JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

Development of an Improved Liquid Phase Microextraction Technique and Its Application in the Analysis of Flumetsulam and Its Two Analogous Herbicides in Soil

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An improved liquid phase microextraction (LPME) technique has been developed. As part of this technique, analytes were extracted into an extractant microdrop which was laid on the cone-shaped bottom of a PCR tube (polychloroprene rubber tube) but not at the needle tip of a microsyringe, and the sample vial and PCR tube were horizontally placed so that the extractant was not affected by the force of vertical orientation (gravity and floating force). The stability of the extractant microdrop increased greatly, and the selection of extractant was extended. In this work, flumetsulam and its two analogous herbicides were chosen as model analytes in investigating the feasibility of the new pretreatment method by coupling it to high-performance liquid chromatography (HPLC). Under the optimized experimental conditions, the linear range and the limits of detection ($S/N = 3$) were 0.01–5 μg/mL ($r = 0.9997$) and 0.8 ng/mL for flumetsulam, 0.002–5 μg/mL ($r = 0.9994$) and 0.5 ng/mL for analogue **1**, and 0.002–1 μg/mL ($r = 0.9993$) and 0.5 ng/mL for analog **2**, respectively. The inter- and intraday reproducibilities (RSD) were below 5.3 and 4.5%, respectively. Good recoveries that ranged from 79.4 to 115.0% were obtained in the analysis of real soil samples. The extraction efficiency of the improved method was 4–8 times higher than that of the conventional liquid phase microextraction method. The novel, simple, rapid, sensitive technique is very suitable for extraction of apolar and medium polar analyte in complex environmental samples.

KEYWORDS: Liquid phase microextraction; high-performance liquid chromatography; flumetsulam and its two analogues; soil analysis

INTRODUCTION

Flumetsulam [*N*-(2,6-difluorophenyl)-5-methyl[1,2,4]triazolo [1,5-*a*]pyrimidine-2-sulfonamide (**Figure 1a**)] and its two analogous herbicides {analogue **1** [*N*-(2,6-dimethylphenyl)-5,7-dimethyl[1,2,4]triazolo[1,5-*a*]pyrimidine-2-sulfonamide] (**Figure 1b**) and analogue **2** [*N*-(2-methylphenyl)-5,7-dimethyl[1,2,4] triazolo[1,5-*a*]pyrimidine-2-sulfonamide] (**Figure 1c**)} are widely used sulfonamide herbicides. They have broad spectrum activity on many broad leaf weeds and good crop selectivity (*1*). However, they are quite persistent in acid soils, and their degradation rate decreases with an increased rate of sorption and a decrease in temperature (*2, 3*). The estimated half-life of flumetsulam ranges from 2 weeks to 4 months across diverse soils of varied pH and organic carbon content (*2*). The residue analyses can be challenged because of the complex environmental matrixes and the trace level of analytes. Therefore, it is urgent to establish a simple and sensitive method for analyzing the trace herbicides in the environmental matrix. One of the most important steps in the development and application of an analytical method is sample preparation. In general, this step is

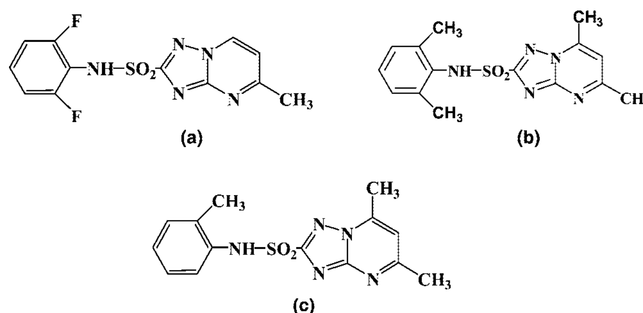

Figure 1. Structure of flumetsulam and its two analogues: (**a**) flumetsulam [*N*-(2,6-difluorophenyl)-5-methyl[1,2,4]triazolo[1,5-*a*]pyrimidine-2-sulfonamide], (**b**) analogue **1** [*N*-(2,6-dimethylphenyl)-5,7-dimethyl[1,2,4]triazolo[1,5-*a*]pyrimidine-2-sulfonamide], and (**c**) analogue **2** [*N*-(2-methylphenyl)-5,7-dimethyl[1,2,4]triazolo[1,5-*a*]pyrimidine-2-sulfonamide].

