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

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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 μg L^{-1}–500 μg L^{-1}, repeatability (RSD 1.1–3.8%), low LODs (0.03–0.05 μg 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 μg 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: δ=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.

2.4. Preparation of honey samples

Three honey samples were purchased from local supermarkets (lime tree honey (Jiamusi, Heilongjiang), Vitex honey (Shunyi, Beijing), and acacia honey (Chengde, Heibei)) to validate the proposed method. Each honey sample (10 g) was mixed with 80 mL deionized water, stirred in a homogeneous solution, and filtered through a 0.22 μm membrane (Agla, USA). All of the samples were stored in darkness at 4 °C.

2.5. Extraction procedure

2.5.1. IL-DLLME step

Aliquots of 70 μL of $[C_6MIM]NTf_2$ were quickly injected into a conical-bottom test tube that contained 10 mL of water to form an emulsified solution. This solution was then sonicated for 4 min to accelerate the formation of the fine droplets of the extraction solvent and to enhance the transfer of the analytes.

2.5.2. D-μ-SPE step

Sixty milligrams of S-BaFe (20 nm) MNPs were added into the tube and then sealed. The mixture was vigorously shaken using a vortex agitator for 100 s at 2800 rpm. The MNPs were able to successfully extract the $[C_6MIM]$ NTf_2 containing the pyrethroids after the high-speed stirring process. A magnet was subsequently held around the test tube to concentrate the nanoparticles. After all of the MNPs were sedimented, the sample solution was then carefully removed using a drip tube and microsyringe. Acetonitrile (50 μL) was injected into the test tube to desorb the IL as well as the pyrethroids from the MNPs by sonication for 150 s. Finally, the nanoparticles were isolated from solution with a magnet, and 10 μL of organic solvent was collected and injected into the HPLC system for analysis.

2.6. Data handling and processing

Experimental design matrices were constructed and the response surfaces were carried out using the Minitab 16 statistical package (Minitab Inc., USA).

3. Results and discussion

3.1. Selection of the non-modified MNPs and the extraction solvent

The IL-DMME method aims to attain the highest possible extraction efficiency in a minimum amount of time with convenient materials. The non-modified MNPs used in this method should have a strong interaction effect on IL so that target analytes extracted by IL can be completely transferred. The size distribution and the type of MNPs are two critical aspects to consider for a high recovery yield of the analytes, Herein, three major types of non-modified commercial MNPs (γ-Fe_2O_3 (20 nm), Fe_3O_4 (20 nm), and spherical barium ferrite (S-BaFe) (30–50 nm)) were chosen in terms of their adsorption behavior to ionic liquids. The results are illustrated in Fig. 1. As is evident from the relative values of recovery observed in the single and dual microextraction, the coupling method could significantly improve the extraction performance of non-modified MNPs. Interestingly, the S-BaFe MNPs, usually inconspicuous in magnetic carrier techniques, exhibited the best performance when combined with the ionic liquid. For the Fe_3O_4 MNPs, as was expected based on a previous report [11], a particle size of approximately 20 nm showed good performance. In this sense, S-BaFe MNPs were chosen for the further experiments.

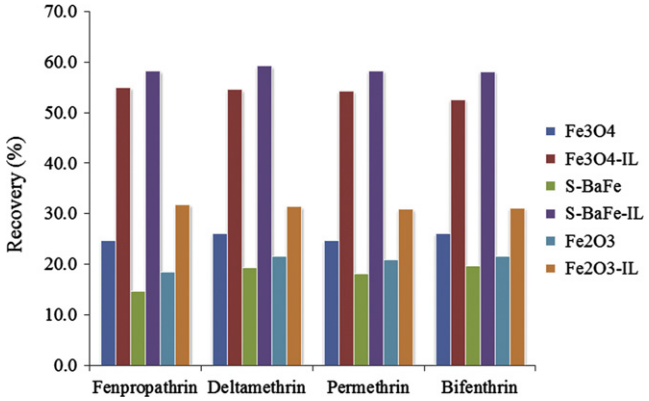

Fig. 1. The effects of various MNPs on the recovery of pyrethroids. The extraction conditions were as follows: water sample volume, 10.00 mL; $[C_6MIM]NTf_2$, 40 μL; MNP dosage, 40 mg; vortex time, 90 s; desorption solvent (acetonitrile), 50 μL; desorption time, 120 s; and concentration level, 50 μg L^{-1}.

