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# POSSIBILITY OF INCREASING THE SELECTIVITY OF CHROMATOGRAPHIC SEPARATION UNDER THE ACTION OF LASER RADIATION

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## SUMMARY

The possibility of increasing the selectivity of chromatographic separation when carried out in a field of laser radiation has been considered. This increase is the result of the selective excitation of one of the types of the molecules to be separated, the sorption of which decreases owing to the excitation. It has been shown that as a result of this effect, the rate of movement of the excited type of molecules along the column under favourable conditions may be nearly twice that of the non-excited variety. The method can be used in a capillary along which the laser beam is propagated and employed, for example, to resolve isotope mixtures.

In the laser chromatographic separation of different varieties of molecules, for instance isotopes, the chromatography is carried out in a field of laser radiation. In such a field, provided there is a corresponding frequency of excitation, some varieties of molecules are excited, while others remain non-excited. It is assumed that upon colliding with the surface of the adsorbent the excited molecules are either not adsorbed or are sorbed with a lower probability than the non-excited molecules[1–4]. The non-adsorbed molecules lose their excitation and return to the gas phase, where they are excited again. As a result of this process, the selectivity of separation ($a$) must be significantly increased.

Let the partition coefficient of a substance, $K$, be equal to $b/a$ (in the absence of laser radiation), where $b$ and $a$ are the concentrations of the substance in the gas and the liquid phase, respectively. As a result of the action of radiation, the concentration of particles in the gas phase will increase by a value $b^*$, and the partition coefficient will be equal to $(b + b^*)/(a - [b^* \kappa]/[\kappa_1])$, where $\kappa$ and $\kappa_1$ are fractions of the column volume occupied by the gas and the liquid phase, respectively. As laser chromatography is more conveniently effected on short columns at low temperatures, it can be assumed that $(a/b) \gg (\kappa/\kappa_1)$; then the partition coefficient, under conditions of laser radiation, will be $(b + b^*)/a$. As it is known that the velocity of movement of the band, $V$, is related to the carrier gas flow-rate, $U$, by

$$V(0) = \frac{U}{1 + \kappa_1/K\kappa}$$

or, taking into account the above inequality,

$$V(0) \approx \kappa U K / \kappa_1$$

then accordingly, under conditions of laser radiation with an intensity $I$

$$V(I) = \frac{U(b + b^*)\kappa}{a\,\kappa_1}$$

The ratio $V(I)/V(0)$ is equal to $\dfrac{b + b^*}{b}$.

As can be seen from the above equation, the acceleration of the band movement under the action of excitation depends on $b^*$. If it is assumed that the excited molecules upon collision with the surface are not sorbed, the ratio $(b + b^*)/b$ will increase with an increase in the laser radiation intensity.

We shall obtain the following relationship, by considering an one-dimensional problem:

$$D\,\frac{\partial^2 b}{\partial y^2} = \sigma I(b - b^*) \tag{1a}$$

$$D\,\frac{\partial^2 b^*}{\partial y^2} = -\sigma I(b - b^*) \tag{1b}$$

with the boundary conditions

$$y = 0: b = Ka,\; D\,\frac{\partial b^*}{\partial y} = b^* \bar{U}/\sigma \tag{2}$$

$$y = d: \frac{\partial b}{\partial y} = 0,\; \frac{\partial b^*}{\partial y} = 0 \tag{3}$$

where $y$ is the distance from the point considered to the phase interface, $D$ the diffusion coefficient of the substance to be resolved, $I$ the intensity of laser radiation, $\sigma$ the cross-section of radiation transition, $\bar{U}$ the heat velocity of the molecules and $d$ the half-thickness of the gas phase layer.

Eqns. 1a and 1b describe the diffusion of the non-excited and the excited particles, their formation and decay under the action of laser radiation being taken into account. The first of the boundary conditions shows that on the phase interface the usual condition of sorption equilibrium for non-excited molecules is maintained. The boundary condition in eqn. 2 expresses that any excited particle that finds its way to the wall loses its excitation and diffuses to the gas phase without being sorbed. The stream of excited particles $b^* \bar{U}$ must be equal to the stream of deactivated particles on the surface. Finally, the boundary condition in eqn. 3 expresses the symmetry of the problem and shows that the concentration of the excited particles is at a maximum in the middle of the column, while that of the non-excited ones is at a minimum.

In eqns. 1a and 1b, the terms describing spontaneous transitions are omitted, which is justified only when the time of diffusion to the wall, $\tau^* = d^2/D$, is much less than the time of spontaneous transition.

Strictly speaking, the condition in eqn. 2, expressing the equality of the diffusion stream to the gas kinetic stream, should be put at a distance from the boundary $\Lambda$ equal to the length of the free path of the molecule, with $\Lambda \ll d$, is practically satisfied with $y = 0$.

On solving eqns. 1–3, we obtain

$$\frac{V(I)}{V(0)} = F(I) = \frac{1 + (6D/\bar{U}d) \sqrt{2\sigma I\tau^*} \text{ tg } \sqrt{2\sigma I\tau^*}}{1 + (3D/\bar{U}d) \sqrt{2\sigma I\tau^*} \text{ tg } \sqrt{2\sigma I\tau^*}} \tag{4}$$

If we reject the assumption of deactivation of any molecule that reaches the phase interface and assume that the probability of its sorption is $\beta$ ($0 \leqslant \beta \leqslant 1$), then instead of eqn. 4 the following is obtained:

$$F(I) = \frac{1 + (6D/\bar{U}d) \sqrt{2\sigma I\tau^*} \text{ tg } \sqrt{2\sigma I\tau^*}}{1 + (1+\beta)(3D/\bar{U}d) \sqrt{2\sigma I\tau^*} \text{ tg } \sqrt{2\sigma I\tau^*}} \tag{5}$$

If $\beta < 1$, the velocity of movement of the chromatographic band changes, reaching a value of $2V(0)/(1 + \beta)$ with $\sigma I\tau^* \gg 1$.

