Effect of the relative pressure on the efficiency and separation properties of open capillary columns

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Wide use of a combination of gas chromatographic (GC) separations with mass spectroscopic detection causes the necessity to study the effect of the relative pressure in a capillary column on its efficiency and separation properties. Using *n*-decane as a sorbate, a decrease in the relative pressure was shown to induce a slight increase in the efficiency of polar capillary columns but results in a considerable decrease in the optimal flow rate of the mobile phase and strongly constricts the Van-Deemter curve profile. In the presence of the restrictor, even minor deviations from the optimal flow rate can result in a considerable decrease in the column efficiency. Since the capillary restrictor is often a component of the interface between the column and mass spectrometer, it is necessary to exactly maintain the optimal operation conditions of the GC column to achieve an optimal efficiency of separation.

Key words: open capillary columns, gas chromatography, column efficiency, pressure of gas carrier.

Efficiency of separatory columns in chromatography is traditionally characterized by the Van-Deemter dependence that relates the height equivalent to a theoretical plate (HETP, H) to the linear flow rate of the mobile phase in the column[1]

$$H = A + B/u + Cu, \quad (1)$$

where u is the linear flow rate of the mobile phase; A, B, and C are constants independent of the rate of mobile phase motion.

This dependence has a shape of unsymmetric parabola and shows that the HETP passes through a minimum (H_{min}) at an optimal value of the linear flow rate of the mobile phase u_{opt} (see Ref. 2)

$$u_{opt} = (B/C)^{0.5}, \quad (2)$$

$$H_{min} = A + 2(BC)^{0.5}. \quad (3)$$

In the presented form Eqs (1)—(3) are applicable to liquid chromatography only, where the mobile phase is considered almost incompressible and the rate of its flow remains constant over the column length. In gas chromatography (GC) using a compressible mobile phase, the rate of gas flow changes along the column length, and the flow rate is averaged along the column length ($\bar{u}$) when constructing the Van-Deemter dependence. The HETP value also remains constant for any region of the column only in liquid chromatography, while in GC it changes along the column length. The HETP value determined in gas chromatographic experiments represents the quotient of the division of the column length (L) into its efficiency (N). This magnitude is also an average value because it indicates the peak broadening observed when the mobile phase diffuses through the whole column and related to its unit region (theoretical plate). Thus, in GC the Van-Deemter equation (1) takes the following form:

$$H = A + B/\bar{u} + C\bar{u}. \quad (4)$$

Since the HETP of the column in GC depends on the average flow rate of the mobile phase changing along the column length, it was assumed that only a small part of the column works under optimal pressure, whereas the major part of the column exists under the conditions far from optimum.[3—6] In this connection, it was proposed to carry out separations at low relative pressures (the relative pressure P in chromatography is equal to the ratio of the pressure at the inlet of the column p_i to the pressure at the outlet of the column p_o, *i.e.*, $P = p_i/p_o$). It is considered[3—6] that at the relative pressure close to unity the major part of the column works at the optimal flow rate of the mobile phase and the column efficiency increases. The experimental checking showed[3—6] that the observed efficiency of the packed chromatographic column increases, in fact, by ~30% with a 4.5-fold decrease in the relative pressure on the column.

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At present open capillary columns, especially in combination with mass spectrometric detectors, should be used at rather high relative pressures, because at the outlet of the column the pressure is close to zero (vacuum).[7] However, special capillaries, whose diameter is smaller, as a rule, than the diameter of the separatory column, are placed between the GC column and mass spectrometer almost in all interfaces. They are used to unify the attachment of columns of different diameter to the mass spectrometer and simultaneously they substantially change the dynamics of operation of the separatory column.

The purpose of the present work is to study the effect of an additional narrow capillary (restrictor) at the outlet of the column on the column efficiency and to determine optimal conditions of its operation, which make it possible to achieve the best resolution of mixtures of compounds to be analyzed.

