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Determination of phenylurea and triazine herbicides in milk by microwave assisted ionic liquid microextraction high-performance liquid chromatography

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ABSTRACT

The determination of phenylurea and triazine herbicides in milk based on microwave assisted ionic liquid microextraction (MAILME) coupled with high-performance liquid chromatographic separation was described. The experimental parameters of the MAILE, including type and amount of ionic liquid, microwave extraction power, extraction time and salt concentration in sample, were evaluated by a univariate method and orthogonal screening. When 60 μL of $[C_6MIM][PF_6]$ was used as extraction solvent the target compounds can be isolated from the 4 mL of milk. The MAILME is quick (7 min) and simple. The detection limits for isoproturon, monolinuron, linuron, propazine, prometryne, terbutryn and trietazine are 0.46, 0.78, 1.00, 1.21, 1.96, 0.84 and 1.28 μg L^{-1}, respectively. The proposed method was applied to the analysis of milk samples and the recoveries of the analytes ranged from 88.4 to 117.9% and relative standard deviations were lower than7.43%.

1. Introduction

Phenylureas and triazines, which are important herbicide used in agriculture worldwide, are ubiquitous environmental pollutants. Humans are exposed to these chemicals mainly through intake of food [1,2]. The milk is an important nutritional food and can provide an essential developmental factor and immunological components for the aged and infants. Therefore monitoring programs of milk samples are performed in many countries. In the EU, maximum residue limits (MRLs) for organochlorine pesticides and other chemical contaminants in milk are provided in several statutes, such as the EU directive 2002/32/EC. Furthermore, a new legislative framework (Commission Directive 2008/149/EC) on pesticide residues is applicable, it required that the contents of pesticide residues in milk and cream are not higher than 50 μg kg^{-1}. The extraction plays a key role in determination of herbicides prior to chromatographic analysis. But it is often difficult to extract the herbicides in the presence of fats, lactose and proteins in the samples, such as milk. The extraction of pesticides in milk was predominantly performed by solid-phase extraction (SPE) [3] and matrix solid-phase dispersion (MSPD) [4]. In the last few years, efforts have been directed towards miniaturizing the extraction procedure by greatly reducing the solvent to aqueous phase volume ratio, leading to the development of the solvent microextraction (SME), including cloud point extraction (CPE) [5] and single-drop microextraction (SDME) [6]. The main advantages of SME over other common methods are reduction of organic solvent consumption and enhancement of sensitivity. Room temperature ionic liquids (RTILs) are a group of new organic salts consisting of the organic cations and various anions that are liquids at room temperature [7]. Important features of RTILs include their immeasurably low vapor pressure, high stability, large viscosity, moderate dissolvability of organic compounds, as well as adjustable miscibility and polarity [8–10]. In recent years, RTILs have been used as acceptor phase for SME in some reports [11–14]. But in these reports, it took long time to finish the extraction and SME did not coupled with other extraction methods, such as ultrasonic extraction (UE) and microwave-assisted extraction (MAE). The rapidity, simplicity, low cost of operation and high sample throughput of MAE make this technique to be developed into a good alternative to traditional extraction methods and become a popular routine technique in environmental analysis, especially in organic analysis [15]. Widespread using of microwaves for analytical purpose has been found in different areas including clinical, food and environmental analysis [16–18]. Considering the central molecules of RTILs are the combination of the organic cations and various anions [19], they are suitable for dissipation of microwave energy. Based on these, studies about using RTILs as solvents in the microwave-assisted extraction (MAE) of organic compounds have been reported [20–22]. But to our knowledge, the reports about the RTIL microwaves extraction of herbicides from milk samples are scarce.

In this paper, a method for isolation, enrichment and determination of phenylureas and triazines in milk samples by microwave

