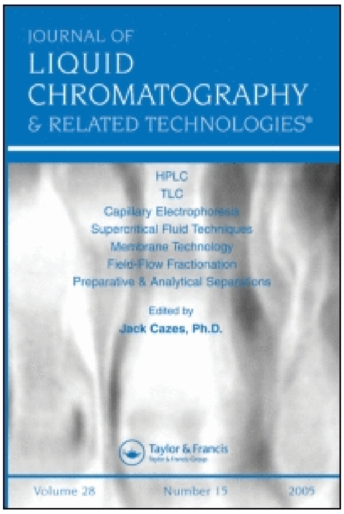

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# Advantages of TLC as a Pilot Technique for HPLC

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# ADVANTAGES OF TLC AS A PILOT TECHNIQUE FOR HPLC

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## ABSTRACT

In the paper two ways of using thin-layer chromatographic data for mobile phase optimization in column chromatography have been presented. The first method is connected with experimental correlations between thin-layer and column retention parameters. This moderately simple method needs to determine the correction parameter to transfer experimental thin-layer data to liquid column technique. In the paper the effects of mobile phase kind and cocentration, as well as chromatographed solute character on this parameter have been presented. The other method is based on thermodynamic description of adsorption systems with mixed mobile phases, i.e., adsorbent + binary solvent+ solute systems. This treatment is very precise, but it needs a lot of experimental thin-layer data.

In the paper the possibility of using TLC experimental data for the choice of optimal mobile phase kind and composition in two-component solvents and some organic model solutes has been presented.

## INTRODUCTION

The problem of using thin-layer chromatography as a pilot technique for liquid column method is connected with two issues of general meaning. At first, it is necessary to solve problems of thin-layer effects, i.e., mobile phase demixing, preadsorption, the presence of gas phase or gradient of phase ratio and the others (1,2), not only to obtain the recurrent experimental data, but for their proper interpretation.

The other problem is to find or choose the best method for transfering TLC experimental data to liquid column technique.

The most popular way of using TLC as a pilot technique for LCC is based on simple experimental correlations between thin-layer and column retention parameters. Different versions of this method have been with details described by Kaiser and Rieder (3), Siouffi and co-workers (4), Soczewiński (5,6), Gołkiewicz (7), Różyło and co-workers (8-10), Jost (11) and Hara (12).

In present paper the correlations between thin-layer and liquid column retention parameters have been described using Kaiser and Rieder relationship (3):

$$k'_{TLC} = c\, k'_{LCC} \qquad (1)$$

where $k'_{TLC}$ is solute capacity factor obtained by TLC and $k'_{LCC}$ by LCC measurements, and c is a constant, or the following modification of this relationship:

$$k'_{LCC} = \frac{1}{c}\, k'_{TLC} \qquad (2)$$

This relationship ( 1 or 2 ) is rather simple, but in practical use it requires evaluation of the value of c ( or 1/c) parameter. As it was realized this parameter depends on mobile phase kind and composition as well as on chromatographed solute character, though from Kaiser and Rieder (3) works appears that it can be evaluated experimentally for standard solute in given chromatographic system.

The other method for using TLC as a pilot technique for LCC is based on thermodynamic description of adsorbent + binary solvent + solute systems. The detail description of this method has been presented in our previous papers (13-18).

In this treatment theoretical solute capacity factors k' in mixed mobile phase can be calculated by the means of the following equation:

$$\log k'_{12} = x_1^l \log k'_1 + x_2^l \log k'_2 + (\, x_1^s - x_1^l\,)\left(\log \frac{k'_1}{k'_2} + A_{s(12)}\right) \qquad (3)$$

TABLE I

Solute Capacity Factors obtained in hexane - carbon tetrachloride mobile phase.

$k'_{TLC}$ - experimental k' values obtained by TLC;

$k'_{LCC}$ - experimental k' values obtained by LCC;

$k'_{(th)}$ - theoretical k' values calculated according to eq. (3).

