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Note

Inexpensive, precise method for the determination of chlorinated pesticide residues in soil

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Chlorinated pesticides are widely used for the protection of crops[1], especially in developing and tropical countries owing to the low cost of their production and their efficacy against malaria[2–5]. Their persistence in the environment leads to their accumulation in different elements of the food chain. Our recent monitoring studies of residues of chlorinated pesticides in different environmental samples showed that the concentrations of DDT and its metabolites in soil, animal feeds and human fat tissue have been increasing in recent years (unpublished data).

One of the elements of the ecosystem that is often contaminated by chlorinated pesticides is soil. In order to analyse its contamination, a method is necessary that would reflect the real content of chlorinated pesticides, both free and bound, in the soil. The residues bound with humins in soil[6] have good opportunities for transition from the soil to different plant elements[7], thus being a source of contamination in animals and humans.

Commonly used methods are based on clean-up of raw extracts of the samples on chromatographic columns filled with adsorbents such as Florisil[8–10], alumina[11,12], Kieselgel[13,14], gel permeation on Bio-Beads SX-3[15,16], and sweep co-distillation[17,18]. Such a clean-up of extracts substantially increases the costs of analysis, as the cost of the adsorbent constitutes over 50% of the entire costs of analysis. For this reason, efforts have been made to develop a less expensive method of extract clean-up using concentrated sulphuric acid[19–22]. To release bound pesticides, however, oxidation with CrO_3 in acetic acid was applied previously[23,24], and more recently, concentrated sulphuric acid was used[25]. The gas chromatographic (GC) method reported here uses acetic acid hydrolysis to release bound pesticides and replaces adsorbents with 1 ml of concentrated sulphuric acid in the clean-up of extracts.

EXPERIMENTAL

Reagents and standards

Acetonitrile, acetic acid, light petroleum (b.p. 40–50°C), distilled water and concentrated sulphuric acid were used. The pesticides examined were hexachlorobenzene (HCB), α-, β-, γ-, δ- and ε-HCH; *p,p'*-DDE, *o,p'*-DDT, *p,p'*-DDT, *p,p'*-DDD, heptachlor, heptachlor epoxide and aldrin.

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Equipment

A Varian 2100 gas chromatograph with a ^{63}Ni electron-capture detector was used. The column was a U-shaped glass tube, 360 cm × 2 mm I.D., packed with 1.5% OV-17 + 1.95% QF-1 on Gas-Chrom Q (80–100 mesh). The carrier gas (nitrogen) flow-rate was 30 ml/min, the injector and detector temperatures 250°C and the column oven temperature 180°C.

Method

An air-dried soil sample (20 g) was weighed into a round-bottomed 250-ml flask, mixed with 50 ml of acetonitrile–acetic acid–water (30:10:10) and were left in the dark for 16 h. The mixture was boiled under reflux for 15 min, cooled and decanted through filter-paper into a 500-ml separatory funnel. The residue in the flask was mixed with 50 ml of the extracting mixture and again boiled under reflux for 15 min.

After cooling, the extract was poured into the previously obtained extract, through the filter-paper used previously. To the combined extracts, 300 ml of distilled water were added and the contents were mixed. The chlorinated pesticides were extracted with three 50-ml portions of light petroleum. The extracts were washed with two 50-ml portions of water to remove residues of acetic acid and acetonitrile.

The extract was dried by passage through a layer of sodium sulphate and concentrated to a small volume in a rotary evaporator. The concentrated extract was transferred quantitatively with light petroleum into a tube with a cut glass stopper and the volume was adjusted to 10 ml.

The extract was cleaned up by intensive shaking of the tube contents with 1 ml of concentrated sulphuric acid for about 1 min. Thereafter, the tube was left for approximately 3 min to ensure good phase separation and the upper organic layer was removed with a pipette. It was then dried by passing it through a layer of sodium sulphate and concentrated to a final volume of 2.0 ml in a rotary evaporator.

The qualitative and quantitative analysis was performed by gas chromatography with electron-capture detection, qualitatively by comparing retention times and quantitatively by measuring the peak heights and peak areas.

TABLE I

ANALYSED COMPOUNDS, FORTIFICATION LEVELS, MEAN RECOVERIES AND STANDARD DEVIATIONS FOR TEN SOIL SAMPLES

Compound	*Fortification level (ppm)*	$\bar{x}$ *(%)*	*S.D.*
α-HCH	0.0053	99.30	1.26
β-HCH	0.0107	98.53	2.39
γ-HCH	0.0113	99.86	0.61
δ-HCH	0.0111	100.40	0.40
ε-HCH	0.0108	98.85	1.64
HCB (hexachlorobenzene)	0.0054	98.28	1.26
Heptachlor epoxide	0.0215	99.51	0.64
p,p'-DDE	0.0300	98.78	0.58
p,p'-DDD	0.0250	98.13	1.65
o,p'-DDT	0.0315	98.55	2.39
p,p'-DDT	0.0450	91.52	1.61

RESULTS AND DISCUSSION

Table I gives the mean recoveries of the individual compounds from ten repeated analyses, plus standard deviation and the fortification levels at which the studies were carried out. The fortification level is relatively high, because a soil with low residues of chlorinated compounds is lacking.

