



# Polypropylene membrane coated with carbon nanotubes functionalized with chitosan: Application in the microextraction of polychlorinated biphenyls and polybrominated diphenyl ethers from environmental water samples



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## ABSTRACT

Acid oxidized multi-walled carbon nanotubes (CNTs) functionalized with chitosan were coated on polypropylene membrane and used as sorbent to extract trace polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) from environmental water samples. The analytes were extracted by the hydrophobic interaction between analytes and the functionalized CNTs. The chitosan polymer coating also contributed to extraction efficiency. Microextraction conditions (different types of desorption solvent, extraction time, salt concentration, stirring rate and desorption time) were optimized by means of orthogonal array design (OAD). A mixed level OAD matrix, OA<sub>16</sub> (4<sup>1</sup> × 2<sup>12</sup>) was employed for the initial optimization. Based on the results of the first step, *n*-hexane was chosen as desorption solvent and 5 min was selected as desorption time. Extraction time, stirring rate and salt concentration were further optimized in the second step by an OA<sub>16</sub> (4<sup>5</sup>) matrix. Under the optimized conditions, calibration curves with coefficients of determination higher than 0.993 over the concentration range of 0.2 and 50 ng/ml. Low limits of detection (<0.60 ng/l) and acceptable reproducibility with relative standard deviations in the range of 0.17% and 5.01%, were achieved. The developed method was applied to extract PCBs and PBDEs from environmental water samples. The relative recoveries of the analytes spiked into the real water samples ranged from 85.6 to 104.1% at 0.2 ng/ml of each analyte, and from 82.4 to 98.6% at 2 ng/ml of each analyte.

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## 1. Introduction

Sample preparation is a critical step for the determination of trace organic pollutants in environmental water samples. In general, liquid–liquid extraction (LLE) [1,2] and solid-phase extraction (SPE) [3–5] are the most widely used sample preparation techniques. However, these methods can be tedious, labor-intensive and time-consuming. They also consume moderate to large quantities of toxic and expensive organic solvents. Solid-phase microextraction (SPME) was introduced as an alternative extraction method in the late 1980s [6]. It is a solvent-free and

environmentally sound extraction technique. SPME has gained extensive applicability in many areas since its introduction [7–11]. Although convenient to use, commercial SPME fibers are, however, still relatively expensive [12]. Moreover, a limited range of sorbents available commercially has led to a very fertile field of research in the in-house synthesis of sorbents and their coating on a variety of fiber types for SPME applications.

Carbon nanotubes (CNTs) have received great attention since their discovery in 1991 by Iijima [13]. There have been an increasing number of applications of CNTs in various fields of chemical analysis because they exhibit unique structural, mechanical and chemical properties [14–18]. According to the carbon layers of the wall of the nanotubes, these materials can be classified as single-walled carbon nanotubes (SW) CNTs [19] or multiwalled (MW) CNTs [20,21]. CNTs as extraction materials have been reported [22–26]. Cai and co-workers [22,23] and Li et al. [24] applied MWCNTs as SPE packing materials for the extraction of alkylphenols, phthalates, and

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volatile organic compounds. Guo and Lee explored the potential of MWCNTs as sorbent for the micro-SPE ( $\mu$ -SPE) of polycyclic aromatic hydrocarbons (PAHs) [25]. Zhang et al. applied functionalized CNTs-coated SPME to the extraction of polybrominated diphenyl ethers (PBDEs) [26].

Chitosan is a linear  $\beta$ -1,4-linked polysaccharide that is obtained by the partial deacetylation of chitin. There are many reactive amino and hydroxyl groups in the chitosan skeleton, which can be cross-linked with covalent or ionic cross-linkers to form chitosan hydrogel. The most common covalent cross-linker is glutaraldehyde, which has been applied to chitosan [27,28]. In the present work, a chitosan functionalized acidic MWCNTs coating on a polypropylene membrane was prepared and used as sorbent for the extraction of polychlorinated biphenyls (PCBs) and PBDEs from environmental water samples. The surface of the MWCNTs was oxidized by a mixture of  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  to give MWCNT-COOH, and then a layer of hydrophilic chitosan was coated on the MWCNT-COOH surface to form a chitosan-CNTs (CC) sorbent, which was subsequently coated on a polypropylene membrane. (Such a coated membrane is henceforth termed as CCMe.)

PBDEs are widely used as flame retardant additives in polymers and textiles which are easily released into the environment [29]. PCBs were employed in many industrial applications as complex commercial mixtures [30] before they were banned under the Stockholm Convention of the United Nations Environment Program [31]. PBDEs and PCBs are lipophilic, resistant to degradation, and are concentrated by organisms. Therefore, PCBs and PBDEs can be present in environmental water at potentially harmful concentrations. The development of a sensitive analytical method to determine the PCBs and PBDEs is therefore desirable.

In the present work, determination of PCBs and PBDEs in water was conducted by gas chromatography mass spectrometry (GC-MS) after extraction by the CCMe material. Extraction parameters: desorption solvent, salt concentration, extraction time, desorption time and stirring rate were optimized by an orthogonal array designs (OADs) procedure with an  $\text{OA}_{16}$  ( $4^1 \times 2^{12}$ ) matrix in the first optimization step. Based on the results obtained from the first step, *n*-hexane was chosen as desorption solvent and 5 min was set as desorption time, and extraction time, stirring rate and salt concentration were further optimized by an  $\text{OA}_{16}$  ( $4^3$ ) matrix. The quantitative performance of the proposed CCMe microextraction, in terms of linearity, coefficients of determination ( $r^2$ ), precision, and limits of detection (LODs), were determined under the optimum conditions. The proposed method was applied to determine PCBs and PBDEs in environmental water samples.