Table 1
Experimental variables and levels of the Plackett–Burman design.

Variable	Key	Level	
		Low	High
IL volume (μl)	A	40	80
MNPs dosage (mg)	B	20	60
Sonication time (min)	C	0	4
Vortex time (s)	D	30	150
Desorption time (s)	E	30	150
Ionic strength (%, w/v)	F	0	8

The selection of an appropriate ionic liquid plays a key role in the entire sample preparation process. In conventional DLLME, a mixture of the disperser and extractant solvents is rapidly injected into the sample, immediately forming a cloudy solution. This chemical dispersion, based on the employment of dispersive solvents, could greatly enhance the mass transfer in DLLME [26]. However, the partition coefficient of the analytes is very critical in microextraction and may decrease with the addition of the disperser solvent [38]. Dispersers employed in DLLME are usually toxic organic solvents, a fact that may overshadow the "green" effect of using an IL. In this work, $[C_6MIM]NTf_2$ was synthesized to avoid this problem. The pre-experiment showed that $[C_6MIM]NTf_2$ could be rapidly dispersed into aqueous solutions to form a cloudy solution without the aid of chemical dispersion because of its low viscosity and surface tension. Herein, the experimental conditions have been optimized using $[C_6MIM]NTf_2$ as the sole extraction solvent.

3.2. Optimization of the experimental conditions

3.2.1. Screening design

Based on preliminary experiments, six factors that may affect the extraction were evaluated by the Plackett–Burman design. The six factors include the volume of the ionic liquid, MNP dosage, sonication time, vortex time, desorption time and salt effect. For each factor, two levels were considered (Table 1). Twelve runs were carried out randomly to nullify the effects of extraneous or nuisance variables. The effects were evaluated using ANOVA tests, and the statistically significant effects were determined using a t-test with a 95% probability. The effects were then visualized using a standardized Pareto chart (Fig. 2). Because all the chosen pyrethroids displayed similar results, only one chart was selected as a representative example of the analytes.

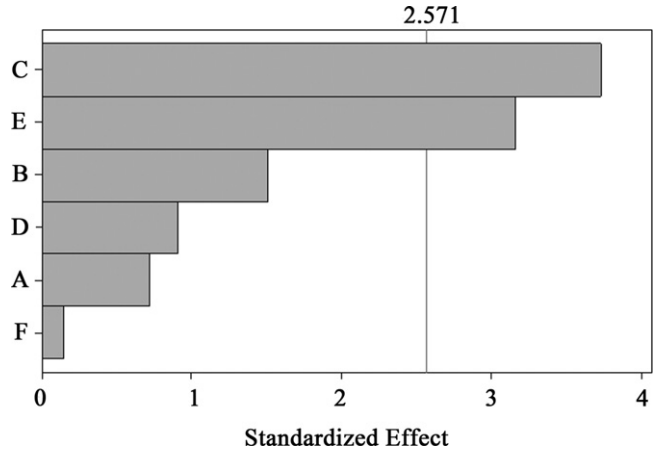

Fig. 2. The standardized effect Pareto chart for the Plackett–Burman design. The vertical line in the chart defines the 95% confidence level.

Table 2
Experimental variables, levels and star points of the central composite design (CCD).

Variables	Key	Level			Star points	
		Lower	Central	Upper	$-\alpha$	$+\alpha$
MNPs dosage (mg)	A	20	40	60	6.36414	73.6359
Sonication time (s)	B	0	2	4	−1.36359	5.36359
Desorption time (s)	C	30	90	150	−10.9076	190.908

According to Fig. 2, the sonication and desorption time had the greatest influence on the system response. This can be explained by the fact that the microextraction technique is a surface area dependent process. Prolonged time in both sonication and desorption, which could result in enlargement of surface area for both the IL and the MNPs, was very beneficial for the mass transfer in the DLLME and the D-μ-SPE step. The amount of S-BaFe was the next most important factor. The greater the amount of MNPs that were used, the more complete the adsorption of the ionic liquid was. The Pareto graph also indicated that vortex time exerts a slightly large effect on the overall extractions. The effect arises because an increased vortex time enhances the diffusion transference. In contrast, the vortex time had little positive effect when it was over 100 s. Both the IL volume and the NaCl concentration had non-significant effects on the extraction efficiency.

