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Short communication

Analysis of flufenacet in soil, wheat grain and straw by gas chromatography

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Abstract

An analytical procedure for detecting residues of a new herbicide, flufenacet, in soil, wheat grain and straw by gas chromatographic method using various solvents and extraction methods was standardized. The best results were obtained when samples fortified with flufenacet and were extracted with acetone–0.2 *M* HCl (95:5) using a horizontal shaker for soil and Soxhlet extractor for plant samples. The clean up was done by partitioning with dichloromethane. The GC equipped with an electron-capture detector and a column packing of HP-1 as stationary phase and nitrogen as a carrier gas at a flow-rate of 15 ml min^{-1} was used. Temperatures of oven, injector and detector were adjusted at 190, 210 and 270°C, respectively. The retention time of flufenacet was 2.07 min. The herbicide recoveries ranged between 81 to 100% from the three matrices.

Keywords: Soil; Pesticides; Flufenacet

1. Introduction

Flufenacet (Foe 5043) {*N*-(4-fluorophenyl)-*N*-(1-methyl-ethyl)-2-[5-(trifuoromethyl)-1,3,4-thiadiazol-2-yl]oxy]acetamide}, a new soil acting herbicide has been introduced recently as a selective herbicide to control grassy weeds in a wide range of crops including cereals [1,2].

Although there are several reports on the efficacy of flufenacet against various weeds in cereal crops, there are very few reports on the method of analysis and its environmental fate in agro ecosystems. Gould et al., (1997) reported a gas chromatography–selected ion monitoring–mass spectroscopy (GC–MS–SIM) for measuring residues of Foe 5043 and its metabolites in different crops [3]. In this method the residues were briefly oxidized and hydrolyzed to the corresponding fluoroaniline by digesting the crop matrix with sulfuric acid. The fluoroaniline was separated from fortified crop matrix by steam distillation, recovered by extraction and derivatized. The derivative was measured by GC–MS–SIM. The method gave recoveries of 67–116% of Foe 5043 and its metabolites at the 0.10 ppm level. The environmental fate of flufenacet in soil under anaerobic and aerobic conditions was studied using labeled [phenyl-U-^{14}C]Foe 5043. It was relatively stable under anaerobic compared to aerobic con-

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ditions [4].The half-life of flufenacet ranged between 33 and 64 days under aerobic conditions [5]. The method described in this paper presents a sensitive and simple procedure for measuring of flufenacet residue in soil as well as wheat grain and straw.

2. Experimental

2.1. Chemicals

The analytical-grade flufenacet (99.6% purity) was supplied by M/S Bayer India Ltd. All solvents were distilled before use.

2.2. Preparation of standards

A stock solution of flufenacet (1000 μg ml^{-1}) was prepared by dissolving 25 mg of analytical-grade herbicide in 25 ml of acetone. Other flufenacet solutions (1, 0.5, 0.1, 0.05, 0.01 μg ml^{-1}) were prepared from the stock solution by dilution with hexane.

2.3. Instrument

The method employed a Hewlet–Packard gas chromatograph, model HP 5890, equipped with a ^{63}Ni electron-capture detector, a 10 m×0.53 mm I.D. column containing HP-1 as stationary phase and nitrogen as carrier gas at a flow-rate of 15 ml min^{-1}. The operating temperatures for oven, injector and detector were 190, 210 and 270°C, respectively. A 3 μl volume of sample was injected on the column by an auto-injector and chromatograms were visualized on a computer. The instrument was connected to a computer having software able to compute detector response in terms of peak area.

2.4. Extraction and cleanup

2.4.1. Extraction from soil

A soil containing 0.33% organic matter with a pH of 7.1 and a sandy loam texture consisting of 19% clay, 21% silt and 60% sand was used. Soil was dried in shade and sieved. Soil samples (50 g) in triplicate were fortified with different concentrations (0.1, 0.25 and 0.5 μg g^{-1}) of flufenacet and extracted using two methods namely shaking on a horizontal shaker for $\frac{1}{2}$ h and Soxhlet extraction.

Two solvent systems (50 ml) viz. acetone–hexane (10:90) and acetone–0.2 *M* HCl (95:5) were separately used to check efficiency of extraction by shaking on a horizontal mechanical shaker for $\frac{1}{2}$ h.

