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CONCEPTUALLY NEW MODEL OF GAS CHROMATOGRAPHY

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Abstract

The paper describes a mathematical model of gas chromatography in terms of a set concentration waves passing through an adsorption column. An analytical solution is derived for the passage of concentration eigenwaves through the entire adsorption column. This makes it possible to find analytical solutions for an arbitrarily shaped concentration signal passing through the adsorption column. To do this, it is necessary to decompose the input concentration signal into a set of adsorption column eigenwaves and to obtain an analytical solution for each of the concentration eigenwaves at the exit of that column. All of the concentration eigenwave solutions are then combined. This is the solution for passing an arbitrary concentration signal through the adsorption column. This approach is suitable for any periodic adsorption process and allows for the variable concentration of components at the entrance to the adsorption layer. The wave approach to the analysis of chromatographic column processes provides an explanation for the empirical Van Deemter equations used in the practice of gas chromatography.

Key words: adsorption; gas chromatography; van Deemter equation; concentration waves.

КОНЦЕПТУАЛЬНО НОВА МОДЕЛЬ ГАЗОВОЇ ХРОМАТОГРАФІЇ

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Анотація

У статті описано математичну модель газової хроматографії як набір концентраційних хвиль, що проходять через адсорбційну колонку. Отримано аналітичне рішення для проходження власних концентраційних хвиль через адсорбційну колонку. Це дозволяє знаходити аналітичні рішення для концентраційного сигналу довільної форми, що проходить через адсорбційну колонку. Для цього необхідно розкласти вхідний концентраційний сигнал на набір власних хвиль конкретної адсорбційної колонки та отримати рішення для кожної з цих власних хвиль на виході з колонки. Потім усі рішення для власних концентраційних хвиль об'єднуються. Це і є рішенням для проходження концентраційного сигналу довільної форми через адсорбційну колонку. Такий підхід може бути використаний для будь-якого періодичного адсорбційного процесу, та дає змогу врахувати змінну концентрацію компонентів на вході в адсорбційний шар. Хвильовий підхід до аналізу процесів хроматографічної колонки дає пояснення емпіричних рівнянь Ван Деемтера, які використовуються в практиці газової хроматографії.

Ключові слова: адсорбція; хвиля; газова хроматографія; рівняння ван Деемтера.

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Introduction

Chromatography is a physical separation method in which the components to be separated are distributed between two phases, one of which is stationary while the other mobile phase moves in a specific direction [1–3].

The various chromatographic methods are named after the physical state of the mobile phase. For example, in gas chromatography (GC) the mobile phase is a gas, and in liquid chromatography the mobile phase is a liquid. A subdivision is made according to the state of the stationary phase. If the stationary phase is a solid, the GC technique is called gas-solid chromatography; if it is a liquid, the technique is called gas-liquid chromatography.

This paper discusses only gas-solid chromatography (GSC).

Separation of components using a gas chromatography process with a solid stationary phase based on a different adsorption value of separated substances.

The mobile phase in gas chromatography is an inert gas, usually helium, but sometimes nitrogen or argon. This mobile phase is often referred to as the carrier gas.

A schematic diagram of a gas chromatograph is shown in Figure 1. The major parts of a gas chromatograph include: carrier gas cylinder, flow controller, injector, chromatographic column, detector, and data system.

Chromatographic analysis begins with the rapid injection of a sample mixture into a stream of carrier gas. As it is transported through the chromatographic column, different components migrate through the column at different rates by interacting differently with the adsorbent in the column. As a result, each component is retained in the column for a different amount of time, known as the retention time. Different retention times cause the components to pass separately through the column outlet.

The initial gas mixture separates into a series of binary mixtures, one component of which is a carrier gas and the other component is from the mixture being analyzed. When these binary mixtures pass through a detector, it produces a response that indicates a change in the properties of the gas mixture.

The way to observe a separation result is through a chromatogram, which is a plot of the detector response versus the time that has elapsed since the injection of a mixture being tested.

The working principle of the gas chromatograph is based on the fact that the retention time of each component is an individual property of this component and does not depend on the composition of the analyzed mixture. Therefore, the peak corresponding to the substance will always be in its own place, if the
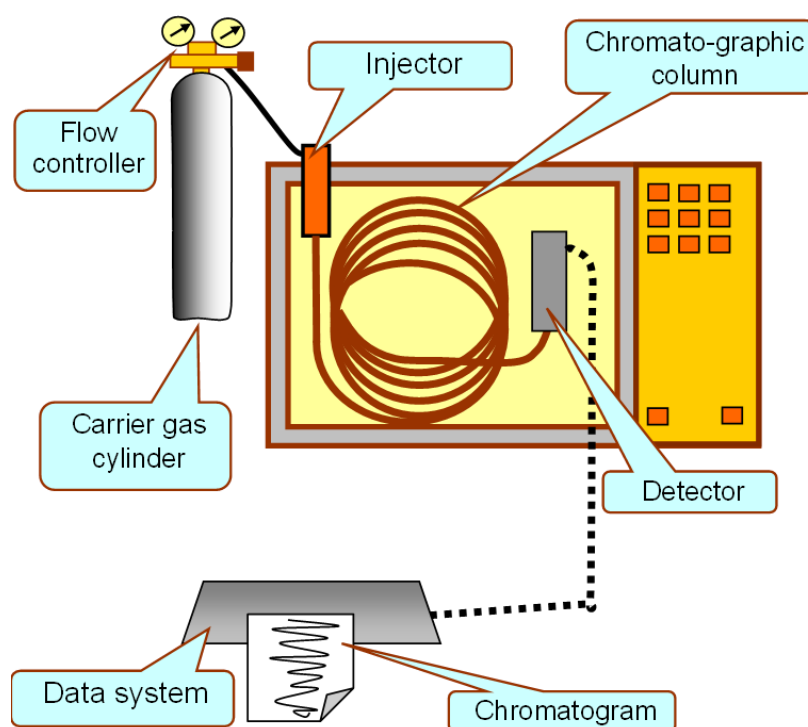

Fig. 1. The schematic diagram of the gas chromatography apparatus

conditions of analysis are constant, regardless of the composition of the initial mixture.

