

Capillary Flow in TLC

• Capillary Flow

- Unlike in gas and liquid column chromatography, where the movement of the mobile phase results from the difference in pressure between column entrance and column exit, the spontaneous solvent flow on a thin layer plate is caused by the capillary effect. **By entering the capillary cavities of the layer the liquid seeks to reduce its surface and hence its free energy.** This energy difference ΔE_m is proportional to the surface tension γ and the mole volume V_m of the solvent and inversely proportional to the capillary radius r

$$\Delta E_m = \frac{2 \gamma V_m}{r}$$

- **The liquid flowing in fills the narrower capillaries first** (see Figure). The larger pores at the solvent front remain empty for some time and fill progressively with the liquid flowing from the smaller pores behind. This differentiation of flow **leads**, by the way, **to a frontal volume gradient** which is dealt with further on.

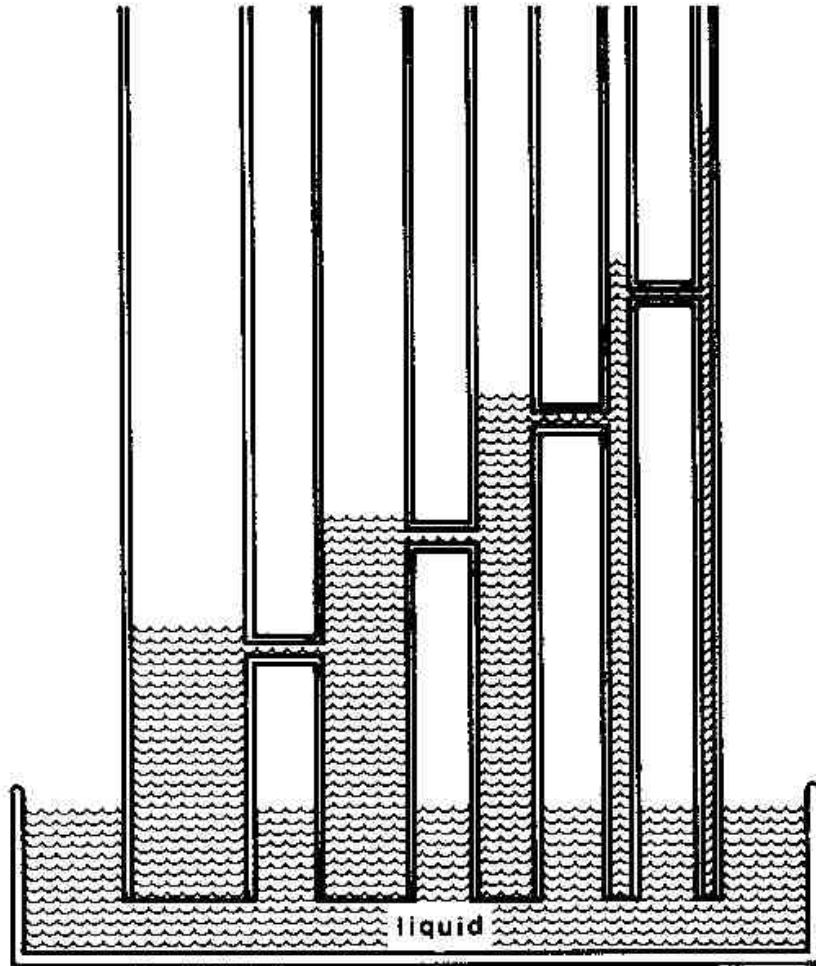


Figure 11. Capillary model for the frontal volume gradient. After Giddings et al¹⁸.