Plots of the function F($I$) with $\beta = 0$ and different values of the dimensionless parameter $3D/\bar{U}d \approx \Lambda/d$, where $\Lambda$ is the length of the free path of the molecules, are given in Fig. 1. It can be seen that the intensity of light required to increase the velocity of movement of the chromatographic band by 10% rapidly increases with an increase in the value of the ratio $d/\Lambda$, tending (with $d/\Lambda \geqslant 100$) to a value independent of $d$, which can be found from the equation $\sigma I\Lambda/\bar{U} \approx 2 \cdot 10^{-3}$.
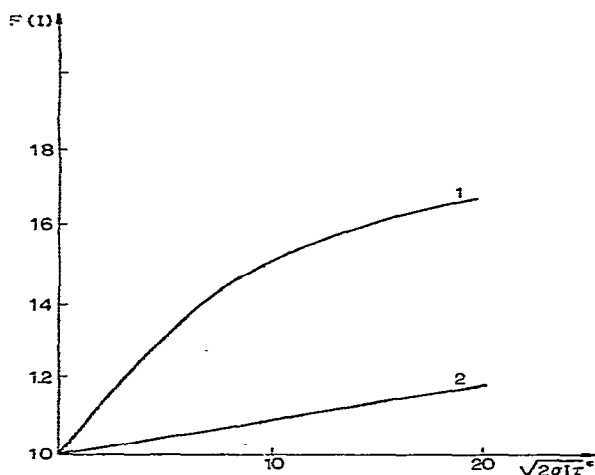


Fig. 1. Plot of function F ($I$) for different values of the parameter 3 $D/\bar{U}d$: (1) 0.1; (2) 0.01.

The life of the oscillatory excitement of molecules may reach values of the order of $10^{-5}$ sec. The average time of diffusion to the wall has the same order of magnitude

for capillaries of radius $10^{-2}$ cm at atmospheric pressure. From the estimates given by Gochelashvili *et al.*[1], it follows that in this instance the powers of gaseous $CO_2$ lasers are sufficient for a marked increase in the rate of movement of a chromatographic band. Thus, the use of lasers for the selective excitation of molecules makes possible the separation of substances that have similar sorption coefficients but different optical properties, even at atmospheric pressure.

The theory presented above is based on a number of assumptions, playing different roles in laser chromatography. For example, taking into account factors such as degeneration of the combining levels, the Poiseuille distribution according to velocities and diffusion of molecules in a liquid film, one merely obtains a more precise form of eqn. 5, without changing the basic deduction of the theory as to the influence of laser radiation upon the velocity of movement of a chromatographic band. The process considered is found to be critical to only one phenomenon, namely weaker sorption of the optically excited molecules.

Laser chromatography could be a sufficiently universal means of separating substances if lasers with a rearranged frequency of sufficient power are used. To demonstrate this possibility, $CO_2$ lasers are suitable for the chromatographic separation of boron isotopes in $BCl_3$. To demonstrate the effect of changing the velocity of movement of a chromatographic band, $SF_6$ could be used if a suitable liquid phase is selected.

In practice, laser chromatography can be carried out in a capillary the inner walls of which are coated with a liquid film, the laser ray being propagated along the capillary. Measures should be undertaken to prevent the evaporation of the liquid phase film under the action of laser radiation. For this purpose, the capillary must be well cooled and the thickness of the liquid phase film must not exceed a few microns.

Let us attempt to evaluate the parameters of the capillary required for detecting the effect discussed.

From purely optical considerations, let us assume that the diameter of the capillary is 1 mm and its length is 20 cm. For such a capillary, the thickness of the stationary phase film being about 2 $\mu$m, $\kappa \approx 1$ and $\kappa_1 = 10^{-2}$, and the retention time, $t_R$, is equal to $20/U$ $(1 + 0.01/K)$. To ensure reliable measurement, it is necessary that the retention time of $SF_6$ should be at least twice that of the non-sorbed component; to ensure this requirement, it is necessary to have $0.01/K \approx 1$, *i.e.*, $K \approx 0.01$. Under this condition, with a rate $U \approx 1$ cm/sec, $t_R \approx 40$ sec. According to the estimates given above, even on such a short capillary the retention time of $SF_6$ after irradiation must decrease by 5–7 sec, which can easily be recorded. Unfortunately, very little information is available on the retention of $SF_6$ on liquid phases. If some literature data[5,6] are used, the value of $K$ for this compound on Kel-F 3 can be estimated at room temperature. This value is about 1, which is obviously insufficient for our purpose. On decreasing the temperature, however, $K$ decreases rapidly. At temperatures below $0°$, using fluorinated hydrocarbons as the stationary phase, it will be possible to attain the required values of $K \leqslant 0.01$.

In conclusion, it can be expected that laser radiation will help to increase the selectivity of chromatography in the multi-stage separation of mixtures that are difficult to resolve, such as mixtures of isotopes.

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