# ADVANCED CONCEPTS IN THIN-LAYER CHROMATOGRAPHY
# A SUMMARY

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Major challenges for experimental and theoretical thin-layer chromatography (TLC) workers remain in several areas. These include: (a) increased resolution (separation) and shorter separation times; (b) improved reproducibility; (c) the prediction of $R_F$ values for sample identification; (d) increase in the capacity of preparative systems; (e) improved quantitation. The present program includes contributions in areas a–d, while an entire later session is devoted to item e.

Increased resolution per unit time in TLC (item a) is now amenable to theoretical analysis, and the results can be compared with corresponding data for column separations[1,2]. At this point it appears that the two techniques can be described by the same basic equations and experimental parameters. Conventional TLC is basically limited in the resolution per unit time it can provide, although the use of plates of varying length or the techniques of stepwise and continuous development allow resolution to be traded for separation time. Thus, very difficult separations can be carried out if long times are allowed, and easy separations can be effected quite rapidly. The recently introduced technique of *drum-TLC* (ref. 2) allows a considerable increase in the resolution per unit time, for the separation of a particular pair of compounds. In this case separations by normal TLC can be duplicated in much shorter times, and separation efficiencies (number of theoretical plates) for difficult separations can be increased by as much as a factor of 10 (with comparable separation times).

The variation of the solvent (and to a lesser extent the adsorbent) in TLC also allows dramatic increase in sample resolution in the case of difficult separations. A large number of such effects have been reviewed earlier[3], and an extension of this work is described in following papers[4,5]. It is found for non-hydrogen bonding solute-solvent systems[4] that the effect of the solvent on relative sample migration (and separation) can be predicted with an accuracy almost as good as the experimentally determined values. The extension of this approach to other solvent systems should result in a general, systematic approach to solvent selection for maximum peak separation.

The systematic characterization of different adsorbents for the purpose of maximizing sample resolution has been discussed[3,6]. Since then, the work of NICO-LAIDES[7] indicates a unique role for the adsorbent magnesia. Apparently, planar sample molecules are preferentially adsorbed, with the consequence that steroids (relatively more planar) can be separated from fatty acid derivatives of the same type (*e.g.* steryl esters from wax esters).

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Reproducibility in TLC (item b) depends upon an appreciation of the various effects which can alter band migration, *i.e.* adsorption and desorption of solvent from the vapor phase, solvent concentration gradients in the direction of solvent flow, variation of adsorbent water content, solvent demixing, and temperature effects associated with the above. In the hands of careful workers, reproducibility of $R_F$ values within a few hundredths of a unit has been possible, even in two-dimensional TLC (*e.g.* ref. 5). The mathematical analysis of these complex TLC systems (*e.g.* ref. 8) seems at present a remote theoretical goal, and an unpromising practical project. The most promising approach is careful control and duplication of all experimental conditions.

A fundamental approach to the prediction of sample $R_F$ values has been presented earlier[3]. Two possibilities exist, *viz.* the use of data reported by other laboratories, or direct calculation from the molecular structure of the sample plus conditions of separation. Each of these methods can be useful in certain situations[9,10], but cannot be extended to all cases. The above complications associated with the problem of reproducibility limit the first approach, while insufficient data have been reported for general application of the second approach. In either case, the systematic measurement of $R_F$ values with attempts at their correlation with solute structure (*e.g.* ref. 11) will continue to be useful in the prediction of $R_F$ values.

Increased sample size in preparative TLC (item d) received considerable emphasis originally (*e.g.* ref. 12), but has since largely given way to column separations, when more than a few milligrams of sample are required. However, the recent introduction of very thick layers[13] permits the separation by TLC of gram quantities of easily resolved mixtures.

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