For quantitative analysis of a mixture the height or area of peaks in the obtained chromatogram is used. The height and area of chromatographic peaks are proportional to the concentration of components in a feed gas mixture.

Despite the fact that gas chromatography is a widely used method, and it is rightly considered one of the most theoretically sound methods, the practice of gas chromatography allows putting a number of questions that are difficult to answer within the framework of existing theoretical concepts. The most obvious of these difficult questions is Why is the chromatographic separation better achieved at high temperature of the absorption column?

It is well known that adsorption of gases increases with decreasing temperature of the adsorbent. If gas chromatography is based on multiple repetitions of adsorption and desorption of a component of a mixture, it would seem reasonable that separation of a mixture would be better at a lower temperature of the adsorption column. However, chromatographic separation processes are usually performed at elevated temperatures, usually around 100–200 °C.

Sometimes a higher temperature of the chromatographic column required that all components of the mixture be in the gaseous state. However, even in a case where the boiling temperature of all components of the mixture was significantly below room temperature, separation of this mixture was still performed at elevated temperature [1–4].

On the other hand, it is known that purification of gases by adsorption is always carried out at lower temperatures, if possible.

The incompleteness of modern concepts of gas chromatography is illustrated by the example of temperature-programmed gas chromatography. The application of temperature programming is a very adequate way to speed up a gas chromatographic analysis. This technique is also used for the analysis of gas mixtures with very different properties [4–6].

Figure 2 shows a typical view of chromatograms obtained at constant and variable temperatures of the adsorption column. It is clearly visible that peaks at the beginning of the chromatogram are completely separated from each other at low column temperatures, but peaks corresponding to the different components at the end of the chromatogram are broadened at this temperature. Conversely, the peaks of the chromatogram become sharper when the temperature of the adsorption column is increased, but the distance between adjacent peaks decreases.
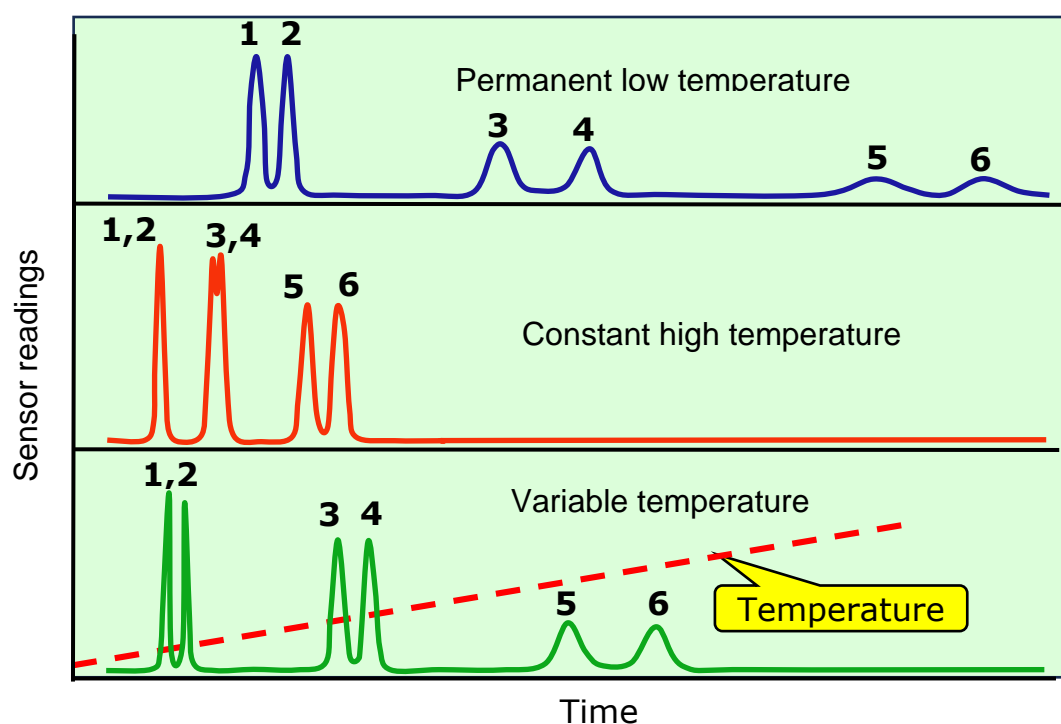

Fig. 2. The typical form of gas chromatograms at a constant and a variable temperature of adsorption column

If in the act of separation the column temperature is gradually increased from minimum to maximum, the shape of the chromatogram will be improved in terms of mixtures quantitative and qualitative analysis.

Gas adsorption increases with decreasing temperature. Therefore, the increasing distance between concentration peaks at low temperature is well explained within the framework of existing ideas about physical mechanisms of gas chromatography.

However, the sharp concentration peaks seem to be related to another factor that increases with increasing temperature. It can be assumed that this factor is the longitudinal diffusion of a component in a carrier gas, since it increases with increasing temperature, but the effect of diffusion usually explains the reverse process of broadening of concentration peaks at the column outlet.

The influence of this factor on the process of gas chromatography is so significant that the separation of gas mixtures at their chromatographic analysis is practically always carried out at increased temperature, despite the fact that in this case the adsorption is significantly reduced.

It follows that our understanding of separation mechanisms in gas chromatography is not complete and needs to be clarified.

