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THIN-LAYER CHROMATOGRAPHY OF CHLORINATED CRESOLS

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SUMMARY

The thin-layer chromatography of four chlorinated cresols was studied on five layer materials using eleven solvent systems. Sharp spots were obtained except on Kieselguhr G layers. The best separation of the individual compounds occurred on silica gel-containing layers with dichloromethane as the solvent. Each solvent system was found to cause a different separation on different layers.

INTRODUCTION

Thin-layer chromatography (TLC) is one of the most widely used analytical techniques¹ and is applied extensively for the separation and identification of pesticides and their residues²⁻⁴ and for their multiple detection⁵⁻⁸. TLC is an inexpensive and sensitive technique for the rapid screening and multiple detection of pesticide residues even at the 0.5- μ g level^{9,10}. TLC procedures devised for organophosphorus and organochlorine pesticides and developed for the detection of common pesticides on a single plate using one or more developing reagents can be adopted for routine toxicological analysis¹¹. TLC is reported¹² to be more suitable for organochlorine than for organophosphorus pesticides. From the different layer materials available for TLC, silica gel, alumina, Kieselguhr and cellulose are the most widely used¹³. In a TLC study of seven pesticides, Narayanaswami *et al.*¹¹ obtained good results on silica gel and silica gel-alumina (7:3) layers with three different solvent systems.

Chlorinated cresols are persistent environmental residues and 4-chloro-*o*-cresol is important in Finland as the first metabolite and impurity of the most used pesticide MCPA¹⁴. No systematic TLC study on chlorinated cresols has been reported, although the TLC separation of some chlorinated cresols was considered together with other chlorinated phenolic compounds on silica gel using both polar and non-polar solvents¹⁵. Our results on the TLC of chlorinated catechols¹⁶ prompted us to undertake the present study for the separation, identification and determination of chlorinated cresols with different layer materials using several solvent systems.

EXPERIMENTAL

Apparatus and methods

The sizes of the standard TLC plates were 20 × 20 cm and five plates were

prepared in a single operation with a Desaga/Brinkmann Model S-11 applicator (Brinkmann Instruments, Westbury, N.Y., U.S.A.). Ascending elution in a closed glass chamber (Desaga, Heidelberg, G.F.R.) was applied. The samples were spotted with a 10- μ l syringe (Hamilton, Whittier, Calif., U.S.A.) to a starting line 1 cm from the bottom of the layer, the first spot 1 cm from the side of the layer and the following three spots at 4-cm intervals. A Desaga scale plate was used to measure the R_F values of the spots.

Layers

The following materials were used: (i) silica gel G ("nach Stahl", Typ 60; Merck, Darmstadt, G.F.R.); (ii) alumina ("150 Sauer", Typ T, Merck); (iii) Kieselguhr G (Merck); (iv) silica gel-alumina (7:3, w/w); and (v) silica gel-Kieselguhr (3:2, w/w).

Samples

The compounds studied were 2-chloro-*p*-cresol (I), 3-chloro-*o*-cresol (II), 4-chloro-*o*-cresol (III) and 4-chloro-*m*-cresol (IV). III was a commercial sample (Fluka, Buchs, Switzerland), which was purified by vacuum distillation, and I, II and IV were synthesized in our laboratory. Proof of their structures obtained by infrared, mass and ^1H and ^{13}C nuclear magnetic resonance spectrometry will be reported elsewhere. The analytical purity of the samples was verified by gas chromatography.

Solvent systems

A preliminary screening of 45 different solvents and solvent mixtures was carried out in order to select those which gave good spots and reasonable R_F values for all of the compounds studied. The 11 most suitable solvents were as follows: 1, light petroleum (b.p. 40–60°)–acetone (80:20, v/v); 2, light petroleum–ethyl acetate (70:30); 3, light petroleum–methanol (75:25); 4, dichloromethane; 5, dichloromethane–benzene–methanol (60:30:10); 6, benzene–ethanol–acetic acid (85:10:15); 7, benzene–chloroform–acetic acid (60:30:10); 8, *n*-hexane–ethyl acetate–acetic acid (80:15:5); 9, light petroleum–ethyl acetate–acetic acid (80:15:5); 10, light petroleum–acetone–acetic acid (80:15:5); and 11, benzene–acetone–acetic acid (80:15:5).