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10.1021/jf0718345 CCC: $37.00 © 2007 American Chemical Society
Published on Web 10/23/2007

the most time-consuming and often the costliest step in an analytical process. It represents a major challenge and bottleneck of an analytical method.

At present, liquid–liquid extraction (LLE) (*4–6*) and solid phase extraction (SPE) (*5–7*) are conventional sample pretreatment methods. However, LLE is time-consuming, labor intensive, and expensive and requires large amounts of highly pure organic solvents, which are expensive and toxic and can cause other problems in the environment. SPE still consumes a considerable amount of toxic organic solvent for analyte desorption, and the small columns or disks that are used are subjected to "plugging" if the aqueous sample contains solid fine particles. Solid phase microextraction (SPME) (*7–12*) and liquid phase microextraction (LPME) (*13–23*) overcome these disadvantages. SPME was introduced by Arthur and Pawliszyn in 1990 (*12*), and it is a useful sample pretreatment method. The extraction fiber is expensive and fragile and also has a limited lifetime. LPME was introduced by Jeannot and Cantwell in 1996 (*16*). It has been developed into static LPME and dynamic LPME with the ability to perform in sample and headspace extraction (*16, 19–23*), continuous-flow LPME (CFME) (*13*), hollow fiber-based LPME (HF-LPME) (*14, 15, 17*), and solvent bar microextraction (SBME) (*18*). These techniques have attracted much attention in recent years because of their advantages such as a short analysis time, minimal use of organic solvent, and a simple experimental setup, but disadvantages of these techniques such as the instability of the microdrop and the relatively low precision and sensitivity are often encountered, especially for direct immersion single-drop microextraction (DI-SDME) (*24*). In DI-SDME, a small drop (0.3–5 μL) of organic solvent is held on the hole at the tip of a microsyringe needle, which is immersed in a stirred aqueous sample solution for extraction (*19–21*). After extraction, the microdrop of organic solvent is retracted back into the microsyringe and transferred to a HPLC system or another for further analysis.

There perhaps are several reasons for the drawbacks of the DI-SDME method. First, the volume of the extractant microdrop is small; it is often no bigger than 5 μL which confines the amount of analytes extracted and the extraction efficiency. Second, the microdrop is unstable and easily dislodged from the tip of the microsyringe needle during the stirring extraction. The microdrop is suspended on the microsyringe needle by the surface tension, which is relatively low because of the small contact area between the microdrop and the tip of the microsyringe needle. Therefore, the stirring velocity cannot be quick due to the instability of the microdrop, so the extraction often cannot reach equilibrium. Third, the kind of available extractant is limited, because the extractant in DI-SDME must satisfy certain conditions such as water immiscibility and appropriate density. Otherwise, the extractant microdrop easily floats away or drops from the tip of needle, which results in a failed experiment. Fourth, reproducibility is often poor due to the serious dissolution loss of organic extractant, which has a small volume and large contact area with the sample solution.

In view of the considerations mentioned above, we developed a new LPME method based on the principle of DI-SDME and investigated the feasibility of the method with flumetsulam and its two analogues as model analytes. At the same time, the technique was applied in determining levels of three sulfonamide herbicides in real soil samples by coupling it to HPLC.