Model of gas chromatography

Gas adsorption in porous adsorbent. Now we consider the adsorption of a component dissolved in the carrier gas.

We will use the following physical interpretation of the component spreading in a microporous adsorbent when constructing the mathematical model of the adsorption process [7; 8].

Carrier gas mixed with the component we want to adsorb is filtered through a porous adsorbent. Near the tangential points of the adsorbent grains are the stagnant zones where the carrier gas is almost stationary.

The gas flow passes through an array of holes in the empty spaces between the adsorbent grains.

Thus, the entire space filled with adsorbent can be divided into two zones: a stationary frame consisting of adsorbent grains and adjacent stagnant zones, and the system of holes and voids in which the carrier gas with the dissolved component moves.

The component in the stationary frame spreads mainly due to its molecular diffusion in the gas, filling the micropores in the adsorbent grains and the stagnant zones around them.

The component spreads by convection in the system, which consists of randomly arranged holes and cavities in the stationary frame.

Thus, the adsorbed component in the stationary frame and the gas flow in the hole system move along paths that are essentially non-intersecting (see Figure 3). The interactions between these flows occur along the boundary of the hole system in which the carrier gas is moving.

This physical pattern of gas propagation through a porous adsorbent bed differs significantly from the conventional scheme of mathematical description of adsorption, provided for example in [9–11]. The traditional approach
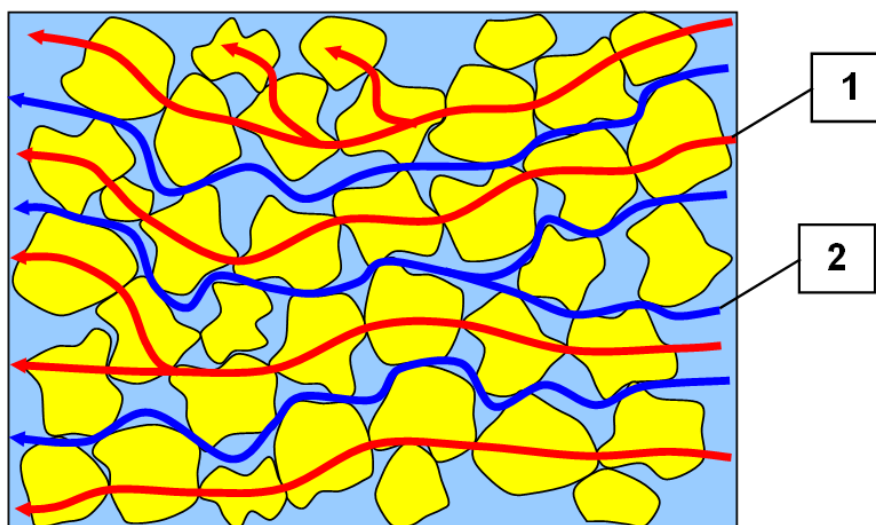

Fig. 3. The component spreading pattern in adsorbent bed.
1 is the motion of the diffusing component in a stationary frame;
2 is the carrier gas line of current

considers the diffusion of the adsorbed component within the moving carrier gas.

In the proposed formulation of this problem, the removal of a component from a moving carrier gas into a stationary frame acts as the absorption of this component in the problem of molecular diffusion in the pores of the adsorbent.

Convection of this component in channels with moving carrier gas is described by the separate equation.

That's why the equation of the molecular diffusion in the stationary frame can be written as follows:

$$D_E \frac{\partial^2 C(x,\tau)}{\partial x^2} - \beta \cdot F\big(C(x,\tau) - Cg(x,\tau)\big) = K_G \frac{\partial C(x,\tau)}{\partial \tau}, \qquad (1)$$

where $C(x,\tau)$ is actual volumetric concentration of the component in the stationary frame (gas in the pores of adsorbent and stagnant areas around the adsorbent particles), [m^3/m^3]; $Cg(x,\tau)$ is an actual volumetric concentration of the component in the moving carrier gas, [m^3/m^3]; β is the kinetic coefficient of mass transfer between the gas in the stationary frame and the moving carrier gas, [$m^3/(s \cdot m^2)$]; F is the specific contact surface of the stationary frame and the moving carrier gas, [m^2/m^3]; D_E is the equivalent value of the diffusion coefficient in the stationary frame, is equal to the product of the diffusion coefficient in the carrier gas and the relative value of the effective pore

cross section in the stationary frame, [m^2/s]; K_G is the nondimensional Henry constant for the adsorption isotherm.

It is noticed that the diffusion equation, recorded for the stationary frame, included the Henry constant. This means that the proposed mathematical model of the adsorption of the gas is a linear model. The isotherm used for this adsorption model is known as Henry's adsorption isotherm.

The material balance of the component in the elementary volume of carrier gas, moving inside the adsorbtion column, can be written in the form of another differential equation:

$$\beta F\big(C(x,\tau) - Cg(x,\tau)\big) - G \frac{dCg(x,\tau)}{dx} = 0; \qquad (2)$$

where G is a volumetric flow rate of carrier gas related to a unit section of the adsorbtion column, [m^3/s].

These two equations, when considered together, make it possible to find the component concentration distribution in the moving carrier gas and in stationary frame [12–14].

Wave Mathematical model of Adsorption. We consider the passage of the component through an adsorption column of width h.

We assume that the volumetric concentration of the component in the carrier gas varies harmonically in the inlet section of the adsorption column. This is shown in Figure 4.

The steady adiabatic adsorption process in the thermally insulated adsorbent bed is considered in this paper.

If we consider a stationary movement of a concentration wave through the adsorption column, according to Prigogine's theorem, the entropy production in this layer should reach its minimum [15].

Since the adsorption process, which is accompanied by heat effect and heat transfer, is basically an irreversible process, the heat that has been given in the adsorption process can never be completely given back in the desorption process.

