



## Determination triazine pesticides in cereal samples based on single-hole hollow molecularly imprinted microspheres



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### ABSTRACT

Single-hole hollow molecularly imprinted microspheres (h-MIMs) were prepared by hard template method and applied to extract six triazine pesticides in cereal samples, followed by HPLC-MS/MS detection. The synthesis mechanism of the h-MIMs has been studied. The h-MIMs exhibited bigger specific surface area and much higher binding capacity than the molecularly imprinted polymers prepared by precipitation polymerization (p-MIPs) and surface polymerization (s-MIPs). Besides, the adsorption rate of h-MIMs to prometryn was significantly higher than that of p-MIPs and s-MIPs. Owing to the hollow structure of the h-MIMs, more binding cavities were located on the inner and outer surfaces of the h-MIMs, which could facilitate the removal of template molecules from the polymers and the rebinding of the target molecules to the polymers. Under the optimal conditions, the detection limits of triazines are in the range of 0.08–0.16 ng g<sup>-1</sup>. At the spiked level (5 ng g<sup>-1</sup>), the recoveries of triazines are in the range of 81 ± 4% to 96 ± 4%. The proposed method was successfully applied to determine six triazines in five cereal samples. Atrazine was found in two rice samples and a wheat sample with the contents of 5.1, 6.7 and 5.6 ng g<sup>-1</sup>, respectively. Ametryn and prometryn were found in a maize sample with the contents of 7.6 and 7.3 ng g<sup>-1</sup>, respectively.

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### 1. Introduction

Triazine herbicides have been widely applied in agriculture to protect crops from undesirable broadleaf weeds by inhibiting photosynthesis [1]. However, such triazine herbicides residues in plant-derived foodstuffs are suspected of resulting in cancers, birth defects and interruption of hormone functions [2,3]. Therefore, the monitoring of pesticide residues in agriculture products is essential to ensure food safety and international trade. For most agriculture products, the Environmental Protection Agency requires that the tolerance of triazine herbicides is 250 ng g<sup>-1</sup>, while the European Union dictates that the maximum residue limits for atrazine and simazine in cereals were 10 and 100 ng g<sup>-1</sup>, respectively.

A variety of analytical techniques have been reported for the analysis of triazines in different complex food matrices, such as high performance liquid chromatography (HPLC) [4,5], gas chromatography [6], capillary electrophoresis [7], gas chromatography tandem mass spectrometry [6,8] and liquid chromatography

tandem mass spectrometry (LC-MS/MS) [3,9,10]. Among these approaches mentioned above, LC-MS/MS is the most selective and sensitive technique for identification and quantification of triazines.

Because of the relatively low concentrations of triazines and the inherent complexity of the food samples, the preconcentration and clean-up steps are necessary for the reliable determination of these compounds, prior to their analysis. Common extraction procedures, such as ultrasound-assisted extraction [10], agitated extraction [3], microwave-assisted extraction [11] and pressurized liquid extraction [12] have been employed for extracting triazines from different food samples. Although these pretreatment methods were simple and widely used, a clean-up step was needed after an extraction procedure to remove some of the co-extracted compounds. Solid phase extraction (SPE) is the most commonly used technique. In SPE procedure, a desired adsorbent is important to obtain good recovery, high enrichment factor and to reduce the interfering substances in samples. Consequently, excellent adsorbents with good adsorption efficiency and high stability, such as carbon nanotubes [13], graphene [14], metallic nanoparticles (TiO<sub>2</sub>, ZrO<sub>2</sub>) [15,16], metal-organic frameworks [17], and molecularly imprinted polymers (MIPs) [18,19] have been developed. Among these adsorbents,

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MIPs are of particular interest because of the high selectivity and universality they exhibit towards target molecules [18].

Although the prepared MIPs have exhibited high selectivity, high stability under extreme conditions of pH and temperature and excellent reusability, some problems of MIPs such as incomplete template removal, low binding capacity, and slow mass transfer were presented and their applications are limited to some extent [20]. To solve these problems and to broaden the scope of the application of MIPs, new preparation methods have been proposed constantly. Although the leakage of the templates has been solved by using the structurally related analog as alternative template molecule [21], the mass transfer rate was still very low. In addition, the leakage of templates has been solved to some extent and the mass transfer rate of templates has been enhanced greatly through the application of surface MIPs [22], but the adsorption capacity of the surface MIPs is relatively low.

Then, the concept of the hollow MIPs was put forward. Zhang et al. first synthesized single hole hollow capsules, which could recognize specific 2, 4, 6-trinitrotoluene molecules through precipitation polymerization in 2007 [23]. The research proved that the rebinding capacity of the hollow capsules could be improved, attribute to their special structures. In 2012, single hole hollow MIPs which could provide specific recognition of sudan I molecules were prepared by Xiong et al. and used as adsorbents [24]. However, the studies are mainly focused on the synthesis mechanism, few attempts have been made for their SPE application.

In this study, single-hole hollow molecularly imprinted microspheres (h-MIMs) were prepared by hard template synthesis method based on polystyrene (PS) particles, and then the PS particles were removed by methylene chloride. The microspheres were subsequently synthesized based on multistep seed swelling polymerization, using prometryn as template molecule, methacrylate (MAA) as functional monomer, divinyl benzene (DVB) as cross linker, and toluene as porogen. Both the adsorbing capacity and the adsorption rate of the h-MIMs were compared with the MIPs prepared by precipitation polymerization (p-MIPs) and surface polymerization (s-MIPs). And the performances of the h-MIMs used as SPE sorbents for specific recognition of triazines in cereal samples were also investigated.

