1026 *Russian Chemical Bulletin, Vol. 46, No. 5, May, 1997*

The method of concentrating a substance from a solution in a stationary sorbent layer and its theoretical basis

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The principle of concentrating a substance from a mixture flow in a stationary sorbent layer of infinite length that was previously developed for gas chromatography is extended to liquid chromatography.

Key words: liquid chromatography, two-column system; two-temperature method of concentrating in a sorbent.

It is known that concentration of a substance from a mixture flowing in a circulation gas-chromatographic system with two moving electric ovens occurs, when the length of the sorbent layer is increased.[1] For the dynamic heating technique developed,[1] high enrichment is typical due to continuous feeding. Previously,[2] the dynamic heating method of concentrating in a stationary sorbent layer of infinite length was extended to gas chromatography with reverse purging of columns. However, the use of moving electric ovens restricts its application.[2] Furthermore, in some cases[3] a change in temperature does not affect the capacity (selectivity) of the sorbent much.

The method of concentrating a substance from a solution in a stationary sorbent layer of infinite length proposed by us is characterized by the fact that the moving electric ovens are replaced by alternating pulse heating and cooling of the two columns.[1,2,4] The two-column system for liquid chromatography with the reversal of the mobile phase flow is schematized in Fig. 1. The devices for pulse heating and cooling of the columns are not shown, because they have been described previously.[5,6]

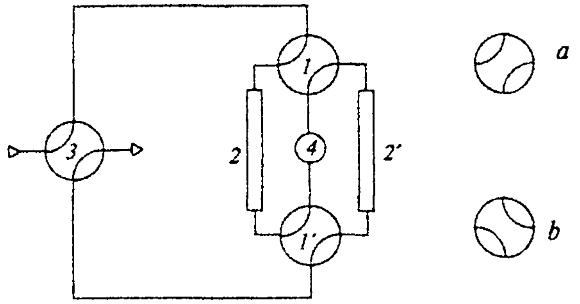

Fig. 1. The system for liquid chromatography with reverse flow of the mobile phase: *1* and *1'*, valves; *2* and *2'*, columns; *3*, the valve for the reversal of flow; *4*, detector.

Initially, the tempetature of the columns is the same and is equal to T_{cold}. With continuous feeding of the solution to the system, equilibrium is attained, *i.e.*, the concentration of the substance in the sorbent over the total length of the columns is in equilibrium with its concentration in the starting mixture. After switching valve *1'* to position "*b*" (see Fig. 1), column *2'* is heated to temperature T_{hot}. Then valve *1'* is returned to the initial position "*a*"; valve *3*, which reverses the flow of the mobile phase, is turned to position "*b*". The desorbed portion of the substance, as a chromatographic band whose length is equal to the length of one column, enters column *2*. This band is compressed when it moves from one column to the other.[5–7]

In the warmer column, the lower boundary of the band after time τ moves to a distance

$$L = \tau u/(1 + k_{\text{hot}}),$$

and in the cooler column, the upper boundary moves a distance

$$l = \tau u/(1 + k_{\text{cold}}),$$

where L is the length of each column (*2*, *2'*) of the system, l is the width of the band after its complete transition from one column to another; k is the capacity coefficient; u is the linear velocity of the moving solvent.

In the case under consideration we accept that $k_{\text{cold}} > k_{\text{hot}}$, hence, $l < L$, and the effect of compression can be described by the following equation:

$$b_T = l/L = (1 + k_{\text{hot}})/(1 + k_{\text{cold}}) = 1/q,$$

where b_T is the factor of pulse-thermal compression of the band,[5,6] and q is the enrichment coefficient.[7]

After the compression of the band is completed, valve *3* is returned to the initial state "*a*", and valve *1* is switched to position "*b*" (valve *1'* remains in position "*a*").

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 5, pp. 1063—1065, May, 1997.

Column *2'* is cooled to the temperature T_{cold} and consumes the adsorbed substance,[1] and column *2* is heated to T_{hot}. Then valve *1* is switched to position "*a*". The chromatographic band is transferred by the reverse flow of the mobile phase from the "hot" column *2* to the "cool" column *2'*. The movement of the concentration wave is accompanied by the repeated compression of the band to $v_1{}^0 = b_T v_1$, where v_1 is the band width at the time at which heating of column *2* is completed. The $v_1 > l$ relation is fulfilled owing to diffusion smearing.[1]

After the transition of the concentration band from column *2* to column *2'*, valve *1'* is turned to position "*b*", and the cycle is repeated according to the above sequence of the operations. Note that when substantial smearing is absent, $q_m = (L/l)^m = q^m$, where m is the number of operations of band compression.[7] Taking into account the regularities of the diffusion smearing of the concentration waves,[1] we obtain

$$v_2 = v_1(b_T{}^2 + 1)^{1/2}.$$

As a result of the subsequent operation of compression,

$$v_2{}^0 = v_1(b_T{}^4 + b_T{}^2)^{1/2}$$

and further

$$v_3 = v_1(b_T{}^4 + b_T{}^2 + 1)^{1/2}.$$

Owing to the multiple alternations of the processes of compression and smearing

$$v_m = v_1[b_T{}^{2(m-1)} + b_T{}^{2(m-2)} + \ldots + b_T{}^2 + 1]^{1/2}$$

or

$$v_m = v_1\left(\frac{1-b_T{}^{2m}}{1-b_T{}^2}\right)^{1/2}.$$

Thus, the increase in the width v_m is restricted by the limit ($b_T < 1$),

$$v_\infty = v_1[1/(1 - b_T{}^2)]^{1/2},$$

which is attained at $m \to \infty$. Hence, $q = L/l > L/v_\infty$.

So far we have described the transformation of a single band formed at the very beginning of the process. It is obvious that each heating of the columns generates new concentration waves of the accumulated substance because it is being continuously fed into the system. When reversal of the mobile phase occurs at a suitable time (with the aid of valve *3*), the concentration waves move along the stationary sorbent layer independently of each other periodically reversing direction (under the condition that Henry's law is fulfilled). On the basis of the results of the theoretical analysis, it is possible to conclude that each concentration wave approaches a steady state as the number of operations of compression is increased. Hence, under this condition, the maximum concentration of the substance in the entire zone formed by the superposition of generated concentration waves will increase and diffusuion smearing will not lead to the limit of increase in the concentration at the maximum of the resulting curve; this is in line with the previous conclusions.[1] The existence of an asymptotic value of the concentration at the maximum of the resulting curve has been established experimentally.[1] This phenomenon is due to the curved shape of the sorption isotherm.[1]

It is noteworthy that the described process can be carried out with a circular flow of the solution[4] and be treated as a version of the separation of a mixture of substances by the sorption two-temperature method of an oscillating wave that was proposed and theoretically justified previously.[8,9] When countercurrent columns are used, the two-temperature method[10] is accomplished either by varying such parameters of the process as the concentration and pH of the solution, the composition of the solvent, or by the introduction of complexation reagents.[3]

In the system under question (see Fig. 1), when changes in temperature have little effect on the capacity coefficient and selectivity, it is useful to combine the thermal and concentration pulses.[2,11,12] The two-temperature method realized in gas, liquid, and supercritical-fluid chromatography is of practical interest for solving problems of ion-exchange technology,[3,8,9] concentrating admixtures from various media,[7] and purifying gases and solvents.[8]

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Received October 18, 1996;
In revised form December 24, 1996