Theoretical analysis

Pressure effect on the column efficiency in the classical Van-Deemter model. Expressions (1) and (4) were obtained[1] by the purely experimental way, and the coefficients A, B, and C were considered as experimental constants independent of the flow rate of the mobile phase. Further the properties of these coefficients were studied in more detail (see, *e.g.*, Ref. 7) and the coefficient values were shown to be determined by a series of properties of the chromatographic system, such as diffusion coefficients of sorbates, retention coefficients of sorbates, *etc*. Under usual chromatographic experiments when the pressure does not exceed 10 atm, it is assumed that these coefficients are constant values[2] independent of the flow rate of the mobile phase. At the same time, the flow rate of the mobile phase in chromatography is not an independent parameter. The rate value is determined by the values of the inlet and outlet pressures applied to the column. The relation of the average linear flow rate of the mobile phase in GC to the pressures at the inlet of the column p_i and at the outlet of the column p_o is given by the Poiseuille—Darcy equation[2]

$$\bar{u} = \frac{B_o}{L\eta}(p_i - p_o)j' = \frac{3B_o}{4L\eta}\frac{(p_o^2 - p_i^2)^2}{(p_i^3 - p_o^3)}, \qquad (5)$$

where $j' = 3(p_i^2 - p_o^2)(p_i + p_o)/[4(p_i^3 - p_o^3)]$ is the Halash compressibility factor,[2] L is the column length, η is the viscosity of the carrier gas at the temperature of the column, and B_o is the permeability of the column.

Substituting Eq. (5) into Eq. (4), one can find the dependence of the HETP on the pressure in the column

$$H = A + B\frac{4L\eta(p_i^3 - p_o^3)}{3B_o(p_i^2 - p_o^2)} + C\frac{3B_o(p_i^2 - p_o^2)}{4L\eta(p_i^3 - p_o^3)}. \qquad (6)$$

Equation (6), as well as Eq. (4), has two extrema: the maximum at $p_i = p_o$ and the minimum at

$$\frac{3B_o(p_i^2 - p_o^2)}{4L\eta(p_i^3 - p_o^3)} = (BC)^{0.5}. \qquad (7)$$

The first extreme is not interesting for chromatography, because it corresponds to the complete diffusion of the chromatographic zone in the absence of a mobile phase flow. This is due to the fact that the mobile phase flow in the column is absent when the pressures at the inlet and outlet of the column are equal. Equation (7) indicates that the minimum HETP value and the optimum value of the linear flow rate of the mobile phase should be retained at different ratios of the inlet and outlet pressures, only if the p_i and p_o values correspond to the conditions (7). Thus, under the condition of constant A, B, and C coefficients, the theoretical analysis of the classical Van-Deemter equation assumes no increase in the column efficiency with a change in the relative pressure. It follows from this analysis that the same optimum $\bar{u}$ and H values can be obtained for many combinations corresponding to the condition (7) rather than for the single combination of p_i and p_o. The experimental verification of these theoretical conclusions is given below.

Determination of the p_m pressure at the outlet of the column in the point of restrictor attachment. The Poiseuille—Darcy equation (5) describes the linear flow rate of the mobile phase as a function of the inlet and outlet pressures. The equation can be transformed into the form valid for the volumetric rate of the mobile phase $\bar{F}$, if the left- and right-side parts of the equation are multiplied by the cross section surface area of the column S accessible to the mobile phase

$$\bar{F} = \bar{u}S = \frac{SB_o}{L\eta}\Delta pj'. \qquad (8)$$

The average volumetric flow rate of the mobile phase $\bar{F}$ is related to the volumetric rate at the outlet of the column F_o, like its linear analog, through the James—Martin compressibility factor $j_3^2 = 3(p_i^2 - p_o^2)/[2(p_i^3 - p_o^3)]$

$$F_o = \frac{SB_o}{L\eta}\Delta p\frac{j'}{j_3^2} = \frac{SB_o}{L\eta}\frac{p_i^2 - p_o^2}{2p_o}. \qquad (9)$$

