Gas-solid elution chromatography in a column with surface-layer biporous packing

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The theory of gas-solid elution chromatography on surface-layer biporous packing was examined. The explicit analytical expressions for the dependences of HETP and retention time on the thickness of the surface porous layer were obtained. The use of the surface-layer packing makes it possible to increase the separation efficiency as compared to the conventional sorbents.

Key words: sorption, chromatography, surface-layer packing, HETP, retention time.

Many works deal with the analysis of gas mixtures by gas-solid chromatography.[1—3] Uniform microporous sorbents, such as active carbons, silica gels, and zeolites,[4] are used conventionally for separation of mixtures in columns. Mass transfer in pellets of these sorbents is insufficiently intense, resulting in an incomplete separation of components of the sample. To increase the efficiency of the chromatographic process, the size of pellets is decreased, *i.e.*, micropacking columns are used. Accordingly, the chromatographic process should be carried out under higher pressures. The absence of micropores decreases the sorption capacity of these sorbents and restricts their use mainly to analysis of strongly sorbing gases, which makes these sorbents almost unsuitable for separation of light gases.

In this work, we studied chromatographic gas separation in a column packed with the surface-layer biporous sorbent. The schematic structure of the sorbent is presented in Fig. 1. Along with micropores that are the source of a high adsorption capacity of the sorbent, this sorbent contains macropores (transport pores) penetrating the pellet of the sorbent, through which a sample of separated substances is more intensely transported to sorption sites, *i.e.*, to micropores (or microzones). The biporous structure can be observed in many kinds of sorbents. For example, in the pellet composed of the zeolite crystallites bound by an inert material, zeolite crystallites are microzones and the space between them form the transport system of pores.[5] In the case of composite polymer materials, the dispersed phase plays the role of sorbing microporous zones, and the matrix itself acts as the transport system.[6]

Let us consider the mass transfer of the probe introduced into the carrier gas flow in a chromatographic column with a biporous packing. It is determined by the transport through the sorbent pellets and the transfer in the voids between the pellets.

The diffusion and sorption process in the pellet of the biporous packing is described by the following system of equations[5—8]:

$$\partial a/\partial t = \frac{1}{r^{\nu}}\frac{\partial}{\partial r}(r^{\nu}D_a\partial a/\partial r),\ 0 < r < r_0, \tag{1}$$

$$\varepsilon_n\partial a/\partial t + \varepsilon_t\partial C_t/\partial t = \frac{1}{R^2}\frac{\partial}{\partial R}(D_t R^2\varepsilon_t\partial C_t/\partial R), \tag{2}$$

where a is the concentration of the sample in microporous regions (zones); ν is the index relating to the shape of the microporous region ($\nu = 0$ is the plate, 1 is the cylinder, and 2 is the sphere); D_a is the diffusion coefficient in the microporous zone; r_0 is the pore radius in the microporous zone; r is the current coordinate in the microporous pellet (zone); C_t is the concentration of an

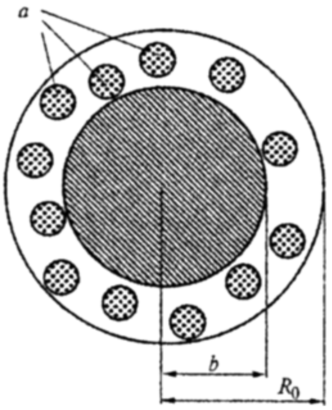

Fig. 1. Schematic view of the surface-layer of biporous packing pellet: a, microporous zone with pores with radii r_0; b, radius of the impermeable pellet core; R_0, pellet radius.

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admixture in the system of transport pores; D_t is the diffusion coefficient in the transport porous system; R is the current coordinate in the sorbent pellet; $\varepsilon_t = V_t/V$ and $\varepsilon_a = V_a/V$ are the volume fractions of the transport porous system and microporous zones, respectively; V_t, V_a, and V are the volumes of the transport porous system, microporous zones, and pellet, respectively; R_0 is the size of the sorbent pellet.

