

Table I. Retention Times Relative to Aldrin

	OV-17 ^a + QF-1	OV-17 ^b	QF-1 ^c	DC 200 ^d	DC 200 ^e + QF-1
Lindane	0.66	0.63	0.77	0.48	0.58
Heptachlor	0.81	0.80	0.77 ^f	0.79	0.81
Aldrin	1.00	1.00	1.00	1.00	1.00
Heptachlor epoxide	1.57	1.50	1.80	1.23	1.46
<i>o,p'</i> -DDE	1.89	1.94	1.44	1.47	1.47
<i>p,p'</i> -DDE	2.30	2.39	1.88	1.81	1.88
Dieldrin	2.47	2.35	2.73	1.82	2.22
<i>o,p'</i> -TDE	2.77	2.83	2.25	1.87	2.04
Endrin	3.05	2.93	3.22	2.04	2.50
<i>p,p'</i> -TDE	3.62	3.60	3.20	2.31	2.70
<i>o,p'</i> -DDT	3.30	3.42	2.33	2.41	2.48
<i>p,p'</i> -DDT	4.36	4.44	2.42	3.07	3.28

^a Equal parts of 7% OV-17 + 9% QF-1 on 100/120 Gas Chrom Q at 200° C. and 20 p.s.i.g. Absolute retention time for aldrin, 7.12 min.

^b 9% OV-17 on 100/120 Gas Chrom Q at 205° C. and 40 p.s.i.g. Absolute retention time for aldrin 12.11 min.

^c 12% QF-1 on 100/120 Gas Chrom Q at 200° C. and 35 p.s.i.g. Absolute retention time for aldrin 2.01 min.

^d 10% DC 200 on 100/120 Gas Chrom Q at 200° C. and 30 p.s.i.g. Absolute retention time for aldrin 6.11 min.

^e Equal parts of 10% DC 200 + 15% QF-1 on 80/100 Gas Chrom Q at 200° C. and 30 p.s.i.g. Absolute retention time for aldrin 8.35 min.

^f Not calculated. Heptachlor very close to lindane.

relative to aldrin are presented in Table I for five packings. Separation factors for adjacent pesticides are shown in Table II for the OV-17 + QF-1 and DC 200 + QF-1 mixed packings.

Literature Cited

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Table II. Separation Factors between Adjacent Pesticides

OV-17 + QF-1		DC 200 + QF-1	
Lindane		Lindane	
Heptachlor	1.23	Heptachlor	1.40
Aldrin	1.24	Aldrin	1.23
Heptachlor epoxide	1.57	<i>o,p'</i> -DDE	1.46
<i>o,p'</i> -DDE	1.20	Heptachlor epoxide	1.01
<i>p,p'</i> -DDE	1.22	<i>p,p'</i> -DDE	1.28
Dieldrin	1.08	<i>o,p'</i> -TDE	1.08
<i>o,p'</i> -TDE	1.12	Dieldrin	1.09
Endrin	1.10	<i>o,p'</i> -DDT	1.12
<i>o,p'</i> -DDT	1.09	Endrin	1.03
<i>p,p'</i> -TDE	1.10	<i>p,p'</i> -TDE	1.06
<i>o,p'</i> -DDT	1.20	<i>p,p'</i> -DDT	1.22

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RESIDUE DETERMINATION

Determination of Small Quantities of 2,6-Dichloro-4-nitroaniline (Dichloran)

A procedure for the colorimetric determination of dichloran and for detecting dichloran spots on thin-layer chromatographs, based on diazotization and dye-coupling, is described. A modification of the Kilgore colorimetric method for dichloran is given.