MATERIALS AND METHODS

Reagents and Chemicals. Methanol was of HPLC grade and was filtered with a 0.45μm membrane; other reagents were of analytical grade. The water used in the experiments was doubly distilled and deionized. Dichloromethane was washed with a 5 μM sodium carbonate solution and distilled water in that order and then dried with anhydrous calcium chloride. Dichloromethane was distilled after being washed, and then the distillation of 40–41 °C was collected for use. Flumetsulam and its two analogues (≥98%) were synthesized in our laboratory (*25*), and the characterization data are given in the Supporting Information.

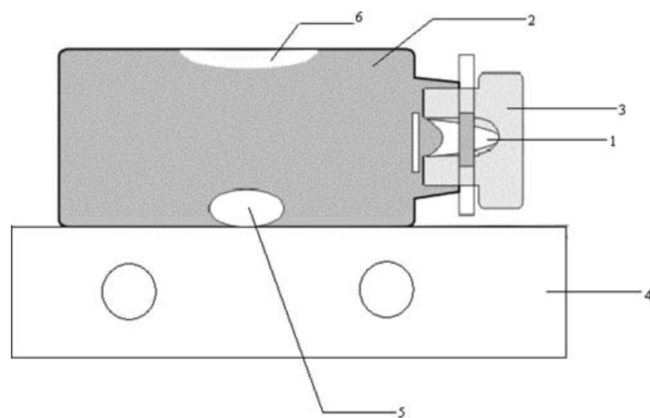

Figure 2. LPME apparatus: (1) PCR tube, (2) sample vial, (3) rubber cover, (4) magnetic stirrer, (5) stirring bar, and (6) air bubble.

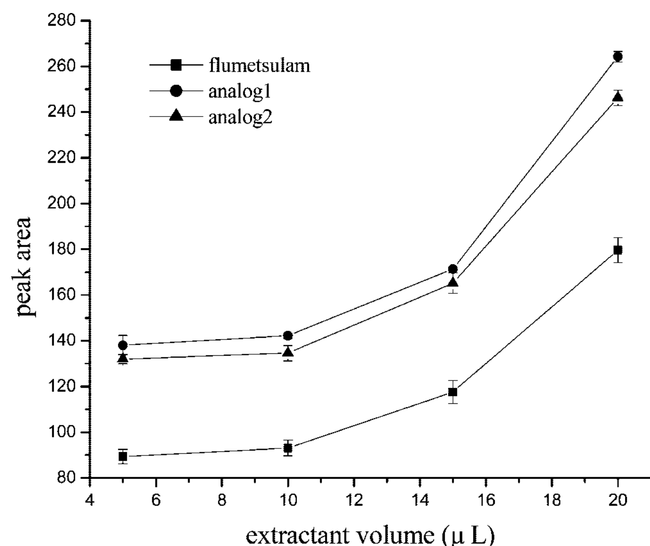

Figure 3. Optimization of extractant volume. The sample concentration was 0.4 μg/mL, the extractant dichloromethane, the sample volume 8 mL of 2% NaCl, the stirring rate 1250 rpm, and the extraction time 20 min.

HPLC Method. The HPLC system equipped with a variable-wavelength detector (VWD), a quatpump, an analytical ChemStation, and a 20 μL injection loop was an Agilent 1100 liquid chromatograph system. The analytes were separated on a Venusil, XBP C_{18} column [250 mm × 4.6 mm (inside diameter), 5 μm]. The mobile phase was a methanol/phosphate buffer solution (55:45, v/v; pH 3.0). The flow rate was kept at 0.8 mL/min. The detection wavelength was 225 nm, and the column temperature was 25 °C.

