Gas Chromatographic Determination of D-D (*cis*- and *trans*-1,3-Dichloro-1-propene and 1,2-Dichloropropane) in Potatoes

A gas chromatographic method utilizing microcoulometric detection for the determination of residues of D-D (*cis*- and *trans*-1,3-dichloro-1-propene and 1,2-dichloropropane) in potatoes is described. In the cleanup procedure, concentration of D-D from the acetone–hexane eluate from the silica gel column is effected by the addition of sodium bisulfite solution. Acetone complexes with bisulfite and the small volume of hexane separating out contains the D-D and is suitable for gas–liquid chromatography. This method of concentration of the highly volatile D-D avoids the losses associated with evaporative concentration. Ten samples of potatoes grown in soils variously treated with D-D were analyzed and no residues were found by the method described.

A mixture of 1,2-dichloropropane and the cis and trans isomers of 1,3-dichloro-1-propene is produced commercially under the trade name D-D, and is used widely for the control of nematodes in soil. It is claimed to be nonpersistent in the soil and therefore it is not expected to be found in potatoes. Another nematocide, Vorlex, contains 80% of the chlorinated 3-hydrocarbons and is similarly considered nonpersistent in soil (Frear, 1955).

A method using thermal conductivity detection has been described by Hannon *et al.* (1963) for the determination of D-D in soil and they found no D-D residue at the microgram level in soils 24 hr after treatment. No investigation, however, has been reported of the possible residue of D-D in potatoes grown in treated soil and no method has been published for the determination of D-D below the microgram level.

The method here described was developed to investigate the residual effect that the various types of soil treatment may have on potatoes. Microcoulometric detection was employed to take advantage of its halogen specificity. No problems were encountered in extracting the D-D from the sample with acetone, partitioning it into hexane, absorbing it on a silica gel column, and eluting it from the column with acetone.

Difficulty was experienced in attempting to concentrate the acetone eluate for injection into the gas chromatograph. D-D is highly volatile and concentration with the aid of heat resulted in a loss of 90% from a beaker and a loss of 50% from a Kuderna-Danish evaporator. Recoveries were no better when the acetone eluate was diluted with water and extracted with several portions of hexane. Concentration of this hexane extract also resulted in considerable loss of D-D.

A hexane solution suitable for gas chromatography without concentration was obtained by adding sodium bisulfite to the acetone eluate. Acetone complexes with bisulfite and this promotes the partitioning of D-D into a separating hexane phase.

The silica gel column holds up to 25 ml of hexane prior to the addition of acetone. The eluate collected after adding 100 ml of acetone to the column contains 25 ml of hexane and 75 ml of acetone. Sodium bisulfite complexes with acetone when added to the solution. The separated hexane phase contains about 88% of the D-D and can be injected directly into the gas chromatograph.

Several gas chromatographic columns were tried. It was necessary to use heavy loading (25%) of the liquid phase to obtain satisfactory resolution of the isomers.

MATERIALS AND METHODS

Reagents. Silica gel, Davison grade 923 (Will), activated at 350° C for 3 hr and cooled in a desiccator. Freshly activated material was used. A solution containing 10 ng per μl of each of the three D-D components was prepared from reference standards supplied by the Shell Chemical Co.

Apparatus. A Microtek 220 gas chromatograph connected to a Dohrmann T-300S titration cell and a Dohrmann C-200A microcoulometer was used. The recorder employed had a span of 100 μV per in. and was fitted with a Disk integrator. The 0.25-in. × 6-ft column was packed with 15% QF-1 + 10% DC-200 on 80 to 100 mesh Gas Chrom Q, and preconditioned overnight at 200° C and a flow of 50 ml N per min. This column is stable for several months. The temperature of the column was 55° C and the temperature of the injection port was 100° C. The flow rate of the nitrogen carrier gas was 50 ml per min. The coulometer bias was set for 240 mV and the range for 200 ohms. The temperature of the combustion furnace was 870° C.

Determination. The D-D was extracted from 200 g of potatoes by blending with 300 ml of acetone. The mixture was filtered through paper covered with a thin layer of Celite, and the filtrate was then poured into a graduated cylinder and its volume noted (F). The filtrate was transferred to a 1-l. separatory funnel and diluted to 800 ml with water. After adding 10 ml of saturated NaCl brine, the solution was extracted with 100 ml of hexane. The aqueous phase was drawn into a second separatory funnel and extracted with a second 100 ml of hexane. The combined extracts were shaken gently with 100 ml of refrigerated 25% $NaHSO_3$ solution. After washing the hexane layer with two 100-ml portions of water, the hexane solution was transferred to a 250-ml glass-stoppered graduated cylinder and its volume noted (H).

The cleanup column was prepared by placing 17 g of activated silica gel in a 22 × 300 mm column and covering it with a 25-mm layer of anhydrous Na_2SO_4. The holdup of this column was determined by pouring on the column 50 ml of hexane and catching the excess in a graduated cylinder. The volume of the hexane collected subtracted from 50 ml was taken as the holdup of the column (V). The extract in the glass-stoppered cylinder was dried by shaking it with 10 g of anhydrous Na_2SO_4 and was quantitatively transferred to the silica gel column.