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$$z_f^2 = \lambda t$$

(1) Darcy's law 1856

$$z_f^2 = \kappa t \quad (1) \text{ Darcy's law 1856}$$

$$z_f = \sqrt{\kappa t} \quad (2) \text{ front position}$$

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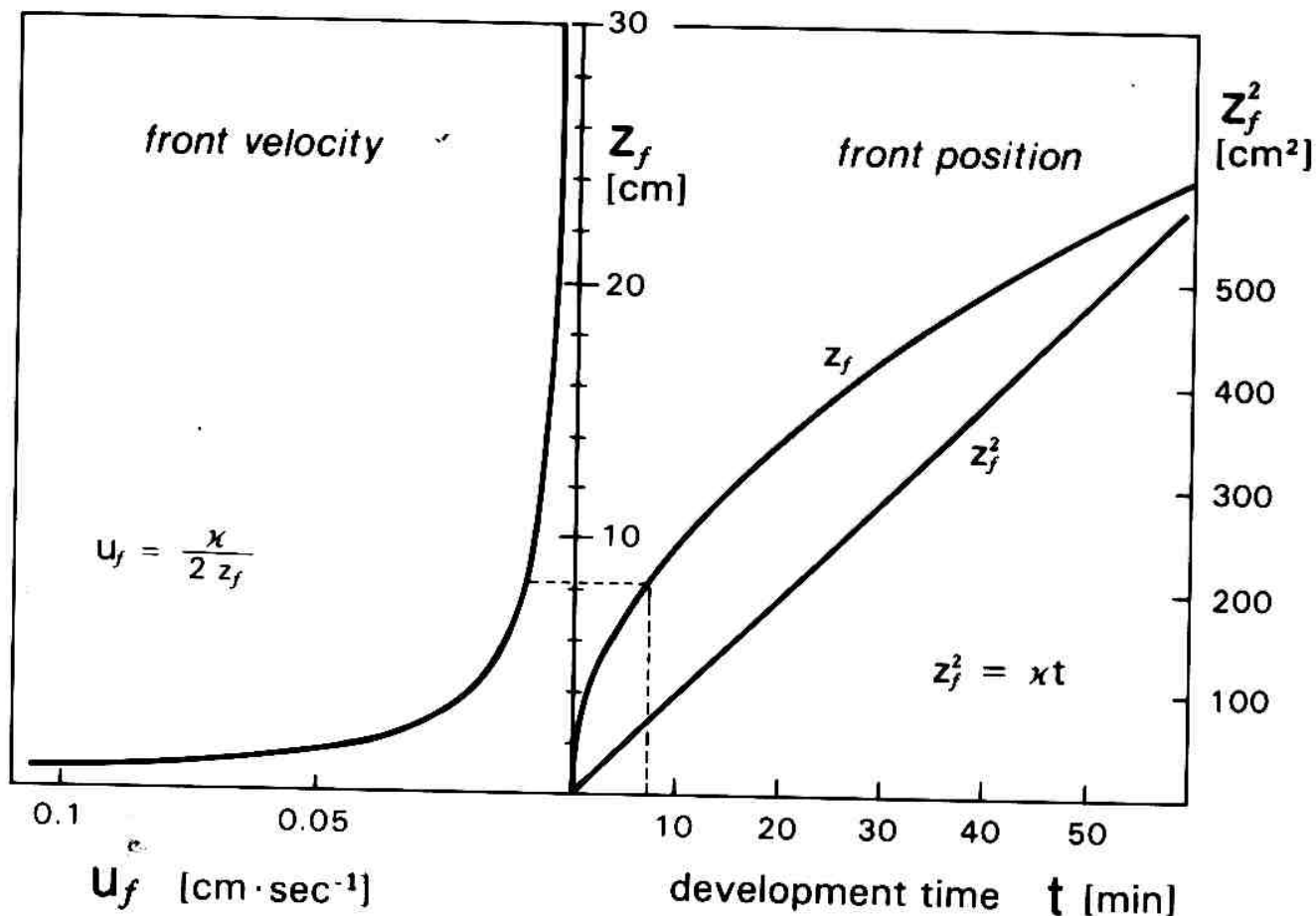


Figure 2. Movement of the solvent front.

Flow constant $x = 0.16 \text{ cm sec}^{-1}$. Data calculated from eq. (2), (3), (4). Linear development, no pre-adsorption of solvent vapors. Example: After 15 sec dev't. the front has reached $z_f = 1.6 \text{ cm}$ height and migrates at a momentary speed of 0.05 cm sec^{-1} , after 7.5 min the front is at 8.5 cm and has a velocity of $0.0094 \text{ cm sec}^{-1}$ (broken line).

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$$\kappa = k_1(\gamma/\eta) \quad (5) \text{ "velocity constant"}$$