LPME Apparatus and Procedure. The schematic diagram of the LPME apparatus is shown in **Figure 2** (*26*). The sample solution (2–8 mL), a stirring bar, and salt (sodium chloride, 2–6%, w/w) were added to a 9 mL sample vial. Water immiscible organic solvent (5–20 μL) was added to a 0.2 mL polychloroprene rubber tube (PCR tube; a picture of a PCR tube is shown in the Supporting Information), and the organic solvent was covered with the sample solution to reduce the volatile loss of extractant and ensure no air bubble between the sample solution and the extractant in the extraction process. Then the PCR tube loaded with the sample solution and extractant was stuffed into the rubber cover of a sample vial and fixed. The sample vial was tightly capped

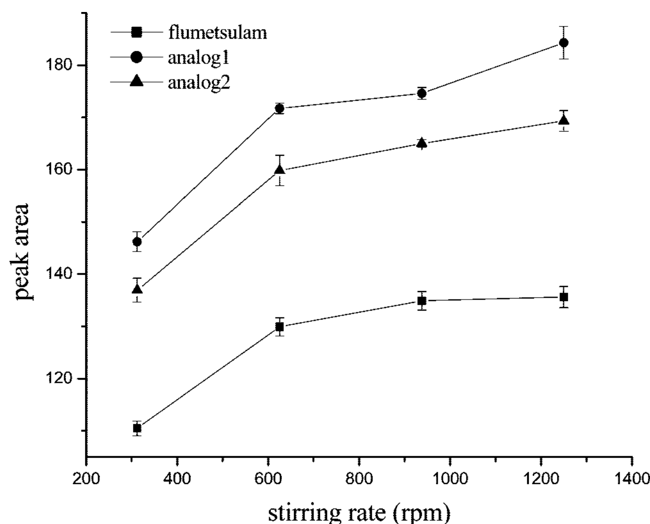

Figure 4. Optimization of stirring rate. The extractant was 20 μL of dichloromethane and the pH 1.3; other conditions were the same as those described in the legend of **Figure 3**.

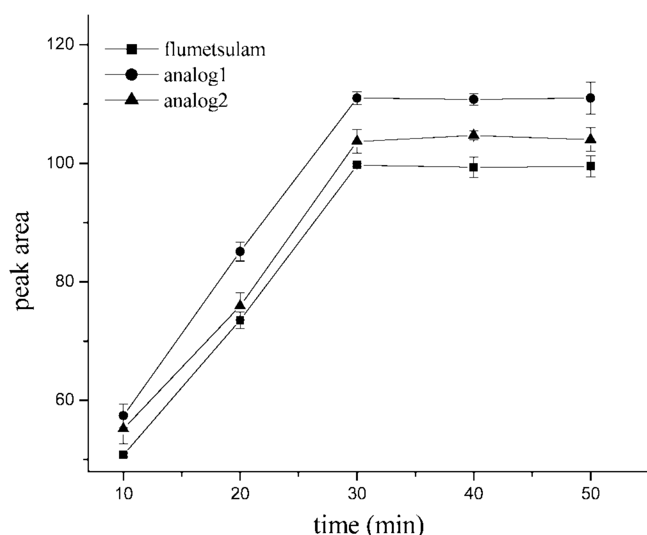

Figure 5. Optimization of extraction time. The sample concentration was 0.25 μg/mL of 4% NaCl; other conditions were the same as those described in the legend of **Figure 4**.

with the cover carefully and horizontally placed on a magnetic stirrer for extraction; after extraction for 10–50 min, the extractant was transferred to the HPLC system for analysis. Each experiment was conducted in triplicate to obtain average data.

DI-SDME Procedure. For DI-SDME, the sample solution (2–8 mL), a stirring bar, and salt (sodium chloride, 2–6%, w/w) were added to a 9 mL sample vial. The microsyringe needle was immersed in the stirred sample solution (stirring rate, 0–312 rpm), and a small drop of extractant (0.3–5 μL) was ejected and suspended at the tip of the microsyringe needle. After extraction for 1–5 min, the extractant microdrop was retracted back into the microsyringe and transferred to the HPLC system for further analysis.

Standard Solutions. Stock solutions (10 μg/mL) of flumetsulam and its two analogues were prepared by dissolving 1.0 mg of the analytes in 100 mL of water. The standard solutions (0.002–5 μg/mL) were prepared by serial dilution of stock solutions with water.

