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A. A. Zhukhovitskii, N. M. Turkel’ taub, V. P. Shvartsman,

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Abstract

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A. A. Zhukhovitskii, N. M. Turkel' taub, V. P. Shvartsman, A. F. Shlyakhov

BROADENING OF FRONTS AND CALCULATION OF THE COMPOSITION OF MIXTURES IN CHROMATOGRAPHY WITHOUT A CARRIER GAS*

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Frontal chromatographic analysis has not found application in industrial control chiefly because the mixtures being analyzed usually require mixing with a carrier gas.

Chromatography without a carrier gas (CWCG) (^{1,2}) is also of interest because it makes it possible to enrich both heavy components (in frontal-desorption analysis) and light components (in frontal-adsorption analysis), and, under certain conditions (^{3}), to enrich all components.

However, in (^{2}) no simple method is given for calculating the composition from the chromatogram, and in (^{1}) doubt is expressed as to the possibility of constructing such a method.

The problem of calculating the composition from a chromatogram was considered by us for the example of a ternary mixture (components 1, 2, 3) passed through a layer filled with a fourth, least adsorbed gas (^{4}). The calculation is carried out for linear isotherms. Figure 1 gives a scheme of the distribution of zones arising in frontal-adsorption analysis, and an experimentally obtained chromatogram of the mixture.

The solution of the balance equations (^{2}) can be expressed in the following two forms:

$$N_3^0 \frac{t_3}{t_2 - t_3} = B\frac{t_1}{t_2} - C, \qquad N_2^0 \frac{t_3}{t_1 - t_2} = E\frac{t_3}{t_2} - F; \tag{1}$$

$$N_2^0 = A\left(\frac{t_1}{t_2} - 1\right) h_2, \qquad \frac{N_1^0}{h_1} = \frac{1}{b_1} - \frac{N_2^0}{h_1} \cdot \frac{b_2}{b_1}. \tag{2}$$

$$A = \frac{\Gamma_2}{b_2(\Gamma_1 - \Gamma_2)}, \qquad C = \frac{\Gamma_3^2}{(\Gamma_2 - \Gamma_3)(\Gamma_1 - \Gamma_3)}, \qquad B = \frac{\Gamma_2\Gamma_3}{(\Gamma_2 - \Gamma_3)(\Gamma_1 - \Gamma_3)},$$

$$E = \frac{\Gamma_2^2}{(\Gamma_2 - \Gamma_3)(\Gamma_1 - \Gamma_2)}, \qquad F = \frac{\Gamma_2\Gamma_3}{(\Gamma_2 - \Gamma_3)(\Gamma_1 - \Gamma_2)},$$

where t_i is the time of appearance of the zone; Γ_i is the Henry coefficient of the component; b_i is the coefficient characterizing thermal conductivity; h_i is the height of the zone step.

In the first form, the composition of the initial mixture is expressed only through the times of appearance of the zones (t_i); in the second form, detector readings are also used.

In this derivation it was assumed that the detector readings are linearly related to concentration for all components.

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* L. G. Novikova and L. G. Kornelyuk took part in carrying out the experimental work.

The systems of equations (1) and (2) provide the basis for the following methods of determining composition. In the first variant, calibration is reduced to obtaining straight lines in the coordinates

$$N_3^0 \frac{t_3}{t_2 - t_3} - \frac{t_1}{t_2} \quad \text{and} \quad N_2^0 \frac{t_3}{t_1 - t_2} - \frac{t_3}{t_2},$$

and in the second—straight lines in the coordinates

$$N_2^0 - \left(\frac{t_1}{t_2} - 1\right) h_2 \quad \text{and} \quad \frac{N_1^0}{h_1} - \frac{N_2^0}{h_1}.$$

After this, the composition is determined from calibration curves. We note that in the second variant there is no need to use a fourth substance, since the column can be washed with the least adsorbed component of the mixture.

