



## Extraction of eight triazine and phenylurea herbicides in yogurt by ionic liquid foaming-based solvent floatation

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### ABSTRACT

The ionic liquid foaming-based solvent floatation (ILF-SF) was developed for extracting triazines and phenylureas from yogurt. These analytes were separated and determined by high performance liquid chromatography. Some experimental parameters, such as the pH value of floatation solution, extraction solvent, kind of ionic liquid and floatation time were investigated and optimized. The mixture of n-propyl alcohol and ethyl acetate was used as extraction solvent and 1-hexyl-3-methylimidazolium hexafluorophosphate was used as foaming agent. The precision and recoveries of eight herbicides vary from 0.17 to 6.90% and from 86.5 to 118.7%, respectively. The detection limits for simeton, simazine, chlortoluron, isoproturon, ametryn, propazine, prometryne and prebana are 0.59, 0.44, 0.44, 0.46, 0.32, 1.01, 0.34 and 0.23  $\mu\text{g L}^{-1}$ , respectively. The enrichment factors for the solvent floatation range from 11.6 to 18.6 for the eight herbicides.

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### 1. Introduction

The herbicides can result in the contamination of the atmosphere, ground and wastewater, agricultural products and, consequently, the direct or indirect pollution of food products and biological systems. Triazine and phenylurea herbicides may be dangerous for human health because they are suspected to cause cancer, birth defects and interruption of hormone functions [1,2]. These herbicides have been proven to be transferred to the dairy products [3–5]. The European Union (EU) legislation harmonizes a maximum residue limits (MRLs) of the pesticides and fixes default value of MRLs at 0.01  $\text{mg kg}^{-1}$  for human food and animal feeding stuffs (Commission Directive 2008/149/EC). Yogurt is a product prepared by fermentation of milk at ambient temperature.

To achieve effective extraction of the pesticides from dairy products, several sample preparation methods have been developed, such as liquid–liquid extraction (LLE) [6], solid-phase extraction (SPE) [7–10], dispersive solid-phase extraction (DSPE) [11], matrix solid-phase dispersion (MSPD) [12], pressurized liquid extraction (PLE) [13] and hollow fiber membrane-protected solid-phase microextraction (HFMS-SPME) [14]. The separation and determination of the pesticides were performed by high performance liquid

chromatography (HPLC) [6,10–13,15], capillary electrophoresis (CE) and gas chromatography (GC) [7,14,16].

Solvent floatation (SF) was originally introduced by Sebba [17] as an improved method for the ion floatation in 1962. In this special adsorptive bubble separation method, some organic solvent placed on the top of aqueous phase is used to collect the compounds adsorbed on the bubble surface of an ascending gas stream. The main advantages of SF are high separation efficiency and concentration coefficient, a small amount of organic solvent, soft separation process without emulsions, simple operation and a large amount of sample. This method has recently attracted much attention on pesticide detection [18–21].

Ionic liquids (ILs) are organic salts consisting of the organic cations and various anions and liquids at room temperature [22]. Important features of ILs include their immeasurably low vapor pressure, high stability, large viscosity, moderate dissolvability of organic compounds, as well as adjustable miscibility and polarity [23–25]. In recent years, ILs have been used as extraction solvents in dispersive liquid–liquid microextraction (DLLME) [26,27], microwave assisted ionic-liquid microextraction (MAILME) [28], ionic liquid–salt aqueous two-phase floatation (ILATPF) [29], ionic liquid solvent floatation [30] and single drop microextraction (SDME) [31]. ILs are not only used as alternative green solvents for synthesis, catalysis and biocatalysis, but also as electrolytes, lubricants or modifiers of mobile and stationary phases in the separation science [32–37]. Because ILs contain a long n-alkyl substituent chain on cation, they are a novel cationic surfactant. Patra

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et al. [38,39] has used ILs as additive of other surfactant solution. Zhang et al. [40] has applied the ILs-based foam floatation-solid phase extraction (FF-SPE) for the extraction and concentration of the steroid hormones in water samples.

In this work, ionic liquid foaming-based solvent floatation (ILF-SF) was applied to the extraction of herbicides in yogurt samples. ILs were used as foaming agent.