Equation (2) describes the transfer in transport pores of the spherical pellet, and Eq. (1) describes the sorption kinetics in the microporous zone. Assume that no sorbed molecule is present in the pellet in the initial moment, and the sorption is described by Henry's isotherm and occurs in microporous zones with $\nu = 2$ and on the surface of transport pores. Then the initial and boundary conditions take the form

$$C_t(r,R,0) = 0;\ (R^2\partial C_t/\partial R)_{R=0} = 0;$$

$$C_t(r,R,t) = K_t C(r,t), \qquad (3)$$

$$a(z,r,R,0) = 0;\ (\partial a/\partial r)_{r=r_0} = 0;$$

$$a(z,r,R,t) = k_a C_t(z,R,t), \qquad (4)$$

where K_t and k_a are Henry's constants for adsorption on the walls of transport pores and microporous zones; and $C(r,t)$ is the concentration of an admixture between the adsorbent pellets.

The mass transfer of an admixture in the chromatographic column is described by the equation

$$(1-\varepsilon)(\partial Q/\partial t) + \varepsilon(\partial C/\partial t) + \varepsilon\upsilon(\partial C/\partial z) =$$

$$= D_L(\partial^2 C/\partial z^2) + D_r\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial C}{\partial r}\right), \qquad (5)$$

where ε is the porosity of packing in the column; D_L is the molecular diffusion coefficient of the gas in the column; C is the concentration of the gas in the column; D_r is the longitudinal diffusion coefficient of an admixture in the column; and $Q = 3\varepsilon_t D_t(\partial C_t/\partial R)_{R=R_0}/(R_0)$. The corresponding boundary and initial conditions have the form

$$C(z,r,0) = (q_0/W)\delta(z)\delta(r).\ C(\pm\infty,t) = 0;\ \partial C/\partial z|_{\pm\infty} = 0, \qquad (6)$$

where q_0 is the amount of the sorbate introduced into the column; $\delta(r)$ and $\delta(z)$ are Dirac delta-functions; and W is the probe volume.

To determine the main parameters of gas chromatographic separation, let us apply the Laplace transform to the system of Eqs. (1)—(6). Then multiply the equations obtained by rz^n and integrate with respect to dr and dz. As a result, we obtain the system of recurrent equations[9]

$$s\varphi(s)\hat{\mu}_n(s) - \upsilon n\hat{\mu}_{n-1}(s) = D_L n(n-1)\hat{\mu}_{n-2}(s) + m_0, \qquad (7)$$

where $\varphi(s) = [1 + (1-\varepsilon)/\varepsilon 3(\beta\mathrm{cth}\beta - 1)]$; $\beta = [\tau_R s\psi(s)]^{1/2}$; $\psi(s) = (1 + \tilde{k}\,\mathrm{th}\sqrt{\tau_a s}\,/\sqrt{\tau_a s})$; $\tau_R = R^2/D_t$ and $\tau_a = r_0^2/D_a$ are the characteristic times of diffusion in the transport porous system and microporous zone in the spherical form ($\nu = 2$); $\tilde{k} = \varepsilon_a k_a/\varepsilon_t$; $\hat{\mu}_n(s) = \int e^{-st}\mu(t_n)\mathrm{d}t$; s is the Laplace parameter; and $\mu_n(t) = \iint C(r,z,t)rz^n\mathrm{d}z\mathrm{d}r$ is the nth moment of the chromatographic peak.

From Eq. (7) we obtain the explicit expressions for the first three moments (n = 0, 1, and 2) at high t ($s \to 0$). For this purpose, assuming n = 0, 1, and 2 in Eq. (7), we perform asymptotic expansions with respect to s of the given equations and apply to them the inverse Laplace transform. As a result, we obtain

$$\mu_0 = m_0/(1+\Gamma);\ \mathrm{M}_1 = \mu_1/\mu_0 = \upsilon/(1+\Gamma)\{t + 2A\}, \qquad (8)$$

$$\mathrm{M}_2 = \mu_2/\mu_0 = \upsilon^2/(1+\Gamma)^2\{t^2 + 6At\}, \qquad (9)$$