These methods were tested by us on the example of a mixture of methane, nitrogen, and hydrogen. A column with SKT charcoal of $L = 60$ cm was preliminarily filled with helium. A katharometer G-10 was used as the detector. The composition of the mixtures was determined on the same column by the elution method. The flow rate of the mixture at the column inlet was 20 ml/min. The measurement results are presented in Fig. 2.

Fig. 1. Frontal-adsorption analysis.
a—scheme of zone distribution, *b*—chromatogram of a mixture of methane (1),

Fig. 1. Frontal-adsorption analysis. a—scheme of zone distribution, b—chromatogram of a mixture of methane (1), nitrogen (2), hydrogen (3), $N_1^0 = 0.28,\ N_2^0 = 0.36,\ N_3^0 = 0.36$

Figure 1: Fig. 1. Frontal-adsorption analysis. a—scheme of zone distribution, b —chromatogram of a mixture of methane (1), nitrogen (2), hydrogen (3), $N_1^0 = 0.28,\ N_2^0 = 0.36,\ N_3^0 = 0.36$

Fig. 2. Calibration graphs for calculation of composition, variant 1 (I), variant 2 (II)

Figure 2: Fig. 2. Calibration graphs for calculation of composition, variant 1 (I), variant 2 (II)

nitrogen (2), hydrogen (3),

$$N_1^0 = 0.28, \quad N_2^0 = 0.36, \quad N_3^0 = 0.36$$

Fig. 2. Calibration graphs for calculation of composition, variant 1 (I), variant 2 (II).

The points fall satisfactorily on straight lines, despite the fact that the methane isotherm is not linear.

We note that systems with a low hydrogen content at a high nitrogen content cannot be calculated, since the hydrogen step is absent on the chromatogram.

The errors in determining composition by the variants considered include calibration errors, measurement errors, and inaccuracies due to the assumptions of the theoretical calculation (linearity of the isotherm, linearity of the detector, and others). In order to reduce the contribution due to inaccuracies in the analysis of calibration mixtures, it is advisable to compare the results of determination by both variants for the same mixtures. Such a comparison showed that, for example, for nitrogen the mean value of the ratio of the modulus of the difference of the concent···

tions determined by both variants, relative to their mean value, is 8.8%. The analogous quantity characterizing the deviation of the concentration found from the initial one is, for nitrogen, 10.7 and 9% for the first and second variants, respectively.

The time-based calculation method has a number of advantages in addition to those indicated. There is no requirement concerning the dynamic range of the detector or the independence of its readings from velocity. Thus, in the calculation by the second variant, because of the nonlinearity of the detector calibration, the points with a high hydrogen content do not fall on straight lines, and the straight line in Fig. 2 IIa does not pass through the origin.

Fig. 3. Elution curves for washing ethane out with argon (a), nitrogen (b), and hydrogen (v) at different gas flow rates at the column inlet.

Figure 3: Fig. 3. Elution curves for washing ethane out with argon (a), nitrogen (b), and hydrogen (v) at different gas flow rates at the column inlet.

Fig. 3. Output elution curves for washing ethane out with argon (a), nitrogen (b), and hydrogen (v) at different gas flow rates at the column inlet.
$1 - \alpha_0 = 258$, $2 - \alpha_0 = 107$, $3 - \alpha_0 = 43$, $4 - \alpha_0 = 8.5$, $5 - \alpha_0 = 274$, $6 - \alpha_0 = 135$, $7 - \alpha_0 = 70$, $8 - \alpha_0 = 25$, $9 - \alpha_0 = 337$, $10 - \alpha_0 = 219$, $11 - \alpha_0 = 127$, $12 - \alpha_0 = 32$ cm/min

The method of analysis considered can be carried out only owing to the presence of steep fronts at the boundaries of the zones.

A specific feature of chromatography without a carrier gas is the increased spreading of desorption fronts when elution is carried out with a less adsorbable gas, and sharp adsorption fronts. The additional physical factors causing spreading in chromatography without a carrier gas reduce to the following: the flow rate changes along the length of the column and with time; in addition, in the process of adsorption and desorption of substances, local pressure gradients must arise, leading to a change in the spreading.