## 2. Materials and methods

### 2.1. Reagents and chemicals

Simeton, simazine, chlortoluron, isoproturon, ametryn, propazine, prometryne and prebane were obtained from National Institute for the Control of Pharmaceutical and Biological Products (Beijing, China) (The structures of these herbicides can be found in Suppl. Fig. 1.). Standard stock solutions for the herbicides at the concentration level of  $100 \mu\text{g mL}^{-1}$  were prepared in acetonitrile. 1-Butyl-3-methylimidazolium hexafluorophosphate ( $[\text{C}_4\text{MIM}][\text{PF}_6]$ ), 1-hexyl-3-methylimidazolium hexafluorophosphate ( $[\text{C}_6\text{MIM}][\text{PF}_6]$ ), 1-octyl-3-methylimidazolium hexafluorophosphate ( $[\text{C}_8\text{MIM}][\text{PF}_6]$ ), 1-butyl-3-methylimidazolium tetrafluoroborate ( $[\text{C}_4\text{MIM}][\text{BF}_4]$ ), 1-hexyl-3-methylimidazolium tetrafluoroborate ( $[\text{C}_6\text{MIM}][\text{BF}_4]$ ) and 1-octyl-3-methylimidazolium tetrafluoroborate ( $[\text{C}_8\text{MIM}][\text{BF}_4]$ ) were obtained from Chengjie Chemical Co. Ltd. (Shanghai, China). Chromatographic grade acetonitrile was from Fisher Scientific Company (Loughborough, 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). Triton X 114 (T-114) was purchased from Beijing Biotechnological Company (Beijing, China). Ethyl trimethyl ammonium bromide (CTAB), sodium dodecyl sulfate (SDS) and sodium dodecyl benzene sulfonate (SDBS) were purchased from Beijing Chemical Factory (Beijing, China).

Fifteen yogurt samples were purchased from local large-scale supermarket and stored at  $4^\circ\text{C}$ .

### 2.2. Apparatus

Chromatographic separation and determination of the 8 herbicides were carried out on the 1100 series liquid chromatograph (Agilent Technologies Inc., USA) equipped with UV detector and quaternary gradient pump. Eclipse XDB-C18 column ( $3.5 \mu\text{m}$ ,  $4.6 \text{ mm} \times 150 \text{ mm}$ , Agilent, USA) was used. The 1100 series liquid chromatograph (Agilent Technologies Inc., USA) equipped with photodiode-array detector (DAD) was used.

The KQ-100DE ultrasonic cleaner was purchased from Kunshan Ultrasonic Instrument Co., Ltd. (Kunshan, China). The frequency and output power of the ultrasonic cleaner are 40 kHz and 100 W, respectively. Allegra™ 64 R Centrifuge was purchased from Beckman Coulter.

### 2.3. Preparation of spiked samples

Five fresh spiked samples (samples 1–5) were prepared by spiking the stock standard solutions of triazines and phenylureas into five yogurt samples and shaking for 10 min.

One aged spiked sample (sample 6) was prepared by the same as the above method except that the spiked sample was kept in sealed bottle and stored for 1, 7, 14, 21 and 40 days at  $4^\circ\text{C}$ , respectively.

### 2.4. Extraction procedure

The schematic diagram of the experimental set-up is shown in Fig. 1. 10 mL of sample, 14 mL of water and  $30 \mu\text{L}$  of perchloric acid

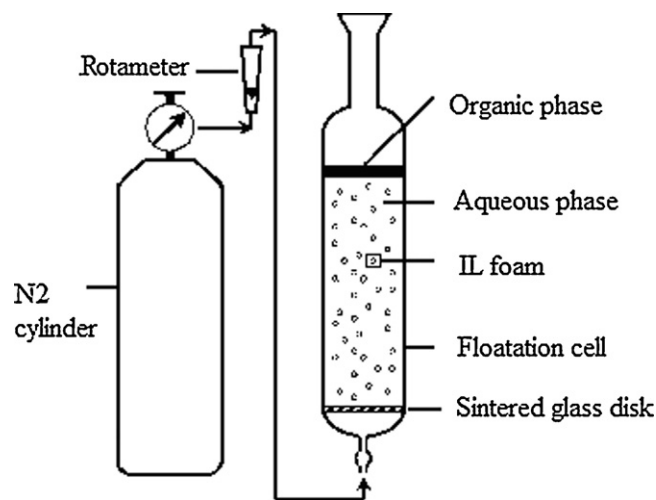


Fig. 1. The schematic diagram of the experimental set-up.

