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Short Communication

Determination of diclofop-methyl and diclofop residues in soil and crops by gas chromatography

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ABSTRACT

A method is described for the determination of residues of the herbicide diclofop-methyl and its metabolite, diclofop, in soil and crops. The residues were extracted with acetone–light petroleum and extracts were concentrated (diclofop was derivatized to its pentafluorobenzyl derivative), and then the products were purified on a chromatographic column containing alumina, silver–alumina and Florisil. Finally, they were determined by gas chromatography using an electron-capture detector. The detection limits of diclofop-methyl and diclofop were between 0.01 and 0.05 mg/kg. The average recoveries were 76.4–97.2% and 72.8–105.2%, respectively, making the method suitable for statutory residue testing purposes.

INTRODUCTION

The selective grass herbicide diclofop-methyl (I), methyl 2-[4-(2,4-dichlorophenoxy)phenoxy]propionate, is the active ingredient of the product Illoxan [1–4]. It is rapidly hydrolysed in the environment to the corresponding acid, diclofop (II), 2-[4-(2,4-dichlorophenoxy)phenoxy]propionic acid [5,6].

Most methods for the determination of diclofop-methyl and diclofop have been developed for water, soil and plant analyses or for formulations, and gas chromatography (GC) and high-performance liquid chromatography (HPLC) are most often used. Diclofop-methyl in formulations can be determined by HPLC [7], but if residue levels are to be detected, *e.g.*, in waters, soils and plants, several GC and HPLC methods [8,9] have been reported. Analysis of soil for diclofop-butyl and diclofop by

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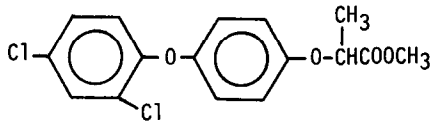

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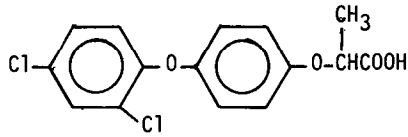

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GC using electron-capture detection (ECD) has also been reported [10]. The determination of diclofop residues in plants has not been reported. As diclofop-methyl undergoes relatively rapid hydrolysis to the free acid, it is necessary to have methods available for the determination of Diclofop residues in plant and grain.

The procedure developed here for the determination of diclofop-butyl and diclofop residues in soil, leaves of wheat and sugar beet, wheat grain and sugar beet root involves (a) acetone–light petroleum extraction; (b) filtration and concentration; (c) derivatization of diclofop to its pentafluorobenzyl derivative; (d) clean-up on a chromatographic column containing alumina, silver–alumina and Florisil; and (e) GC–ECD. This work is part of a wider study on the movement and degradation of diclofop-methyl and diclofop in Chinese agrosystems [11].

EXPERIMENTAL

Reagents and materials

Light petroleum (b.p. 68–70°C) and other solvents used were of analytical-reagent grade (Hangzhou Oil Refining Plant and Shanghai Chemical Reagent Plant). A pure standard of diclofop-methyl (99.0%) was supplied by Hoechst (Frankfurt/M, Germany). Diclofop was obtained by refluxing Diclofop-methyl for 3 h in 3 *M* sodium hydroxide solution containing sufficient acetonitrile to dissolve the compound. The purity of diclofop was checked by thin-layer chromatography (TLC) and UV and IR spectroscopy. Pentafluorobenzyl bromide was kindly supplied by PCR Research.

Neutral alumina, (200–300 mesh) (Shanghai Wu Si Chemical Reagent Plant) was heated at 500°C for 3 h, cooled to 50°C, mixed with 8 g of water per 100 g and stored in air-tight containers overnight. Silver–alumina was obtained by adding 10 g of neutral alumina (containing 8% of water) a mixture of silver nitrate (0.75 g), water (0.75 g) and acetone (4 ml) and shaking until no smell of acetone remained. Florisil (120–160 mesh) (Floridin, Berkeley Springs, WV, USA) was heated at 650°C for 3 h, cooled to 50°C, mixed with 2 g of water per 100 g and stored in a desiccator overnight.

