



## Analytical Methods

## Development of magnetic micro-solid phase extraction for analysis of phthalate esters in packaged food

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## ABSTRACT

A novel, simple and low cost magnetic multi-walled carbon nanotubes-poly (vinyl alcohol) cryogel-micro-solid phase extraction (magnetic-MWCNTs-PVA cryogel- $\mu$ -SPE) sorbent was synthesized by incorporating magnetic particles and MWCNTs into a PVA cryogel. The magnetic-MWCNTs-PVA cryogel- $\mu$ -SPE sorbent developed, with a large surface area and macro-porous structure, provided good sorbent-to-sorbent reproducibility (%RSD < 8) and each sorbent could be used up to 30 times (%RSD < 6). This sorbent was applied for the extraction of dibutyl phthalate (DBP) and di-2-(ethylhexyl) phthalate (DEHP) in packaged food prior to analysis by gas chromatograph coupled with flame ionisation detector (GC-FID). The concentration of DBP and DEHP in hot-water samples from plastic bags were found in the range 0.04–0.15  $\mu\text{g mL}^{-1}$  and 0.03–0.20  $\mu\text{g mL}^{-1}$ , respectively, but only DEHP was found in clear chicken soup samples in the range 0.02–0.07  $\mu\text{g mL}^{-1}$ .

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## 1. Introduction

In order to analyse trace level of contaminants in a complex matrix, sample preparation is one of the most important steps prior to any instrumental analysis. The most commonly used sample preparation techniques are solid phase extraction (SPE), solid phase microextraction (SPME) and liquid liquid extraction (LLE). Even though these techniques can be very successfully used in pre-concentrating target analytes for analysis, they still have some drawbacks. For example, LLE is time consuming and requires a large amount of sample and organic solvent while SPME fibres are relatively expensive, break easily and carry-over during extraction. The conventional SPE technique is also time-consuming and relatively expensive because it requires both an SPE manifold and a vacuum pump (Ahmadi, Assadi, Hosseini, & Rezaee, 2006; He et al., 2010; Prosen & Zupančič-Kralj, 1999; Wu, Zhao, Feng, Wang, & Wang, 2011). Therefore, any modification that might overcome some of the drawbacks would be useful.

Recently, there have been some developments in the SPE method, based on modifications to the sorbent materials using

magnetic particles (Meng, Bu, Deng, & Zhang, 2011; Wu et al., 2011), leading to the so-called magnetic solid phase extraction process (MSPE). With MSPE, the extraction process simply involves adding the magnetic adsorbent to the sample solution. After the analytes are adsorbed, the adsorbent can be, rapidly and simply, separated from the sample solution using an external magnet. The target compounds are then eluted from the magnetic adsorbent with a very small volume of an appropriate organic solvent (Zhang, Niu, Hu, Cai, & Shi, 2010). This technique has more advantages than the use of a conventional SPE sorbent packed in an SPE column or SPE cartridge, where high back pressure and clogging of the sorbent during loading can occur resulting in an unstable loading flow rate that affect the extraction efficiency (Chu, Lou, Yu, Hu, & Shen, 2011; Zhang & Shi, 2012).

Additional materials facilitating the adsorption of the analytes may be considered to further improve the MSPE technique. Among these, nanomaterial sorbents have attracted attention because of their high surface area-to-volume ratio, which results in a high extraction efficiency and an adsorption capability (Sha, Deng, & Liu, 2008; Song, Zhao, Tchounwou, & Liu, 2007). There have been many reports on the use of magnetic particles incorporated with nanomaterials such as graphene (Wu et al., 2011), single-walled carbon nanotubes (SWCNTs) (Rastkari, Ahmadvaniha, Samadi, Shafiee, & Yunesian, 2010) and multi-walled carbon nanotubes (MWCNTs) (Guan, Jiang, Hu, & Jia, 2010; Iijima, 1991) as magnetic

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nanosorbents. Among these, MWCNTs are the most widely used because of their hydrophobic property, adsorption capacity and large surface area. MWCNTs are particularly suited for adsorption of aromatic compounds because of  $\pi$ - $\pi$  interaction and Van der Waals force (Saridara, Brukh, Iqbal, & Mitra, 2005; Wang, 2000). However, the use of MWCNTs as an adsorbent alone can be problematic due to their very small size resulting in the loss of the sorbent during extraction and elution. Alternatively, immobilization of the MWCNTs onto or within an appropriate material may be a good approach.