Preparation of Soil Samples. The preparation method for the soil samples was the method described in ref *27* with a minor modification. Three different soil samples were collected [vegetable plot at the Central China Agricultural University (soil 1), the experimental farm at the College of Life Sciences of Central China Normal University (soil 2), and forest at the Central China Normal University (soil 3)] and dried naturally. The soil was smashed, sieved to pass 2 mm, and weighed; 40 mL of water and 0.3 mL of 0.1 M sodium hydroxide were added to 2 g of soil. The 40 mL sample was ultrasonically vibrated for 20 min and centrifuged duplicately at 3000 rpm for 20 min. The supernatant liquid was separated and washed with 2 × 25 mL of petroleum ether. Then, the petroleum ether was discarded and the supernatant liquid used for extraction.

RESULTS AND DISCUSSION

Principle of the Method. In this technique, the analyte is distributed between the sample solution and the organic phase. When equilibrium is reached, the amount of analyte (n) is described by the following equation (*28*):

$$n = K_{odw}V_dC_0V_s/(K_{odw}V_d + V_s) \quad (1)$$

where n is the amount of analyte extracted, K_{odw} is the distribution coefficient for the analyte between the sample solution and the organic phase, C_0 is the initial concentration of the analyte in the matrix, and V_d and V_s are the volumes of the organic phase and sample solution, respectively. As indicated by eq 1, n increases with an increase in K_{odw}, C_0, V_d, and V_s. K_{odw} is affected by the extractant characteristics, pH, and ionic strength (*29*). The increase in C_0 and V_s can be simply realized in the experiment. However, the increase in V_d is not so easy to realize because of the instability of the microdrop on the microsyringe needle. In the conventional DI-SDME method, V_d is no larger than 5 μL; therefore, the amount extracted and the sensitivity are limited.

In the proposed LPME method, three main modifications were made. (a) A 0.2 mL PCR tube was selected as the extractant container in place of a microsyringe so more extractant could be loaded. The surface tension between the microdrop and the cone-shaped bottom of the PCR tube increased largely because of the increased contact area; as a result, the stability of the microdrop was improved. For example, 20 μL (even 100 μL) of dichloromethane could be loaded in the PCR tube as extractant, while the volume of dichloromethane suspended at the tip of microsyringe was no more than 5 μL. (b) The sample vial and PCR tube were horizontally placed so that the extractant was not affected by the forces of vertical orientation (gravity and floating force), and the density of the organic solvent had no effect on the choice of extractant. Therefore, the extractant microdrop was more stable than that suspended at the tip of the microsyringe needle, and the selection of the extractant was extended greatly. (c) The stirring rate could be increased markedly due to the improved stability of the extractant microdrop. The greater stirring rate shortened the time it took to reach equilibrium; thus, the total analysis time was shortened. The reproducibility of the method was enhanced greatly because of the smaller dissolution loss of extractant with the reduced analysis time and large extractant volume.

Selection of the Organic Solvent. The selection of an appropriate extraction solvent is of great importance for the experiment. First, the extraction solvent is immiscible with water. Second, analytes can be dissolved in it, and the distribution coefficients of analytes between the extraction solvent and the water sample are sufficiently large. Third, the peak of the extractant must be separated from the analyte peaks in the chromatogram. With regard to the solubility and polarity of the organic solvent, several organic solvents were selected as the extractant, including ethyl acetate, cyclohexane, toluene, and dichloromethane. The extraction efficiencies of different extractants were compared, and the results showed that the peak of ethyl acetate overlaps with that of analogue **1**. The extraction

Table 1. Linear Equation, Limits of Detection, and Limits of Quantification

analyte	linear range (μg/mL)	linear equation	r	LOD (ng/mL)	LOQ (ng/mL)
flumetsulam	0.01–5	$Y = 176.18x - 1.38$	0.9997	0.8	2.7
analogue **1**	0.002–5	$Y = 345.82x + 4.55$	0.9994	0.5	1.7
analogue **2**	0.002–1	$Y = 260.37x + 11.50$	0.9993	0.5	1.7

efficiencies of three analytes were the best with dichloromethane as the extractant, so dichloromethane was selected as the extractant in the subsequent experiments.

