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## Note

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### Rapid simultaneous determination of residues of MCPA, mecoprop and MCPB in soil by gas chromatography of the pentafluorobenzyl ester

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The monochlorinated phenoxyalkanoic acids are widely used in agriculture as herbicides for the control of broad leaved weeds in cereals and other crops. Specific detectors such as microcoulometric, electrolytic conductivity or electron capture give only a low response to these compounds. This has led to the preparation of many derivatives particularly those with enhanced electron-capture response. Bache *et al.*<sup>1</sup> have prepared nitro compounds while Mattinen *et al.*<sup>2</sup> have brominated the herbicides. However, reactions involving ring substitutions have two disadvantages. Firstly reaction conditions need to be carefully controlled to avoid the formation of more than one isomer and secondly, since the derivatives are insufficiently volatile to chromatograph as acids, they must then be esterified. Esterification with a reagent containing an electron capturing group can achieve both objects at once. Mierza and Witek<sup>3</sup> and Gutenmann and Lisk<sup>4</sup> have used halogenated alkyl esters while Chau and Terry<sup>5</sup> have prepared the pentafluorobenzyl (PFB) esters. Halomethyldimethylsilyl derivatives have also been used<sup>6</sup>.

These methods while increasing the response to the herbicide have the disadvantage that they increase the background by producing derivatives of co-extractants from the soil. This is usually overcome by a clean-up procedure which is time consuming and multiplies the opportunity for error because of the large number of manipulations.

In this work an extraction method is used that produces a sufficiently low background after pentafluorobenzylation that a clean-up is not normally necessary.

## MATERIALS AND METHODS

### *Soils*

Soils from two locations were used. Table I gives some details of the composition of these soils. Both soils were air dried and passed through a 3-mm sieve prior to fortification with herbicide.

### *Soil fortification*

Aqueous solutions of the sodium salts of MCPA, mecoprop and MCPB were prepared so that when sufficient solution was added to the dry soils to achieve field

TABLE I  
SOME PROPERTIES OF THE TWO SOILS USED

	Soils	
	1	2
Organic carbon (%)	1.6	4.1
pH	7.0	5.1
Clay (%)	16	16
Silt (%)	11	16
Sand (%)	73	68
Field capacity (moisture, %)	16.6	27.0

capacity, the concentration was 1.0 or 0.1 ppm acid equivalent. All samples were prepared in triplicate and allowed to stand for 48 h before extraction.

#### Extraction

A 10-g amount of the soil was shaken with 25 ml of 0.25 *M* sulphuric acid and 10 ml of toluene for 1 h in a 50-ml stoppered centrifuge tube using a reciprocating flat-bed shaker. After shaking the tube was centrifuged at 1500 *g* for 5 min and the supernatant liquid decanted into a test tube.

#### Esterification

The method used was that of Chau and Terry<sup>5</sup>. An aliquot of the upper toluene layer was evaporated to dryness in a test tube by blowing with a gentle stream of dry air while warming the tube in a water bath at 50°. The residue was dissolved in 4 ml of acetone and 30  $\mu$ l of 30% potassium carbonate in water and 200  $\mu$ l of 1% PFB bromide in acetone were added. Contents of the tube were mixed thoroughly and allowed to stand. After 3 h, 10 ml of water and 5 ml of toluene were added and the tube shaken vigorously for 30 sec. The esters partitioned into the toluene layer and after suitable dilution 5- $\mu$ l aliquots of this layer were injected into the chromatograph.

#### Preparation of standards

A solution of the herbicides as acids was prepared containing 1 mg of each herbicide in 100 ml of methanol. Aliquots of this solution were taken through the esterification procedure to give standards with concentrations of 0.01 ng/5  $\mu$ l to 0.2 ng/5  $\mu$ l.

#### Chromatography

A Pye chromatograph fitted with a <sup>63</sup>Ni electron-capture detector and a 1.5 m  $\times$  4 mm I.D. glass column was used for estimation of the esters. The conditions employed were: column packing, 5% SE-30 on Chromosorb W HP (80–100 mesh); carrier gas, oxygen-free nitrogen at 50 ml/min; temperatures, column 200°, injector 250°, detector 350°; attenuation 10  $\times$  10<sup>2</sup>; pulse time 150  $\mu$ l.

Injections were made by using a Pye S4 Autojector and peak areas measured with an Infotronics CRS 108 digital integrator. Logarithmic graphs of peak area vs. amount (ng) were linear for the three herbicides in the range 0.01 to 0.2 ng injected. Under these conditions the PFB esters elute with retention times of 276, 134 and 624 sec for MCPA, mecoprop and MCPB, respectively.

## RESULTS AND DISCUSSION

Table II shows recoveries from both soils at both levels of fortification.