Therefore, the steady-state process in which

the mass of the adsorbed substance is periodically changed will, by definition, be essentially irreversible. It follows that the minimum entropy produced in the steady-state movement of the concentration wave will be achieved when the mass of the adsorbed component remains unchanged. Therefore, in this mathematical model, the convention of constancy of the mass of the component adsorbed in the adsorbent bed is used.

Constant component weight is achieved only for the oscillation frequencies at which the instantaneous values of component concentration at the adsorbtion column inlet are equal to the instantaneous value of its concentration at the column outlet. This is only possible if the wavelength of the concentration in the stationary frame is equal to the thickness of the adsorbtion column.

Following the conventional terminology, we call these oscillations of the concentration – eigenmodes of this adsorption column, and the frequency of these oscillations – eigenfrequencies of the adsorption column.

In the considered mathematical model, it is also assumed that the gas filling the pores of the adsorbent and the gas adsorbed on its surface are in thermodynamic equilibrium.

The initial condition of equation (1) for this physical interpretation of the dispersion of the component in the porous adsorbent can be written as:

$$C(x,0) = Co(x). \tag{3}$$

Neumann boundary condition is:

$$\frac{\partial C(0,\tau)}{\partial x} = 0; \qquad \frac{\partial C(h,\tau)}{\partial x} = 0. \tag{4}$$

The physical significance of these boundary conditions is that the end surfaces of the adsorbed column are not absorbed and do not leave the component of interest.

Mass transfer occurs only between a moving carrier gas and the stationary frame of the adsorbtion column.

We write equation (1) in operator form (S is the operator used to differentiate in time) [15]:

$$D_E \frac{\partial^2 C(x,s)}{\partial x^2} - \beta F\big(C(x,s) - Cg(x,s)\big) = sK_G C(x,s) - Co(x). \tag{5}$$

The boundary conditions can also be written in the operator form:

$$\frac{\partial C(0,s)}{\partial x} = 0; \qquad \frac{\partial C(h,s)}{\partial x} = 0. \tag{6}$$

We construct the finite integral cosine transform for the coordinate *x*:

$$\overline{C}_k(s) = \int_0^h C(x,s)\cos(\mu_k \frac{x}{h})dx, \ k = 0,1,2... \tag{7}$$

The inversion formula is:

$$C(x,s) = \sum_{k=0}^{\infty} \frac{\overline{C}_k(s)}{\|\psi_k\|^2}\cos(\mu_k \frac{x}{h}). \tag{8}$$

Where $\|\psi_k\|^2$ is the square of the norm of the integral transform kernel:

$$\|\psi_k\|^2 = \int_0^h \cos^2(\mu_k \frac{x}{h})dx. \tag{9}$$

The last expression is the tabular integral:

$$\|\psi_k\|^2 = \int_0^h \cos^2\left(\mu_k \frac{x}{h}\right)dx = \left(\frac{x}{2} + \frac{h}{2\mu_k}\sin\left(2\mu_k \frac{x}{h}\right)\right)\Big|_0^h = \frac{h}{2} + \frac{h}{2\mu_k}\sin(2\mu_k) \tag{10}$$

Let the image of the expression for the second derivative of the component concentration be converted by the integration by parts formula:

$$\int_0^h \frac{\partial^2 C(x,s)}{\partial x^2}\cos\left(\mu_k \frac{x}{h}\right)dx = \frac{\partial C(x,s)}{\partial x}\cos\left(\mu_k \frac{x}{h}\right)\Big|_0^h + \frac{\mu_k}{h}\int_0^h \frac{\partial C(x,s)}{\partial x}\sin\left(\mu_k \frac{x}{h}\right)dx =$$
$$= \left[\frac{\partial C(x,s)}{\partial x}\cos\left(\mu_k \frac{x}{h}\right) + C(x,s)\left(\frac{\mu_k}{h}\right)\sin\left(\mu_k \frac{x}{h}\right)\right]\Big|_0^h - \frac{\mu_k^2}{h^2}\int_0^h C(x,s)\cos\left(\mu_k \frac{x}{h}\right)dx. \tag{11}$$

Let us find the eigenvalues μk of the integral transform to ensure that the boundary conditions are satisfied.
The boundary condition at *x=0*:

$$\left[\frac{\partial C(x,s)}{\partial x}\cos\left(\mu_k \frac{x}{h}\right) + C(x,s)\left(\frac{\mu_k}{h}\right)\sin\left(\mu_k \frac{x}{h}\right)\right]\Big|_{x=0} = \frac{\partial C(0,s)}{\partial x} = 0. \tag{12}$$

Therefore, the boundary condition at *x=0* for a cosine transform is automatically applied.
The boundary condition at *x=h*:

$$\left[\frac{\partial C(x,s)}{\partial x}\cos\left(\mu_k \frac{x}{h}\right) + C(x,s)\left(\frac{\mu_k}{h}\right)\sin\left(\mu_k \frac{x}{h}\right)\right]\Big|^{x=h} = \left[\frac{\partial C(h,s)}{\partial x}\cos(\mu_k) + C(h,s)\left(\frac{\mu_k}{h}\right)\sin(\mu_k)\right]. \tag{13}$$

Find the eigenvalues of the integral transform that satisfy the condition:

$$\frac{\partial C(h,s)}{\partial x}\cos(\mu_k) + C(h,s)\left(\frac{\mu_k}{h}\right)\sin(\mu_k) = 0. \tag{14}$$

Then dividing right and left sides of this equation to $\cos(\mu_k)$, we obtain:

$$\frac{\partial C(h,s)}{\partial x} = -C(h,s)\cdot\left(\frac{\mu_k}{h}\right)\cdot tg(\mu_k) = 0. \tag{15}$$

