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Dissipation and Residues of Flumetsulam in Wheat and Soil

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Abstract A residue analytical method for the determination of flumetsulam in wheat and soil was developed using gas chromatography with electron capture detector (GC-ECD). The limit of detection of the analytical method was 0.001 ng, and the limit of quantification was 0.005, 0.01 mg/kg for soil and wheat grain, respectively. The mean recoveries from soil and wheat ranged from 83.85 % to 107.2 % with average relative standard deviation ranging from 1.87 % to 8.09 %. The method was successfully applied to determine the residual level and dissipation rate of flumetsulam in the soil and wheat. The half-life in soil was 23.1 days with a dissipation rate of 69 % over 35 days. At harvest time, the residue levels of flumetsulam in wheat grain and soil from high dosage plot were 0.031 and 0.045 mg/kg, respectively. The flumetsulam residues could not be detected from low dosage plot. Direct confirmation of the analyte in real samples was achieved by GC-ECD.

Keywords Flumetsulam · Pesticide residue · Wheat · GC-ECD

Flumetsulam, N-2,6-difluorophenyl-5-methyl-1,2,4-triazolo [1,5-a]Pyrimidine-2-Sulfonamide, is the first triazolopyrimidine sulfonanilide herbicide developed by DowElanco. Flumetsulam is a weak acid (pKa = 4.6), with water solubility of 5,600 mg/L at pH 7. Like the sulfonylureas, flumetsulam is an acetolactate synthase (ALS) inhibitor of the biosynthesis of branched chain amino acids (valine, leucine, and isoleucine). Flumetsulam has a broad spectrum activity on many broad leaf weeds and shows selectivity on several major agronomic crops such as corn, soybean, wheat and barley (Felix et al. 2005; Chen et al. 2009).

To the best of our knowledge and available literatures, analytical procedures for the quantitative analysis of flumetsulam residues employing techniques such as high performance-liquid chromatography (HPLC) (Baskaran et al. 1996; Moawad and Khoo 2005; Xu et al. 2007), gas chromatography with electron-capture detection (GC-ECD) or GC-mass spectrometric (GC-MS) detection after derivatization (Olberding et al. 1991; Qu et al. 1999; Yang et al. 2000; Rouchaud et al. 2002) have been reported so far. These methods were unsuitable for determination of flumetsulam owing to lengthy clean-up steps, high organic solvent consumption and low sensitivity. Although the residue and degradation of flumetsulam have been studied in some environmental materials, such as soil, soybean, and corn (Lehmann et al. 1993; Li et al. 2000; Rouchaud et al. 2002; Zhang et al. 2003). We were unable to find any published information on flumetsulam residues in wheat.

In this work, a simple method was developed for the analysis of flumetsulam in wheat and soil using GC-ECD after its methylation by methyl iodide into flumetsulam-methyl. The purpose was to study the ultimate residue and dissipation rate of flumetsulam in a wheat field ecosystem.

Materials and Methods

Reference standards of flumetsulam was purchased from the Institute of Agro-environmental Protection, Ministry of Agriculture of China (Tianjin, China), its commercial formulation (WG, 80 %) was provided by Qingdao Hansen

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Biologic Science Co., Ltd. (Shandong, China). Other chemicals and solvents were from Dikma Limited (Beijing, China) and were of analytical-grade. Florisil (500 mg/3 mL) cartridge was purchased from Agela Technologies (Beijing, China).

A Shimadzu 2014 gas chromatograph equipped with an electron capture detector (ECD) and a Rtx-5 capillary column (30 m × 0.25 mm × 0.25 μm) was used for separation and determination of the derivatization product of flumetsulam residues. Nitrogen (>99.999 %) was used as the carrier gas at the constant flow rate of 20 cm/s, and the injection volume was 1 μL. The injection port temperature was held at 280°C at the split mode with the split ratio 10:1. The detector temperature was held at 320°C. The oven temperature program: 120–280°C (20°C/min, hold for 1 min), 280–300°C (5°C/min, hold for 5 min). The approximate retention time of the flumetsulam-derivatization was 16.3 min.