*Chromogenic reagent*¹⁷

A 2% solution of 3,5-dichloro-*p*-benzoquinonechlorimine in benzene was used for spot detection.

Development of chromatograms

A slurry of the absorbent was applied to the glass plates to form a 1-mm thick layer. The plates were activated at 110°C for 12 h and spotted with 10 μ l of 0.1% (w/v) solutions in diethyl ether of each cresol studied. The elution was continued up to a height of the solvent front of 15 cm. The plates were then dried in air and sprayed with the chromogenic reagent.

RESULTS AND DISCUSSION

The R_F values and colours of the spots obtained using the 11 solvent systems are given in Tables I–V.

(i) Silica gel G layer (Table I)

All four chlorinated cresols formed sharp spots with all solvent systems. After elution with acetic acid-containing solvent mixtures (6–11) all spots gave yellow colour reactions, whereas variable colours were obtained when the eluent was a neutral organic solvent (1–5). The elution times at room temperature (20°) varied from 30 to 70 min.

TABLE I

R_F VALUES OF CHLORINATED CRESOLS (I–IV) ON A SILICA GEL G LAYER (i) WITH DIFFERENT SOLVENT SYSTEMS (1–11)

Solvent	I	II	III	IV	Elution time (min)
1	0.33	0.36	0.33	0.30	30
2	0.56	0.56	0.56	0.56	40
3	0.23	0.26	0.26	0.26	70
4	0.56*	0.46	0.43	0.36	30
5	0.73	0.66	0.66	0.63	30
Colour	Yellow	Dark blue	Brown	Brown	
6	0.63	0.60	0.60	0.60	50
7	0.53	0.50	0.50	0.53	50
8	0.50	0.40	0.36	0.33	40
9	0.52	0.46	0.43	0.43	35
10	0.26	0.26	0.23	0.23	35
11	0.66	0.63	0.63	0.63	40
Colour	Yellow	Yellow	Yellow	Yellow	

* Brown spot.

The fastest ascending solvent (5) had the greatest eluting power, giving R_F values of 0.63–0.73. The best separation of the individual compounds from each other was obtained with eluents 4 and 8. These solvents could therefore be used for the identification of chlorinated cresols on silica gel. Solvent 2 eluted all four compounds at the same speed, giving R_F values of 0.56, and seems to be very suitable for the group separation of chlorinated cresols from other components in a clean-up process in residue analysis.

(ii) Alumina layer (Table II)

All spots with all 11 solvent systems were sharp and yellow, except for the dark blue colour produced with II and brown with III when a neutral eluent (1–5) was used. The elution times were 50–65 min.

The eluting powers of the different solvents varied considerably, being greatest with solvent 5 and least with solvent 3.

None of the eluents was suitable for the separation of the compounds I–IV from each other. However, all compounds had identical R_F values with eluents 2 and 11 (0.63 and 0.73, respectively), and hence elution on an alumina layer using solvent 2 or 11 seems to be applicable for group separation purposes.

(iii) Kieselguhr G layer (Table III)

The ascending elution was rapid with all solvents, being completed in 25–60

TABLE II

R_F VALUES OF CHLORINATED CRESOLS (I-IV) ON AN ALUMINA LAYER (ii) WITH DIFFERENT SOLVENT SYSTEMS (1-11)

Solvent	I	II	III	IV	Elution time (min)
1	0.73	0.70	0.70	0.66	50
2	0.63	0.63	0.63	0.63	60
3	0.36	0.16	0.16	0.13	65
4	0.73	0.60	0.60	0.50	55
5	0.86	0.83	0.83	0.80	60
Colour	Yellow	Dark blue	Brown	Yellow	
6	0.76	0.73	0.73	0.73	50
7	0.76	0.70	0.70	0.70	55
8	0.63	0.60	0.60	0.60	50
9	0.60	0.56	0.56	0.56	50
10	0.51	0.43	0.43	0.43	55
11	0.73	0.73	0.73	0.73	55
Colour	Yellow	Yellow	Yellow	Yellow	