Overall, the data of this first screening study indicated that three variables could be fixed at appropriate values (vortex time: 100 s; ionic liquid volume: 40 μL; and no addition of NaCl) to optimize the method.

3.2.2. Optimization design

In the next step, a central composite design (CCD) was employed to optimize the significant factors (the dosage of S-BaFe, sonication and desorption time) that were chosen from the first screening design to obtain the best response. The levels used to examine these parameters are summarized in Table 2.

The CCD permits the response to be modeled by a polynomial fit, which can be expressed as the following equation:

$$y = \beta_0 + \beta_1 x + \beta_2 x + \beta_3 x + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{23} x_2 x_3 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \beta_{33} x_3^2$$

where y is the response, x_i are the independent variables, and β_0 through β_3 are the coefficients of the polynomial equation. This design consists of a factorial (2^k) augmented with ($2k$) star points, where k is the number of factors to be optimized, and with a central point (C), which can be run n times (generally, $n=2^k+2k+C$) [39].

In this study, f and C were set at 3 and 4, respectively, showing that 20 experiments were required in this procedure. The results, including the regression coefficients for each term in the model and the analysis of Students t distribution using the Minitab program, are listed in Table 3. The experimental data exhibited good agreement with the second-order polynomial equations. The R-squared statistic indicated that the model explained 95.94% of the variability in recovery. The adjusted R-squared statistic was 92.94% for recovery, showing a good correlation between the experiment data and the fitted model.

Table 3 indicates that all of the chosen factors (MNPs quantity, sonication and desorption time) and their quadratic terms, with p-values less than 0.05, had significant effects on the extraction efficiency. The interactions of the sonication time and the MNP dosage are also significant. Fig. 3 depicts the response surface plots of the extraction recovery modeling for the three significant factors. Accordingly, the curvatures of the plots given in Fig. 3 graphically show the variation of the relative areas as a function of each pair of independent variables. In Fig. 3C, the interaction between the quantity of MNPs and the sonication time can be observed, indicating that longer sonication time is more favorable in forming a cloudy solution in the DLLME step. Fig. 3A and C demonstrate that the surface plot of the peak area responses increase significantly as the quantity of MNPs increases. This result suggested that complete adsorption of the IL to the MNPs in the D-μ-SPE step can be achieved by applying a larger dosage of MNPs. Fig. 3B shows that the extraction efficiency increased as the sonication time increased from 0 s to 100 s. However, a prolonged sonication time has little positive effect on the response surface. This finding may be because 120 s is long enough for the pyrethroids to reach desorption equilibrium in the D-μ-SPE step. On the basis of the CCD experiments, the following optimal extraction conditions for the IL-DMME method were chosen: MNP quantity, 60 mg; sonication time, 4 min; and desorption time, 130 s.

3.3. Method validation

A series of experiments were performed using the optimum conditions obtained by the response surface model (i.e., 40 μL $[C_6MIM]NTf_2$, 60 mg S-BaFe, 4 min sonication, 100 s vortex shaking, 150 s desorption time and no addition of salt) to validate the proposed method. The pertinent results were calculated and are summarized in Table 4. The calibration curves gave a high level of linearity, yielding correlation coefficients (r^2) of 0.9992, 0.9999, 0.9998 and 0.9993 for fenpropathrin, deltamethrin, permethrin and bifenthrin, respectively. The LODs for the pyrethroids, calculated at

Table 3
Estimated regression coefficients and analysis of variance of the predicted model for analyte recoveries.