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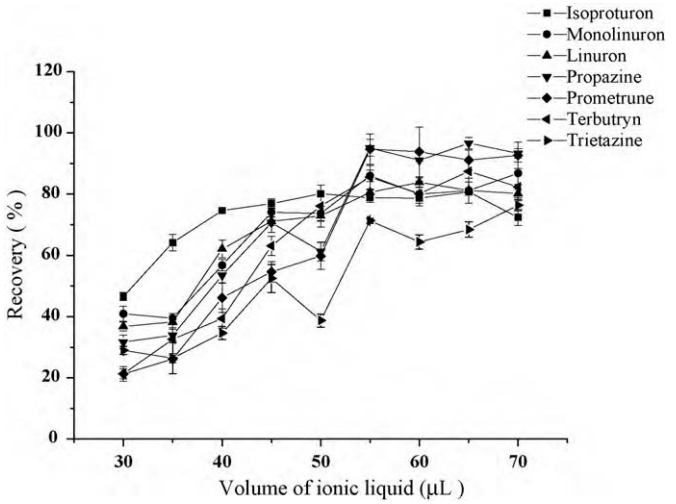

Fig. 1. Effect of ionic liquid volume. Sample volume, 4 mL; spiked concentration, 70 μg L^{-1}; microwave power, 150 W; extraction time, 5 min.

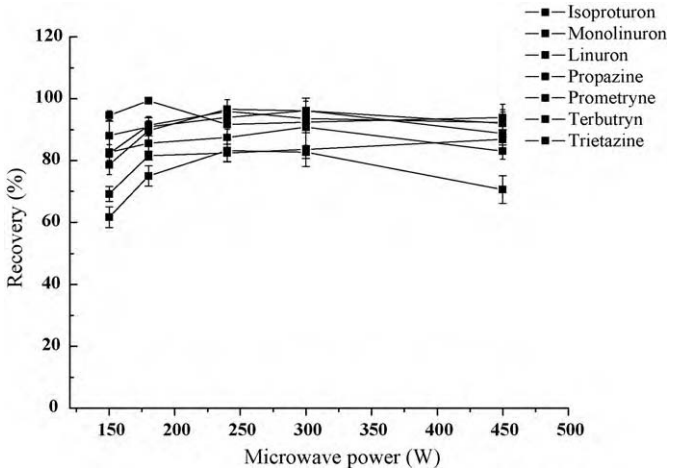

Fig. 2. Effect of microwave power. Volume of [C_6MIm][PF_6], 60 μL; volume of sample, 4 mL; spiked concentration, 70 μg L^{-1}; extraction time, 5 min.

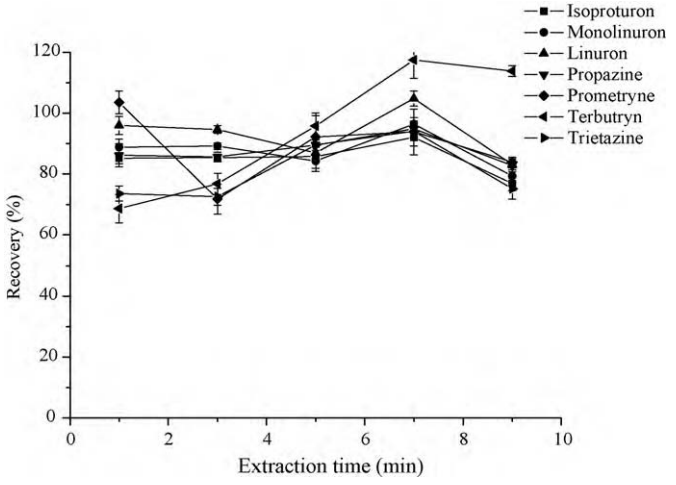

Fig. 3. Effect of extraction time. Volume of [C_6MIm][PF_6], 60 μL; volume of Sample, 4 mL; spiked concentration, 70 μg L^{-1}; microwave power, 240 W.

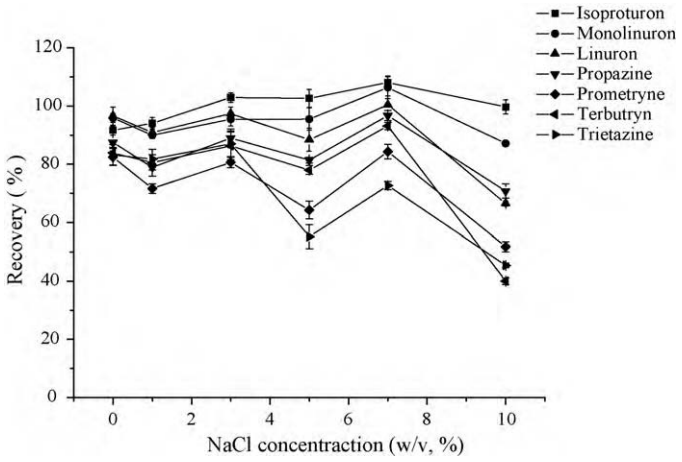

Fig. 4. Effect of NaCl concentration. Volume of [C_6MIm][PF_6], 60 μL; volume of sample, 4 mL; spiked concentration, 70 μg L^{-1}; microwave power, 240 W; extraction time, 7 min.