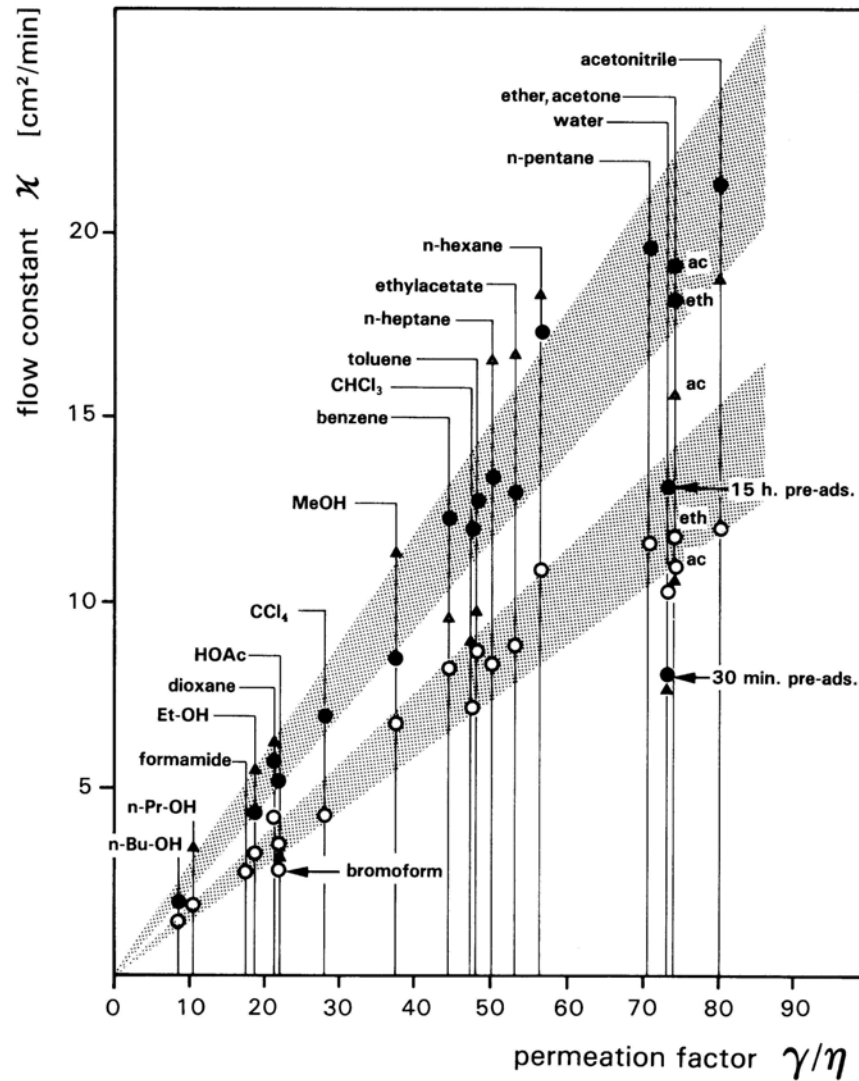


Figure 5b. Flow velocity κ as a function of the parameters surface tension γ /viscosity η for different solvents, as in Figure 3a, but for different degrees of pre-adsorption. Upper fan: (●) saturated N-tank, 30 min pre-adsorption to "sorption saturation" increased front velocity. Lower fan: unsaturated S-tank with no pre-adsorption leads to lower front velocity. Literature values (Δ)¹⁰ obtained in sat'd. N-tanks with immediate start of development scatter between the extremes because of varying degree of pre-adsorption.

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$$\kappa = k_1 (\gamma/\eta) \quad (5) \text{ "velocity constant"}$$

$$\kappa = k_2 \cdot d_p \quad (6) \text{ infl. particle diameter}$$

$$\kappa = k_1 (\gamma/\eta) [V_m / V_m - V_v] \quad (7) \text{ infl. pre-ads.}$$

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(permeation factor)

$$\kappa = \Theta \cdot d_p \quad (6) \text{ infl. particle diameter}$$

$$\kappa = k_1 (\gamma/\eta) [V_m / (V_m - V_v)] \quad (7) \text{ infl. pre-ads.}$$

$$\Theta = \kappa/d_p \quad (6a) \text{ "flow coefficient" (Guio.)}$$

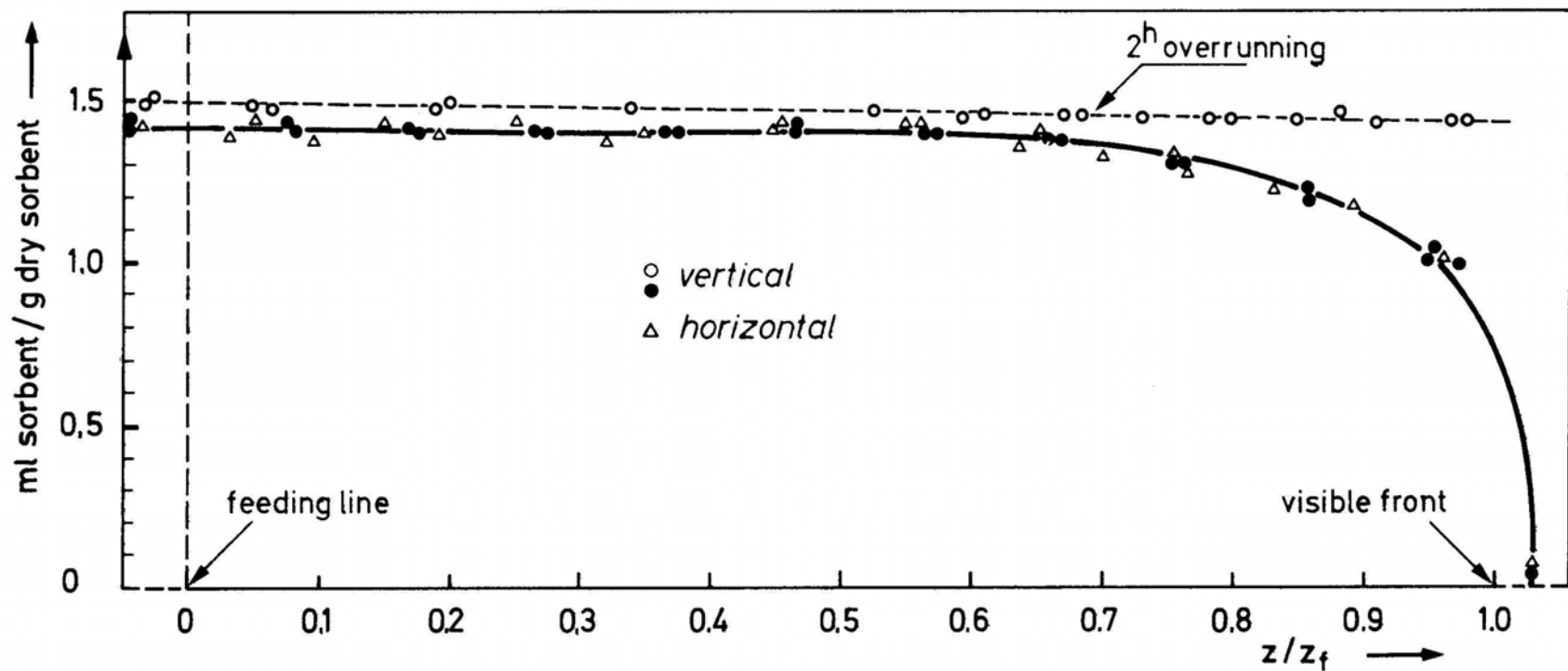


Figure 12. Reduced volume profile. Silicagel Alu sheet (Merk, 1968), benzene, BN and Vario-KS tank. From⁴.

