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Ionic liquid coated magnetic nanoparticles for the gas chromatography/mass spectrometric determination of polycyclic aromatic hydrocarbons in waters

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ABSTRACT

In this paper, ionic liquid coated magnetic nanoparticles (IL-MNPs) have been prepared by covalent immobilization. The as-synthesized MNPs have been successfully used as sorbent for the extraction of polycyclic aromatic hydrocarbons (PAHs) from water samples, the analytes being finally determined by gas chromatography/mass spectrometry. The influence of several experimental variables (including the ionic strength, amount of MNPs, sample volume, agitation time and desorption solvent) has been considered in depth in the optimization process. The developed method, which has been analytically characterized under its optimal operation conditions, allows the detection of the analytes in the samples with method detection limits in the range from 0.04 $\mu g\,L^{-1}$ (fluoranthene) to 1.11 $\mu g\,L^{-1}$ (indeno(1,2,3-cd)pyrene). The repeatability of the method, expressed as relative standard deviation (RSD, $n = 7$), varies between 4.0% (benzo[b]fluoranthene) and 8.9% (acenaphthene), while the enrichment factors are in the range from 49 (naphthalene) to 158 (fluoranthene). The proposed procedure has been applied for the determination of thirteen PAHs in water samples (tap, river, well and reservoir ones) with recoveries in the range from 75 to 102%.

1. Introduction

The tremendous potential of ionic liquids (ILs) as an alternative to environmentally harmful ordinary organic solvents is well recognized [1–3]. ILs have attracted extensive attention and gained popularity in analytical chemistry [4] covering different application fields like chromatography, electrochemistry or extraction techniques [5]. This applicability is based on their unique properties, such as low volatility, high thermal and chemical stability, and electrolytic conductivity. Furthermore, some of the IL properties, including their polarity, hydrophobicity or viscosity, can be tuned by the proper selection of the building cations and anions. This tunable nature allows the synthesis of task-specific solvents for different applications.

Despite the general advantages previously described, ILs present some shortcomings that may limit their potential. Among them, the low mass-transfer rates, the long equilibrium times and the difficulty in phases' separation can be highlighted [6]. These limitations can be overcome by immobilizing ILs on solid supports generating therefore new materials with interesting properties. These new materials have been successfully applied as stationary phases in liquid chromatography (LC) [7,8] and as sorbents in solid-phase extraction (SPE) [9–18]. The usefulness of these materials rests on their dual nature: they act as low-polarity phases for non-polar compounds and in the opposite manner for compounds bearing strong proton-donor groups [17].

Magnetic solid-phase extraction (MSPE) [19], which is based on the use of sorbents with paramagnetic properties, has been successfully applied to solve different analytical problems [20–24]. In addition to its excellent extraction efficiency, MSPE simplifies the overall procedures. On one hand, the sorbent is dispersed in a sample solution instead of being packed into a SPE cartridge, improving the contact area between the sorbent and the sample and therefore increasing the extraction rates. On the other hand, the sorbent recovery after the extraction is easily performed by the application of an external magnetic field which is a simpler alternative compared to filtration or centrifugation. The success of MSPE has been based on two basic aspects. First of all, the evolution of the sorbents from the micrometer-sizes to the nanometer-size has led to an increase of the extraction efficiency thanks to the enhancement of the superficial area of the particles. Secondly, the easy chemical modification of the magnetic nanoparticles (MNPs) surfaces

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increases the versatility of the technique even improving the selectivity of the extraction procedures [25]. In this context, the use of octadecyl groups [26–28], polymeric surfactants [29,30] or carbon nanotubes [31–33] can be highlighted.

In this article, the use of functionalized MNPs has been applied for the extraction of polycyclic aromatic hydrocarbons (PAHs) from water samples. According to the literature, several MNPs with different coatings such as graphene [34], carbon [35], polymers [36], bis-(2,4,4-trimethylpentyl)-dithiophosphinic acid [37] or octadecyl groups [38] have been already proposed to solve the same analytical problem. In our proposal, the great affinity of ionic liquids toward this type of hydrocarbons [39] has been exploited. Up to date, the use of ILs in MSPE has been restricted to the extraction of three polycyclic aromatic hydrocarbons (PAHs) from water samples [40] and the extraction of cadmium and lead from milk and water samples [41]. In both cases, the IL is physically absorbed on the surface of the MNP and therefore it may be present in the final extract. This aspect limits the compatibility of the procedures with certain techniques like gas chromatography. In the present article, the covalent immobilization of IL in the surface of silica coated Fe_3O_4 tries to avoid this limitation.

2. Experimental

2.1. Reagents and samples

All reagents were of analytical grade or better. Polycyclic aromatic hydrocarbons (naphthalene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz[a] anthracene, chrysene, benzo[b]fluoranthene, benzo[a]pyrene, indeno (1,2,3-cd)pyrene, dibenz[a,h]anthracene) were purchased from Sigma–Aldrich (Madrid, Spain). Stock standard solutions of each analyte were prepared in methanol (Panreac, Barcelona, Spain) at a concentration of $1000\,mg\,L^{-1}$ and stored at 4 °C. Working solutions were prepared by dilution of the stocks in Milli-Q water (Millipore Corp.; Madrid, Spain) or hexane (Panreac) as required. In the extraction procedure, sodium chloride from Sigma–Aldrich was used to adjust the ionic strength and hexane was employed as eluent.

