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Fig. 1. Column scheme.

Figure 1: Fig. 1. Column scheme.

Abstract

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DEVELOPMENT CHROMATOGRAPHY IN COLUMNS WITH A MOVING SORBENT

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Various variants of gas chromatography are used in scientific practice. Depending on the nature of the motion of the sorbent in the column and on the method of introducing the sample to be separated, four variants may be considered (see Table 1). All these variants, with the exception of variant III, have been described in the literature (1-3).

In the present article the results of work on the practical implementation of development chromatography with a moving sorbent are set forth, and a brief theoretical justification of the method is given.

The proposed method, depending on the direction of motion of the carrier gas relative to the direction of motion of the sorbent, may be carried out in two variants: 1) the carrier gas and the sorbent move in the same direction; 2) the carrier gas and the sorbent move in opposite directions.

The experimental verification of the proposed method was carried out using a column whose scheme is shown in Fig. 1. The chromatograms obtained in the separation of hydrocarbon gases on a column with moving and stationary sorbent are presented in Figs. 2 and 3. As follows from Fig. 2, the retention time and asymmetry (4) of the peak for the case of coinciding directions of motion of the carrier gas and sorbent decrease in comparison with the corresponding data for chromatography on a stationary sorbent. The relative retention time also decreases. In the case of opposite directions of motion of the carrier gas and sorbent (Fig. 3), separation of α- and β-butylenes occurs considerably better than on a stationary sorbent. In this case the relative retention time of the β-butylenes (α-butylene as standard) increased from 1.35 to 1.58.

Fig. 1. Column scheme.
1 –working part of the column (630 × 5 mm), 2 –branch pipe, 3,4 –upper and lower reservoirs for sorbent, 5 –valve, 6 –diaphragm, 7 –heater for complete desorption, 8 –vibration device

Fig. 2. Chromatograms of the separation of a gas mixture for the case of coincident directions of motion of the carrier gas and sorbent: methane (1), ethylene (2), acetylene (3), propylene (4), butylene (5) on ASK silica gel. a —the sorbent moves, b —the sorbent is stationary.

Figure 2: Fig. 2. Chromatograms of the separation of a gas mixture for the case of coincident directions of motion of the carrier gas and sorbent: methane (1), ethylene (2), acetylene (3), propylene (4), butylene (5) on ASK silica gel. a —the sorbent moves, b —the sorbent is stationary.

In separations on a column with a moving sorbent, the reproducibility of the retention-time values of various compounds did not differ from the reproducibility of the corresponding values obtained on a column with a stationary sorbent.

The principal characteristics of chromatographic separation are the value of the retention time $t_d = L/(u + w)$, where L is the length of the chromatographic column; u is the velocity of displacement of the zone (or of a given concentration C) of the compound in the column; w is the linear velocity of displacement of the sorbent; $k_1 = \Delta t/2\mu$ is the separation criterion, Δt is the difference in retention times of the separated compounds, and μ is the band width.

Let us find expressions for these quantities under the conditions of chromatography with a moving sorbent, assuming that broadening due to additional causes arising in connection with displacement of the sorbent is small.

Table 1

Classification of chromatographic methods

Method of introducing the sample to be separated	Mobile phases: carrier gas	Mobile phases: carrier gas and sorbent
Instantaneously, periodically	I. Elution chromatography	III. Elution chromatography with a moving sorbent
Continuously	II. Frontal chromatography	IV. Continuous frontal chromatography with a moving sorbent

The retention time t_{d} in chromatography on a column with a moving sorbent is determined by the sum of the velocities of motion along the column of the zone of the given compound due to the carrier gas and of the displacement of the sorbent with linear velocity w. In this case w, in accordance with the two variants of the method, may be either positive or negative. For the case of a linear isotherm $u = \alpha/\Gamma$, where α is the velocity of the carrier gas, and Γ is Henry’ s adsorption coefficient.

Fig. 2. Chromatograms of the separation of a gas mixture for the case of coincident directions of motion of the carrier gas and sorbent: methane (1), ethylene (2), acetylene (3), propylene (4), butylene (5) on ASK silica gel. *a* –the sorbent moves, *b* –the sorbent is stationary.

For Δl under the conditions of a moving sorbent we obtain the expression

$$t_{\mathrm{d}} = \frac{L}{u+w} = \frac{L}{\alpha/\Gamma + w}, \qquad \frac{\partial t}{\partial \Gamma} = \frac{L}{\alpha(1+w/u)^2};$$

for small values of Δt

$$\Delta t_{\mathrm{d}} = \frac{L}{\alpha}\frac{\Delta\Gamma}{(1+w/u)^2};$$

for a stationary sorbent

$$\mu_{\mathrm{n}} = \frac{4}{u}\sqrt{\frac{Dt}{\Gamma}},$$

where D is the coefficient of effective diffusion;

with motion of the sorbent

$$\mu_{\mathrm{d}} = \frac{4}{u+\omega}\sqrt{\frac{DL}{\Gamma(u+\omega)}} = \frac{4}{u}\frac{1}{(1+\omega/u)^{3/2}}\sqrt{\frac{DL}{a}},$$

$$K_{1\mathrm{d}} = \frac{\Delta t_{\mathrm{d}}}{2\mu} = \frac{1}{8}\frac{\Delta\Gamma}{\Gamma}\sqrt{\frac{aL}{D}}\frac{1}{(1+\omega/u)^{1/2}}.$$

Since

$$K_{1\mathrm{n}} = \frac{1}{8}\frac{\Delta\Gamma}{\Gamma}\sqrt{\frac{aL}{D}}$$

(for a stationary sorbent), then

$$\frac{K_{1\mathrm{d}}}{K_{1\mathrm{n}}} = \frac{1}{(1+\omega/u)^{1/2}}.$$

Thus, in comparison with chromatography on a stationary sorbent, for coinciding directions of motion of the carrier gas and the sorbent, the retention time and the separation coefficient should decrease in accordance with the formulas given.

