



## Enrichment of polycyclic aromatic hydrocarbons in seawater with magnesium oxide microspheres as a solid-phase extraction sorbent

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### ABSTRACT

The enrichment of polycyclic aromatic hydrocarbons (PAHs) in water samples with magnesium oxide (MgO) microspheres was evaluated, and four 3–5-ring PAHs were used as probes to validate the adsorption capacity of the material. Factors affecting the recovery of PAHs were investigated in detail, including the type and concentration of organic modifiers, elution solvents, particle size of the adsorbent, volume and flow rate of the samples, and the lifetime of MgO cartridges. The recoveries of four PAHs extracted from 20 mL of seawater spiked with standard PAHs ranged from 85.8% to 102.0% under the optimised conditions. The limits of detection varied from 1.83 ng L<sup>-1</sup> to 16.03 ng L<sup>-1</sup>, indicating that the analytical method was highly sensitive. Additionally, the proposed method was successfully used to enrich PAHs in seawater. Compared to conventional methods, the proposed method consumed less organic modifier (5% acetone), and cheaper sorbents with comparable extraction efficiency were employed.

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### 1. Introduction

In recent years, polycyclic aromatic hydrocarbons (PAHs), a class of organic compounds with two or more fused aromatic rings, have drawn a considerable amount of attention due to their carcinogenicity and mutagenicity [1,2]. They are formed mainly as a result of pyrolytic processes, especially the incomplete combustion of organic materials during industrial activities. For instance, PAHs are formed from the processing of coal and crude oil, the combustion of natural gas and refuse, and vehicular traffic. Moreover, they can be formed from natural processes such as carbonisation. The United States Environmental Protection Agency had designated 16 PAHs as priority pollutants.

However, due to their non-polar structure and extremely low water solubility, the concentration of PAHs in natural water is extremely low. To improve the sensitivity of analysis, solid-phase extraction (SPE) techniques are often used to enrich PAHs at trace levels in various environmental matrices such as soil [3,4], water [5–7], and air [8]. Sorbents are the most important component

of SPE; thus, these materials have received a significant amount of attention from various research groups. A variety of different SPE sorbents have been developed, including silica-based matrices [9–12], multiwalled carbon nanotubes [13], octadecyl functional magnetic ferrite microspheres [7], molecularly imprinted polymers [6], and tetradecanoate hemimicelles [14]. In the past few years, C18 bonded silica has become the most important SPE adsorbent. To improve the recoveries of 2–6-ring PAHs, optimal parameters for various C18 SPE cartridges have been determined [4,10–12,15]. For example, Buseti and coworkers [4] tested three different sorbents (StrataE, StrataM, and Supelclean Envi-18) and demonstrated that StrataE exhibited superior recovery (83–102%) and reproducibility for a variety of different PAHs; however, poor results (83–87%) were obtained for 5–6-ring PAHs. Interactions between organic analytes and C30, a hydrophobic SPE sorbent, are superior to that of other materials; thus, Li et al. [9] developed a method for the determination of PAHs in airborne particulates and obtained satisfactory results for high-ring PAHs using C30 bonded silica. Recently, Krupadam et al. [6] successfully synthesised a molecularly imprinted polymer using standard PAHs as a template, and obtained excellent recoveries of nearly 100% for PAHs standard and 71–98% for environmental samples using fluorescence spectrophotometry, including coastal sediments, atmospheric particulates, and industrial effluents. Additionally, Liu et al. [7] and Ballesteros-Gómez and Rubio [14] prepared C18 magnetic ferrite microspheres and tetradecanoate hemimicelles on Fe<sub>3</sub>O<sub>4</sub> nanoparticles to determine the concentration of PAHs in aqueous samples, respectively. The results of the aforementioned study indicated that the proposed

**Abbreviations:** PAHs, polycyclic aromatic hydrocarbons; MgO, magnesium oxide; SPE, solid-phase extraction; PHEN, phenanthrene; ANTH, anthracene; PYR, pyrene; BaP, benzo[a]pyrene; ACN, acetonitrile; MeOH, methanol; DCM, dichloromethane; HPLC, high-performance liquid chromatography; LOD, limits of detection; LOQ, limits of quantification; RSD, relative standard deviation; PF, pre-concentration factor.