## 2. Experiment

### 2.1. Chemicals and materials

The standards (purity >98%) of ametryn, atrazine, desmetryn, prometryn, propazine, simazine and pirimicarb were obtained from the Dr. Ehrenstorfer (Augsburg, Germany). The standard of melamine was purchased from National Institute for the Control of Pharmaceutical and Biological Products (Beijing, China). Aniline and p-aminothiophenol of analytical grade were purchased from Beijing Chemical (Beijing, China). Their chemical structures are shown in Fig. 1. Chromatographic grade acetonitrile (ACN) was obtained from Fisher (Pittsburgh, PA, USA). Ethylene glycol dimethacrylate (EGDMA), MAA, polyvinylpyrrolidone (PVP), azobisisobutyronitrile (AIBN), styrene, acrylic acid (AA), sodium bicarbonate ( $\text{NaHCO}_3$ ), styrene, ammonium persulfate (APS), sodium dodecyl sulfate (SDS), dibutyl phthalate (DBP) and DVB were obtained from Guangfu (Tianjin, China). Methanol, ethanol, acetic acid and ACN of analytical grade were purchased from Beijing Chemical Reagents Co. (Beijing, China). The Milli-Q water was obtained from a Millipore purification system (Billerica, MA, USA) operating at a resistivity of  $18.2 \text{ M}\Omega \text{ cm}^{-1}$ .

Individual triazine stock standard solutions ( $500 \mu\text{g mL}^{-1}$ ) were prepared in methanol and stored at  $-18^\circ\text{C}$ . A mixed stock solution ( $20 \mu\text{g mL}^{-1}$ ) of six triazines was prepared by diluting individual

stock solutions with methanol and stored at  $4^\circ\text{C}$  in a dark glass bottle. The mixed solution should be replaced every two weeks. The working standard solutions were daily prepared by diluting mixed solution using deionized water.

The cereal samples including rice, millet, wheat and maize were purchased from local supermarket (Changchun, China). All the samples were powdered using a cyclone mill and passed through a sieve (40 mesh). The spiked cereal samples were made by adding certain amounts of triazine standard solution to blank cereal samples and stored at  $4^\circ\text{C}$ .

### 2.2. The preparation of h-MIP microspheres

#### 2.2.1. Preparation of carboxylated PS particles

Monodisperse carboxylated PS particles were prepared using emulsion polymerization, which was similar to the reported method [23] with minor modification. First, 0.15 g  $\text{NaHCO}_3$  was dissolved in 100 mL distilled water and the aqueous solution was stirred at  $60^\circ\text{C}$  under a nitrogen atmosphere. Then, AA (1 mL), styrene (5 mL) and APS (0.08 g) were stepwise added into it and the polymerization reaction was carried out at  $70^\circ\text{C}$  for 20 h under nitrogen atmosphere. Subsequently, the obtained PS particles were separated through centrifugation and washed with ethanol for several times. Finally, the PS particles were dried at  $60^\circ\text{C}$  and stored in a sealed brown flask for further use.

#### 2.2.2. Synthesis of prometryn imprinted h-MIMs

The PS particles (0.4 g) were uniformly dispersed in 100 mL 0.25% SDS aqueous solution by ultrasonic treatment and the mixture was added into a 250 mL three-necked flask. Then 0.7 mL DBP was added into the emulsion, the swelling step was carried out for 24 h. Subsequently, a second-step swelling was carried out for another 24 h by adding 8.0 mL toluene, 450  $\mu\text{L}$  MAA and 360 mg prometryn. After adding 6.0 mL DVB and 0.08 g AIBN into the mixture solution, the polymerization reaction was first initiated at  $43^\circ\text{C}$  for 8 h under nitrogen atmosphere. Then the reaction system was heated up to  $60^\circ\text{C}$  for polymerization/cross-linking reaction. After reacting for 20 h, the product was further aged at  $80^\circ\text{C}$  for 2 h. The polymers obtained were centrifuged and washed with ethanol. Finally, the h-MIMs were fabricated through the removal of the PS particles using methylene chloride and the removal of prometryn templates with a mixture of methanol/acetic acid (8:2, v/v).

Hollow non-imprinted microspheres (h-NIMs) were prepared and processed in the same way as h-MIMs, except not adding the template molecule prometryn. And the s-MIPs were prepared in the same way as the h-MIMs, except that the PS core particles were not removed from the polymers. The surface NIPs (s-NIP) were prepared in the same way as the s-MIPs, except that the template molecule prometryn was not added.

### 2.3. Preparation of the MIPs by precipitation polymerization (p-MIPs)

The p-MIPs were prepared as follows: the prometryn (1.0 mmol) was dissolved in 20 mL ACN, then MAA (4.0 mmol) was added into it. In order to prepare pre-assembly solution, the mixture was sonicated for 10 min. After adding the EGDMA (20.0 mmol), the mixture was stirred for 30 min for preparation of the prepolymerization solution. Then PVP (0.4 g) used as dispersant was dissolved into 80 mL of ACN in a three-necked flask. Finally, the prepolymerization solution and 0.1 g of AIBN were added into the flask, respectively. The mixture was stirred at 300 rpm and purged with nitrogen gas for 24 h, while the temperature was kept at  $60^\circ\text{C}$ . When the polymerization process was completed, the polymers were separated and washed with methanol: acetic acid (8:2, v/v) solution by soxhlet extraction until the template molecule could not be detected

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