GC/MS analysis was performed with a Shimadzu GCMS-QP2010E system, equipped with a mass selective ion detector and a capillary column (Rtx-5, 30 m × 0.25 mm × 0.25 μm). The GC column and oven temperature program described above were used. Injector and interface temperatures were 280 and 260°C, respectively. Eluent from the GC column was fed into a 70-eV electron-impact ionization source maintained at 200°C. The acquisition was performed in scan mode in the ranges m/z 50–500. Helium (>99.999 %) was used as the carrier gas at the constant flow rate of 29.3 cm/s.

The field trials including the dissipation experiment and residue experiments were carried out in an experimental plot located at Changping District of Beijing, China. Each experiment field contained three replicate plots and a control plot which was separated by irrigation channels, and the area of each plot was 30 m^2.

To investigate the dissipation of flumetsulam in soil, flumetsulam (WG, 80 %) was dissolved in water and sprayed in the wheat field after the emergence of the first two leaves of the broadleaf weeds. The dose of application was 4.6875 g a.i.ha^{-1} (1.5 times the recommended dosage). Representative soil samples (0–10 cm) were collected at intervals of 2 h, 1, 3, 5, 7, 14, 21 and 35 days after spraying. The samples were stored in a freezer at −20°C for analysis.

The ultimate residue experiment was performed at two dosage levels: lower dosage of 46.85 g a.i.ha^{-1} (the recommended high dosage), and a higher dosage level of 70.275 g a.i.ha^{-1} (1.5 times the recommended high dosage), respectively. After the emergence of two leaves of the broadleaf weeds in the wheat field, the high and low dosage treatment groups were sprayed one time. At the time of the harvest, both wheat grain and soil were sampled to determine the final residues of flumetsulam. All the collected samples were stored in a freezer at −20°C for further analysis.

For long-term storage, a stock solution (200 μg/mL) of flumetsulam was prepared in acetonitrile. Working calibration solutions (0.01, 0.05, 0.1, 0.5, 1.0, 5.0 μg/mL), used for sample spiking and for preparation of standard curve, were obtained from stock solution by volumetric serial dilution. The derivatization procedures were performed as described for the soil samples.

Soil sample was dried at room temperature and screened through 40-mesh sieves. A portion (10 g) of homogenized soil sample was put in a 250 mL flask. Flumetsulam was extracted by adding 40 mL methanol–water (1/1, v/v), and the mixture was shaken on a mechanical horizontal shaker for 30 min. The extract was filtered through a Buchner funnel and washed with another 20 mL methanol–water (1/1, v/v), and then the combined filtrate was transferred quantitatively to a separator funnel containing 30 mL 2 % aqueous sodium sulfate solution. This filtrate was added with 3 M NaOH to pH 9.0–10.0, and then followed by liquid–liquid partition with dichloromethane for three times at the volume of (30 + 30 + 30) mL. The dichloromethane layer was discarded, and the aqueous layer containing the analyte was acidified to pH 2.0–3.0. Then the filtrate was again partitioned with dichloromethane three times sequentially (3 × 20 mL). The dichloromethane phase was collected after partitioning and transferred to a funnel with anhydrous sodium sulfate. The resultant solution was then filtered with 10 mL dichloromethane. All extracts were combined and concentrated to near dryness with a vacuum rotary evaporator at 40°C, and the drying was completed under a nitrogen stream. This concentrated extract was then dissolved with 2 mL acetonitrile and subjected to derivatization.

Chopped and homogenized wheat grain sample (10 g) was extracted with 40 mL methanol–water (3/1, v/v) by shaking thoroughly in a 250 mL flask for 30 min on a mechanical horizontal shaker. The sample was filtered through a Buchner funnel into a filtrate flask and washed with another 20 mL methanol–water (3/1, v/v). The combined filtrate was transferred to a separatory funnel with 5 g sodium chloride. The filtrate was added with 4 M HCl to pH 2.0–3.0, and then extracted by liquid–liquid partition with 3 × 20 mL dichloromethane. The dichloromethane layer containing the analyte was collected. The next steps were the same as the soil samples.

