ELSEVIER
Available online at www.sciencedirect.com
ScienceDirect
Journal of Chromatography A, 1165 (2007) 10–17
JOURNAL OF CHROMATOGRAPHY A
www.elsevier.com/locate/chroma

Oxidized multiwalled carbon nanotubes as a novel solid-phase microextraction fiber for determination of phenols in aqueous samples

Xiaoyan Liu, Yongsheng Ji, Yonghui Zhang,
Haixia Zhang*, Mancang Liu

College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, China

Received 10 May 2007; received in revised form 7 July 2007; accepted 10 July 2007

Abstract

A simple and environmentally friendly method for determination of seven phenols using solid-phase microextraction (SPME) coupled to high-performance liquid chromatography (HPLC) has been developed. Several materials were used as stationary phase of SPME fibers and an oxidized multiwalled carbon nanotubes material was found to be effective in carrying out simultaneous extraction of phenols in aqueous samples. Compared with the widely used commercially available SPME fibers, this proposed fiber had much lower cost, longer lifetime (over 150 times), shorter analysis time (30 min of extraction and 3 min of desorption time) and comparable or superior extraction efficiency for the investigated analytes. The extraction and desorption conditions were evaluated and the calibration curves of seven phenols were linear ($R^2 \geq 0.9908$) in the range from 10.2 to 1585 ng mL^{-1}. The limits of detection at a signal-to-noise (S/N) ratio of 3 were 0.25–3.67 ng mL^{-1}, and the limits of quantification calculated at S/N = 10 were 0.83–12.25 ng mL^{-1} for these compounds. The possibility of applying the proposed method to environmental water samples analysis was validated.

Keywords: Phenols; Oxidized multiwalled carbon nanotubes; Solid-phase microextraction–high performance liquid chromatography

1. Introduction

Phenol and substituted phenols are important pollutants in water due to their widespread use in industrial processes [1–3]. Because of their high toxicity, as well as their unpleasant organoleptic properties, some phenols have been included in the priority pollution list of the European Union (EU) and US Environmental Protection Agency (EPA).

The determination of phenols is usually accomplished by chromatographic techniques, which involve a previous extraction step that traditionally has been carried out with liquid–liquid extraction [4,5], solid-phase extraction (SPE) [6–8], steam distillation extraction (SDE) [9,10], and liquid-phase microextraction (LPME) [11–13]. Solid-phase microextraction (SPME) is a solvent-free and miniaturizable extraction technique that represents a convenient alternative to most of conventional extraction method. SPME was initially applied to analyze phenols in water by Buchholz and Pawliszyn [14]. Since then this technique has been widely used to determine phenols in environmental water [15–21], soil [22] and landfill leachates samples [23]. In these methods, several kinds of fibers including commercial SPME fibers such as 50 μm carbowax/templated resin (CW-TPR), 60 μm polydimethylsiloxane/divinylbenzene (PDMS-DVB) and 85 μm polyacrylate (PA) [15–17,21,22,23], and other custom-made SPME fibers such as 25,27-dihydroxy-26,28-oxy(2′,7′-dioxo-3′,6′diazaoctyl) oxy-*p*-*tert*-butylcalix [4] arene/hydroxy-terminated silicone oil (amide bridged-C [4] /OH-TSO) coating [18], electropolymerized aniline-based fiber [19], polyethylene glycol-coated solid-phase microextraction fiber [24], and poly(acrylamide-vinylpyridine-*N*,*N*-methylenebisacrylamide) monolithic capillary for in-tube solid-phase microextraction [25] were employed. However, to achieve a more selective determination of these compounds, it is still significant to prepare an efficient

---

* Corresponding author. Tel.: +86 931 4165997; fax: +86 931 8912582.
E-mail address: zhanghx@lzu.edu.cn (H. Zhang).

0021-9673/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.chroma.2007.07.057

SPME fiber for the maximum utilization of its analytical potential.

Carbon nanotubes (CNTs), first observed by Iijima [26], are large moleculars with thousands of carbon atoms in an electronically aromatic delocalized system which are rolled up into a cylinder and closed by two caps. They can be divided into single-walled carbon nanotube and multiwalled carbon nanotube according to the carbon atom layers in the wall of the nanotubes. CNTs have high surface area, mechanical strength and chemical stability. Due to their unique characteristic and strong adsorption ability [27], they have been successfully used to remove many kinds of pollutants such as dioxin [28] from air and lead [29], cadmium [30], zinc [31,32], fluoride [33], 1,2-dichlorobenzene [34] and trihalomethanes [35] from water. Furthermore, multiwalled carbon nanotubes (MWCNTs) have also been proven to possess great potential to be used as SPE sorbent [36–48] and SPME fiber coating [49] for analysis of organic compounds. In general, CNTs materials can be obtained from the Chemical Reagent Co. (example, Shenzhen Nanotech Port Shenzhen, China) and are directly utilized. However, when these materials are treated by mixture of acids of H_2SO_4 (98%)/HNO_3 (70%), some of physical chemistry properties change, owing to the carboxyl group is partially induced at the sidewall of CNTs. Thus, the presence of oxygenated functional groups serves as the starting point for binding a variety of different chemical moleculars on the nanotubes surface [50–52] and these oxidized multiwalled carbon nanotubes (MWCNTs-COOH) used as the sorbent for sample pretreatment should have different adsorption selectivity from the raw MWCNTs.

