Journal of Chromatography, 387 (1987) 541–545
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 19 158

Note

High-performance liquid chromatographic determination of Fluazifop-butyl and Fluazifop in soil and water

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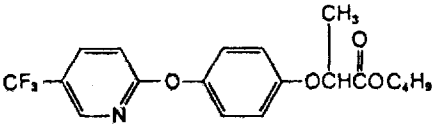
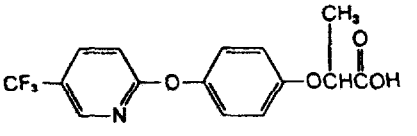
(First received June 10th, 1986; revised manuscript received October 14th, 1986)

The selective grass herbicide Fluazifop-butyl (I), butyl 2-[4-(5-trifluoromethyl-2-pyridyloxy)phenoxy]propionate, is the active ingredient of the product Fusilade[1,2]. It is rapidly hydrolyzed in the environment to the corresponding acid, Fluazifop, 2-[4-(5-trifluoromethyl-2-pyridyloxy)phenoxy]propionic acid (II).

(I)



(II)



Most methods for the determination of Fluazifop-butyl and Fluazifop have been developed for vegetables or formulations and gas–liquid chromatography (GLC) and high-performance liquid chromatography (HPLC) are most often used. Fluazifop-butyl in formulations can be determined by GLC with a flame ionization detector[3], but if residual levels are to be detected, *e.g.*, in vegetables, the derivatization of Fluazifop-butyl to its bromide derivative[4] and of Fluazifop to its pentafluorobenzyl derivative[5] is recommended in order to use the more sensitive electron-capture detector. Several methods have been reported for the HPLC determination of Fluazifop-butyl[4,6] or Fluazifop-butyl and Fluazifop plus conjugated esters through hydrolysis of all the compounds to Fluazifop[7]. These procedures do not require derivatization and an UV detector can be used.

Difficulties in the extraction of residues of pesticides or their metabolites from soil arise from their tendency to bind to the organic and clay fractions. Moreover, together with the analyte, soil compounds are extracted that can interfere with the analysis whether by GLC or HPLC and must be eliminated by sample clean-up. The choice of the most suitable extractant is therefore of great importance. Molinari *et al.*[8] found methanol–1 *M* hydrochloric acid (1:1, v/v) saturated with dichloromethane to be most effective for the contemporaneous extraction of Fluazifop-butyl

0021-9673/87/$03.50

and Fluazifop. In this work, which is part of a wider study on the environmental behaviour of Fluazifop-butyl and Fluazifop, we used a method for the determination of these two compounds in soil and water based on the one proposed by Molinari *et al.*[8].

MATERIALS AND METHODS

Apparatus

A Varian 5000 liquid chromatograph equipped with a 250 mm × 4 mm I.D. LiChrosorb RP-18, 10-μm analytical column, a multiwavelength Varian UV detector and a Varian 4290 integration system was used.

Reagents

Standards of Fluazifop-butyl and Fluazifop (97.4% pure) were kindly supplied by ICI Solplant, Italy. Analytical reagent grade dichloromethane, 85% orthophosphoric acid, anhydrous sodium sulphate, HPLC grade methanol and acetonitrile were obtained from Carlo Erba. Water was purified with a Milli Q Water System (Millipore). The stock standard solutions contained 500 μg/ml of Fluazifop-butyl and Fluazifop in methanol. The extraction solutions were methanol–1 *M* hydrochloric acid (1:1, v/v) saturated with dichloromethane, methanol–0.1 *M* hydrochloric acid (1:1, v/v) saturated with dichloromethane and methanol–1 *M* hydrochloric acid (9:1, v/v).

Soil

The soil used, containing 1% organic carbon, 8% clay and with a pH of 5.2, was sieved to 2 mm and maintained at about 10% of moisture.

Water and soil fortification

Samples of distilled water (50 ml) or of soil (50 g) were spiked with 1 ml methanolic solutions of Fluazifop-butyl and Fluazifop (5–500 μg/ml), shaken and extracted immediately.

Extraction from water

Samples of spiked water were transferred to a separating funnel, acidified to pH 2–3 with 1 *M* hydrochloric acid and extracted three times with dichloromethane (50 ml). The pooled extract was dried by filtration over anhydrous sodium sulphate, concentrated to about 5 ml in a rotary evaporator (water-bath at 30°C), then added to 5 ml of methanol. The final solution was concentrated to about 1 ml in a rotary evaporator. The residue was transferred to a volumetric flask and brought to volume (2–20 ml) with methanol.

Extraction from soil

The extraction solution (50 ml) was added to the soil and the mixture was shaken for 30 min on a mechanical shaker, then centrifuged at 3000 rpm for 5 min. The entire procedure was repeated three times on the same soil sample. The extracts were pooled, diluted in 60 ml water and extracted three times with dichloromethane (50 ml). The organic phase, dried by filtration over anhydrous sodium sulphate, was

evaporated to about 1 ml in a rotary evaporator (water-bath at 30°C). The residue was transferred to a volumetric flask and brought to volume with methanol (2–20 ml).

Determinations

A 10-μl methanolic sample solution was injected in the chromatographic column. The amounts in residues were determined by comparison with peaks obtained from known amounts of reference substances of appropriate concentrations. The separation conditions are given in Figs. 1 and 2.

