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Abstract

Full Text

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STEPWISE CHROMATOGRAPHY

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The most important tasks that industry poses for gas chromatography are its applications in automatic control and in the analysis of impurities. However, development chromatography has so far been developed as applied to problems of laboratory analysis of complex mixtures of components similar in their properties. In developing variants corresponding to the two tasks indicated above, it is necessary to keep in mind the following requirements. The signal transmitted by the detector in the form of a command must be stable and must not depend on changes in the experimental parameters; it must be directly and easily interpreted and must not require complex calibrations. The problem of impurity analysis requires preservation of the concentration of substances in the initial sample during development, i.e., elimination of the decrease in concentration due to dilution. All these requirements can be satisfied when samples of large volumes are used.

Fig. 1. Schematic of a stepwise chromatogram of a binary mixture

The introduction of small quantities is justified by the desire to obtain good separation of difficult-to-separate substances and leads to a substantial decrease (by tens and hundreds of times) in the concentration at the maximum as compared with the initial concentration (1). The problem therefore arises of an isothermal variant of development chromatography in which, even at the cost of poorer separation, the initial concentration η would be preserved and, consequently, the possibility of analyzing impurities and obtaining stable signals would be retained. Such a formulation of the problem is justified by the fact that, in automation practice, it is often necessary to determine a comparatively small number of substances that are very different in their properties and, in a number of cases, are present in small concentrations. The tasks posed are solved by the method of stepwise chromatography.

Two variants of stepwise development chromatography are possible. In the first, the chromatogram has the form of separated bands that have retained regions of constant (initial) concentration. In the second variant, a region of zero concentrations between all bands is not attained.

Figure 1 schematically presents a chromatogram containing two separated steps. From the figure, the conditions for preservation of a step during development are evident. They reduce to the requirement:

$$V_0 > 2v.$$

Here V_0 is the introduced volume of the sample, and v is the volume in which spreading occurred during development.

The solution of the diffusion equation for the problem of spreading of the boundary of a sharp change in concentration leads to the following formula for v:

$$v = 1.6\Gamma\sqrt{HL}. \tag{1}$$

Here Γ is the Henry coefficient, H is the plate height, and L is the length of the layer.

The condition for separation of steps, taking into account spreading beyond the limits of the applied step,

$$V_0 < L\Delta\Gamma - 0.74\Gamma\sqrt{HL}. \tag{2}$$

Thus,

$$3.2\Gamma\sqrt{HL} < V_0 < L\Delta\Gamma - 0.74\Gamma\sqrt{HL}. \tag{3}$$

From the compatibility condition for these inequalities we obtain the value of the smallest length L_{min} at which two separated steps can be obtained:

$$L_{\text{min}} = 4H/K_c^2. \tag{4}$$

Here $K_c = \Delta\Gamma/2\Gamma$ is the selectivity coefficient (^{2}).

If $L > L_{\text{min}}$, then, owing to (3), a range of values of V_0 is possible that leads to separated steps. Substituting (4) into either side of the inequality, we obtain the characteristic value of the smallest volume V_0 (V_{0x}) that must be applied in order to obtain separated steps:

$$V_{0x} = 6.5\Gamma H/K_c. \tag{5}$$

These formulas were obtained for the case in which the concentration ratio is close to unity. If it is equal to B, then the first of the conditions will not change, while the second is written as follows:

$$V_0 < L\Delta\Gamma - 1.4\sqrt{HL}\left[\operatorname{arc}\Phi\left(1 - \frac{2}{eB}\right) + \operatorname{arc}\Phi\left(1 - \frac{2B}{e}\right)\right]. \tag{6}$$

Here e is the base of natural logarithms, and $\operatorname{arc}\Phi$ is the inverse of Kramp' s function.

Calculation of $L_{\min}$ in accordance with (6) shows that at $B = 10$ the minimum length increases by a factor of 3 in comparison with $B = 1$. Let us determine the conditions for the presence on the chromatogram of n separated steps. Suppose that all n components fit between the maxima of the first and last components on the chromatogram:

$$L(\Gamma_n - \Gamma_1) > (n-1)V_0. \tag{7}$$

This condition is necessary but not sufficient, since the components may fit within the indicated interval but still not be separated. In addition, we neglect the term $0.74\Gamma\sqrt{HL}$, which describes the spreading of the step beyond the initial band. It is sufficient to impose the condition of preservation of the step for the most strongly sorbed component, since the width of its initial step is minimal:

$$V_0 > 3.2\Gamma_n\sqrt{HL}. \tag{8}$$

From (8) and (7) it follows that

$$n \leq 1 + 0.3\sqrt{L/H}\,(1 - \Gamma_1/\Gamma_n). \tag{9}$$

The factor $(1 - \Gamma_1/\Gamma_n)$ is close to 1 if $\Gamma \gg \Gamma_1$.

