Journal of Chromatography, 107 (1975) 407–410

CHROM. 8148

Note

Method for determining trace quantities of the herbicide chlortoluron in soils by liquid chromatography

ALLAN E. SMITH* and K. A. LORD
Rothamsted Experimental Station, Harpenden, Herts. (Great Britain)
(Received December 23rd, 1974)

The herbicide chlortoluron —N-(3-chloro-4-methylphenyl)-N'-dimethylurea— is used as a pre- and post-emergence herbicide, applied at rates of up to 4.5 kg/ha, for the control of grasses and broad-leaved weeds in winter cereal crops.

Two principal methods have been developed for analysing substituted urea herbicide residues in soils. The first involves hydrolysis of the extracted chemicals to produce an aniline which is then determined colorimetrically[1–3]. The second procedure, which is more rapid and specific, entails direct gas chromatography (GC) of the unchanged residues. This latter method has recently been extensively reviewed[4]. However, in our experience the GC method is not satisfactory for chlortoluron, which contains only one chlorine atom per molecule and does not give a large response with electron-capture detectors.

Liquid chromatography (LC) is increasingly used for analysing trace amounts of various compounds, including herbicides[5]. The following procedure was developed for the routine extraction and LC estimation of chlortoluron residues from soils.

EXPERIMENTAL

Materials

Table I shows the composition and properties of the soils used in these studies.

Technical-grade chlortoluron was obtained from Ciba–Geigy, Agrochemical Division (Cambridge, Great Britain) and recrystallised from a mixture of acetone and *n*-hexane to a constant melting point of 148°. A solution was prepared containing 0.5 mg chlortoluron per ml in methanol.

For the column clean-up procedure, *n*-hexane was glass-distilled and the silica gel (100–200 mesh) was of chromatographic grade.

Soil treatment

To 40-g samples of the sieved air-dried soils in 250-ml capacity screw-capped glass bottles were added 200 or 80 μl of solution, containing 100 or 40 μg chlor-

* Currently on sabbatical leave from Agriculture Canada, Research Station, Regina, Sask. S4P 3A2, Canada.

TABLE I

SOIL CHARACTERISTICS

Soil	*% clay*	*% silt*	*% sand*	*% organic matter*	*pH in water (1:1)*
Rothamsted, silty loam	20	65	15	1.5	7.0
Woburn, sandy loam*	14	14	72	6.0	6.8
Barnfield, silty clay loam	35	22	43	1.2	7.5

* With added peat.

toluron, to give soil concentrations of 2.5 or 1.0 μg/g herbicide. In addition, samples of Rothamsted and Woburn soils were treated with 20 μl solution (10 μg chlortoluron) to give 0.25 μg/g herbicide, whilst the Barnfield soil was fortified at the 0.5 μg/g level with 40 μl (20 μg) of the chemical. After mixing to ensure distribution of the chlortoluron throughout the soil samples, the bottles were kept at room temperature for at least 48 h, to equilibrate, before extraction and analysis. There were four replicates for each soil type and herbicide concentration.

Extraction procedure

Air-dried soil (40 g) was placed in a glass-stoppered 250-ml flask with 100 ml methanol and shaken for 1 h on a wrist-action shaker. The soil slurry was then filtered using suction through a Whatman No. 1 filter paper and an 80-ml aliquot, corresponding to 32 g of the air-dried soil, was evaporated to dryness at 55° using a rotary evaporator. When all the solvent had been removed the residue was further heated under vacuum for 10 min at 55° and then extracted by shaking vigorously with 4.0 ml *n*-hexane. The hexane extract was transferred to a 5-ml glass-stoppered tube and 3-μl aliquots taken for liquid chromatographic analysis.

Silica gel clean-up procedure

The residue, following evaporation of the methanolic extract as above, was shaken with 5, 2, 2 and finally 1 ml of hexane and the combined extracts were transferred to a column packed with 10 g silica gel. The column was eluted with 200 ml of a solution containing 2% 2-propanol, in hexane, to remove interfering soil material. Any chlortoluron was eluted with 100 ml of a 2-propanol–*n*-hexane mixture (1:3). This eluate was evaporated to dryness using the rotary evaporator and the residue shaken with three 5-ml portions of hexane. The combined *n*-hexane extracts were evaporated to dryness in a 20-ml capacity flask and any chlortoluron present was dissolved in 1.0 ml hexane, 3-μl samples being taken for analysis.

Liquid chromatographic analysis

The chromatograph used was constructed at Rothamsted Experimental Station and had a variable-wavelength ultraviolet detector, with a 1-cm light path and 10-μl cell capacity. The absorbance was measured at 240 nm, the absorption maximum of chlortoluron. The 20 cm × 4 mm stainless-steel column was packed with Merckosorb SI 60 having a 10-μm particle size. The eluting solvent was *n*-hexane containing 15% (by volume) of 2-propanol at a flow-rate of 1.1 ml/min under a pressure of 480 lb./sq. in. At room temperature the retention time for chlortoluron was 3.7 min.