were added into 25 mL centrifuge tube. The mixture was vigorously shaken for 30 s, ultrasonicated for 10 min at  $20^\circ\text{C}$  and then centrifuged at 15,000 rpm for 8 min at  $4^\circ\text{C}$ . The supernatant was transferred into a beaker. 0.5 g of NaCl, 14 mL of water and  $30 \mu\text{L}$  of perchloric acid were added into the centrifuge tube and treated by the method mentioned above. The obtained supernatant was also added into the beaker. The pH value of combined supernatant was adjusted to 5 with  $1 \text{ mol L}^{-1}$  NaOH and  $1 \text{ mol L}^{-1}$  HCl. 8 g of  $(\text{NH}_4)_2\text{SO}_4$  and  $1 \mu\text{L}$  of IL were added into the beaker. The resulting solution was referred to as floatation solution. The floatation solution was transferred into the floatation cell. The extraction solvent (n-propyl alcohol: ethyl acetate = 1:1, v/v) was added into the floatation cell. The N<sub>2</sub> flow rate was 50 mL/min and ILF-SF started. 10 min later, the organic phase was transferred into a glass flask and evaporated to dryness. The residue was dissolved in  $250 \mu\text{L}$  of methanol. The resulting solution was referred to as analytical solution and filtered through a  $0.22 \mu\text{m}$  PTFE filter membrane.

### 2.5. HPLC conditions

The HPLC analysis was conducted in gradient mode. Mobile phases A and B are acetonitrile and water, respectively. The gradient conditions are as follows: 0–3 min, 25–30% A; 3–5 min, 30–40% A; 5–10 min, 40–48% A; 10–18 min, 48–50% A; 18–20 min, 50% A; 20–30 min, 50–60% A and 30–33 min, 67% A. The column temperature was kept at  $30^\circ\text{C}$  and the flow rate of mobile phase was kept at 0.5 mL/min. Injection volume of analytical solution was  $20 \mu\text{L}$ . The monitoring wavelengths were 222 nm for simeton, simazine, ametryn, propazine, prometryne, prebane and 244 nm for chlortoluron, isoproturon. The reference wavelength and bandwidth were 360 and 4 nm, respectively.

## 3. Results and discussion

### 3.1. Optimization of ILF-SF conditions

#### 3.1.1. Effect of amount of NaCl

To investigate the influence of amount of NaCl on the extraction of analytes, a series of experiments were performed by adding different amounts of NaCl (0.3–1.5 g). The recoveries of the analytes increase when the amount of NaCl increases from 0.3 to 0.5 g. When the amount of NaCl increases from 0.5 to 1.5 g, the recovery of propazine decreases, the one of isoproturon increases slightly and that of other analytes are unchanged (The detailed information can be found in Suppl. Fig. 2.). When the amount of NaCl is 0.5 g, the

**Table 1**  
Analytical performance.

Analyte	Regression equation	Correlation coefficient	Liner range ( $\mu\text{g L}^{-1}$ )	LOD ( $\mu\text{g L}^{-1}$ )	LOQ ( $\mu\text{g L}^{-1}$ )
Simeton	$A = 3.10383c + 0.97563$	0.9999	2.10–250	0.59	1.96
Simazine	$A = 4.97425c + 25.13336$	0.9997	1.95–250	0.44	1.46
Chlortoluron	$A = 2.2826c + 2.7305$	0.9992	1.95–250	0.44	1.45
Isoproturon	$A = 4.7915c - 0.08405$	0.9993	1.95–250	0.46	1.52
Ametryn	$A = 5.8536c + 10.39624$	0.9997	1.50–250	0.32	1.08
Propazine	$A = 2.43383c - 3.4654$	0.9995	3.90–250	1.01	3.37
Prometryne	$A = 5.83646c + 1.56528$	0.9985	1.50–250	0.34	1.15
Prebane	$A = 4.39567c - 2.8325$	0.9997	0.97–250	0.23	0.78

recoveries range from 87.4 to 119.1% and the mean recovery for the analytes is 101.0%. Therefore, the 0.5 g of NaCl is suitable.

### 3.1.2. Effect of pH value of floatation solution

The pH value of floatation solution is an important factor. The effect of the pH values of floatation solution ranging from 3 to 11 on recoveries was studied. The recoveries obviously increase with the pH increase from 3 to 5 and then decrease when pH value is higher than 5 (The detailed information can be found in Suppl. Fig. 3.). When the pH values are excessively low and high, the foaming rate is very rapid. The excessively rapid foaming rate can limit the loading capacity of IL foam [40]. The herbicides are weak bases and can be hydrolyzed at excessively low pH value. On the other hand, when the pH value is higher than 5, the interaction of  $\text{OH}^-$  with IL may predominate, which is not beneficial to the formation of herbicide-IL complex. Therefore, we carried out all subsequent experiments at pH 5.

