The use of vacuum in thin-layer chromatography with a forced flow of the mobile phase on plates with covered polymer layer

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A new version of TLC with a forced flow of the mobile phase has been suggested. The variant involves the use of a TLC plate, the sorption layer on which is covered with a polymer film, and evacuation as an additional driving force for the mobile phase. The advantages of the new method were analyzed; the velocity coefficient of the movement of the mobile phase front was found to be linearly dependent on the rarefaction at the end of the plate.

Key words: thin-layer chromatography; mobile phase, forced flow, vacuum.

The separation of a mixture in the traditional TLC occurs as a rule with a noncontrolled and nonoptimal velocity of the flow of the mobile phase (see, for example, Refs. 1—4). To accelerate the separation, a variant of TLC with a forced flow of the mobile phase under pressure has been suggested.[5—7] The use of the forced flow of the mobile phase makes it possible, first, to increase substantially the efficiency of the separation, second, to accelerate it, and, third, to carry out chromatographic processes in those cases when the mobile phase does not wet the sorbent layer (*i.e.*, the processes that in principle cannot be realized within the framework of the traditional TLC). However, this method is rather complex and expensive.

The purpose of the present work is to develop a more facile procedure for the realization of TLC with a forced flow, which, unlike that described previously, is based on the use of a special plate with a polymeric coating over the sorption layer and involves evacuation as the driving force for the mobile phase. The plate with the sorption layer covered with a polymer film[9,10] is actually a flat column.

The traditional TLC, the TLC with a forced flow of the mobile phase under pressure, and the variant of TLC we developed are described in Table 1. It can be seen that the simple TLC procedure proposed by us allows the chromatographic process to be substantially accelerated and its efficiency to be increased. Note that the simple setup needed to carry out separation with the use of evacuation can be produced virtually in any chemistry laboratory.

Experimental

The separation under the conditions of a forced flow of the mobile phase was carried out on plates with a Kieselgel layer covered with a polyethylene film.[9,10]

The scheme of the setup used for the chromatographic separation is shown in Fig. 1. Methanol was used as the mobile phase. The plates with covered layers were obtained from standard TLC plates with open adsorbent layers: Silufol UV-254 (Kavalier, Czechia), Kieselgel 60F254 (Merck, Germany), Armsorb TSKh-S (Erevan, Armeniya), HPTLC SIL G-25 (Macherei-Nagel, Germany).

A plate and a polyethylene film pressed to the sorption layer were heated to a temperature several degrees below the melting point of polyethylene.

Our variant of TLC with a forced flow of the mobile phase involved, unlike the known TLC variants of this type,[2] the use of a vacuum source. One end of the plate was immersed into the liquid mobile phase, and the other one was connected to a vacuum source.[8]

The dimensions of the plates were (6×6)—(6×12) cm^2 or 10×20 cm^2, and the fractions of the sorbent particles varied

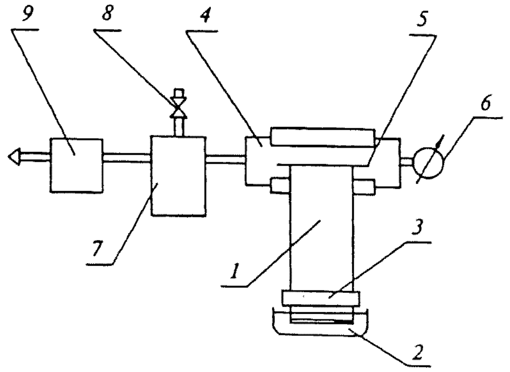

Fig. 1. The scheme of the setup for the TLC procedure with evacuation to produce a forced flow of the mobile phase: *1*, thin-layer chromatographic plate with a covered sorbent layer (the modification for linear chromatography); *2*, vessel with the mobile phase; *3*, sealing clamp; *4*, chamber; *5*, sealable slit for connecting the plate to the evacuation system; *6*, vacuum gage; *7*, surge tank; *8*, valve; *9*, vacuum pump.