The samples of soil, leaves of wheat and sugar beet, wheat grain and sugar beet root were obtained by Zhejiang Agricultural University.

Apparatus

A chopper, ultrasonic bath, shaker, water-bath, vacuum pump, 500-ml separating funnels, Kuderna–Danish evaporators and chromatographic columns (15 cm × 1 cm I.D.) for clean-up were used for the sample pretreatment. The GC system consisted of a Shimadzu Model GC-7A gas chromatograph, an ECD-7 nickel-63 electron-capture detector and a C-R1B integration system.

Standard solutions

Stock standard solutions (0.1 g/l) of diclofop-methyl and diclofop in light petroleum were prepared. Working standard solutions were obtained by suitable dilution with light petroleum and stored at 0°C. Fresh solution were prepared every 3 months.

Procedure

After chopping, a representative sample of 10 g was weighed into a 250-ml conical flask.

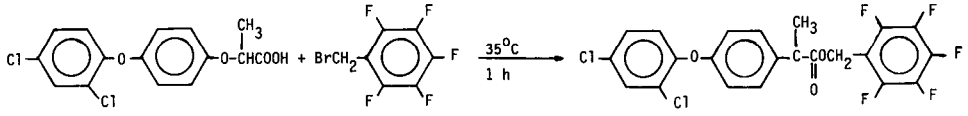
Extraction of diclofop-methyl. Add 100 ml of acetone–light petroleum (1:1) and 2 g of Celite, place the flask in an ultrasonic bath filled with sufficient water and sonicate for 30 min.

Extraction of diclofop. Add 10 ml of 4 *M* hydrochloric acid and 60 ml of acetone–light petroleum (2:1), place the flask in an ultrasonic bath filled with sufficient water and sonicate for 30 min.

Filtration. Filter the extract through a Büchner funnel fitted with a filter-paper (prewashed with 10 ml of acetone) and transfer the filtrate into a 500-ml separating funnel. Add 100 ml 2% sodium sulphate solution and 50 ml of light petroleum (for extraction of diclofop, add 60 ml of chloroform) and shake. Discard the aqueous layer and wash the organic layer with 50 ml of 2% sodium sulphate solution and 40 ml of 2% sodium carbonate solution.

Dry the organic layer by filtration through 10 g of anhydrous sodium sulphate into a Kuderna–Danish evaporator and concentrate the extract to 5 ml (for the determination of diclofop, concentrate the extract to dryness).

Derivatization of diclofop. Add 2 ml of 2% pentafuorobenzyl bromide in acetone and three drops of triethylamine to the dry residue. Mix and heat at 35°C in waterbath for 1 h in the dark. The reaction is as follows:



After cooling in ice, add 50 ml of light petroleum and transfer the mixture into a 500-ml separating funnel. Wash the product with 50 ml of 1% hydrochloric acid and then 70 ml of 2% sodium sulphate solution. Transfer the organic phase into a Kuderna–Danish evaporator and concentrate it to 50 ml at 40°C.

Clean-up. Prepack a chromatographic column as described in Tables I and II and prewash the column with 10 ml of light petroleum. Add the sample extract and allow the solvent to settle and run off at the rate of 90–100 drops/min. Elute the

TABLE I

COLUMNS AND ELUENTS FOR CLEAN-UP OF DICLOFOP-METHYL

Sample	Column	Eluent	Volume collected (ml)
Soil	2 g anhydrous Na_2SO_4, 15 g neutral Al_2O_3	50 ml acetone–light petroleum (1:99)	40
Leaves of wheat and sugar beet	2 g anhydrous Na_2SO_4, 15 g neutral Al_2O_3, 2g Ag–Al_2O_3	80 ml acetone–light petroleum (1:99)	50
Wheat grain and sugar beet root	2 g anhydrous Na_2SO_4, 10 g neutral Al_2O_3, 5 g Florisil	80 ml acetone–light petroleum (0.7:99.3)	50

products from the column using the solvents and collecting volumes listed in Tables I and II. Finally, concentrate the collected liquid to 10–50 ml using a Kuderna–Danish evaporator at 40°C.

