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# Ionic liquid-based foam flotation followed by solid phase extraction to determine triazine herbicides in corn

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## ABSTRACT

Ionic liquid-based foam flotation followed by solid phase extraction was developed for extraction of eight triazine herbicides, including cyanazine, metribuzin, desmetryn, sebumeton, terbumeton, terbuthylazine, dimethametryn and dipropetryn in corn samples. When the extraction was completed, the analytes were separated from the sample matrix by foam flotation and introduced into the solid phase extraction cartridge. The separation and concentration of target analytes were performed simultaneously. The analytes eluted from the solid phase extraction cartridge were determined by high performance liquid chromatography. The effects of experimental parameters of extraction and flotation were examined. Under the optimized experimental conditions, a good linearity was obtained in the range of 2.50–150 µg/kg. The detection limits of the triazine herbicides were in the range of 0.74–1.62 µg/kg. The present method was successfully applied to the analysis of corn samples. The recoveries ranged from 85.9% to 104.0% and the relative standard deviations were lower than 5.6%.

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## 1. Introduction

The triazine herbicides have been used widely throughout the world [1–3]. However, a large number of present researches have proven the toxicity of triazine herbicides [4–6]. On one hand, the triazine herbicides have been suspected to cause endocrine disruption, give rise to cancer and congenital defect and so on [7–10]. On the other hand, triazine herbicides and their metabolic degradation products could contaminate crop themselves and their surroundings environment, such as soil and water [11,12]. Therefore, the harm of triazine herbicides to humans and environment could not be ignored.

Many countries have formulated maximum residue limits (MRLs) of the triazine herbicides [13–15]. In the European Union (EU), MRLs for pesticides in corn, vegetable and other agriculture products are provided in several statutes (EU directive 2002/32/EC, Regulation (EC) No. 396/2005, Commission Directive 2008/149/EC and Commission Regulation (EU) No. 212/2013) and the MRLs of eight triazine herbicides were ranged from 0.05 to 0.1 mg/kg. The Environmental Protection Agency (EPA) requires that MRLs of triazine herbicides are 0.25 mg/kg for most agriculture products. The MRLs were used as an important technical barrier in import

and export of agricultural products. Therefore, effective control and detection of triazine herbicide residues are very important.

The extraction of triazine herbicides from a variety of matrices can be carried out by solid phase extraction (water, rice and corn, honey) [16–18], solid phase micro-extraction (water, soil) [19,20], magnetic solid phase extraction (water) [21], molecularly imprinted solid phase extraction (water, rice and onion) [12], liquid–liquid extraction (food) [22], microwave-assisted extraction (infant nutrient cereal-based foods) [23], matrix solid phase dispersion (milk) [24] and pressurized liquid extraction (potato, carrot, lettuce, zucchini, runner beans, oranges and wheat) [25]. Generally, high performance liquid chromatography (HPLC) [26] was applied to the determination of these polar and thermally stable herbicides. To our knowledge, the HPLC using reversed phase columns was widely used. In addition, gas chromatography [27], liquid chromatography–mass spectrometry [28], gas chromatography–mass spectrometry [29] and micellar electrokinetic capillary chromatography [30] were used to determine herbicide residues.

Ionic liquids (ILs) are semi-organic molten salts, which consist of organic cations and various anions. Because of their low vapor pressure, non-flammability, low melting point, good thermal stability and ability to dissolve various organic and inorganic substances, ILs have been widely used as extraction solvents in the recent years [31–33]. The IL-based aqueous two-phase system was widely applied for purification, extraction and biocatalysis [34]. The foam flotation (FF) based on IL was recently reported [35–37]. The FF coupled with solid phase extraction (SPE) was

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successful applied to the extraction, separation and enrichment of steroid hormones in water samples [35] and ginsenosides in extract of *Panax quinquefolius* L. [36]. The ionic liquid foaming-based solvent flotation was applied to the extraction of herbicides in yogurt [37]. In these researches, the foaming property of ILs was found and the factors that can influence foaming property of the ILs were investigated. The FF based on ILs can be applied to the extraction, separation and concentration of analytes.