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extraction method was an effective procedure for sample pretreatment. Although these novel materials could improve recovery rates, multiple steps must be conducted to properly prepare samples. Therefore, new, simple, and alternative SPE methods for the enrichment of PAHs in water samples must be developed.

In a previous report, MgO microspheres were successfully prepared by seed-induced precipitation, and excellent efficiency in the separation of PAHs was obtained [16]. In contrast to conventional silica, MgO displays unique selectivity for the separation of basic compounds in normal-phase liquid chromatography, including aniline, quinoline, and pyridine derivatives [17]. The high adsorption capacity for electron-rich compounds is attributed to interactions between oxygen vacancies at the surface or sub-surface of MgO and lone pairs of electrons on the analyte [17]. In addition, MgO microspheres were successfully used to preconcentrate benzo[a]pyrene (BaP) in environmental water, and recovery rates of 94–101% were obtained [18]. However, the performance of MgO as a SPE sorbent for enriching multifold PAHs has not yet been investigated. In this study, the extraction efficiencies of MgO for four 3–5-ring PAHs were studied systematically. Parameters affecting the extraction efficiency of the material were investigated in detail, including the type and concentration of organic modifiers, elution solvents, particle size of the adsorbent, volume and flow rate of the sample, and the lifetime of MgO cartridges. In addition, the optimised method was used to enrich PAHs in seawater.

## 2. Experimental

### 2.1. Chemicals and materials

Magnesium nitrate ( $\text{Mg}(\text{NO}_3)_2$ ) and potassium carbonate ( $\text{K}_2\text{CO}_3$ ) were purchased from Kermel Chemical Reagent Co., Ltd. (Tianjin, China). Sodium polyphosphate and  $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$  seeds were obtained from Beijing Chemical Reagent Co., Ltd. (Beijing, China) and Beijing Shuanghuan Chemical Reagent Factory (Beijing, China), respectively. HPLC-grade acetonitrile (ACN) and methanol (MeOH) were purchased from Shandong Yuwang Industrial Co., Ltd. Chemical Branch (Yuwang, China), and HPLC-grade dichloromethane (DCM), isopropanol and *n*-hexane were purchased from Tianjin Chemical Reagents Institute (Tianjin, China), Shenyang Chemical Reagents Institute (Shenyang, China), and Tianjin Kermel Chemical Reagents Co., Ltd. (Tianjin, China), respectively. Reagent grade ethyl acetate and acetone were purchased from Shenyang Chemical Reagents Factory (Shenyang, China). Phenanthrene (PHEN), anthracene (ANTH), pyrene (PRY), and BaP (>98%) were obtained from Fluka (Buchs, Switzerland), Beijing Chemworks (Beijing, China), BDH Laboratory Chemicals Group (Poole, England), and Fluka (Buchs, Switzerland), respectively. Ultrapure water was obtained from a Millipore system, and Sep-Pak cartridges (Vac C18 3cc) were purchased from Waters (Milford, MA, USA).

### 2.2. Preparation of standard PAH solutions

Stock solutions of PHEN ( $72 \text{ mg L}^{-1}$ ), ANTH ( $68 \text{ mg L}^{-1}$ ), PYR ( $72 \text{ mg L}^{-1}$ ), and BaP ( $16 \text{ mg L}^{-1}$ ) were prepared in MeOH, respectively. PAHs standard #1 ( $0.28 \text{ mg L}^{-1}$  PHEN,  $0.22 \text{ mg L}^{-1}$  ANTH,  $0.63 \text{ mg L}^{-1}$  PYR, and  $0.33 \text{ mg L}^{-1}$  BaP) and PAHs standard #2 ( $54 \mu\text{g L}^{-1}$  PHEN,  $17 \mu\text{g L}^{-1}$  ANTH,  $144 \mu\text{g L}^{-1}$  PYR, and  $9.5 \mu\text{g L}^{-1}$  BaP) were prepared by diluting the standard stock solution with ACN. The solutions were stored in a refrigerator at  $4^\circ\text{C}$  to reduce losses by evaporation.

