

CHROM. 15,496

## THIN-LAYER CHROMATOGRAPHY ON CHEMICALLY BONDED PHASES: A COMPARISON OF PRE-COATED PLATES

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(First received October 19th, 1982; revised manuscript received November 5th, 1982)

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### SUMMARY

The characteristics of eight types of commercially available thin-layer plates pre-coated with non-polar chemically bonded phases are compared. Phthalate esters, aromatic acids, chlorophenols, chloroanilines and aminophenols were used as test compounds.

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### INTRODUCTION

In modern thin-layer chromatography (TLC), silica is the stationary phase material preferred by most workers, and TLC on chemically bonded phases has had limited use. This is in marked contrast with the situation in column liquid chromatography (LC), where a considerable proportion of the work has been carried out using chemically bonded phases, especially non-polar C<sub>18</sub>- and C<sub>8</sub>-modified silicas. However, in recent years the widespread use of these apolar chemically bonded stationary phases in what is often called reversed-phase column liquid chromatography (RP-LC) has promoted interest in their utilization in TLC, and a recent review<sup>1</sup> on reversed-phase thin-layer chromatography (RP-TLC) on chemically bonded phases featured over 90 references. For the sake of clarity, it is emphasized that RP-TLC as such can be subdivided into two categories, on physically coated and on chemically bonded stationary phases, and that it is only the latter type that is considered in this paper.

In previous papers<sup>2,3</sup> we discussed the relative merits of various types of commercially available pre-coated plates for RP-TLC, with emphasis on aspects such as development time of the chromatogram and compatibility of the RP-TLC plates with mobile phases containing a relatively large proportion of water. Since then, several new types of commercial RP-TLC plates have become available. These have been included in this study which, for the rest, has mainly been directed at the separation of rather polar compounds such as chloroanilines, chlorophenols and aminophenols.

## EXPERIMENTAL

*RP-TLC plates\**

Commercial HPTLC-quality plates pre-coated with RP-8- and RP-18-modified silica (HPTLC-Fertigplatten RP-8 F<sub>254s</sub> and RP-18 F<sub>254s</sub>; product nos. 13725 and 13724, respectively) and samples of, meanwhile become commercially available, TLC-quality plates pre-coated with RP-8- and RP-18-modified silica (DC-Fertigplatten RP-8 F<sub>254S</sub> and RP-18 F<sub>254S</sub>; product nos. 15424 and 15423, respectively) were obtained from Merck (Darmstadt, G.F.R.). The TLC-quality plates were received as gifts in September 1980 (RP-8a), July 1981 (RP-18b) and October 1981 (RP-8c and RP-18c), the suffixes a, b and c having been added by us in order to distinguish between them.

Pre-coated KC<sub>18</sub> plates were obtained from Whatman (Springfield Mill, Great Britain; KC<sub>18</sub>F plates, product no. 4803-800), Si-C<sub>18</sub>F pre-coated plates from Baker (Deventer, The Netherlands; product no. 7013-4), OPTi-UP C<sub>12</sub> pre-coated plates from Antec (Bennwil, Switzerland; OPTi-UP C<sub>12</sub> DC Trägerplatten L 254; product no. 1028) and Nano-SIL C18-50 pre-coated plates from Macherey, Nagel & Co. (Düren, G.F.R.; product no. 811.064). All of these 20 × 20, 20 × 10 or 10 × 10 cm plates contain a fluorescent indicator. They were used without pre-treatment.

TLC plates of a size appropriate for our experimental work were obtained using the simple device shown in Fig. 1. A sheet of millimetre graph paper is glued on to a metal or wooden plate. A thin-layer plate is placed on this base plate, with its pre-coated side down, so that it touches the metal guides a and b. The metal cutter guide c is moved into the desired position and secured by means of the two screws d. Continuous scores are made in the glass backing of the thin-layer plate by moving a glass cutter with its flat side along the edge of c. The slides are then broken off at the edge of the base plate. This procedure can conveniently be performed with less than 5% loss of material.

*Materials*

The phthalate esters, aromatic acids, chloroanilines, chlorophenols, aminophenols and further test solutes and all solvents and other chemicals were of normal analytical-reagent grade. Approximately 1% sample solutions in dioxane were used for spotting. Dioxane was preferred to ethanol<sup>2</sup> in order to prevent any esterification reactions with the phthalate ester and aromatic acid stock solutions.

*TLC*

TLC was routinely carried out on rectangular plates of about 6.5 × 1.5 cm. After the application of about 0.5–1.0 mm spots using a pointed paper wick partly impregnated with the sample solution or a fine-tipped melting-point capillary, ascending development was carried out in Hellendahl staining jars over a distance of 5.0 cm. Saturation of the chromatographic chamber was achieved by lining its wider upper part with filter-paper impregnated with the mobile phase. Detection was accomplished by viewing the plates under 254-nm UV light. The aminophenols were

\* For further details on plate characteristics, see the next section.

