Determination of Terbacil in Soil by Gas-Liquid Chromatography with ^{63}Ni Electron Capture Detection

S. U. Khan
Chemistry and Biology Research Institute
Canada Agriculture, Ottawa, Ontario
Canada K1A OC6

Terbacil, 3-tert-butyl-5-chloro-6-methyluracil, is used for weed control in crops such as sugar cane, citrus, pineapples, peppermint, apples and peaches. Application at the rate of 4.48 kg/ha may result in its persistence in some soils for more than one year (GARDINER et al. 1969). PEASE (1968) developed a method for the determination of terbicil residues in a variety of substrates. The procedure made use of programed temperature microcoulometric gas chromatography and has the sensitivity of about 0.04 ppm with an average recovery of better than 90% (based on a 25 g sample). Radium-226 electron capture (EC) detection of terbacil has been described by GUTENMANN and LISK (1968) and the method has a sensitivity of 0.5 to 1.0 ppm with recoveries ranging from 78 to 98% (based on a 25 g soil sample). The procedure involves evaporative co-distillation for isolation of the herbicide residue.

The two methods described above (PEASE 1968; GUTENMANN and LISK 1968) involve time consuming steps in the extraction, isolation and cleanup of the herbicide residue. Furthermore, under the gas chromatographic conditions described terbacil gave a peak with a retention time of about 13 - 15 min. A relatively faster method, with an improved sensitivity and reproducibility, was desired for determining terbacil residues in soils. While the availability of ^{63}Ni EC detector has facilitated the work of pesticide residue analysis in many laboratories, determination of terbacil residues using this detector has not been attempted.

This report describes a method applied to the determination of terbacil residue in soil using a ^{63}Ni EC detector. The method has a sensitivity of 0.01 ppm based on 20 g soil sample. The procedure described here has been applied successfully to field treated soil containing different amounts of organic matter. The extraneous materials from the latter which interferred with electron capture detection were effectively removed by column cleanup.

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Materials and Methods

Chemicals. All solvents were pesticide grade and used as received. Anhydrous sodium sulfate (reagent grade) was heated at 300°C for 24 hr and stored in dessicator. Florisil (60-100 mesh, PR grade) was activated at 130°C for 4 hr and stored in dessicator. Terbacil reference standard (99% pure) was supplied by E.I. du Pont de Nemours & Co., Inc., Wilmington, Del., 0.1 μg/ml in hexane.

Apparatus. (a) Gas chromatograph. - Pye series 104, Model 74 fitted with ^{63}Ni electron capture detector and 150 x 0.4 cm i.d. coiled glass tube packed with 1.5% XE-60 coated on 80-100 mesh Chromosorb W(HP). Operating conditions: flow rate (ml/min) - nitrogen 40, purge 5; temperatures (°C) - column 200, injector 200, detector 290; detector operated in pulse mode at 150 μsec and at amplifier attenuation of 10×10^{-10} amp.

(b) Recorder.- Fisher Recordall, series 500; chart speed 0.5 inch/min.

(c) Chromatographic column.- 30 x 1.9 cm i.d. glass tube with a fritted disk.

(d) Gas chromatograph.- mass spectrometer (GC-MS). - A Finnigan Model 3100D quadrupole mass spectrometer with electron impact ion source, equipped with venting system and glass jet separator to interface with gas chromatographic column. GC condition: glass column 150 cm x 0.4 cm i.d. packed with 3% OV-17 coated on 80-100 mesh Chromosorb W (HP), column temperature 215°C, helium carrier flow 35 ml/min. The mass spectrum were recorded at 70 ev on Zeta, series 100 printer/plotter.

Preparation and Fortification of Sample. The soil was air-dried at room temperature, pulverized, screened through a 20-mesh screen, and mixed thoroughly by tumbling. The sample (20 g, oven-dry basis) was fortified with terbacil at 0.1, 0.05, and 0.01 ppm levels. The soil was mixed thoroughly and the solvent was allowed to evaporate.

Extraction. Twenty g of soil (oven-dry basis) was shaken in a 250 ml glass stoppered Erlenmeyer flask with 100 ml of 1.5% NaOH solution for 1 hr on a mechanical shaker. The soil suspension was transferred into a 250 ml centrifuge bottle and the flask rinsed with two 25 ml portions of 1.5% NaOH solution. The sample was centrifuged at 2000 rpm for 15 min and the supernatant liquid decanted through glass wool (pre-washed with ethyl acetate) into a 500 ml separatory funnel. The soil residue in centrifuge bottle was shaken vigorously twice with 50 ml of 1.5% NaOH solution and each time centrifuged as before. The supernatant liquids were combined with the content of the separatory funnel and the aqueous solution was extracted with 75 ml of ethyl acetate. This step was repeated with two more 75 ml portions of ethyl acetate. The ethyl acetate extracts were filtered through 5 cm anhydrous Na_2SO_4 in a round bottom flask and combined. The solvent was evaporated to a small volume using a flash evaporator. The last 1-2 ml were removed with a jet of dry filtered air. The aqueous phase was discarded.

