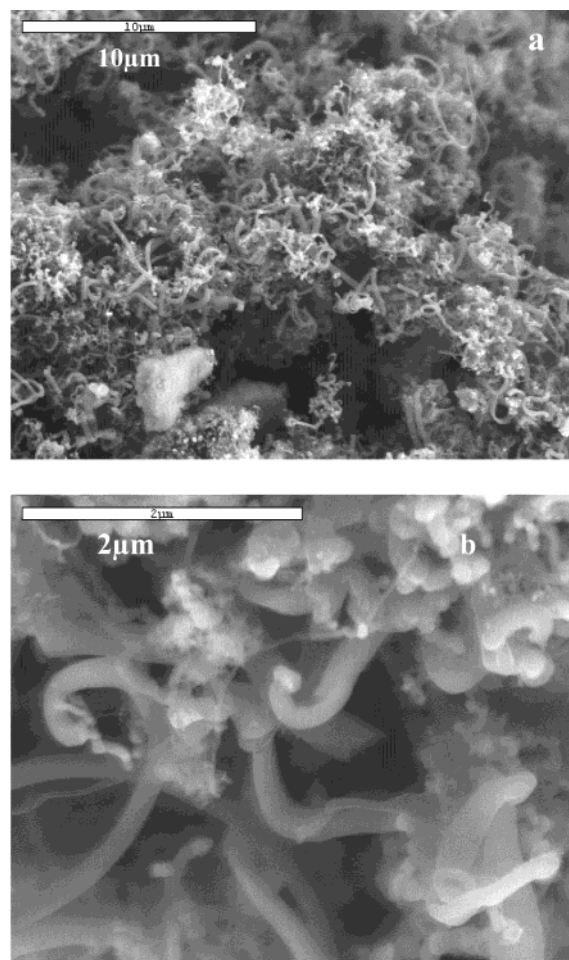


Figure 1. SEM image of the MWNTs powder.

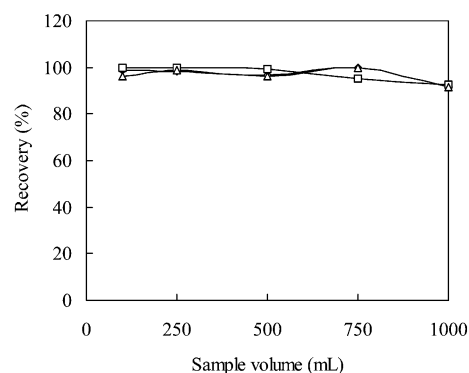


Figure 2. Effect of volume of water sample solutions on the recoveries of bisphenol A, 4-*n*-nonylphenol, and 4-*tert*-octylphenol by using a MWNTs-packed cartridge. \diamond , bisphenol A; \square , 4-*tert*-octylphenol; \triangle , 4-*n*-nonylphenol. Concentration of the three analytes, 2 ng/mL; volume of eluent, methanol, 2.5 mL; flow rate of sample solutions, 8 mL/min. See text for the other experimental conditions.

good recoveries (>95%) were obtained for all three analytes when the volumes of sample solutions were under 750 mL. Although a slight decline of recoveries was observed for the three analytes in 1000 mL of sample solutions, the recoveries for all three analytes were still above 90%, which was acceptable in trace analysis. A sample volume of 500 mL was selected in the subsequent analysis of several environmental water samples.

In a solid-phase extraction system, the flow rate of sample solution not only affects the recoveries of analytes, but also

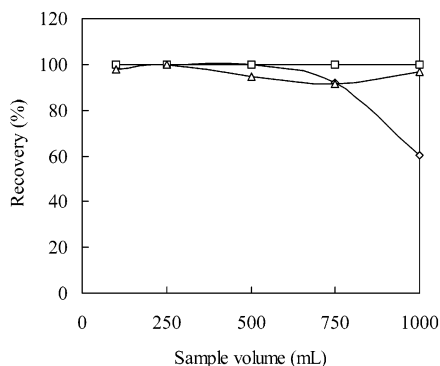


Figure 3. Effect of volume of sample solutions on the recoveries of bisphenol A, 4-*n*-nonylphenol, and 4-*tert*-octylphenol by using a C₁₈ silica-packed cartridge. ◇, bisphenol A; □, 4-*tert*-octylphenol; △, 4-*n*-nonylphenol. Concentration of the three analytes, 2 ng/mL; volume of eluent, methanol, 2.5 mL; flow rate of sample solutions, 8 mL/min. See text for the other experimental conditions.

