Short Communication

Gas chromatographic method for the determination of anilophos in soil

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ABSTRACT

The gas chromatographic determination of anilophos was studied using four different detectors and it was found that flame photometric and nitrogen–phosphorus detection (NPD) were more sensitive than flame ionization and electron-capture detection. The method was extended to the determination of anilophos residues in soil using NPD. The recoveries of anilophos from soil with ethyl acetate (95–102%) were significantly higher than those with dichloromethane (80–88%) and methanol (44–49%).

INTRODUCTION

Anilophos [(S-4-chlorophenyl-N-isopropylcarbaniloylmethyl) O,O-dimethylphosphorodithioate] (Fig. 1) is a recently introduced herbicide which effectively controls grassy and some broad-leaved weeds in rice (*Oryza sativa*) crops [1,2] either alone [3–5] or as a mixed herbicide [6,7]. There is, however, no information available on the persistence of this herbicide in soil or on methods for its detection.

This paper presents a gas chromatographic (GC) method for the determination of anilophos. The method is simple and sensitive and is conveniently used for the detection of the herbicide at microgram levels. Further, the technique was extended to the determination of residues of the herbicide in soils to evaluate its persistence in the agro-ecosystem.

EXPERIMENTAL

Preparation of standards

Anilophos (90%, technical) obtained from Gharda Chemicals (Bombay, India) was recrystallized from benzene–hexane before use. Distilled analytical-reagent grade acetone, hexane, ethyl acetate, methanol and dichloromethane were used. Anhydrous sodium sulphate was used as a drying agent for soil samples.

Anilophos (25 mg) was dissolved in hexane–acetone (8:2) in a 25-ml volumetric flask and diluted to volume to give a 1000 μg/ml stock solution. A 1-ml volume of this stock solution was diluted to volume in a 100-ml volumetric flask with the same solvent mixture to give a 10 μg/ml stock standard solution of anilophos. Solutions of different concentrations were pre-
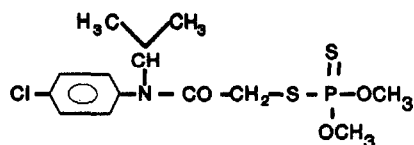
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Fig. 1. Anilophos.

pared by diluting this stock standard solution. A 3-μl volume of each sample was injected accurately. The method was quantitatively validated by running solutions of 0.01, 0.02, 0.05, 0.1, 0.2, 0.5, 1.0, 2.0, 5.0 and 10.0 μg/ml of anilophos. Each run was performed in duplicate and the detector response was measured in terms of peak area.

Calibration of instruments

Hewlett-Packard Model 5890A and 5890 Series II, Varian Model 3400 and Nucon Model 5700 gas chromatographs were used. The detectors, columns, packing materials and other chromatographic conditions used were as given in Table I.

Extraction of anilophos from soil

The soil was a sandy loam with a composition of 19% clay, 21% silt, 60% sand and 0.35% organic carbon and had a pH of 7.2. The

recovery of anilophos was checked at three different concentrations, each replicated three times. A 10-g amount of dried and sieved soil was fortified with anilophos separately at 1, 5 and 10 μg/g. Three different solvents (methanol, dichloromethane and ethyl acetate) were used separately for the extraction of soil.

The soil was extracted with 50 ml (25 + 15 + 10) of solvent by shaking on a wrist-action shaker for 0.5 h each time, filtered and then passed through anhydrous sodium sulphate (3 g). The extract was evaporated to dryness on a rotary evaporator at 35–40°C. The residue was dissolved in hexane–acetone (8:2) to make a solution of 0.5 ppm. A 3-μl volume of the extract was injected and chromatographed. This was preceded by the injection of a standard solution of known concentration.

The concentration of analyte in the extracted sample of soil was calculated by comparing the peak area of the sample with that of the standard using the equation

$$C = A \cdot RF$$

where C is the concentration of anilophos, A is the area of the peak corresponding to anilophos in the extract and RF (response factor) is the concentration of standard/area of standard.