Determination by GLC–ECD. A glass column (1.6 m × 7.0 mm O.D. × 3.2 mm I.D.) packed with 2% OV-17 on Chromosorb W DMCS (60–80 mesh) was used. The oven temperature was 215°C and the injector and detector temperatures 260°C. The carrier gas was nitrogen at a flow-rate of 60 ml/min and the injection volume was 1 μl.

RESULTS AND DISCUSSION

Under the above chromatographic conditions the chromatograms shown in Figs. 1 and 2 were obtained.

The linearity of ECD was checked by injecting 2-μl aliquots of diclofop-methyl and diclofop (pentafluorobenzyl ester) standard solutions with concentrations ranging from 0.01 to 21.0 mg/l and 0.008 to 46.0 mg/l, respectively. The regression equations for peak area *vs.* amount injected were C (mg/l) $= 0.0041 + 8.59 \cdot 10^{-6} A$ (μV s) ($r = 0.9997$) and C(mg/l) $= 0.0029 + 7.51 \cdot 10^{-6} A$($\mu$V s) ($r = 0.9984$), respectively. The minimum detectable amount of both standards (signals-to-noise ratio = 4) was 0.02–0.016 ng per injection.

TABLE II

COLUMNS AND ELUENTS FOR CLEAN-UP OF DICLOFOP

Sample	Column	Eluent	Volume collected (ml)
Soil	2 g anhydrous Na_2SO_4, 10 g Florisil	70 ml acetone–light petroleum (2:98)	60
Leaves of wheat and sugar beet	2 g anhydrous Na_2SO_4, 2 g neutral Al_2O_3, 8 g Florisil	30 ml acetone–light petroleum (2:98) and 60 ml (1:99)	70
Wheat grain and sugar beet root	2 g anhydrous Na_2SO_4, 4 g neutral Al_2O_3, 8 g Florisil	120 ml acetone–light petroleum (2:98)	80

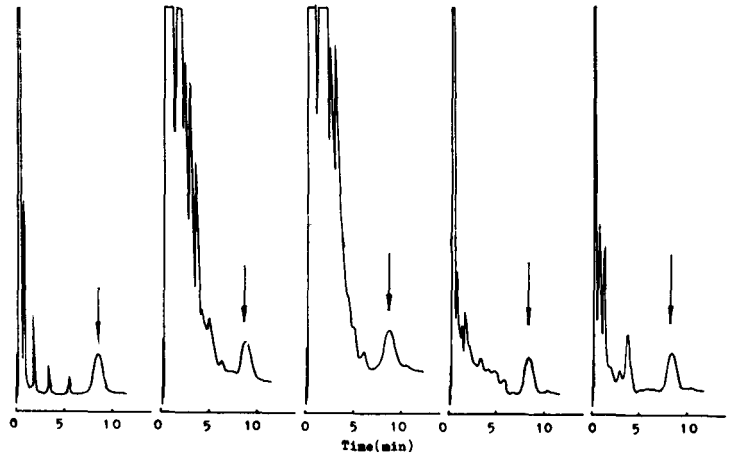


Fig. 1. Chromatograms of diclofop-methyl residues in soil and crops. Residual level in samples, 0.10 mg/kg; final volume, 20 ml; injection volume, 1 μl; detection current, 2.0 nA; range, 10; attenuation, 4.

The detection limits (for real samples) were calculated by using the following equation:

$$\text{Detection limit (mg/kg)} = \frac{\text{minimum detectable amount (ng)}}{\text{injection volume } (\mu l)} \cdot \frac{\text{final volume (ml)}}{\text{sample weight (g)}}$$

The results for various samples are given Table III.