Optimization of Extractant Volume. As indicated in eq 1, the amount extracted increases with the increase in extractant volume. The experimental results validate the theory. The effect of the extractant volume on extraction efficiency was studied in the range of 5–20 μL. The analytical signals increase with the increase in solvent volume (**Figure 3**). Consequently, 20 μL of dichloromethane was selected so that a high extraction efficiency and a short analysis time could be achieved; additionally, it was matched up to a common 20 μL injection loop.

Optimization of Sample pH and Volume. The pH value of the sample solution also directly affects the extraction efficiency. The results showed an initial increase in extraction efficiency with an increase in pH, with a maximum being reached at 1.3, followed by a decrease in extraction efficiency with a further increase in pH. The decrease in extraction efficiency at high pH results from the deprotonation of analytes, which has pK_a values of approximately 4.6. The proper sample pH can keep the analytes in an electrically neutral form, which has a relatively higher affinity for the organic phase than in the ionized form according to “like dissolves like”. It was unclear why the efficiency decreased when the acidity of the sample solution was greater than 1.3; therefore, pH 1.3 solutions were used in all experiments.

It is known that the more analyte is present in the sample, the more analyte can be extracted. The influence of sample volume on the extraction efficiency was investigated in the range of 2–8 mL. The peak area increased with an increase in sample volume from 2 to 8 mL, but an excess of sample will lead to an increase in the time required to reach equilibrium and to consume the sample. Therefore, an 8 mL sample was selected.

Optimization of Stirring Rate. On the basis of the penetration theory of mass transfer of solute (*30*), stirring will weaken the diffusing layer between the sample solution and extractant, increase the mass transfer coefficient of the analytes, shorten the time required to reach equilibrium, and improve the extraction efficiency. In the proposed LPME technique, the stability of the extractant microdrop was enhanced greatly because of the large contact area between the microdrop and PCR tube and the fact that the PCR tube lies horizontally. The influence of stirring rate on extraction efficiency was studied in the range of 312–1250 rpm. The extraction efficiencies are enhanced with an increase in the stirring rate (**Figure 4**); the maximum peak signal is obtained at a stirring rate of 1250 rpm (the largest stirring rate for our stirrer), so it was chosen in the following experiments.

Salt Addition. Sodium chloride was added to the sample solution to increase the ionic strength of the sample solution. It can keep the analytes in an electrically neutral form, reduce the solubility of the analytes in sample solution, and dissolve more in the extractant (*29*). However, too much salt can lead to an increase in the amount of analyte dissolved in the sample solution and a decrease in extraction efficiency. The influence

Table 2. Reproducibility of the Method

	intraday RSD (%) ($n = 6$)		interday RSD (%) ($n = 6$)	
analyte	0.5 μg/mL	0.05 μg/mL	0.5 μg/mL	0.05 μg/mL
flumetslam	3.8	4.5	4.7	5.3
analogue **1**	3.4	4.3	4.1	5.1
analogue **2**	1.4	3.2	2.6	4.0

Table 3. Recovery of the Method

			recovery (%) (spiked soil sample)	
soil sample[a]	analyte	blank soil	0.5 μg/mL	0.05 μg/mL
soil 1	flumetsulam	–[b]	110.0	91.2
	analogue **1**	–[b]	95.5	95.0
	analogue **2**	–[b]	90.2	96.0
	flumetsulam	1.5	115.0	114.2
soil 2	analogue **1**	1.5	112.3	110.7
	analogue **2**	5.8	110.2	103.8
	flumetsulam	–[b]	105.0	100.7
soil 3	analogue **1**	–[b]	90.3	92.1
	analogue **2**	–[b]	85.2	79.4

[a] The characterization data of soil samples (including pH, percent of organic matter, clay, and sand) are given in the Supporting Information. [b] Not detected.

of the percent of sodium chloride on the extraction efficiency was investigated in the range of 2–6%. The peak area increased first with the increase in salt concentration; it reached the maximum at 4% NaCl for all three analytes, and then it decreased at higher salt concentrations. Therefore, 4% NaCl was used in the following work.