The derivatization process followed the method described by Olberding et al. (1991) with slight modifications. 120 μL methyl iodide-triethylamine (1/1, v/v) was added to the above extracts of soil sample. The mixture was held for 30 min at room temperature for derivatization, and then evaporated to dryness under vacuum. The derivatized sample was dissolved in 2 mL 5 % sodium chloride solution and transported to a 10 mL centrifuge tube. 5 mL

methyl-t-butyl ether was subsequently added, and the tube was shaken vigorously by hand for 1 min and centrifuged at 4,000 rpm for 2 min. The methyl-t-butyl ether layer was transferred into a clean 100 mL evaporating flask. This procedure was repeated two times. The solution was evaporated under nitrogen and redissolved in 2 mL acetone-petroleum ether (5/95, v/v) prior to GC-ECD analysis.

The above wheat extract was placed in a 250 mL screw-cap bottle, and 400 μL methyl iodide-triethylamine (1/1, v/v) was added. After that the same derivatization procedure was followed as described for soil. The derivatized wheat sample was dissolved with 10 mL acetone-petroleum ether (5/95, v/v) and for purification by Florisil cartridges before GC-ECD detection.

A Florisil cartridge was preconditioned with petroleum ether (2 mL). After loading 2 mL wheat sample solution, the cartridge was washed with 5 mL acetone-petroleum ether (5/95, v/v). The analyte was eluted with 8 mL acetone-petroleum ether (35/65, v/v), and the eluted was concentrated to dryness at 40°C under a stream of nitrogen. The resulting residue was redissolved in 2 mL acetone-petroleum ether (5/95, v/v) for GC-ECD analysis.

Different amounts of standard flumetsulam were spiked to the blank samples of wheat grain and soil. Spiked samples were left to stand for 30 min to allow flumetsulam absorption onto the sample. Afterward, they were processed according to the above-described procedure. Three replicates for each concentration were analyzed. Blank analyses were performed in order to check interference from the matrix. Recovery and the flumetsulam residues in these samples were determined with single-point calibration and the external standard method.

The residual amount and half-life of flumetsulam were calculated by the equations, $C_T = C_0 e^{-KT}$ and $T_{1/2} = \ln 2/K$, respectively, where C_T represented the concentration of the pesticide residue at time T, C_0 represented the initial concentration after application, K is a dissipation coefficient and $T_{1/2}$ is the time required for the pesticide residue level being degraded to half of the initial post application level.

Results and Discussion

Direct determination of flumetsulam by gas chromatography has not been possible due to its thermal unstability and non-volatile nature. Derivatization is often used in GC to increase the volatility of an analyte, to improve its thermal stability and to enhance the sensitivity or selectivity of the detection.

Derivatisation product of flumetsulam is formed as shown in Fig. 1. The flumetsulam was converted into N-methyl derivative which has a molecular mass of m/z 339. In this procedure, the amount of derivatization agent appeared to be a rather critical factor. Increasing the amount of derivatization reagent increases the yield of derivatives until the reaction is completed, but at times it increases the amount of by-products. The amount of the derivatization agent required to complete the derivatization was 120, 400 μL for soil and wheat grain, respectively.

Gas chromatography-mass spectrometry (GC-MS) was used to verify whether the derivatization proceeded as expected or not. The results are shown in Fig. 2, which confirm the structure of the generated derivative. The molecular ion peak of N-methyl derivative was 338 (M-H, 0.13). The characteristic ions were 134 (($C_5H_3N_4$)(CH_3), 100), 142 ((C_6H_3)F_2(NCH_3), 47) and 247 (($C_6H_3F_2$)($C_5H_2N_4$)(CH_3) + H, 10).

During initial method development, the low recoveries of flumetsulam from wheat grain were found to be due to the different ratios of methanol–water. In ratios 1/1 (v/v) and 2/1 (v/v), the fortified recoveries were blow 71.41 %, but in 3/1 (v/v) the recoveries were above 83.85 %. In order to improve the selectivity and reproducibility of the method, cleanup procedures were implemented. As for soil cleanup, liquid–liquid partition was employed to separate the pesticide using dichloromethane, which gave good

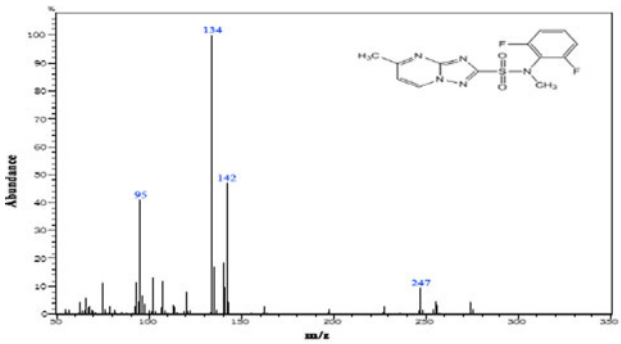

Fig. 2 Gas chromatography-mass spectrum of the derivatization product of flumetsulam