1/c correction factor from eq. (1)

| Solutes | $x_1^1=0.3$ | | | | $x_1^1=0.5$ | | | |
|---|---|---|---|---|---|---|---|---|
| | $k'_{TLC}$ | $k'_{(th)}$ | $k'_{LCC}$ | 1/c | $k'_{TLC}$ | $k'_{(th)}$ | $k'_{LCC}$ | 1/c |
| Naphtalene | 1.32 | 1.30 | 1.05 | 0.80 | 1.16 | 0.94 | 0.83 | 0.72 |
| Anthracene | 2.00 | 1.97 | 1.58 | 0.79 | 1.62 | 1.60 | 1.23 | 0.76 |
| Pyrene | 1.95 | 2.20 | 1.78 | 0.91 | 1.86 | 1.70 | 1.38 | 0.74 |
| Fluoranthen | 2.19 | 2.73 | 2.45 | 0.90 | 1.74 | 2.01 | 1.82 | 1.05 |
| 2,3-dichlorophenol | 4.79 | 12.60 | 12.30 | 1.12 | 11.48 | 10.01 | 9.33 | 0.81 |
| 2,4-dichlorophenol | 15.14 | 16.62 | 16.60 | 1.10 | 11.75 | 12.39 | 11.75 | 1.00 |
| 2,5-dichlorophenol | 12.30 | 11.22 | 11.48 | 0.93 | 9.12 | 8.40 | 8.51 | 0.93 |
| 2,6-dichlorophenol | 6.46 | 10.19 | 10.00 | 1.55 | 5.07 | 7.61 | 7.41 | 1.46 |

where $k'_1$, $k'_2$ and $k'_{12}$ are capacity factors of given solute in solvents 1 and 2, and in their mixture 1+2, respectivelly; $x_1^1$ and $x_2^1$ are molar fractions of solvents 1 and 2 in bulk phase; $x_1^s$ is a molar fraction of solvent 1 in surface phase; $A_{s(12)}$ is a parameter describing molecular interactions existing in bulk phase.

The method of $x_1^s$ and $A_{s(12)}$ parameters calculation from thin-layer experimental data are presented in papers (13-18). It is obvious that theoretical predictions of k' values according to equation (3) needs a lot of of TLC experimental data, i.e., not only $k'_1$ and $k'_2$ values, but a number of $k'_{12}$ capacity factors in the mixed mobile phase 1+2, for the estimation of $x_1^s$ and $A_{s(12)}$ parameters.

TABLE II.

Solute Capacity Factors obtained in hexane - benzene mobile phase.
$k'_{TLC}$ - experimental k' values obtained by TLC;
$k'_{LCC}$ - experimental k' values obtained by LCC;
$k'_{(th)}$ - theoretical k' values calculated according to eq.(3).
1/c correction factor from eq.(1)

| Solutes | $x_1^l=0.1$ | | | | $x_1^l=0.3$ | | | |
|---|---|---|---|---|---|---|---|---|
| | $k'_{TLC}$ | $k'_{(th)}$ | $k'_{LCC}$ | 1/c | $k'_{TLC}$ | $k'_{(th)}$ | $k'_{LCC}$ | 1/c |
| Naphtalene | 1.34 | 0.78 | 0.78 | 0.58 | 0.95 | 0.38 | 0.35 | 0.37 |
| Anthracene | 1.82 | 1.09 | 1.29 | 0.71 | 1.05 | 0.37 | 0.48 | 0.46 |
| Pyrene | 1.70 | 1.24 | 1.34 | 0.79 | 1.12 | 0.44 | 0.54 | 0.48 |
| Fluoranthene | 2.04 | 1.33 | 1.58 | 0.77 | 1.20 | 0.38 | 0.60 | 0.50 |
| 2,3-dichlorophenol | 14.79 | 11.00 | 10.97 | 0.74 | 8.51 | 4.37 | 4.79 | 0.56 |
| 2,4-dichlorophenol | 15.14 | 12.06 | 12.59 | 0.93 | 8.13 | 5.00 | 5.62 | 0.69 |
| 2,5-dichlorophenol | 12.02 | 9.52 | 8.71 | 0.72 | 6.76 | 4.10 | 4.17 | 0.62 |
| 2,6-dichlorophenol | 6.31 | 7.15 | 6.92 | 1.10 | 3.89 | 2.70 | 2.95 | 0.76 |

In the paper these two ways of using thin-layer chromatography for the choice of optimal mobile phase in liquid column chromatography in systems with two-component mobile phases and some organic model substances have been presented.