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Table 1. Comparison of TLC with a forced flow of the mobile phase with the traditional TLC

Description of the method	TLC with a forced flow of the mobile phase		Traditional TLC
	under pressure[5]	under vacuum[8]	
Plate	TLC plate with an open sorption layer	TLC plate with a covered слоем[9,10]	TLC plate with an open sorption layer
Main stages of the chromatographic separation	1. Elastic gasket is held down under pressure on the plate, which is thus transformed into a flat chromatographic column. 2. The sample is separated by supplying the mobile phase under pressure onto the TLC plate	One edge of the TLC plate with the sorption layer covered with the film is connected to the vacuum pump, and the other edge is connected to the mobile phase supply	One edge of the TLC plate in the traditional special unit (a chamber) is placed into the mobile phase supply
Variation of the pressure of the mobile phase	At the beginning of the plate, pressure exceeds the atmospheric pressure (input pressure 5—18 atm); at the end of the plate, it is approximately equal to the atmospheric pressure	At the beginning of the plate, the pressure is equal to the atmospheric pressure, and at the front, it is markedly lower than the atmospheric pressure (the pressure drop does not exceed 1 atm)	Does not change
Complexity of the setup	Very complex	Simple	Very simple
Cost of the setup	High (comparable to the cost of a simple chromatograph)	Not very high	Low

from 5—10 to 5—20 and 5—40 μm (see, for example, Ref. 4). Mobile phases with various viscosities were used, $\eta/10^{-3}$ Pa s = 0.586 (toluene), 0.584 (methanol), 1.19 (ethanol), 2.20 (propanol), and 2.95 (butanol).[11] The range of pressures studied was 0.1—1.0 atm.

Results and Discussion

The use of evacuation as an additional driving force for the mobile phase allows the chromatographic process to be substantially accelerated. For example, without additional driving factors ($\Delta p = 0$), it takes ~510 min to move the front of *n*-butanol on a Kieselgel 60F254 plate with a covered sorbent layer by 150 mm. When evacuation is used in the above-described setup (Δp = 0.5 kg cm^{-2}), the time required for elution decreases by a factor of more than 4 and is equal to ~120 min. When a higher vacuum is used, the duration of the movement of the mobile phase front can be reduced to ~70 min. In the traditional chromatography,[2] the dependence of the distance by which the front of the mobile phase is moved (Z_f) on the elution time (t) is expressed by the following equation:

$$Z_f^2 = Kt, \qquad (1)$$

where K is the velocity coefficient.

However, in the chromatography with a forced flow under pressure, the $Z_f = f(t)$ dependence is linear and is described by the equation[6]

$$Z_f = Kt. \qquad (2)$$

The theoretical justification of this dependence was presented in one in our papers.[7] In the new variant of TLC proposed by us, the $Z_f = f(t)$ dependence can be nonlinear, because, first, the additional force that causes the accelerated movement of the mobile phase does not exceed 1.0 atm, and, second, vacuum rather than pressure is used as the driving force. In fact, in this paper, we have shown that in the case of TLC where evacuation is used to create a forced flow of the mobile phase, the movement of its front is described by the following equation:

$$Z_f^2 = K_p t, \qquad (3)$$

where $K_p = f(\Delta p)$.

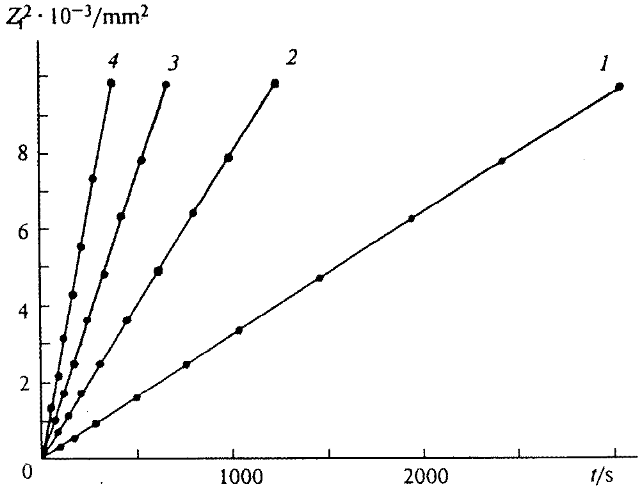

Fig. 2. Dependence of Z_f^2 on the time of elution at various Δp. TLC conditions: a Kieselgel 60F254 plate (Merck) with covered sorbent layer, methanol as the mobile phase, Δp/kg cm^{-2} = 0.0 (*1*), 0.2 (*2*), 0.5 (*3*), and 1.0 (*4*).