The D-D was eluted with 100 ml of acetone and the eluate was slowly added to 500 ml of refrigerated 25% sodium bi-

Table I. Recovery of D-D from Potatoes

Added, mg/kg	1,2-dichloropropane		*cis*-1,3-Dichloro-1-propene		*trans*-1,3-Dichloro-1-propene	
	Found, mg/kg	Recovery %	Found, mg/kg	Recovery %	Found, mg/kg	Recovery %
0.500	0.334	66.8	0.383	76.6	0.432	86.5
1.000	0.834	83.4	0.844	84.4	0.946	94.6
1.500	1.509	100.5	1.590	105.9	1.445	96.5
2.000	1.910	95.6	1.630	81.5	1.882	94.1
Average recovery 86.6		86.6		87.1		92.9

sulfite solution contained in a 1-l. separatory funnel. After shaking well, the phases were allowed to separate and the aqueous phase was discarded. The hexane phase was washed with two 25-ml portions of water, transferred to a glass-stoppered cylinder, and dried with 5 g of anhydrous Na_2SO_4. Four microliters of the solution were injected into the gas chromatograph. Aliquots of 1, 2, 3, and 4 μl of the standard D-D solution were also injected and the areas under the peaks plotted against the concentration.

Calculation. Since 200 g of potatoes contain on the average 160 g of water (Barry *et al.*, 1968), blending it with 300 ml of acetone produces 460 ml of extract, of which F ml of filtrate is collected. The filtrate is extracted with 200 ml of hexane, of which H ml is collected. The D-D contained in this solution is the amount of V ml of the assay solution. The portion of the sample represented in the assay solution is calculated from the following values.

200 g (F ml/460 ml) × (H ml/200 ml) =

aliquot sample weight in V ml

Results. VALIDATION OF METHOD. Recoveries obtainable by the method were tested by fortifying potatoes at various levels ranging from 0.5 to 2.0 ppm of each of the three components of D-D. Results are summarized in Table I.

Recoveries at the 0.5-ppm level were rather low but satisfactory at the higher levels. Overall recovery for the isomers at the levels tested was 88%. No interfering peaks were noted when untreated potatoes were put through the procedure. Figure 1 shows the chromatograms of a potato sample before and after fortification with D-D.

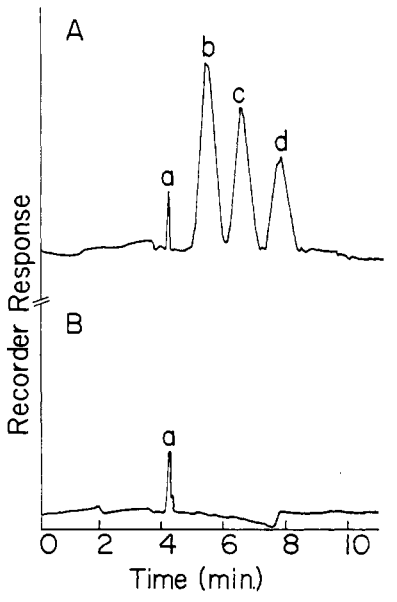

Figure 1. Gas chromatogram of a potato sample: A, fortified with D-D and B, untreated control. The 2 μl-aliquot of the fortified extract injected contained 20 ng of commercial D-D per 12.4 mg sample. Peak (a) air vent, (b) 1,2-dichloropropane, (c) *trans*-1,3-dichloro-1-propene, and (d) *cis*-1,3-dichloro-1-propene

Table II. Nematocide Applied to Soil, Two Treatments

Field no.	Area, acres	Material used	Application per acre, each time, gal
I	35	D-D	45
II	54	Vorlex	10
III	7	Vorlex, tarped[a]	15
IV	15	Vorlex/D-D, combined	15/45
V	22	Vorlex	10
VI	27	D-D, tarped[a]	45
VII	20	Vorlex	15
VIII	41	D-D	45
IX	34	D-D	45
X	69	D-D	45

[a] Field was covered with plastic after application.

ANALYSIS FOR RESIDUES. Ten fields were treated for nematode control in June 1968 in the manner indicated in Table II. Average size of the plots was 37 acres. In each case the treatment consisted of two applications of the quantities shown in the last column.

Potatoes were planted in these plots in April 1969. Samples were taken from the fields in a random manner, placed in plastic bags, and taken to the laboratory where they were analyzed without delay. No D-D residue was found in these samples by the method described.

ACKNOWLEDGMENT

The authors are indebted to R. E. Hanson, Shell Chemical Co., for the pure 1,2-dichloropropane and the cis and trans isomers of 1,3-dichloropropene needed for this study.

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Received for review July 15, 1970. Accepted April 19, 1971.