Recently, Kueseng and co-workers have developed a multi-walled carbon nanotubes/poly (vinyl alcohol) (PVA) cryogel composite sorbent by entrapping MWCNTs in a high porosity PVA cryogel and used the resulting sorbent in a conventional SPE procedure for extracting polycyclic aromatic hydrocarbons (PAHs) in water samples. Although this SPE sorbent can solve clogging problem, due to its super-macro-porous structure, the extraction process is still time consuming and laborious. Moreover, it still requires a large volume of sample (500 mL) and/or organic solvent (15 mL) (Kueseng, Thammakhet, Thavarungkul, & Kanatharana, 2010).

In order to simplify the extraction/desorption procedure, and to make it more environmentally-friendly, a novel magnetic-MWCNTs-PVA cryogel- $\mu$ -SPE sorbent was developed by incorporating MWCNTs and magnetic particles into a PVA cryogel microbar. The magnetic-MWCNTs-PVA cryogel- $\mu$ -SPE sorbent developed was used to extract dibutyl phthalate (DBP) and di-2-(ethylhexyl) phthalate (DEHP) from food packed in plastic containers. These model chemicals and samples were selected because phthalate esters are the most widely used plasticizers in plastics production (Farahani, Ganjali, Danarvand, & Norouzi, 2008; Lau & Wong, 2000; Tsumura, Ishimitsu, Kaihara, Yoshii, & Tonogai, 2002) and they could migrate from the container to food and beverages (Balafas, Shaw, & Whitfield, 1999; Jen & Liu, 2006; Rios, Morales, & Márquez-Ruiz, 2010). To obtain the best extraction efficiency with the magnetic- $\mu$ -SPE sorbent developed, various parameters affecting adsorption efficiency such as time, type and volume of the desorption solvents, and the amount of MWCNTs used were optimised, and the analytical performance of the method developed was evaluated and validated.

## 2. Experimental

### 2.1. Chemicals and reagents

All chemicals used in this study were of analytical grade. Di-2-(ethylhexyl) phthalate (DEHP) (97% purity) and 25% glutaraldehyde were from Fluka (Buchs, Switzerland). Dibutyl phthalate (DBP) (99% purity), ferric chloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ) and ferrous chloride tetrahydrate ( $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ) were from Sigma-Aldrich (St. Louis, Missouri, USA). Acetone, hydrochloric acid (HCl), sodium chloride (NaCl) and sodium hydroxide (NaOH) were from Lab-Scan (Bangkok, Thailand). Hexane was from CARLO ERBA (Rodano, USA). PVA (MW 96,000  $\text{g mol}^{-1}$ , 98% hydrolysed) and ethyl acetate were from Merck (Darmstadt, Germany). Ultrapure water was obtained from a maximum ultrapure water system (18.2 M $\Omega$  ELGA, England). MWCNTs ( $\geq 95\%$  purity) with diameters of 60–100 nm and lengths of 2–5  $\mu\text{m}$  were from Shenzhen Nanotech Port Co., Ltd (Shenzhen, China).

### 2.2. Instrumentation

Gas chromatographic studies were performed using a gas chromatograph coupled with a flame ionisation detector (GC-FID) (Shimadzu 14B, Kyoto, Japan) with a DB-5 fused silica capillary column

(30 m length, 0.25 mm I.D. and 0.25  $\mu\text{m}$  film thickness; J&W Scientific, CA, USA). Scanning electron microscope (SEM) images of the magnetic-MWCNTs-PVA cryogel- $\mu$ -SPE sorbent were obtained using a JSM 5200 (JEOL, Japan). The extraction of DBP and DEHP using the magnetic-MWCNTs-PVA cryogel- $\mu$ -SPE sorbent under sonication was carried out in an ultrasonic bath at 37 kHz (Ultrasonic Cleaning Units, Model Elmasonic S 100H, Singen, Germany).

