Optimization of derivatization procedure and gas chromatography–mass spectrometry method for determination of bensulfuron-methyl herbicide residues in water

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ABSTRACT

A simple and efficient technique based on liquid phase extraction with CH_2Cl_2 solvent followed by derivatization with $(C_2H_5)_2O \cdot BF_3$ solution and confirmation analysis with GC–MS analytical method was developed for detecting the bensulfuron-methyl (BSM) residues in water. Box-Behnken response surface methodology was employed for optimization of the derivatization efficiency. According to the optimization model, the derivatization time of 45 min, derivatization temperature at 55 °C and 0.2 mL $(C_2H_5)_2O \cdot BF_3$ solvent were selected as the optimal derivatization condition for obtaining the maximum desirability of response. Method validation was performed at 6 working standard levels (0.05, 0.1, 0.2, 0.5, 1.0, 5.0 μg/mL) and the linearity of the calibration curve was linear well over the 6 fortification levels with the squared correlation coefficient of determination $r^2 = 0.998$ and the LOD was found to be 0.1 μg/L for BSM herbicide. The mean value of BSM was detected from 0.0414 to 4.7542 μg/mL at levels from 0.05 to 5 μg/mL with the recoveries remained at the acceptable level (42.8–95.0%) with the RSD values from 3.5% to 6.2%, which is more accptable and desirable than the results obtained by LC methods. Moreover, the method allowed the determination of BSM residue in real paddy field water samples at concentrations between 0.0902 and 3.4605 μg/L. Average recovery rates of the BSM spiked at levels 0.1, 0.2, 0.5, 1.0 μg/mL into thirty water samples ranged from 74.1% and 94.1% with the relative standard derivation (RSD) values from 1.9% to 6.7%.

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1. Introduction

With the modernization of agriculture, a number of low dose and high potency pesticides were introduced to enhance the yields of crop. Although herbicides have played a significant part in boosting agricultural production, more and more attention have been drawn for the hazards they have brought to water, soil, argricultural products and human health. Bensulfuron-methyl (BSM), a low-application-rate sulfonylurea herbicide, is widely used to control broad-leaved weeds in cereals and plantation crops [1–5], especially in paddy fields. However, due to its selective and persistent characteristic, the residues at phytotoxic level in soil or water could pose phytotoxicity for the next crop in rotation [6–8]. Therefore, it has stimulated the pursuit of more effective and sensitive methods

to determine the low level herbicide residues in the environment medium [5,9].

Recently, the determination of sulfonylurea herbicide residues has been focused on the methods of high performation liquid chromatography (HPLC) [1–5,10], biossay [1], capillary electrophoresis [11] and liquid chromatography/mass spectroscopy (LC/MS) [12–14]. HPLC method as the most common analytical approach for the detection of sulfonylurea herbicide residues in different matrices [2,15,16], however, is not sensitive enough to detect sulfonylurea residues at lower levels owing to their low application rate, complexity and instability in samples, and a series of crucial pretreatment procedure must be performed for samples before HPLC analysis [5,17]. Therefore, it is desirable that simpler and more sensitive analytical method to be employed to complement the shortcomings of previous methods. Gas chromatographic (GC) is a classic method to analyze the pesticide residues, however, direct detection of sulfonylurea herbicides is restrained by GC because of its low volatility and thermal unstability. Only after derivatization

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could sulfonylurea herbicides be detected by GC method suggested by Singh [18], who has investigated metsulfuron methyl residues by GC after derivatization by diazomethane solvent.

BSM herbicide could be accessible to gas chromatography–mass spectrometry (GC–MS) analysis after derivatization to a methyl compound using boron trifluoride diethyl ether ($(C_2H_5)_2O·BF_3$) solvent that is an esterification catalyst with the advantages of stability, better catalytic effect and lower price. The main objective of present work was to evaluate and optimize the efficiency of the derivatization process of BSM herbicide for determination by GC–MS method. Box-Behnken response surface methodology was employed to investigate the optimum level of the impact factors of the derivatization procedure, including derivatization time, derivatization temperature and volume of $(C_2H_5)_2O·BF_3$ solvent, which resulted in the maximum response. The method evaluation and a comparison with LC methods were carried out to judge the reliability and accuracy of the method for detecting sulfonylurea residues by spiked water samples. Moreover, the analysis of real water samples performed under the selected derivatization conditions also shows satisfying analytical performance by GC–MS.

2. Materials and methods

2.1. Chemicals and reagents

Analytical grade BSM (99.3%) was supplied by Shenyang Research Institute of Chemical Industry (Shenyang, China), and standard solution of 100 μg/mL was prepared in acetonitrile and serially diluted to working standards of 0.05, 0.1, 0.2, 0.5, 1.0, 5.0 μg/mL for linearity analysis and method validation. Sodium sulfate (Na_2SO_4) chemical, acetonitrile, $(C_2H_5)_2O·BF_3$, dichlorometane (CH_2Cl_2), methyl alcohol (MeOH) solventsand acetic acid, all of analytical grade, were purchased from Beijing Chemical Reagent Co. Ltd (Beijing, China). All of the solvents were distilled before use and the Na_2SO_4 chemical was dried in muffle furnace for 24 h at 400 °C and kept in desiccators for storage.