### 3.1.3. Effect of extraction solvent

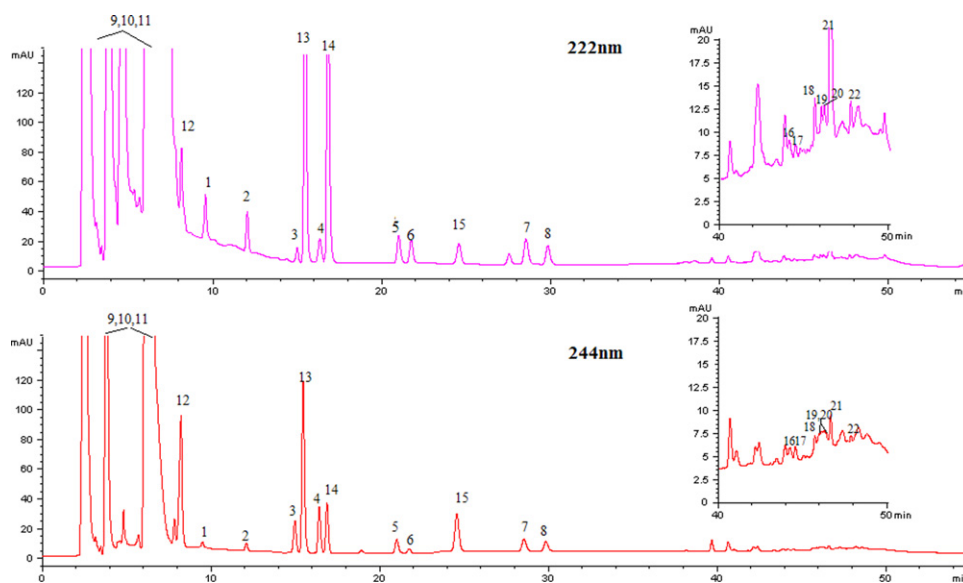
The recoveries depend on the solubility of the analytes in the extraction solvent. The effect of kinds of extraction solvents, including ethyl acetate (EA), n-butyl alcohol (BA), n-propyl alcohol (PA) and n-propyl alcohol-ethyl acetate (PE, 1:1, v/v), was investigated. The highest recoveries for the analytes were obtained when PE was used as extraction solvent. The recoveries obtained with PA, BA and EA are ranked in descending order (The detailed information can be found in Suppl. Fig. 4.). Therefore, the PE was used for further ILF-SF investigations.

### 3.1.4. Effect of the kinds of ILs

It is necessary to consider the relationship of the extraction capacity and the length of alkyl chain of ILs [41].  $[\text{C}_4\text{MIM}][\text{BF}_4]$ ,  $[\text{C}_6\text{MIM}][\text{BF}_4]$  and  $[\text{C}_8\text{MIM}][\text{BF}_4]$  are hydrophilic and  $[\text{C}_4\text{MIM}][\text{PF}_6]$ ,  $[\text{C}_6\text{MIM}][\text{PF}_6]$  and  $[\text{C}_8\text{MIM}][\text{PF}_6]$  are hydrophobic. ILs have suitable surface activity and good extraction ability. The effect of the kinds of ILs on the recoveries of the analytes was investigated. The experimental results indicated that compared with the other ILs when  $[\text{C}_6\text{MIM}][\text{PF}_6]$  was used the recoveries for all analytes were higher. The mean recovery for the analytes obtained with  $[\text{C}_6\text{MIM}][\text{PF}_6]$ ,  $[\text{C}_4\text{MIM}][\text{BF}_4]$ ,  $[\text{C}_4\text{MIM}][\text{PF}_6]$ ,  $[\text{C}_8\text{MIM}][\text{PF}_6]$ ,  $[\text{C}_6\text{MIM}][\text{BF}_4]$  and  $[\text{C}_8\text{MIM}][\text{BF}_4]$  is ranked in descending order (The detailed information can be found in Suppl. Fig. 5.). Therefore  $[\text{C}_6\text{MIM}][\text{PF}_6]$  was used as foaming agent. The foaming ability of ILs increases with the increase of alkyl chain length (n) at the 1-position of the cation. The higher foaming ability is beneficial to the extraction of these analytes. However, excessively high foaming ability can result in high foaming rate that can limit the loading capacity of IL foam. So, compared with  $[\text{C}_4\text{MIM}][\text{PF}_6]$  and  $[\text{C}_8\text{MIM}][\text{PF}_6]$ ,  $[\text{C}_6\text{MIM}][\text{PF}_6]$  should be more suitable. The solubility of ILs in extraction solvent can also affect the recoveries of the analytes. The hydrophobic ILs can easily be extracted into the extraction phase compared with the hydrophilic ones. Considering both foaming ability in aqueous phase and solubility in organic phase  $[\text{C}_6\text{MIM}][\text{PF}_6]$  should be the more suitable than other ILs.

