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## THIN-LAYER CHROMATOGRAPHY OF CHLORINATED CATECHOLS

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### SUMMARY

The thin-layer chromatography of catechol and six chlorinated catechols has been studied on five adsorbents. Acetic acid in the developing solvent was essential for the production of sharp zones. The best separation of the individual compounds occurred on alumina, whereas silica gel appeared to be good for group separation (clean-up) from other compounds.

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### INTRODUCTION

The literature on both qualitative and quantitative analysis of pesticides and their metabolites is extensive<sup>1,2</sup>, and thin-layer chromatography (TLC) is one of the most widely used techniques in separation and analysis of individual members of different groups of pesticides<sup>3-6</sup>.

Walker and Beroza studied 62 chlorinated or organophosphorus pesticides by TLC, with three pure solvents (chloroform, benzene and hexane) and mixtures of each of these with ethyl ether, ethyl acetate, acetone, methanol or acetic acid for development<sup>7</sup>. Kovacs reported that better resolution was achieved in the separation of chlorinated pesticides by TLC than in that of organophosphorus pesticides<sup>8</sup>. Blinn has determined residues of phorate by TLC<sup>9</sup>. In all these studies<sup>7-9</sup>, standard glass plates (20 × 20 cm) were used.

The most widely used adsorbents are silica gel, alumina, kieselguhr and cellulose; they offer a wide range of properties and are suitable for the analysis of most pesticides and their residues<sup>10a</sup>.

Waldi *et al.*<sup>11</sup> compared silica gel G, aluminium oxide G and kieselguhr G, representing an acidic, a basic and a neutral adsorbent, respectively; the capacity of these materials for pesticides decreased in the order silica gel, alumina, kieselguhr.

Although TLC has been applied to a wide variety of separations, we have found no information on the TLC of chlorinated catechols, which are of interest to us as potent environmental residues. The work described here was carried out in an attempt to separate, identify and determine chlorinated catechols, and catechol itself, in different TLC systems.

## EXPERIMENTAL

### *Apparatus and methods*

Standard chromatoplates (20 × 20 cm) were used, and five plates were prepared in a single operation with a Desaga-Brinkmann model S-11 applicator (Brinkmann, Westbury, N.Y., U.S.A.). Ascending development was carried out in a closed glass chamber (Desaga) after application of the samples with a 10- $\mu$ l syringe (Hamilton, Whittier, Calif., U.S.A.) on a line 1 cm from the bottom of the layer, the first spot being 1 cm from the side of the plate and the following six spots at 3-cm intervals. A Desaga scale plate was used to measure the  $R_F$  values of the spots.

### *Layers*

The following layer materials were used: silica gel G ("nach Stahl", Type 60, Merck), alumina ("150 Sauer", Type T, Merck), kieselguhr G (Merck), silica gel-alumina (7:3, w/w), and silica gel-kieselguhr (3:2, w/w).

### *Samples*

Except for catechol itself, which was a commercial sample (Fluka), the compounds studied were synthesized in our laboratory; proof of their structures by IR spectroscopy, and mass and NMR ( $^1\text{H}$  and  $^{13}\text{C}$ ) spectrometry will be reported elsewhere. The purity of the samples was verified by gas chromatography. The following compounds were used: (I) catechol, (II) 3,4-dichlorocatechol, (III) 3,5-dichlorocatechol, (IV) 3,6-dichlorocatechol, (V) 3,4,5-trichlorocatechol, (VI) tetrachlorocatechol, (VII) 5-chloro-3-methylcatechol.

### *Solvent systems*

A preliminary screening of 60 different solvents or solvent mixtures was carried out to select those giving good spots and reasonable  $R_F$  values with all the compounds studied. All solvent mixtures that gave sharp spots without tailing contained acetic acid; the compositions (by volume) of the 12 most suitable solvents all of which were mixtures, are listed below:

- (1) Benzene-acetone-acetic acid (80:15:5)
- (2) Light petroleum (b.p. 40-60°)-acetone-acetic acid (80:15:5)
- (3) Light petroleum (b.p. 40-60°)-ethyl acetate-acetic acid (80:15:5)
- (4) *n*-Hexane-ethyl acetate-acetic acid (80:15:5)
- (5) Benzene-chloroform-acetic acid (60:30:10)
- (6) Benzene-ethanol-acetic acid (85:10:5)
- (7) Chloroform-ethyl acetate-acetic acid (80:15:5)
- (8) Chloroform-diethyl ether-acetic acid (85:10:5)
- (9) Benzene-acetic acid (85:15)
- (10) Chloroform-acetic acid (80:20)
- (11) Light petroleum (b.p. 40-60°)-dichloromethane-acetic acid (40:40:20)
- (12) *n*-Hexane-acetone-acetic acid (75:20:5).

### *Chromogenic reagent*

A 2% solution of 3,5-dichloro-*p*-benzoquinonechlorimine in benzene was used for spot detection.<sup>10b</sup>

*Development of chromatograms*

A slurry of the absorbent was applied to the glass plates to form a 1-mm layer; the plates were then activated at 110° for 12 h and spotted with 10  $\mu$ l of a 0.1% (w/v) solution (in diethyl ether) of each catechol. Development was continued until the solvent front had ascended 15 cm, then the plates were dried in air and sprayed with chromogenic reagent.

## RESULTS AND DISCUSSION

The  $R_F$  values obtained in the various systems are shown in Tables I–V.

*Silica gel layer (Table I)*

All the compounds formed sharp spots, those for catechol (I) and 5-chloro-3-methylcatechol (VII) being pink, and those for the chlorinated catechols green to brown. All the solvent mixtures gave sharp spots, and the development time at room temperature (20°) varied from 30 to 60 min.