It follows from (9) that separation of a multicomponent system into individual steps is possible only in the case where $\Gamma_n \gg 1$. Hence it also follows that weakly sorbed components ($\Gamma \sim 1$) will not give individual steps. In particular, in capillary chromatography weakly sorbed–

substances will not give separated steps, since in this case the value of Γ is closer to unity than for gas-liquid chromatography. However, at small Γ the need for the method under discussion decreases, since broadening only slightly reduces the initial concentration.

Even if the formation of separated steps is not feasible, the type of analysis under consideration is nevertheless feasible if the number of components is small. In the absence of separation, the chromatogram will contain a number of steps. However, in all cases only the first and the last steps, for a linear isotherm, contain pure components. This circumstance is a consequence of the fact that in frontal-adsorption analysis the first component is isolated in pure form, whereas in frontal-desorption analysis the last component is isolated in pure form.

Thus, the composition of a two-component system is determined directly by the method of stepwise-development chromatography even in the absence of complete separation of the steps.

Fig. 2. Stepwise chromatogram of a mixture ethane –propylene –butane –isopentane –pentane

In the case of a three-component mixture, in order to obtain the concentrations of all three components it is sufficient to obtain on the chromatogram, in addition to the steps at the edges, a step in the middle, provided that the concentration increases on both sides of this step. In this case the concentrations of all three components in the introduced mixture are determined by the height of these steps.

As a rule, the problem of determining impurity concentrations arises for systems with few components. If the number of components to be determined is greater than three, the following two methods may be used. By increasing the length of the layer or decreasing the sample volume, one should obtain a zero zone. Then, for each system on both sides of the zone, the considerations given above are applicable. The presence of a zone thus increases the number of components determined by the indicated method. On the other hand, from the magnitudes of the steps it is easy, in the case of linear isotherms, to calculate the concentrations of the components, since the heights of the steps are determined by the sum of the corresponding concentrations.

Let us note, however, that calculations according to equations (3)–(8) show that obtaining separated steps, even for multicomponent systems, is a realistic task, feasible at comparatively small layer lengths.

Thus, taking $H = 0.3$ cm and $K_c = 0.1$, from (4) we obtain

$$L_{\text{min}} = 4 \cdot 0.3/0.1^2 = 120 \text{ cm}.$$

The characteristic volume per unit cross section according to (5) (at $\Gamma = 5$):

$$V_{0x} = \frac{5.5 \cdot 5}{0.1} \simeq 270 \text{ cm}^3.$$

Finally, for substances that differ greatly in properties, for an attainable number of separated steps at $L = 300$ cm, from (9) we obtain

$$n \leq 1 + 0.3\sqrt{300/0.3}, \qquad n < 11.$$

Fig. 3. Step chromatogram of a mixture of ethane—propane—isobutane—butane—isopentane—pentane

Figure 2: Fig. 3. Step chromatogram of a mixture of ethane—propane—isobutane—butane—isopentane—pentane

Experiment confirms the feasibility of obtaining separated steps for comparatively complex systems.

Figure 2 presents a step chromatogram of a five-component mixture (ethane, propylene, butane, isopentane, pentane). The sorbent is Inza brick impregnated with Vaseline oil, $L = 340$ cm; the detector is a katharometer, $V_0 = 170$ cm^3. Complete separation of the components takes place, with the steps preserved in the band of each of them.

Figure 3 presents a step chromatogram, obtained on Inza brick impregnated with hexadecane (35 wt. %), of a six-component mixture (ethane, propane, isobutane, butane, isopentane, pentane). The detector is flame-ionization, $L = 300$ cm, $V_0 = 16$ cm^3. Although, as is evident from the chromatogram, the first two components did not separate, their concentrations can be determined quite accurately from the horizontal sections.

The main advantage of step chromatography is the presence of a steady signal. The height of the step is determined without any additional operations (integration, multiplication, etc.) and depends on the experimental parameters only if the detector readings depend on them. This distinguishes this characteristic from the peak-maximum height of an ordinary chromatogram, which cannot be used as a signal.

Fig. 3. Step chromatogram of a mixture of ethane—propane—isobutane—butane—isopentane—pentane

Calibration in a step chromatogram is reduced to calibration of the detector, which in most cases can be based on literature data on the physical properties of the components. Thus, the numerous difficulties associated with the instability of calibration curves in ordinary chromatography are eliminated. The absence of band broadening in step chromatography raises the sensitivity of the chromatographic apparatus to the sensitivity of the detector, which is especially important for the analysis of impurities. Finally, since in step chromatography there is no need for complete separation of the components, this gives a decisive advantage for a number of systems. In this connection it should be noted that step chromatography makes it possible to use adsorbents with a developed surface; since broadening caused by nonlinearity of the isotherm is not only reduced because of the position of the unseparated components, but also does not prevent formation of a step on one side of the band. It should be noted that the use of step chromatography will make it possible to substantially increase the productivity of preparative chromatography.

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