## MATERIALS AND METHODS

All experimental data presented in the paper have been obtained using adsorption liquid chromatography. Two techniques of this analytical method have been used, i.e., column chromatography and

TABLE III.

Solute Capacity Factors obtained in hexane - etylene chloride mobile phase.

$k'_{TLC}$ - experimental k' values obtained by TLC;

$k'_{LCC}$ - experimental k' values obtained by LCC;

$k'_{(th)}$ - theoretical k' values calculated according to eq. (3).

1/c correction factor from eq. (1)

| Solutes | $x_1^1=0.3$ | | | | $x_1^1=0.5$ | | | |
|---|---|---|---|---|---|---|---|---|
| | $k'_{TLC}$ | $k'_{(th)}$ | $k'_{LCC}$ | 1/c | $k'_{TLC}$ | $k'_{(th)}$ | $k'_{LCC}$ | 1/c |
| Naphtalene | 1.20 | 0.68 | 0.58 | 0.48 | 0.89 | 0.30 | 0.27 | 0.30 |
| Anthracene | 1.35 | 0.92 | 0.89 | 0.66 | 0.81 | 0.32 | 0.25 | 0.31 |
| Pyrene | 1.41 | 0.88 | 0.79 | 0.56 | 0.95 | 0.44 | 0.32 | 0.34 |
| Fluoranthene | 1.78 | 1.10 | 1.00 | 0.56 | 1.17 | 0.38 | 0.35 | 0.30 |
| 2,3-dichloro-phenol | 8.91 | 5.60 | 5.62 | 0.63 | 4.07 | 1.89 | 2.00 | 0.49 |
| 2,4-dichloro-phenol | 9.55 | 6.18 | 6.31 | 0.66 | 4.27 | 2.00 | 2.34 | 0.55 |
| 2,5-dichloro-phenol | 7.76 | 4.92 | 4.79 | 0.62 | 3.89 | 1.74 | 1.78 | 0.46 |
| 2,6-dichloro-phenol | 4.37 | 4.10 | 4.17 | 0.95 | 2.45 | 1.32 | 1.41 | 0.58 |

Techma Robot Type 302 liquid chromatograph ( Warsaw, Poland ) equipped with UV detector ( Labmim, Hungary ). The column was fitted with Lichrosorb Si-60, $d_p$= 5μm ( Merck ). Mobile phase flow rate was v = 1 ml/min.

In thin-layer measurements sandwich chambers and precoated ( Merck ) silica gel ( Si-60, $d_p$ = 5μm ) plates have been used.

Thin-layer chromatograms were visualized by Scanning Densitometer Cs-9000 ( Shimadzu ).

All substances and solutes used in TLC and LCC measurements were identical.

For detailed information see previous papers ( 14-18).