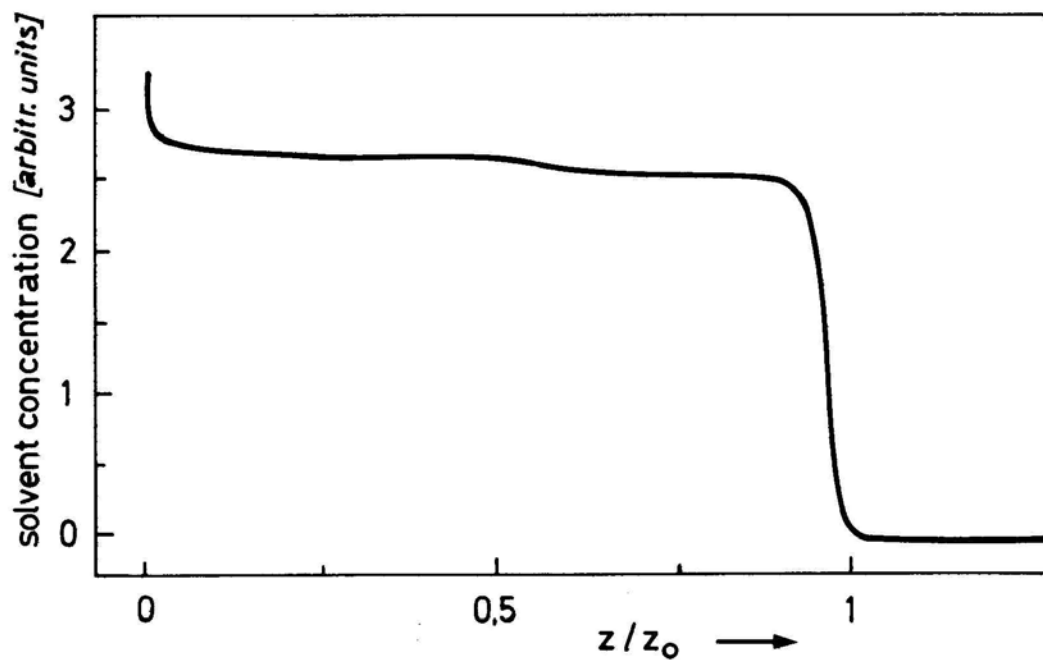


Figure 12a. Solvent volume profile obtained with the “dye- $R_f = 1$ method”. N-chamber, 10 min pre-loading, acetone; $z_f - z_0 = 5$ cm.