In this work, we first report the preparation of a novel SPME fiber based on MWCNTs-COOH materials for extraction of phenols in environmental samples. Several extraction variables and desorption conditions were optimized. Compared with other laboratory-made SPME fibers and commercial SPME fibers, the developed MWCNTs-COOH fiber had the highest extraction efficiency for phenols. Finally, the developed method was applied for the determination of phenols in river and wastewater.

2. Experimental

2.1. Chemicals and materials

Phenol (>98%) (P) was purchased from Tianjin Guangfu Chemical Reagent Co. (Tianjin, China). 2-Nitrophenol (2-NP), 4-nitrophenol (4-NP), 2,4-dinitrophenol (2,4-DNP), 2,4-dichlorophenol (2,4-DCP) and 2,4-dimethylphenol (2,4-DMP) (>98%) were obtained from Shanghai Chemical Reagent Co. (Shanghai, China) except for 2,4,6-trichlorophenol (2,4,6-TCP) (>98%) from Alfa Aesar a Johnson Mattey. (MA, USA). Acetonitrile of HPLC grade was from Dima Technology. (VA, USA). All the other reagents were of analytical-reagent grade (Tianjin Chemicals, Tianjin, China) and purified water by Milli-Q system was used throughout the experiments. The standard mixtures of seven phenols were prepared by dissolving 10.0 mg of each compound in acetonitrile in 10.0 mL volumetric flask. The stock solution was stored at 4 °C and diluted with ultrapure water to give the required concentration.

Fused silica Capillary (75 μm internal diameter, 375 μm external diameter) was from Yongnian Photoconductive Fiber Factory (Handan, China). MWCNTs (10–20 nm external diameter, 5–15 μm length, >95% purity) were purchased from Shenzhen Nanotech Port (Shenzhen, China). The special surface area and thermal conductivity of the MWCNTs are 40–300 m^2/g and ∼2000 W/(mk) (Watt per meter-kelvin), respectively.

SPE Alumina N and Carbograph cartridge were kindly provided by Vertical Chromatography (Bangkok, Thailand) and the packings were used to prepare the SPME fiber coatings.

The commercial SPME fiber used included PDMS/DVB (60 μm/partially crosslinked) and CW/TPR (50 μm/partially crosslinked) from Supelco (Belletonte, PA, USA).

2.2. Instrumentation

The HPLC–UV analyses were performed on a Varian 210 high-performance liquid chromatograph (CA, USA) equipped with 325 UV–vis detector and Varian Star Chromatographic workstation.

Chromatographic conditions included C 18 column at 30 °C (5 μm, 250 × 4.5 mm, Hanbon Science & Technology, Jiangsu, China) and gradient elution (A, 1% aqueous acetic acid solution; B, acetonitrile; 0–5 min A = 80%, B = 20%; 20 min A = 20%, B = 80%; 25 min A = 10%, B = 90%; 26 min stop) with a flow-rate of 1.0 mL min^{-1}. Both solutions were filtered through a 0.22-μm nylon membrane filter (Varian).

The optimum UV wavelength for each compound was: P at 268 nm, 4-NP at 311 nm, 2,4-DNP, 2-NP, 2,4-DMP, 2,4-DCP and 2,4,6-TCP at 280 nm.

Hot plates stirrers from Corning Global Business Operations (Milan, Italy) and a Leici PHS-3B pHmeter (Shanghai, China), equipped with a combination electrode, Leici, E-201-C, were used.

2.3. Procedures

2.3.1. Preparation of SPME fibers coating

The method developed by Saito et al. [53] has been used for the preparation of MWCNTs-COOH materials. In brief, after being purified by concentrated HCl (36.5%) (sonicated in a water bath for 24 h), 200 mg of the purified MWCNTs were suspended in 400 mL of a 3:1 mixture of concentrated H_2SO_4 (98%)/HNO_3 (70%) and sonicated in a water bath for 22 h at 50 °C. The resultant MWCNTs-COOH were collected on a polytetrafluoroethylene (PTFE) filter with the pore size of 500 nm and washed four times with water and methanol, respectively. The CNTs were left to dry overnight at room temperature and finally recovered from the filter by scraping them off.

Capillary-fused silica tubing was employed as the needle tip of the device. After burning off the external polyimide coating (2 cm length) and sealing both ends of the tubing with a microflame torch, the fused-silica tube was cleaned in ultrapure water and ethanol, and then dried at 60 °C. The fiber was prepared according to Ref. [54]. Briefly, the purified MWCNTs, MWCNTs-COOH, Alumina N and Carbograph materials (2.0 mg) were immobilized onto the fused-silica tube by epoxy