### 3.1.5. Effect of the volume of ILs

The effect of the volume of ILs was investigated. The recoveries of the analytes increase when the volume of ILs increases from 0.1



**Fig. 2.** Chromatograms of yogurt sample spiked with the target analytes and other compounds. (1) Simeton; (2) simazine; (3) chlortoluron; (4) isoproturon; (5) ametryn; (6) propazine; (7) prometryne; (8) prebane; (9) sulfacetamide; (10) sulfadiazine; (11) sulfamerazine; (12) fenarone; (13) simetryn; (14) prometon; (15) linuron; (16) prothiofos; (17) sulprofos; (18) cyhalothrin; (19) deltamethrin; (20) fenvalerate; (21) chlorpyrifos and (22) bifenthrin.

to 1  $\mu\text{L}$ . There is no obvious change in recoveries when the volume is between 1.0 and 10  $\mu\text{L}$  (The detailed information can be found in Suppl. Fig. 6.). There were significant interference peaks in the chromatogram when the volume of  $[\text{C}_6\text{MIM}][\text{PF}_6]$  was larger than 5  $\mu\text{L}$ . The recoveries range from 91.2 to 110.3% and the mean recovery for the analytes is 98.0% when the volume is 1  $\mu\text{L}$ . So we carried out the experiments with 1  $\mu\text{L}$  of IL.

### 3.1.6. Effect of amount of $(\text{NH}_4)_2\text{SO}_4$

The effect of amount of  $(\text{NH}_4)_2\text{SO}_4$  was investigated. The recoveries for most analytes increase at first and then decrease with the increase of the amount of  $(\text{NH}_4)_2\text{SO}_4$  (The detailed information can be found in Suppl. Fig. 7.). The competitive hydration of salt and the floatation solvent is beneficial to the phase separation. Ammonium sulfate is a kind of kosmotropic salt and  $\Delta G_{\text{hyd}}$  value of the salt is low due to the structured water “lattice” around the ion [42]. The increase of amount of the salt results in the decrease of free water in the aqueous phase, which surely brings about the decrease of the analyte solubility in water phase and the transfer of the analyte from water phase to the organic phase. Therefore, the recoveries of these herbicides increase with the increase of salt amount. However, when salt concentration is excessively high, the viscosity of the solution increases, which would weaken the mass transfer of the analyte to air–water interface. The mean recovery for the analytes is the highest when the amount of  $(\text{NH}_4)_2\text{SO}_4$  is 8 g. Therefore, 8 g of  $(\text{NH}_4)_2\text{SO}_4$  is most suitable.

### 3.1.7. Effect of gas flow rate

Gas flow rate is very important operation parameter in ILF-SF which directly affects the area of air–water interface. The recoveries of the analytes increase at first and then decrease or are unchanged with the increase of gas flow rate and when the flow rate is 50 mL/min, the mean recovery for the analytes is the highest (The detailed information can be found in Suppl. Fig. 8.). Mass transfer of the analytes to air–water interface of rising bubble in the aqueous phase is the dominant transport process. The area of air–water interface at high gas flow rate is larger than that at low one. As a result, floatation efficiency increases with the increase of gas flow rate and more analytes can be transferred into organic phase which results in the increase of the recoveries. However, when gas flow rate is excessively high, the water–organic interface is drastically destroyed and the part of organic phase can be returned to the water phase, which results in the decrease of the recoveries. The recoveries ranging from 99.7 to 118.5% are obtained when the gas flow rate is 50 mL/min. Therefore, the gas flow rate of 50 mL/min is suitable.