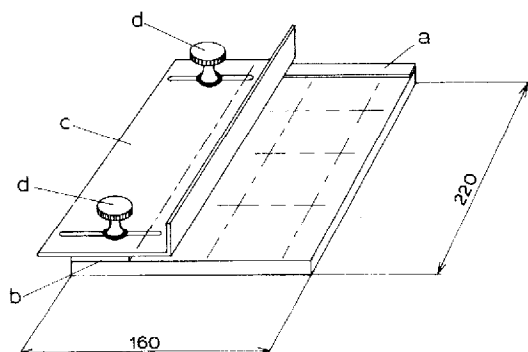


Fig. 1. Device used for cutting TLC plates to appropriate size. a, b, Metal guides; c, metal cutter guide; d, screws. Dimensions, 220 × 160 mm. For further explanation, see text.

detected as brown spots after irradiation of the RPTLC plates for 3–5 min with a medium-pressure mercury lamp.

## RESULTS AND DISCUSSION

### *RP-TLC plate characteristics*

A wide variety of good-quality pre-coated plates for RP-TLC are commercially available, as is evident from the summary in Table I. As most of these types of plates were used in this work, a few pertinent comments will be added (for the abbreviations used in the text, see Table I). The data given in this section have mainly been derived from product information bulletins or have been supplied by the manufacturers. For all references on the use of the RP-TLC plates in analysis, a recent review<sup>1</sup> should be consulted.

The Antec  $C_{12}$  plates have been commercially available for several years and they have been used in various studies. Recently, the manufacturing process of

TABLE I

### COMMERCIALY AVAILABLE APOLAR CHEMICALLY BONDED RP-TLC PLATES

Manufacturer	Plate designation	Carbon chain length	Abbreviation in text	$F_{254}$ indic.*	Miscellaneous
Antec	OPTi-UP $C_{12}$	12	$C_{12}$	+	Inorganic binder
Baker	Si- $C_{18}$	18	—	±	± Pre-scored
Macherey, Nagel & Co.	Nano-SIL C18-100, -75, -50	18	MN-100, -75, -50	±	—
Merck	Kieselgel silanisiert	2	—	±	—
	RP-2, -8, -18 (HPTLC)	2, 8, 18	—	+	Acid-resistant $F_{254}$ ; TLC plates have
	RP-8, -18 (TLC)	8, 18	—	+	improved water compatibility
Whatman	KC $_{18}$	18	—	±	End-capped with $C_2$ ; ± pre-adsorbent strip

\* ±, With or without.

these plates appears to have been changed: the newer plates are much softer and migration times are considerably shorter; unfortunately, however, the separation efficiency seems to have deteriorated. The average particle diameter,  $d_p$ , of the stationary phase material on the latter type of plates (which were mainly used in this study) is 10–20 (80%: 10–15)  $\mu\text{m}$ . The  $C_{12}$  plates use silica silanized with dodecyltrichlorosilane, with no subsequent end-capping, and an inorganic binder. This may explain why the sorption of polar solutes such as nitrobenzene and acetophenone from apolar mobile phases<sup>4</sup> in our experience was much stronger with the Antec  $C_{12}$  plates than with any other RP-TLC plate tested.

The Baker Si- $C_{18}$  plates are the most recent addition to the list of pre-coated RP-TLC plates. As yet, their use has not been described in the literature, and data on plate characteristics are still lacking.

Macherey, Nagel & Co., who market a series of three bonded-phase plates, use high-performance TLC-grade silica (HPTLC silica;  $d_p$  stated to be 5–10  $\mu\text{m}$ ) as the base material. The silanol groups on this silica are totally or partly (75 or 50%) reacted with a  $C_{18}$  alkylsilane. No details are known about the methods used to control and/or determine the degree of silanization, and the real degree of silanization of the MN-75 and MN-50 materials is assumed by some workers to be much higher, *e.g.*, of the order of 90–95% for MN-75.

