Ionic liquid-linked dual magnetic microextraction: A novel and facile procedure for the determination of pyrethroids in honey samples

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ARTICLE INFO

ABSTRACT

A novel and facile microextraction technique, termed as ionic liquid-linked dual magnetic microextraction (IL-DMME), was developed for the determination of pyrethroids in honey samples. The distinct advantage of the proposed method is that high recoveries can be readily achieved through the combination of dispersive liquid–liquid microextraction (DLLME) and dispersive microsolid-phase extraction (D-μ-SPE) with the aid of synthetic ionic liquid and non-modified magnetic nanoparticles (MNPs), respectively. In the first DLLME step, $[C_6MIM]NTf_2$ was used to extract the pyrethroids without the addition of any toxic dispersive solvent. In the following D-μ-SPE steps, non-modified MNPs were added to retrieve the ionic liquid. The effect of different variables on the extraction efficiency was studied simultaneously using the response surface methodology. The Plackett–Burman design was first employed to screen for the variables that significantly affected the extraction efficiency. Central composite design (CCD) was then introduced to optimize the significant factors using a polynomial fit. The optimal experimental conditions obtained from this statistical evaluation included: ionic liquid volume, 75 μL; S-BaFe quantity, 60 mg; sonication time, 4 min; vortex time, 100 s; desorption time, 150 s; and no addition of salt. Under the optimal conditions, good linearity in the range of $0.5\ \mu g\,L^{-1}$–$500\ \mu g\,L^{-1}$, repeatability (RSD 1.1–3.8%), low LODs (0.03–$0.05\ \mu g\,L^{-1}$) and good recovery (86.7–98.2%) were obtained. Finally, the developed method was evaluated for the extraction and determination of four pyrethroids in real honey samples.

1. Introduction

Pyrethroids, with structures typically containing 2–3 asymmetric carbon atoms (chiral centers), are synthetic pyrethrins that present a high stability and insecticidal activity for a large spectrum of pests [1,2]. Therefore, pyrethroids are regarded as the fourth major generation of synthetic organic insecticides developed after organonitrogen, organochlorine and organophosphorus compounds [3]. In recent decades, pyrethroids have attracted much more attention and have been widely used due to their selectivity in action, their relatively lower mammalian toxicity and lower environmental persistence compared to their predecessors [4]. However, the widespread residue from pyrethroids in the environment could lead to chronic exposure and long-term toxicity effects [5]. Additionally, the toxicity effects of pyrethroids on aquatic organisms and insects, including fish and some arthropods, is of great concern because of their very low LC_{50} values (less than $0.5\ \mu g\,L^{-1}$) [6]. In this scenario, the

development of precise, accurate and ultra-sensitive analytical methods, associated to simplicity and celerity for environmental and food-containing pyrethroids monitoring is essential.

Magnetic carrier technology (MCT), consisting of the synthesis and processing of nano (or micro) magnetic carriers, holds promise for interesting environmental and bio-applications [7]. A feature of MCT is the utilization of magnetic materials. These magnetic materials can be readily isolated from sample solutions by the application of an external magnetic field, which significantly facilitates the sample preparation because no additional centrifugation or filtration is needed after extraction [8]. Of the various possible carriers, magnetic nanoparticles (MNPs), such as Fe_3O_4, are promising candidates in terms of the several unique properties: (i) Adsorption capacity is expected to be high with the large surface area to volume ratio of the NPs [9]; (ii) MNPs possess superparamagnetic properties and low toxicity [10]; (iii) MNPs can be synthesized and functionalized in large quantities using a wide range of techniques [11]. Since the pioneering study by Robinson et al. in 1973 [12], a wide range of applications hitherto have borne testimony to the fact that MNPs are portable, economical, and effective for sample preparation [13,14]. However, to enhance the capacity of MNPs for the adsorption of target analytes, considerable time must be dedicated to the surface

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chemical modification by the attachment of inorganic shells or/ and organic molecules in common method [15–17]. For example, over 24 h must be taken on the preparation of grapheme-based MNPs for the extraction of carbamate pesticides in environmental water samples [18]. Moghaddam et al. have spent more than 36 h for the preparation of silica-coated MNPs modified with quercetin as a selective sorbent for the extraction of uranyl ions from water samples [19]. In spite of these innovations, enforcements are still necessary to improve the efficiency and simplicity in the analytical magnetic carrier technology.

Very recently, a novel extraction method based on non-modified MNPs has been successfully developed [20]. In this technique, satisfactory enrichment factor and recovery can be readily achieved through the a two-step microextraction linked by MNPs. i.e. 1-octanol was utilized as an extractant in the dispersive liquid–liquid microextraction (DLLME) mode [21,22] and thereafter extracted and retrieved by MNPs in the dispersive microsolid-phase extraction (D-μ-SPE) step. In the light of the results, this dual microextraction is a very powerful technique for the development of timesaving and efficient sample pretreatments. Nevertheless, it is also noteworthy that for most of DLLME, extraction solvents with densities higher than water, rather than 1-octanol, were applied [23–25]. Therefore, expansion of this two-step microextraction with more extensive extractants, which altogether may provide an access to more sophisticated methods, should also be considered.