The method makes it possible to carry out chromatographic separation of mixtures of substances differing considerably in retention time, for example, the joint separation of gases and liquids. In this case the duration of separation is shortened and the asymmetry of the peaks of the chromatographed compounds is reduced. This variant of the method makes it possible to solve problems typical of thermochromatography. However, the proposed method can be applied to the separation of mixtures at lower temperatures than in thermochromatography, which is important for thermally unstable substances.

Table 2

Substance	Retention time, calc.	Retention time, exp.	Deviation, %
Butylene	305	282	8.5
Propylene	171	167	2.5
Acetylene	107	106	1

For opposite directions of motion of the carrier gas and the sorbent, the retention time and the separation coefficient of the chromatographed compounds should increase in accordance with the same formulas. When this variant of the method is used, the separation of the chromatographed compounds is improved. Let us note that, with small geometric dimensions of the column, it is possible to sharply increase the retention times of the chromatographed compounds without increasing the resistance of the column to the carrier-gas flow, i.e., the pressure difference at the inlet and outlet of the column is minimal. This latter circumstance, apparently, makes it possible easily to realize the optimal regime of chromatographic separation with respect to the carrier-gas velocity over the entire length of the column.

To verify the theoretical regularities derived above, it was necessary to compare the expected (i.e., calculated from the formulas) retention times with those obtained experimentally. Such a comparison for coinciding directions of motion of the carrier gas and the sorbent is given in Table 2. As follows from the data in the table, the calculated values of the retention times are very close to the experimental ones.

For opposite directions of motion of the carrier gas and the sorbent, the calculated values of the retention times are significantly greater than the values obtained experimentally. The reason for the discrepancy between calculation and experiment apparently consists in the fact that, when the column is shaken by the vibrational device, and especially under conditions of comparatively large and oppositely directed velocities of motion of the sorbent and the carrier gas, the density of the sorbent becomes lower than under conditions of an immobile stationary phase. As a result, the velocity of motion of the zone increases, and the corresponding retention times decrease.

Fig. 3. Chromatograms of the separation of a gas mixture for the case of opposite directions of motion of the carrier gas and sorbent: air (1), propylene (2), α- and β-butylenes (3) and (4) on 20% Vaseline oil on diatomaceous brick. a –sorbent moving, b –sorbent stationary

Figure 3: Fig. 3. Chromatograms of the separation of a gas mixture for the case of opposite directions of motion of the carrier gas and sorbent: air (1), propylene (2), α- and β-butylenes (3) and (4) on 20% Vaseline oil on diatomaceous brick. a –sorbent moving, b –sorbent stationary

To confirm the correctness of the explanation given, on the basis of the data for β-butylene the proportionality coefficient was calculated, correspond-

corresponding to the transition from the rate of motion of the zone at the density of the stationary sorbent to the corresponding rate under conditions of a moving sorbent, which proved to be equal to 1.3. In this case, the retention-time values of the compounds calculated taking into account the coefficient 1.3 are very close to the experimental ones.

The proposed method of elution chromatography with a moving sorbent in the column, in terms of the results achieved, differs fundamentally from chromatography in columns with a stationary sorbent and from continuous frontal chromatography. The proposed method is characterized by the fact that the chromatographed compounds of one and the same sample mixture undergo separation on columns of different effective length, with other experimental conditions equal, determined by the retention time of each compound. At the same time the relative retention time changes, which gives the proposed method fundamentally new possibilities. The application of the method is promising for the separation of complex mixtures whose components differ sharply in their properties (the motion of the carrier gas and of the sorbent coincide in direction), and for the separation of difficult-to-separate mixtures (the motion of the carrier gas and of the sorbent are opposite in direction).

Fig. 3. Chromatograms of the separation of a gas mixture for the case of opposite directions of motion of the carrier gas and sorbent: air (1), propylene (2), α- and β-butylenes (3) and (4) on 20% Vaseline oil on diatomaceous brick. *a* –sorbent moving, *b* –sorbent stationary.

It should also be noted that the design and the procedure for carrying out the experiments may be highly varied: the column may be fitted with various plugs, have forced feeding of sorbent, be thermostated at one temperature or (which is easily feasible) have a temperature gradient along the length of the column. In one experiment the rate of sorbent motion may be constant, may vary, or may be zero, which practically does not entail a change in the zero line of the chromatogram when a katharometer is used (the stationary regime is established within several minutes). In specific applications it is possible to combine the proposed variants (or one of them) with ordinary chromatography on columns with a stationary sorbent, and also to combine them with thin-layer chromatography. Apparently, the use of a moving sorbent (thread) in capillary chromatography is also promising.

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Note: Figure translations are in progress. See original paper for figures.