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THE DETERMINATION OF SOME SUBSTITUTED UREA HERBICIDE RESIDUES IN SOIL BY ELECTRON-CAPTURE GAS CHROMATOGRAPHY

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SUMMARY

A method is described for the direct determination of eight substituted urea herbicides at the 0.1 to 1.0 p.p.m. level in soil using electron-capture gas chromatography. Residues of linuron were determined at 0.1, 0.5 and 1.0 p.p.m. in three soils of different organic matter content. Benzomarc, chlorbromuron, diuron, fluometuron, metobromuron, metoxymarc and neburon were determined at 0.1 and 1.0 p.p.m. in a single soil. The mean recovery for linuron was 88%. The recoveries obtained for the other seven herbicides ranged from 73 to 104%.

INTRODUCTION

Methods for the analysis of substituted urea herbicide residues in soil have been reported using a variety of techniques. Some methods involve hydrolysis of the herbicide to produce an aniline derivative which is determined colorimetrically after diazotisation and coupling to produce an azo dye[1–3]. Thin-layer chromatography has been used to measure residues of several urea herbicides in soil[4]. Other workers have used gas chromatography to measure aniline derivatives after hydrolysis of the herbicide[5,6]. Halogenated aniline derivatives have been used to improve the sensitivity and specificity of residue determinations using electron-capture gas chromatography[7,8]. More recently the gas chromatography of twelve unchanged substituted urea herbicides has been described[9]. Eight of these compounds containing either three fluorine, two chlorine or one bromine atom were considered suitable candidates for residue methods based on their measurement by direct electron-capture gas chromatography. This paper describes a method for the determination of linuron residues in soil that is also suitable for benzomarc, chlorbromuron, diuron, fluometuron, metobromuron, metoxymarc and neburon in soils.

EXPERIMENTAL

Materials

The following herbicides were evaluated:

Benzomarc	N-benzoyl-N-(3,4-dichlorophenyl)-N',N'-dimethylurea
Chlorbromuron	N-(4-bromo-3-chlorophenyl)-N'-methoxy-N'-methylurea
Diuron	N'-(3,4-dichlorophenyl)-N,N-dimethylurea
Fluometuron	N'-(3-trifluoromethylphenyl)-N,N-dimethylurea
Linuron	N'-(3,4-dichlorophenyl)-N-methoxy-N-methylurea
Metobromuron	N'-(4-bromophenyl)-N-methoxy-N-methylurea
Metoxymarc	N'-(3,4-dichlorophenyl)-N-(4-methoxybenzoyl)-N',N'-dimethylurea
Neburon	N-butyl-N'-(3,4-dichlorophenyl)-N-methylurea

Some properties of the soils are listed in Table I.

TABLE I

CHARACTERISTICS OF SOILS

Source	*Parent material*	*Texture*	*% organic carbon*	*% clay (<0.002 mm)*	*pH in water (1:2.5)*	*Cation exchange capacity (mequiv./100 g)*
Hollow (Weed Res. Org.)	Calcareous gravel	Sandy loam	1.9	15.6	7.1	11
Trawscoed	Alluvium from greywacké	Silty clay loam	3.7	32.6	6.2	12
Helmshore	Boulder clay	Clay loam	12	6.6	6.3	18

Fortification of the soil

Aqueous solutions were prepared containing 2.5, 12.5 and 25 μg herbicide in 2.5 ml. Solutions of neburon were prepared in 10% methanol to overcome its low water solubility. Portions of 25 g of air dry soil were weighed into shallow 7-cm aluminium dishes and 2.5 ml of aqueous herbicide solution was added with a pipette uniformly over the surface of the soil. The fortified soil now containing approximately 9% moisture was allowed to air dry naturally and was extracted after an interval of one