So far, the Merck RP-coated plates (RP-2, -8 and -18) have been most widely used. Production started about 5 years ago, the bonded phases being HPTLC ( $d_p$  *ca.* 5–7  $\mu\text{m}$ ) quality. With these pre-coated plates severe problems arose, however, when mobile phases containing over 30–40% of water were used. In such instances, the non-wettability of the apolar stationary phase prevented normal chromatographic development; the addition of salts such as sodium or lithium chloride to the mobile phase, a well known remedy<sup>2,5</sup> (see below), did not improve the situation. In order to extend the application range of their pre-coated RP-TLC plates, Merck has recently marketed plates pre-coated with  $C_8$ - and  $C_{18}$ -alkyl-modified silica that feature a slightly larger particle size of the silica used as base material ( $d_p$  *ca.* 11–12  $\mu\text{m}$ ) while silanization is not completely exhaustive. These are therefore called chemically bonded TLC (in contrast with the above-mentioned HPTLC) plates. They are essentially comparable to the well known silanized silica pre-coated plates manufactured since 1972 (Kieselgel silanisiert F<sub>254</sub>), which also feature a particle size of 11–12  $\mu\text{m}$ . It should be added that both these plates and the RP-2-coated HPTLC plates are prepared via silanization with dimethyldichlorosilane, so that they are (di-)RP-1- rather than RP-2-coated plates.

A survey of the literature reveals that an increasing number of workers prefer to use  $KC_{18}$  plates (the  $KC_2$  and  $KC_8$  plates mentioned in a single recent paper are not commercially available). As with the RP-coated HPTLC plates, the  $KC_{18}$  plates cannot be used with mobile phases that contain over about 40% of water. With the  $KC_{18}$  plates it has been amply demonstrated, however, that the addition of about 3% of sodium chloride to the mobile phase suffices to extend the application range to at least 80–90% of water in methanol–water and acetonitrile–water mixtures without any undue increase in the time of development. For the rest, the manufacturer has repeatedly stated that the silica base material of the  $KC_{18}$  plates has a particle size of about 10  $\mu\text{m}$ . Surprisingly, in a single recent brochure, 20  $\mu\text{m}$  is mentioned instead; this seems to fit well with provisional results from particle size measurements<sup>6</sup>.

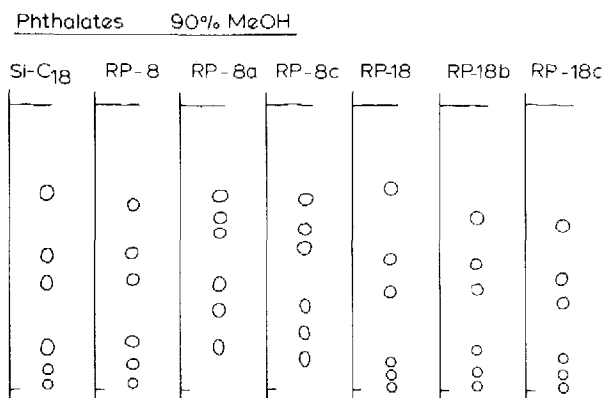


Fig. 2. RP-TLC, on Si-C<sub>18</sub> and various types of RP-coated plates, of six phthalate esters using methanol (MeOH)-water (90:10) as the mobile phase. Phthalate esters, in order of decreasing  $hR_F$ : di-C<sub>2</sub>, di-C<sub>4</sub>, di-C<sub>5</sub>, di-C<sub>8</sub>, di-C<sub>10</sub>, di-C<sub>11</sub>.

Finally, the following characteristics of the RP-TLC plates should be mentioned. When plates containing a fluorescent indicator are viewed under 254-nm UV light, the KC<sub>18</sub> and Si-C<sub>18</sub> plates display a strong, and the C<sub>12</sub> plates a weaker, yellow fluorescent background; the (TLC) RP- and MN-type plates show a weak blue fluorescence. The KC<sub>18</sub> and, slightly less so, the Si-C<sub>18</sub> plates have a hard surface, which, especially in the case of the Baker plates, has a fairly coarse structure. The RP- and MN-type layers are distinctly softer materials, which display a very smooth surface. With none of these four types of plates does writing on the layer surface pose a problem. The C<sub>12</sub> layers are smooth and extremely soft; small amounts of stationary phase material easily come off when they are touched, and writing cannot conveniently be done.

#### RP-TLC plate quality

*Model separations.* A rapid test for the assessment of the separation efficiency of the various types of pre-coated plates is provided by, *e.g.*, the analysis of a mixture of phthalate esters using a suitable methanol-water mixture as the mobile phase. Results for seven types of plates, with emphasis on the RP-coated HPTLC and TLC plates, are shown in Fig. 2. Combination of these data with those previously published<sup>2,3</sup> for, *e.g.*, KC<sub>18</sub> and MN plates demonstrates that all pre-coated plates tested so far pass the said test.

