



# Sensitive monitoring of benzoylurea insecticides in water and juice samples treated with multiple monolithic fiber solid-phase microextraction and liquid chromatographic analysis



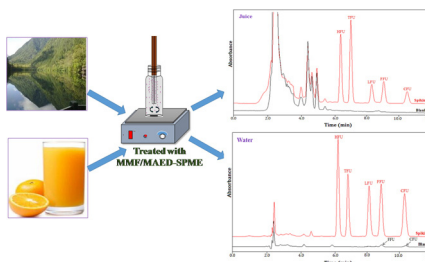
Meng Mei, Xiaojia Huang\*, Keren Liao, Dongxing Yuan

State Key Laboratory of Marine Environmental Science, Key Laboratory of the Ministry of Education for Coastal and Wetland Ecosystem, College of the Environment and Ecology, Xiamen University, Xiamen 361005, China

## HIGHLIGHTS

- A new MMF/MAED-SPME was designed and prepared.
- Preparation and extraction conditions were studied thoroughly.
- MMF/MAED-SPME can extract benzoylurea insecticides (BUs) effectively.
- Sensitive determination method for BUs in water and juice samples was developed.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 16 November 2014  
 Received in revised form 22 December 2014  
 Accepted 26 December 2014  
 Available online 30 December 2014

### Keywords:

Multiple monolithic fiber solid-phase microextraction (MMF-SPME)  
 Monolith  
 Sorbent  
 Benzoylurea insecticide  
 High performance liquid chromatography

## ABSTRACT

In present study, a convenient, sensitive and environmentally friendly method for the determination of five benzoylurea insecticides (BUs) in water and juice samples was developed. To extract trace benzoylurea insecticides effectively, poly(methacrylic acid-co-ethylene dimethacrylate) monolith was prepared and used as the sorbent of multiple monolithic fiber solid-phase microextraction (MMF-SPME). The influences of preparation conditions of monolith and extraction parameters of MMF-SPME on BUs were studied thoroughly. Under the optimized conditions, the combination of MMF-SPME with high performance liquid chromatography-diode array detection (MMF-SPME-HPLC-DAD) showed expected analytical performance for target analytes. The limits of detection ( $S/N = 3$ ) of the developed method were  $0.026\text{--}0.075\ \mu\text{g L}^{-1}$  in water and  $0.053\text{--}0.29\ \mu\text{g L}^{-1}$  in juice samples. Good linearity was obtained for analytes with the correlation coefficients ( $R^2$ ) above 0.99. Satisfactory repeatability and reproducibility was achieved, with relative standard deviations (RSD) of both less than 10%. Finally, the established MMF-SPME-HPLC-DAD method was successfully applied for the determination of BUs residues in juice and environmental water samples. Recoveries obtained for the determination of BUs in spiking samples ranged from 65.1% to 118%, with RSD below 10% in all cases.

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## 1. Introduction

Benzoylurea insecticides (BUs) have been widely used for the control of insects and act as powerful insect growth regulators because of their attractive properties, which include their insecticidal activities, tremendous selectivity and rapid degradation [1–3]. However, the presence of residues in foods and the

\* Corresponding author at: Xiamen University, P.O. Box 1009, Xiamen 361005, China. Tel.: +86 592 2189278.

E-mail address: [hxj@xmu.edu.cn](mailto:hxj@xmu.edu.cn) (X. Huang).

environment due to their great consumption on agrochemical could lead to chronic exposure and long-term toxicity effects [4]. Therefore, developing sensitive, simple and environmentally friendly analytical techniques for the monitoring of BUs are necessary.

Among the analytical methods developed for the determination of BUs, high-performance liquid chromatography (HPLC) is the most commonly used technique for the analysis of BUs in different samples because of its simplicity, high sensitivity and broad linear range [5,6]. However, sample pretreatment steps are required before the analysis because of the complexity of the matrices in real samples and the trace level of BUs. So far, liquid–liquid extraction (LLE) [7], liquid-phase microextraction (LLME) [8,9], solid-phase extraction (SPE) [6,10] and solid-phase microextraction (SPME) [11] have been applied for the analysis of BUs in all kinds of samples. However, LLE and SPE are slow, labor-intensive and environmentally unfriendly. The extraction capacity of LLME is limited because of the low extractant is used. Compared with other extraction methods, SPME is simple, convenient, flexible and environmentally friendly. Vázquez et al. used commercial polydimethylsiloxane/divinylbenzene (PDMS/DVB, 60  $\mu\text{m}$ ) coated fiber to extract six BUs from orange juice [11]. However, the extraction capacity was limited because the coatings were thin and low extraction media were employed. Furthermore, in their study, non-equilibrium extraction was utilized because some BUs did not reach extraction equilibrium even if the extraction time was prolonged to 60 min. There are some disadvantages of non-equilibrium extraction. For example, to obtain satisfactory precision, the extraction time should be controlled strictly. However, it is inconvenient in experimental operation. Therefore, to utilize the SPME to extract BUs from complicated samples matrices, developing new extraction fibers with high extraction performance is highly desired.