Terms	Coefficients	t Value	p
Constant	88.354	42.555	0.000
B	12.669	9.197	0.000
A	11.131	6.081	0.000
C	5.810	4.218	0.002
B^2	−5.011	−3.737	0.004
A^2	−6.242	−4.655	0.001
C^2	−8.031	−5.989	0.000
AB	4.491	2.495	0.032
BC	1.887	1.049	0.319
AC	1.997	1.109	0.293

a signal-to-noise ratio of 3, ranged from 0.03 to 0.05 μg L^{-1}. The LOQs, calculated at a signal-to-noise ratio of 10, were in the range of 0.10–0.18 μg L^{-1}. Taking all results into consideration, the IL-DMME method can be considered a sensitive and facile method that not only presents satisfactory detection limits and high recovery but is also easy to operate given that no complicated surface chemical modification is necessary and the ionic liquid is purified in advance to eliminate possible interferences during extraction.

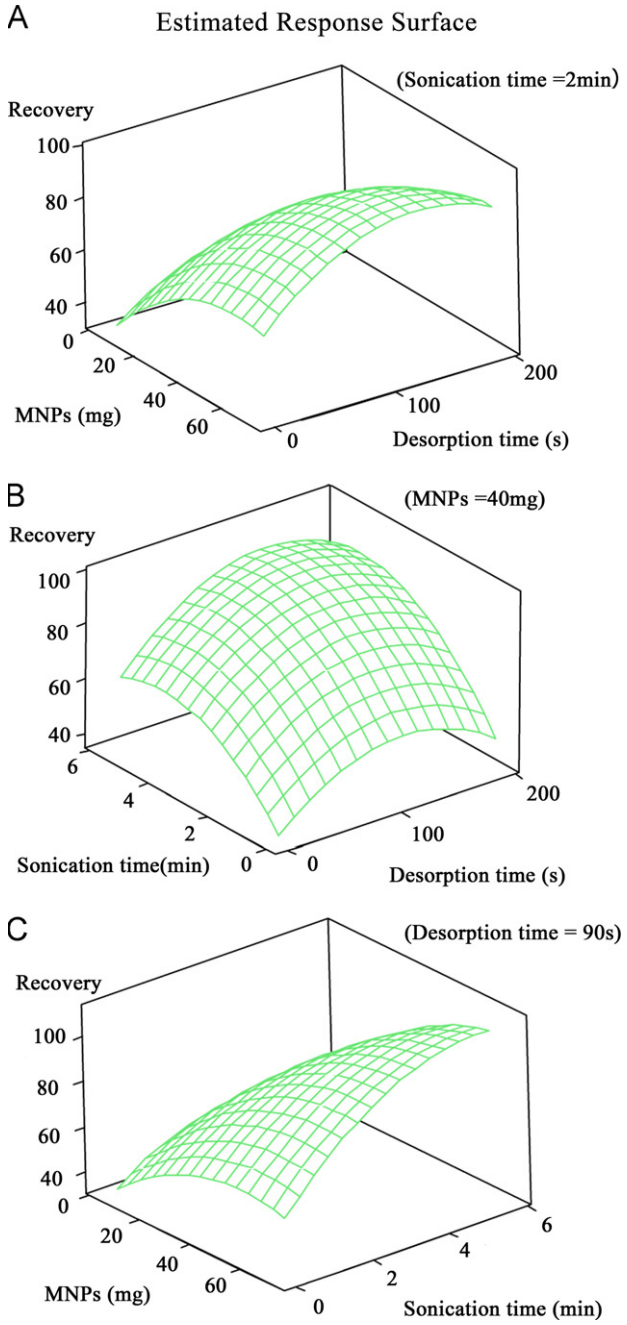

Fig. 3. Response surfaces for pyrethroids using the central composite design obtained by plotting (A) MNPs vs. desorption time, (B) sonication time vs. desorption time, and (C) MNPs vs. sonication time.

3.4. Analysis of honey samples

The control of pesticides in honey has become an issue of primary health importance in recent years as a consequence of the extensive distribution and increasing content of these chemicals in bee products [39]. Honey, therefore, may serve as an indicator of environmental pollution. However, the fact that honey is a complex biological matrix blocks the development of suitable analytical methods [40]. In such cases, the IL-DMME method is very desirable for such samples. The suspended matrices that may be present in honey cannot affect the determination of target analytes because the dual microextraction is in dispersive mode and $[C_6MIM]NTf_2$ is recovered by a magnet.