The above test, in other words, is too simple to be really valuable and, in its stead, a separation of three aromatic acids was therefore selected that requires the use of a much more polar mobile phase (Fig. 3). The differences between the two types of separation are obvious. In Fig. 3, with Si-C<sub>18</sub>, development of the plate poses no problem, but the separation is poor. With the RP-8- and RP-18-coated HPTLC plates development does not occur at all, which is in agreement with earlier results. The introduction of the RP-8- and RP-18-coated TLC plates is seen to effect a considerable improvement: the flow of the mobile phase is now uninterrupted and an adequate separation of *o*-nitrobenzoic, acetylsalicylic and *p*-hydroxybenzoic acid (in order of increasing  $hR_F$ ) is observed in all instances. From previous work it is

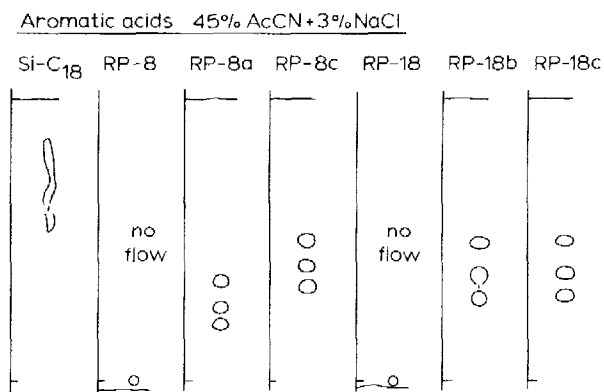


Fig. 3. RP-TLC, on Si-C<sub>18</sub> and various types of RP-coated plates, of three aromatic acids using acetonitrile (AcCN)-water (45:55) + 3% sodium chloride as the mobile phase. Acids, in order of increasing  $R_F$ : *p*-nitrobenzoic, acetylsalicylic, *p*-hydroxybenzoic acid.

known<sup>2,3</sup> that efficient separations of the aromatic acids can also be created on KC<sub>18</sub> and MN-50 layers.

With the C<sub>12</sub> plates (data not shown) the results of the phthalate ester separation were satisfactory, although it is interesting that optimal separation was achieved at 80% methanol compared with 90–95% for all other RP-TLC plates. With the aromatic acids no separation worth mentioning was achieved with any of the mobile phases tested.

*Migration time.* The dependence of migration time, for a 5-cm run, on the mobile phase composition was systematically studied for several types of pre-coated plates. Methanol-water and acetonitrile-water mixtures were routinely used, both with and without added sodium chloride. Development was carried out in saturated Hellendahl jars, but without previous accommodation of the pre-coated plates.

In Fig. 4 results for the two available batches of RP-18-coated TLC plates and

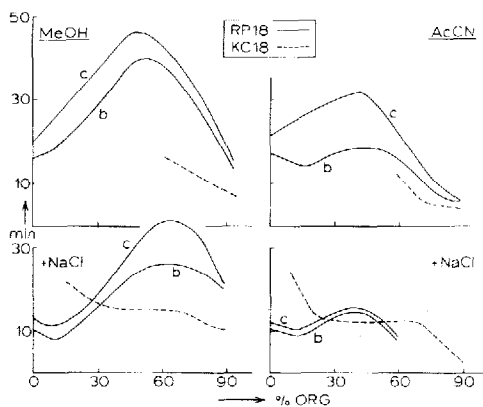


Fig. 4. Dependence of migration time, for a 5-cm run, on the organic modifier (methanol or acetonitrile) and sodium chloride content of the mobile phase for two types of TLC-quality RP-18 (solid lines) and for KC<sub>18</sub> (broken lines) plates.

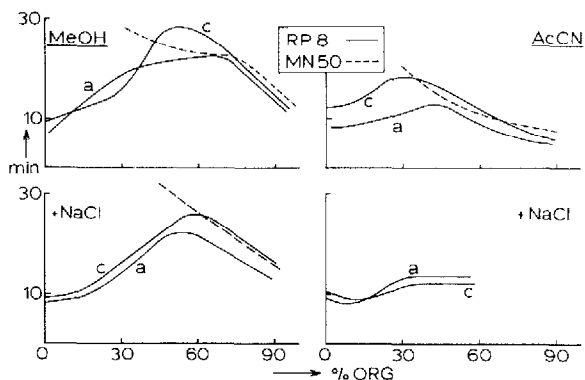


Fig. 5. Dependence of migration time, for a 5-cm run, on the organic modifier (methanol or acetonitrile) and sodium chloride content of the mobile phase for two types of TLC-quality RP-8 (solid lines) and for MN-50 (broken lines) plates.

$KC_{18}$  plates are compared. The data for the  $KC_{18}$  plates are in good agreement with those published in ref. 2: when using over about 40% of water in the mobile phase, addition of sodium chloride is required and, provided this is done, high migration rates are obtained up to at least 80–90% of water. With RP-18b and c, normal development of the plates occurs at all mobile phase compositions (including 100% water) even without added sodium chloride (such an addition, however, generally increases the speed of migration to some extent). The reproducibility of the results between batches varies between fair and excellent. For the rest, it is noteworthy that the shape of the migration time *versus* mobile phase composition plots is completely different for the RP-coated TLC plates and the  $KC_{18}$  plates. With the latter type, the time of development is virtually independent of the mobile phase composition between about 30 and 70% of organic modifier (in the presence of sodium chloride), whereas there is a distinct maximum in the plots for the RP-coated plates. This more or less coincides with the maximum in the viscosity *versus* composition plot of the mobile phase mixtures used.

