



# Magnetic ionic liquid in stirring-assisted drop-breakup microextraction: Proof-of-concept extraction of phenolic endocrine disruptors and acidic pharmaceuticals



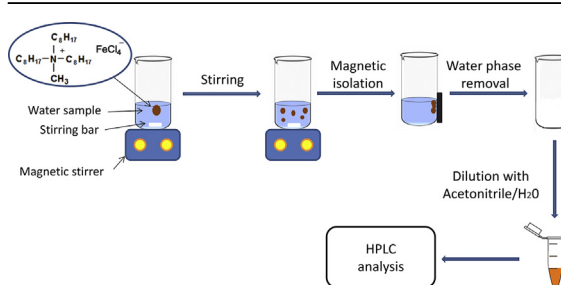
Theodoros Chatzimitakos, Charalampos Binellas, Katerina Maidatsi, Constantine Stalikas\*

Laboratory of Analytical Chemistry, Department of Chemistry, University of Ioannina, 451 10 Ioannina, Greece

## HIGHLIGHTS

- a magnetic ionic liquid-based procedure for microextraction purposes is proposed.
- the term 'magnetic ionic liquid in stirring-assisted drop-breakup microextraction' is coined for this novel procedure.
- it extracts phenolic compounds and acidic pharmaceuticals from aqueous matrixes.
- it uses low volumes of ionic liquid, avoids the use of toxic solvents and exhibits high extraction efficiency.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The use of magnetic ionic liquids (MILs) is in constant growth due to their switchable properties in the presence of an external magnetic field along with the outstanding properties of ionic liquids. In this study, a novel stirring-assisted drop-breakup microextraction (SADBME) approach is put forward, based on the synthesis and utilization of methyltrioctylammonium tetrachloroferrate ( $[N_{8,8,1}][FeCl_4]$ ), as a MIL. The proposed procedure complies with the principles of the green chemistry, since it uses low volumes of easily synthesized ILS-based magnetic extracting phases avoiding the use of toxic solvents. To demonstrate its applicability, the proposed microextraction procedure is studied in conjunction with HPLC for the determination of selected phenols and acidic pharmaceuticals in aqueous matrixes, taking into account the main experimental variables involved. The results obtained are accurate and highly reproducible, thus making it a good alternative approach for routine analysis of phenols and acidic pharmaceuticals. The low-cost approach is straightforward, environmentally safe and exhibits high enrichment factors and absolute extraction percentages and satisfactory recoveries. To the best of our knowledge, this is the first time that a MIL is used for analytical purposes in a practical, efficient and environmentally friendly drop-breakup microextraction approach for small molecules.

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## 1. Introduction

The role of sample preparation is widely recognized as being of outstanding importance in chemical analysis [1]. Research in the field has contributed to giving sample preparation the attention it

\* Corresponding author.

E-mail address: [cstalika@cc.uoi.gr](mailto:cstalika@cc.uoi.gr) (C. Stalikas).

deserves rendering the saying 'if you fail to prepare, prepare to fail' an important adage to keep in mind. Among the existing sample preparation techniques, single-drop microextraction (SDME) has been recognized as a popular liquid-phase microextraction technique because it is rapid, inexpensive, effortless and easy to operate with minimal volumes of solvent and samples [2,3]. Analytes are extracted from a sample solution into the solvent microdrop, which is suspended from a microsyringe needle and immersed into a sample solution [1,4,5]. It is typically performed by using a water-immiscible (organic phase) microdrop (0.5–2.0  $\mu\text{L}$ ), as a solvent for the extraction of analytes from an aqueous phase (1–30 mL).

Dispersive liquid–liquid microextraction (DLLME) is an alternative to the classical liquid–liquid extraction and includes solvent volumes, at microliter levels [6]. Briefly, a mixture of an extracting and a dispersing solvent is rapidly injected in an aqueous sample and a cloudy solution is formed. In this way, the contact area between the sample and the extracting solvent is maximized, the extraction time is limited and the efficiency is increased [7]. Phases can be separated after extraction by centrifugation. Most of the time, high-density chlorinated solvents are used, as it is easy to collect them from the bottom of a centrifuge tube [8]. These types of solvents are toxic and therefore, counterbalance the intrinsic advantages of the technique.

Ionic liquids (ILs) are a broad class of organic salts or salt mixtures that do not crystallize at room temperature. They are liquids composed solely of cations and anions [9]. In most cases, they are non-toxic and easily synthesized. Therefore, they can be claimed as 'green alternative solvents' compared to the classical organic ones for reactions and separations [10–12]. Apart from that, they possess fascinating properties, including low volatility, tunable viscosity and miscibility, as well as high solvation interactions both with polar and non-polar compounds. These characteristics make ILs unique and useful for many applications in chemical analysis [13–16]. As a consequence of the evolution of analytical chemistry towards automation and simplification, new miniaturized extraction procedures, based on the principles of liquid-phase microextraction, were recently introduced with ILs as extractants, under the extraction principles of SDME and DLLME [15]. The use of ILs as a replacement to the traditional solvents in SDME has resulted in higher extraction efficiencies albeit with longer extraction times [17]. The volume of the IL microdrop suspended from the needle, is larger compared to conventional organic solvents resulting in a more efficient enrichment. Nonetheless, the IL-SDME mode has some drawbacks. In direct immersion-SDME mode, apart from the relatively high price of ILs, instability of the IL microdrop is sometimes observed, especially when particles are present in solution, making troublesome the application of this technique to translucent samples. In addition, due to the intrinsic limitation of SDME, volumes larger than 10  $\mu\text{L}$  are difficult to handle and can result in loss of the drop.