Florisil Chromatography. Ten g Florisil was placed onto the chromatographic column. The column was topped with 1 cm anhydrous Na_2SO_4 and prewashed with 100 ml hexane. The residue was dissolved in the round bottom flask in about 2 ml hexane, mixed and added to column. This step was repeated several times. The column was eluted with 200 ml of 5% ethyl acetate in hexane and the eluate discarded. Then the column was eluted with 200 ml of ethyl acetate, the eluate was collected in a round bottom flask, dried with anhydrous Na_2SO_4 and finally evaporated to a small volume under reduced pressure on rotating evaporator. The last 1-2 ml were removed with a jet of dry filtered air. The residue was dissolved in hexane and the solution was diluted to required volume with hexane to give suitable concentration of GLC injection.

Analysis. An aliquot (1-5 µl) of the sample and standard solution was injected into gas chromatograph operated as described under apparatus. Terbacil present was determined by comparing peak height with standard solution of about same peak height.

To obtain mass spectrum, an aliquot of the sample solution containing approximately 0.5 - 1 µg of the herbicide was injected onto chromatographic column of GC-MS. To confirm identity of the terbacil peak in the sample (retention time - 3.8 min, OV-17), its mass spectrum was compared with that of pure terbacil injected on the chromatographic column of GC-MS in the same manner.

Results and Discussion

Under the gas chromatographic conditions described terbacil requires 1.9 ng for a peak height of 100 mm with a retention time of 3.5 min. The response of the ^{63}Ni EC detector was linear in the range of 0.05 to 2.25 ng and the least detectable amount of terbacil (2 x noise level) was 1.02×10^{-12} g/sec.

Sample chromatograms of check and field treated soils are shown in Fig. 1. The compound extracted from the treated soils (GC peak with retention time of 3.5 min) was identified by comparing its retention time and mass spectra with that of reference standard and by co-chromatography. A GC-MS of the compound showed a molecular ion $M^{+\cdot}$ at m/e 216, a chlorine isotopic $M^{+\cdot} - 2$ ion, an intense $M^{+\cdot} - 55$ ion and a less abundant $M^{+\cdot} - 56$ ion, as well as other characteristics $M^{+\cdot} - 15$, $M^{+\cdot} - 97$

and $M^{+\cdot}$ - 98 ions. This fragmentation pattern was similar to that of authentic terbacil.

Terbacil extracted from soil containing high organic matter (Bookton loam, Table 1) did not completely separate on the gas chromatograph from an interferring peak with a retention time of 3.15 min (Fig. 1 a,c). However, cleanup column removed the interferring peak from the extract (Fig. 1 b,d). The first eluting solvent (5% ethyl acetate in hexane) also removed some of the other coextracted peaks. A comparison of the gas chromatograms of extracts from the field treated soil samples, with and without cleanup, demonstrate the effectiveness of the Florisil column procedure used in this study (Fig. 1). However, it should be noted that the procedure does not necessitate column cleanup for extracts from soils containing low organic matter. Preliminary experiments showed that 98% (± 2.5) of the terbacil reference standard (0.1 ppm) was recovered from the column by eluting with ethyl acetate.

In the preliminary experiments no measurable loss was observed when pure terbacil was shaken with 1.5% NaOH up to 4 hr. Furthermore, shaking treated soil with 1.5% NaOH for longer than 1 hr did not result in an increased yield of the terbacil residue. There was a slight increase in the recovery of terbacil residues when the concentration of NaOH was increased from 0.5 to 1.5% (20 g soil, 100 ml NaOH). Further increase in the concentration of NaOH did not increase the recovery. The efficiency of the procedure was tested by adding known amounts of terbacil to check soil samples before extraction. The recoveries from the three soils are shown in Table 1. In order to separate terbacil from other coextractives it was found necessary to subject extracts from soils containing more than 5% organic matter (Table 1) for column cleanup. With the sample size and dilution used, residue at 0.01 ppm level can easily be determined. However, sensitivity can be increased by using a more concentrated extract for injection into the gas chromatograph.

TABLE 1

Recoveries (%) of terbacil from fortified soils.

Soil type	Organic matter	Column cleanup	Terbacil added (ppm)		
	%		0.1	0.05	0.01
Fox sandy loam	1.8	No	94.4±3.2	87.0±1.7	82.8±3.8
Bookton sandy loam	5.2	Yes	88.3±4.8	80.8±5.5	78.9±4.4
Bookton loam	10.9	Yes	89.7±6.8	77.9±8.1	76.4±6.1

The procedure has been used for the residue determination in treated orchard soils. The samples were obtained from fields

