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# Magnetic ionic liquids as non-conventional extraction solvents for the determination of polycyclic aromatic hydrocarbons



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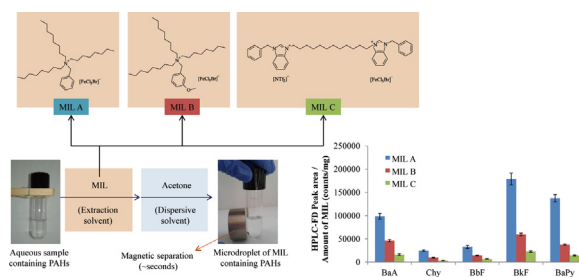
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## HIGHLIGHTS

- MILs of hydrophobic nature and low water solubility have been used in microextraction.
- MILs are used for 1st time in an analytical method for hydrophobic analytes (PAHs).
- The magnet-based MILs in microextraction-HPLC-FD method was optimized and validated.
- ~20  $\mu\text{L}$  of MILs were adequate for PAHs in waters & tea infusions with LODs ~ low  $\text{ng L}^{-1}$ .

## GRAPHICAL ABSTRACT



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## ABSTRACT

This work describes the applicability of magnetic ionic liquids (MILs) in the analytical determination of a group of heavy polycyclic aromatic hydrocarbons. Three different MILs, namely, benzyltrioctylammonium bromotrichloroferrate (III) (MIL A), methoxybenzyltrioctylammonium bromotrichloroferrate (III) (MIL B), and 1,12-di(3-benzylbenzimidazolium) dodecane bis[(trifluoromethyl)sulfonyl]imide bromotrichloroferrate (III) (MIL C), were designed to exhibit hydrophobic properties, and their performance examined in a microextraction method for hydrophobic analytes. The magnet-assisted approach with these MILs was performed in combination with high performance liquid chromatography and fluorescence detection. The study of the extraction performance showed that MIL A was the most suitable solvent for the extraction of polycyclic aromatic hydrocarbons and under optimum conditions the fast extraction step required ~20  $\mu\text{L}$  of MIL A for 10 mL of aqueous sample, 24  $\text{mmol L}^{-1}$  NaOH, high ionic strength content of NaCl (25% (w/v)), 500  $\mu\text{L}$  of acetone as dispersive solvent, and 5 min of vortex. The desorption step required the aid of an external magnetic field with a strong NdFeB magnet (the separation requires few seconds), two back-extraction steps for polycyclic aromatic hydrocarbons retained in the MIL droplet with n-hexane, evaporation and reconstitution with acetonitrile. The overall method presented limits of detection down to 5  $\text{ng L}^{-1}$ , relative recoveries ranging from 91.5 to 119%, and inter-day reproducibility values (expressed as relative standard derivation) lower than 16.4% for a spiked

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level of  $0.4 \mu\text{g L}^{-1}$  ( $n = 9$ ). The method was also applied for the analysis of real samples, including tap water, wastewater, and tea infusion.

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## 1. Introduction

Trends in sample preparation are focused on the development of non-conventional solvents as well as novel solid materials in extraction and preconcentration schemes to improve limitations and toxicity issues of current organic solvents and common sorbents [1–4]. Within non-conventional solvents, ionic liquids (ILs) have been widely studied in recent years due to their interesting structures and unusual properties [5]. These non-molecular solvents exhibit melting points below  $100^\circ\text{C}$ , low to negligible vapor pressure at room temperature, high chemical stability as well as wide electrochemical windows. They have also been pointed out as green solvents because select classes of ILs do not generate volatile organic compounds and are hydrolytically stable [6,7]. Their structures can be easily modified by changing the nature of the cation/s and/or anion/s of the IL, or by incorporating different functional groups to the cationic/anionic moieties [8,9]. This simple structural versatility is accompanied by important modification of their properties, from low to high viscosity, moderate to high conductivity, and miscibility in water or in organic solvents, among others [10].

Several derivatives of ILs have been also designed with the purpose of combining some of their unique properties with those derived from other types of materials. Thereby, polymeric ionic liquids (PILs) combine the inherent properties of polymers as well as IL character [11,12], while IL-based surfactants offer the possibility to form a micellar media when dissolved in an aqueous media at a certain concentration [13,14]. Following this idea, magnetic ionic liquids (MILs) exhibit paramagnetic behavior under the application of an external magnetic field [15], and can be designed to incorporate paramagnetic metal anions or metal complexes. Tetrachloroferrate (III) ( $[\text{FeCl}_4]^-$ ) and tetrabromoferrate (III) ( $[\text{FeBr}_4]^-$ )-based MILs are among those that are more commonly studied [15]. In recent years, other MILs containing anions based on Fe (III) [16,17], Co (II) [17], Mn (II) [17,18] and lanthanide [17,19] complexes have also been reported.

