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Abstract

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ON THE APPLICATION OF THE THERMAL FACTOR IN GAS CHROMATOGRAPHY

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Despite the appearance of a considerable number of studies in which the thermal factor is employed in adsorption separation ($^{1-3,\ 8-9}$), there is no physicochemical analysis of the question.

The introduction of the thermal factor leads to a number of advantages in chromatography. Changing the temperature of the adsorbent layer makes it possible to vary its capacity, which makes it possible to separate, on a single adsorbent, a large number of components and to carry out a continuous separation process ($^{4,\ 5}$). However, of greatest importance is the increase in the distance between the adsorbate bands and their narrowing. In addition, in adsorption analysis the thermal factor can sharply reduce the requirements imposed on the sensitivity and inertia of the recording instrument.

The advantages of chromatography are used most fully when the thermal factor is introduced into development chromatography. The combined action of the solvent stream and of any temperature field varying in time and space is called thermochromatography (^{6}).

It is expedient first to consider the dependence of the separating power in development analysis on temperature.

Separation in development analysis depends little on the temperature of the layer. A simple calculation leads to the following relations for the distance between the components (Δx) and the band width () in a layer:

$$\Delta x = L\Delta Q/RT, \qquad = mDL/\alpha)^{1/2}.$$

Here ΔQ is the difference between the heats of adsorption of the components, D is the coefficient of longitudinal diffusion, L is the length of the layer, α is the linear flow velocity, $m = 4\ln(c_{\max}/c)$, where $c_{\max}$ and c are the concentrations, respectively, at the maximum and at the edge of the band. On the effluent curve all distances are changed by a factor Γ (Γ is the adsorption coefficient) as compared with the adsorbent layer. Therefore the recorder plays the role of a certain magnifier, changing both Δx and . To characterize separation in the layer from the data of the effluent curve, it is expedient to consider the coefficient K, which is independent of the effluent temperature:

$$K = \Delta x/({}_1 + {}_2).$$

It is not difficult to show that, for a linear isotherm, the purity of the fractions is simply expressed through the coefficient K:

$$\delta = e^{-4K^2}/4K\sqrt{\pi},$$

where δ is the fraction of foreign component in the fraction.

Gluckauf (7) and other authors (8) proposed analogous criteria for the operation of a layer on the basis of the concept of theoretical plates. It seems to us more expedient to use the consideration of the physical processes of separation and broadening of the adsorbate bands.

In partition chromatography the diffusion coefficient D decreases with decreasing temperature and, just as with a curvilinear isotherm, the width of the bands sharply increases with decreasing temperature.

A temperature field independent of time does not lead to an improvement in separation. In this case

$$\Delta x = \frac{\overline{\Delta Q}}{R}\left(\frac{1}{T}\right)$$

and the process proceeds in the same way as with an un-

of that mean temperature. An analogous result is obtained for a field depending only on time (9,10).

However, the simplicity of implementing such a field and the possibility of separating a large number of components in a short time create a number of practical advantages for this variant.

Figure 1 gives the elution curve for the separation of a mixture

$$\mathrm{CH_4—C_2H_6—C_3H_8—C_4H_{10}—C_5H_{12}—C_6H_{14}}$$

in 3 min, with the temperature varied from 20 to 100°.

Increasing the separating power through the use of the thermal factor can be achieved only on the condition that, throughout the experiment, the components are at different temperatures and that the mean development temperature, accordingly, is different for each component. This is accomplished in the two most expedient variants of chromatothermography. In stationary chromatothermography, the adsorbent is acted upon, in addition to the solvent stream,

Fig. 1

Figure 1: Fig. 1

by a temperature wave moving in the direction of the stream. The sign of the temperature gradient also coincides with the sign of the velocity of the developer stream. In this case all components, in the stationary regime, are at their characteristic temperatures. The principal advantages of this variant consist in the compression of bands about their characteristic position in the temperature field to some stationary width. This makes the method especially useful for the analysis of substances at low concentrations. Its use substantially reduces the demands placed on the sensitivity of recording devices.

As was shown ([5]), on this basis continuous analysis can be carried out. As in elution chromatography, in stationary chromatothermography, in principle, any binary mixture can be separated, since the distance between bands is inversely proportional to the temperature gradient, while the band width ([12]) is inversely proportional to the square root of this quantity. Therefore, by decreasing the gradient (i.e., by increasing the length of the furnace), one can in principle achieve separation of bands of substances as close as desired in adsorbability.

Fig. 1

However, for a given layer length, in stationary chromatothermography the distance between bands will be smaller than in the elution method, since the better-adsorbed component is at a higher temperature than the more poorly adsorbed one. This does not mean, generally speaking, that the separating power ([13]) in stationary chromatothermography is lower than in the elution method, since in the former case narrowing occurs, whereas in the latter, spreading of bands occurs.