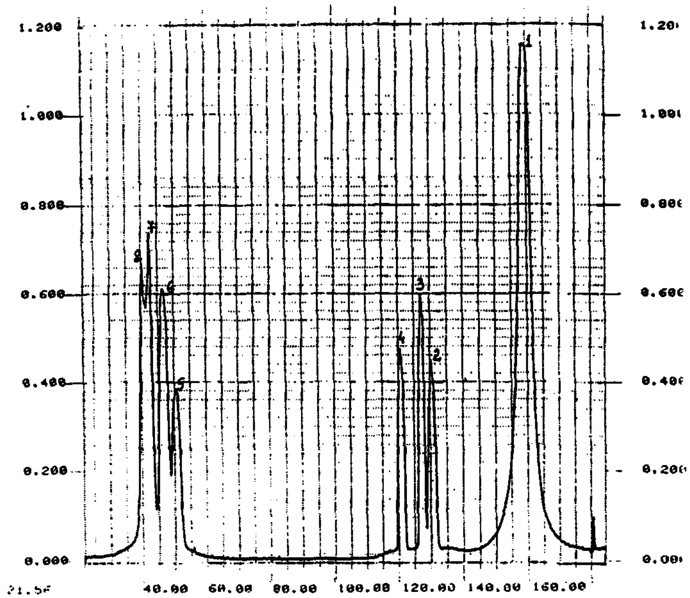

Fig. 1
Chromatogram obtained by TLC technique ( Scanning Densitometer Cs-9000, Shimadzu, $\lambda$ = 287 nm ).
Mobile phase: hexane - carbon tetrachloride, $x_1^1 = 0.3$
solutes: (1)naphthalene, (2) anthracene, (3) pyrene, (4) fluoranthene, (5) 2,6-dichlorophenol, (6) 2,5-dichlorophenol, (7) 2,3-dichlorophenol, (8) 2,4-dichlorophenol

## RESULTS AND DISCUSSION

Using TLC measurements experimental capacity factors k' of studied substances for all mobile phases have been obtained. These values are presented in Tables I-III as $k'_{TLC}$ parameters. Experimental capacity factors of the same substances and mobile phases obtained by column chromatography are presented in Tables I-III as $k'_{LCC}$ values.

Thin-layer chromatograms are presented on Figs 1-5, for chosen mobile phase systems.

For comparing experimental capacity factors corresponding to both techniques, 1/c correction factors have been calculated according to Kaiser and Rieder equation (1).

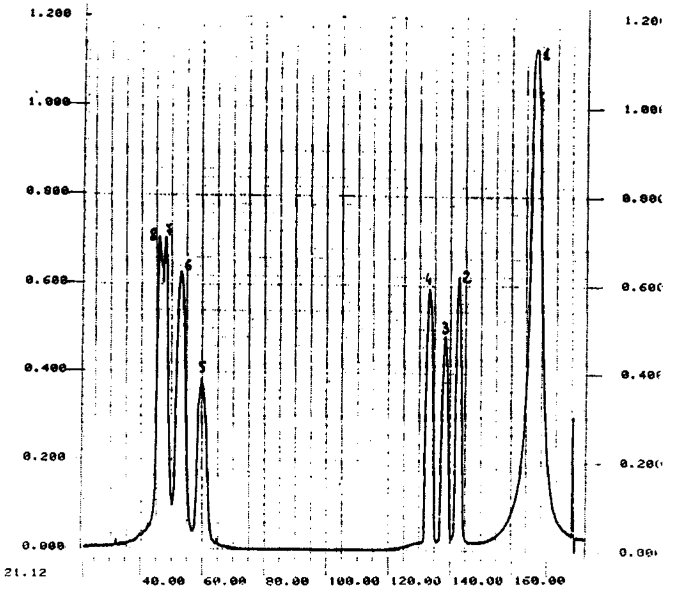

Fig. 2
Chromatogram obtained by TLC technique ( Scanning Densitometer Cs-9000, Shimadzu, λ = 287 nm ).
Mobile phase: hexane - carbon tetrachloride, $x_1^1 = 0.5$
solutes: (1)naphthalene, (2) anthracene, (3) fluoranthene, (4) pyrene, (5) 2,6-dichlorophenol, (6) 2,5-dichlorophenol, (7) 2,3-dichlorophenol, (8) 2,4-dichlorophenol

These parameters are listed in Tables I-III for all studied substances and mobile phases.

Analysing these 1/c parameters it is obvious that they depend not only on chromatographed substances but on mobile phase properties as well. But, for given two-component mobile phase one can notice that:

- 1/c values change with mobile phase composition;
- 1/c values are very similar to each other for the given group of chromatographed substances, i.e., for aromatic hydrocarbons or chlorophenols, especially in more active mobile phases hexane-benzene and hexane-ethylene chloride.