By comparison with the second boundary condition, we obtain the formula for finding the eigenvalues: $tg(\mu_k) = 0; \mu_k = \pi k.$ $\qquad k = 0,1,2...$ $\qquad\qquad$ (16)

Taking this into account, we obtain an expression for the integral transform:

$$\int_0^h \frac{\partial^2 C(x,s)}{\partial x^2}\cos\left(\pi\cdot k\frac{x}{h}\right)dx = -\frac{(\pi\cdot k)^2}{h^2}\int_0^h C(x,s)\cos\left(\pi\cdot k\frac{x}{h}\right)dx = -\frac{(\pi\cdot k)^2}{h^2}\overline{C}_k(s). \tag{17}$$

The diffusion equation in the stationary frame (1) takes the form, after the cosine transform, of the following $\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ equation:

$$-\frac{(\pi k)^2}{h^2}\overline{C}_k(s) = \left(s\frac{K_G}{D_E} + \frac{\beta F}{D_E}\right)\overline{C}_k(s) + \frac{1}{D_E}\int_0^h Co(x)\cdot\cos\left(\pi k\frac{x}{h}\right)dx - \frac{\beta F}{D_E}\overline{Cg}_k(s). \tag{18}$$

In this way, we can find the image of the function that describes the concentration of the component in a stationary frame:

$$-\overline{C}_k(s) = \frac{1}{\left(\frac{(\pi k)^2}{h^2} + s\frac{K_G}{D_E} + \frac{\beta F}{D_E}\right)}\int_0^h Co(x)\cos\left(\pi k\frac{x}{h}\right)dx - \frac{\beta F}{\left(\frac{(\pi k)^2}{h^2} + sK_G + \frac{\beta F}{D_E}\right)}\overline{Cg}_k(s); \tag{19}$$

For simplicity, we choose zero value of the initial temperature distribution: $Co(x) = 0$.

With this in mind, we obtain:

$$\overline{C}_k(s) = \frac{\beta F\cdot\overline{Cg}_k(s)}{\left(\frac{(\pi k)^2}{h^2} + \frac{s}{D_E}K_G + \frac{\beta F}{D_E}\right)}; \tag{20}$$

or

$$\overline{C}_k(s) = \frac{D_E\cdot\frac{\beta F}{K_G}\cdot\overline{Cg}_k(s)}{\left(s + \frac{\beta F}{K_G} + \frac{(\pi k)^2 D_E}{h^2 K_G}\right)}. \tag{21}$$

For further investigation, we specified the wave nature of the concentration oscillation in the carrier gas. This means that if we know the period of the oscillations, we can find the length of the concentration eigenwave by knowing the width of the adsorbtion column:

$$Cg_k(x,\tau) = A_k\cos\left(2\pi k\left(\frac{x}{h} + \frac{\tau}{T}\right)\right) = A_k\left[\cos\left(2\pi k\frac{x}{h}\right)\cos\left(2\pi k\frac{\tau}{T}\right) - \sin\left(2\pi k\frac{x}{h}\right)\sin\left(2\pi k\frac{\tau}{T}\right)\right], \tag{22}$$

where T is the period of oscillations in the main concentration wave, [s]. A_k is the amplitude of the k-th harmonic of the concentration oscillations, [m³/m³].

transformation in coordinate *x*, considering that the concentration wavelengths are multiples of the adsorption column length:

We construct the finite cosine integral

$$\overline{Cg}_m(\tau) = \int_0^h Cg_k(x,\tau)\cos\left(\pi n\frac{x}{h}\right)dx = A_k\cos\left(2\pi k\frac{\tau}{T}\right)\int_0^h\cos\left(2\pi k\frac{x}{h}\right)\cos\left(\pi n\frac{x}{h}\right)dx -$$

$$- A_k\sin\left(2\pi k\frac{\tau}{T}\right)\int_0^h\cos\left(2\pi k\frac{x}{h}\right)\sin\left(\pi n\frac{x}{h}\right)dx. \tag{23}$$

To find these integrals we use the frequency selection rule:

$$\int_0^h \cos\left(2\pi k \frac{x}{h}\right) \cos\left(\pi m \frac{x}{h}\right) dx = \left\{\begin{array}{l} 2m = k \Rightarrow \dfrac{h}{2} \\ 2m \neq k \Rightarrow 0 \end{array}\right\} \tag{24}$$

$$\int_0^h \cos\left(2\pi k \frac{x}{h}\right) \sin\left(2\pi n \frac{x}{h}\right) dx = 0$$

With this in mind: $\overline{Cg}_k(\tau) = A_k \cos\left(2\pi k \dfrac{\tau}{T}\right) \dfrac{h}{2}$. (25)

Next, convert this expression to the operator form using the differentiation operator with respect to time:

$$\overline{Cg}_k(s) = \frac{A_k h}{2} \frac{s}{\left(s^2 + \left(\dfrac{2\pi k}{T}\right)^2\right)}. \tag{26}$$

Substituting this expression into equation (21), after some elementary transformations, we obtain the expression that can easily be returned to its original form:

$$\overline{C}_k(s) = \frac{D_E \dfrac{\beta F}{K_G} \dfrac{Ah}{2} s}{\left(s + \dfrac{\beta F}{K_G} + \dfrac{(\pi k)^2 D_E}{h^2 K_G}\right)\left(s^2 + \left(\dfrac{2\pi k}{T}\right)^2\right)}. \tag{27}$$

Let it be transformed by the original. The resulting expression is the sum of two terms.

The first term is an inverse exponential function over time. The stationary value of this function is zero. The second summand of this original is the sum of the sine and cosine.