To study the applicability of the proposed IL-DMME method, three honey samples from a local market were evaluated. As seen in Table 5, all of the honey that was selected contained low concentration of deltamethrin or/and permethrin. Three replicates of these samples were spiked at 2, 50 and 200 μg L^{-1} with all of the target analytes and were extracted under the optimized experimental conditions. Recovery values ranged from 85.3% to 95.9%, 88.0% to 95.3%, and 85.8% to 95.8% for samples spiked with 2, 50 and 200 μg L^{-1}, respectively. The typical chromatograms of the pyrethroids in the spiked and blank honey samples are illustrated in Fig. 4.

3.5. Comparison of IL-DMME with other analytical methodologies

A comparison of the proposed IL-DMME with other analytical methodologies was summarized in Table 6. It can be observed that the analytical performance for IL-DMME is superior in the following ways: (i) The utilization of ionic liquids as extractants without adding any toxic dispersive solvents, IL-DMME makes the real 'green' microextraction possible; (ii) With the aid of MNPs, the present method greatly simplifies sample pretreatment and eliminates the necessary centrifugation procedures in most DLLME to separate extractants from water samples. (iii) Dual microextraction allows the analytical ranges and LOD moderate among these microextraction techniques. In conclusion, we have demonstrated that the IL-DMME method is simple, rapid and effective, and this work may provide a potential platform for developing a unique route for the determination of pesticides in environmental water samples.

4. Conclusions

In the present study, a new sample preparation methodology, ionic liquid-linked dual magnetic microextraction (IL-DMME), was developed for the determination of pyrethroids in honey

Table 4
The performance characteristics of the proposed IL-DMME method combined with HPLC-VWD.

Analytes	Linearity equation	Linearity (μg/L)	R^2	RSD (%)	LOD (μg/L)	LOQ (μg/L)	Recovery (%)
Fenpropathrin	$Y=1.6988X+0.8098$	0.5–500	0.9992	1.6	0.05	0.18	90.8
Deltamethrin	$Y=2.6299X-0.9636$	0.5–500	0.9999	3.8	0.05	0.16	93.9
Permethrin	$Y=2.4177X-2.5005$	0.5–500	0.9998	1.1	0.03	0.10	86.7
Bifenthrin	$Y=2.4021X+3.9898$	0.5–500	0.9993	3.3	0.04	0.13	98.2

RSD: relative standard deviation; LOD: limits of detection (S/N=3); LOQ: limits of quantitation (S/N=10).

Table 5
Results of the determination and recoveries of honey samples spiked with pyrethroids.

Samples	C_{found}[b] (μg/L)	C_{found}[c] (μg/L)	RSD%	C_{found}[d] (μg/L)	RSD%	C_{found}[e] (μg/L)	RSD%
1							
Fenpropathrin	ND[a]	1.8	2.8	47.0	2.8	182.7	3.8
Deltamethrin	3.3	1.8	2.0	47.6	3.9	171.5	3.7
Permethrin	ND[a]	1.9	1.9	46.9	3.0	180.2	2.7
Bifenthrin	ND[a]	1.7	2.2	45.6	2.1	179.4	1.4
2							
Fenpropathrin	ND[a]	1.8	1.8	44.7	2.0	186.0	3.7
Deltamethrin	3.1	1.9	2.6	45.1	1.6	177.6	2.5
Permethrin	ND[a]	1.8	1.2	45.5	1.9	177.4	3.3
Bifenthrin	ND[a]	1.9	1.4	44.9	1.1	182.4	3.8
3							
Fenpropathrin	ND[a]	1.9	2.0	46.7	1.5	191.5	1.5
Deltamethrin	3.4	1.8	5.7	44.0	2.4	175.0	4.9
Permethrin	1.8	1.8	1.9	44.8	5.3	182.3	1.1
Bifenthrin	ND[a]	1.8	4.1	44.6	1.3	184.8	3.7

[a] Not detected.
[b] Spiked concentration of honey is 0 μg L^{-1}.
[c] Spiked concentration of honey is 2 μg L^{-1}.
[d] Spiked concentration of honey is 50 μg L^{-1}.
[e] Spiked concentration of honey is 200 μg L^{-1}.