Samples were injected as *n*-hexane solutions and concentrations of chlortoluron calculated by comparison of peak heights with those of appropriate standards. The standard curve was linear over the range 5–80 ng.

RESULTS AND DISCUSSION

Typical liquid chromatograms obtained from 3 μl of a standard solution containing 8 ng/μl of chlortoluron, and from 3 μl of hexane extracts from untreated Rothamsted silty loam and the same soil fortified at the 1.0 μg/g level are shown in Fig. 1. Although the chlortoluron was not completely separated from the background soil extract, elution with 15% 2-propanol in *n*-hexane through the Merckosorb column did provide sufficient separation for quantitative measurements. Decreasing the proportion of 2-propanol in the eluting solvent broadened the chlortoluron peak and reduced sensitivity without markedly improving the separation from material extracted from the soil.

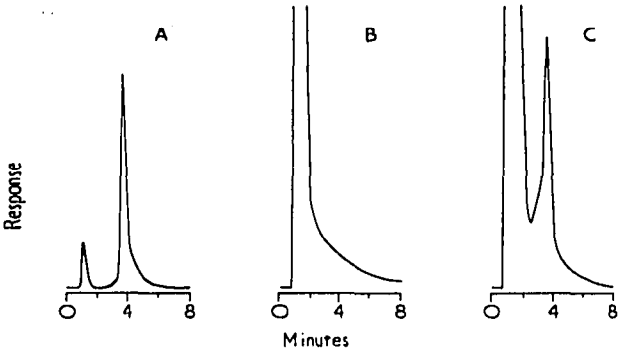

Fig. 1. Liquid chromatograms from (A) 3 μl standard solution containing 24 ng of chlortoluron, (B) 3 μl extract from control Rothamsted clay loam, and (C) 3 μl extract from control Rothamsted clay loam fortified with 1 ppm chlortoluron.

More than 85% of the added chlortoluron was consistently recovered from the treated Rothamsted and Woburn soils at all three concentrations (Table II) without recourse to the silica gel clean-up procedure. Recovery from Barnfield silty loam was less, but still greater than 70% and very reproducible (Table II). Despite the imperfect separation of chlortoluron from the tailing band of material extracted from the soil (Fig. 1), the extracts from untreated control soils did not contain substances which would interfere with the determination of chlortoluron at the 0.25-ppm level with the Rothamsted and Woburn soils, and at the 0.5-ppm rate with the Barnfield silty clay loam.

A more extensive preliminary separation of the co-extracted UV absorbing materials from the chlortoluron-soil extracts permitted greater concentration of the extract with increased herbicide sensitivity. Thus, using the silica gel column clean-up procedure the limits of assay were 0.1 ppm for Rothamsted and Woburn soils and 0.2 ppm for the Barnfield silty clay loam, with reproducible recoveries of 77, 73 and 64%, respectively.

TABLE II

PERCENTAGE RECOVERY OF CHLORTOLURON FROM FORTIFIED SOILS

Soil	*Added (ppm)*	*Found (ppm)*	*Recovery* (%)*	
			Mean	*Standard deviation*
Rothamsted, silty loam	2.5	2.23	89	3.8
	1.0	0.95	95	1.5
	0.25	0.22	86	3.8
Woburn, sandy loam	2.5	2.25	90	3.5
	1.0	0.85	85	2.4
	0.25	0.21	85	5.5
Barnfield, silty clay loam	2.5	1.78	71	2.5
	1.0	0.73	73	1.7
	0.5	0.37	74	1.4

* Average of four replicate samples.

Under the chromatographic conditions described the peaks for the commonly used area herbicides diuron and monuron (retention times 4.2 and 5.0 min) overlap that of chlortoluron (retention time 3.7 min). The method can therefore only be used for the quantitative assay of chlortoluron in the absence of diuron and monuron, which are also extracted from soils by methanol[6].

ACKNOWLEDGEMENT

We thank Mr. J. J. B. Tinkler for his assistance.

REFERENCES

1 W. E. Bleidner, H. M. Baker, M. Levitski and W. K. Lowen, *J. Agr. Food Chem.*, 2 (1954) 476.
2 R. Bock, W. Berndt and S. Gorbach, *Z. Anal. Chem.*, 198 (1963) 235.
3 S. E. Katz, *J. Ass. Offic. Anal. Chem.*, 49 (1966) 452.
4 W. P. Cochrane and R. Purkayastha, *Toxicol. Environ. Chem. Rev.*, 1 (1973) 137.
5 J. A. Schmit, in J. J. Kirkland (Editor), *Modern Practice of Liquid Chromatography*, Wiley, New York, 1971, p. 398.
6 C. E. McKone, *J. Chromatogr.*, 44 (1969) 60.