RESULTS AND DISCUSSION

Extraction from water

The recovery of Fluazifop-butyl and Fluazifop from water appears to be satisfactory (Table I). The dichloromethane solution must not be evaporated to dryness because a loss up to 10% can occur. On the other hand, this solvent interferes with the chromatographic separation: a concentration greater than 5% causes deformation of the peak and reduction of the retention time of Fluazifop, making impossible its separation from interferences. The same effects are exerted on Fluazifop-butyl by higher concentrations (50%) of dichloromethane. A similar phenomenon was reported previously in the HPLC determination of dioxine[9]. It is probabily due to the good solubility of Fluazifop-butyl and Fluazifop in dichloromethane. This drawback was overcome by adding 5 ml methanol to the concentrated dichloromethane solution and evaporating the mixture to 1 ml so as to achieve almost complete removal of the dichloromethane. Addition of methanol prior to concentration proved ineffective in removing the dichloromethane.

Extraction from soil

The proposed methanol–1 *M* hydrochloric acid mixture[8] does not appear to be effective in extracting Fluazifop-butyl from soil. With this extractant, the recovery of Fluazifop-butyl spiked at levels of 0.1–10 ppm averaged 54 ±10.2%. No improvement was noted when 0.1 *M* hydrochloric acid was employed in the mixture. An extraction with methanol alone allowed the recovery of the Fluazifop-butyl not extracted by the mixture, thus indicating the higher effectiveness of the organic solvent.

TABLE I

RECOVERY OF FLUAZIFOP-BUTYL AND FLUAZIFOP FROM WATER

n = 3 in each case.

Spiking level (mg/l)	*Recovery (%) ± S.D.*	
	Fluazifop-butyl	*Fluazifop*
10	102.3 ±2.5	97.2 ±1.3
1	95.7 ±3.2	95.3 ±1.0
0.1	95.0 ±6.2	99.5 ±1.0

TABLE II

RECOVERY OF FLUAZIFOP-BUTYL AND FLUAZIFOP FROM SOIL

Extracting solution: methanol–1 *M* hydrochloric acid (9:1, v/v). $n = 4$ in each case.

Spiking level (mg/kg)	*Recovery (%) ± S.D.*	
	Fluazifop-butyl	*Fluazifop*
10	93.8 ±1.6	98.0 ±2.1
3	102.0 ±4.3	94.5 ±3.5
1	97.3 ±2.8	99.1 ±1.7
0.1	95.0 ±4.8	85.5 ±11.2

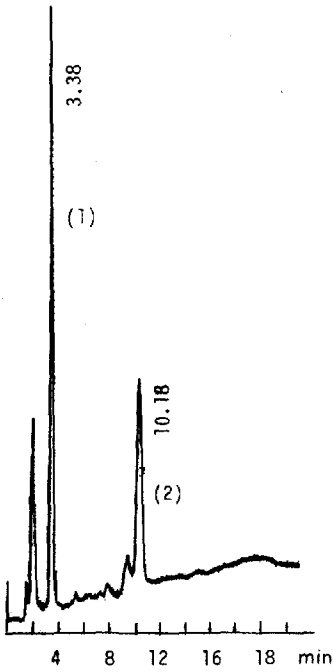


Fig. 1. Chromatogram of water extract spiked (1 mg/l) with Fluazifop-butyl (2) and Fluazifop (1). Wavelength: 270 nm. Flow-rate: 1.0 ml/min. Volume injected: 10 µl. Mobile phase: water acidified to pH 3 with orthophosphoric acid–acetonitrile (29:71, v/v).

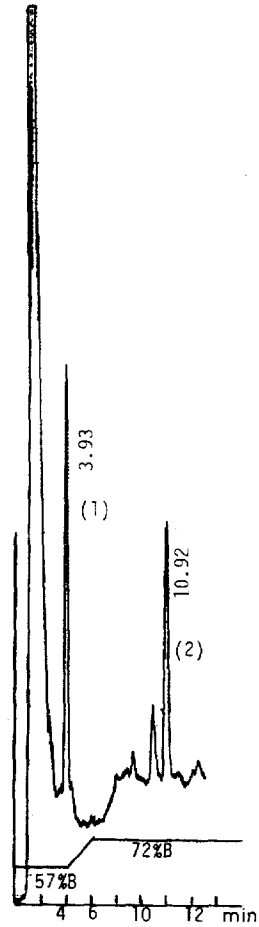


Fig. 2. Chromatogram of soil extract spiked (1 mg/kg) with Fluazifop-butyl (2) and Fluazifop (1). Flow-rate: 1.5 ml/min. Mobile phase: water acidified to pH 3 with orthophosphoric acid (A)–acetonitrile (B); gradient as indicated. Other details as in Fig. 1.

An extraction mixture enriched in methanol (90%) was therefore used with 10% of 1 *M* hydrochloric acid to prevent hydrolysis of Fluazifop-butyl, which is favoured by alkaline conditions. Also, since the undissociated form of Fluazifop is more stable under these conditions, its tendency to bind to soil components is presumably reduced and the recovery more complete. The proposed mixture yielded a good recovery of both Fluazifop-butyl and Fluazifop (Table II). It is advisable, as in the case of water, not to evaporate the extract to dryness. In this case, the addition of methanol prior to concentration is not necessary because the organic phase resulting from the liquid–liquid partitioning is enriched in the methanol used as extractant.

HPLC analysis

The determination of the compounds in the extracts from water can be carried out under isocratic conditions due to the low concentration of interfering substances (Fig. 1). For soil, a elution gradient must be used to achieve an effective separation of the peaks (Fig. 2). Under the described conditions the detection limit is 10 ng for both the ester and the acid (signal-to-noise ratio 2:1).

Fluazifop-butyl and Fluazifop have two absorbance maxima at 225 and 270 nm. The absorbance at 225 nm is twice that at 270 nm, but the latter wavelength was preferred owing to the lower effect of the interfering substances in the extracts from both water and soil. Under these conditions, clean-up of the extracts is not required.

ACKNOWLEDGEMENTS

This work was supported by grants from Regione Piemonte Assessorato Sanità and CNR.

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