Using Eq. (9), one can easily determine the product $F_o p_o$, which is constant for any combination column—restrictor, because for the ideal gas it is proportional to the molar flow μ (mol (time unit)$^{-1}$) of the carrier gas in the system, which, according to the law of conservation of mass, is constant in the stationary system

$$F_o p_o = F_i p_i = \bar{F}P_{\bar{F}} = \mu RT. \qquad (10)$$

Therefore, the following expression is valid for two parts (column and restrictor) of the system considered:

$$\frac{S_1 B_{o1}}{L_1}(p_i^2 - p_m^2) = \frac{S_2 B_{o2}}{L_2}(p_m^2 - p_o^2), \quad (11)$$

where indices 1 and 2 refer to the separatory column and restrictor, p_i is the pressure at the inlet of the column, p_o is the pressure at the outlet of the restrictor, and p_m is the pressure at the outlet of the column and at the inlet of the restrictor.

Equation (11) can be solved with respect to p_m

$$p_m = \sqrt{\frac{p_i^2 + \Lambda p_o^2}{1 + \Lambda}}, \quad (12)$$

where $\Lambda = S_2 B_{o2} L_1/(S_1 B_{o1} L_2)$.

If both the column and restrictor are open capillary of different diameters and lengths, then, as it is known, the permeability of the capillary is given by the expression[2] $B_o = d_c^2/32$ and the cross section surface area of the capillary is $S = \pi d_c^2/4$. In this case,

$$\Lambda = d_2^4 L_1/(d_1^4 L_2). \quad (13)$$

Experimental

All experiments were carried out on an LKhM-8MD chromatograph and a capillary column (Zebron, 30 m×0.235 mm, covered with a film of the polydimethylsiloxane stationary phase, thickness 0.25 μm). The carrier gas was helium, the sorbate was *n*-decane, and the isothermal regime (70 °C) was used (flame-ionization detector, sensitivity scale of the electric meter 10^{-11} A, temperature of the injector 250 °C). Restrictors, being sections of capillaries of small diameter, were used to maintain a pressure at the outlet of the capillary column. The sizes of the restrictors are listed in Table 1.

Results and Discussion

The Van-Deemter dependences for the open capillary column under study were measured both in the absence of a restrictor and with attached restrictors (Fig. 1). As can be seen from Fig. 1, the attachment of the restrictor induces, first of all, the shift of the optimal flow rate of the mobile phase to the smaller value of flow rate, whereas the HETP in the minimum of the Van-Deemter curve only slightly changes with an increase in the restrictor resistance.

Table 1. Dimensions (length and diameter) of restrictors used for the calibration of the system

Length/cm (±0.1)	Diameter[a]/mm (±10%)	d^b/mm
5.0	0.10	0.097±0.001
10.0	0.10	0.096±0.001
20.0	0.10	0.097±0.001
10.0	0.075	0.074±0.001
15.0	0.162	0.161±0.001

[a] Nominal diameter given by the manufacturer.
[b] Diameter of the restrictor determined by the approximation of experimental points by Eq. (12).

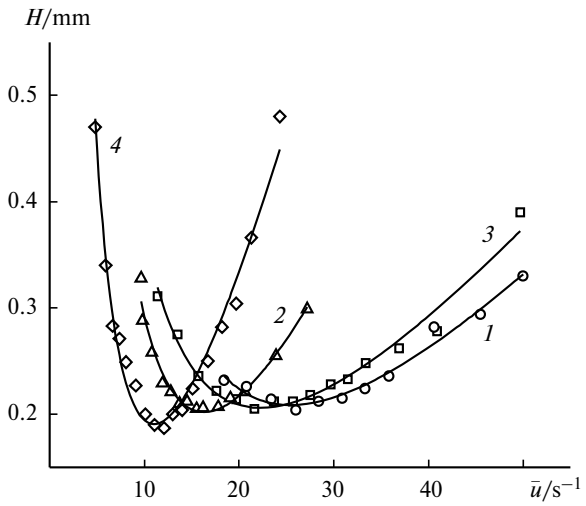

Fig. 1. Plots of the HETP (H) of an open capillary column *vs* average linear flow rate ($\bar{u}$) of the carrier gas in the absence (*1*) and in the presence of attached restrictors with the dimensions 10 cm×0.075 mm (*2*), 10 cm×0.1 mm (*3*), and 18 cm×0.05 mm (*4*). The conditions of measurement of the curves are given in Experimental.