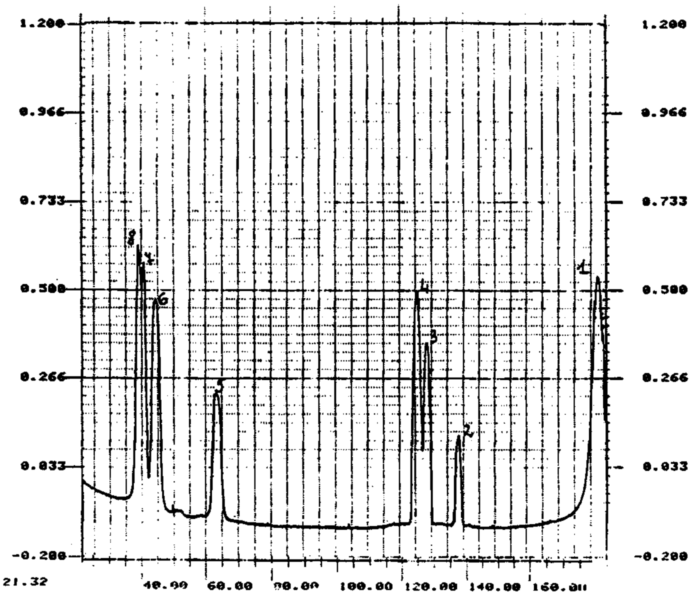

Fig. 3
Chromatogram obtained by TLC technique ( Scanning Densitometer Cs-9000, Shimadzu, λ = 287 nm ).
Mobile phase: hexane - benzene, $x_1^1 = 0.1$
solutes: (1)naphthalene, (2) pyrene, (3) anthracene, (4) fluoranthene, (5) 2,6-dichlorophenol, (6) 2,5-dichlorophenol, (7) 2,3-dichlorophenol, (8) 2,4-dichlorophenol

In the paper theoretical capacity factors $k'_{(th)}$ of studied substances ( Table I-III ) have been calculated using equation (3) resulting from thermodynamic description of adsorption chromatographic system.
These $k'_{(th)}$ values are capacity factors of studied substances in liquid column technique evaluated on the bases of experimental thin-layer data.
From the data presented in Tables I-III it seems that there is a very good agreement between theoretical and experimental k' values for all studied substances and mobile phases.
In the paper two ways of the choice of optimal mobile phase in LCC technique from TLC experimental data are presented.

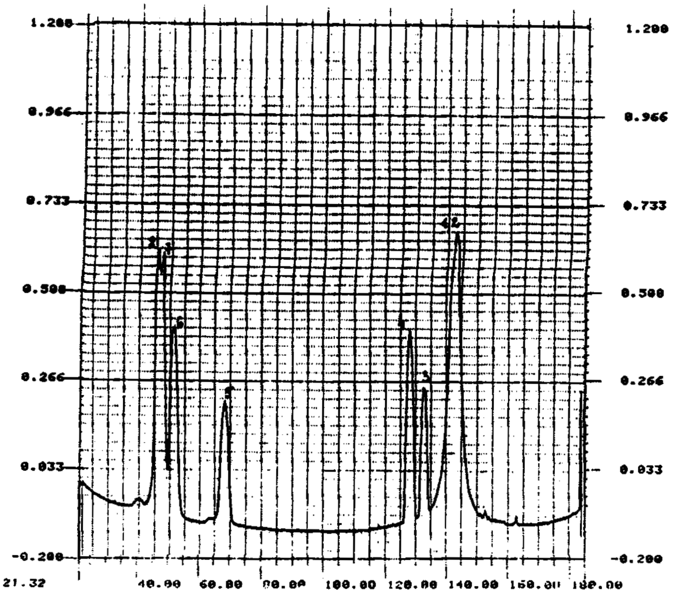

Fig. 4
Chromatogram obtained by TLC technique ( Scanning Densitometer Cs-9000, Shimadzu, λ = 287 nm ).
Mobile phase: hexane - benzene, $x_1^1 = 0.3$
solutes: (1) naphthalene, (2) anthracene, (3) pyrene, (4) fluoranthene, (5) 2,6-dichlorophenol, (6) 2,5-dichlorophenol, (7) 2,3-dichlorophenol, (8) 2,4-dichlorophenol

At first, for this purpose there have been used the correlations between experimental thin-layer and column retention parameters, i.e., between $k'_{TLC}$ and $k'_{LCC}$ values.