assisted ionic liquid microextraction (MAILME), coupled with high-performance liquid chromatographic separation, was developed. Variables influencing the MAILME were evaluated. The proposed method was also applied to the analysis of some milk samples and the analytical results were satisfactory.

2. Materials and methods

2.1. Reagents and chemicals

Isoproturon (N,N-dimethy-1-N-[4-(1-methylethy) phenyl]-urea), monolinuron (3-[4 chlorophenyl]-1-methoxy-methyl-urea), linuron (1-methoxy-1-methyl 1-3-[3,4-dichorophenyl]-urea), terbutryn (2-N-tert-butyl-4-N-ethyl-6-methylsulfanyl-1,3,5-triazine-2,4-diamine), trietazine (6-chloro-2-N,2-N,4-N-triethyl-1,3,5-triazine-2,4-diamine), propazine (6-chloro-N,N-bis[1-methylethyl]-1,3,5-triazine-2,4-diamine) and prometryne (2-methylthio-4,6-bis[isopropylamino]-1,3,5-triazine) were obtained from National Institute for the Control of Pharmaceutical and Biological Products (Beijing, China). Standard stock solutions for the herbicides at the concentration level of 500 μg mL^{-1} were prepared in acetonitrile. Synthesis-grade RTILs, 1-butyl-3-methylimidazolium hexafluorophosphate ([C_4MIM][PF_6]), 1-hexyl-3-methylimidazolium hexafluorophosphate ([C_6MIM][PF_6]) and 1-octyl-3-methylimidazolium hexafluorophosphate ([C_8MIM][PF_6]) were obtained from Chengjie Chemical Co. Ltd. (Shanghai, China). Chromatographic grade acetonitrile was from Fisher Scientific Company (UK). All other reagents were of analytical-reagent grade and from Beijing Chemical Factory (Beijing, China). Pure water was obtained with a Milli-Q water purification system (Millipore Co., USA). Analytical pure sodium chloride was used to adjust the ionic strength of the sample solution. All milk samples were purchased from local large-scale supermarket and stored at 4 °C.

2.2. Sample preparations

In the study, eight milk samples (1–8) were analyzed. Except for the experiments mentioned in Section 3.3.2, which were performed on all eight samples, all other results were obtained with sample 1.

The fresh spiked samples (1–4) containing phenylureas and triazines at the concentration levels of 10 and 70 μg L^{-1} were prepared by spiking the stock standard solutions into milk samples and shaking for 10 min.

Table 1
Orthogonal screening results.

No.	(A) Volume of $[C_6MIm][PF_6]$ (μL)	(B) Microwave power (W)	(C) Extraction Time (min)	(D) The concentration of NaCl (w/v, %)	Recovery (%)
1	A_1	B_1	C_1	D_1	57.3
2	A_1	B_2	C_2	D_2	48.2
3	A_1	B_3	C_3	D_3	74.4
4	A_1	B_4	C_4	D_4	64.8
5	A_2	B_1	C_2	D_4	81.3
6	A_2	B_2	C_1	D_3	98.8
7	A_2	B_3	C_4	D_2	110.6
8	A_2	B_4	C_3	D_1	118.1
9	A_3	B_1	C_3	D_2	112.4
10	A_3	B_2	C_4	D_1	118.8
11	A_3	B_3	C_1	D_4	112.4
12	A_3	B_4	C_2	D_3	105.5
13	A_4	B_1	C_4	D_3	112.5
14	A_4	B_2	C_3	D_4	108.3
15	A_4	B_3	C_2	D_1	115.2
16	A_4	B_4	C_1	D_2	82.8
K1	61.2	92.3	85.7	98.9	
K2	93.6	88.2	87.6	87.0	
K3	113.7	101.8	102.9	94.1	
K4	104.7	90.9	97.1	93.3	
R	52.5	13.6	17.2	11.9	