To estimate the dependence of changes in $\bar{u}$ and H on the relative pressure on the column, it is necessary to determine the pressure p_m at the point of restrictor attachment to the column. This can be done on the basis of the preliminary calibration of the system, placing a tee joint at the point of attachment of restrictor to the column and installing a pressure gauge, or using theoretical calculations based on the constant molar flow of the carrier gas (*i.e.*, the number of moles per time unit) in the whole column—restrictor system. The theoretical and experimental data are compared in Fig. 2. The experimental points are well described by Eq. (12), and the restrictor diameters calculated by Eq. (13) are well consistent with the data presented by the manufacturer (see Table 1). Therefore, Eq. (12) was used further for the calculation of the pressure p_m; the found p_m values are listed in Table 2. The optimal flow rate of the carrier gas and the HETP values at the minimum of the Van-Deemter curve for the column—restrictor combinations studied are also given in Table 2 (only several curves are shown in Fig. 1).

As can be seen from Table 2, the HETP of the column only slightly depends on the relative pressure. This result does not agree with the literature data.[3–6] In our experiments the relative pressure on the column changes at most twofold; the HETP of the open capillary column

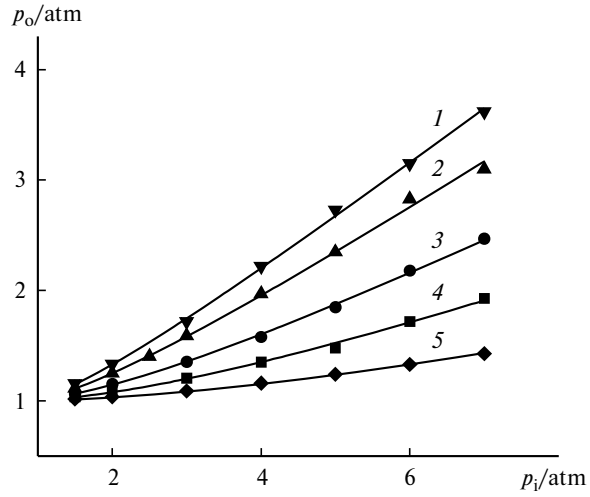

Fig. 2. Plots of the pressure at the outlet of the column (at the point of restrictor attachment) p_o *vs* pressure at the inlet of the column p_i for different restrictors. Dimensions of the restrictors: 10 cm×0.075 mm (*1*), 20 cm×0.1 mm (*2*), 10 cm×0.1 mm (*3*), 5 cm×0.1 mm (*4*) and 15 cm×0.162 mm (*5*).

decreases from 0.22 to 0.19 mm, *i.e.*, by ~16%. These changes are almost within the error of our measurements of the HETP, which was ~10%. The divergence with the literature data[3–6] can be due to several factors.

First of all, the range of changes in the relative pressure for the packed column was noticeably broader in Ref. 6 than that for the open capillary column in our study. Probably, because of the low efficiency of the packed column and the broad range of changes in the relative pressure in Ref. 6 the HETP of the column decreased considerably more strongly with a decrease in the relative pressure. It is most likely that these changes are not so significant with small changes in the relative pressure for highly efficient open capillary columns. The expression that assumes no pressure effect on the column efficiency was obtained in the later works.[8] According to these calculations, the HETP in the optimum of the Van-Deemter curve depends only on the retention factor of the substrate, which is pressure-independent[9,10] in the case of ideal gases. At the same time, the optimal flow rate of the carrier gas changes[8] in direct proportion to the change in the diffusion coefficient of the sorbate. The latter, as it is known,[2] changes in inverse proportion to the pressure change and, hence, the optimal flow rate of the carrier gas should decrease with the pressure increase.