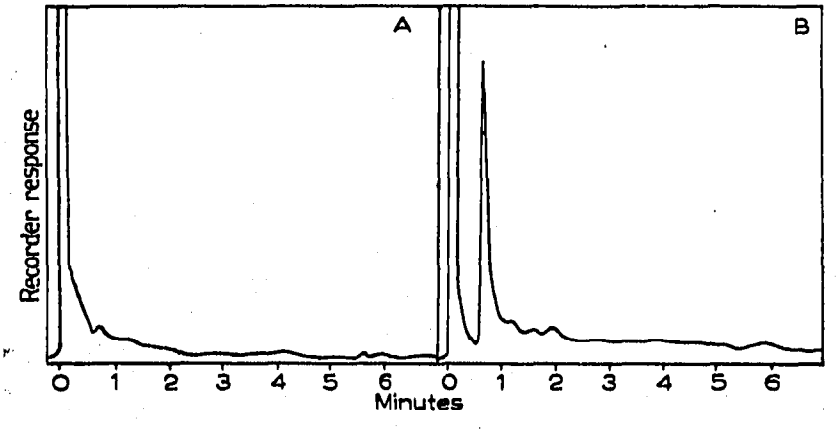

Fig. 1. Chromatogram of (A) control Hollow soil and (B) control Hollow soil fortified with 1 p.p.m. linuron.

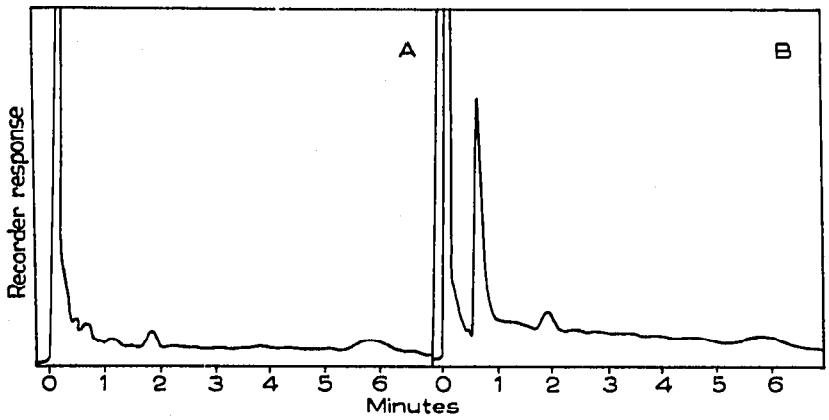

Fig. 2. Chromatogram of (A) control Trawscoed soil and (B) control Trawscoed soil fortified with 1 p.p.m. linuron.

week. The soil was mixed with a spatula once during this time to facilitate drying. The average moisture content of the 'air dry' soil at the time of extraction was 1.2, 2.2 and 3.3% for Hollow, Trawscoed and Helmshore respectively.

Extraction procedure

Air dried soil (25 g) was placed in a stoppered 250-ml conical flask with 50 ml of re-distilled methanol and shaken on a wrist-action shaker for 1 h. After shaking, the soil slurry was allowed to settle and the supernatant liquid was filtered through a fluted Whatman No. 1 filter paper into a stoppered tube. As soon as 10 to 15 ml of filtrate had been collected, the filter funnel was removed and the tube was stoppered to prevent evaporation. A 5-ml aliquot was transferred with a pipette to a 100-ml stoppered conical flask, a clean glass bead was added and the solution was concentrated to about 0.5 ml under reduced pressure in a water bath at 50°. The flask was then taken from the water bath and the remaining methanol removed with a gentle stream of dry air. The residue was dissolved in 5 ml of redistilled 2,2,4-trimethylpentane; 0.5 g of anhydrous sodium sulphate was added and the flask was stoppered and shaken vigorously for 1 min. Aliquots of this solution were taken for gas chromatography.

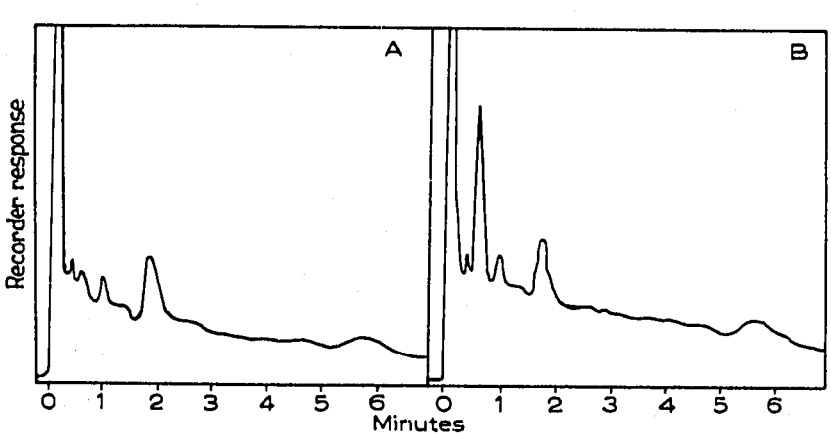

Fig. 3. Chromatogram of (A) control Helmshore soil and (B) control Helmshore soil fortified with 1 p.p.m. linuron.

