

in a flask supplied with a magnetic stirrer and a reflux condenser. A suspension of Na (1.3 g) in xylene (5 mL) was added to the solution with vigorous stirring for 0.5 h, and then allyl bromide (7.3 g, 0.06 mol) was added dropwise. The reaction was accompanied by heating. The reaction mixture was stirred for 1 h at 60 °C, left for 12 h, and after that filtered. The residue on the filter was washed with xylene. After the solvent was removed, the residue was distilled *in vacuo* to give 9.2 g (93 %) of ether 3, b.p. 126–127 °C (1 Torr), n^{20}_{D} 1.4730. Found (%): C, 60.40; H, 7.66; N, 7.10. $\text{C}_{10}\text{H}_{15}\text{NO}_3$. Calculated (%): C, 60.89; H, 7.66; N, 7.10. IR, ν/cm^{-1} : 1640 (C=O), 1690 (CONH), 1755 (COOR). ^1H NMR, CDCl_3 , δ : 1.05 (t, 3 H, CH_3); 3.30 (m, 1 H, CH); 3.95 (m, 2 H, CH_2O); 4.96 (m, 2 H, $=\text{CH}_2$); 5.5 (m, 1 H, $=\text{CH}$).

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Over-pressure TLC variant on a plate with an enclosed sorbent layer

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An over-pressure TLC variant with an enclosed sorbent layer and forced flow of the mobile phase was suggested. A simple new type device for its realization was developed.

Key words: over-pressure TLC, plate with closed sorbent layer, device for over-pressure TLC.

Thin-layer chromatography is widely used in science and industry for determination of the composition of various objects.^{1–6} However, the most popular TLC variant has several restrictions: (1) rather long duration of analysis; (2) low reproducibility of the chromatographic parameters of the process; and (3) nonoptimum efficiency of the process, which is explained by a sharp change in the flow rate of the mobile phase during experiments.

Hungarian researchers (see, e.g., Refs. 5–9) suggested a TLC variant with forced flow of the mobile phase, in which the plate placed in a special device becomes a planar column during chromatographic separation due to application (under high pressure) of a polymeric material on its sorption layer, and the mobile phase under the action of pressure is supplied to the beginning of this planar column. Despite fine results, the method described did not find wide application, because the device is rather expensive and complicated. In this work, a new simplified TLC variant with forced

flow of the mobile phase is proposed. The method is based on the use of TLC plates with the standard plate adsorption layer enclosed in a transparent polymeric film.^{10,11}

The device,¹² which allows one to realize TLC with forced flow of the mobile phase using the new type plates, is presented in Fig. 1. Its work is based on creation of a pressure drop on the layer, because an eluent is supplied at an elevated pressure equal to an excessive gas pressure in the chamber, and the air space of the layer is connected with the atmosphere and exists at normal pressure. The value of the pressure drop (≤ 4 atm) depends on the pressure of the gas supplied from the pressure source and is determined by the design of the chamber (ability to "hold" pressure).

The demountable hermetic chamber is made of organic glass and consists of the body (1) and transparent lid (2), which are sealed with screw clamps (3) by the gasket (4) that has the form of a rectangular frame. The chamber contains the plate (5) with an enclosed sorbent

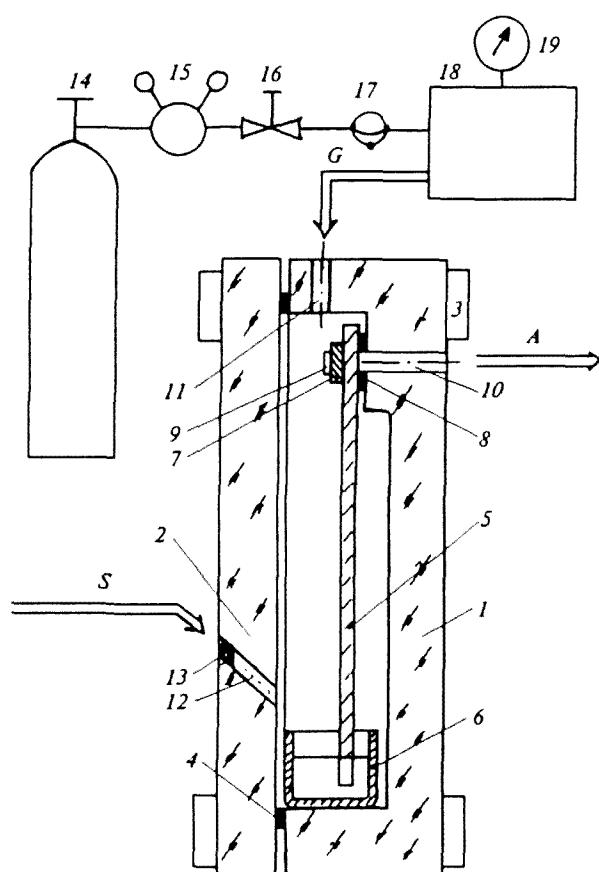


Fig. 1. Scheme of the device for realization of TLC variant with forced flow of the mobile phase using plates with a sorption layer enclosed in a polymeric film. S is solvent, A is atmosphere, G is gas.