We can accept the relative pressure as an independent variable, since, as can be seen from Table 2, the decrease in relative pressure at the optimal flow rate of the carrier gas is accompanied by the pressure increase both at the inlet and outlet of the column. Accordingly, the optimal flow rate of the mobile phase should decrease with a decrease in the relative pressure. This is confirmed by the experimental data, which show that the optimal flow rate of the carrier gas decreases with a decrease in the relative pressure (see Table 2), and the optimal rate decreases linearly with an increase in the value inverse to the relative pressure (Fig. 3).

The restrictor at the end of the column increases the dynamic resistance of the column and, as it is experimentally shown (see Fig. 1), induces the substantial compression of the Van-Deemter curve. It is caused by the increase in the *C* coefficient in the Van-Deemter equation (Table 3) and, therefore, in the slope of the right-side branch of the curve of the dependence of the HETP on $\bar{u}$

Table 2. Dependence of the HETP (*H*) and the optimal flow rate of the carrier gas on the restrictor resistance (measurement accuracy ±10 rel.%)

Dimensions of restrictor		B_o[a]·10^4/mm^2	Λ[b]	Optimal rate/cm s^{-1}	p_i[c]	p_m[d]	P[e] = p_i/p_m	H/mm
Length/cm	Diameter/mm				atm			
18	0.050	0.78	0.34	11.2	3.87	3.38	1.14	0.19
6	0.050	0.78	1.02	15.7	2.69	2.02	1.33	0.20
10	0.075	1.76	3.11	19.3	2.52	1.54	1.63	0.20
10	0.100	3.12	9.84	22.4	2.04	1.15	1.77	0.20
5	0.100	3.12	19.7	22.9	1.96	1.12	1.75	0.20
15	0.162	8.20	45.2	23.8	1.92	1.03	1.86	0.21
6.5	0.162	8.20	104.2	23.5	1.93	1.01	1.91	0.23
—[f]	—	17.26	—	23.9	1.92	1.00	1.92	0.22

[a] Permeability of the restrictor calculated according to the equation $B_o = d_c^2/32$.[2]
[b] Calculated by Eq. (13).
[c] Optimal pressure at the inlet of the column providing the optimal flow rate of the mobile phase.
[d] Optimal pressure at the outlet of the column complementary to the inlet pressure.
[e] Ratio of the pressure at the inlet of the column to the pressure at the outlet of the column in the minimum of the Van-Deemter curve.
[f] In the absence of a restrictor.

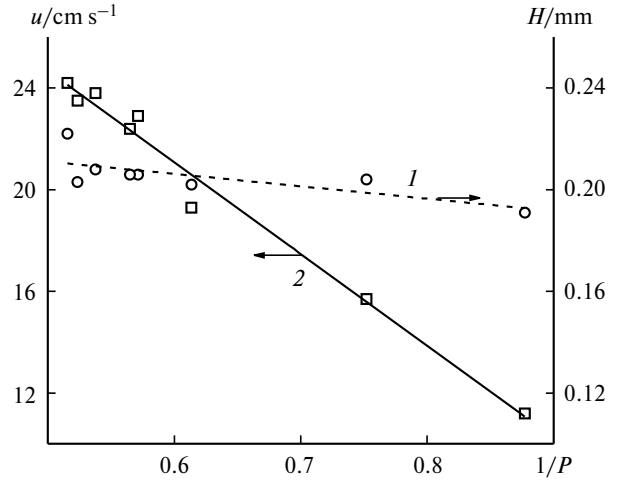

Fig. 3. Plots of the HETP of the column (*1*) and optimal rate (u) of the carrier gas flow (*2*) *vs* inverse relative pressure $1/P$.