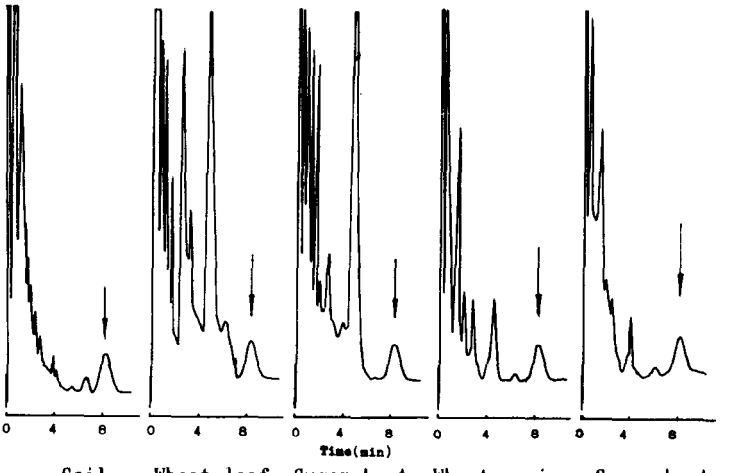


Fig. 2. Chromatograms of diclofop (pentafluorobenzyl ester) residues in soil and crops. Conditions as in Fig. 1.

TABLE III

DETECTION LIMITS FOR VARIOUS SAMPLES

Sample	Detection limit (mg/kg)	
	Diclofop-methyl	Diclofop
Soil	0.01	0.02
Wheat leaf	0.05	0.05
Sugar beet leaf	0.05	0.05
Wheat grain	0.03	0.04
Sugar beet root	0.04	0.04

The recoveries and precisions for diclofop-methyl and diclofop in various samples at three residual levels appeared to be satisfactory (Table IV).

In the study, the detection limit of diclofop as its pentafluorobenzyl ester in soil was 0.02 mg/kg compared with 0.05 mg/kg obtained by Johnstone *et al.* [10] for the methyl ester. The efficiency of conversion of diclofop to its pentafluorobenzyl ester at the 0.10-, 0.36- and 0.72-μg levels was more than 90%.

The average recoveries for diclofop-methyl and diclofop in soil were 88.8% and 76.2%, respectively, which is consistent with the results cited by Schwalbe *et al.* [12] and Johnstone *et al.* [11]. The precisions of the procedure for various samples were satisfactory, the standard deviations being less then 15%.

In conclusion, the described method has high sensitivity and gives high recoveries. It is now used routinely in our laboratory for studies on the movement and degradation of diclofop-methyl and diclofop in Chinese agrosystems and for statutory chemical confirmation of their residue levels in wheat grains and sugar beet. We have found it to be equally suitable for other vegetables and soybean samples.

TABLE IV

RECOVERIES FOR VARIOUS SAMPLES IN A STANDARD ADDITION TEST

Sample	Amount added (mg/kg)	Recovery ± S.D. (%) ($n=5$)	
		Diclofop-methyl	Diclofop
Soil	0.10	86.9 ± 12.7	77.2 ± 7.6
	0.36	95.5 ± 7.1	76.4 ± 10.1
	0.72	83.9 ± 5.4	75.1 ± 9.7
Wheat leaf	0.10	84.8 ± 11.2	78.9 ± 7.0
	0.36	86.5 ± 8.3	79.2 ± 15.5
	0.72	93.3 ± 4.1	90.7 ± 9.8
Sugar beet leaf	0.10	76.4 ± 5.7	78.9 ± 7.2
	0.36	84.6 ± 6.8	80.1 ± 8.1
	0.72	89.3 ± 4.6	81.1 ± 16.9
Wheat grain	0.10	79.2 ± 10.4	72.8 ± 6.6
	0.36	81.0 ± 2.8	103.4 ± 8.8
	0.72	84.6 ± 9.3	105.2 ± 7.7
Sugar beet root	0.10	97.2 ± 8.6	78.5 ± 14.9
	0.36	87.5 ± 6.4	75.8 ± 9.0
	0.72	79.3 ± 7.0	77.3 ± 8.2

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