Of extraction solvents with higher densities than water, chlorinated solvents have been widely exploited. However, the concerns connected with toxicity of chlorinated solvents have led to the search of less toxic solvents or potentially 'green' solvents [26]. Room-temperature ionic liquids (RTILs) are gaining worldwide attention as excellent replacement for toxic organic solvents in separations. The unique properties of RTILs, such as low volatility (negligible vapor pressure), chemical and thermal stability, and good solubility for both organic and inorganic molecules [27,28], make them promising solvents with respect to the safety to operators and the environment. Since 2008, numerous DLLME techniques based on ILs have been developed for the determination of organic and inorganic analytes in different matrices [29–31]. However, the main drawback of the IL-DLLME method is the necessity of using a large quantity of dispersive solvents (such as 200 μL of methanol [6]), which commonly decreases the partition coefficient of the analytes [32]. This negative effect has been overcome by another IL-based microextraction known as in-situ solvent formation microextraction (ISFME) [33]. In ISFME, a water-miscible IL such as $[C_6MIM][BF_4]$ is added to the sample, being completely dissolved, and thereafter a common ion reagent such as $LiNTf_2$ is added to form a water-immiscible IL for the extraction of analytes vial inducing metathesis reaction. Nevertheless, the generated electrolytes by-product in aqueous solutions such as $LiBF_4$ is problematic since the solubility of the given IL in water dramatically depends on the ionic strength [34–36]. Complicated matrices in the extraction systems may also block the metathesis reaction. In comparison with the ISFME, the synthesis of the $[NTf_2]^-$ based IL and its direct use appear to be a good strategy to make the best of both worlds.

Herein, we report on a novel and facile sample preparation method, ionic liquid-linked dual magnetic microextraction (IL-DMME), for the determination of pyrethroids in honey samples. This method aims to expand MCT and DLLME, as well as their combined use in the field of separation. In this method, the IL ($[C_6MIM][NTf_2]$) was chosen and synthesized based on the good performance of $[C_6MIM]$ PF_6 in our previous study [37]. It was then employed in DLLME for the extraction of four pyrethroids under sonication. It is worth noting that no dispersive solvent is needed in this step. Subsequently, non-modified MNPs were added into the samples for the microextraction of the IL from the aqueous samples. After the dual microextraction, only 50 μL of acetonitrile was introduced into the vial to desorb the IL and the target analytes from the aqueous samples. The factors that could possibly affect the microextraction efficiency such as the volume of the ionic liquid, sonication time, vortex time and desorption time were assessed using the Plackett–Burman design (PB) and central composite design (CCD). Finally, the optimized procedure was employed to determine the pyrethroids in real honey samples.

2. Experimental

2.1. Chemicals and samples

All pesticide standards (fenpropathrin, deltamethrin, permethrin, and bifenthrin) were obtained from Aladdin Reagent Corporation (Shanghai, China). The acetonitrile for spectroscopy was purchased from Dikma Limited (Beijing, China), and the deionized water was purified using a Milli-Q SP Reagent Water System (Millipore, Bedford, MA, USA). 1-Hexyl-3-methylimidazolium chloride ($[C_6MIM]Cl$) was purchased from the Center for Green Chemistry and Catalysis, LICP, CAS (Lanzhou, China). Lithium bis (trifluoromethanesulfonimide) ($LiNTf_2$) was purchased from Zhejiang Jiuzhou Pharmaceutical (Zhejiang, China). Sodium chloride (analytical grade) was purchased from Beijing Chemical Reagent Company. Stock solutions of three types of magnetic nanoparticles (γ-Fe_2O_3 (20 nm), Fe_3O_4 (20 nm), and spherical barium ferrite nanoparticles (S-BaFe) (30–50 nm)) were purchased from Aladdin Reagent Corporation. Standard stock solutions were prepared in acetonitrile at a final concentration of 100 mg L^{-1}. Working standard solutions were freshly prepared by dilution of an appropriate amount of the standard stock solutions in deionized water.

2.2. Synthesis of the ionic liquid

$[C_6MIM]NTf_2$ was prepared by anion exchange from the corresponding chloride salt of the imidazolium cation ($[C_6MIM]Cl$) with one equivalent of lithium bis(trifluoromethylsulfonyl)amide in deionized water. The higher density hydrophobic IL phase $[C_6MIM]NTf_2$ was decanted and washed with water 6 to 8 times. The product was then dried at 50 °C for at least 48 h. 1H NMR chemical shifts (relative to TMS internal standard) and coupling constants J/Hz: $\delta = 8.65$ (s, 1H), 7.39 (t, 1H, $J = 1.76$), 7.37 (t, 1H, $J = 1.48$), 4.17 (t, 2H, $J = 7.4$), 3.93 (s, 3H), 1.87 (m, 2H), 1.32 (m, 6H), 0.87 (t, 3H, $J = 6.53$).

2.3. Instruments

Chromatographic analysis was performed on an Agilent 1200 HPLC system (California, USA) equipped with a variable-wavelength detector (VWD) and an automatic sample injector. The separation of the analytes was performed on a Spursil C18 column (5 μm, 4.6 mm × 250 mm, Dikma Limited) with Spursil C18 Guard Cartridges (5 μm, 2.1 mm × 10 mm, Dikma Limited). The mobile phase was an acetonitrile–water mixture (83/17, v/v) delivered at a flow rate of 1 mL min^{-1}, and the column temperate was 25 °C. The VWD wavelength was 230 nm. A high-speed refrigerated centrifuge (Baiyang 52A, Baoding, China), a vortex shaker (QL-861, Haimen, China) and ultrasonic equipment (KQ3200DE, Kunshan, China) were used for the sample treatment. All glassware used in the experiments was washed with deionized water and acetone and then dried at room temperature.