matography

. Varian Aerograph 1520 gas chromatograph was used fitted with the electron- detector previously described in detail[9]. The Aerograph electron-capture r was not found to be suitable. The performance of other electron-capture rs has not been evaluated but it seems probable that any design that includes its specification will not be suitable.

The operating conditions were as follows: Column, 1.5 m × 3.5 mm O.D. stainless cked with 5% E301 (methyl silicone) on 60–80 mesh Gas-Chrom Q; flow rate, nin oxygen-free nitrogen; injector temperature, 265°; column temperature, 240° used for fluometuron), detector temperature, 200°; detector voltage, 90 V nsitivity, × 1; attenuation, 4 and 8; recorder, Leeds and Northrup Speedomax art speed, 30 in./h.

The ends of the column were packed with steel wool that had been washed with . A stainless steel injector insert was fitted and injections were made with the the needle just entering the column. It is essential to exclude glass from the and to adhere strictly to the conditions described[9].

tion standards

olutions of herbicides containing 1 mg/ml were prepared in re-distilled meth- Using a Hamilton syringe, 50 μl of the solution was transferred to a 100-ml etric flask and diluted to volume with re-distilled 2,2,4-trimethylpentane. This n, containing 2.5 ng herbicide in 5 μl was diluted with 2,2,4-trimethylpentane a range of standards containing 0.1–1.0 ng herbicide in 5 μl. The graph of log eight *vs.* log nanograms herbicide was essentially linear for each compound over ge 0.1 ng to 1.0 ng. The 2,2,4-trimethylpentane solutions obtained from extracts soil were diluted where necessary so that the standard injection volume of 5 μl ed a herbicide concentration within the calibration range.

E II

COVERY OF LINURON FROM THREE SOILS FORTIFIED WITH THREE HERBICIDE CONCENTRA-

	Amount added (p.p.m.)	*Amount found (p.p.m.)*	*% recovery*	
			Mean	*S.D.*
	0	0.05	—	—
	0.1	0.08[a]	80	3.1
	0.5	0.43	86	0.0
	1.0	0.79	79	1.7
oed	0	0.08	—	—
	0.1	0.10	100	11.7
	0.5	0.52	104	4.0
	1.0	0.91	91	1.7
ıore	0	0.30	—	—
	0.1	0.08	80	16.2
	0.5	0.38	76	5.3
	1.0	0.94	94	6.9

[a] Corrected for blank values.

RESULTS

In Tables II and III the recoveries given are based on three replicates at each level.

TABLE III

THE RECOVERY OF SEVEN SUBSTITUTED UREA HERBICIDES FROM TRAWSCOED SOIL FORTIFIED WITH TWO HERBICIDE CONCENTRATIONS

Herbicide	*Amount added (p.p.m.)*	*Amount found (p.p.m.)*	*% recovery*	
			Mean	*S.D.*
Benzomarc	0	0.06	—	—
	0.1	0.07[a]	70	4.6
	1.0	0.77	77	4.6
Chlorbromuron	0	0.03	—	—
	0.1	0.08	80	29.5
	1.0	0.84	84	12.3
Diuron	0	0.03	—	—
	0.1	0.08	80	9.7
	1.0	0.86	86	6.7
Fluometuron	0	0.02	—	—
	0.1	0.10	100	10.4
	1.0	0.90	90	3.5
Metobromuron	0	0.06	—	—
	0.1	0.08	80	3.5
	1.0	0.73	73	8.0
Metoxymarc	0	0.06	—	—
	0.1	0.09	90	15.0
	1.0	0.99	99	16.0
Neburon	0	0.04	—	—
	0.1	0.09	90	9.1
	1.0	1.04	104	7.6

[a] Corrected for blank values.