## 2. Experimental

### 2.1. Chemicals and materials

PBDEs (BDE-47, BDE-49 and BDE-99) and PCB-35 were obtained from Aldrich (Steinheim, Germany). HPLC grade organic solvents methanol, *n*-hexane and acetonitrile were purchased from Tedia (Fairfield, OH, USA) and isooctane was bought from Merck (Darmstadt, Germany). Sodium chloride was purchased from GCE (Chula Vista, CA, USA). Nitric acid ( $\text{HNO}_3$ ) and sulfuric acid ( $\text{H}_2\text{SO}_4$ ) were bought from Merck. Ultrapure water was produced on a Milli-Q water purification system (Millipore, Milford, MA, USA).

MWCNTs were bought from Sigma Aldrich (Milwaukee, WI, USA). Chitosan was obtained from Aldrich. The porous flatsheet polypropylene membrane (157  $\mu\text{m}$  thickness, 0.2  $\mu\text{m}$  pore size) was purchased from Membrana (Wuppertal, Germany). Individual stock solutions of pure PCB-35 and PBDEs were prepared in *n*-hexane at 2 mg/ml concentrations and stored at  $-20^\circ\text{C}$ . Working solutions containing all analytes at different concentrations in ultrapure water were prepared from the stock solution. The

concentrations of working solutions used for the optimization procedure were 0.2 ng/ml.

### 2.2. Apparatus

Analysis of PCB-35 and PBDEs was performed on a Shimadzu QP 2010 GC-MS system (Kyoto, Japan) equipped with a Shimadzu AOC-201 autosampler and a DB-5MS (J&W Scientific, Folsom, CA, USA) fused-silica capillary column (15 m  $\times$  0.25 mm internal diameter). Helium was employed as the carrier gas at a flow rate of 2 ml/min. The GC-MS interface was maintained at a temperature of  $260^\circ\text{C}$ . The injector temperature was held at  $280^\circ\text{C}$  and all injections were made in the splitless mode. The oven temperature programme applied was as follows: the initial temperature was  $80^\circ\text{C}$ , held for 2 min, then an increase to  $250^\circ\text{C}$  at  $25^\circ\text{C}/\text{min}$  and further to  $300^\circ\text{C}$  at  $5^\circ\text{C}/\text{min}$ , held for 10 min. All standards and samples were analyzed in selective ion monitoring (SIM) mode.

### 2.3. Preparation of CCMe

To functionalize the MWCNTs, 100 mg of the material was stirred in a 3:1 (v:v) mixture of  $\text{H}_2\text{SO}_4$  (98%)/ $\text{HNO}_3$  (65%) for 12 h at  $70^\circ\text{C}$ . A 1.0% chitosan stock solution was prepared by dissolving 100 mg of the material in 10 ml of 1.0% (v/v) acetic acid solution. A dispersion of 0.5% (m/v) functionalized MWCNTs in 1% (m/v) chitosan solution was prepared by mixing 10 mg of functionalized MWCNTs in 2 ml of the 1.0% (m/m) chitosan solution, and then 0.4 ml of 0.5% glutaraldehyde was added into the prepared solution under vigorous mechanical stirring and aged for 3 h. The detailed procedure has been previously reported [32]. The polypropylene membrane was trimmed to a size of 1 cm  $\times$  0.4 cm, followed by ultrasonic cleaning with acetone and then air dried. It was then immersed in the chitosan-CNT solution for 30 s. The prepared CCMe was then removed and dried in an oven at  $60^\circ\text{C}$  for 4 h to evaporate the solvent completely.

### 2.4. Extraction procedure

For the microextraction procedure, 10 ml of sample solution was added to a 15 ml sample vial containing a 15 mm  $\times$  6 mm magnetic stirring bar and then one piece of the CCMe was added to the sample. The sample vial was then placed on a magnetic stirrer plate. The CCMe in the sample tumbled freely during extraction. The membrane was removed with a pair of tweezers after the extraction and placed in a 300  $\mu\text{l}$  glass insert for desorption. Desorption was conducted by sonication for 5 min in 30  $\mu\text{l}$  of desorption solvent for 5 min. One microliter of the extract was injected into the GC-MS system for analysis.

### 2.5. Calculation of extraction efficiency

The definition of the extraction efficiency is given as the ratio of the amount of analyte present in the extracted solution to the amount of analyte in the standard solution which was injected directly into GC-MS without any extraction [33]. Extraction efficiency ( $E$ ) was calculated according to the following equation:

$$E\% = \frac{A_2}{A_s} \times \frac{C_s}{C_a} \times \frac{V_a}{V_s} \times 100\%$$

where  $A_s$  and  $A_2$  represent peak areas obtained for standard solutions and extracted solutions respectively,  $C_s$  and  $C_a$  represent concentrations of standard solution and analyte in the spiked solution used for extraction, and  $V_s$  and  $V_a$  represent volumes of sample solution and desorption solvent.

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