For simplicity, we introduce the following notation:

$$B_{ok} = \left(\frac{D_E \cdot \beta F \cdot A_k h}{2 K_G}\right); \tag{28}$$

$$B_{ck} = \frac{\left(\dfrac{\beta F}{K_G} + \dfrac{(\pi k)^2 D_E}{h^2 K_G}\right)}{\left(\left(\dfrac{2\pi k}{T}\right)^2 + \left[\dfrac{\beta F}{K_G} + \dfrac{(\pi k)^2 D_E}{h^2 K_G}\right]^2\right)}; \tag{29}$$

$$B_{sk} = \frac{\left(\dfrac{2\pi k}{T}\right)^2}{\left(\left(\dfrac{2\pi k}{T}\right)^2 + \left[\dfrac{\beta F}{K_G} + \dfrac{(\pi k)^2 D_E}{h^2 K_G}\right]^2\right)}. \tag{30}$$

With conside ration of this, the original is:

$$\overline{C}_k(\tau) = B_{ok}\left\{B_{ck} \cos\left(2\pi k \frac{\tau}{T}\right) + B_{sk} \sin\left(2\pi k \frac{\tau}{T}\right)\right\}. \tag{31}$$

Thus, we find a simple solution to the diffusion equation as its eigenwave passes through the adsorbent bed:

$$C_k(\tau, x) = \frac{2 B_{ok}}{h} \sqrt{B_{ck}^2 + B_{sk}^2} \cos\left(2\pi k \left(\frac{x}{h} + \frac{\tau}{T}\right) - \varphi_k\right); \tag{32}$$

where

$$\varphi_k = arctg\left(\frac{B_{sk}}{B_{ck}}\right). \tag{33}$$

The physical meaning of this formula is obvious. The oscillation amplitude of the component concentration in a stationary frame is proportional to the amplitude of its oscillation in a

carrier gas (at the entrance of the adsorbtion column) multiplied by a coefficient that depends on the carrier gas velocity and the adsorbent properties.

The phase of concentration oscillations in a stationary frame lags behind the phase of oscillation in a carrier gas at the entrance of the adsorbtion column.

In other words, at the same carrier gas velocity, the velocity of the concentration wave in the adsorbtion column is less than the velocity of the concentration wave out of the adsorbent bed. Moreover, this velocity difference is influenced by many factors, including the Henry's law constant for gas adsorption. It is easy to verify that the larger the value of Henry's constant, the larger the value of B_{sk} and therefore more phase shift, and is less the velocity of a concentration wave in the adsorbtion column.

The mass balance of a component in an elementary volume of carrier gas moving inside the adsorption column can be written in the form

$$C_k(x, \tau) = Ac_k \cdot \sin\left[2\pi k\left(\frac{x}{h} + \frac{\tau}{T}\right)\right].$$

For functions of the selected type, the mass balance equation (2) takes the form:

of a first-order differential equation (2). The physical meaning of this equation is that the change of concentration of the gas moving in the pores occurs only by mass exchange with the gas in a stationary frame.

We search for the solutions of this equation for the k-th wave of the adsorbtion column:

$$Cg_k(x, \tau) = A_k \cos\left[2\pi k\left(\frac{x}{h} + \frac{\tau}{T}\right)\right]. \qquad (34)$$

The component from the carrier gas can only go into the stationary frame; and vice versa, the component from the stationary frame can only go into the carrier gas. It follows that if the concentration of the component in a carrier gas decreases, it can only increase in the stationary frame, and vice versa, if the concentration of the component in a stationary frame decreases, it should increase in a carrier gas.

To satisfy this condition, represent the concentration waves in a stationary frame as a function of sine:

$$\qquad (35)$$

$$\frac{\beta F}{G} Ac_k \sin\left[2\pi k\left(\frac{x}{h} + \frac{\tau}{T}\right)\right] - \frac{\beta F}{G} A_k \cos\left[2\pi k\left(\frac{x}{h} + \frac{\tau}{T}\right)\right] = -\frac{2\pi k}{h} A_k \sin\left[2\pi k\left(\frac{x}{h} + \frac{\tau}{T}\right)\right]. \qquad (36)$$

We transform the last expression into a form suitable for analysis by grouping the similar terms and using the formula of difference identities for sine:

$$A_k \sin\left[2\pi k\left(\frac{x}{h} + \frac{\tau}{T}\right) - \phi_k\right] = \frac{\dfrac{\beta F}{G}}{\sqrt{\left(\dfrac{2\pi k}{h}\right)^2 + \left(\dfrac{\beta F}{G}\right)^2}} Ac_k \sin\left[2\pi k\left(\frac{x}{h} + \frac{\tau}{T}\right)\right]. \qquad (37)$$

The above expression can be interpreted as a spatial delay between the concentration wave in the carrier gas and the concentration wave in the stationary frame.

The tangent of the phase angle between the concentration of the component in a stationary frame and in a carrier, gas is equal to:

$$\psi_k = arctg\left\{\frac{\beta Fh}{2\pi k G}\right\}. \qquad (38)$$

The main difference between concentration waves and sound or electromagnetic waves is that in the case of superposition of ordinary waves, their amplitudes add up. In the case of superposition of concentration waves, a completely different law applies.

When two streams are combined or mixed, the concentration of a component in the combined stream is determined as the weighted average of its concentrations in the two mixed streams.

Let's assume that when we decompose a periodically changing concentration signal entering the adsorption column into a Fourier series, each harmonic corresponds to a portion of the carrier gas flow, and these portions of the carrier gas flow are the same for all harmonics. Then the amplitude of the concentration fluctuations after mixing two flows can be found by the formula

$$\frac{B_k + B_n}{2} = \frac{B_k}{2} + \frac{B_n}{2} \qquad (39)$$

Therefore, to obtain the correct value of the amplitude of the concentration wave after summing the two harmonics, it is sufficient to add the concentration waves whose amplitudes are equal to half of their amplitudes before mixing.