The recovery study was carried out by adding an *n*-hexane solution of pesticide mixture to the soil sample, evaporating the *n*-hexane and leaving the fortified sample for several hours so that the binding reaction of pesticides with particles of soil could take place. Subsequently, the extracting mixture was added, followed by the above procedure of extraction and evaporation. The recoveries ranged from 98% to 99% with the exception of *p,p'*-DDT, for which it was 91.52%, owing to contamination of the sample with this compound. The standard deviation did not exceed 2.4%,

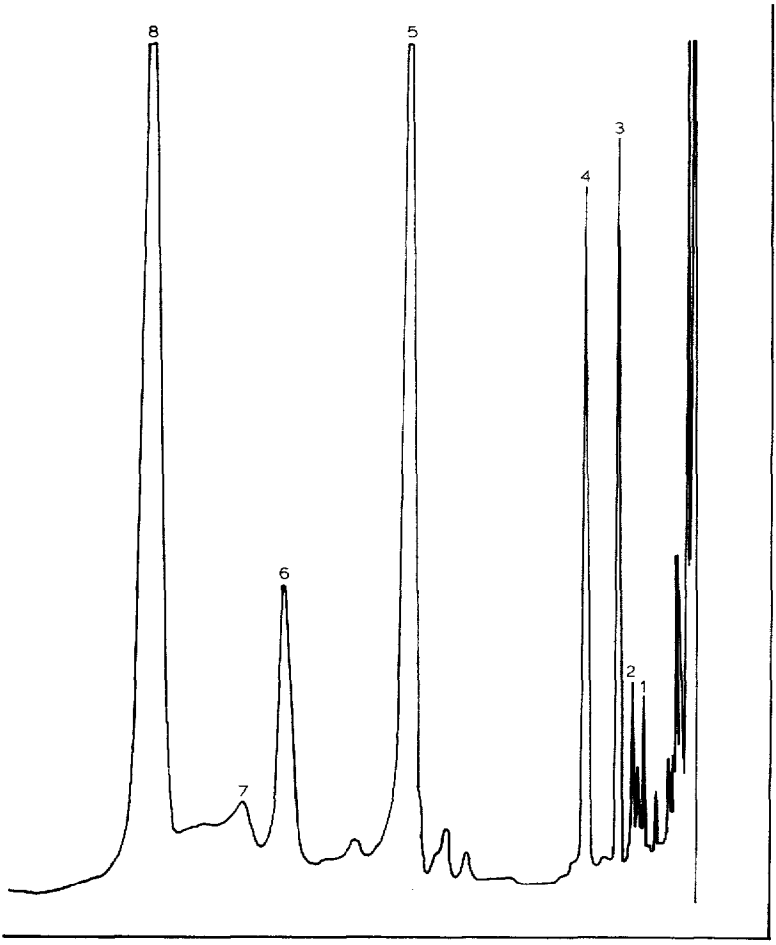

Fig. 1. Gas chromatogram of soil sample chosen at random and analysed by the proposed method (values in ppm). 1, HCB (0.0006); 2, HCH (0.0004); 3, γ-HCH (0.0057); 4, aldrin (0.0103); 5, *p,p'*-DDE (0.050); 6, *o,p'*-DDT (0.039); 7, *p,p'*-DDD (0.008); 8, *p,p'*-DDT (0.163).

indicating a high precision for the method. The recovery study was carried out on ten samples taken within a period of a few days. A typical gas chromatogram of a soil sample is presented in Fig. 1. The peaks are symmetrical and have a narrow width at the base, which indicates good separations of the compounds studied from other substances that may interfere in the analysis.

When the GC column was packed with 1.5% OV-17 + 1.95% QF-1, it was not possible to analyse heptachlor and aldrin because their peaks covered partially the peaks of the HCH isomers. Therefore, some control samples without HCH isomers and fortified with heptachlor and aldrin were tested in the recovery analysis and their mean values were 97.85% and 98.23%, respectively. As these samples were not analysed ten times the standard deviation was not calculated and they are not included in Table I.

Almost no differences were observed in the gas chromatograms between soil samples with high and low contents of organic substances, which indicates that the extract clean-up with concentrated sulphuric acid is very effective. The cost of a single analysis is much less than that of analyses carried out according to commonly used methods for the determination of residues of chlorinated pesticides. This is due to the use of reduced amounts of solvents for extraction and to the replacement of the adsorbents commonly used in sample extract clean-up with 1 ml of concentrated sulphuric acid.

The high precision and low cost of the proposed method for the measurement of soil contamination with chlorinated compounds recommend it for use in soil monitoring studies.

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