The method developed for linuron was applied to seven other substituted urea herbicides and determinations were made on Trawscoed soil fortified with 0.1 and 1.0 p.p.m. herbicide.

Samples of Hollow soil fortified with approximately 1 p.p.m. linuron were stored for two years and analysed during storage. The results are shown in Table IV.

DISCUSSION

Three soils of widely different organic matter content were chosen in order to test the method with soils likely to produce different background responses. The method of extraction was primarily developed for linuron and extraction experiments were first carried out on soil fortified with this herbicide. Dichloromethane, methanol,

TABLE IV

THE ANALYSIS OF HOLLOW SOIL FORTIFIED WITH LINURON AND STORED FOR TWO YEARS
(A) Stored air dry; (B) stored deep frozen (−10°) (14% moisture).

Date	*Amount linuron found (p.p.m.)*	
	A	*B*
23. 1.67	1.12	1.12
2.10.67	1.11	1.13
21. 2.69	0.97	1.03

acetone and dichloromethane containing 10% acetone or 10% methanol were evaluated as extraction solvents by shaking 25 g of field treated soil with 50 ml of solvent for 1 h and overnight for 16 h. Of these solvents, methanol gave the highest recovery of linuron with the lowest background from coextracted material. Extraction with methanol for 1, 2 and 3-h periods showed that increased recoveries were not obtained by shaking for more than 1 h. Extraction of linuron from moist soil (14 to 16% moisture) with methanol gave low recoveries but on mixing the soil with its own weight of anhydrous sodium sulphate before extraction, recoveries were similar to those obtained with dry soil.

Fortification of the soil with herbicides in volatile solvents immediately prior to extraction gave consistent recoveries of around 100% but using the fortification method adopted for this work, lower recoveries were generally obtained. It is therefore considered important to leave an interval of at least one week or longer after fortifying a soil before attempts are made to measure extraction efficiency. The results in Table IV illustrate the storage stability of soil samples containing linuron. In Table II the mean recoveries differed somewhat between levels and between soils. The standard deviation of the linuron recoveries tended to rise with increasing soil organic matter. Some of the variations obtained in the recovery experiments may be due in part to the difficulty of selecting a method for reproducibly fortifying soils with herbicides that bears a reasonable resemblance to practical field application procedures. Since replicate injections of linuron standards gave a coefficient of variation of 5.1%, some of the variations in the recoveries may be assigned to the final measurement and probably reflect the chromatographic instability of this compound.

In Table III the standard deviations have been calculated at both levels for each of the seven herbicides. Some of these figures, *e.g.* for chlorbromuron and metoxymarc, are high in comparison with those for linuron, but the method may not be ideal for all of the herbicides tested as it was basically developed for linuron. However, it is likely that only minor modifications would be necessary to establish satisfactory procedures for these herbicides. It cannot be judged whether the standard deviations obtained in this work are typical of those obtained by other workers for herbicide residue methods, since standard deviations for recoveries at individual levels are rarely if ever quoted in the literature.

Linuron, diuron, neburon and metoxymarc were not resolved from each other on the 5% E301 column and it would be necessary to confirm the identity of residues of unknown origin by an alternative technique. Thin-layer chromatography meth-

ods[4,10,11] would probably be suitable. In order to improve the sensitivity of the method a clean-up procedure would be required particularly for very high organic matter soils. The analyses reported in this work were obtained without clean-up. The minimum detectable linuron concentration in all three soils was considered to be 0.05 p.p.m. The minimum detectable levels of diuron, fluometuron, neburon, metoxymarc and benzomarc were slightly lower than 0.05 p.p.m. because of the greater sensitivity of the electron-capture detector to these compounds[9].

The method has been in routine use for over two years in this laboratory, analysing soil samples for linuron residues. Soil samples from the field are sieved, subsampled and allowed to air dry naturally. They are stored at room temperature while awaiting analysis.

This method has considerable advantages over existing methods for estimating some substituted urea herbicides in soil. The extraction from the soil is simple and rapid and final measurement is made of the original herbicide. It avoids the preliminary separations often required to distinguish the original molecule from aniline derivatives that may also be present in the soil.

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