Magnet-based separations constitute a quite interesting and evolving advancement in sample preparation [20]. These methods utilize an extractant material with magnetic properties. Analytes are enriched in the material, which can be further separated from the remaining components of the sample with the aid of a strong magnet [21,22]. Analytes are finally eluted from the material and subjected to quantification. Thus, the overall method is quite simple because it does not require centrifugation or filtration to separate the magnetic material from the sample once extraction has been accomplished. ILs [23,24] and IL-based surfactants [25–27] have been described as extractants presenting a magnetic core (normally magnetite:  $\alpha\text{-Fe}_3\text{O}_4$ ) in a number of magnet-based extraction approaches. Bare  $\text{Fe}_3\text{O}_4$  MNPs tend to aggregate, they easily oxidize in air, or they experience biodegradation, and thus coatings are required in an attempt to increase their stability [20]. Applications using  $\text{Fe}_3\text{O}_4$ @ILs (or @IL-based surfactants) require more than one synthetic step (that of the IL and that of the  $\text{Fe}_3\text{O}_4$  magnetic nanoparticles, MNPs); and in some cases the whole extraction efficiency of the hybrid material is lower than that of the neat IL (or IL-based surfactant). In some approaches, dispersive solvents or agitation may be needed to disperse the extraction phase and

improve the mass transfer of the analytes to the micro-amounts of material [20].

MILs have been utilized as extraction solvents for the pre-concentration of DNA from a cell lysate [28]. They have also been shown to be highly compatible with the polymerase chain reaction thereby permitting high throughput DNA amplification from template DNA enriched in the MIL microdroplet [29]. MILs have been also used for the removal of certain compounds [17,30–34]. In these cases, there was no elution of the trapped analytes from the MIL prior to downstream analysis. In fact, there are few studies in the literature that exploit the use of neat MILs (paramagnetic MILs that do not combine ILs with  $\alpha\text{-Fe}_3\text{O}_4$ ) in analytical microextraction approaches involving further determination of analytes [35–37]. Two of these studies required the addition of carbonyl iron powder to the MIL because the paramagnetism of the tested MILs (1-hexyl-3-methylimidazolium  $[\text{FeCl}_4]^-$  [35] and 1-butyl-3-methylimidazolium- $[\text{FeCl}_4]^-$  [36]) was not sufficient to enable the magnetic separation under the application of an external magnetic field. The remaining report was applied to the determination of polar analytes (phenols) using methyltrioctylammonium  $[\text{FeCl}_4]^-$  [37].

A main challenge encountered when working with MILs in microextraction approaches is the need to minimize water solubility of the MIL. This can largely be achieved by incorporating nonpolar moieties into the cation and/or using non-coordinating anions. The main aim of this work is the development of a MIL-based analytical microextraction approach devoted to the determination of hydrophobic analytes because so far the unique analytical determination study for small molecules with neat MILs has been devoted to the determination of polar compounds (phenols) [37]; and the majority of studies with MILs do not imply the further analytical determination of target compounds [17,30–34]. A group of five heavy polycyclic aromatic hydrocarbons (PAHs) was selected as test analytes, as model hydrophobic compounds widely determined using ILs or any other novel material [38–41]. The method was combined with high performance liquid chromatography and fluorescence detection (HPLC-FD) for the determination of these compounds within various aqueous samples.

## 2. Experimental

### 2.1. Chemicals, reagents, materials, and samples

Benzo(a)anthracene (BaA,  $\geq 99.0\%$ ), chrysene (Chy,  $\geq 99.0\%$ ), and benzo(a)pyrene (BaPy,  $\geq 99.0\%$ ) were supplied by Sigma-Aldrich (St. Louis, MO, USA). Benzo(b)fluoranthene (BbF,  $\geq 99.0\%$ ) was purchased from Supelco (Bellefonte, PA, USA) whereas benzo(k)fluoranthene (BkF,  $\geq 99.0\%$ ) was purchased from Fluka (St Louis, MO, USA). Ultrapure water ( $18.2 \text{ M}\Omega \text{ cm}$ ) was obtained from a Milli-Q water purification system (Millipore, Watford, UK).

All PAHs were individually dissolved in acetonitrile ( $\geq 99.9\%$ ), supplied by VWR International Eurolab S.L. (Barcelona, Spain) at a concentration of  $1200 \text{ mg L}^{-1}$  for BaA,  $760 \text{ mg L}^{-1}$  for Chy, and  $1000 \text{ mg L}^{-1}$  for the remaining PAHs. Three intermediate solutions of all PAHs at  $1 \text{ mg L}^{-1}$ ,  $0.5 \text{ mg L}^{-1}$ , and  $0.25 \text{ mg L}^{-1}$ , in acetonitrile, were prepared by dilution of the individual standards. All experi-

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