Let us consider the theory of the first of these effects and, on the basis of comparison with experiment, show that at small values of the Henry coefficients this effect determines the spreading.

The equations of sorption dynamics for the process of washing out a well-adsorbed component by a less adsorbable one, at constant pressure and temperature, may be written in the following form:

$$-\frac{1}{\Gamma_1}\frac{\partial}{\partial x}(\alpha N_1) = \frac{\partial N_1}{\partial t}, \tag{3}$$

$$-\frac{1}{\Gamma_2}\frac{\partial}{\partial x}(\alpha N_2) = \frac{\partial N_2}{\partial t}, \tag{4}$$

where α is the linear flow velocity, depending on the coordinate x and time t; N_1 and Γ_1 are the mole fraction and Henry coefficient of the eluting gas; N_2 and Γ_2 are the same characteristics of the gas being eluted.

An analogous problem for eluent analysis, taking into account longitudinal diffusion and sorption kinetics, has already been considered in the literature ([4]).

The boundary and initial conditions are written as follows:

$$N_1(x=0,t) = 1, \qquad N_1(x,t=0) = 0,$$

$$\alpha(x=0,t)=\alpha_0, \qquad \alpha(x,t\to 0)=\alpha_0\frac{\Gamma_2}{\Gamma_1},$$

where α_0 is the linear flow velocity at the entrance to the column.

Adding and integrating equations (3) and (4), we obtain:

$$\frac{\alpha N_1}{\Gamma_1}+\frac{\alpha N_2}{\Gamma_2}=f(t)$$

or, after taking the boundary conditions into account:

$$\alpha=\frac{\alpha_0}{N_1+\delta N_2}, \tag{5}$$

where $\delta=\dfrac{\Gamma_1}{\Gamma_2}$.

Substituting equation (5) into equation (3), we obtain:

$$-\frac{\alpha_0}{\Gamma_1}\frac{\partial N_1}{\partial x}=\frac{1}{\delta}\left[\delta+N_1(1-\delta)\right]^2\frac{\partial N_1}{\partial t}. \tag{6}$$

Thus,

$$U_{N_1}=\frac{\alpha_0}{\Gamma_2[N_1+\delta N_2]^2}. \tag{7}$$

Here U_{N_1} is the velocity of motion of the point with concentration N_1.

Comparison of the theory with experiment was carried out for ethane washed from a chromatographic column by nitrogen, argon, or hydrogen ($l=3.4$ m, $d=5$ mm, fraction 0.5-0.25 mm of Inza brick with 35% vaseline oil, $t=22^\circ$, $\Gamma_1=0.60$; $\Gamma_2=1.06$).

Figure 3 shows the outlet curves for the case of ethane being washed out by argon (4a), nitrogen (4b), and hydrogen (4c).

Since it follows from equation (7) that N_1 and N_2 are determined by the product $\alpha_0 t$, this quantity was chosen as the abscissa axis. The points on the graph represent the experimental values of N_1 and N_2 for a wide range of velocities. On the whole, there is good agreement between experiment and theory, which predicts the dependence of the outlet curve on the velocity and the nature of the washing gas. It should be noted, however, that in the case of hydrogen the deviations substantially exceed the experimental errors.

Equation (6) is equivalent to the equation for ordinary development chromatography with a concave isotherm, for which

$$\frac{\partial a_1}{\partial N_1} = \frac{1}{\delta}\left[\delta + N_1(1-\delta)\right]^2.$$

Therefore the leading front of nitrogen (the closing front of ethane) is diffuse. In frontal-adsorption analysis, on the contrary, the closing front of nitrogen (the leading front of ethane) will be steep. This circumstance leads to a substantial advantage of carrier-gas-free gas chromatography in comparison with eluent chromatography.

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