TABLE I

OPERATING CONDITIONS OF DIFFERENT GC INSTRUMENTS

Model	Detection method	Column	Packing material	Temperature (°C)			Carrier gas (nitrogen) flow-rate (ml/min)
				Oven	Injector	Detector	
Hewlett-Packard 5890A	ECD	Coiled glass, 2 m × 2 mm I.D.	3% OV-25	270	300	300	46
Varian 3400	ECD	As above	As above	270	300	300	46
Hewlett-Packard 5890A	FID	Megabore, 10 m × 0.53 mm I.D.	OV-17	250	250	250	34
Nucon 5700	NPD	Coiled glass, 2 m × 2 mm I.D.	3% OV-25	260	270	280	40
Hewlett-Packard 5890-II	FPD	Megabore, 10 m × 0.53 mm I.D.	HP-1	230	250	250	20

RESULTS AND DISCUSSION

Anilophos could be resolved as a single, sharp peak using a gas chromatograph equipped with detectors for either electron-capture (ECD), nitrogen–phosphorus (NPD), flame photometric (FPD) or flame ionization (FID) detection (Table I). The maximum sensitivity of 0.06 ng of anilophos was obtained by GC–FPD using a megabore column. Next in sensitivity were ECD and NPD, both with detection limits of 0.6 ng of anilophos. Both of these instruments had coiled glass columns. FID exhibited the lowest sensitivity (300 ng). FID was therefore considered suitable for macro analysis of anilophos whereas the other three detection methods were suitable for microanalysis. The better sensitivity of FPD than ECD and NPD could be due to the presence of the more efficient megabore column (HP-1, Table I).

It was observed during bulk analysis of anilophos samples by GC–ECD that the results obtained on the following day were erratic and irreproducible when the same anilophos solutions were injected. It appeared that with continued use anilophos was deposited in the detector, making it unfit for further analysis. This observation was recorded on both the Hewlett-Packard and Varian instruments. ECD was therefore considered unsuitable for the determination of anilophos residues in soil. This erratic behaviour was not observed with NPD or FPD, with which a solution of 0.02 μg/ml anilophos was clearly resolved and a large number of soil extracts could be analysed continuously over several days without losing reproducibility.

The calibration graphs obtained by plotting concentration *versus* average peak area (each sample injected in duplicate) were linear over the range 0.02–10 μg/ml with both FPD and NPD. However, for the simultaneous determination of anilophos and its degradation products, NPD was finally selected and the conditions standardized.

After optimizing the GC conditions (Tables I and II), the method was extended to the determination of anilophos residues in soil. There was no interfering peak in the soil blank (Fig. 2). Of the three solvents used for extraction

TABLE II

RETENTION TIME AND SENSITIVITY OF ANILOPHOS IN GC WITH DIFFERENT DETECTION METHODS

Other conditions are as given in Table I.

Detection	Retention time (min)	Sensitivity (ng)
FID	1.69	300
ECD	3.78	0.6
NPD	6.30	0.6
FPD	2.72	0.06

(methanol, dichloromethane and ethyl acetate), ethyl acetate gave the highest and quantitative recoveries (95–102%) from soil (Table III). The limit of determination of anilophos in soil was 1 μg/g.
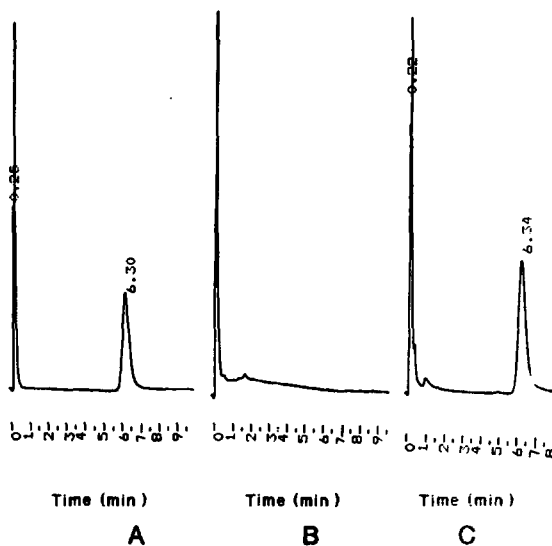
Fig. 2. Gas chromatograms of anilophos: (A) standard solution; (B) blank soil; (C) treated soil.

TABLE III

RECOVERY OF ANILOPHOS FROM SOIL USING DIFFERENT SOLVENTS

Results are averages of three replicates.

Soil sample	Solvent used for extraction	Concentration of anilophos in soil (μg/g)		Retention time (min)	Average recovery (%)
		Added	Found		
Control	Methanol	–	–	–	–
Treated		1	0.485	6.30	48.5 ± 0.8
Treated		5	2.175	6.31	43.5 ± 0.5
Treated		10	4.500	6.30	45.0 ± 1.0
Control	Dichloromethane	–	–	–	–
Treated		1	0.880	6.30	88.0 ± 0.9
Treated		5	4.005	6.29	80.1 ± 0.7
Treated		10	7.990	6.31	79.9 ± 1.1
Control	Ethyl acetate	–	–	–	–
Treated		1	1.018	6.34	101.8 ± 0.5
Treated		5	4.845	6.30	96.9 ± 0.4
Treated		10	9.460	6.31	94.6 ± 1.4

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