It is expedient to consider variants of chromatothermography in which there is an increase in the distance between bands compared with the elution method. To accomplish this, it is necessary to localize the more poorly adsorbed component in a region of higher temperatures than the better-adsorbed one. This means that the temperature gradient must have a sign opposite to the flow velocity. In this case the process ceases to be stationary. The "reverse" gradient can be produced in two ways. In the **first** of them, the direction of motion of the temperature wave coincides with the direction of the stream. Then the better-adsorbed components are progressively cooled, and the mov—

their movement is retarded. This variant has been called adsorption retardation (14). Only those components whose initial temperature is below the characteristic temperature will be accelerated.

The drawback of this variant is the difficulty of ensuring the appropriate conditions successively for different components. The method of selecting the optimal initial temperature (14) presents a number of practical inconveniences. In addition, the danger that the band of a component may split into several bands should be taken into account.

Fig. 2.
Time in min.; readings of the potentiometer in conventional units. Peak labels: n-pentane, isopentane, cis-2-butylene, trans-2-butylene, isobutylene, n-butane, isobutane, propylene, propane, ethylene, ethane, methane, hydrogen.

In the second variant, the direction of the temperature wave is opposite to the direction of the solvent flow. In this case all components move with acceleration and are washed out in one operating cycle.

It can be shown that, with a small reverse gradient, the acceleration is related in the following way to the flow velocity α and the Henry coefficient $q = \alpha^2\sigma/\Gamma$. Here $\sigma = Q\gamma/RT^2$, where Q is the heat of adsorption, γ is the temperature gradient.

Thus, the additional acceleration, which also decreases with increasing adsorbability, will improve the separation. This circumstance is illustrated by the data of Table 1, from which it is evident that the distance between the bands increases when the sign of the gradient is changed. This increase cannot be attributed entirely to the action of the outlet temperature, as is evident from the sharp increase in K.

Let us note that the use of nonstationary chromatothermography makes an adsorption column in some respects more advantageous than a partition column, since in this case not only isomers of butane and pentane are separated, but also saturated and unsaturated hydrocarbons and low-boiling gases. Figure 2 presents the outlet curve of such a mixture.

The drawback of the method under consideration for using the reverse gradient is that all components pass through identical temperature regions. The retardation variant can be used only under conditions of automation, which may be achieved by returning the furnace to the initial temperature with repetition of the cycle. In this case, owing to the advance of the components deeper into the furnace, they will gradually find themselves in the critical state, and their motion will be accelerated.

The thermal effect may be used not only in the form of a continuously acting field, but also in the form of brief heating (a pulse) followed by cooling. In the displacement method, an increase in the length of the adsorbent layer cannot practically be achieved because of the blurring

Table 1

Adsorbent Al_2O_3, 16.55 g. Tube length 250 cm; cross section 0.125 cm^2; $w = 20.8$ cm/min; $\alpha = 320$ cm/min; $\eta = 0.065$

Experiment no.	Mixture component	Temperature gradient character	Oven temperature, °C	Peak height, cm	Retention volume per 1 cm of section, v'_g, cm	Band width L/l, cm	Distance between maxima, Δx, cm	K
20	Propane	Forward	120	33	2640	91	240	1.39
20	Butane	Forward	120	46.8	2910	82	240	1.39
21	Propane	Reverse	120	9.2	2016	272	1920	4.1
21	Butane	Reverse	120	23	4250	205	1920	4.1
23	Propane	Forward	78	45.6	2640	82	368	1.7
23	Butane	Forward	78	21.6	3008	120	368	1.7
22	Propane	Reverse	78	16.8	2350	228.5	2240	4.5
22	Butane	Reverse	78	20.9	4500	183	2240	4.5
24	Propane	Forward	40	67.2	2570	64	640	2.8
24	Butane	Forward	40	46.4	3312	137	640	2.8
25	Propane	Reverse	40	16.8	2590	320	3250	5
25	Butane	Reverse	40	5.1	5840	330	3250	5

of bands and the limited sensitivity of the recorder. If, however, after development over a certain length of the adsorbent layer the adsorbate is subjected to pulsed "collecting" heating, then the length of the adsorbent layer can be increased without limit.

In pulse chromatography of a mixture it is expedient to carry out circulation, returning the component after the pulse to the beginning of the layer. At the end of the layer there should be a thin "collecting" layer of adsorbent with high adsorption capacity, to which the pulse is applied at the necessary moment. The application of the pulse must be regulated depending on the required degree of separation. At the moment of the minimum on the output curve, a pulse should be applied, and the enriched mixture should enter the adsorbent for subsequent circulation. Such a type of temperature field, dependent on the degree of separation, we call "self-consistent." On the basis of such fields one can obtain the best separation and draw up a program for a separating adsorption-thermal machine.

Automatic devices should have at their disposal such factors as temperature distribution, variation of speed, and so forth. On the basis of the automatic calculation of the quantity K, or of a similar quantity, after some period during which a simple test analysis is carried out, a temperature field with a reverse gradient will be automatically applied to the layer of adsorbed substance; the magnitude of this gradient will be automatically varied as a function of time, and K will continuously increase.

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