TABLE III

R_F VALUES OF CHLORINATED CRESOLS (I-IV) ON A KIESELGUHR G LAYER (iii) WITH DIFFERENT SOLVENT SYSTEMS (1-11)

Solvent	I	II	III	IV	Elution time (min)
1	—	0.93	0.93	—	25
2	—	0.96	0.96	—	30
3	0.96	0.96	—	—	60
4	—	0.96	0.96	0.96	25
5	—	0.96	0.96	0.96	25
Colour	Yellow	Blue	Brown	Yellow	
6	—	0.96	—	—	40
7	—	0.96	—	—	25
8	—	0.98	0.98	—	40
9	—	0.96	0.96	—	25
10	—	0.96	0.96	—	30
11	—	0.96*	0.98	—	25
Colour	Yellow	Brown	Yellow	Yellow	

* Yellow spot.

min. The chlorinated cresols were eluted very rapidly, giving high or unmeasurable R_F values. Hence one could conclude that Kieselguhr alone is not a useful layer material for the TLC of chlorinated cresols.

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

The sharpness of the spots and their colour reactions were the same as on the alumina layer but the R_F values were significantly different. Dichloromethane (4) appeared to be a suitable eluent for identification purposes, all four R_F values being different. For group separations, solvents 3, 6 and 10 seem to be the best, the R_F values of the individual chlorinated cresols being identical.

TABLE IV

R_F VALUES OF CHLORINATED CRESOLS (I-IV) ON A SILICA GEL-ALUMINA (7:3) LAYER (iv) WITH DIFFERENT SOLVENT SYSTEMS (1-11)

Solvent	I	II	III	IV	Elution time (min)
1	0.50	0.46	0.43	0.43	60
2	0.40	0.40	0.43	0.50	30
3	0.23	0.23	0.23	0.23	50
4	0.56	0.43	0.40	0.33	40
5	0.66	0.66	0.60	0.60	50
Colour	Yellow	Dark blue	Brown	Yellow	
6	0.60	0.60	0.60	0.60	50
7	0.60	0.53	0.53	0.50	50
8	0.43	0.33	0.33	0.30	40
9	0.60	0.53	0.53	0.50	35
10	0.26	0.26	0.26	0.26	30
11	0.70	0.66	0.66	0.63	35
Colour	Yellow	Yellow	Yellow	Yellow	

(v) Silica gel-Kieselguhr G (3:2) layer (Table V)

Sharp spots were obtained with solvents 1-8, 10 and 11. With solvent 9 the compounds were eluted with the solvent front. The colours of the spots were same as on the alumina (ii) and silica gel-alumina (iv) layers, but the R_F values were different. Dichloromethane (4) proved to be a suitable solvent for identification purposes, giving a different R_F value for each chlorinated cresol. With the other solvents, the differences in the R_F values were too small for the separation of the individual chlorinated cresols from each other, but these solvents could be applied for group separations in some instances. The elution times varied from 30 to 60 min.

TABLE V

R_F VALUES OF CHLORINATED CRESOLS (I-IV) ON A SILICA GEL-KIESELGUHR G (3:2) LAYER (v) WITH DIFFERENT SOLVENT SYSTEMS (1-11)

Solvent	I	II	III	IV	Elution time (min)
1	0.46	0.43	0.43	0.40	35
2	0.70	0.70	0.63	0.60	40
3	0.33	0.33	0.30	0.26	60
4	0.66	0.56	0.53	0.46	35
5	0.73	0.66	0.66	0.60	35
Colour	Yellow	Dark blue	Brown	Yellow	
6	0.76	0.73	0.73	0.73	60
7	0.66	0.60	0.63	0.63	60
8	—	0.56	0.53	0.53	30
9	—	—	—	—	30
10	0.40	0.36	0.36	0.36	30
11	0.66	0.76	0.76	0.76	30
Colour	Yellow	Yellow	Yellow	Yellow	

CONCLUSIONS

Chlorinated cresols can be detected and analyzed by TLC. Separation of the individual compounds can be achieved by elution with dichloromethane on silica gel or on mixtures of silica gel with alumina or Kieselguhr G. Elution with light petroleum-ethyl acetate (70:30) on silica gel or alumina is applicable for the group separation (clean-up) of the chlorinated cresols from other compounds.

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