Data for the two available batches of RP-8-coated TLC plates and for MN-50 plates are shown in Fig. 5. With the RP-8-type plates, salt addition is again seen to be superfluous; the reproducibility between batches now is excellent in all four instances shown, and the migration times are distinctly shorter than with the RP-18-coated TLC plates. As for the MN-50 plates, with down to about 30% of organic modifier their behaviour is closely analogous to that of the RP-8-type plates. If, however, over 70% of water is present in the mobile phase, the migration times increase rapidly, with the addition of salt detracting from rather than improving the performance of the system, and the plates can no longer be used conveniently.

The  $C_{12}$  plates display very favourable migration characteristics. Migration times for the 5-cm run do not exceed 15 min over the whole 0:100 to 95:5 range for methanol–water and acetonitrile–water mixtures. Addition of sodium chloride does not significantly influence the speed of migration. The behaviour of the Si- $C_{18}$  plates is closely analogous to that of the  $KC_{18}$  plates, shown in Fig. 4.

On the basis of the above data, all further work was limited to RP-TLC of rather polar test solutes because, with these, the effect of a high water content of the

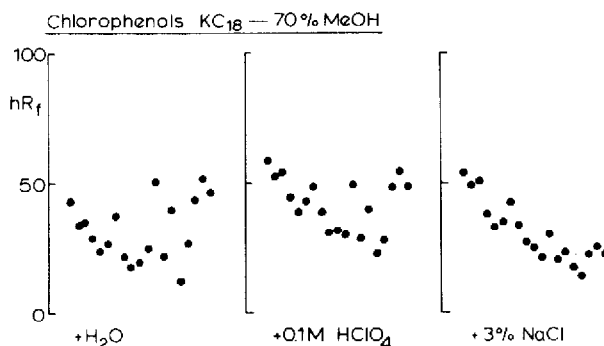


Fig. 6. RP-TLC, on  $KC_{18}$  plates, of 19 chlorophenols using methanol-water (70:30) (left), with added acid (centre) or added sodium chloride (right), as the mobile phase. Sequence of chlorophenols, from left to right: 2-, 3-, 4-; 2,3-, 2,4-, 2,5-, 2,6-, 3,4-, 3,5-; 2,3,4-, 2,3,5-, 2,3,6-, 2,4,5-, 2,4,6-, 3,4,5-; 2,3,4,5-, 2,3,4,6-, 2,3,5,6-; penta.

mobile phase and pH or ionic strength (sodium chloride) variation on chromatographic behaviour can be more easily studied.

### Chlorophenols

From reversed-phase column LC with, *e.g.*, methanol-water mixtures as the mobile phase, it is known<sup>7,8</sup> that for lower (mono- to tri-) chlorinated phenols the capacity factor,  $k'$ , increases with increasing number of chlorine substituents. With the tetra- and pentachlorophenol(s), however, such a relationship does not hold: the retention starts to decrease and becomes irreproducible, and the peak shapes tend to be poor. This anomalous behaviour is caused by the relatively strong acidity of the higher chlorinated phenols, which are partly ionized under the experimental conditions. Acidification of the water used as (part of) the mobile phase to a pH of about 3 completely suppresses ionization and the capacity factors now increase almost linearly with increasing chlorine content through to the pentachlorophenol.

In this work, all 19 chlorophenols were chromatographed on  $KC_{18}$  plates with methanol-water (70:30) as the mobile phase (Fig. 6; in this and the subsequent Figs. 7, 8, 10 and 11 the chlorine content of the test solutes invariably increases from left to right). With methanol water, the result is according to expectation. The  $hR_f$  values decrease on going from the mono- to the trichlorophenols and then increase again

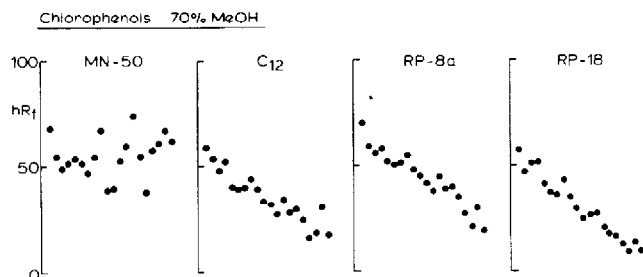


Fig. 7. RP-TLC, on MN-50,  $C_{12}$ , RP-8a and RP-18 (HPTLC) plates, of phenol and 19 chlorophenols (for sequence, see Fig. 6) using methanol-water (70:30) as the mobile phase.