In this paper, IL-based FFSPE was applied for extraction of eight triazine herbicides, including cyanazine, metribuzin, desmetryn, secbumeton, terbumeton, terbuthylazine, dimethametryn and dipropetryn from corn samples. As far as we know, studies on extraction and detection of triazine herbicides mainly focused on the environmental samples and studies on the corn samples were rare. HPLC was applied to the determination eight triazine herbicides. ILs were used as the extraction solvents and foaming agents. The effect of experimental parameters were investigated and optimized.

## 2. Experimental

### 2.1. Chemicals and reagents

Cyanazine, metribuzin, desmetryn, secbumeton, terbumeton, terbuthylazine, dimethametryn and dipropetryn were obtained from National Institute for the Control of Pharmaceutical and Biological Products (Beijing, China). 1-Ethyl-3-methylimidazolium tetrafluoroborate ( $[\text{C}_2\text{MIM}][\text{BF}_4]$ , >98.0% purity), 1-butyl-3-methylimidazolium tetrafluoroborate ( $[\text{C}_4\text{MIM}][\text{BF}_4]$ , >99.0% purity), 1-hexyl-3-methylimidazolium tetrafluoroborate ( $[\text{C}_6\text{MIM}][\text{BF}_4]$ , >98.0% purity), 1-octyl-3-methylimidazolium tetrafluoroborate ( $[\text{C}_8\text{MIM}][\text{BF}_4]$ , >99.0% purity), 1-ethyl-3-methylimidazolium hexafluorophosphate ( $[\text{C}_2\text{MIM}][\text{PF}_6]$ , >98.0% purity), 1-butyl-3-methylimidazolium hexafluorophosphate ( $[\text{C}_4\text{MIM}][\text{PF}_6]$ , >98.0% purity), 1-hexyl-3-methylimidazolium hexafluorophosphate ( $[\text{C}_6\text{MIM}][\text{PF}_6]$ , >98.0% purity), 1-octyl-3-methylimidazolium hexafluorophosphate ( $[\text{C}_8\text{MIM}][\text{PF}_6]$ , >97.0% purity) and 1-hexyl-3-methylimidazolium chloride ( $[\text{C}_6\text{MIM}]\text{Cl}$ , 98.0%) were obtained from Chengjie Chemical Co. Ltd. (Shanghai, China). Methanol and acetonitrile of chromatographic grade were purchased from Dikma Technologies Inc. (USA). All other reagents of analytical grade were purchased from Beijing Chemical Factory (Beijing, China). Pure water was obtained with a Milli-Q water purification system (Millipore Co., USA).

Standard stock solutions for the triazine herbicides at the concentration level of 500  $\mu\text{g}/\text{mL}$  were prepared in methanol and standard working solutions were prepared every week by diluting the standard stock solutions with methanol. Mixed standard working solutions at different concentrations were prepared by the same method as the standard working solutions. All the standard and working solutions were stored at 4 °C and protected from light.

### 2.2. Material and instrumentation

The 1200 series liquid chromatograph (Agilent Technologies Inc., USA) equipped with multi-wavelength detector was used. Chromatographic separation of target analytes was performed on Agilent Eclipse XDB-C18 column (150 mm  $\times$  4.6 mm i.d., 3.5  $\mu\text{m}$ , Agilent, USA). The column temperature was kept at 30 °C and sample injection volume was 20  $\mu\text{L}$ . The mobile phases A and B were water and acetonitrile, respectively. The gradient conditions are as follows: 0–5 min, 40–60% B; 5–10 min, 60–80% B; 10–15 min, 80–80% B; 15–25 min, 80–40% B. The flow rate of the mobile phase was 0.50 mL/min. The detection of the analytes was carried out at the