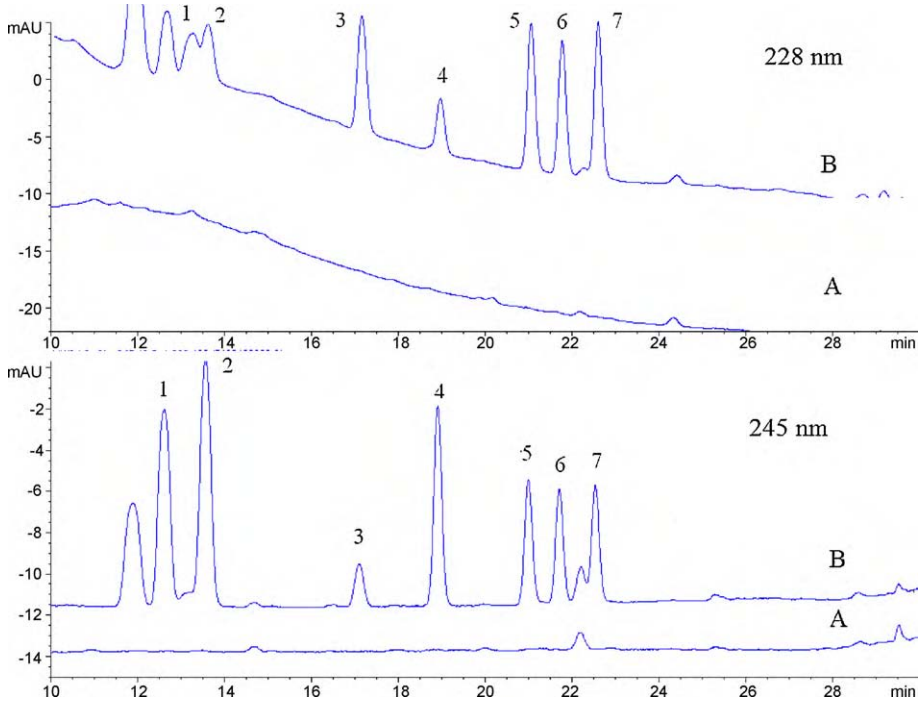

Fig. 5. Chromatograms of blank milk sample 1 (A) and spiked sample 1 (B): (1) isoproturon; (2) monolinuron; (3) propazine; (4) linuron; (5) prometryne; (6) terbutryn; and (7) trietazine. Volume of $[C_6MIm][PF_6]$, 60 μL; volume of sample, 4 mL; spiked concentration, 70 $\mu g\,L^{-1}$; microwave power, 240 W; extraction time, 7 min.

The aged spiked samples (5–8) were prepared the same as the above method. Then the samples were kept in sealed bottle and stored for 1, 7, 14, 21 and 30 days at 4 °C, respectively.

2.3. Instrumentations

The extraction was performed on a modified household microwave oven (NN-MX25WF, Shanghai, China) with the out-

Table 2
Analytical performances.

Compound	Regression equation	Correlation coefficient	Liner range ($\mu g\,L^{-1}$)	LOD ($\mu g\,L^{-1}$)	LOQ ($\mu g\,L^{-1}$)
Isoproturon	$A = 1.11787 + 3.19117c$	0.9996	3.5–140	0.46	1.53
Monolinuron	$A = -0.42142 + 3.63785c$	0.9997	3.5–140.0	0.78	2.62
Linuron	$A = 0.46612 + 2.42466c$	0.9994	3.0–123.7	1.00	3.35
Propazine	$A = 2.13387 + 1.40122c$	0.9993	3.5–140.0	1.21	4.03
Prometryne	$A = 10.42353 + 1.30512c$	0.9996	3.84–153.5	1.96	6.52
Terbutryn	$A = 12.93808 + 1.44324c$	0.9997	3.37–135	0.84	2.79
Trietazine	$A = 18.19211 + 2.16197c$	0.9991	3.44–137.5	1.28	4.26

put maximum power of 800W. The output power of ultrasonic generator (KQ2200E Kunshan Ultrasonic Instrument Co. Ltd., Kunshan, China) was 100W. The 1100 series liquid chromatograph (Agilent Technologies Inc., USA) equipped with photodiode-array detector (DAD) was used. Chromatographic separation of target analytes was performed on Zorbax Eclipse XDB-C18 column (3.5 μm, 4.6 mm × 150 mm, Agilent, USA).