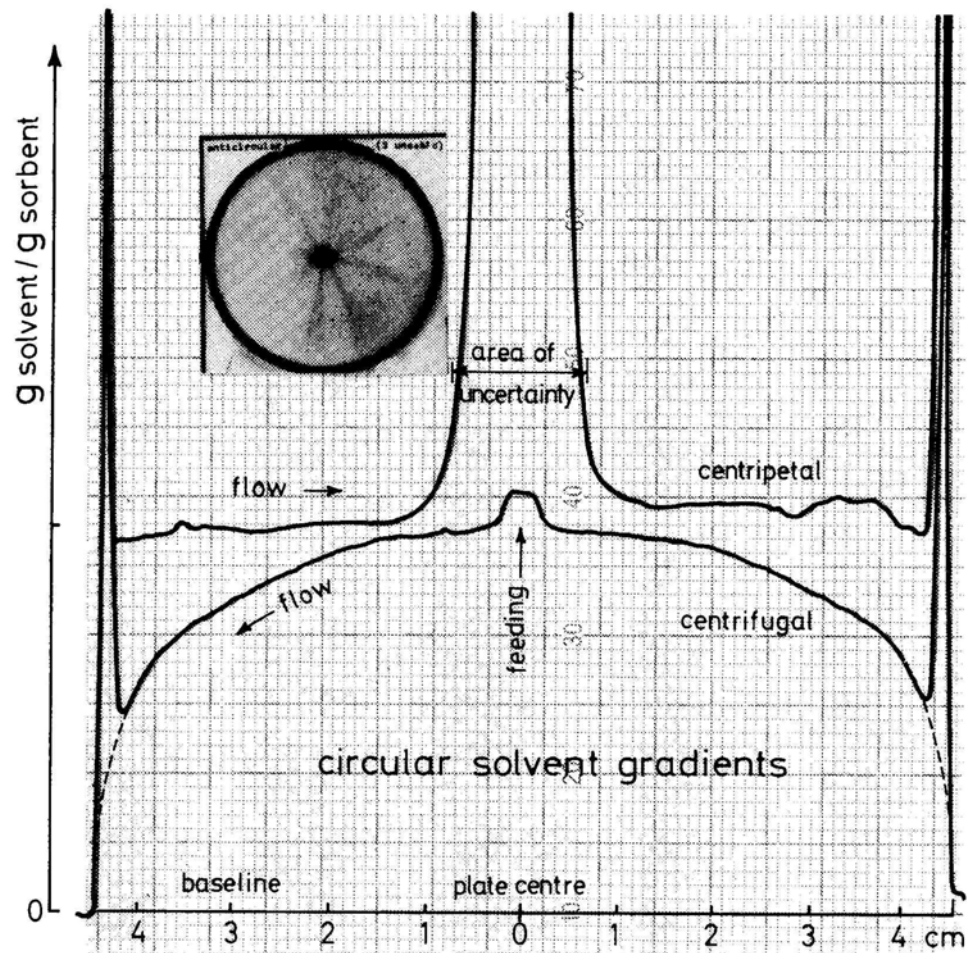


Figure 41. Solvent profiles in circular TLC. Dye- $R_f = 1$ method. Solvent: solution of 0.006% Sudan red in acetone. Centrifugal mode with CAMAG U-Chamber, centripetal mode with CAMAG Anticircular U-Chamber. *Insert*: “ancircular” chromatogram with central color spot (see text). ● Unpublished data, ⊙ precoated silica gel 60. See also Fig. 72a.

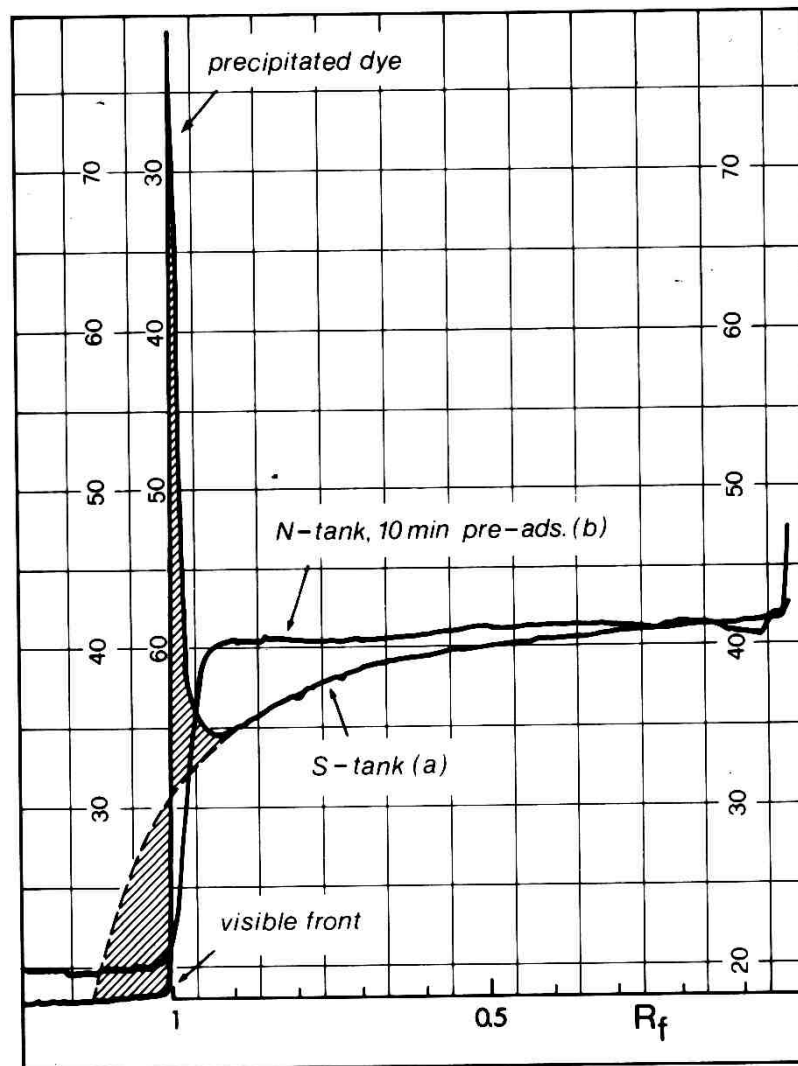


Figure 14. Volume profiles (frontal gradients) obtained using the "dye- $R_f = 1$ method". Scanner curves of a) and c) in Figure 12. The area under the frontal peak equals the (otherwise invisible) amount of solvent that has evaporated across the front line.