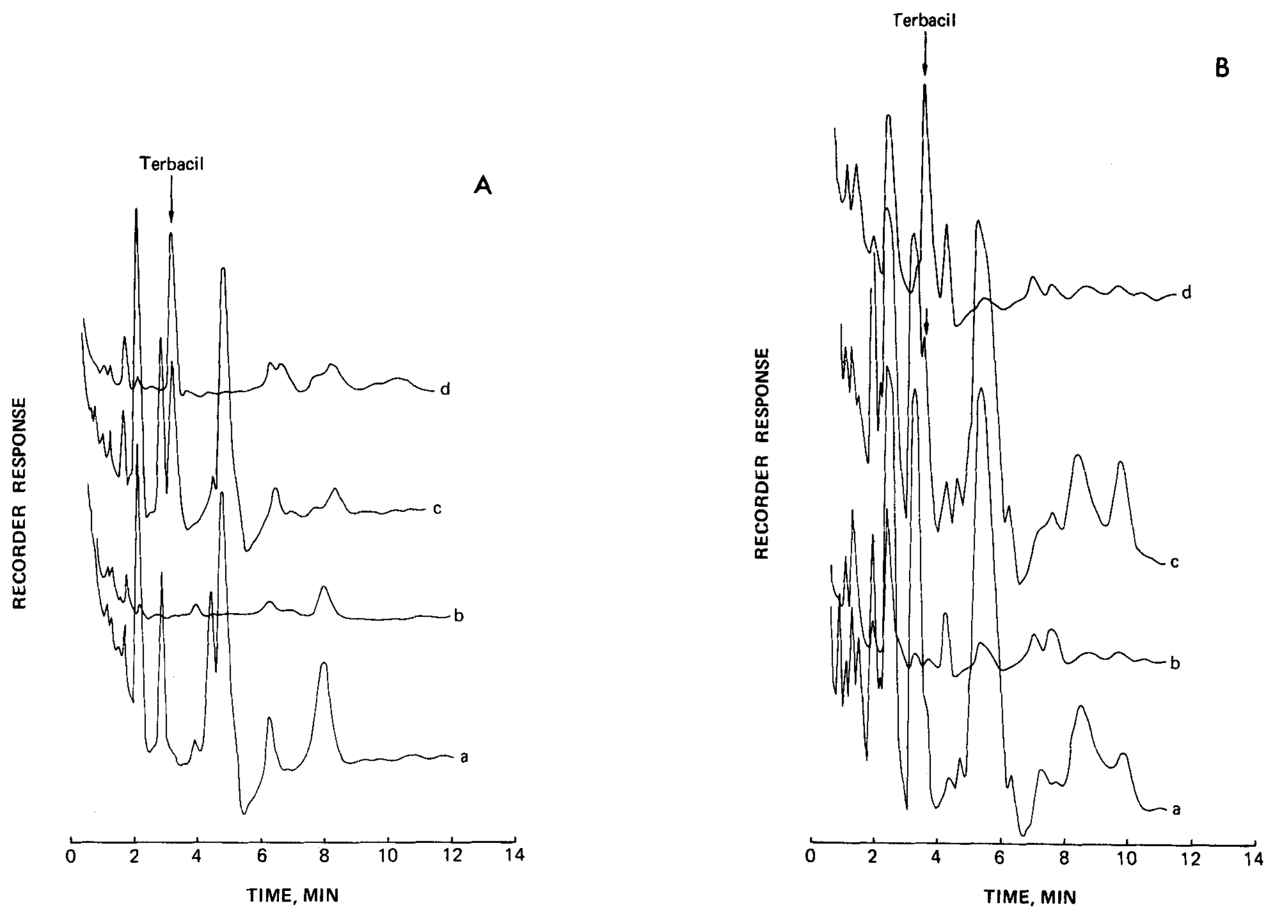

Fig. 1. Gas chromatograms of extracts from soils: (a) control soil; (b) control soil after cleanup on Florisil column; (c) treated soil; and (d) treated soil after cleanup on Florisil column. (A) Fox sandy loam; (B) Brookton loam.

treated annually with terbacil at the rate of 4.5 kg/h. Composite soil samples of Fox sandy loam (5-cm depth), Bookton sandy loam (5-cm depth), and Bookton loam (15-cm depth) were taken about 1, 6 and 6 months, respectively, after the herbicide application. Table 2 shows the residue levels obtained by the method described in this paper. The residue method developed is reasonably simple and faster to perform and an analyst should be able to use it with no difficulty.

TABLE 2

Residues of terbacil in the orchard soils (mean values for duplicate samples from each of three replicates with standard errors.

Soil type	Terbacil residue (ppm)
Fox sandy loam	2.53 ± 0.06
Bookton sandy loam	1.47 ± 0.09
Bookton loam	0.49 ± 0.07

Summary

A method is described for the determination of terbacil residue in soil. The herbicide residue is extracted with 1.5% NaOH, partitioned into an organic phase and subsequently cleaned up by passing through a Florisil column. Extract is analyzed by gas-liquid chromatography using a ^{63}Ni electron capture detector. The procedure has a sensitivity of about 0.01 ppm, based on a 20 g sample. The method was used for the analysis of terbacil residues in the field treated soil samples.

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