2.4. Extraction procedure

4 mL of milk sample, 0.28 g of NaCl and 60 μL of $[C_6MIM][PF_6]$ were placed into the 5 mL polytetrafluoroethylene (PTFE) tube, respectively. In order to make the ionic liquid disperse into the sample, the tube was immersed into the ultrasonic bath for 5 min and shaken strongly once a minute by hand during the ultrasonic treatment. The resulting suspension was intermittently irradiated by microwave under the microwave power of 240 W for 16 min. The microwave extraction was performed intermittently, i.e. irradiation–shaking–irradiation, and the irradiation time was maintained for 2 min, during which 2 min was taken for shaking the sample between two irradiation processes. Then the suspension was centrifuged at 15,000 rpm for 10.0 min. After centrifugation, the RTILs settled on the bottom of the tube. Then the upper aqueous phase was dumped completely. In order to reduce the loss of RTILs, acetonitrile was added to dilute the RTIL to 150 μL. Finally, the organic phase was homogenized manually and filtered by 0.22 μm PTFE filter membrane.

2.5. Determination of target compounds by HPLC

The flow rate of mobile phase was kept at 0.5 mL min^{-1}. Mobile phases A and B were acetonitrile and water, respectively. The gradient conditions are as follows: 0–5 min, 40% A; 5–9 min, 40–47% A; 9–20 min, 47–65% A; 20–24 min, 65–67% A; 24–28 min, 67–100% A; 28–33 min, 100–40% A. The temperature of column was controlled at 30 °C. Injection volume was 20 μL. The monitoring wavelength was 228 nm for propazine, prometryne, terbutryn, trietazine and 245 nm for isoproturon, monolinuron and linuron. The reference wavelength and bandwidth were 360 and 4 nm respectively.

3. Results and discussion

3.1. Optimization of MAILME conditions

In this extraction, the influence of experimental parameters, such as types and amount of RTILs, time and power of microwave irradiation and ionic strength in the sample, was investigated. The parameters were first studied separately for finding out the optimum ranges of the parameter values. Then the most relevant parameters were studied with an orthogonal model.

3.1.1. Selection of RTILs

Characteristics of RTILs, such as solubility in water, the viscosity, extraction capacity and chromatographic behavior, play a key role in influencing the recovery and enrichment factor. It was necessary to consider the relationship of the extraction capacity and the length of alkyl chain of RTIL [23]. When the microwave power was 150 W and extraction time was 5 min, the effect of $[C_4MIM][PF_6]$, $[C_6MIM][PF_6]$ and $[C_8MIM][PF_6]$ on the extraction yields was studied. The results indicated that, the recovery obtained with $[C_4MIM][PF_6]$ was lower than those obtained with $[C_6MIM][PF_6]$ and $[C_8MIM][PF_6]$. But there were significant interference peaks in the chromatogram when $[C_8MIM][PF_6]$ was used as the extraction solvent. Abraham et al. calculated the partition coefficients for the $[C_4MIM][PF_6]$/water and $[C_6MIM][PF_6]$/water system, respectively [24]. The solubility of the $[C_4MIM][PF_6]$ in water (1.88 g/100 mL)

Table 3
Analytical results for fresh spiked samples.

Sample	Added (μg L^{-1})	Isoproturon		Monolinuron		Linuron		Propazine		Prometryne		Terbutryn		Trietazine	
		Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
1	10	101.0	3.39	102.7	5.03	97.7	3.33	109.4	5.41	104.2	3.75	110.1	3.42	111.4	7.20
	70	89.8	3.18	95.7	4.15	91.5	5.20	107.7	6.34	108.5	5.74	101.9	1.27	92.3	6.51
2	10	106.9	5.98	104.8	2.71	105.0	6.28	114.2	6.56	102.9	4.46	91.4	4.55	93.2	4.88
	70	102.1	5.82	105.9	2.88	108.0	2.96	111.4	2.96	114.6	2.84	99.5	2.22	103.8	3.80
3	10	111.2	4.45	107.1	6.82	104.1	3.60	111.2	4.28	104.6	8.01	99.2	4.44	88.4	4.84
	70	102.7	0.85	109.6	2.47	103.5	6.64	111.7	4.35	104.8	4.84	103.3	3.09	98.1	5.44
4	10	108.1	5.41	105.8	4.98	102.2	3.20	115.5	6.48	101.6	3.53	99.2	4.44	106.0	6.41
	70	100.1	1.39	104.2	1.54	100.8	2.18	111.2	3.95	104.8	1.91	104.5	4.05	92.2	1.71

Table 4
Analytical results for the aged spiked samples.

