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Note

Rapid high-performance liquid chromatographic method for determining trace levels of fluometuron in soil

J. D. MATTICE* and T. L. LAVY
Altheimer Laboratory, Department of Agronomy, University of Arkansas, Route 11, Box 83, Fayetteville, AR 72701 (U.S.A.)
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Crop production systems often involve rotations of species from year to year, replanting to a different crop, or double-cropping within the same year. Fluometuron [1,1-dimethyl-3-(α,α,α-trifluoro-*m*-tolyl)urea], commonly used as a pre-emergence herbicide for cotton, can be injurious to soybeans used as a replacement crop when cotton stands fail. A rapid method for analyzing residual concentrations of fluometuron and a knowledge of the threshold level for crop damage would give the producer an estimate of the influence which this herbicide could have in cotton fields replanted to soybeans or other sensitive crops.

There are several analytical methods for fluometuron from various sources[1–8]. Guth and Voss[1] reported a colorimetric procedure for fluometuron from soil; however, it is for the unchanged urea and the corresponding hydrolysis product. Analysis of the unchanged urea requires thin-layer chromatography to separate it from metabolites. A reversed-phase high-performance liquid chromatographic (HPLC) method is available for the separation of carbamates and ureas from each other and from some of their metabolites[2].

Many of the procedures available for analyzing fluometuron cannot be applied easily to a large number of samples per day because they involve extensive clean-up, large pieces of glassware, or Soxhlet extraction. The objective of this study was to develop a method for the rapid analysis of fluometuron residues in a large number of soil samples.

EXPERIMENTAL

Chemicals

Fluometuron (99.2%) was obtained from Ciba-Geigy (Greensboro, NC, U.S.A.). Working solutions of 0.3, 3.0, and 15 ppm were prepared by making appropriate dilutions of a 100-ppm stock solution in ethanol with deionized water. Propachlor (2-chloro-N-isopropylacetanilide) was obtained from Monsanto (St. Louis, MO, U.S.A.) and was used as a 50-ppm solution in 5% methanol in deionized water. The 20% saturated ammonium chloride was prepared by diluting saturated ammonium chloride (1:5). Diethyl ether was reagent grade and methanol and acetonitrile were HPLC grade.

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Apparatus

The extraction bottles were 175 ml square, linear polyethylene Nalgene® with polypropylene caps. The samples were filtered through 0.22-μm aqueous 13-mm diameter Millipore filters in a Swinney adapter fitted to a 10-ml syringe. The HPLC system consisted of a Waters Assoc. (Milford, MA, U.S.A.) Model 6000A solvent delivery system, Model 710A WISP, Data Module, Model 440 UV detector fixed at 254 nm, and a Radial Compression Module with a 5-mm I.D. Radial-Pak 10-μm C_8 cartridge. A wrist-action shaker operating at 3 to 4 shakes per sec and a N-Evap (Organomation Assoc., Northborough, MA, U.S.A.) were also used.

Sample preparation

The samples were fortified with fluometuron in a manner that put them through a wet–dry cycle to simulate the "aging process" which occurs under field conditions. Dry soil (30 g) was placed in a polyethylene bag, and the desired volume of fluometuron solution was applied in drops evenly over the soil. Additional water was added in the same manner to make a total of 4 ml of water added to the soil. The bags were closed, shaken by hand for *ca.* 10 sec at a rate of 2 to 3 shakes per sec, and then opened and allowed to dry. Each sample was extracted and analyzed within 4 days of fortification.

Extraction

The soil was placed in a 175-ml plastic bottle. Then 25 ml of 20% saturated aqueous ammonium chloride and 50 ml of ether were added in sequence. The cap was screwed on securely, and the bottle was shaken for 30 min on a wrist-action shaker. The bottle was removed, and the soil was allowed to settle into the aqueous layer. The ether layer was transferred to a 20 × 2.5 cm I.D. test tube by means of a disposable Pasteur pipet. (When 30 samples were to be run, the second fifteen were shaking while the ether layers were being removed from the first fifteen). The volume of ether was reduced to *ca.* 10 ml on a 35°C N-Evap under a stream of dry nitrogen. The sample was extracted with two additional 50-ml portions of ether in the same manner with the ether portions being combined and reduced in volume. After the third extraction the ether was completely removed by evaporation. An internal standard of 2 ml of 50-ppm propachlor in 5% methanol in water was added, followed by 1 ml of methanol. The sides of the test tube were washed down with the solution by means of a Pasteur pipet, and the tube was placed in a warm water bath for 5 min with occasional swirling. The sample was filtered into a sample vial through a 0.22-μm Millipore filter in a Swinney adapter and analyzed by HPLC.