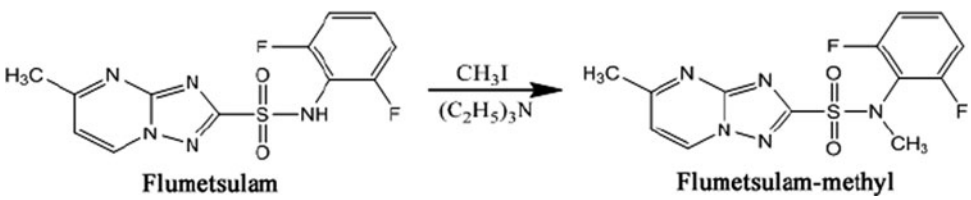

Fig. 1 The derivatization process of flumetsulam

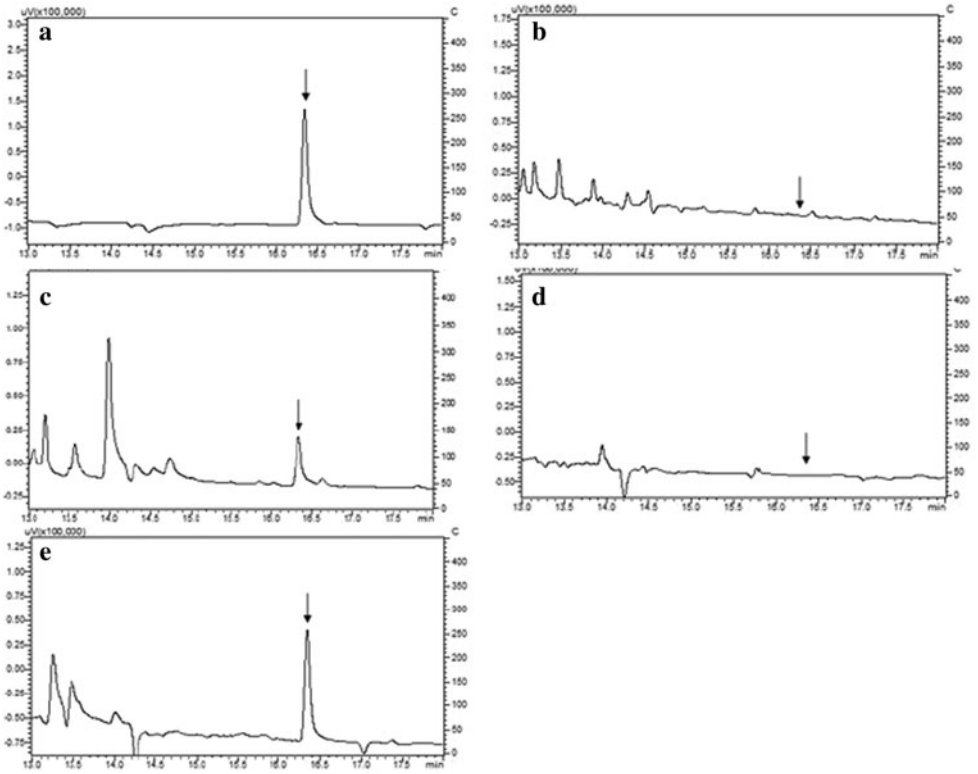

Fig. 3 Chromatograms obtained from the target pesticides: **a** flumetsulam standard solution, **b** blank soil sample, **c** soil spiked with flumetsulam at 0.1 mg/kg, **d** blank wheat sample, **e** wheat spiked with flumetsulam at 0.1 mg/kg

recoveries and little interference in the chromatogram and did not need further purification. As for wheat grain, additional Florisil cartridge cleanup procedure was required after derivatization.