Table 6
Comparison of the IL-DMME with other methods for the determination of pyrethroids.

Methods	Extraction solvents	Dispersive solvents	ET (min)	Analytical ranges	LODs	Recoveries (%)	Ref.
TC-IL-DLLME -HPLC	$[C_8MIM]PF_6$	–	45	1.00–100 μg L^{-1}	0.34–0.48 μg L^{-1}	89.2–102.7	[41]
LLME-SFO -GC-ECD	1-dodecanol	–	25	0.15–80 μg L^{-1}	2.0–50 ng L^{-1}	79.0–113.6	[42]
DLLME-HPLC	Chloroform	Methanol	10	2.00–1000 μg L^{-1}	2–5 μg L^{-1}	85.8–94	[2]
MSPD-DLLME -GC-ECD	C_2Cl_4	Acetone	15	5.0–500 ng g^{-1}	0.45–1.13 ng g^{-1}	83.6–98.5	[43]
IL-DMME-HPLC	$[C_6MIM]NTf_2$	–	10	0.5–500 μg L^{-1}	0.03–0.05 μg L^{-1}	86.7–98.2	Present work

LLME-SFO, Liquid–liquid microextraction based on solidification of floating organic droplet; MSPD, Miniaturized matrix solid-phase dispersion.

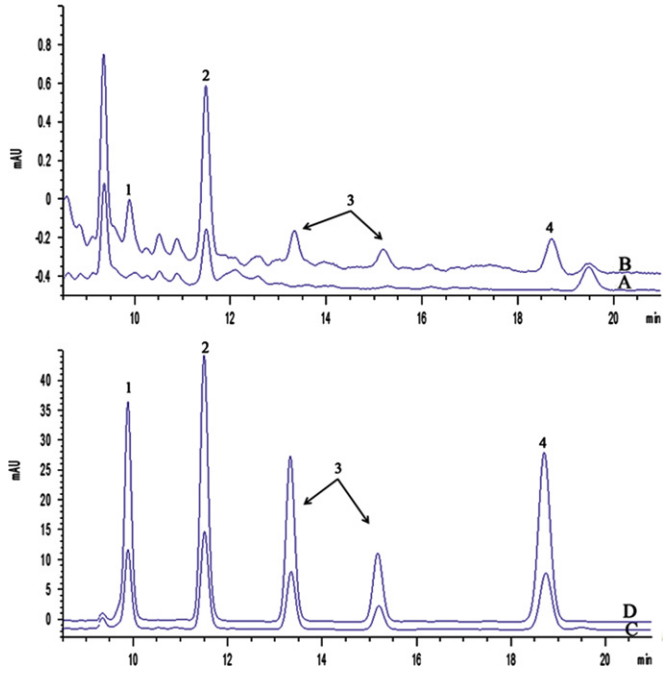

Fig. 4. Typical chromatograms of pyrethroids in the spiked and blank honey from the local market: (1) fenpropathrin; (2) deltamethrin; (3) permethrin; (4) bifenthrin. Chromatograms A–D: spiked levels were 0, 2, 50 and 200 μg L^{-1}, respectively.

samples. $[C_6MIM]NTf_2$, employed as extractant for the pyrethroids in the DLLME step, was fabricated to eliminate the possible negative effects with respect to the ion effect. In the D-μ-SPE step that followed, hydrophobic non-modified magnetic nanoparticles were utilized to retrieve $[C_6MIM]NTf_2$. Due to the rapid mass transfer associated with the DLLME and the D-μ-SPE steps, satisfactory extraction performance could be achieved. All of the results demonstrated that this method is sensitive, efficient and easy-to-operate because no complex surface chemical modification is required and the ionic liquid can be synthesized and purified in advance to avoid possible interference during extraction that may occur in the previous in-situ metathesis reaction of the DLLME step. In general, the proposed method may be of great interest in both MCT and routine analytical laboratories.

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