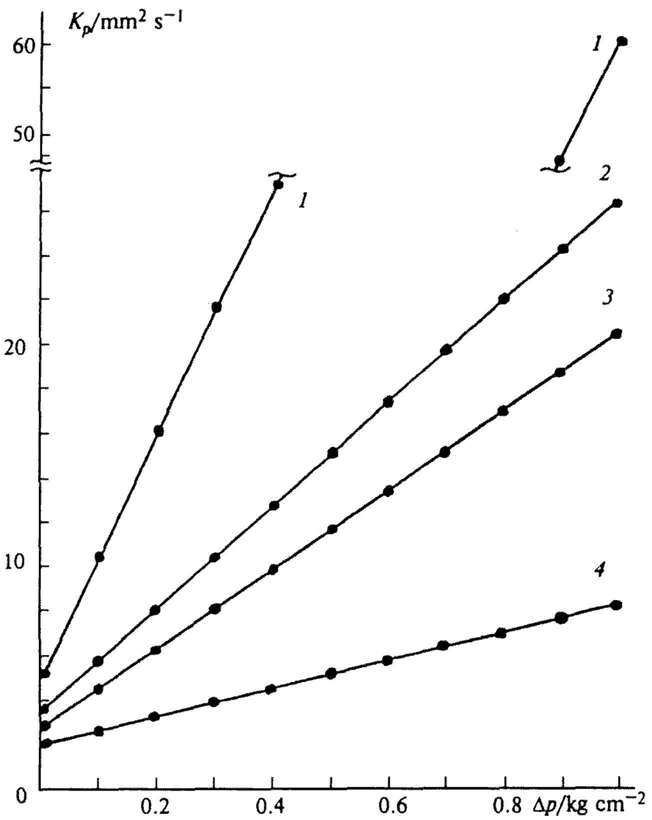

Fig. 3. Dependence of K_p on Δp for various plates with silica gel (covered layer). TLC conditions: methanol as the mobile phase, Silufol UV-254 (*1*), Kieselgel 60F254 (*2*), Armsorb TSKh-S (*3*), and HPTLC SIL G-25 plates (*4*).

Figure 2 shows the $Z_f^2 = \varphi(t)$ plots at various Δp values. As follows from Fig. 2, the movement of the mobile phase in the variant of TLC under consideration follows regularities differing from those obeyed in the case of TLC with a forced flow under pressure and is described by Eq. (3).

Our studies showed that in the suggested variant of TLC, the velocity coefficient K_p in Eq. (3) increases with an increase in Δp:

$$K_p = A + B\Delta p, \qquad (4)$$

where A and B are constants peculiar to a particular mobile and stationary phases and particular experimental conditions. At $\Delta p = 0$, we obtain $K_p = A = K$, and, therefore,

$$K_p = K + B\Delta p. \qquad (5)$$

Figure 3 presents the experimental data obtained in the $K_p = f(\Delta p)$ coordinates. It can be seen that Eq. (5) is in good agreement with the experimental results.

The dependence (4) established by us holds for plates of various types and for various mobile phases. The coefficients A and B from Eq. (4) and correlation coefficients for the description of the experimental K values in terms of this equation are listed in Table 2. These data indicate that Eq. (4) is in very good agreement with the experimental results: the correlation coefficients for all the plates and mobile phases studied were no less than 0.99.

The velocity at which the front of the mobile phase moves varies in conformity with the following equation:

$$\frac{dZ_f}{dt} = \frac{\sqrt{K_p}}{2}\cdot\frac{1}{\sqrt{t}} \qquad (6)$$

or, taking into account Eq. (5),

Table 2. Parameters for the dependences of the velocity constants for the movement of the mobile phase on the pressure drop (Eq. (4)) and correlation coefficients (r) for these dependences obtained for plates with covered sorbent layers