The linear calibration curve was obtained by plotting concentration against average peak area. Good linearity was achieved between the ranges 0.01–1 μg/mL with a correlation coefficient of 1,000. The standard curve equation was $y = 2{,}707{,}155.58x + 7{,}536.05$. The limit of detection (LOD) of flumetsulam was 1×10^{-7} mg at a signal-to-noise (S/N) ratio of 3, and the limit of quantification (LOQ) was 0.005 and 0.01 mg/kg for soil and wheat, respectively.

Recoveries were determined at three fortification levels (Table 1). The mean recoveries from three replicates of the fortified wheat and soil samples were in the range of 83.85 %–107.2 %. The relative standard deviations (RSDs) ranged from 1.87 % to 8.09 %. The recoveries and precision results showed that it was a reliable method for determination of flumetsulam in wheat and soil samples (Fig. 3).

The dissipation data of flumetsulam in soil were listed in Table 2. The dissipation dynamics of flumetsulam could be described by the following first-order rate equation: $C_T = 0.56e^{-0.03t}$ with the square of coefficient (R^2) of 0.87. The initial residue of flumetsulam in soil was 0.71 mg/kg with a half-life of 23.1 days; 69 % of this residue had dissipated after 35 days. This indicates that flumetsulam degrades a little more slowly in soil. In

Table 1 Fortification and recovery of flumetsulam in wheat and soil samples

Sample type	Fortification levels (mg/kg)	Recovery (%)				RSD (%)
		1	2	3	Average	
Wheat	0.5	80.93	83.09	87.52	83.85	4.01
	0.1	98.52	99.31	102.9	100.2	2.33
	0.01	101.6	102.8	117.2	107.2	8.09
Soil	0.5	96.63	102.6	108.4	102.5	5.74
	0.1	85.20	87.84	88.83	87.29	2.15
	0.005	91.73	94.72	94.80	93.75	1.87

Table 2 Dissipation of flumetsulam residues in soil in Beijing, China in 2011

Days after spraying	Residue (mg/kg)	Dissipation (%)
2 h	0.71	–
1	0.23	67.6
3	0.49	31.0
5	0.48	32.4
7	0.43	39.4
14	0.30	57.7
21	0.27	62.0
35	0.22	69.0

Table 3 Final residues of flumetsulam in wheat and soil in Beijing, China in 2011

Sample type	Application	Dosage (g a.i/ha)	Days after spraying	Residue (mg/kg)
Wheat	One time	High dosage (4.6875)	53	0.031
	One time	Low dosage (3.125)	53	<0.01
Soil	One time	High dosage (4.6875)	53	0.045
	One time	Low dosage (3.125)	53	<0.005

previous reports, the estimated half-life of flumetsulam in the soil ranges from 2 weeks to 4 months, depending on soil organic carbon content and soil pH (Lehmann et al. 1992). Soil moisture and temperature also influence microbial activity and consequently flumetsulam degradation. Low rainfall and low temperatures contribute to slower dissipation of flumetsulam (Murphy and Shaw 1997). Flumetsulam soil residues decrease rapidly during the warm summer months and more slowly during the fall (Lehmann et al. 1993).

Data of the ultimate residues are shown in Table 3. The residue levels of flumetsulam in wheat grain and soil from high dosage plot were 0.031 and 0.045 mg/kg, respectively. The flumetsulam residues could not be detected from low dosage plot. The maximum residue limit (MRL) is the safety limit of pesticides in agricultural products and food. There has been no MRL of flumetsulam set by Chinese legislation or FAO (Food and Agriculture Organization)/WHO (World Health Organization) yet. The MRL for flumetsulam for wheat in the Japan is 0.05 mg/kg (Zhuang 2010). From the results of final residue experiments, the terminal residues of flumetsulam in wheat grain and soil were below 0.05 mg/kg (the MRL of Japan) at both recommended high dosage and 1.5 times the recommended high dosage. Therefore this study provides evidence that flumetsulam is acceptable to apply for wheat under the recommended dosage.

A relatively simple and fast residue analytical method using GC-ECD for the detection and monitoring of flumetsulam in wheat and soil was established. The method shows satisfactory validation parameters in terms of linearity, lower limits, accuracy and precision. The developed method was successfully applied to determine the fate of flumetsulam in wheat and soil. This work will aid in the establishment of a maximum residue limit and the safe and proper use of flumetsulam in wheat in China.

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