TABLE I

 $R_F$  VALUES OF CATECHOL AND CHLORINATED CATECHOLS ON SILICA GEL

Solvent No.	Compound No.							Development time, min
	I	II	III	IV	V	VI	VII	
1	0.43	0.40	0.46	0.46	0.40	0.43	0.50	40
2	0.10	0.13	0.13	0.17	0.17	0.20	0.26	35
3	0.26	0.20	0.26	0.30	0.20	0.26	0.30	35
4	0.20	0.17	0.20	0.23	0.17	0.17	0.25	40
5	0.20	0.23	0.26	0.26	0.20	0.26	0.30	50
6	0.46	0.43	0.50	0.50	0.43	0.46	0.53	50
7	0.56	0.40	0.60	0.60	0.40	0.53	0.60	60
8	0.46	0.53	0.53	0.50	0.53	0.50	0.63	60
9	0.30	0.30	0.30	0.36	0.26	0.36	0.40	40
10	0.53	0.66	0.60	0.63	0.63	0.56	0.63	60
11	0.40	0.40	0.56	0.60	0.46	0.53	0.60	60
12	0.16	0.16	0.23	0.23	0.16	0.23	0.26	40
Colour	Pink	Pale green	Brown	Brown	Brown	Pale green	Pink	

Chloroform–acetic acid (80:20) (solvent 10) showed the greatest eluting power, the  $R_F$  values ranging from 0.53 to 0.63; the lowest  $R_F$  values were obtained with light petroleum–acetone–acetic acid (80:15:5) (solvent 2). Variations in  $R_F$  value in each run were small. Thus, pure silica gel is not suitable for the identification of individual compounds in this group, but can be used for the separation (clean-up) of this group from its mixtures with other compounds. For this purpose, benzene–acetone–acetic acid (80:15:5) (solvent 1) and benzene–ethanol–acetic acid (85:10:5) (solvent 6) would be particularly useful, as when these solvents are used, the individual components differ little in  $R_F$  value.

*Alumina layer (Table II)*

The sharpness of the spots and their colour reactions were the same as on



*Silica gel-alumina (7:3) layer (Table IV)*

Sharp spots were obtained, and the colours were the same as on silica gel and alumina. The  $R_F$  values indicated some overlap of spots with all the solvents. Thus, such a layer is unsuitable for identification, but, with solvents 2 or 4, could be used for the group separation of catechols from faster-moving contaminants.

TABLE IV

$R_F$  VALUES OF CATECHOL AND CHLORINATED CATECHOLS ON SILICA GEL-ALUMINA (7:3)

Solvent No.	Compound No.							Development time, min
	I	II	III	IV	V	VI	VII	
1	0.46	0.33	0.46	0.46	0.26	0.16	0.53	35
2	0.13	0.20	0.13	0.20	0.20	0.10	0.23	30
3	0.30	—	0.30	0.33	—	0.16	0.40	35
4	0.13	0.13	0.16	0.16	0.13	0.10	0.20	40
5	0.23	—	0.23	0.33	0.23	0.16	0.30	50
6	0.43	0.40	0.43	0.40	0.33	0.16	0.53	50
7	0.50	—	0.50	0.46	—	0.33	0.60	60
8	0.43	0.36	0.43	0.43	0.33	0.23	0.53	50
9	0.23	0.16	0.26	0.36	0.13	0.16	0.30	90
10	0.73	—	—	0.70	—	0.23	0.80	70
11	0.46	—	0.56	0.60	—	0.36	0.63	45
12	0.23	—	0.26	0.23	—	0.16	0.26	40
Colour	Pink	Pale green	Brown	Brown	Brown	Pale green	Pink	

*Silica gel-kieselguhr G (3:2) layer (Table V)*

Sharp spots were obtained, and the colours were the same as on silica gel, alumina and silica gel-alumina (7:3). The  $R_F$  values show that solvents 3–7 and 12 could be used for group separation in certain clean-up processes for catechols on

TABLE V

$R_F$  VALUES OF CATECHOL AND CHLORINATED CATECHOLS ON SILICA GEL-KIESELGUHR G (3:2)

Solvent No.	Compound No.							Development time, min
	I	II	III	IV	V	VI	VII	
1	0.63	—	0.66	0.66	—	0.56	0.66	30
2	0.20	—	0.23	0.23	0.20	0.20	0.26	30
3	0.26	0.26	0.33	0.30	0.26	0.26	0.60	30
4	0.23	0.23	0.26	0.30	0.26	0.23	0.33	30
5	0.30	0.30	0.36	0.43	0.26	0.33	0.40	60
6	0.63	0.56	0.63	0.63	0.53	0.56	0.70	60
7	0.66	0.53	0.70	0.70	0.53	0.60	0.73	50
8	0.66	—	0.70	0.70	—	0.60	0.76	55
9	0.16	—	0.33	0.33	0.33	0.33	0.33	30
10	0.50	—	0.66	0.66	—	0.66	0.70	60
11	0.60	—	0.66	—	—	0.70	0.73	30
12	0.20	0.20	0.26	0.26	0.23	0.26	0.30	35
Colour	Pink	Pale green	Brown	Brown	Brown	Pale green	Pink	

this layer, but the material is unsuitable for the identification of individual compounds.

## CONCLUSIONS

Chlorinated catechols can be detected and analyzed by TLC with developing solvents containing acetic acid. Separation of the individual compounds can be achieved with benzene-acetone-acetic acid (80:15:5) or light petroleum-acetone-acetic acid (80:15:5) on an alumina layer. Development on silica gel is useful for separation of the catechols, as a group, from other compounds.

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