## Chlorophenols MN-50 — 70% MeOH

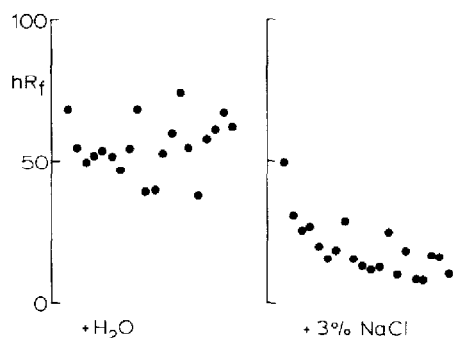


Fig. 8. RP-TLC, on MN-50 plates, of phenol and 19 chlorophenols (for sequence, see Fig. 6) using methanol-water (70:30), without and with added sodium chloride, as the mobile phase.

with the higher chlorinated compounds. Surprisingly, however, on acidification of the mobile phase (with 0.1 *M* perchloric acid), the general picture remains essentially the same. If, on the other hand, sodium chloride is added, the retention of the tetra- and pentachlorophenol(s) distinctly increases.

The unexpected results obtained with the  $KC_{18}$  plates prompted us to repeat this study with four more chemically bonded phases (Fig. 7). Three of these, *viz.*,  $C_{12}$ , RP-8a and RP-18 (HPTLC), yield the "normal"  $hR_f$  sequence, *i.e.*, increasing retention from mono- to pentachlorophenol, even without acidification of the mobile phase. A confused picture emerges with the other plate tested, MN-50. Here, results

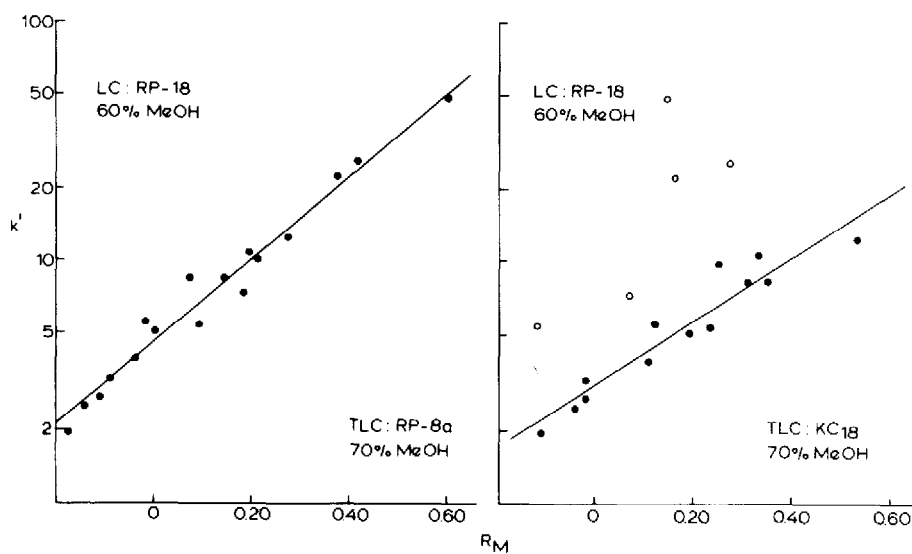


Fig. 9. Plots of  $k'$  from RP-LC on LiChrosorb RP-18 using acidified methanol-water (60:40) as the mobile phase<sup>7</sup> versus  $R_M$  from RP-TLC on RP-8a and  $KC_{18}$  plates using methanol-water (70:30) as the mobile phase. Test compounds: chlorophenols; open circles denote outliers.

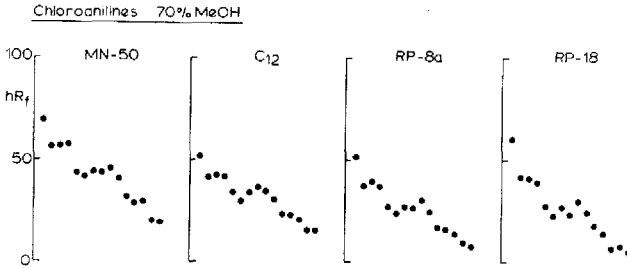


Fig. 10. RP-TLC, on MN-50,  $C_{12}$ , RP-8a and RP-18 (HPTLC) plates, of aniline and 14 chloroanilines using methanol-water (70:30) as the mobile phase. Sequence of chloroanilines: see Fig. 6 (2,3,5-, 2,3,6- and 3,4,5-tri-, 2,3,4,6-tetra- and pentachloroaniline not included).

slightly improved on addition of sodium chloride to the mobile phase (Fig. 8), but in fact the distinct decrease in the  $hR_F$  values for *all* chlorophenols is a much more striking phenomenon.