### 3.1.8. Effect of floatation time

The effect of floatation time was examined. The recoveries of analytes increase sharply with the increase of the floatation time when the time is shorter than 10 min and when the time is longer than 10 min, the recovery of propazine decreases sharply and that of other analytes increase slightly (The detailed information can be found in Suppl. Fig. 9.). So the floatation time of 10 min was selected.

### 3.1.9. Effect of the volume of extraction solvent

The effect of the volume of extraction solvent was studied. The recoveries obviously increase when the volume increases from 2 to 3 mL and change slightly when the volume is larger than 3 mL. The recoveries range from 97.4 to 104.9% and the mean recovery for the analytes is 100.4% when the volume is 3 mL (The detailed information can be found in Suppl. Fig. 10.). Therefore, the optimum volume of extraction solvent is 3 mL.

**Table 2**  
Analytical results for fresh spiked samples.

Sample	Added ( $\mu\text{g L}^{-1}$ )	Simeton		Simazine		Chlortoluron		Isoproturon		Ametryn		Propazine		Prometryne		Prebane	
		Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
1	10	95.6	1.85	95.6	2.60	102.9	0.56	88.9	1.46	94.7	1.71	89.3	0.76	91.1	3.16	89.2	1.77
	70	90.9	4.37	93.8	0.7	95.7	4.45	95.2	4.80	103.6	3.13	95.7	3.30	86.7	6.76	100.9	1.01
2	10	86.9	0.85	89.1	2.83	100.0	1.36	96.0	1.53	90.3	2.30	93.7	0.47	99.6	1.73	96.3	1.87
	70	87.6	3.10	93.9	3.05	88.9	1.70	96.9	2.70	103.8	1.30	93.9	0.75	99.4	4.60	97.8	0.30
3	10	97.3	1.02	98.9	4.66	100.6	1.83	95.2	1.05	91.2	3.60	93.1	0.64	92.1	0.91	98.9	2.75
	70	90.0	2.95	98.0	1.35	102.9	0.45	97.0	1.65	102.3	2.85	100.7	2.90	103.9	3.45	114.3	6.33
4	10	110.0	0.82	110.0	3.37	118.9	1.30	108.0	3.68	91.3	3.31	105.9	1.14	93.8	0.75	102.3	2.92
	70	95.2	6.90	98.1	2.60	99.5	0.30	98.6	3.45	103.8	6.49	98.4	1.43	95.1	2.70	101.2	1.55
5	10	96.0	1.35	99.4	4.20	97.3	0.75	106.6	0.40	95.5	2.40	117.5	1.95	102.3	2.92	108.1	1.56
	70	105.2	4.10	100.4	2.75	100.2	0.5	92.0	5.30	106.0	3.89	108.0	1.25	101.2	1.55	108.2	0.80

**Table 3**  
Analytical results for the aged spiked sample.

Stored time (day)	Added ( $\mu\text{g L}^{-1}$ )	Simeton		Simazine		Chlortoluron		Isoproturon		Ametryn		Propazine		Prometryne		Prebane	
		Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
1	10	103.3	1.83	101.2	0.75	94.80	0.49	87.1	0.25	108.8	1.90	100.5	1.25	95.7	2.93	99.8	3.19
	70	96.0	0.60	100.8	0.70	98.10	4.00	93.3	2.30	100.7	4.90	105.0	1.75	100.7	1.75	107.6	6.85
7	10	104.2	1.30	90.2	1.70	118.2	2.10	97.4	1.70	95.7	2.90	92.9	2.10	96.0	0.75	111.1	1.61
	70	93.1	5.15	97.1	1.30	100.8	2.15	100.9	6.00	105.1	0.75	108.0	1.25	100.2	5.56	109.1	5.17
14	10	110.2	1.10	93.6	2.14	94.7	1.70	87.3	0.49	87.5	3.59	108.9	1.21	91.2	2.14	96.0	1.32
	70	93.2	1.25	100.0	4.84	91.0	2.56	93.0	3.34	107.7	5.37	98.4	3.55	99.4	3.64	111.9	6.38
21	10	100.9	0.45	101.4	3.42	101.0	2.35	91.5	0.95	95.8	2.65	118.7	1.06	108.1	3.30	91.4	1.80
	70	92.1	4.85	100.0	1.71	107.8	2.40	97.7	1.35	109.3	5.85	99.9	4.19	100.1	0.80	112.7	2.50
40	10	86.5	0.39	96.8	3.17	94.3	0.29	102.7	0.17	86.9	5.02	106.2	0.81	112.6	3.41	97.2	1.67
	70	94.6	1.73	99.1	3.83	108.6	6.41	97.5	6.52	104.9	2.85	100.7	2.72	106.2	6.35	109.9	5.89