Optimization of Extraction Time. LPME is an equilibrium process for the analytes between the sample solution and extractant. The influence of extraction time on extraction efficiency was tested in the range of 10–50 min. The amount extracted increases with an increase in extraction time from 10 to 30 min and levels off after 30 min as shown in **Figure 5**. The time required to reach extraction equilibrium is 30 min, so it was selected as the optimized extraction time.

Comparison with DI-SDME. To test the feasibility of the proposed LPME method, its merit was compared with that of the conventional DI-SDME method. In conventional DI-SDME, several parameters that influence the extraction efficiency were optimized systemically. The extraction efficiency was increased with an increase in extractant volume, stirring rate, and extraction time. Four microliters of dichloromethane was the largest volume, which could be suspended at the tip of a microsyringe needle. Therefore, 4 μL of dichloromethane was selected as the extractant for DI-SDME. The greatest stirring rate was 312 rpm, and the longest extraction time was 5 min. Otherwise, the microdrop will drop from the tip of the microsyringe needle at a higher stirring rate and longer extraction time. Therefore, the amount extracted and the sensitivity of the method were limited. In the improved approach, the stability of the extractant microdrop was enhanced markedly with the PCR tube as an extractant holder. Therefore, the extractant volume, stirring rate, and extraction time can increase greatly; even 100 μL of dichloromethane, a stirring rate of 1250 rpm, and an extraction time of 50 min can be used.

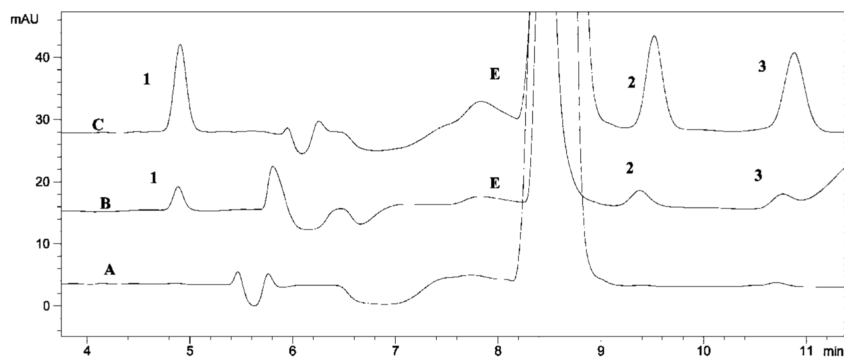

Figure 6. Chromatograms of blank and spiked soil samples. The mobile phase was a methanol/phosphate buffer solution (55:45, v/v; pH 3.0), with a flow rate of 0.8 mL/min. The detection wavelength was 225 nm and the temperature 25 °C. Peak identification: (1) flumetsulam, (2) analogue **1**, (3) analogue **2**, (E) extractant. (**A**) Blank soil sample (soil 2). (**B**) Soil sample (soil 2) spiked with 0.5 μg/mL herbicides analyzed by DI-SDME–HPLC. (**C**) Soil sample (soil 2) spiked with 0.5 μg/mL herbicides analyzed by our method. The conditions are the same as those described in the legend of **Figure 5**.

Under the optimal conditions, the extraction efficiency of the two methods was compared, and the extraction efficiency of the proposed method was 4–8 times higher than that of DI-SDME for the three herbicides.