The IL-based DLLME was introduced in 2008 as a temperature-controlled IL-DLLME mode and was applied using a water-insoluble IL, as an extraction solvent [18]. Heating was necessary to disperse the water-insoluble IL in the solution negating the need for a dispersing solvent but cooling was applied to separate the IL.

The use of magnetic materials as sorbents has been another great advancement in sample preparation. Their ability to be isolated from a solution by applying an external magnetic field and the fact that they retain no residual magnetism after the field is removed, are some of the merits that rendered magnetic materials useful in chemical and biological analyses [19–23]. Another reason for the plethora of their applications is their reusability, which can be accomplished after proper regeneration of the material. During the last decade, the development of magnetic ILs (MILs) urged a new wave of research, full of opportunities to create innovative

devices and develop processes and products [24–27]. The MILs are primarily based on high-spin d5 iron(III), in the form of tetrachloro- or tetrabromoferrate(III), with various counter cations. Common cations used in the synthesis of MILs are 1-ethyl-3-methylimidazolium and 1-butyl-3-methylimidazolium [27]. The ILs containing fluorinated anions, such as hexafluorophosphate or bis(trifluoromethylsulfonyl)imide are usually expensive; furthermore, the former ions can undergo hydrolysis leading to the formation of hydrofluoric acid. Because of their availability at reasonable prices, the most preferred salts used are those with trihexyl(tetradecyl)phosphonium [28,29], choline [30] and aliquat [31].

The publications describing magnetic retrieval of MILs in IL-based procedures are scarce [26,32]. Unlike conventional IL-DLLME, where a dispersing solvent and centrifugation are often required to extract the analytes and separate the extracting phase from aqueous solutions,  $\text{Fe}_3\text{O}_4$  magnetic nanoparticles are used to render the phase magnetic and achieve separation [33]. In the study reported herein, a novel stirring-assisted drop-breakup microextraction (SADBME) is put forward based on the extraction properties of the MIL methyltrioctylammonium tetrachloroferrate ( $\text{N}_{8,8,8}[\text{FeCl}_4]$ ). The MIL drop is subjected to limited breakage events during extraction and hence, it resembles more the IL-SDME than the DLLME, where a cloudy solution is formed. Then, the MIL is harvested by an ordinary magnet, thereby separating it from the continuous large-volume aqueous phase. To explore the applicability of the concept, the simultaneous extraction of six phenolic compounds and four acidic pharmaceuticals was carried out (see details about structure and physicochemical properties of the analytes in [Table S1 of Supplementary material](#)). The presence of both classes in the environment can be hazardous and even fatal for the living organisms [34–36]. For this reason, regulatory agencies, such as the European Union and the US Environmental Protection Agency have included phenolic compounds and pharmaceuticals in their list of priority pollutants [37]. The extraction procedure was optimized considering the main variables involved (e.g. loading of the extracting phase, pH, stirring rate, extraction time, temperature and salt concentration). A proof-of-concept application in three different aqueous matrixes (municipal treatment plant, river and lake water) showcases the applicability of the concept in real world matrixes and demonstrates that the proposed procedure functions as intended. To the best of our knowledge, this is the first time that a MIL is used for analytical purposes in a drop-breakup microextraction process for small molecules.

## 2. Materials and methods

### 2.1. Chemicals and reagents

All chemicals and reagents used were at least of analytical grade and the solvents were of HPLC grade. Anhydrous ferric chloride was purchased from Merck (Darmstadt, Germany). Methyltrioctylammonium chloride (>97%), methyltridodecylammonium chloride (98%), methyl paraben, 3-nitrophenol, bisphenol A, irgasan, 17 $\beta$ -estradiol, 2,3,5-trichlorophenol, 4-*tert*-butyl phenol and 4-octylphenol were purchased from Sigma–Aldrich (Steinheim, Germany). Dichlofenac sodium salt and ibuprofen (99%) were purchased from Alfa Aesar (Karlsruhe, Germany). Individual stock standard solutions of each compound were prepared in methanol, at a concentration of 200 mg/L. The solutions were stored in capped glass vials, at  $-18^\circ\text{C}$ .

### 2.2. Synthesis of the MIL

Anhydrous ferric chloride (0.13 mmol) predissolved in 1 mL of

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