where $A = \tau_R(1+\tilde{k})^2 f(x)/15 + [\tilde{k}\tau_a/15](1-x^3)$; $\Gamma = [(1-\varepsilon)/\varepsilon]k\cdot(1-x^3)$; $x = b/R$; b is the radius of the impermeable core of the surface-layer biporous sorbent; $k = (\varepsilon_t + \varepsilon_a\cdot k_a) = \varepsilon_t(1+\tilde{k})$; $\tilde{k} = \varepsilon_a k_a/\varepsilon_t$; $f(x) = (1 - 5x^3 + 9x^5 - 5x^6)$. From where we find that at greater times

$$t_R = L(1+\Gamma)/\upsilon, \qquad (10)$$

$$H = 2D_L/\upsilon + 2\upsilon(1-\varepsilon)\varepsilon_t/[\varepsilon(1+\Gamma)^2]\times$$
$$\times\{[\tau_R(1+\tilde{k})^2/30]\cdot f(x) + [k\tau_a/15](1-x^3)\}, \qquad (11)$$

where t_R is the retention time; Γ is the distribution coefficient; $H = \sigma^2/L$ is the height equivalent to the theoretical plate (HETP); $\sigma^2 = (\mu_2/\mu_0 - \mu_1{}^2/\mu^2)$; σ is the dispersion of the chromatographic peak; and L is the column length.

Let us analyze the effect of the porous layer thickness on the parameters obtained. It can be easily shown that ε_t and ε_a are related by the correlation

$$\varepsilon_t + \varepsilon_a = 1 - x^3. \qquad (12)$$

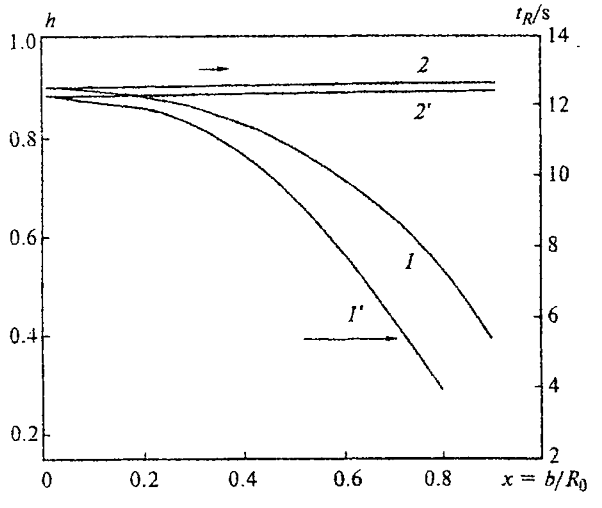

Fig. 2. Dependences of HETP ($H/2R_0 = h$) and retention time on the porous layer thickness (b): *1* and *1'*, surface-layer biporous packing; *2* and *2'*, volume biporous packing ($b = R_0$).

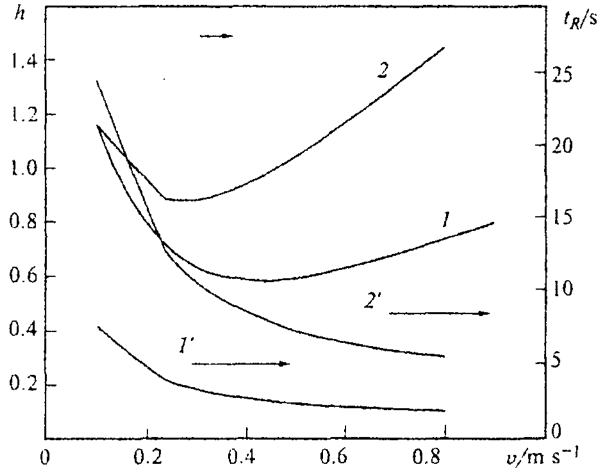

Fig. 3. Dependences of HETP ($H/2R_0 = h$) and retention time on the flow rate of the carrier gas (v): *1* and *1'*, surface-layer biporous packing; *2* and *2'*, volume biporous packing ($b = R_0$).

