Quasi-thin layer chromatography with forced flow of the mobile phase in microchannels packed with a sorbent

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A version of the thin-layer chromatography with forced flow of the mobile phase in microchannels packed with a sorbent is proposed. The dependences of retention parameters R_f and the number of theoretical plates in the course of the elution of hydrophilic dyes (naphthol red and methyl red) on the eluent (propan-2-ol) pressure and developing time were studied. The method can be of interest as a simplified version of the forced-flow TLC and would be useful as a micropilot technique for liquid chromatography.

Key words: forced-flow thin layer chromatography, retention parameters, efficiency, eluent pressure.

One of the promising directions of the TLC technique is the development of versions with a controlled flow of the mobile phase (MP).[1,2] Optimization of the conditions of separation provides a significant decrease in the duration of analysis and an improvement of the efficiency of the method.

Different versions of TLC with the forced flow of an eluent make it possible to separate rapidly and efficiently a great number of samples. The TLC under pressure is characterized by the following advantages: 1) the possibility of elution of the samples to be analyzed to great distances (when microdispersed sorbents and viscous eluents are used) as well as of realization of a flow version of analysis; 2) high efficiency; 3) small expenditure of time; 4) good reproducibility of the results.[2—4]

A number of commercial instruments and developing chambers for different modifications of the TLC method under pressure are available.[2,5] However, the relatively complicated construction and high cost of the equipment restrict their wide practical application. Recently, a simpler instrument for the realization of TLC under pressure has been proposed; however, it requires special plates the upper layer of which is coated with a polymer film.[6]

The development of the experimental conditions for more complex processes of separation by the column LC method is one of the most important practical uses of TLC.[7] However, due to the nonidentity of sorbents used in both TLC and LC as well as due to other reasons (*e.g.*, due to the contact of the mobile phase with the dry sorbent and its evaporation in TLC), it is impossible to achieve quite complete correspondence of the processes in both versions of chromatography.

In order to approach the conditions of separation in the above-mentioned methods to those in the column LC, we proposed the system for the chromatographic separation in thin layers of a sorbent that allows, in our opinion, TLC to be used more efficiently as the micropilot method for LC. In this version, TLC is applied for the preliminary ("rough") development of the procedure of the separation of the mixture to be analyzed and the results obtained are taken into account during the final realization of separation on the liquid chromatograph.

Experimental

A chromatographic system consists of a cell, *i.e.*, a set of parallel microcolumns used for separation,[7] and a vessel with an eluent that is positioned somewhat higher. The height of the vessel position determines the eluent pressure at the column inlet. The cell is a plate of stainless steel (20×5 cm), along which channels of 1 mm width and length are cut. The through holes are bored at the both end of the channels. Stainless steel capillary tubes of ~40 cm length for supply and drain of the eluent are soldered to these holes. The sorbent layer is introduced to the channels by the known methods;[2,7] after this the top of the plate with channels (columns) is covered with a film of a transparent material, *e.g.*, polyethylene, which is fixed by a stainless steel plate. The sorbent is activated by drying in vacuum. A vessel of Marriott's bottle type is best for feeding the eluent.

In all the experiments performed a silica gel L for TLC (Chemapol, Czech Republic) of 5—40 μm granule size was used. Samples (hydrophilic dyes naphthol red and methyl red) were deposited preliminarily on a sorbent layer at the beginning of the column as 0.1% solutions in propan-2-ol using a

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Table 1. Dependence of retention parameters (R_f) and the number of theoretical plates (N) on the eluent pressure at the inlet

h/mm	L/mm	X_1/mm	X_2/mm	ω_1/mm	ω_2/mm	R_{f1}	R_{f2}	N
240	18	11	9	1.0	1.0	0.61	0.50	1300
340	23	17	14	1.0	1.0	0.74	0.60	2400
440	28	21	17	1.2	1.1	0.75	0.61	4600
540	33	24	21	1.3	1.2	0.73	0.66	7000

Note. h is the height of liquid column, elution time is 10 s. The subscripts of the values to be determined correspond to the two substances undergoing chromatography: *1*, naphthol red; *2*, methyl red.

microsyringe (sample volume was 0.5 μL). Propan-2-ol of chromatographic purity was used as the mobile phase.

Results and Discussion

The values of the retention parameter R_f for the alcohol-soluble dyes naphthol red and methyl red were estimated at different eluent pressures, which were determined by the height of the solvent column, as well as at different widths of the zones of the separated compounds. The numbers of theoretical plates were calculated on the basis of the results of elution of a mixture of the dyes to be separated according to the formula[2,8] $N_i = 16(X_i/\omega_i)^2$ (i = 1, 2), where X_i is the distances between the starting line and the centers of the zones of the compounds under separation, and ω_i are the corresponding values of the zone widths. The experimental results are presented in Table 1 (the average values obtained from the four parallel experiments are shown; the relative standard deviations of the parameters calculated did not exceed 3%).

As can be seen in Table 1, with increasing eluent pressure at the inlet, the R_f values increase only slightly, while the number of the theoretical plates increases significantly. It is noteworthy that the chromatographic zones are slightly broadened and this fact is undoubtedly an advantage of the method as compared to the conventional version of TLC on the plates.

The retention parameters R_f of naphthol red and methyl red determined by chromatography under the conditions of the conventional developing TLC on "Silufol Cavalier" plates were equal to 0.58 and 0.34, respectively (mobile phase, propan-2-ol, developing time > 3 min).

Table 2. Dependence of retention parameters (R_f) and the number of theoretical plates (N) on developing time (t)

t/s	L/mm	X/mm	ω/mm	R_f	N
10	18	9	1.0	0.50	1300
20	32	16	1.0	0.50	4100
30	47	25	1.1	0.54	8900
40	63	33	1.2	0.53	12000
50	91	45	1.2	0.49	22000
60	112	58	1.3	0.51	31500

A comparison of the results obtained when the elution was carried out with forced flow of the eluent with the data of conventional TLC indicates the above-mentioned advantages of the improved version. Dependence of the chromatogrphic parameters on the duration of retention is presented in Table 2. The relatively high efficiency of the method is seen when the time of elution increases within the limits of 10—60 s.

Thus, a new version of the liquid quasi-TLC in thin layers of a sorbent combines the advantages of both LC and TLC with a forced flow of the eluent. These advantages are the following: 1) the possibility of improving the sensitivity of the quantitative determination due to a decrease in zone broadening during chromatography and 2) acceleration of the elution.

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