### 2.3. Preparation of MgO microspheres

MgO microspheres were prepared according to the method described in our previous report [16]. To synthesise MgO spheres,

$20.52 \text{ g}$  of  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  was dissolved in  $100 \text{ mL}$  of ultrapure water. The resulting solution was transferred to a  $500\text{-mL}$  three-necked flask and heated to  $70^\circ\text{C}$ . In a separate flask,  $0.3 \text{ g}$  of sodium polyphosphate was added to  $200 \text{ mL}$  of a  $0.4 \text{ M}$  solution of  $\text{K}_2\text{CO}_3$ , and the mixture was heated to  $70^\circ\text{C}$ . Under vigorous stirring, the  $\text{K}_2\text{CO}_3$  solution was added into the solution of  $\text{Mg}(\text{NO}_3)_2$  over  $4\text{--}5 \text{ s}$ . Next, two drops of  $0.4 \text{ mg mL}^{-1}$  of  $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 6\text{H}_2\text{O}$ , which had been dispersed in water by ultrasonication, was rapidly added to the reaction mixture, and the resulting solution was stirred for  $1 \text{ min}$ . The mixture was maintained at  $70^\circ\text{C}$  for  $1 \text{ h}$  under static condition, and the temperature of the reaction was increased to  $100^\circ\text{C}$  for  $1 \text{ h}$ . Finally, the product was collected, filtered, and washed with ultrapure water and ethanol. The material was calcined in air from room temperature to  $300^\circ\text{C}$  at a rate of  $2^\circ\text{C min}^{-1}$  for  $2 \text{ h}$ . Upon completion, the product was calcined from room temperature to  $550^\circ\text{C}$  in a muffle furnace for  $7 \text{ h}$  to obtain MgO microspheres.

### 2.4. Chromatographic measurements of PAHs on MgO column

The SPE sorbent was packed into stainless-steel tubes by applying a slurry of MgO microspheres ( $100 \text{ mm} \times 4.6 \text{ mm i.d.}$ ). Standard solutions of PHEN, ANTH, PYR, and BaP were analysed with a Waters high-performance liquid chromatography (HPLC) system. The flow rate of the mobile phase (100% of MeOH) was set to  $0.8 \text{ mL min}^{-1}$ .

### 2.5. SPE procedure

#### 2.5.1. Preparation of SPE columns

The SPE columns were prepared by packing  $0.2 \text{ g}$  of spherical MgO into an empty cartridge ( $6 \text{ mL}$ , polypropylene). Upper and lower frits were placed at each end of the cartridge to hold the packing material in place. Next, the cartridge was conditioned by sequentially eluting with DCM ( $5 \text{ mL}$ ), organic modifiers ( $4 \text{ mL}$ , e.g., acetone, MeOH, and isopropanol), and a solution of ultrapure water and organic modifiers ( $4 \text{ mL}$  of 5:95 (v/v); 15:85 (v/v); 25:75 (v/v), respectively).

#### 2.5.2. The analysis of synthetic water samples via SPE

To obtain synthetic water samples, aliquots of organic modifiers (e.g., 0, 5, 15, and 25% (v/v) of MeOH, acetone, and isopropanol, respectively) and  $1 \text{ mL}$  of PAH standard #1 were added to ultrapure water, and the resulting suspension was ultrasonicated. The synthetic water samples were passed through each cartridge at a specific flow rate (e.g., 1.0, 2.5, and  $5.0 \text{ mL min}^{-1}$ ). After loading the samples, the cartridges were washed with  $3 \text{ mL}$  of ultrapure water and were dried thoroughly with a vacuum pump. Subsequently, the target compounds were eluted with different elution solvents ( $2 \times 2.5 \text{ mL}$  of DCM, *n*-hexane, or ethyl acetate) and the volume of the elutant was evaporated to  $<100 \mu\text{L}$  with a gentle stream of nitrogen. Finally, the volume of the elutant was reconstituted to  $2 \text{ mL}$  with 80% (v/v) ACN- $\text{H}_2\text{O}$ , and the solution was stored in  $2 \text{ mL}$  Teflon-lined screw capped glass vials at  $4^\circ\text{C}$ .

#### 2.5.3. The analysis of spiked seawater via SPE

Prior to SPE, seawater was filtered through a solvent filtration apparatus to remove suspended sediments and solid materials. To prepare  $20 \text{ mL}$  of spiked seawater, a procedure similar to the method described in Section 2.5.2 was employed; however, ultrapure water and PAHs standard #1 was replaced with seawater and PAHs standard #2, respectively. SPE was carried out under the optimised conditions, and the elutant was treated as described in Section 2.5.2.

### 2.6. Instrumental analysis

Pretreated samples were analysed with a Waters HPLC system consisting of a Waters 2695 separations module and a Waters

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