Another way to explain how two appears in the denominator of Formula (39) is as follows. In the steady-state motion of a concentration wave,

multiple component exchanges occur between the carrier gas and the adsorbent. As a result, the amplitudes of the component mass oscillations in the carrier gas and in the adsorbent are identical. It follows that the amplitude of the natural oscillations of the component concentration at the

$$Cg_k(x,\tau) = \frac{A_k}{2}\cos\left[2\pi k\left(\frac{x}{h}+\frac{\tau}{T}\right)-\varphi_k-\psi_k\right].$$

The physical sense of this formula is obvious: for eigenwaves propagating through the adsorbent bed, their frequency remains the same and the phase of the wave is delayed in time by an angle φk and in space by the angle ψk. Furthermore, the phase angles are different for different concentration waves.

For the mathematical model considered, it is essential that the system of eigenfunctions is complete. This means that any periodic sequence of arbitrarily shaped pulses can be expanded in a finite series of these eigenfunctions with any degree of accuracy. This position has been proven by mathematical analysis.

Thus, any concentration signal entering the adsorption column can be decomposed into the finite series of eigenfrequencies of that column. Furthermore, after separately passing through the adsorption column, we can combine these eigenmodes back into the output concentration signal at the column outlet.

Thus, having the analytical solution for the set of eigenfrequencies in the adsorption column, we can relatively easily obtain a solution for any periodic sequence of concentration pulses.

Results of calculations

To test the capabilities of the resulting mathematical model, previously published experimental data on the chromatographic separation of hydrogen isotopes were used.

Chromatographic isotope separation is one of the most promising methods for solving this important and complex problem [17-25].

As an example of these solutions, we calculate the passage of a pulse of a hydrogen and deuterium mixture through an adsorption column filled with zeolite 5a.

Helium is chosen as the carrier gas. The pressure in the adsorption column is assumed to be 1.0 bar. The Henry constant of zeolite 5a for the adsorption of hydrogen and deuterium is taken from and is assumed to be 1.0 m³/(m³·bar) for hydrogen and 1.0 m³/(m³·bar) for deuterium. The temperature of the adsorption column is taken as in experimental work [] -160°C. The formulas defining the mass transfer coefficient are taken

exit from the adsorbtion column will be equal to half of the oscillation amplitude at the entrance to this adsorbtion column.

Considering this, we obtain a relatively simple solution for the concentration eigenwaves exiting the adsorptive column:

$$(40)$$

from [26].

The adsorption column length is assumed to be 2.0 m, the carrier gas velocity in the column is assumed to be 60 mL/min. The Gaussian curve shape is given by the input concentration signal.

First, decompose the Gaussian impulse response of the nitrogen partial pressure into a Fourier series. To determine the expansion coefficients, we use well-known mathematical analysis formulas:

$$a_k = \int_0^{2\pi x/h} f(x)\sin\left(2\pi k\frac{x}{h}\right)dx\,;$$

$$b_k = \int_0^{2\pi x/h} f(x)\cos\left(2\pi k\frac{x}{h}\right)dx\,;\qquad(41)$$

where f(x) is a function expanded in Fourier series.

Thus, since we have a sine and cosine sum representation of an input concentration signal, we can easily predict the steady-state output concentration signal. To do this, we use equations (32; 33) and (38; 39) to find the Fourier series for the hydrogen and deuterium concentrations in the stationary frame and in the carrier gas leaving the adsorption column.

In this example, the calculation is performed for the first two hundred members of the Fourier series. The terminating effects of the Fourier series can thus be eliminated.

Figure 5 shows the calculated curves for the non-adsorptive gas concentration in the outlet of the adsorption column 1, and in the hydrogen 2 and deuterium 3 pulses.

As expected, during the passage of the concentration pulse through the adsorption column, the phases of individual harmonics of the concentration signal are shifted. This results in a delay of the concentration signal in time and space.

The initial data for the calculation are the same as in the article devoted to the chromatographic separation of hydrogen isotopes on a column of 2 mm diameter and 3 m length filled with zeolite 5a. In the experiment, the hydrogen retention time at a carrier gas velocity of 60 ml/min was 42.0

minutes, and the deuterium retention time was 63.2 minutes. The experiment was performed at a constant column temperature of −160°C [27].

The calculation gave a hydrogen retention time of 46 minutes and a deuterium retention time of 66 minutes.

The differences obtained are easily explained by the error in determining the adsorption of zeolite 5a at low temperatures in the calculations.

Discussion

Analysis of the mathematical model of gas chromatography

To analyze the solutions obtained using the wave model, we start from the concentration wave of the non-sorbent component, which has the same period and initial phase of oscillation as the component under study. This approach is generally accepted in analytical gas chromatography.

The wave model of gas chromatography assumes that the carrier gas, like the unsorbed component, does not interact with the adsorbent. Therefore, the velocity of the unsorbed solute is equal to the velocity of the carrier gas.

The concentration wavelength of the unabsorbed component can be found as the product of the carrier gas velocity and the period of the concentration wave for the unabsorbed component.

It is well known that the height of the equivalent theoretical plate and therefore the separation efficiency of the chromatographic column depends on the carrier gas velocity. The nature of this dependence is such that there is an

$$\varphi_k = arctan\left(\frac{\left(\frac{2\pi k}{T}\right)^2}{\left(\frac{\beta F}{K_\Gamma} + \frac{(\pi k)^2 D_э}{h^2 K_\Gamma}\right)}\right).$$

Since the kinetic mass transfer coefficient β for laminar flow is independent of the carrier gas velocity, the denominator in this expression is a constant. The only variable in the numerator is a period of the main eigenmode T, which is inversely proportional to the carrier gas velocity.