### 3.1.10. Comparison of IL and conventional surfactants

In this work, IL was used as a kind of surfactant. To examine the property of the IL, other surfactants, including CTAB (cationic), SDBS (anionic), SDS (anionic) and T-114 (neutral) were used. The recoveries obtained with IL are much higher than those obtained with other surfactants in the same floatation time. The mean recovery obtained with IL, T-114, CTAB, SDBS and SDB is ranked in descending order (The detailed information can be found in [Suppl. Fig. 11.](#)). IL should be an effective and green surfactant compared to the conventional surfactants.

### 3.2. Evaluation of the method

#### 3.2.1. The enrichment factor

In order to evaluate the performance of the proposed method, the enrichment factor (EF) for the solvent floatation is obtained based on the following equation:

$$EF = \frac{C_{or}}{C_{aq}}$$

where  $C_{aq}$  is the concentration of the analyte in the aqueous phase and  $C_{or}$  is concentration of the analyte in the organic phase (extraction solvent).

The EF values are 11.6, 12.9, 14.0, 16.5, 16.2, 17.9, 18.6 and 18.5 for simeton, simazine, chlortoluron, isoproturon, ametryn, propazine, prometryne and prebane, respectively.

#### 3.2.2. Limits of detection and quantification

The working curves were constructed by plotting the peak areas measured versus the concentrations of analytes. The linear regression equations and correlation coefficients are listed in [Table 1](#). The limits of detection (LODs) and quantification (LOQs) indicated in [Table 1](#) are determined as the lowest concentrations yielding a signal-to-noise (S/N) ratio of 3 and 10, respectively. The LOQs of all analytes are lower  $0.01 \text{ mg kg}^{-1}$  which is the MRL default value mentioned above. So the LOQs and linear equations are appropriate to the goal of the proposed method.

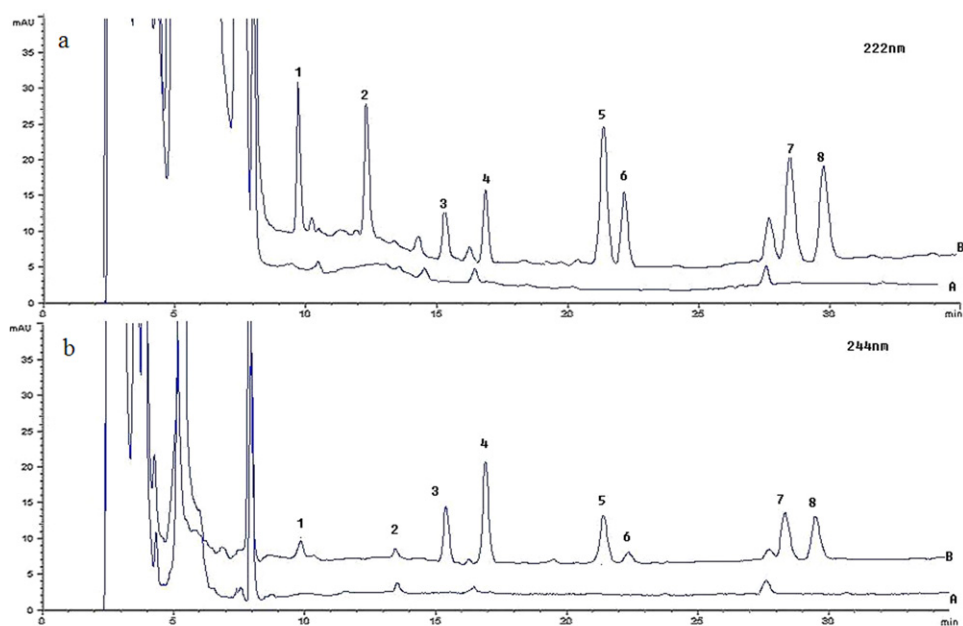
#### 3.2.3. Selectivity

Selectivity was evaluated by analyzing the samples spiked with the target analytes at the concentration of  $50 \mu\text{g L}^{-1}$  and other compounds, including some antibiotics and pesticides, at the concentration of  $500 \mu\text{g L}^{-1}$ . The representative chromatograms of the spiked sample are shown in [Fig. 2](#). The result indicates that these antibiotics and pesticides, including sulfacetamide, sulfadiazine, sulfamerazine, fenarone, simetryn, prometone, linuron, prothiofos, sulprofos, chlorpyrifos, cyhalothrin, deltamethrin, bifenthrin and fenvalerate, do not interfere with the determination of the target analytes. Therefore, the selectivity of the proposed method should be satisfactory.