Table 3. Change in the coefficients in the Van-Deemter equation for the capillary column (30 m×0.235 mm) upon the attachment of restrictors (the standard deviation is given in the last significant digit in parentheses)

Dimensions of restrictor		Coefficient in the Van-Deemter equation		
Length /cm	Diameter /mm	$-A$/mm	B/mm^2 s^{-1}	C/s^{-1}
—		0.25(5)	55(7)	0.0010(1)
6.5	0.162	0.39(3)	72(5)	0.0013(1)
15	0.162	0.27(4)	55(5)	0.0011(1)
5	0.1	0.34(3)	62(4)	0.0012(1)
10	0.1	0.28(3)	54(3)	0.0011(1)
10	0.075	0.54(5)	60(4)	0.0023(1)
6	0.05	0.30(4)	39(3)	0.0026(1)
18	0.05	0.59(4)	43(2)	0.0036(1)

(see Fig. 1). As a consequence, in the presence of the restrictor, even small deviations from the optimal flow rate can considerably decrease the column efficiency.

Thus, the studies performed did not confirm the concept on the strong effect of the relative pressure on the column efficiency for at least open capillary columns in the studied range of changing P. The change in the relative pressure exerts a considerably stronger effect on the shape of the Van-Deemter curve and the optimal flow rate of the carrier gas, which requires rigid fulfillment of the optimal parameters of the work of the column to achieve the optimal efficiency of separation. The pressure effect is due to the change in the diffusion coefficients of the sorbates with the pressure change in the system. In this case, the coefficients in the Van-Deemter equation depend on the carrier gas pressure and, therefore, are dependent variables,[11,12] which requires particular consideration.

References

1. J. J. Van-Deemter, F. C. Zuiderweg, A. Klinkenberg, *Chem. Eng. Sci.*, 1956, **5**, 271.
2. L. S. Ettre, J. V. Hinshaw, *Basic Relationships of Gas Chromatography*, Advanstar, Cleveland, 1993.
3. R. P. W. Scott, J. D. Cheshire, *Nature*, 1957, **180**, 702.
4. R. P. W. Scott, in *Vapour Phase Chromatography*, Ed. D. H. Desty, Butterworths Sci. Publ., London, 1957, 131.
5. J. Cazes, R. P. W. Scott, *Chromatography Theory (Chromatographic Science, 88)*, Marcel Dekker, Inc., New York, 2002, 496.
6. *Gas Chromatography*, Ed. D. H. Desty, Butterworth Sci. Publ., London, 1958.
7. C. Poole, S. Poole, *Chromatography Today*, Elsevier, Amsterdam, 1991.
8. B. A. Rudenko, G. I. Rudenko, *Vysokoeffektivnye khromatograficheskie protsessy* [*Highly Efficient Chromatographic Processes*], Nauka, Moscow, 2003, **1**, p. 79 (in Russian).
9. A. A. Korolev, V. E. Shiryaeva, T. P. Popova, A. V. Kozin, A. A. Kurganov, *Zh. Fiz. Khim.*, 2009, **83**, 670 [*Russ. J. Phys. Chem.* (*Engl. Transl.*), 2009, **83**, 776].
10. A. V. Kiselev, A. V. Iogansen, K. I. Sakodynskii, V. M. Sakharov, Ya. I. Yashin, A. P. Karnaukhov, N. E. Buyanova, G. A. Kurkchi, *Fiziko-khimicheskoe primenenie gazovoi khromatografii* [*Physicochemical Application of Gas Chromatography*], Khimiya, Moscow, 1973, 255 pp. (in Russian).
11. G. H. Stewart, S. L. Seager, J. C. Giddings, *Anal. Chem.*, 1959, **31**, 1738.
12. J. C. Giddings, S. L. Seager, L. R. Strucki, G. H. Stewart, *Anal. Chem.*, 1960, **32**, 867.

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