



Comparison of the solid-phase extraction efficiency of a bounded and an included cyclodextrin-silica microporous composite for polycyclic aromatic hydrocarbons determination in water samples



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ABSTRACT

Solid-phase extraction is one of the most important techniques for sample purification and concentration. A wide variety of solid phases have been used for sample preparation over time. In this work, the efficiency of a new kind of solid-phase extraction adsorbent, which is a microporous material made from modified cyclodextrin bounded to a silica network, is evaluated through an analytical method which combines solid-phase extraction with high-performance liquid chromatography to determine polycyclic aromatic hydrocarbons in water samples. Several parameters that affected the analytes recovery, such as the amount of solid phase, the nature and volume of the eluent or the sample volume and concentration influence have been evaluated. The experimental results indicate that the material possesses adsorption ability to the tested polycyclic aromatic hydrocarbons. Under the optimum conditions, the quantification limits of the method were in the range of 0.09–2.4 $\mu\text{g L}^{-1}$ and fine linear correlations between peak height and concentration were found around 1.3–70 $\mu\text{g L}^{-1}$. The method has good repeatability and reproducibility, with coefficients of variation under 8%. Due to the concentration results, this material may represent an alternative for trace analysis of polycyclic aromatic hydrocarbons in water through solid-phase extraction.

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1. Introduction

Polycyclic aromatic hydrocarbons are pollutants whose presence in the environment is widespread and they have boiling points over 200 °C. These organic compounds are semi-volatile and they can remain in the atmosphere for a long time [1]. PAH are thermodynamically stable but they may suffer from photochemical decomposition [2]. These compounds are nonpolar and their polarity decreases when their molecular mass increases [3]. Furthermore, polycyclic aromatic hydrocarbons with largest

molecular masses tend to be more stable and toxic [4]. Its origin is mainly anthropogenic [5], but they can also be generated by natural sources such as volcanic emissions. Consequently, they are present in the atmosphere as gaseous phase and adsorbed in atmospheric particles, whereas in water samples the concentration of these organic pollutants is found in $\mu\text{g L}^{-1}$ due to their low solubility [6–8].

There has been growing interest in monitoring PAH in environmental samples in recent years [9,10] due to their harmful effects on health and the ecosystem. In fact, it has been shown that these compounds are carcinogenic and/or mutagenic [8] and some of them are considered priority pollutants by the EPA. For this reason, some regulations regarding emissions and contents of polycyclic aromatic hydrocarbons in water have been established. In order to control the PAH presence in different environments, benzo[a]pyrene was chosen as the main representative of the group, establishing its equivalent toxicity as 1. Therefore, contents of PAH are often expressed based on the concentration of this compound, obtained as the sum of benzo[ghi]perylene, benzo[b]fluoranthene, benzo[k]fluoranthene and indeno[1,2,3-cd]pyrene

Abbreviations: SPE, Solid-phase extraction; HPLC, High-performance liquid chromatography; PAH, Polycyclic aromatic hydrocarbons; HRTEM, High-Resolution Transmission Electron Microscopy; EPA, Environmental Protection Agency; LLE, Liquid-liquid extraction; LPME, Liquid-phase microextraction; SPME, Solid-phase microextraction; SBSE, Stir-bar sorptive microextraction; CD, Cyclodextrin; VOC, Volatile organic compound; LOD, Limit of detection; LOQ, Limit of quantification; CF, Concentration factor; NMR MAS, Nuclear magnetic resonance with magic-angle spinning

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[11–13]. There is a PAH limit of $1.7 \cdot 10^{-4} \mu\text{g L}^{-1}$ expressed in annual average levels and of $0.27 \mu\text{g L}^{-1}$ as the maximum permissible concentration in inland surface waters [14]. For European member states, there is an upper limit of $0.1 \mu\text{g L}^{-1}$ for these organic compounds presence in drinking water [15].

The polycyclic aromatic hydrocarbons determination in water requires previous preconcentration. The main problem hindering PAH determination concerns the lack of accuracy and precision of results, mainly derived from the sampling and sample preparation stages. For this reason, there is a need of analytical procedures with low detection and quantification limits [3,7].

There are several procedures for PAH preconcentration and for interferences elimination, but they all present advantages and disadvantages [13]. Liquid-liquid extraction [16] uses toxic solvents and for membrane-based extraction methods [17] the selection of the most appropriate membrane type is critical. Solid-phase microextraction [18], liquid-phase microextraction and stir bar sorptive extraction are subjected to the matrices effects [3,19,20]. Solid-phase extraction [3,13] uses time-consuming procedures but it constitutes a good alternative to other proposed methods for PAH preconcentration in water samples. For this reason, developing new materials for its application in SPE is a new challenge that must be overcome.

Cyclodextrins have been widely used in Analytical Chemistry as chromatographic column fillers [21,22]. They have the property to form host-guest complexes, whereas the ability to be modified, changing the physical and chemical properties of the natural cyclodextrins [23,24]. Nowadays, there exist a wide variety of researches on solid-phase extraction using materials synthesized from cyclodextrins that allow the organic compounds extraction from urine samples [25], water samples [26] or soil samples [27], among others.

Immobilization of CD and modified CD by binding or by inclusion in inert materials has been studied, being silica supports the most extensively used due to the wide variety of possible siliceous structures and its thermal stability [28]. In this case, the sol-gel chemistry allows to synthesize siliceous structures with controlled composition, morphology and porosity at low temperatures [29]. Recently, we have designed samplers for determining VOCs in air samples based on the use of solid phase containing included CD in a silica network [30–32].