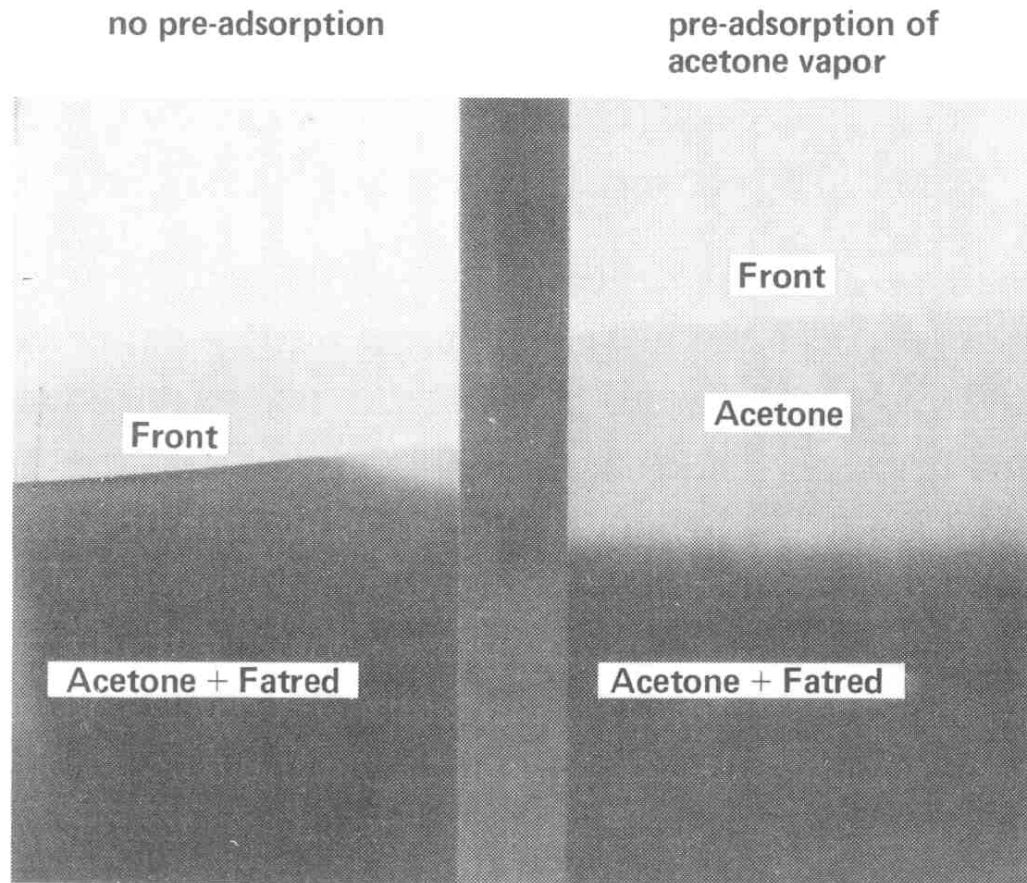


Figure 131. Pre-loading generates virtual front. Developing solvent: acetone + 0.01 % Fat Red ($R_f = 1.00$), dissolved in the solvent. *Left:* Without pre-loading of the adsorbent with acetone gas molecules the dye Fat Red with $R_f = 1.00$ stretches up to the front. *Right:* The dye stops at the virtual front to which its R_f should be related ($R_f < 1$ but $R'_f = 1$). The colorless liquid ahead is pushed-up pure acetone from pre-loading.

