



# Double-functionalized magnetic nanoparticles for preconcentration and determination of polycyclic aromatic hydrocarbons in water samples



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## ABSTRACT

A rapid and simple method for the separation and determination of five polycyclic aromatic hydrocarbons (PAHs) in water is described. The procedure is based on the selective extraction of the PAHs on the surface of modified magnetic nanoparticles using a solid-phase dispersion technique. The PAHs-loaded magnetic nanoparticles were separated from the aqueous phase with a magnet and then quantified by HPLC. The modified extraction method successfully replaced conventional extraction methods. The partitioning of the analyte between the sub-micron magnetic nanoparticles (solid phase) and the liquid phase occurs as the solid moves through the samples as a colloidal sol. The detection limits were in the range 0.14–0.31 ng/L, with recoveries ranging from 88% to 96%. The as-synthesized magnetic nanoparticles showed good stability and high extraction recoveries for the adsorption-desorption of PAHs, even after recycling four times. The procedure was successfully applied to PAHs determinations in real water samples.

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## 1. Introduction

The term ‘polycyclic aromatic hydrocarbon (PAH)’ is a colloquial descriptor that refers to a large group of organic compounds that typically contain two or more fused benzene rings, although there is no single classification that collectively describes these compounds. PAHs are widespread and ubiquitous contaminants of the natural environment [1], and are an important class of marine organic pollutants. High-molecular-weight PAHs have demonstrated carcinogenicity in experimental animals, as well as genotoxicity and mutagenicity *in vitro* and *in vivo* [2–5], whilst lower molecular weight species are known to be narcotic to marine organisms [6]. PAHs are introduced into aqueous media by numerous pathways, including gas emissions from industrial combustion, in the discharge of fossil fuels, and from residential heating [7–9]. The reliable quantification of PAHs in environmental samples, particularly in water, is still difficult for a number of reasons. First, they are usually present in natural water as extremely complex mixtures

that contain many isomeric structures and alkylated isomers [10]. Second, their contamination levels in environmental water samples are usually below the detection limits of current analytical methods [11]. Finally, no certified reference standards for water are available. Under standards adopted by the European Union (EU), the maximum allowable concentration of PAHs in drinking water is 200 ng/L [12].

To measure the low concentrations of these compounds that occur in water samples, most of the methods developed so far have applied different extraction and preconcentration techniques, including Soxhlet extraction [13], ultrasound-assisted extraction [14], and liquid-liquid extraction (LLE) [15]. These extraction techniques require large amounts of toxic organic solvents and are time-consuming. Solid-phase extraction (SPE) [16], supercritical fluid extraction (SFE) [17], and cloud-point extraction are good replacements [18], as they require lower volumes of organic solvents; however, they are also expensive and complicated procedures. Solid-phase microextraction (SPME) is a solvent-free extraction method that has been used as a concentration technique for the quantification of PAHs in water samples [19]. SPME simplifies sample handling and manipulation by integrating sampling, extraction, concentration, and sample introduction into one step

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with a single device. However, some degradation of the solid-phase microextraction fibers occurs during repeated usage [20]. In recent years, a novel extraction approach based on the solid-phase dispersion extraction (SPDE) technique was developed by Howard and Khadry [21]; this method employs carefully size-selected modified spherical silica particles functionalized with different chemical groups as the extracting agent. Conceptually, this method is based on the partitioning of the analyte between a sub-micron solid and a liquid phase as a colloidal sol. By tailoring the size of the particles to approximately 50 nm diameter, they can be easily dispersed in aqueous solution, without the need for any mechanical or hand shaking, and the solid can then be readily recovered, together with the analytes, by simple filtration, centrifugation, or magnetic force [22].

Iron oxide magnetic nanoparticles (MNPs) have emerged as a new type of important functional sub-micron nanoparticles [23]. Unmodified MNPs have some limitations, as they aggregate in aqueous solution, and thus, lose the ability to extract the analytes from the solutions [24]. In addition, the MNPs have high chemical activity and are easily oxidized when exposed to air. Therefore, the suitable coating of the MNPs, such as by silanization, is essential to protecting and maintaining their chemical stability. Another advantage of silica-coating iron oxide MNPs is that the silanol-terminated surface groups may be modified with various coupling agents to covalently bind to specific ligands for selective analyte extraction.