Sample	Added ($\mu g\ L^{-1}$)	Stored time (day)	Isoproturon		Monolinuron		Linuron		Propazine		Prometryne		Terbutryn		Trietazine	
			Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
5	10	1	108.0	3.34	98.6	3.17	114.7	3.07	109.6	6.07	102.0	2.71	90.1	6.03	95.6	5.24
		7	111.3	5.47	104.1	1.36	93.7	5.90	100.6	7.00	100.5	6.92	98.0	2.88	96.4	5.97
		14	103.9	5.68	97.2	4.57	92.1	3.36	97.6	6.69	98.5	4.52	117.8	5.78	114.4	4.75
		21	107.5	2.26	102.4	2.55	97.5	1.25	103.2	3.05	101.1	3.40	114.8	4.17	103.0	4.91
		30	91.1	6.41	101.4	4.75	94.9	3.32	98.7	4.93	96.2	4.17	107.0	3.89	109.0	4.35
	70	1	112.9	1.25	105.0	3.54	106.8	4.74	92.5	1.24	116.7	5.22	92.8	5.60	92.5	3.71
		7	100.5	0.72	105.4	1.21	103.6	0.78	89.4	4.30	93.2	3.88	94.2	5.63	92.9	5.13
		14	101.7	2.41	108.9	3.87	116.0	4.67	89.5	5.31	92.6	4.62	92.4	4.30	91.3	5.44
		21	106.4	4.96	106.9	5.33	114.8	5.86	102.2	6.79	90.2	5.75	98.7	3.09	91.0	3.85
		30	103.8	3.10	99.1	5.12	101.2	3.69	105.0	3.90	95.7	3.41	103.2	3.47	95.3	6.02
6	10	1	98.6	5.11	104.7	3.35	108.8	7.11	117.9	7.43	108.1	5.44	107.7	6.71	100.0	4.79
		7	112.2	2.45	109.7	4.46	115.3	7.43	111.4	4.00	95.4	0.70	103.6	1.59	95.1	6.23
		14	108.3	1.76	109.0	5.13	112.1	4.07	97.1	5.86	101.3	3.55	99.7	3.44	116.2	4.77
		21	116.9	3.19	112.3	2.21	106.0	3.58	99.1	2.87	107.5	3.95	95.1	3.96	96.2	2.81
		30	101.7	3.12	102.0	4.34	104.4	3.35	91.0	5.61	93.7	3.11	104.4	5.48	92.1	5.68
	70	1	104.3	2.65	105.6	1.80	105.5	0.90	107.0	1.88	110.2	5.68	96.5	5.65	95.4	1.39
		7	109.3	2.74	115.1	2.13	114.9	3.62	109.7	3.40	106.1	5.12	105.3	3.83	113.3	5.87
		14	104.9	2.92	115.4	0.88	117.1	4.39	93.8	3.21	91.5	3.28	90.2	4.73	104.4	2.03
		21	105.9	4.96	110.2	2.56	114.6	5.88	103.1	4.11	114.1	1.66	88.8	3.79	105.1	4.74
		30	105.0	3.51	114.5	4.91	111.4	3.21	98.4	4.01	104.2	2.52	92.7	3.02	101.6	0.86
7	10	1	110.8	3.61	109.0	0.54	119.8	3.03	117.8	2.40	93.5	6.12	102.8	5.36	111.4	1.98
		7	117.8	3.57	110.7	4.64	111.6	3.65	97.9	5.93	103.3	0.50	111.5	4.65	100.2	5.12
		14	107.8	2.98	109.4	4.01	107.3	6.06	101.2	5.29	107.5	1.16	91.8	3.64	103.0	2.78
		21	110.4	5.16	111.7	4.46	114.5	5.03	96.2	1.77	115.7	2.81	97.6	1.22	112.0	4.91
		30	91.1	6.41	101.4	4.75	103.0	2.43	96.0	5.61	93.2	6.08	100.9	2.48	95.6	2.52
	70	1	100.7	3.00	104.5	1.95	117.9	1.21	117.2	0.13	110.1	2.11	116.7	3.77	110.7	5.43
		7	106.7	1.56	116.5	1.00	116.7	3.41	103.5	2.24	103.7	4.87	100.7	7.08	108.6	5.32
		14	112.7	1.22	112.7	2.63	112.4	2.87	102.1	3.94	98.3	1.56	102.2	5.35	109.9	4.16
		21	104.4	3.48	92.1	6.51	114.4	6.32	110.2	1.19	110.3	5.93	101.2	6.13	110.2	3.31
		30	100.7	4.96	109.8	5.05	113.3	3.72	95.6	3.14	104.5	2.27	92.2	2.03	108.9	2.79
8	10	1	102.3	0.81	108.6	1.92	114.0	5.41	107.2	1.17	96.6	0.98	98.1	3.59	106.7	6.07
		7	116.8	5.64	112.6	2.58	113.0	5.79	103.7	4.52	115.3	2.65	112.8	3.40	114.3	7.49
		14	115.9	1.96	104.0	0.99	110.3	3.22	105.8	6.02	106.7	3.25	91.2	4.31	106.1	4.32
		21	104.8	5.56	115.0	5.35	110.5	2.85	107.5	5.58	117.3	2.63	101.4	2.18	109.0	5.57
		30	109.3	3.91	106.6	5.07	101.7	2.61	105.3	4.06	98.8	5.53	92.6	6.42	96.5	4.41
	70	1	117.2	5.73	113.1	4.54	116.0	4.22	110.5	4.81	104.9	4.51	116.7	4.81	103.4	3.99
		7	108.5	0.97	115.9	0.85	112.8	1.13	102.3	1.26	106.1	4.20	96.4	1.46	99.9	0.69
		14	107.8	4.66	113.1	3.55	108.8	3.53	94.2	1.61	102.2	3.30	93.7	2.63	103.2	2.12
		21	93.2	0.66	106.1	1.84	99.7	2.66	106.8	1.82	109.5	0.71	102.5	3.57	104.3	2.08
		30	100.6	6.52	97.0	4.56	105.5	6.11	98.7	4.42	96.3	3.22	101.5	5.37	108.8	2.19