The aim of this work is to study the potential use of new solid phases containing modified CD bounded to a silica network as fillers of solid extraction cartridges for the isolation and preconcentration of polycyclic aromatic hydrocarbons in water samples.

2. Material and methods

2.1. Instrumentation and reagents

PAH standards were bought from Supelco (Bellefonte, Pennsylvania, USA) as a PAH $10 \mu\text{g mL}^{-1}$ calibration mix in acetonitrile. All solvents used in the extraction and analysis procedures were of HPLC grade quality (Merck, Darmstadt, Germany). Sodium chloride, sodium hydroxide and hydrochloric acid 37% were purchased from Panreac (Montcada i Reixac, Spain). Tetraethyl orthosilicate, β -cyclodextrin (Fluka, Buchs, Switzerland) and 3-isocyanatopropyltriethoxysilane (Sigma-Aldrich) were used. Nanopure water from a Brastead (Boston, MA, USA) purification system was employed.

A Vac Elut 20 connected to a diaphragm vacuum pump (CKNF model N 0.26.3 AN 18) was employed to treat the samples through solid phase extraction with a 3.5 mL min^{-1} flow. Solvent evaporation in the concentration step was carried out using an

evaporator (miVac DUO concentrator). Samples were previously filtered with Nylon $0.45 \mu\text{m}$ Sartorius Stedim Biotech filters.

Analytes were separated using a LC-2000 Plus Jasco liquid chromatograph, equipped with a FP-2020 Plus Intelligent Fluorescent Detector, a PU-2089 Plus Quaternary Gradient Pump with integrated degasser and I/F LC-NetII/ADC interface. Detection was carried out by using an excitation and emission wavelength program (0–19.5 min $\lambda_{\text{excitation}}/\lambda_{\text{emission}}$ 280/330 nm; 19.5–39 min $\lambda_{\text{excitation}}/\lambda_{\text{emission}}$ 280/410 nm; 39–41 min $\lambda_{\text{excitation}}/\lambda_{\text{emission}}$ 280/485 nm). The analytical column SUPELCOSIL™ LC-PAH (25 cm x 4.6 mm I. D., $5 \mu\text{m}$ particle size) was C₁₈ Supelco. Separation was carried out at a constant flow of 1.5 mL min^{-1} with acetonitrile: water as mobile phase working with elution gradient (0–5 min CH₃CN-H₂O 40:60; 5–30 min from CH₃CN-H₂O 40:60 to 100% CH₃CN; 30–41 min 100% CH₃CN). Injection volume was $20 \mu\text{L}$ in a Supelco six-way injection valve.

2.2. Solid phase synthesis and characterization

Recently, we described a new family of solid phases based on cyclodextrin-silica hybrid microporous nanocomposites [30]. The stoichiometry of these materials, which can incorporate a diversity of cyclodextrin and modified cyclodextrin in variable amounts, correspond to the general formula $(\text{CD})_x\text{SiO}_{1.5}(\text{OH})_{0.5} \cdot 0.7\text{H}_2\text{O}$, where the x value depends, among other parameters, on the cyclodextrin type. In this case, it was of interest to use a CD that possessed good properties to bound it to the material silica network. For this reason, a modified β -CD was chosen.

Modified β -CD was synthesized by adding 9.3 mL of 3-isocyanatopropyltriethoxysilane to a stirred solution of 10.7 g of dried β -CD (Telstar LyoAlfa 10/15 lyophilizer) in 132 mL of dried pyridine. The solution was stirred at 70°C under N₂ for 48 h. The solvent was removed under reduced pressure (rotary evaporator Büchi-Switzerland) [33].

Hence, the bounded cyclodextrin-silica microporous composite was synthesized as follows: a 0.015 M aqueous solution of modified β -CD (40 mL) was mixed with variable volumes of tetraethyl orthosilicate (32 mL, 16 mL, 11.5 mL and 7.6 mL to F1, F2, F3 and F4, respectively) under vigorous stirring to select the appropriate nature of the solid phase. Small amounts of a 2 M solution of sodium hydroxide were added to favour the cyclodextrin precursor dissolution. Then, the pH was adjusted in the 1.7–2.0 range by adding diluted hydrochloric acid. Under these conditions, hydrolysis and condensation of the silicon alkoxide is favoured and an evolution from an immiscible mixture to a homogeneous solution occurs. Finally, in order to favour the condensation procedure and the subsequent bounding of modified β -CD molecules in the silica support network, the ethanol, generated through the tetraethyl orthosilicate hydrolysis, was removed by letting it evaporate for 24 h at room temperature. The formed gel was dried at 40°C for another 24 h, crushed and sieved to adjust particle size below $600 \mu\text{m}$. This solid was thoroughly washed with water and it was finally introduced in the oven at 40°C for 24 h. Cartridges containing 200 mg of this solid phase were prepared by using cylindrical 3 mL beds of polypropylene and $20 \mu\text{m}$ of polyethylene filters.

The resulting solid-phase architecture consisted of an inorganic silica network containing bounded modified β -CD molecules trapped inside cage-like interconnected micropores. Material characterization was carried out using elemental CNH analysis, X-Ray Diffraction using Cu K α radiation (Seifert 3000TT θ - θ), thermogravimetric analysis (Setaram Setsys 16/18 TGA), N₂ adsorption-desorption at -196°C (Micromeritics ASAP-2010), High Resolution Transmission Electron Microscopy (Tecnai G2F20[F1]) and ²⁹Si and ¹³C NMR (Varian Unity 300). The porosity and easy accessibility to CD molecules in the material was supported by

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