2.2. GC–MS method

2.2.1. Sample preparation and extraction procedure

To prepare the spiked water samples, 1.0 mL working standard solution of BSM at levels of 0.05, 0.1, 0.2, 0.5, 1.0, 5.0 μg/mL was added to 1 L of blank water samples, respectively. Each spiked sample was prepared three times. Real water samples for evaluating the methodology were collected from an irrigation farmland sprayed with BSM herbicide. All water samples were stored in refrigerator at 4 °C. The prepared samples (1 L) were extracted three times with 20 mL CH_2Cl_2 solvent, respectively. The extracts were combined after filtration with anhydrous Na_2SO_4 and concentrated to dry residue using N_2 stream.

2.2.2. Design of optimal derivatization experiments

Derivatization time (A), derivatization temperature (B), volume of $(C_2H_5)_2O·BF_3$ solvent (C) as the main influence factors on derivatization process were investigated. In order to select the appropriate derivatization conditions, derivatization time of 20, 40 and 60 min, derivatization temperature of 25, 45 and 60 °C and volume of $(C_2H_5)_2O·BF_3$ solvent (C) at 0.1, 0.2 and 0.3 mL were selected for design of optimal derivatization experiments (Table 1). The standard and randomized run order of the experiment as well as coded and real levels of the studied facors were designed by Design Expert software, version 8.0.5 from Stat-Ease (USA) (Table 1). Box-Behnken response surface methodology was employed to analyze the experimental data and thereby carry out the optimisation of the derivatization conditions.

Table 1
Box-Behnken Design matrix.

Run order		Factors coded level			Response
Standard	Random	A	B	C	Sum of peak area (Y)
1	2	1	1	0	662.2
2	3	−1	1	0	324
3	4	1	0	1	555.8
4	16	0	0	0	658.2
5	5	−1	0	−1	302
6	14	0	0	0	673.6
7	15	0	0	0	656.2
8	11	0	−1	1	478.8
9	17	0	0	0	640.6
10	7	−1	0	1	322.5
11	1	−1	−1	0	295.5
12	6	1	0	−1	468
13	13	0	0	0	695.5
14	10	0	1	−1	492.9
15	8	1	−1	0	430.4
16	9	0	−1	−1	408
17	12	0	1	1	627.9
Factor code levels:				−1	0	1
Derivative time (A; min)				20	40	60
Derivative temperature (B; °C)				25	45	60
Volum of $(C_2H_5)_2O·BF_3$ solvent (C; mL)				0.1	0.2	0.3

2.2.3. Derivatization procedure

The dry recidue obtained above was reconstructed in 1.0 mL MeOH, and optimal volume of $(C_2H_5)_2O·BF_3$ solvent was added, and refluxed in a water bath under optimisation of the derivatization time and temperature. After derivatization, the solvent was concentrated to about 1.0 mL and rinsed to separating funnels with 20 mL CH_2Cl_2 solvent and added 50 mL deionized water and shaked thoroughly for extracting the derivative of bensulfuron-methyl. After standing a few minutes, the extracts were filtrated with anhydrous Na_2SO_4, concentrated to 1.0 mL and transferred to glass vials for GC–MS analysis.

2.2.4. GC–MS analysis condition

The prepared samples were analyzed by GC–MS (QP5050A, Shimadzu, Japan) system equipped with a DB-5MS fused quartz capillary column (30 mm × 0.25 mm × 0.25 μm). The temperature programe was set as following: initial temperature 150 °C held for 2 min up to 250 °C at 10 °C/min (maintained 10 min). Injector temperatures was maintained at 280 °C. Helium was used as carrier gas at a flow rate of 1.2 mL/ min. The mass spectrometer was operated in the electron ionization (EI) mode with the ionization energy at 70 eV. The ion source and MS transfer temperature was 250 °C and 230 °C, respectively. 1 μL sample solution was injected in pulsed splitless mode, and the chromatograms were recorded on computer recorder, which allows calculation of the detector response in terms of peak area.

2.3. HPLC method

2.3.1. Sample preparation and extraction procedure

The sample preparation and extraction procedure for HPLC analysis were the same as GC–MS analysis described above. The spiked water samples were extracted three times with 20 mL CH_2Cl_2 solvent, and the extracts were combined after filtration with anhydrous Na_2SO_4 and concentrated to about 1 mL and transferred to glass vials for HPLC analysis.

2.3.2. HPLC analysis condition

A LC-20A HPLC system (Shimadzu, Japan) equiped with a SPD-20A ultraviolet detector was used for HPLC analysis. A XDB-C_{18} colomn (4.6 mm × 150 mm, 5 μm) from Agilent Tecnologies was