is higher than that of $[C_6MIM][PF_6]$ in water (0.75 g/100 mL), and the viscosity of $[C_4MIM][PF_6]$ (450 mPa s at 25 °C) is lower than that of $[C_6MIM][PF_6]$ (586 mPa s at 25 °C) [25–27]. The low viscosity should be beneficial to the extraction time. However, compared with viscosity, the solubility of ionic liquids in water should be more significant for improving the performances of the MAILME. Based on these reasons, $[C_6MIM][PF_6]$ was selected as the extraction solvent.

The effect of volume of $[C_6MIM][PF_6]$ on extraction yields was also studied. As shown in Fig. 1, the recoveries show an increase with the increase of the volume from 30 to 55 μL. The recoveries are almost constant when the volume increases from 55 to 70 μL. Therefore, 55 μL of $[C_6MIM][PF_6]$ was selected in the work.

3.1.2. Selection of microwave power

The RTILs are the molten salts and have larger thermal capacity (>2000 J kg^{-1} K^{-1} at 25 °C) compared with water (1600 J kg^{-1} K^{-1} at 100 °C) [28], which makes the RTILs have high viscosity and difficult for thermal diffusion at normal temperature. As a result, the low diffusion rate of RTILs is an important drawback which can influence the partition equilibrium of analytes between the IL and water. Increasing temperature can decrease the viscosity of the RTILs drastically and therefore, increase the diffusion rate and extraction efficiency. Because the temperature of sample solution is strongly related with the microwave irradiation power and time, the microwave power and irradiation time can affect the extraction recoveries. The effect of extraction power on the recoveries was studied when the extraction time was set at 5 min and 55 μL $[C_6MIM][PF_6]$ was used as extraction solvent. As shown in Fig. 2, the recoveries of the target analytes increase from 150 to 240 W and slowly decrease thereafter. So 240 W was selected for further experiments.