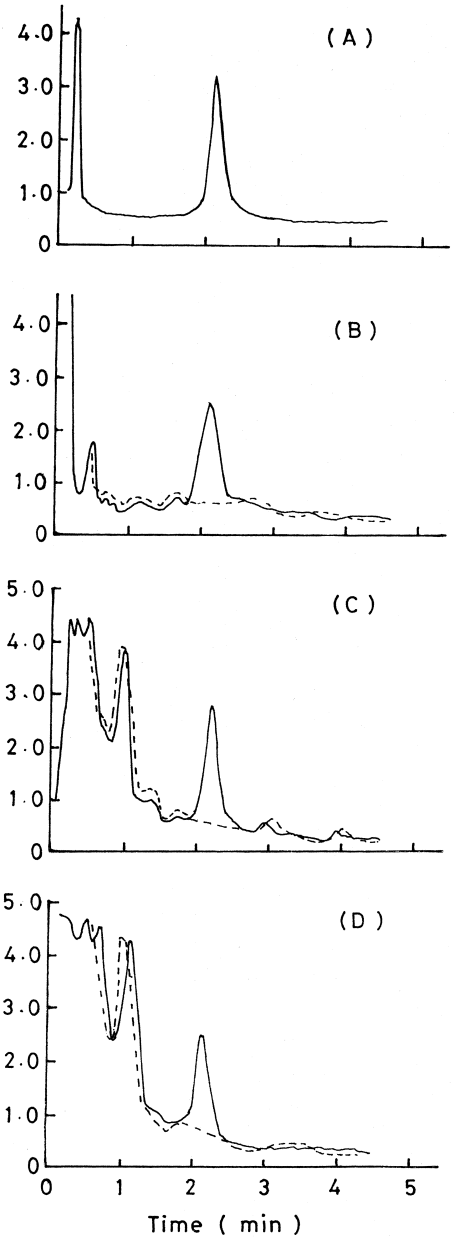

Fig. 1. Gas chromatograms of flufenacet. (A) Standard solution (0.1 μg ml), (B) soil, (C) grain, (D) straw. ---- Blank sample, ——— treated sample).

Table 1
Calibration of flufenacet by GC method

Concentration ($\mu g\ ml^{-1}$)	Area[a]	Average
1	11 185 245	11 409 783±517 523
	12 001 653	
	11 042 452	
0.5	5 043 141	5 220 138±158 770
	5 267 263	
	5 350 011	
0.1	1 053 767	1 054 397±53 689
	1 001 026	
	1 108 398	
0.05	592 197	564 050±29 427
	533 492	
	566 461	
0.01	108 701	108 503±6 295
	102 112	
	114 697	

[a] Three injections.

The contents were filtered through a büchner funnel. The extraction was repeated twice more (50+25 ml). The filtrates were combined and the solvent was evaporated on a rotary evaporator to about 10 ml.

2.4.2. Extraction from wheat straw and grain

Powdered wheat grain and straw samples (50 g) spiked with known quantities (0.1, 0.25 and 0.05 $\mu g\ g^{-1}$) of flufenacet were separately placed in a thimble contained in a Soxhlet apparatus. To this was added 150 ml of (acetone–0.2 *M* HCl; 95:5) and extraction was carried out for 4 h. The contents were collected and the solvent was evaporated to about 10 ml on a rotary evaporator.

2.4.3. Clean up

The first solvent mixture (Acetone–hexane, 10:90) concentrate did not require any clean up. The acidic concentrate was transfered to a separating funnel, diluted with water (70 ml) and extracted three times with methylene chloride (25+10+5 ml). The combined extract was dried by passing through anhydrous sodium sulfate and evaporated to dryness on a rotary evaporator. The residues were dissolved in hexane prior to analysis.

3. Results and discussion

Flufenacet was resolved as a single peak by GC and had a retention time (R_t) of 2.07 min (Fig. 1A). The method showed linearity over a range from 0.01 to 1.0 $\mu g\ ml^{-1}$ (Table 1). The limit of determination of the technique was 0.03 ng of flufenacet.

Three-fold injections of flufenacet (0.01 to 1 $\mu g\ ml^{-1}$) were used to determine the standard deviation. It was observed that triplicate injections of each sample were optimum for operating in a 95% confidence interval. It was found that limit of detection was also satisfactory at level down to 0.01 ppm.

Following optimization of instrument operation conditions, the method was extended to the analysis of flufenacet in soil, straw and grain. Although there was no interference in any extract in the gas chromatogram (Fig. 1B,C,D), the extraction efficiency of the herbicide from soil (Table 2) in acetone–hexane by shaking was rather low (average 56.4%) as compared to acetone –0.2 *M* HCl (average 95.2%).

Table 2
Recovery of flufenacet from fortified soil

Method of extraction	Solvent fortified	Amount recovered ($\mu g\ g^{-1}$)	Amount[a] ($\mu g\ g^{-1}$)	Recovery (%)
Shaking	Hexane–acetone	0.10	0.04±0.002	44.8
Shaking	Hexane–acetone	0.50	0.34±0.016	68.0
Soxhlet	Hexane–acetone	0.10	0.07±0.004	69.2
Soxhlet	Hexane–acetone	0.50	0.34±0.015	67.9
Shaking	Acidified acetone	0.10	0.09±0.005	91.5
Shaking	Acidified acetone	0.25	0.24±0.011	95.3
Shaking	Acidified acetone	0.50	0.49±0.023	98.7

[a] Average of three replicates.

Table 3
Recovery of flufenacet from fortified wheat grain and straw

Matrix	Amount added ($\mu g\ g^{-1}$)	Amount found[a] ($\mu g\ g^{-1}$)	Recovery (%)
Wheat grain	0.10	0.10±0.005	100.5
	0.25	0.23±0.010	92.1
	0.50	0.42±0.021	85.0
Wheat straw	0.10	0.09±0.004	92.7
	0.25	0.22±0.010	87.4
	0.50	0.40±0.020	81.2

[a] Average of three replicates.

The extraction from soil matrix was quantitative only when acetone–0.2 *M* HCl was used as an extraction solvent. While mechanical shaking was found satisfactory for soil, Soxhlet gave quantitative recoveries (81–100%) for wheat grain and straw (Table 3).

Due to the short retention time of the herbicide (<3 min) and the absence of interfering peaks in the area of herbicide for the matrices analyzed, each sample injection could be completed within 5–8 min and it was possible to analyze a large number of samples in a short time. In other words, the method was suitable for batch analyses.

It may be concluded that the described extraction procedure is simple and gives good recoveries for the fortified samples. The GC method is thus sensitive, specific, quick and can be successfully used to quantitatively estimate the residues of flufenacet in soil as well as crop samples.

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