### 2.3. Optimisation of GC-FID conditions

To obtain the best performance (high response, good peak resolution and short analysis time), analysis conditions were optimised including: flow rates of the carrier ( $\text{He}$ ), make up ( $\text{N}_2$ ), fuel ( $\text{H}_2$ ) and oxidant (air) gases, and temperatures of the injector, detector and column. In this study, 1  $\mu\text{L}$  of the DBP and DEHP working standard solution (10  $\mu\text{g mL}^{-1}$ ) was injected into the GC-FID to optimise each parameter (five replications for each tested value). One parameter at a time was varied to optimise performance. When one value was obtained, it was fixed and the next parameter was optimised.

### 2.4. Preparation of the magnetic-MWCNTs-PVA cryogel- $\mu$ -SPE sorbent

To obtain the novel magnetic-MWCNTs-PVA cryogel- $\mu$ -SPE sorbent, the magnetic particles ( $\text{Fe}_3\text{O}_4$ ) were synthesized using the co-precipitation method reported by Wang, Guo, Yu, and He (2006). In brief 5.2 g of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and 2.0 g of  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  were dissolved in 25 mL of ultrapure water under a stream of  $\text{N}_2$  gas for 30 min followed by the addition of 0.85 mL of concentrated HCl. The resulting solution was added dropwise into 250 mL 1.5  $\text{mol L}^{-1}$  NaOH using vigorous stirring. The magnetic particles produced were separated from the solution using an external magnet. Finally the magnetic particles were washed with ultrapure water before further use.

PVA solution (3.3% w/v) was prepared by dissolving PVA powder in ultrapure water at 90  $^\circ\text{C}$ , stirred for 60 min to obtain a clear viscous solution, and left to cool at room temperature before the pH was adjusted to 1 using 5.0  $\text{mol L}^{-1}$  HCl (Kueseng et al., 2010). Then, 0.1 g synthesized  $\text{Fe}_3\text{O}_4$  and 0.03 g of MWCNTs were added to 1.5 mL PVA, thoroughly mixed using a vortex mixer and sonicated for 30 min in an ultrasonic bath to ensure the homogeneous dispersion of  $\text{Fe}_3\text{O}_4$  and MWCNTs. This composite was cooled in an ice bath for 5 min before adding 30  $\mu\text{L}$  of glutaraldehyde as a cross-linking agent, to obtain a final concentration of 0.5% v/v. Then the solution was stirred for 1 min, poured into the  $\mu$ -SPE template (a 4.0 cm  $\times$  5.0 cm  $\times$  0.60 cm acrylic plastic plate with 20 holes, each with an I.D. of 0.30 cm and a length of 0.60 cm) and kept at  $-20^\circ\text{C}$  for 12 h. The frozen composite microbars were removed from the template, thawed at room temperature for 10 min and washed with ultrapure water until the eluted water was neutral. This procedure provided 20 pieces of the magnetic-MWCNTs-PVA cryogel- $\mu$ -SPE sorbent with 1.5 mg of MWCNTs for each sorbent (as described in Section 3.3.5). The sorbent morphology was investigated using a scanning electron microscope (SEM).

### 2.5. Adsorption and desorption procedures for the magnetic-MWCNTs-PVA cryogel- $\mu$ -SPE sorbent

The extraction procedure for the analytes using the magnetic-MWCNTs-PVA cryogel- $\mu$ -SPE sorbent is shown in Fig. 1A. First, a piece of the sorbent (Fig. 1B) was placed in a 2 mL amber vial containing 1 mL of 10  $\mu\text{g mL}^{-1}$  standard solution. The vial was then closed with a PTFE-silicone septum before being sonicated in an ultrasonic bath for 30 min during which time the analytes were adsorbed by the sorbent. After that, the solution was removed

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