Chromatography

The injection volume was 40 μl. The sample was eluted with a mixture of acetonitrile–water (30:70) at a flow-rate of 2 ml/min. The retention times were 9.3 min for fluometuron and 12.0 min for propachlor.

RESULTS AND DISCUSSION

The results are given in Table I. Typical chromatograms of blanks and soil samples fortified at 0.02 and 0.1-ppm fluometuron in soil are shown in Fig. 1. The

TABLE I

RECOVERY OF FLUOMETURON FROM LORING AND CROWLEY SILT LOAMS

Soil	*ppm in soil*	*Recovery ± S.D. (%)**
Crowley	0.00	nd**
	0.02	88 ± 4
	0.10	91 ± 3
	0.50	91 ± 1
	1.00	91 ± 7
Loring	0.00	nd
	0.02	114 ± 13
	0.10	91 ± 2
	0.50	91 ± 5
	1.00	94 ± 2

* Seven replicate samples were analyzed at each concentration for each soil type.
** Not detected.

limit of detection was 0.02 ppm for both soil types. The 91 % recovery was the same for both soils at concentrations of 0.1–1.0 ppm in soil. The only difference in the results for the two soil types was at the lowest concentration of fluometuron (0.02 ppm in soil). The higher percentage recovery and larger standard deviation for the Loring soil at this level indicated higher and more varied background interferences. However, there was a difference in the results for the blank soil and the soil that was fortified at the 0.02-ppm level.

The method has limits of detection comparable to or better than most fluometuron techniques in the literature; it is simple and adaptable to running a large number of samples per day. One person can quickly learn to perform analyses of fifteen samples per day and after becoming more familiar with the procedure can analyze as many as 30 samples per day. This ability to analyze soil samples rapidly is important to farmers using rotational or double-cropping systems or those who wish to replant during the same season.

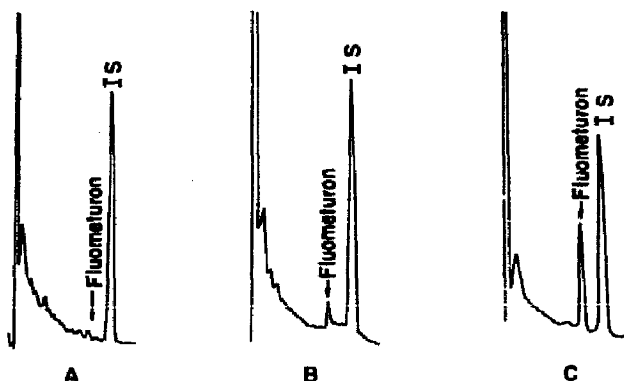

Fig. 1. Chromatograms of soil samples fortified with fluometuron. A, blank; B, 0.02 ppm in soil; C, 0.1 ppm in soil. The retention times for fluometuron and the internal standard (IS) are 9.3 and 12.0 min, respectively.

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REFERENCES

1 J. A. Guth and G. Voss, *Weed Res.*, 11 (1971) 111–118.
2 C. F. Aten and J. B. Bourke, *J. Agr. Food Chem.*, 25 (1977) 1428–1430.
3 A. H. Hofberg, L. C. Heinrichs, V. M. Barringer, M. Tin and G. A. Gentry, *J. Ass. Offic. Anal. Chem.*, 60 (1977) 716–719.
4 H. Buser and K. Grolimund, *J. Ass. Offic. Anal. Chem.*, 57 (1974) 1294–1299.
5 W. P. Cochrane and B. P. Wilson, *J. Chromatogr.*, 63 (1971) 364–369.
6 J. F. Lawrence and G. W. Laver, *J. Agr. Food Chem.*, 23 (1975) 1106–1109.
7 F. S. Tanaka and R. G. Wien, *J. Chromatogr.*, 87 (1973) 85–93.
8 W. H. Gutenmann and D. J. Lisk, *J. Gas Chromatogr.*, 4 (1966) 424–425.