Table 1. Slopes, Correlation Coefficients, and Detection Limits

compd	slope	<i>R</i>	LOD (ng/mL)
bisphenol A	237.8	0.9999	0.083
4- <i>tert</i> -octylphenol	132.6	0.9987	0.024
4- <i>n</i> -nonylphenol	103.0	0.9984	0.018

Table 2. Results of Determination and Recoveries of Real Water Samples Spiked with Three Target Analytes

water sample	added (ng/mL)	found ^a (ng/mL)	recovery ^b (%)
tap water			
bisphenol A		nd ^c	
4- <i>tert</i> -octylphenol	0.40	0.36	89.8 ± 2.0
4- <i>n</i> -nonylphenol	0.40	0.42	104.4 ± 2.5
4- <i>n</i> -nonylphenol	0.40	0.37	93.5 ± 5.2
river water I			
bisphenol A		nd	
4- <i>tert</i> -octylphenol	0.40	0.41	101.4 ± 3.9
4- <i>n</i> -nonylphenol	0.40	0.40	100.0 ± 4.4
4- <i>n</i> -nonylphenol	0.40	0.39	98.4 ± 7.4
seawater			
bisphenol A		nd	
4- <i>tert</i> -octylphenol	0.40	0.41	102.8 ± 4.0
4- <i>n</i> -nonylphenol	0.40	0.38	96.5 ± 3.3
4- <i>n</i> -nonylphenol	0.40	0.39	98.6 ± 5.7
wastewater			
4- <i>tert</i> -octylphenol		nd	
4- <i>n</i> -nonylphenol	0.40	0.36	90.4 ± 1.9
4- <i>n</i> -nonylphenol	0.40	1.69	
4- <i>n</i> -nonylphenol	0.40	2.05	90.1 ± 6.7

^a Mean for five determinations. ^b Mean and standard deviation for five determinations. ^c Not detected.

controls the analysis time. It was found that flow rates up to 8 mL/min (the maximum flow rate of our vacuum pump) for water sample loading on the cartridge had no effect on the recoveries of the three analytes. Therefore, 8 mL/min was chosen as the flow rate of sample solutions.

In a preliminary test, it was found that methanol was an effective eluent for the three analytes, and therefore, it was accepted as an eluent. To find the required volume of methanol to elute all three of the analytes from the cartridge, eluent volumes up to 10 mL were investigated. The experimental results indicated that quantitative recoveries (95%) could be achieved when the volume of methanol was in the range 2–10 mL. Because application of a smaller volume of eluent contributes to obtaining a higher preconcentration factor, 2.5 mL of methanol was adopted as the eluent throughout the experiments. Because the carryover is very harmful to the next extraction, it was also examined in our studies. Experiments indicated that complete desorption (100%) made carryover very minor. Despite no carryover being observed, to obtain quantitative analytical result for the next extraction, the cartridge was washed further with another 3 mL methanol at the end of each extraction. In this way, the cartridge was immediately available for the next extraction.

Changing the pH of the sample solutions results in protonation or deprotonation of the hydroxy of the phenols, so it could be expected that the pH of the sample solutions could affect the extraction efficiencies. It was found that the pH of sample solutions in the range pH 3–11 has no significant influence on the recoveries of 4-*n*-nonylphenol and 4-*tert*-octylphenol. For the extraction of bisphenol A, however, the situation was slightly different: the pH of the sample solutions had no effect on the recoveries of bisphenol A in range of pH 3–8, although a dramatic decrease in recoveries of bisphenol A was observed due to deprotonation of the hydroxy of the phenol when the pH of the sample solutions was above pH 8. On the basis of the experimental results above-mentioned, pH 5–8 was chosen as the pH of the sample solutions.

Comparison Studies. For comparative studies, the most commonly used solid-phase extraction sorbent, C₁₈ and XAD-2 PS-DVB copolymer, were selected as references. Following the same experimental procedure and conditions as the MWNTs-packed cartridge, the recoveries of the three analytes at 2.00 ng/mL concentration levels in different volumes by using an Agilent ZORBAX SPE C₁₈ (EC) cartridge (0.5 g, 6 mL) and a XAD-2 copolymer-packed cartridge (0.5 g) were obtained.

Figure 3 showed the case of extraction of the three analytes by using a C₁₈ cartridge. It was observed that good recoveries (>90%) were still obtained for 4-*n*-nonylphenol and 4-*tert*-octylphenol when the volumes of the sample solutions went up to 1000 mL, which was very similar to the situation for the use of the MWNTs-packed cartridge. For the extraction of bisphenol A, the recoveries were still acceptable (>90%) when the volume of the sample solutions went up to 750 mL. But further increasing the sample volume resulted in serious deterioration of the recoveries of bisphenol A. When the sample volume went up to 1000 mL, the recoveries of bisphenol A fell to 60%, which is a much lower value than that obtained when using the MWNTs-packed cartridge.