Fig. 1 shows the response from (a) untreated soil (b) soil fortified at 0.1 ppm and (c) a standard solution of the three herbicides PFB esters. The figure shows the low background response without clean-up.

The limit of detection based on a response of approximately twice the background signal was 0.05 ppm.

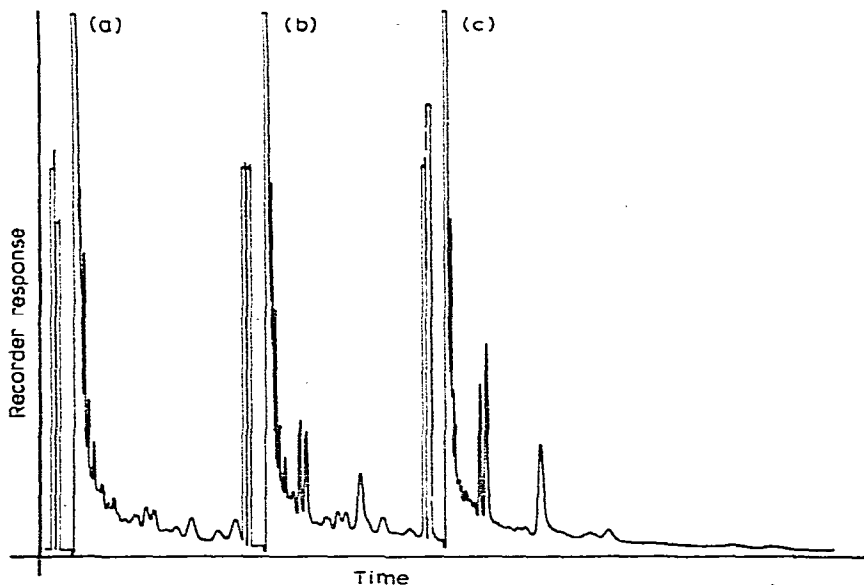


Fig. 1. Chromatograms of PFB esters. (a) Untreated soil extract, (b) soil treated at 0.1-ppm extract, (c) standard solution of herbicide PFB esters.

TABLE II

RECOVERY OF HERBICIDES FROM FORTIFIED SOILS

Soils	Fortification (ppm)	Mean recovery (%) $\pm$ SD		
		MCPA	Mecoprop	MCPB
1	0.1	90 $\pm$ 3.5	85 $\pm$ 8.3	86 $\pm$ 3.3
	1.0	100 $\pm$ 5.6	102 $\pm$ 2.5	93 $\pm$ 2.9
2	0.1	80 $\pm$ 3.5	102 $\pm$ 8.3	72 $\pm$ 2.9
	1.0	107 $\pm$ 0.9	102 $\pm$ 6.4	85 $\pm$ 2.5

During development of the extraction method several other solvent systems were tried. The methods of Kahn<sup>7</sup>, Gutenmann and Lisk<sup>4</sup> and Bache *et al.*<sup>6</sup> which use acidified acetone gave an unsatisfactory background response after pentafluorobenzoylation as did that of Abbott *et al.*<sup>8</sup> which uses diethyl ether and 3 M sulphuric acid. Sattar *et al.*<sup>9</sup> evaluated several methods of extraction for MCPA and achieved good recovery with a satisfactory background using diethyl ether-acetone-hexane-

heptane (2:1:1:1) although a clean-up was necessary. However, it was less efficient than toluene-sulphuric acid in extracting residues from the soils studied here.

Table III summarizes these methods using the recovery of mecoprop to indicate the efficiency of extraction.

TABLE III

## AVERAGE RECOVERIES OF MECOPROP FROM SOIL USING DIFFERENT EXTRACTION METHODS

a = Acceptable, u = unacceptable.

Reference	Extractant	Background	Recovery (%)
	Toluene-H <sub>2</sub> SO <sub>4</sub>	a	98
6	Acetone-H <sub>2</sub> SO <sub>4</sub>	u	60
7	Acetone-HCl	u	60
8	Diethyl ether-H <sub>2</sub> SO <sub>4</sub>	u	40
	Diethyl ether-acetone-hexane-heptane	a*	80

\* Includes clean-up.

Experiments aimed at further reducing the background signal showed it was essential to extract the 30% K<sub>2</sub>CO<sub>3</sub> solution with toluene since some peaks of coincident retention time to mecoprop PFB ester occurred if this step was left out.

Sattar *et al.*<sup>9</sup> found that the optimum time for esterification of MCPA was 3 h while Chau and Terry<sup>5</sup> found that no further derivatization occurred after 5 h. In this work 3 h was selected because additional peaks appeared after longer periods while peak height of standards did not increase after this time whether in the presence of soil extract or in pure solution.

The procedure described is rapid, reproducible and simple to use and gives good recovery for all three herbicides at the 0.1-ppm level.

## ACKNOWLEDGEMENTS

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