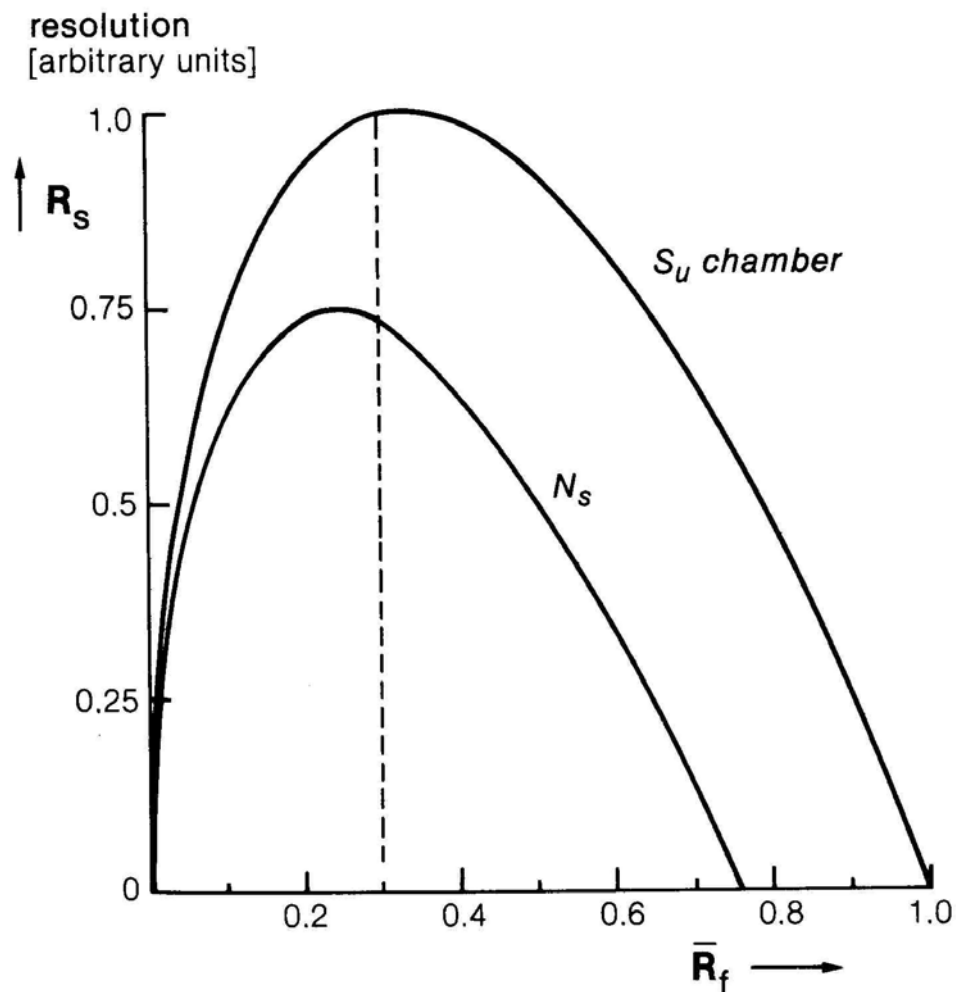


Figure 52. Resolution of a neighboring pair of substances at varying R_f . Optimum is at $R_f \approx 0.3$ if K_1/K_2 is kept constant. Calculated from eq. 54 with $K_1/K_2 = 1.33$, $N = 1000$. With pre-loading (N-chamber), the maximum is lower and displaced to lower R_f ; for $R_f > 0.75$, $R_s = 0$.

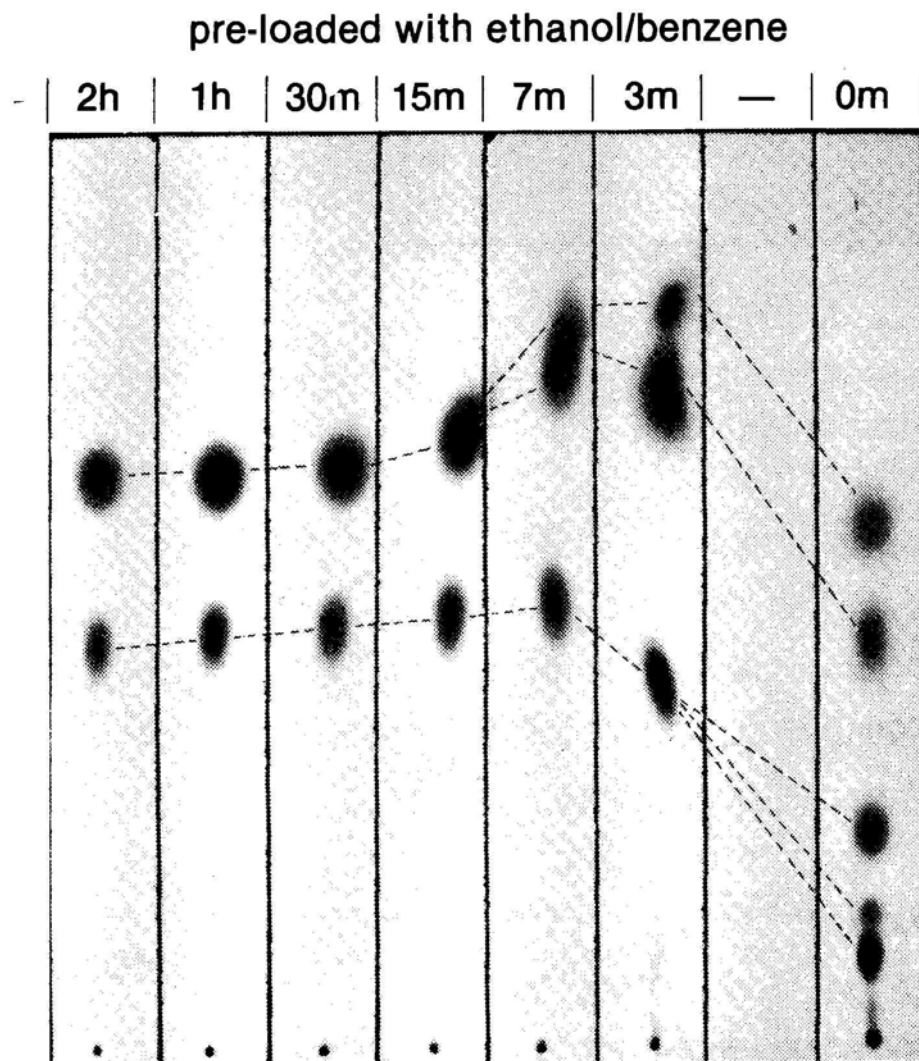


Figure 139b. Pre-loading with solvent mixture. Influence of the time of pre-loading. Silica, developing solvent benzene. Vario-KS-chamber. R_f values pass a maximum.