This method is rather simple, but for precise prediction of $k'_{LCC}$ values it requires evaluation of 1/c correction factors. Though from the study appears that these 1/c values depend not only on the mobile phase kind but on its composition as well, they are characteristic for some groups of studied substances.

The other method is based on thermodynamic description of chromatographic systems. This method is very precise, but it needs much more experimental TLC information than the first one.

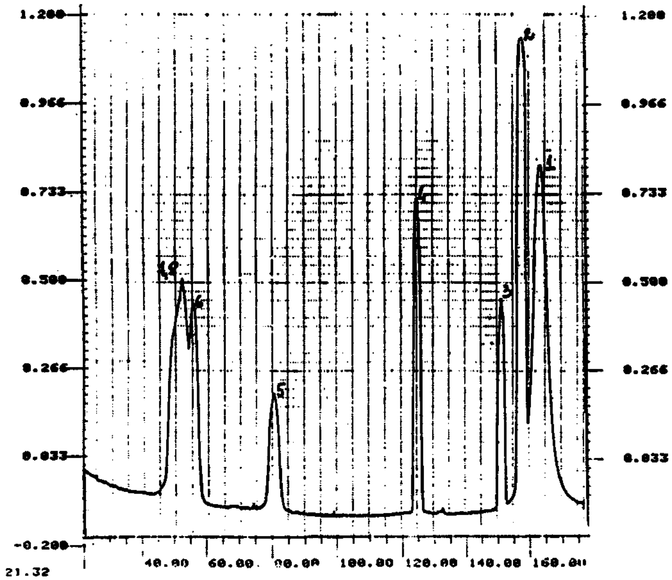

Fig. 5
Chromatogram obtained by TLC technique ( Scanning Densitometer Cs-9000, Shimadzu, $\lambda$ = 287 nm ).
Mobile phase: hexane - ethylene chloride, $x_1^1$ = 0.1
solutes: (1)naphthalene, (2) anthracene, (3) pyrene, (4) fluoranthene, (5) 2,6-dichlorophenol, (6) 2,5-dichlorophenol, (7) 2,3-dichlorophenol, (8) 2,4-dichlorophenol

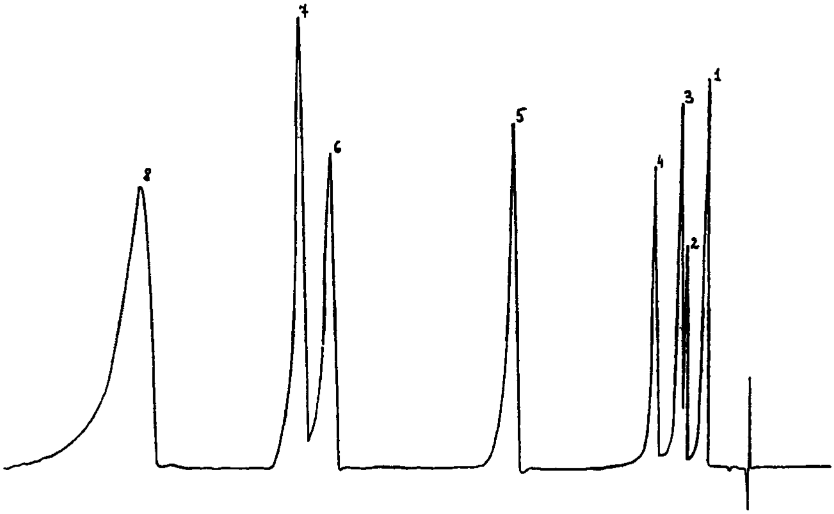

Fig. 6
Chromatogram obtained by LCC technique.
Mobile phase: hexane - carbon tetrachloride, $x_1^1$ = 0.3
solutes: (1)naphthalene, (2) anthracene, (3) pyrene, (4) fluoranthene, (5) 2,6-dichlorophenol, (6) 2,5-dichlorophenol, (7) 2,3-dichlorophenol, (8) 2,4-dichlorophenol