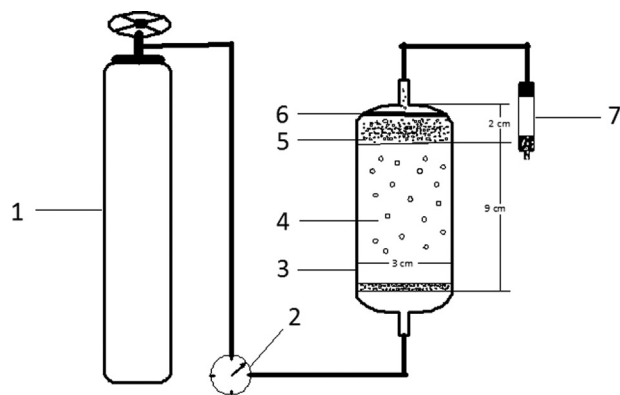


Fig. 1. The IL-based FFSPE system. (1) Nitrogen cylinder; (2) flowmeter, (3) flotation vessel; (4) sample solution; (5) foam; (6) glass cotton; (7) SPE cartridge.

wavelength of 228 nm. The reference wavelength and bandwidth were 360 nm and 4 nm, respectively.

The IL-based FFSPE system was assembled in our laboratory. A schematic diagram of the system is shown in Fig. 1. The glass flotation vessel is cylindrical in shape. The diameter and height are 3 cm and 11 cm, respectively. A 40 kHz, 100 W ultrasonic cleaner (KQ2200E Kunshan Ultrasonic Instrument Co. Ltd., Kunshan, China) was used in an extraction procedure. HR-2870 Philips mill (Philips, Zhuhai, China), CL-2 magnetic stirrer (Great wall, Zhengzhou, China) and RE-52AA vacuum rotatory evaporator (Yarong, Shanghai, China) were used.

Oasis HLB (3 mL, 100 mg) and MCX (3 mL, 100 mg) extraction cartridges were purchased from Waters (Milford, MA, USA). SPE cartridges, including SuperClean  $\text{Al}_2\text{O}_3$  (3 mL, 100 mg), SuperClean C18 (3 mL, 100 mg), and SuperClean Si (3 mL, 100 mg), were purchased from Supelco (Bellefonte, PA, USA).

### 2.3. Sample preparation

Corn samples, including white waxy corn (Sample 1), yellow waxy corn (Sample 2), purple waxy corn (Sample 3) and color waxy corn (Sample 4) were purchased from local supermarkets in Daqing, Heilongjiang Province, in November 2012. All corn samples were pulverized using a HR-2870 Philips mill and passed through a 80-mesh sieve to obtain the powered samples. Except for the experiments mentioned in Section 3.2.3, which were performed with all four samples, all other experiments were performed with Sample 1. The fresh spiked samples containing triazine herbicides were prepared by spiking the stock standard solutions into milled corn mentioned and shaking for 3 min. To ensure the herbicides to be well distributed, a reasonable amount of acetone was added to moisten the milled corn and careful agitation was performed followed by an air-drying for 24 h at room temperature before extraction.

The aged spiked sample was prepared by the same method as mentioned above. Then the samples were kept in sealed bottle and stored for 1, 7, 14, 28, 56 and 70 days at 4 °C. All samples were refrigerated at 4 °C and stored at room temperature before use.

### 2.4. IL-based FFSPE

The IL-based FFSPE system is shown in Fig. 1. 10.0 g of corn sample, 30.0  $\mu\text{L}$  of IL and 50.0 mL of water were placed into the polytetrafluoroethylene (PTFE) tube and blended with the CL-2 magnetic stirrer at 2400 rpm for 3.0 min to obtain a homogeneous mixture. The tube was immersed into the ultrasonic bath for 10.0 min at room temperature. After the extraction was completed, the mixture in the PTFE tube was transferred to a flotation vessel.

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