Therefore, the phase shift angle of a concentration wave in the stationary frame is the arctangent function of the square of the carrier gas velocity:

$$\varphi \approx arctan\left(const \cdot V^2\right). \qquad (44)$$

The spatial phase shift at the output of a chromatographic column is defined by the expression:

optimum carrier gas velocity at which a minimum equivalent theoretical plate height or minimum peak broadening is achieved.

The height equivalent to the theoretical plate for a packed column and the carrier gas velocity are related by the empirical Van Deemter equation, which has the form [6]:

$$h_T = A_D + \frac{B}{V} + CV , \qquad (42)$$

where AD, B and C are constants; V velocity of a carrier gas.

Since optimal values of the carrier gas velocity are important for chromatography, the literature gives various hypotheses about the physical meaning of the constants AD, B and C, as well as recommendations for determining their value.

A minimum height equivalent to a theoretical plate obtained by the van Deemter equation, explained by the fact that this equation is the sum of a decreasing hyperbolic function and an increasing straight line.

Figure 6 shows graphs of the phase shift of the concentration eigenwave in the stationary frame (φ_1), in the carrier gas, exiting the chromatography column (ψ_1), and the total phase shift angle ($\varphi_1+\psi_1$) as functions of the velocity of the carrier gas.

It is clear that the graph of the total phase shift for the concentration wave is similar to the function which is the sum of hyperbole and a straight line.

The expression for the phase shift of the eigenwaves in the stationary frame, after simplification, takes the form:

$$(43)$$

$$\psi \approx arctan\left(\frac{const}{V}\right). \qquad (45)$$

This conclusion is that the spatial phase shift is a decreasing function of the carrier gas velocity, like a hyperbola.

The implication of this analysis is that the phase shifts in space and time with respect to the velocity of the carrier gas are decreasing and increasing functions that have a minimum.

As shown in Figure 6 (gray area), for small values of the argument, the resulting function is well approximated by the van Deemter equation, which is the sum of the hyperbola and a straight line.

The summary phase angle ($\varphi i+\psi i$) for each eigenmode of the concentration signal finally defines the shape of the concentration pulse leaving the chromatography column. The smaller the phase shift angle between individual eigenmodes, the less blurred the peaks on the gas chromatogram, and therefore is less height equivalent to a theoretical plate.

Thus, the proposed mathematical model gives results that are in good agreement with the totality of experience in analytical gas chromatography.

Similarly, due to different speed of concentration waves of different substances, a short pulse of gas mixture passing through a chromatographic column stretching in a gas chromatogram.

From this point of view, it is quite natural similarity between optical spectrum of gas mixtures and view of a chromatogram, obtained by gas chromatography.

Similarly to the refraction of light waves, we could talk about the refraction of concentration waves in a chromatography column.
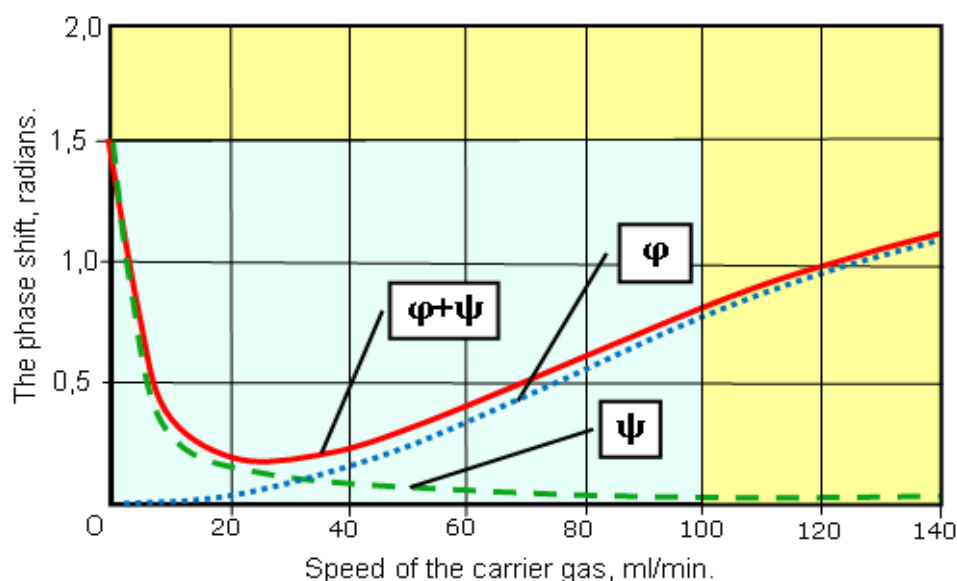

Fig. 6. The graphs of phase angle shift of concentration eigenwave as a function of the velocity of carrier gas.
φ – in a stationary frame; ψ – in a carrier gas, filling the adsorbent bed;
($\varphi+\psi$) is a total phase shift.

There are parallels between the movement of concentration waves and the propagation of various natural waves, such as a light.

The motion of concentration waves in the adsorbent is similar to the motion of light waves in a transparent medium.

Light waves are slowed down when they pass through a transparent medium. This effect depends on a nature of this medium. Similarly, a slowing down of concentration waves depends on a nature of the adsorbent.

The deceleration of light waves also depends on their frequency. Spectral analysis is based on this property of light. Due to different speeds of light waves in a transparent medium, a narrow light beam, in which mixed radiation from different atoms, decomposed into a spectrum.

Therefore, the wave approach to the consideration of gas chromatography is not only a new method of calculation, but it is the same kind of a new paradigm.

Conclusion

The mathematical model of wave adsorption produces reasonable results that well agred with empirical data to have accumulated in analytical gas chromatography.

Wave approach to the analysis of periodic adsorption processes enables to beter understanding process of analytical gas chromatography.

The mathematical model of wave absorption can improve methods of calculating the sorption dynamic for a broad class of batch action adsorption apparatus.

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