Plate (producing company)	Mobile phase	A	B	r
Kieselgel 60F254 (Merck)	MeOH	3.30	23.50	0.9996
	EtOH	1.52	10.92	0.9995
	Pr^{n}OH	0.95	6.35	0.9993
	Pr^{i}OH	0.82	6.08	0.9997
	Bu^{n}OH	0.74	4.83	0.9998
	MePh	4.20	27.80	0.9992
	MeC(O)Me	6.19	42.90	0.9994
SIL G-25 (Macherei-Nagel)	MeOH	3.20	22.41	0.9997
	EtOH	1.48	10.63	0.9995
	Pr^{n}OH	0.92	6.13	0.9996
	Pr^{i}OH	0.80	5.83	0.9997
	Bu^{n}OH	0.71	4.57	0.9993
	MePh	4.15	26.21	0.9993
	MeC(O)Me	6.09	41.20	0.9995
Silufol UF254 (Kavalier)	MeOH	4.92	55.60	0.9991
	EtOH	2.52	29.21	0.9989
	Pr^{n}OH	1.36	14.64	0.9990
	Pr^{i}OH	1.18	13.89	0.9992
	Bu^{n}OH	1.07	11.11	0.9988
Cellulose (Merck)	MeOH	4.26	40.47	0.9991
	EtOH	1.98	19.26	0.9989
	Pr^{i}OH	1.07	10.57	0.9994
	MeC(O)Me	8.09	73.21	0.9986
ATSKh (Haapsalu)	MeOH	3.45	25.88	0.9992
	EtOH	1.60	12.31	0.9994
	Pr^{n}OH	0.99	7.07	0.9995
	Pr^{i}OH	0.86	6.71	0.9991
	Bu^{n}OH	0.78	5.38	0.9994
Armsorb TSKh-S (Erevan)	MeOH	2.91	18.04	0.9995
	EtOH	1.35	8.58	0.9996
	Pr^{n}OH	0.84	4.97	0.9993
	Pr^{i}OH	0.73	4.69	0.9995
	Bu^{n}OH	0.65	3.72	0.9993
HPTLC SIL G-20 UF254 (Macherei-Nagel)	MeOH	2.12	8.90	0.9998
	EtOH	0.98	4.21	0.9996
	Pr^{n}OH	0.61	2.46	0.9997
	Bu^{n}OH	0.48	1.87	0.9998
	MeC(O)Me	4.04	16.24	0.9996
Cellulose (Kavalier)	MeOH	2.62	16.23	0.9989
	Pr^{i}OH	0.66	4.26	0.9990
	MeC(O)Me	5.02	29.71	0.9993

Table 3. The value of HETP (*H*) for fat-soluble dyes obtained in a chromatographic experiment with unsaturated (run *1*) and saturated (run *2*) chambers and on plates with covered sorbent layers under the conditions of TLC under vacuum (run *3*)

Dye	$H/\mu m$		
	run *1*	run *2*	run *3*
Azobenzene	50	38	24
Oily yellow	62	49	38
Sudan III	57	43	27
Victoria blue	42	34	20
Sudan red	55	49	31

Note. The optimal elution conditions are: a Kieselgel 60F254 plate (Merck), toluene as the mobile phase, a path length of the mobile phase of 80 mm.

$$\frac{dZ_f}{dt} = \frac{\sqrt{K + B\Delta p}}{2} \cdot \frac{1}{\sqrt{t}}. \qquad (7)$$

Thus, the velocity decreases proportionally to $1/\sqrt{t}$ and increases when higher vacuum is used. The velocity at which the front of the mobile phase moves is higher than that in the classical variant of TLC by a factor of $\sqrt{(K + B\Delta p)/K} = \sqrt{1 + B/K \cdot \Delta p}$.

It should be noted that to carry out this process with a nearly optimal velocity, the pressure drop Δp needs to be linearly (quasilinearly) programmed, since the resistance to the flow increases with an increase in the length of the path covered by the mobile phase front.

The application of an additional force for increasing the velocity of the movement of the mobile phase in a covered sorption layer on a TLC plate in the region where the path of the mobile phase front is already rather long (>10—20 mm) makes it possible to increase substantially (Table 3) the efficiency of separation (as in other variants of TLC with forced flow).

It follows from the data of Table 3 that average height equivalent to a theoretical plate (HETP) in the separation of fat-soluble dyes on normal plates is 2 times greater in an unsaturated chamber (or 1.5 times greater in a saturated chamber) than that for the TLC separation on plates with covered layers under vacuum, when the pressure drop (rarefaction) is the optimal. The duration of the analysis (for the path covered by the mobile phase equal to 80 mm) was 14.4 min in an unsaturated chamber or 11.0 min in a saturated chamber, whereas on plates with covered sorbent layers (at $\Delta p = 0.35$ kg cm^{-2}) it amounted to 7.6 min. Thus, the variant of TLC proposed by us makes it possible to accelerate substantially the separation and to increase its efficiency.

The above data indicate that the TLC variant developed by us has a number of considerable advantages over the traditional procedures. The new procedure for TLC is simpler and cleaner from the ecological viewpoint than the previously described methods with a controlled flow. The velocity at which the mobile phase moves in the TLC variant being discussed is markedly higher than that in the traditional TLC, because in the present case, the movement is due to both the impregnation of the sorption layer with the mobile phase and the use of evacuation.

In our opinion, further development of this method, in particular its application to paper chromatography or to electrophoresis, is of interest. It would also be expedient to attain the accelerated movement of the mobile phase on plates with covered sorption layers by supplying it to the sorption layer under pressure.

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