Determination of 3,6-Dichloropicolinic Acid Residues in Soil by Gas Chromatography of the 1-Butyl Ester

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INTRODUCTION

The herbicide 3,6-dichloropicolinic acid may be estimated in soil by the method of Pik & Hodgson (1976) which involves extraction with M NaCl followed by gas chromatography of the methyl ester. The percentage recovery obtained by this method is dependent on soil type and some samples analysed in this laboratory have given unacceptably high background response.

Since 3,6-dichloropicolinic acid is similar to picloram, the method developed previously for picloram by McKone and Cotterill (1974) was examined. This method, like that of Pik and Hodgson, uses diazomethane for methylation. However, the methyl ester of 3,6-dichloropicolinic acid is sufficiently volatile for losses to occur during the final concentration step. This report shows how the difficulty can be overcome by preparing the 1-butyl ester.

MATERIALS AND METHODS

Soils

Three soils were used (Table I). Soils 1 and 2, were sandy loam soils and soil 3 was an organic sandy loam. All soils were air dried and passed through a 3 mm sieve prior to fortification.

TABLE I

Soil Properties

Soil	1	2	3
% Organic Carbon	1.6	4.1	25
pH	7.0	5.1	5.9
Field capacity (% moisture)	16.6	27.0	38.9

Soil fortification

Aqueous solutions of the herbicide were added to the dry soil so that, when sufficient solution had been added to the soil to

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achieve field capacity, the concentration was 1.0, 0.1 or 0.05 ppm. Samples were prepared in triplicate at all levels and allowed to stand for 24 h before extraction.

Extraction

10g wet soil was allowed to stand overnight with 1g calcium hydroxide and 50ml distilled water prior to shaking for 1 hour on a wrist action shaker. After shaking the soil slurry was left to settle and the supernatant liquid was filtered through a fluted Whatman No. 42 filter paper. A 25ml aliquot of the filtrate was transferred to a separating funnel and sufficient 2M H_2SO_4 added to adjust to below pH2. The acidified extract was shaken with two 25ml portions of chloroform containing 5% ethanol (Cheng, 1971). The chloroform layers were combined and transferred to a 100ml flask through a funnel containing about 2g sodium sulphate supported by a wad of non-adsorbent cotton-wool. The filter was rinsed with 10ml of chloroform. A glass still head was fitted to the flask and the solution concentrated to about 2ml under reduced pressure on a water bath at 50°C. The residual solution was transferred to a stoppered test tube, the flask was rinsed twice with 2ml chloroform, and the rinses added to the test tube. The contents of the tube were evaporated to dryness using a gentle stream of dried air whilst warming the tube in a water bath.

Esterification

The method used was that of McKone and Hance (1972). The residue in the test tube was dissolved in 1ml of 1-butanol, three drops of concentrated sulphuric acid were added and the tube stoppered and placed in a boiling water bath for 30 min. After cooling, 20ml of water and 5ml of hexane were added and the tube shaken vigorously. An aliquot of the organic phase was suitably diluted for chromatography.

Chromatography

A Pye 104 gas chromatograph fitted with a ^{63}Ni electron capture detector and a 1.5m x 4mm i.d. glass column packed with 2% OV17 on 80/100 mesh Chromosorb W(HP) was used to estimate the ester. The conditions employed were:

Injector temperature: 250°C. Attenuation: 10×10^2.

Column temperature: 195°C. Carrier gas: O_2free nitrogen at 40ml min^{-1}.

Detector temperature: 300°C. Detector mode: 150µs pulsed.

Injection volume: 5µl.

Standards were prepared from analytically pure acid and taken through the butylation procedure. A graph of log peak height vs. log ng of herbicide was linear for standards ranging from 0.02 ng/5µl to 0.2 ng/5µl. Under these conditions the ester elutes with a retention time of 2 min 12s.

RESULTS AND DISCUSSION

Table II shows the recovery of the herbicide from the three soils.

TABLE II

Recovery of 3,6-dichloropicolinic acid from soil.

Soil	Fortification (ppm)	Mean Recovery (%)	Standard error (±)
1	1.0	96.7	0.8
	0.1	92.3	1.4
	0.05	93.7	1.1
2	1.0	91.3	0.9
	0.1	93.1	1.2
	0.05	93.8	2.0
3	1.0	94.7	2.0
	0.1	96.6	3.3
	0.05	94.8	3.0

With the soils investigated recovery seems to be independent of soil type or organic matter content. An overnight soak was included in the extraction since Pik and Hodgson showed that it increased recovery using their extraction procedure. Table III shows that inclusion of the soak had little effect on the recovery of 3,6-dichloropicolinic acid from freshly fortified soil but it did increase the recovery of residues from soil treated five months before extraction.

TABLE III

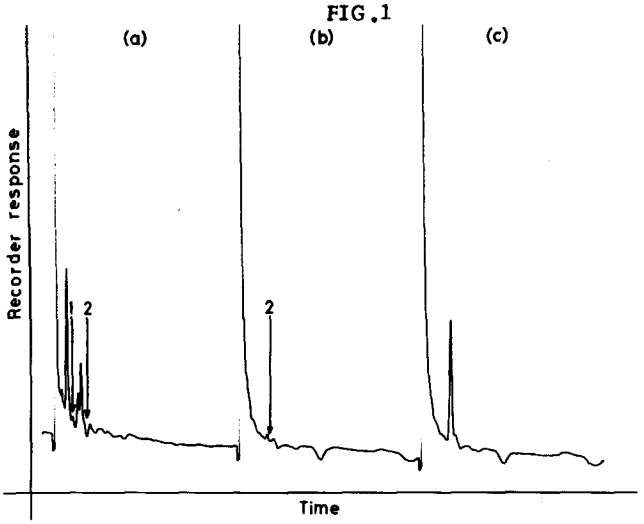
Residues (ppm) in soil (a) with overnight soak, and (b) without soak.

	a	b
Freshly fortified soil	0.047	0.046
Residue after 5 months	0.046	0.037

Use of the butyl ester has several advantages over the methyl ester. Losses due to the volatility of the methyl ester are eliminated, toxic reagents are no longer required and the 1-butyl ester elutes from the glc column with a retention time that does not coincide with that of the coextractants from the soils studied.

Standards were prepared by taking the free acid through the butylation procedure since, though reproduceable, the yield of 1-butyl ester was only 90% (S.E. ± 1.3). Taking the limit of detection as the amount of herbicide which produces a response of twice the background signal gives a limit of 0.005 to 0.01 ppm depending on the soil extracted.

FIG.1



Gas chromatograms of extracts of soil (3). (a) control (Pik and Hodgson extraction methylated). (b) control (proposed method). (c) fortified at 0.05 ppm (proposed method).

The gas chromatograms shown in Fig. 1 clearly show the reduction in background obtained with the method reported here which make a cleanup unnecessary. Arrowed on Fig. 1 are (1) retention time of the methyl ester and (2) retention time of butyl ester.

CONCLUSION

Although this method gives similar limits of detection and recoveries to that of Pik and Hodgson, the reduced background and introduction of the less volatile ester gives it some advantage especially for soils with high organic matter content with their associated high background response.

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