In the case of the XAD-2 copolymer-packed cartridge, it was observed that good recovery (>90%) was obtained for bisphenol A only when the volumes of the sample solutions were below 100 mL. When the sample volume further increased to 1000 mL, the recoveries of bisphenol A fell gradually from 92 to 66%. For the extraction of 4-*n*-nonylphenol and 4-*tert*-octylphenol, the recoveries

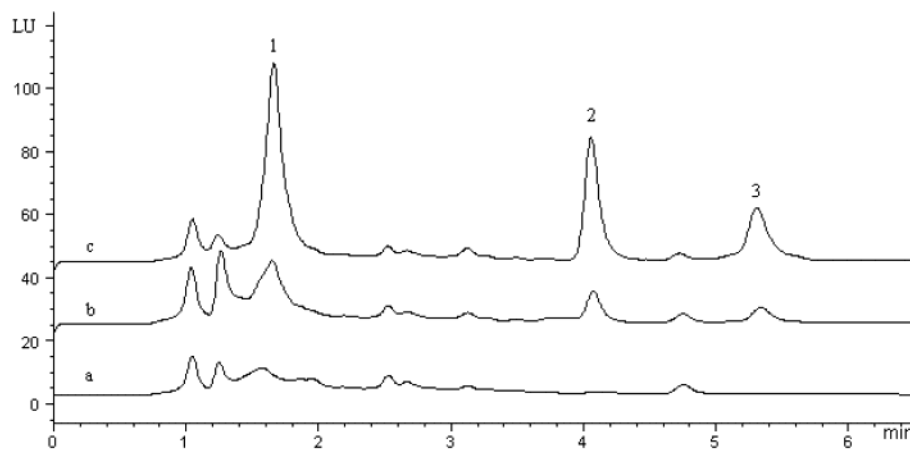


Figure 4. Solid-phase extraction/LC-FLD chromatograms of river water samples. (a) River water sample, (b) river water sample spiked with 0.040 ng/mL of each compound, and (c) river water sample spiked with 2.00 ng/mL of each compound. 1, bisphenol A; 2, 4-*tert*-octylphenol; 3, 4-*n*-nonylphenol. Volume of water sample solutions, 500 mL; flow rate of sample solutions, 8 mL/min; volume of eluent, methanol, 2.5 mL. See text for the other experimental conditions.

obtained in all cases were below 87%. When sample volume increased from 100 to 1000 mL, the recoveries of 4-*n*-nonylphenol and 4-*tert*-octylphenol fell gradually from 87 and 84% to 71 and 73%, respectively.

The above results showed that MWNTs were at least as effective as C_{18} for the solid-phase extraction of 4-*n*-nonylphenol and 4-*tert*-octylphenol, but they were more effective than C_{18} for the solid-phase extraction of bisphenol A. Compared with XAD-2 copolymer, they exhibited better ability for the extraction of all three analytes. In comparison with some reports, it appears that these recoveries are rather good. In Miguel Valcárcel's report,³⁸ it is found that the sorption efficiencies of ordinary organic compounds on C_{60} fullerene never exceed 60%. The reason that the MWNTs have a stronger interaction with the three analytes perhaps is that the hexagonal arrays of carbon atoms in graphene sheets in their structures may have a strong interaction with the benzene rings of bisphenol A, 4-*n*-nonylphenol, and 4-*tert*-octylphenol.

Analytical Performance and Real Sample Analyses. Under the conditions selected above, effective enrichment and matrix separation can be obtained for bisphenol A, 4-*n*-nonylphenol, and 4-*tert*-octylphenol. The analytical performance of the proposed method was assessed with spiked water samples, and the results are given in Table 1. There is a linear correlation between peak area and concentration of the three analytes from 0.2 to 200 ng/mL. The limits of detection for an extraction of 500 mL of water are calculated as 3 times the standard deviation of six replicate runs of procedure blanks. From the above experimental results, it can be seen that the present method exhibited high sensitivity and a wide linear range.

The proposed method was applied to the analysis of some real environmental water samples, and the experimental results are shown in Table 2. No bisphenol A, 4-*n*-nonylphenol, and 4-*tert*-octylphenol were found in the tap water, river water, and seawater samples. For the case of wastewater samples, only 4-*n*-nonylphenol

was found. Recovery tests were carried out with standard phenol mixture-spiked water samples, and the results are fairly satisfactory. The chromatograms of a river water sample and its spiked standard solution are shown in Figure 4.

CONCLUSIONS

A simple, rapid and reliable method was developed for the solid-phase extraction of bisphenol A, 4-*n*-nonylphenol, and 4-*tert*-octylphenol in several environmental water samples by using a MWNTs-packed cartridge. As far as we know, this is the first time that MWNTs have been used as packing material for the solid-phase extraction of organic pollutants from aqueous solutions before they are analyzed by chromatographic methods. The results obtained show that MWNTs have high analytical potential for preconcentration of microorganic pollutants from water samples. For the extraction of 4-*n*-nonylphenol and 4-*tert*-octylphenol, good recoveries that are comparable with C_{18} have been obtained. For the more polar analytes, bisphenol A, MWNTs as solid-phase extraction adsorbents are more powerful than C_{18} , because they possess a higher capability to extract bisphenol A from larger volume of water solutions. That the analytes retained on MWNTs can be easily desorbed and no carryover is observed in the next analysis is another advantage of the present method. In summary, we have preliminarily demonstrated that as promising sorbents, MWNTs have great potential for SPE of some pollutants.

ACKNOWLEDGMENT

This work was jointly supported by the National Natural Science Foundation of China, the National High Technology Project and the Chinese Academy of Sciences.

Received for review November 27, 2002. Accepted March 13, 2003.

AC0263566