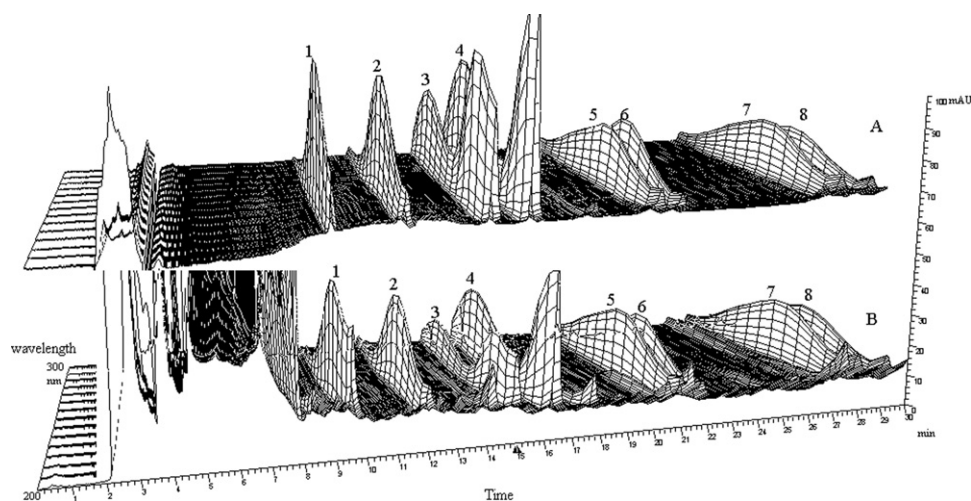
### 3.3. Analysis of samples

The proposed method was applied to the analysis of 15 yogurt samples. The triazine and phenylurea herbicides in the yogurt samples were not detectable. The practical applicability of the proposed method was evaluated by determining eight triazines and phenylureas from five fresh spiked yogurt samples and one aged spiked sample. The recoveries and precision of analytes in the five fresh spiked samples are listed in [Table 2](#). The results indicate that the proposed method provides good recoveries (86.7–117.5%) and acceptable precision ( $\leq 6.90\%$ ) at two concentration levels. The recoveries and precision of the analytes in aged spiked sample are listed in [Table 3](#). The recoveries are in the range of 86.5–118.7% and precision in the range of 0.17–6.85%. The chromatograms of blank yogurt sample and spiked sample are shown in [Fig. 3](#). Because of





**Fig. 3.** Chromatograms of blank yogurt sample (A) and spiked sample (B). (1) Simeton; (2) simazine; (3) chlortoluron; (4) isoproturon; (5) ametryn; (6) propazine; (7) prometryne and (8) prebana.



**Fig. 4.** Absorption spectra of the eluates from the standard solution (A) and spiked yogurt sample (B). (1) Simeton; (2) simazine; (3) chlortoluron; (4) isoproturon; (5) ametryn; (6) propazine; (7) prometryne and (8) prebana.

the lack of selectivity and specificity of the UV detector, the DAD was used to identify the herbicides. The spiked sample and the standard solution of analytes were analyzed and the results are shown in Fig. 4. The target analytes can be identified by comparing their retention times and absorption spectra with those of authentic standard analytes.

#### 4. Conclusion

It is found that the ILs have the foaming property and the foaming ability and extraction ability of ILs are higher than those of conventional surfactants. Because there are many kinds of ILs and the chemical structures of the ILs are adjustable, the IL-based foam floatations can extend the application for floatation separation.

The proposed method has some advantages in the expenditure of organic solvent and extraction time and was successfully applied to the extraction of the triazine and phenylurea herbicides in yogurt samples. The experimental results indicated that ILs have good

foaming property. The proposed method is suitable for the analysis of a large amount of sample because a large amount of sample matrix can be removed by the floatation. So it seems possible to extend this method to the extraction of triazine and phenylurea herbicides in both complex samples and the large volume of aqueous samples by varying the extraction conditions.

#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chroma.2011.12.019.

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