Finally, Fig. 9 demonstrates the excellent agreement between the column LC data and the RP-TLC data obtained with the RP-8a plates. The results clearly are less satisfactory in RP-TLC on  $KC_{18}$  plates. Here, there are at least five outliers, which are indicated in the figure by open circles.

### Chloroanilines

In order to establish whether the above results must be attributed to the unique behaviour of the chlorophenols, a similar study was made with chloroanilines. Here, all RP-TLC plates tested show the same trend of increasing retention with increasing chlorine content of the substituted anilines, as is evident from the results for MN-50,  $C_{12}$ , RP-8a and RP-18 (HPTLC) shown in Fig. 10. Besides, no changes occur on the addition of either acid or sodium chloride to the mobile phase, as illustrated by the  $hR_F$  plots for  $KC_{18}$  and RP-18 (HPTLC) in Fig. 11.

In agreement with the above results, plots of  $k'$  from column LC on LiChrosorb RP-18 *versus*  $R_M$  from RP-TLC on RP-8b and  $KC_{18}$  plates for mobile

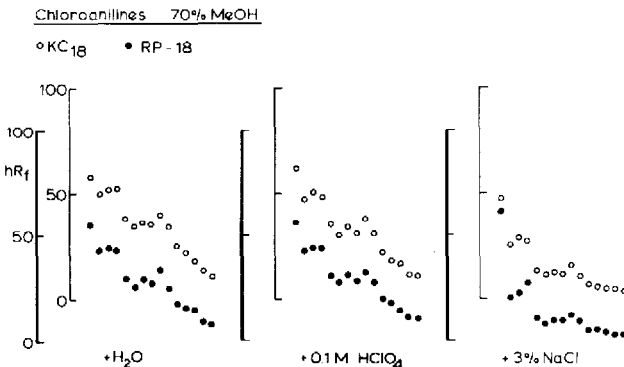


Fig. 11. RP-TLC, on  $KC_{18}$  (○) and RP-18 (HPTLC) (●) plates, of aniline and 14 chloroanilines (for sequence, see Fig. 10) using methanol-water (70:30) (left), with added acid (centre) or added sodium chloride (right), as the mobile phase.

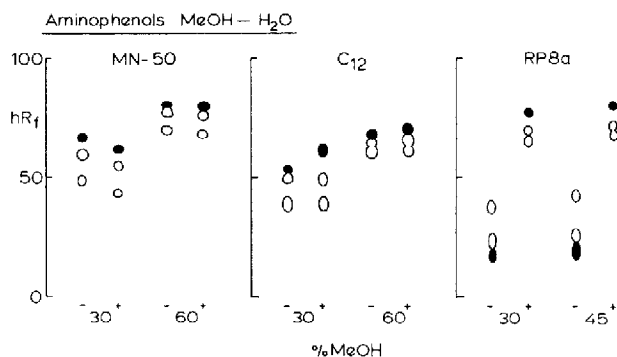


Fig. 12. RP-TLC, on MN-50,  $C_{12}$  and RP-8a plates, of *p*- (●), *o*- and *m*-aminophenol (○) ( $hR_{F,m} < hR_{F,o} < hR_{F,p}$ ) using various methanol-water mixtures (30, 45 or 60% methanol) without (–) or with (+) sodium chloride as the mobile phase.

phases containing 50 or 60% of methanol showed straight-line relationships with correlation coefficients of over 0.985 in all instances.

### Aminophenols

The three isomeric aminophenols were selected as the last group of test solutes. They were separated on all types of plates available to us, using methanol-water mixtures, both with and without sodium chloride, as mobile phase. In all but two instances, the  $hR_F$  values were found to increase in the order *ortho* < *meta* < *para*. Examples of this “normal” sequence are shown in Fig. 12 for MN-50 and  $C_{12}$ , for various percentages of methanol.

Exceptional behaviour was observed for the RP-8- and RP-18-coated TLC (but not the RP-8- and RP-18-coated HPTLC) plates, and in the absence of sodium chloride only (*cf.*, Fig. 12). With these, in the presence of sodium chloride, the “normal” order of separation is obtained. When the salt is left out, however, two

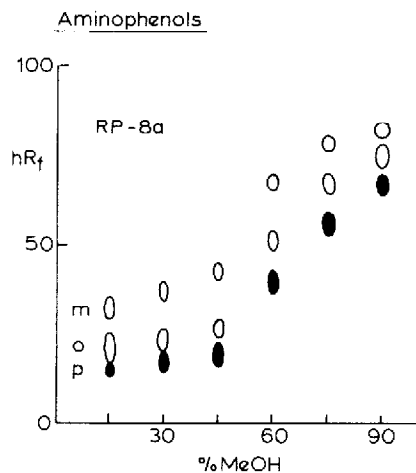


Fig. 13. RP-TLC, on RP-8a plates, of *o*-, *m*- and *p*-aminophenol using methanol water mixtures as the mobile phase.