layer, whose one end is immersed in the vessel with an eluent (6). The opposite sorption layer is connected with the hole (10) in the wall of the chamber (with the output to the atmosphere) through the hole in the polymeric coating by the cleat (7), seal (8), and screws (9). The chamber also has the hole (11) for gas supply and the hole (12) for supply of an eluent enclosed with the membrane. The gas is supplied to the chamber by a simple scheme, whose main units (in addition to the chamber itself) are the gas cylinder (14) and pressure regulator (reductor) (15). The addition of the regulator of gas flow rate (16), switching valve (17), and buffer vessel (18) with manometer (19) to the scheme facilitates pressure control.

In order to carry out chromatographic separation, one or several samples of mixtures to be separated are applied on the sorption layer region, which is free of the polymeric coating. The vessel for an eluent is placed inside the chamber, and the free end of the plate is let down into the vessel without the eluent. The chamber is sealed, and a portion of the eluent is injected into the vessel. Then the valve (17) is switched to the position connecting the gas source with the chamber. When the

Table 1. Time of movement of the eluent front (t , min) to a distance of 80 mm at various excessive pressures (ΔP) at the beginning of the enclosed layer plate

Sys- tem	Plate	Eluent	Time at ΔP /atm			
			0.5	1.0	1.5	2.0
1	I	Toluene	21.0	8.5	6.0	4.8
2	II	Benzene	11.5	6.2	5.0	4.1
3	II	Benzene	10.5	5.8	4.6	4.0
4	I	Toluene	35.0	15.0	9.0	6.5

Note. I is the plate (Myaake Kapur, Estonian Republic); II is the plate from Macherey Nagel (Germany).

Table 2. R_f values for components of a mixture of dyes, using various separating systems (see Table 1)

Component	Separating system (plate—eluent)		
	1	2	3
Azobenzene	0.91	0.83	0.86
Oil yellow	0.52	0.39	0.45
Sudan III	0.28	0.21	0.26
Victoria blue	0.21	0.16	0.17
Sudan red	0.14	0.11	0.14

process is ceased, the valve is switched to the initial position, the chamber is opened, the plate is taken out, and the qualitative and quantitative composition of the analyzed mixture is determined.

The time of movement of the eluent front along the plate at various values of excessive gas pressure was determined to estimate the possible acceleration of separation. The results are presented in Table 1. The time (t) dependence of the movement of the eluent front (Z) is described by the equation:

$$Z^2 = k't,$$

where k' is the rate constant, which depends on the excessive pressure (ΔP) and is related to the rate constant (k) in the absence of pressure by the dependence

$$k' = k + b(\Delta P),$$

b is constant characteristic of the given mobile and stationary phases.

The results of separation of the testing mixture of fat-soluble dyes, using toluene and benzene as a mobile phase, at the excessive pressure of 1 atm are presented in Table 2. The sizes of chromatographic zones depend on the ΔP value (Table 3). The minimum dispersion at constant pressure was observed at $P = 0.5$ atm. When pressure programming is used and the pressure linearly increases in time as the eluent moves, this results in stabilization of the rate of the eluent movement. The results obtained under these conditions turned out to be the best.

Table 3. Longitudinal size of chromatographic zones (mm) with various pressure drops (size of the starting spot is 3 mm)

ΔP /atm	Oil yellow	Sudan red
0.5	6.2	4.2
1	5.8	4.6
1.5	6.3	6.1
2.0	6.8	6.5
(0-1)*	5.2	4.0

* Linear pressure increase with time.

It should be noted in conclusion that the use of the TLC variant on plates with the sorption layer enclosed by the polymeric film and with forced flow of the mobile phase (when the pressure at the beginning of the plate is higher than atmospheric pressure) makes it possible to substantially accelerate the process of chromatographic separation in thin-layer chromatography.

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Reactions of α -halonitrosoalkanes with resorcinol

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α -Halonitrosoalkanes react with resorcinol as nitrosylating agents to form 3-hydroxy-*N*-(2,4-dihydroxyphenyl)-1,4-quinone imine.

Key words: α -halonitrosoalkanes, resorcinol, 3-hydroxy-*N*-(2,4-dihydroxyphenyl)-1,4-quinone imine.

It is known that in the presence of strong mineral acids aromatic nitroso compounds C-amine phenols at the *para*-position to the hydroxyl group to form *N,N*-diarylhydroxylamines, which after elimination of water

transform to indophenols or cyclize to phenoxazine derivatives.¹⁻²

We have found that 1,2-dichloro-1,2,2-trifluoronoitrosoethane **1a** readily reacts with resorcinol in the