Linearity, Limits of Detection (LOD), and Reproducibility. To test the linearity of the calibration curves, various concentrations of the standard solution ranging from 0.002 to 5 μg/mL were extracted by the improved LPME method and analyzed by HPLC. An 8 mL sample solution (containing 4% NaCl, pH 1.3) was extracted for 30 min at 1250 rpm with 20 μL of dichloromethane as the extractant; all dichloromethane was injected for HPLC analysis. The calibration curves were constructed from peak areas counts. As shown in **Table 1**, a good linearity relationship is observed for all analytes with the correlation coefficients (r) ranging from 0.9993 to 0.9997. The limits of detection (LOD) based upon a signal-to-noise ratio of 3:1 ($S/N = 3$) are 0.8 ng/mL for flumetsulam, 0.5 ng/mL for analogue **1**, and 0.5 ng/mL for analogue **2**. The limits of quantification (LOQ) based upon a signal-to-noise ratio of 10:1 ($S/N = 10$) are 2.7, 1.7, and 1.7 ng/mL for flumetsulam, analogue **1**, and analogue **2**, respectively. The interday and intraday reproducibility (RSD; $n = 6$) of the method are less than 5.3 and 4.5%, respectively (**Table 2**). Good reproducibility is obtained due to little dissolution loss, which results from a larger extractant volume and a short analysis time.

Real Soil Sample Analysis. The proposed method was applied to the analysis of real soil samples from three different sources [vegetable plot at the Central China Agricultural University (soil 1), experimental farm at the College of Life Sciences of Central China Normal University (soil 2), and forest at the Central China Normal University (soil 3)]; 1.5 μg/mL flumetsulam, 1.5 μg/mL analogue **1**, and 5.8 μg/mL analogue **2** were detected in soil 2. No analyte was found in the other soil samples. Recovery experiments were performed at two different levels (0.5 and 0.05 μg/mL) to test the application of the method. Satisfied recoveries were obtained in the range of 79.4–115.0% (**Table 3**). These results demonstrate that the method is a reliable technique for the analysis of trace analytes in environmental and agricultural samples. The chromatograms of blank and spiked soil samples are shown in **Figure 6**.

Conclusion. An improved LPME method is described herein. A PCR tube was first utilized to hold extractant in place of a microsyringe, so the stability of the extractant microdrop was improved markedly compared with that in DI-SDME. A larger volume of extractant could be used for extraction, and the available kinds of the extractant were extended largely. The elevated stirring rate could be performed to shorten analysis time and enhance extraction efficiency. The reproducibility is excellent due to little dissolution loss of extractant. Additionally, there was no need to adopt an expensive membrane or a hollow fiber to support the extractant microdrop; the cheap PCR tube is disposable. Therefore, there is no risk of cross-containment. Compared with that of DI-SDME, the extraction efficiency of the proposed method is 4–8 times higher under the optimal experimental conditions. The improved method was successfully applied in determining the levels of flumetsulam and its two analogues in real soil samples by coupling it to HPLC. Satisfied recoveries ranging from 79.4 to 115.0% were obtained. The new LPME method is simple, rapid, economical, and efficient, consumes a small amount of organic solvent, and does not involve cross-containment. The extraction efficiency can be improved further by controlling the temperature of the sample solution and extractant independently. The method is very suitable for extraction of apolar and medium polar analytes in complex environmental samples.

Supporting Information Available: Characterization of flumetsulam, analogue **1**, and analogue **2**, a picture of a PCR tube, and characterization data of soil samples. This material is available free of charge via the Internet at http://pubs.acs.org.

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Received for review June 21, 2007. Revised manuscript received September 21, 2007. Accepted September 22, 2007. This work was support by Key Laboratory of Pesticide and Chemical Biology of the Ministry of Education and the National "973" Project (2003CB114400), the National NSFC (20528201 and 20432010), and the Cultivation Fund of the Key Scientific and Technical Innovation Project, Ministry of Education of China (705039).

JF0718345