DICHLORAN, 2,6-dichloro-4-nitroaniline, DCNA, Botran (The Upjohn Co.) has been used for the control of certain fungus diseases of fruits and vegetables, and gas chromatographic and colorimetric methods for its determination in small quantities have been developed. Beckman and Bevenue (1) reported the determination of dichloran by gas chromatography with a thermal conductivity detector, and recently, Cheng and Kilgore (2) reported a similar determination with greater sensitivity using an electron-

capture detector. The gas chromatographic determination of dichloran has been reported by The Upjohn Co. (4), and, in this laboratory, the method using both detectors has been used for the past 2 years. The sensitivity and rapidity of the electron-capture gas chromatography method for the determination of dichloran often makes it the method of choice in spray residue work.

Kilgore, Cheng, and Ogawa (3) have described a colorimetric method for dichloran in processed fruits based on

the yellow color formed by adding potassium hydroxide to a solution of the sample in acetone. In applying this method, the authors found that the samples as prepared for the spectrophotometer were frequently fogged due to the precipitation of carbonate, which is insoluble in acetone. Furthermore, acetone containing an alkali may develop a yellow color on standing.

The authors modified the Kilgore method by substituting dimethylformamide (5) for acetone as the sample solvent, and Hyamine 10-X hydroxide

(Rohm and Haas, Inc.) for the potassium hydroxide. The carbonate of the Hyamine 10-X is soluble in dimethylformamide, and the samples show no fogging, and blanks do not turn yellow on standing.

In a search for a reagent for detecting dichloran spots on thin-layer chromatograms, the work of Roburn (6) was noted. Roburn developed a method for the colorimetric determination of dichloran based on the reduction of the fungicide to the diamine, followed by oxidation in the presence of aniline to form a blue indamine dye. In his preliminary work, Roburn diazotized dichloran and coupled it to 1-naphthol to form a strong, but variable, color. The authors diazotized dichloran and coupled it to *N*-(1-naphthyl)ethylenediamine, forming a strong purplish red color. This reaction is suitable as a detecting agent for chromatograms, and for the colorimetric determination of dichloran. The maximum absorption is at 515 m μ , and 17 μ g. gives an absorbance of 0.5, while Roburn's method requires more than 160 μ g. to give that absorbance.

Detection of Dichloran Spots on Chromatograms

The chromatogram is sprayed with sulfuric acid (3 + 1) followed by a spray of 0.5% sodium nitrite. After standing for 10 minutes, the chromatogram is sprayed with 5% sulfamic acid, followed by a spray of 1% naphthylethylenediamine. A spot containing 0.5

μ g. of dichloran is easily detected. This procedure also forms colored spots with *p*-nitroaniline and 2-chloro-4-nitroaniline, distinguishable from dichloran spots by their colors.

Colorimetric Determination of Dichloran

Strong acid is required for the diazotization of dichloran. The procedure is similar to that used for aminotriazole by Storherr and Burke (7). Benzene extracts of plant samples are cleaned up on a Florisil (Floridin Co., N. Y.) column (3). An aliquot of the sample containing 5 to 15 μ g. of dichloran is placed in a 25-ml. glass-stoppered Erlenmeyer flask and evaporated to dryness. Three milliliters of sulfuric acid (3 + 1) is added and mixed, then 1 ml. of 0.5% sodium nitrite; after mixing, let stand 10 minutes. One milliliter of 5% sulfamic acid is added, the flask is shaken, and 1 ml. of 1% *N*-(1-naphthyl)ethylenediamine dihydrochloride is added and mixed. After 10 minutes, the sample is read in a spectrophotometer at 515 m μ against a water reference. Standards are prepared using appropriate amounts of pure dichloran (Eastman Kodak Co. No. 1033, 2,6-dichloro-4-nitroaniline) instead of the sample for a range of 0 to 20 μ g. The absorbance-concentration relationship is linear, and the color is stable.

The sensitivities of the modified Kilgore and the dye-coupling methods are nearly the same. With both methods

interferences have been encountered in some samples of soils and plants. A choice of the methods can be made in some instances to avoid the interferences, since the reactions involved in the color formations are different.

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