3.1.3. Selection of extraction time

The effect of extraction time was studied under the microwave power of 240 W. As can be seen from Fig. 3, the recoveries of the target analytes increase gradually with increase of extraction time from 1 to 7 min and then decrease quickly with the increase of the time. On the one hand, the increase of extraction time was beneficial to the decrease of viscosity of RTILs, the acceleration in the rate of the mass transfer of the analytes and improvement of extraction yields of analytes. On the other hand, the increase of extraction time resulted in the increase of solubility of $[C_6MIM][PF_6]$ in the samples [29,30], which resulted in the decrease of recoveries. Based on the experimental results, the extraction time was selected to be 7 min.

3.1.4. Selection of salt concentration

In the extraction, solubility of target analytes in the aqueous phase will be decreased and their partitioning in the extraction phase will be enhanced at the same time [28]. Generally NaCl was used to adjust the ionic strength. The effect of the concentrations of NaCl on the recoveries of target analytes was investigated when the other experimental conditions were constant. The results shown in Fig. 4 indicate that the recoveries increase with the increase of NaCl concentration, reach maximum at NaCl concentration of 7% and then decrease. The salt out effect was enhanced with the increase of the salt concentration. However, when the salt concentration was too high, the ion exchange between $[PF_6]^-$ in $[C_6MIM][PF_6]$ and Cl^- in solution occurred and the resulting $[C_6MIM]Cl$ is soluble in water. This process may lead to the decrease of the amount of settled IL phase and the poor extraction performance. At the same time, the too high salt concentration would influence the phase separation [31–33].

3.2. Orthogonal screening

Based on the experimental results obtained by the univariate method, orthogonal experiment (L_{16} (4^4)) was carried out in order to determine the optimum operating conditions. In the orthogonal screening, the terbutryn was used as the target analyte. The effects of volume of $[C_6MIM][PF_6]$ (A) (A_1, 45 μL; A_2, 55 μL; A_3, 60 μL; A_4, 65 μL), microwave power (B) (B_1, 150 W; B_2, 180 W; B_3, 240 W; B_4, 300 W), microwave extraction time (C) (C_1, 3 min; C_2, 5 min; C_3, 7 min; C_4, 8 min) and concentration of NaCl (D) (D_1, 0%; D_2, 3%; D_3, 7%; D_4, 9%) on the recoveries are shown in Table 1. In the table, K_n is the mean effect of each factor at the different levels and R is the range. The experimental results indicate that the volume of $[C_6MIM][PF_6]$ plays an important role in the extraction followed by extraction time of microwave, microwave power and concentration of NaCl. Based on the experimental results, volume of $[C_6MIM][PF_6]$, microwave power, microwave extraction time and concentration of NaCl were selected as 60 μL, 240 W, 7 min and 7%, respectively. Table 1 also exhibits that the volume of $[C_6MIM][PF_6]$ was the most significant factor and the other factors have not significant effect on extraction yields of the target analytes.

3.3. Evaluation of the method

3.3.1. Analytical performances

The working curves were constructed by plotting the peak areas measured versus the concentration of analytes. The linear regression equations and correlation coefficients are listed in Table 2. The limits of detection (LODs) and quantification (LOQs) indicated in Table 2 are determined as the lowest concentration yielding a signal-to-noise (S/N) ratio of 3 and 10, respectively. The concentrations of the target analytes in the extract are higher than the LOQs and lower than upper limits of determination for the proposed method. So the LOQs and linear equations are appropriate to the goal of the proposed method.

3.3.2. Analysis of samples

The phenylurea and triazine herbicides in the milk samples were not detectable. In order to evaluate the accuracy, repeatability and selectivity of the proposed method, firstly, the phenylurea and triazine herbicides in the fresh spiked samples were determined and the results are listed in Table 3. The results indicate that the proposed method provides good recoveries (88.4–115.5%) and acceptable precisions (≤7.20%). Secondly, the proposed method was applied to the analysis of the aged samples to further evaluate the performances of the method. The results shown in Table 4 are satisfactory. The chromatograms of blank milk sample and spiked sample are shown in Fig. 5

4. Conclusions

The MAILME was successfully applied to the extraction of the phenylurea and triazine herbicides from milk samples. The results indicated that the proposed method has some advantages in respect of extraction efficiency, extraction time and organic solvent consumption. So it seems possible to extend this method to the extraction of phenylurea and triazine herbicides in other similar samples by varying the extraction conditions.

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