



Rapid analysis of phthalates in beverage and alcoholic samples by multi-walled carbon nanotubes/silica reinforced hollow fibre-solid phase microextraction



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ARTICLE INFO

Article history:

Received 14 April 2013

Received in revised form 2 June 2013

Accepted 10 June 2013

Available online 24 June 2013

Keywords:

Multi-walled carbon nanotubes

Silica

Hollow fibre

Solid phase microextraction

Phthalate acid ethers

ABSTRACT

A novel procedure based on multi-walled carbon nanotubes (MWCNTs)/silica reinforced hollow fibre solid-phase microextraction combined with gas chromatography–mass spectrometry has been developed to analyse trace phthalate acid esters in beverage and alcoholic samples. Because of their excellent adsorption capability towards hydrophobic compounds, functionalized MWCNTs, acting as solid-phase sorbent, were co-deposited with silica particles in the pores of polypropylene hollow fibre through a layer-by-layer self-assembly technique. The parameters influencing the extraction efficiency, such as pH values and ionic strength of sample solution, extraction time, temperature and desorption solvent were optimised. Recoveries for phthalates at spiking levels in different matrices were satisfactory (between 68% and 115%). Moreover, the results were further confirmed by comparing them with those obtained using a solvent extraction method according to the national standard of China.

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1. Introduction

In 2011, plasticisers, a group of harmful chemicals, were detected in some beverages produced in Taiwan, causing a health scare (Li, 2011). News stories about the contamination of white liquor with plasticisers in China emerged in November 2012, and an unacceptable amount of plasticisers was found in Jiugui white liquor produced in Hunan Province (Ye, 2013).

These plasticisers, commonly known as phthalate acid esters (PAEs) or phthalates, are widely used in many consumable and household products, such as industrial plastics, polyvinyl chloride (PVC) products and personal care products. PAEs with high molecular weight, such as bis(2-ethylhexyl) phthalate (DEHP), are primarily used to soften PVC products while PAEs with low molecular weight, such as diethyl phthalate (DEP) and dibutyl phthalate (DBP), are widely used as solvents to hold colour and scent in various consumable and personal care products (Cao, 2010). Due to their extensive use and possible migration, PAEs could be released from these products. In recent years, the widespread presence of PAEs has attracted notable public attentions because of their suspected carcinogenic properties (Rios, Morales, & Marquez-Ruiz, 2010). Most PAEs are semi-volatile, thermostable and non-polar compounds with low solubility and high hydrophobicity. Because of the low concentration of PAEs in real samples and complex interference, it is often essential to

perform enrichment of the analytes before analysis. So far, there has been no national standard in China for the determination of PAEs in alcoholic products. Therefore, a reliable and sensitive method for the identification and quantification of PAEs from all kinds of food, water and other matrices is particularly important.

A common sample pretreatment technique is solid-phase microextraction (SPME), which is a solvent-less extraction procedure that involves the exposure of a coated fused silica fibre to a gaseous or liquid sample or the headspace above a liquid or solid sample (Arthur & Pawliszyn, 1990). Among the different approaches to stationary phase development for SPME fibres, Xu and Lee (2007) introduced a novel SPME technique that used ZrO₂ hollow fibre as sorbent and opened the possibility to fabricate numerous interesting inorganic hollow fibres with a homogeneous controllable wall and porous substructure, i.e. hollow fibre solid phase microextraction (HF-SPME). This technique has been shown to be simple, accurate, time-efficient, low-cost and environmentally friendly.

In various fields of chemical analysis, there have been an increasing number of applications of multi-walled carbon nanotubes (MWCNTs), which exhibit a range of structural, mechanical and electronic properties, so they have the potential to be useful in nanotube-reinforced materials as sorbents for SPME and the like (Bashier, Alnedhary, Madhava-Rao, Valliyaveetil, & Lee, 2006; Sae-Khow & Mitra, 2010). Recently, a silica-based, organic-inorganic polymer containing carbon nanotubes, which was prepared based on sol–gel technique, was injected into a piece of polypropylene hollow fibre and a process of *in situ* gelation occurred to give a fibre suitable for an HF-SPME procedure (Ebrahimi,

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Es'haghi, Samadi, & Hosseini, 2011; Es'haghi, Ebrahimi, & Hosseini, 2011; Yang, Chen, & Shi, 2012).

Novel composite hollow fibres with MWCNTs and mesoporous nanoparticles of inorganic oxides (ZrO₂, TiO₂ and SiO₂) co-deposited on the porous surface of polypropylene (PP) hollow fibre through a layer-by-layer self-assembly technique have been prepared. However, MWCNTs/ZrO₂ and MWCNTs/TiO₂ reinforced hollow fibres had much worse extraction capacities in milk than MWCNTs/SiO₂, probably due to specific enrichment of phosphorylated peptides in milk (Nawrochi, Dunlap, McCormick, & Carr, 2004), which blocked up the structural channels in MWCNTs, resulting in extraction amounts of analytes decreasing dramatically.

Therefore, representative PAEs (i.e. DEP, DBP, and DEHP) with different lengths of alkyl chains were selected as model analytes to investigate the extraction efficiency of HF-SPME. Reusable MWCNTs/SiO₂ reinforced hollow fibres were fabricated and used for the extraction of PAEs in beverage and alcoholic samples, followed by gas chromatography–mass spectrometry (GC–MS) analysis. Several factors influencing the extraction and desorption process were optimised. A direct immersion HF-SPME method was finally applied to determine typical phthalate acid esters in real food samples.