Recently, a novel extraction approach based on magnetic solid-phase extraction (MSPE) has been developed. The MSPE method employed carefully size-selected magnetic nanoparticles (MNPs) functionalized with different chemical groups (extracting agent) and dispersed into aqueous solutions to adsorb target compounds, then the sorbent is isolated rapidly and conveniently by an external magnetic field without the need of additional centrifugation or filtration. MSPE has several advantages, such as, high extraction efficiency, low consumption of organic solvents and convenience of operation. Various MNPs were synthesized and functionalized for the extraction of PAHs from different environmental samples. For example, carbon coated  $\text{Fe}_3\text{O}_4$  MNPs ( $\text{Fe}_3\text{O}_4/\text{C}$ ) [25,26]  $\text{C}_{18}$ -functionalized  $\text{Fe}_3\text{O}_4$  MNPs ( $\text{Fe}_3\text{O}_4\text{-C}_{18}$ ) [27,28], diphenyl functionalization of MNPs ( $\text{Fe}_3\text{O}_4$ -diphenyl) [29], *n*-octadecylphosphonic acid modified MNPs [30], cholesterol- functionalized MNPs [31], polydopamine coated  $\text{Fe}_3\text{O}_4$  nanoarticles ( $\text{Fe}_3\text{O}_4/\text{PDA}$ ) [32], Fluorenyl -functionalized  $\text{Fe}_3\text{O}_4$  MNPs [33] and naphthyl- functionalized  $\text{Fe}_3\text{O}_4$  MNPs [34]. However, most of these MNPs are hydrophobic materials, which difficult to disperse in aqueous samples leading to decrease their extraction ability. In the present work, a novel solution to this disadvantage was developed. This involves the synthesized of a new kind of MNPs termed as *n*-hexadecylsilanol-diol magnetic nanoparticles ( $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{C}_{16}\text{-HO}$ ) and this material has been employed for the pre-concentration and extraction of PAHs compounds from water samples. The hydrophobic  $\text{C}_{16}$  groups are functionalized for extraction while the hydrophilic diol groups are designed for dispersing.  $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{C}_{16}\text{-HO}$  has several advantages over other MNPs. Solid phase dispersion extraction using the  $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{C}_{16}\text{-HO}$  magnetic nanoparticles was significantly improved by the incorporation of the diol groups during the modification, as this resulted in magnetic nanoparticles that could be easily dispersed in water samples. Sample handling steps are minimized since the magnetic sorbent can dispersed directly into the aqueous samples without any additional treatment. Since the ( $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{C}_{16}\text{-HO}$ ) can be dispersed easily in aqueous solution, the contact surface between analytes and sorbent is very large, which results in a rapid mass transfer and fast extraction equilibrium. Thus, large numbers of samples can be quickly and simultaneously treated even at the sampling site. In addition, the specially

designed material could ensure operational convenience and improve reproducibility during extraction. All of these advantages combine to make the  $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{C}_{16}\text{-HO}$  solid phase dispersion extraction a powerful tool in the analysis of PAHs in water samples and very useful in monitoring programs assessing PAHs contamination in natural water systems.

The entire procedure (extraction plus concentration plus quantification) takes less than 30 min, and allows the determination of PAHs at low levels. The analytes are first collected on the surface of the modified MNPs and then selectively determined by HPLC-UV. Extraction conditions and chromatographic parameters were optimized to achieve maximum sensitivity with minimum analysis time. Special attention was paid to the synthesis and characterization of the MNPs due to their influence on the extraction efficiency of the proposed procedure.

## 2. Experimental

### 2.1. Apparatus

Chromatographic separations of the PAHs were performed with a Perkin-Elmer 200 HPLC system (Germany) equipped with a vacuum degasser, binary pump, heated column compartment, and an injection loop of 20  $\mu\text{L}$  nominal volume. The UV-Vis detector (Perkin-ElmerSeries20) was set at 230 nm. The chromatographic column was a Waters NOVA PAK  $\text{C}_{18}$  (5  $\mu\text{m}$  particle size, 150 mm  $\times$  3.9 mm, Milford, MA, USA). The mobile phase comprised 60% acetonitrile and 40% doubly distilled water filtered through a 0.45  $\mu\text{m}$  filter before use. Separations were performed with a constant flow rate of 1.0 mL/min. The column temperature was set at 40  $^\circ\text{C}$  in a thermostatically controlled oven.

### 2.2. Materials and reagents

The glassware used for the standards preparation and PAHs extraction was washed with detergent, rinsed with tap water and deionized water, left in a 5% nitric acid bath for at least 24 h, dried in an oven at 50  $^\circ\text{C}$  for 8 h, and finally rinsed thoroughly with deionized water before use. Purified water (conductivity > 18 M $\Omega$ /cm) was distilled and deionized using a Millipore 60 system (Bedford, MA, USA). Toluene (99.99%, HPLC grade) was purchased from Fisher (Loughborough, UK) and dried by fractional distillation under  $\text{N}_2$  from over  $\text{P}_2\text{O}_5$ . Fluorene, anthracene, fluoranthene, pyrene, and chrysene were obtained from Sigma-Aldrich (Stockholm, Sweden). [ $2\text{H}^7$ ]Ropivacaine, supplied by the Department of Medicinal Chemistry, AstraZeneca (Sweden), was used as an internal standard (I.S.). HPLC-grade methanol and ethanol were obtained from Merck (Darmstadt, Germany). Glacial acetic acid and sodium acetate were purchased from Aldrich (Milwaukee, WI, USA), and ferric chloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\geq 98\%$ ), ethyl alcohol (99%, analytical grade) sodium sulfite ( $\text{Na}_2\text{SO}_3$ ,  $\geq 98\%$ ), and anhydrous ammonia (99.5%, analytical grade) were purchased from Sigma-Aldrich (Stockholm, Sweden). Sodium hydroxide (laboratory grade) and hydrochloric acid (37% w/v, laboratory grade) were purchased from Fisher Scientific (Loughborough, UK). Tetramethoxysilane (TMOS, 98%) and *n*-hexadecyltrichlorosilane ( $\text{C}_{16}\text{SiCl}_3$ , 90+%) were obtained from Sigma (Gillingham, UK).

### 2.3. Standard solutions of PAHs

Individual stock solutions of the PAHs were prepared by dissolving each compound (1 mg) in methanol (100 mL). These standards were kept in the dark at 4  $^\circ\text{C}$  and were stable for approximately three months. To prepare the calibration curves and calculate the limits of detection (LODs) for all compounds, mixed

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