Multiple monolithic fiber SPME (MMF-SPME) with porous monolith as extractive medium is a new extraction format which developed in our group [12,13]. Compared with coating-based SPME fiber, there are several distinct advantages of MMF-SPME. Firstly, the MMF-SPME is consisted of four independent thin monolithic fibers. The total amount of sorbent in MMF-SPME is larger than that of coating-based fiber. Hereby, the MMF-SPME possesses high extraction capacity. Secondly, the porous monolith material possesses expected mass-transfer speed. At the same time, the aqueous samples can form convection during extraction because there are gaps between fibers in MMF-SPME. The formation of convection accelerates the extraction procedure.

Therefore, the extraction speed of MMF-SPME is faster than that of coating-based fiber. Thirdly, the MMF-SPME is very flexible. According to the character of target analytes, the extraction medium-monolithic fiber can be easily designed and prepared to realize effective extraction of analytes. At present work, five BUs were selected as target analytes. It can be seen from their molecular structure (Table S1), there are hydrophobic groups–phenyl groups and strongly polar amide groups, amino groups and halogen atoms. According to the structural characters of these BUs, a porous poly(methacrylic acid-co-ethylene dimethacrylate) (MAED) monolith was prepared and used as the sorbent of MMF-SPME. In the monolith, the alkyl groups can interact with the analytes through hydrophobic interactions. The carboxyl groups in the sorbent can produce ion-exchange interactions with amide and amino groups in BUs. Therefore, the MMF/MAED-SPME is expected to extract BUs effectively through multi-interactions. After the optimization of extraction conditions, a simple and sensitive methodology combining the MMF/MAED-SPME and liquid desorption (LD), followed by high performance liquid chromatography with diode array detection (MMF/MAED-SPME-LD-HPLC/DAD) for the direct analysis of trace BUs in water and juice samples was developed.

## 2. Experimental

### 2.1. Chemicals

Methacrylic acid (98%) (MA) and ethylene dimethacrylate (EDMA) (97%) were purchased from Alfa Aesar (Tianjin, China). Azobisisobutyronitrile (AIBN) (97%, recrystallized before use), 1-propanol (97%), 1,4-butanediol (98%) and acetic acid (96%) were purchased from Shanghai Chemical Co. (China); HPLC-grade acetonitrile (ACN) and methanol were purchased from Tedia Company (Fairfield, USA); Water used throughout the study was purified using a Milli-Q water purification system (Millipore, USA). The MMF/VI-SPME based on poly(vinyl imidazole-co-ethylene dimethacrylate) monoliths and MMF/AMIED-SPME based on poly(1-allyl-3-methylimidazolium bis [(trifluoro methyl) sulfonyl] imide-co-ethylene dimethacrylate) monoliths were prepared according to our previous studies [12,13].

Hexaflumuron (HFU), teflubenzuron (TFU), lufenuron (LFU), flufenoxuron (FFU) and chlorfluazuron (CFU) were supplied by national institute for the control of pharmaceutical and biological products. The chemical properties of the above analytes are shown in Table S1. River water and farmland water samples were collected from Xiamen city and filtrated through 0.45  $\mu\text{m}$  membranes, and their resistivity were 6250  $\Omega\text{ cm}$  and 1320  $\Omega\text{ cm}$ , respectively. Juice

**Table 1**  
Extraction efficiency of different MMF/MAED-SPMEs for BUs.

No	Monomer mixture		Polymerization mixture		Peak area ( $\times 10^4$ )				
	MA (% w/w)	EDMA (% w/w)	Monomer mixture (% w/w)	Porogen solvent (% w/w)	HFU	TFU	LFU	FFU	CFU
1	10	90	45	55	2.69	3.18	1.24	1.36	0.92
2	15	85	45	55	1.53	1.78	0.73	0.80	0.62
3	20	80	45	55	1.54	1.81	0.69	0.77	0.53
4	25	75	45	55	1.98	2.00	1.06	1.20	0.97
5	30	70	45	55	3.33	3.38	1.55	1.75	1.14
6	35	65	45	55	1.60	1.56	0.81	0.95	0.76
7	40	60	45	55	1.76	1.55	1.01	1.16	1.02
8	45	55	45	55	1.65	1.36	0.86	0.99	0.80
9	30	70	40	60	2.31	2.35	1.21	1.34	0.99
10	30	70	50	50	2.52	2.42	1.24	1.42	1.05
11	30	70	55	45	2.82	3.07	1.30	1.44	1.06
12	30	70	60	40	2.49	2.23	1.33	1.50	1.23

Note: the sample matrix was ultrapure water and the spiked concentration for each compound was 100  $\mu\text{g L}^{-1}$ .

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