2. Experimental

2.1. Reagents and materials

Tetraethyl orthosilicate (TEOS), hydrochloric acid, sulfuric acid, *n*-hexane, chloroform, ethyl acetate, acetone, methanol, ethanol, citric acid, sodium chloride, monosodium phosphate, and anhydrous sodium sulfate, all of analytical grade, were purchased from Tianjin No.3 Chemical Reagent Factory (Tianjin, China). Accurel Q3/2 polypropylene (PP) hollow fibre membrane (600 µm i.d., 200 µm wall thickness, and 0.2 µm pore size) was bought from Membrana (Wuppertal, Germany). Hydroxylated multi-walled carbon nanotubes (OD, 30–50 nm; –OH content, 1.06 wt%; purity >95%) were purchased from Chengdu Organic Chemical Co. Ltd., Chinese Academy of Sciences (Chengdu, China). High purity deionised water was used in the whole experiments. Diethyl phthalate (DEP), dibutyl phthalate (DBP) and bis (2-ethylhexyl) phthalate (DEHP), all of analytical grade, were purchased from Sinopharm. Chemical Reagent Co. Ltd (Shanghai, China). All of the samples, i.e. milk, juice, carbonated drink, beer, red wine and white wine, were purchased from a supermarket in Lanzhou (Gansu Province, China).

2.2. Preparation of standard solutions

For GC–MS analysis, the mixed standards were diluted with *n*-hexane to give a concentration of 1000 ng mL⁻¹. The stock solution was diluted with *n*-hexane to obtain an eight-point calibration standard solution, 0.02, 0.1, 0.5, 1, 10, 20, 100, and 1000 ng mL⁻¹.

2.3. Apparatus

Thermo Scientific DSQ™ II GC–MS system (Thermo Fisher Scientific, Waltham, MA) was employed for DEP, DBP and DEHP analysis. A Thermo TR-5 MS column, 30 m × 0.25 mm i.d., 0.25 µm film thickness (Thermo Fisher Scientific) was applied to analyse the extracts. Helium (99.999%) was used as the carrier gas and kept at a flow rate of 1.0 mL min⁻¹. MS transfer line heater was 280 °C; ion source temperature was 250 °C; inlet temperature was 250 °C; electron energy was 70 eV. The GC–MS temperature program used was as follows: initial temperature 60 °C, increased to 240 °C at 20 °C min⁻¹ and held for 1 min, then raised to 270 °C at

10 °C min⁻¹ and held for 1 min, then increased to 280 °C at 5 °C min⁻¹ and held for 2 min. Standards and samples were analysed in full scan mode with a scan range of *m/z* 50–650. Samples were injected in splitless mode.

A JSM-5600 (Jeol, Tokyo, Japan) scanning electron microscope (SEM) was used for the SEM experiments. To prepare samples for SEM, composite hollow fibres were fixed on the stub by double-sided sticky tape and then coated with gold by a JFC-1600 Auto Fine sputter coater (Jeol) for 30 s.

2.4. Preparation of MWCNTs/SiO₂ reinforced hollow fibre

Silica sol (Li, Zhang, & Shi, 2011): 30 mL TEOS were added into the mixed solvent of 30 mL absolute ethanol and 9 mL deionised water at room temperature. 38% hydrochloric acid (1 mL) was added to the above solution dropwise under vigorous stirring. The sol was finally transferred to a closed glass container and aged at room temperature for 24 h. Fifty milligrams of hydroxylated MWCNTs were added to 5 mL of silica sol with stirring for 30 min. MWCNTs/silica composite sol solution was formed.

Polypropylene hollow fibres were cut into small segments with a length of 1 cm and rinsed in acetone for 5 min to remove any possible impurities in the fibre. The polypropylene hollow fibre was then entirely immersed in the above-prepared MWCNTs/SiO₂ composite sol for 30 min under sonication at room temperature to allow MWCNTs and silica particles to co-deposit on the porous surface of PP hollow fibre through layer-by-layer self-assembly, followed by a drying procedure with temperature controlled at 120 °C and maintained for 30 min. Subsequently, the above immersion and drying process were performed repeatedly, and MWCNTs/SiO₂ reinforced hollow fibres of about 8 mm length were obtained. Fig. 1 shows the SEM images of MWCNTs/SiO₂ reinforced hollow fibres at different view angles, which clearly represented the presence of MWCNTs in the outer surface and wall pores of the composite hollow fibre.

2.5. Extraction and desorption procedure

Prior to use, MWCNTs/SiO₂ reinforced hollow fibre was rinsed with acetone and dried in order to remove impurities. Extraction was carried out as follows: the composite hollow fibres were first immersed in the sample matrix (1.0 mL) in a small glass vial under sonication for a prescribed time. After extraction, the fibre was taken out from the sample carefully and gently dried with a filter paper. Finally, the fibre was directly placed in a centrifuge tube (1.5 mL) to desorb with desorption solvent (0.30 mL) under sonication at 40 °C for 10 min. Of the 0.30 mL final desorption solution, 1 µL was directly injected into the GC–MS system for analysis. After desorption, the extraction fibre was washed repeatedly with sulfuric acid and absolute ethanol to remove any possible residual analytes or other substances. The fibre was then dried in the oven at 120 °C for 30 min to avoid carry-over effects. Thus, the extraction fibre can be repeatedly used without reduction in extraction efficiency.

While agitation of the sample solution enhances mass transfer to the aqueous phase, the use of a stirrer could potentially damage and break the MWCNTs/SiO₂ hollow fibre by colliding with it repeatedly. Therefore, instead of a stirrer, an ultrasonic bath was used in our study to facilitate the extraction process.

3. Results and discussion

The adsorption of organic substances depends on the size of their molecules, chemical structures and polarity. Usually, the larger the molecule, the better is the sorption. Due to hydrophobic interaction of PAEs, as well as π – π interactions between the ben-

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