All the reagents required for the synthesis of the magnetic nanoparticles were purchased from Sigma–Aldrich. Ferric chloride ($FeCl_3{\cdot}6H_2O$), ferrous chloride ($FeCl_2{\cdot}4H_2O$) and ammonia were used for the synthesis of the magnetic core (Fe_3O_4). Tetraethylorthosilicate (TEOS) and ethanol were employed for covering the magnetic core with a protective silica-based coating. Hydrochloric acid, 3-chloropropyltrimethoxysilane, *N*-methylimidazole, triethylamine, potassium hexafluorophosphate (KPF_6) and toluene were used to introduce methylimidazolium hexafluorophosphate (MIM-PF_6) functional groups on the nanoparticles surface.

River, tap, reservoir and well water samples were collected in amber-glass bottles without headspace. The samples were stored in the dark at 4 °C until their analysis.

2.2. Apparatus

Gas chromatographic/mass spectrometric analyses were carried out on an Agilent (Palo Alto, CA) HP6890 gas chromatograph equipped with an HP5973 mass spectrometric detector based on a quadrupole analyzer and an electron multiplier detector. System control and data acquisition was achieved with an HP1701CA MS ChemStation software.

A pulsed splitless mode (pulse time = 0.5 min) was selected for the injection of 2 μL of extracts, using helium (6.0 grade, Air liquid, Seville, Spain) at a flow rate of $1\,mL\,min^{-1}$ as carrier gas. Chromatographic separations were performed on a fused silica capillary column (30 m × 0.25 mm i.d.) coated with 5% phenyl-95% methyl polysiloxane (film thickness 0.25 μm) (Supelco, Madrid, Spain). The column temperature program was as follows: 2.5 min at 80 °C, raised up to 200 °C at $25\,°C\,min^{-1}$ (kept for 1 min), then immediately ramped at $10\,°C\,min^{-1}$ up to 250 °C and raised up to 285 °C at $5\,°C\,min^{-1}$ (kept for 5 min). Finally, the temperature increased up to 330 °C at $30\,°C\,min^{-1}$ (kept for 1 min). The quadrupole mass spectrometer detector was operated in selected ion monitoring mode, recording the following fragment-ions characteristic of each analyte: 128 and 129 (from 2.5 to 6.0 min) for naphthalene, 153 and 154 (from 6.0 to 7.4 min) for acenaphthene, 165 and 166 (from 7.4 to 8.0 min) for fluorene, 178 and 179 (from 8.0 to 10.5 min) for phenanthrene and anthracene, 202 and 203 (from 10.5 to 13.0 min) for fluoranthene and pyrene, 228 and 229 (from 13.0 to 16.0 min) for benz[a]anthracene and chrysene, 252 and 253 (from 16.0 to 20.0 min) for benzo[b]fluoranthene and benzo[a]pyrene, 276 and 277 for indeno(1,2,3-cd)pyrene and 278 and 279 for dibenz[a,h]anthracene (from 20.0 min to the end of the chromatogram). Electron impact ionization (70 eV) was used for analytes fragmentation. The injector, MS source and quadrupole temperatures were kept at 270 °C, 230 °C and 150 °C, respectively. The peak areas were used for quantification of individual analytes.

A vortex stirrer from J. P. Selecta (Barcelona, Spain) and a ultrasonic bath (100 W, 42 KHz) form Branson (CT, USA) were also used in the extraction procedure. An external magnet (60 mm × 30 mm × 15 mm and 549.4 N of maximum magnetic force), purchased from Supermagnete (Gottmadingen, Germany) was employed for the MNPs recovery after the extraction procedure.

2.3. Synthesis of the magnetic nanoparticles

The synthesis of the MNPs was carried out following four defined steps. First of all, Fe_3O_4 was prepared by coprecipitation. Briefly, $FeCl_3{\cdot}6H_2O$ (24 g) and $FeCl_2{\cdot}4H_2O$ (9.8 g) were dissolved in 100 mL of water under nitrogen atmosphere. The mixture was vigorously stirred and maintained at 80 °C in a water bath for 30 min. Later on, 50 mL of ammonia (25 wt%) were dropwise added producing a black precipitate of iron oxide. The magnetic nanoparticles were separated by an external magnet, washed with water to remove the unreacted chemicals, and finally dried.

In a second step, the MNPs were covered with silica. Silica has been considered as one of the most ideal shell materials due to its reliable chemical stability and versatility in surface modification via silanol groups [42]. For this purpose, 1 g of MNPs were placed in a beaker containing 50 mL of ethanol and 4 mL of water, the pH of the suspension being adjusted to 9.0 with ammonia. Later on, 2 mL of TEOS were added and the suspension was stirred overnight under a nitrogen atmosphere. Finally, the protected magnetic nanoparticles (Fe_3O_4@SiO_2) were recovered with an external magnet, thoroughly washed with water and dried. The obtained Fe_3O_4@SiO_2 presented a high stability in acidic media, necessary for the next synthetic step, which corroborates the successful silica-coating.

Thirdly, methylimidazolium-chloride functionalized magnetic nanoparticles (Fe_3O_4@SiO_2@MIM-Cl) were synthesized following a procedure described elsewhere [43] for silica microparticles. The Fe_3O_4@SiO_2 (5 g) MNPs were dispersed in $1\,mol\,L^{-1}$ hydrochloric acid solution for 24 h in order to activate the superficial silanol groups. The MNPs were washed with water up to neutral pH and dried in an oven for 8 h. Then, the activated MNPs were dispersed in 60 mL of dry toluene in the presence of 5 mL of 3-chloropropyltrimethoxysilane and 0.5 mL of triethylamine, the dispersion being refluxed during 48 h. After a washing procedure involving different solvents (toluene, ethanol:water (1:1, v/v), water and methanol), the chloropropyl derivatized nanoparticles were dried at 60 °C during 8 h. Finally, the solid was