It follows from Eq. (12) that ε_t and ε_a depend on the porous layer thickness. Let us introduce new quantities of porosity of transport pores and microporous zones, which are independent of the pellet core size: $\tilde{\varepsilon}_t = V_t/(V - V_p)$ and $\tilde{\varepsilon}_a = V_a/(V - V_p)$ (V_p is the volume of the pellet core). Evidently, the following correlations are valid:

$$\tilde{\varepsilon}_t + \tilde{\varepsilon}_a = 1;\ \varepsilon_t = \tilde{\varepsilon}_t(1 - x^3);\ \varepsilon_a = \tilde{\varepsilon}_a(1 - x^3). \qquad (13)$$

The results of analysis of the effect of the surface layer thickness on the retention time and HETP are presented in Fig. 2. As seen in Fig. 2, this parameter affects substantially t_R and HETP. As $R_0 - b$ increases, the t_R and HETP values decrease. It follows from Fig. 3 that the optimum HETP value for the surface-layer sorbent is lower than that for the bulk (without an impermeable core) biporous sorbent, and it is achieved at a higher value of the flow rate of the carrier gas. Consequently, chromatographic analysis on this sorbent can be accomplished with a higher efficiency, *i.e.*, with a lower retention time and at a higher selectivity. The behavior of these parameters (t_R and H) are qualitatively confirmed by the experimental data presented previously.[10]

It is of interest that the use of the biporous sorbent makes it possible to apply two possible methods of chromatographic analysis. In conventional[10] gas-solid chromatography, macroporous sorbents are usually used; they have an insignificant fraction of microporous zones and are pre-modified by solvents, which efficiently sorb gases, thus increasing the K value. However, these columns lose their efficiency with time, because liquid sorbents are gradually removed with a carrier gas. As the analysis of the equations obtained shows, the use of the biporous sorbent in the case where $\tau_a \approx \tau_t$ does not involve modification of the surface of transport pores, since microporous zones themselves (for example, fine zeolite crystals) act as sorbing sities.

References

1. K. A. Gol'bert and M. S. Vigdergauz, *Vvedenie v gazovuyu khromatografiyu* [*Introduction to Gas Chromatography*], Khimiya, Moscow, 1990, 480 (in Russian).
2. *Rukovodstvo po gazovoi khromatografii* [*The Guide on Gas Chromatography*], Eds. E. Leibnits and Kh. G. Shtruppe, Mir, Moscow, 1988, vol. **1**, 480 pp. (Russ. Transl.).
3. N. Petsev and N. Kotsev, *Spravochnik po gazovoi khromatografii* [*Manual on Gas Chromatography*], Mir, Moscow, 1987, 260 pp. (Russ. Transl.).
4. Yu. A. Kokotov, P. P. Zolotarev, and G. E. El'kin, *Teoreticheskie osnovy ionnogo obmena* [*Theoretical Foundations of Ion Exchange*], Khimiya, Leningrad, 1986, 280 pp. (in Russian).
5. A. E. Chalykh, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1976, 735 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1976, **25** (Engl. Transl.)].
6. P. P. Zolotarev and M. M. Dubinin, *Dokl. Akad. Nauk SSSR*, 1973, **210**, 136 [*Dokl. Chem.*, 1973, **210** (Engl. Transl.)].
7. V. V. Ugrozov, Ph. D. (Phys.-Math.) Thesis, Institute of Physical Chemistry, Academy of Sciences of the USSR, Moscow, 1983 (in Russian).
8. L. I. Kataeva and V. I. Ulin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1977, 975 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1977, **26** (Engl. Transl.)].
9. V. V. Ugrozov, *Zh. Fiz. Khim.*, 1987, **61**, 1025 [*Sov. J. Phys. Chem.*, 1987, **61** (Engl. Transl.)].
10. Ya. I. Yashin, *Fiziko-khimicheskie osnovy khromatograficheskogo razdeleniya* [*Physicochemical Foundations of Chromatographic Separation*], Khimiya, Moscow, 1976, 216 pp. (in Russian).

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