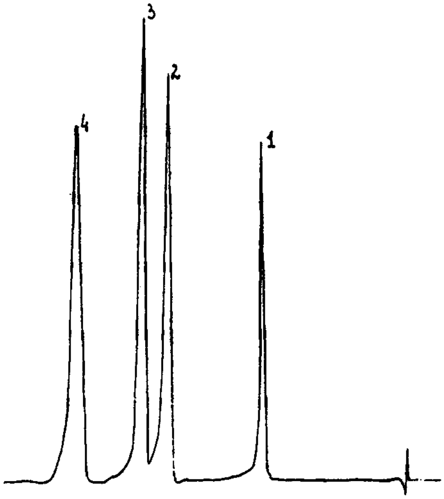

Fig. 7
Chromatogram obtained by LCC technique.
Mobile phase: hexane - carbon tetrachloride, $x_1^1 = 0.5$
solutes: (1) 2,6-dichlorophenol, (2) 2,5-dichlorophenol,
(3) 2,3-dichlorophenol, (4) 2,4-dichlorophenol

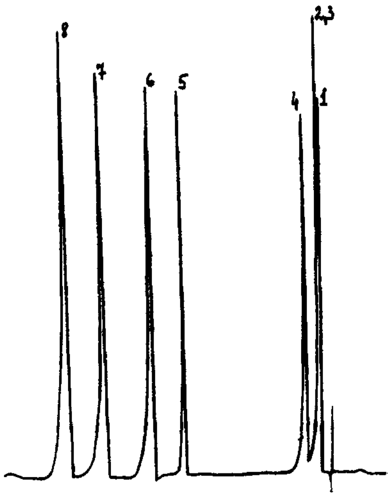

Fig. 8
Chromatogram obtained by LCC technique.
Mobile phase: hexane - benzene, $x_1^1 = 0.1$
solutes: (1) naphthalene, (2) anthrecene, (3) pyrene, (4) fluoranthene,
(5) 2,6-dichlorophenol, (6) 2,5-dichlorophenol, (7) 2,3-dichlorophenol,
(8) 2,4-dichlorophenol

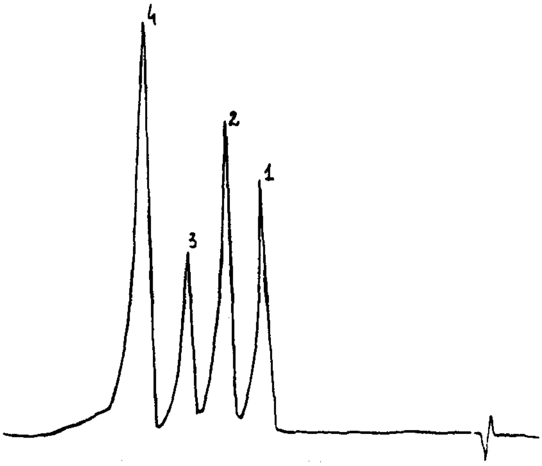

Fig.9

Chromatogram obtained by LCC technique.
Mobile phase: hexane - ethylene chloride, $x_1^1 = 0.1$
solutes: (1) 2,6-dichlorophenol, (2) 2,5-dichlorophenol,
(4) 2,3-dichlorophenol, (5) 2,4-dichlorophenol

From all experimental thin-layer measurements that have been performed in the study, four different mobile phases have been chosen as the most appropriate for liquid column measurements. Liquid column chromatograms obtained in these chosen systems are presented on Figs 6-9.

From LCC experimental data it appears that the best resolution for all studied substances has been obtained in hexane - carbon tetrachloride ( $x_1^1 = 0.3$ ) as mobile phase. This mobile phase seems to be the most comfortable for the separation of aromatic hydrocarbons as well.

For the best separation of the group of chlorophenols it is much better to use hexane - benzene ( $x_1^1 = 0.1$ ) as mobile phase.

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