vol. - % methanol in benzene

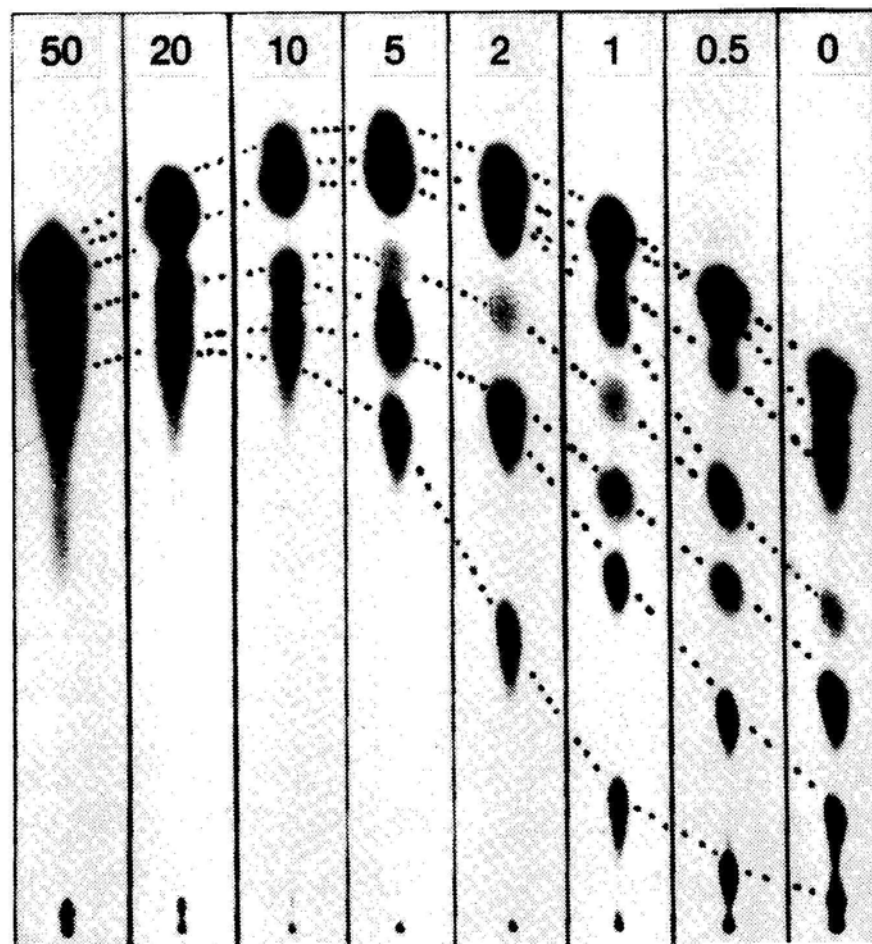


Figure 139a. Pre-loading with solvent mixtures. Silica gel G, Merck; developing solvent benzene; pre-loading mixtures as indicated; Vario-KS-chamber. Pre-loading time 7 minutes. The uppermost spots pass through a maximum. Beyond R_f reduction due to pre-loading outweighs retention weakening by methanol.

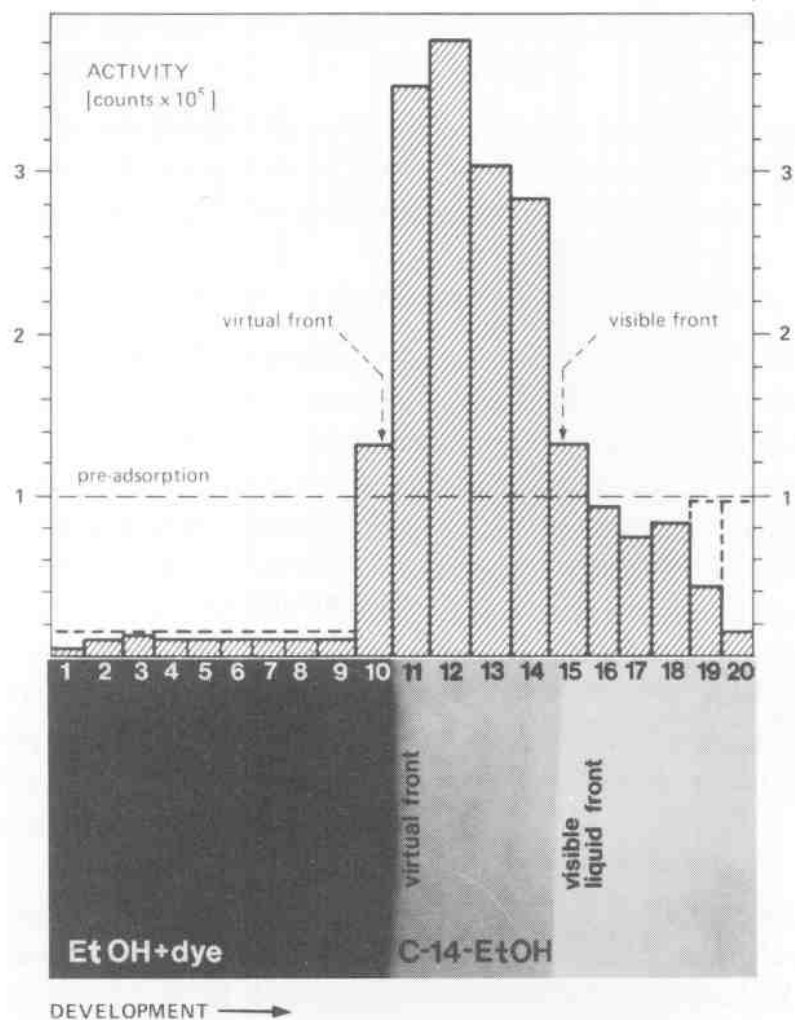


Figure 133. Displacement of pre-loaded gas molecules by the liquid front. Another experimental proof for Figure 130. Pre-loading with $1\text{-}^{14}\text{C}$ -ethanol, development with ethanol containing 0.1% of a dyestuff with $R_f = 1.00$. Fractions 2–9: 10% residual adsorbed fraction from pre-loading, fractions 11–14: pushed-up and condensed pre-loaded solvent molecules, fractions 15–19: “dry” pre-loaded zone. For details see text.

THE END