striking changes occur: (1) the retention increases considerably for all aminophenols, whereas salt addition hardly affects the  $hR_F$  values with the other stationary phases tested; (2) with the *para* isomer the retention increases much more drastically than it does with *o*- and *m*-aminophenol. As a consequence, the order of separation now becomes *para* < *ortho* < *meta*. Similar results were obtained on substituting acetonitrile for methanol. The order of separation did not change on changing the organic modifier content of the mobile phase; pertinent data for the RP-8a plates are shown in Fig. 13.

Experiments similar to the above were carried out for *o*-, *m*- and *p*-nitroaniline, *o*-, *m*- and *p*-chlorophenol and *o*- and *p*-nitrophenol on RP-8a-, RP-18b- and KC<sub>18</sub> plates. With these classes of compounds, and with methanol-water (60:40 and 75:25) as the mobile phase, the order of elution was invariably the same, both with and without added salt. In other words, a relative increase in the retention of the *para* isomer in the absence of sodium chloride was never observed.

## CONCLUSION

Most of the wide variety of commercially available thin-layer plates pre-coated with chemically bonded stationary phases appear to be of normal TLC quality ( $d_p \geq ca. 10 \mu\text{m}$ ), the exceptions being the RP-coated HPTLC-quality plates ( $d_p = 5-7 \mu\text{m}$ ) and, possibly, the MN-type layers ( $d_p = 5-10 \mu\text{m}$ ). Satisfactory overall separation efficiency is combined with compatibility with mobile phases containing up to at least 80-90% of water for the newly introduced RP-8- and RP-18-coated TLC plates, and with the KC<sub>18</sub> plates provided that about 3% of, *e.g.*, sodium chloride is added to the mobile phase. The MN-50 plates can be used up to about 70% of water. The Merck RP-coated HPTLC plates and the MN-75 and MN-100 plates can be used over only a limited range of mobile phase compositions (less than 30-40% of water). With the Si-C<sub>18</sub> (salt addition!) and C<sub>12</sub> plates, migration does not pose a serious problem at any mobile phase composition, but here resolution of the test solutes is often less good than with the other types of plates. For the rest, for the pre-coated plates tested, the plots of migration time *versus* mobile phase composition are strikingly different [RP (TLC) KC<sub>18</sub> and Si-C<sub>18</sub>-MN-C<sub>12</sub>], which seems to indicate fundamental differences in the manufacturing process.

The advantage of the RP-18-coated TLC plates of unlimited use without added sodium chloride is partly offset by the shorter migration time observed with the KC<sub>18</sub> plates in the often used 30-70% methanol range. The combined advantages can possibly be enjoyed when using the Merck RP-8-coated TLC layers (*cf.*, Figs. 4 and 5). Lastly, it is obvious that replacing methanol by the unfortunately more toxic acetonitrile will decrease the time of development substantially. In this respect, it may be worth studying a number of other organic modifiers such as acetone and dioxane.

All types of pre-coated plates display identical separation sequences with test solutes such as the phthalate esters and the chloroanilines. Considerable, and often unexplainable, differences occur, however, in the separation of, *e.g.*, chloro- and aminophenols. As will be evident from the discussion in the previous sections, no general conclusion can be reached here as regards the preferred type of RP-TLC plate. To quote one example, the RP-8- and RP-18-coated TLC plates should be recommended on the basis of the data reported for the chlorophenols; however, with

the aminophenols, it is precisely these two types of plates that produce anomalous results. It seems more appropriate to conclude that, from the point of view of RP-TLC separation studies, the varied, if unpredictable, behaviour of the commercially available pre-coated plates adds to the potential of the technique as a tool for creating separations. When using RP-TLC as a screening technique for a rapid preliminary evaluation of mobile phase systems suitable for use in column LC, on the other hand, one should proceed with caution. Problems are most apt to occur in studies on the RP-(T)LC of polar solutes. Here, mutual differences in interactions with residual silanol groups and/or binders, different pH values and effects caused by the addition of neutral salts or ion-pairing agents may ruin the hoped for similarity between RP-TLC and RP-LC retention data.

#### ACKNOWLEDGEMENTS

We thank Antec (Bennwil, Switzerland), Baker (Deventer, The Netherlands), Macherey, Nagel & Co. (Düren, G.F.R.) and Merck (Darmstadt, G.F.R.) for supplying us with gifts of their pre-coated chemically bonded plates.

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