



Optimization of performance of monolithic capillary column in gas chromatographic separations

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ABSTRACT

Dependence of monolithic column efficiency on column pressure was analyzed using modified Van Deemter relationship with incorporated inlet and outlet column pressures as independent variables. It was demonstrated that the highest column efficiency is observed at high pressures. Inlet and outlet pressure increase has to be controlled in such a way that the relative pressure approaches 1 and the pressure drop across the column is close to zero. Experimental results obtained for open and monolithic capillary columns confirm up to 50% higher column efficiency as compared to column efficiency under standard conditions found using conventional Van Deemter plot. Pressure increase also results in a decrease in the optimal carrier gas velocity and corresponding increase in the analysis time. This drawback can be compensated via an increase in the column temperature.

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1. Introduction

Column efficiency in gas chromatography can be significantly increased using packing the column with small diameter particles (for packed columns) or by reducing capillary diameter (for open capillary columns). Careful control of separation conditions is also an important factor affecting column performance. Widely applied tool to optimize separation conditions is Van Deemter plot [1], which represents a relationship between the height equivalent to the theoretical plate (HETP) and the velocity of carrier gas. Van Deemter plot enables finding an optimal velocity of the carrier gas u_{opt} at which the column efficiency is largest.

However, the carrier gas velocity is not the only operating parameter affecting column efficiency. The inlet-to-outlet pressure ratio (relative pressure) has also been recognized as an important parameter affecting the column efficiency [2–4] and speed of analysis [5–8]. Theoretical considerations of impact of relative pressure on column performance were presented by Giddings [2,3] and later by Cramers et al. [5,6]. These authors predicted that the column efficiency would drop by up to 12.5% when relative pressure varies from 1 (most favorable case) to indefinitely high value (the worst case).

Experimental proof of impact of pressure on column performance provided controversial results. For example, Scott [9,10]

found that HETP of a packed column decreased from 0.056 to 0.04 cm (i.e. by 28%) with the relative pressure decrease from 8.2 to 2.6. Even larger changes were observed by DeFord et al. [11] who varied outlet column pressure from vacuum (0.167 atm) to 5 atm. At the same time Giddings [5,12] claimed that even severe pressure gradients led to small loss of resolution.

This research was extended to capillary columns and vacuum outlet as soon as capillary columns and mass-spectrometric detectors emerged in GC praxis. However, the discrepancy in the reported data was not eliminated. For example, Hatch et al. [13] and Vangaever et al. [14] reported up to 30% loss in separation efficiency due to an increase in pressure gradient with vacuum column outlet. Others reported no loss [15] or even improved resolution [16]. However, all reports agreed that the optimum gas velocity is shifted to higher values with vacuum column outlet [4–7,14,15].

Last two decades monolithic stationary phases are intensively investigated in HPLC [17]. Sykora et al. [18] introduced monolithic columns in GC. This publication encouraged other researchers to investigate potential of monolithic column in GC and comprehensive review on the topic can be found in [19]. Monolithic columns in GC afford HETPs comparable with those typically found for liquid separations. However, they require large pressure gradient due to low column permeability. Therefore, pressure optimization is an important factor for GC use of monolithic columns. The report discusses use of an extended model of the Van Deemter relationship. In contrast to previous investigations with capillary columns in which the column pressures did not exceed a few bar, experimental data in this work were collected at pressures ranging from 1 to 150 bar.

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Table 1
Characteristics of restrictors used in combination with capillary columns in the study.

Column/restrictor		B_o^a mm ²	Λ^b	Optimal column parameters ^c				
Length cm	Diameter mm			Velocity cm/s	Inlet pressure p_i , bar	Outlet pressure p_m , bar	Relative pressure $P = p_i/p_m$	HETP mm
Open capillary column		17.26×10^{-4}	–	23.9	1.92	1.00	1.92	0.22
14.8	0.025	0.195×10^{-4}	0.026	4.6	14.8	14.6	1.01	0.16
22.9	0.050	0.78×10^{-4}	0.25	9.4	3.49	3.16	1.10	0.19
18	0.050	0.78×10^{-4}	0.34	11.2	3.87	3.38	1.14	0.19
6	0.050	0.78×10^{-4}	1.02	15.7	2.69	2.02	1.33	0.20
10	0.075	1.76×10^{-4}	3.11	19.3	2.52	1.54	1.63	0.20
10	0.100	3.12×10^{-4}	9.84	22.4	2.04	1.15	1.77	0.20
5	0.100	3.12×10^{-4}	19.7	22.9	1.96	1.12	1.75	0.20
15	0.162	8.20×10^{-4}	45.2	23.8	1.92	1.03	1.86	0.21
6.5	0.162	8.20×10^{-4}	104.2	23.5	1.93	1.01	1.91	0.23
Monolithic capillary column		0.165×10^{-6}	–	97.4	76.9	1.0	76.9	0.043
10	0.005	0.78×10^{-6}	0.06	– ^d	– ^d	– ^d	– ^d	– ^d
30	0.01	3.12×10^{-6}	0.20	– ^d	– ^d	– ^d	– ^d	– ^d
20	0.01	3.12×10^{-6}	0.23	31.5	113.1	102.0	1.10	0.034
10	0.01	3.12×10^{-6}	0.69	45.0	104.7	80.5	1.30	0.035
5	0.01	3.12×10^{-6}	1.51	59.7	98.3	62.0	1.59	0.039
50	0.025	1.95×10^{-5}	5.38	79.8	75.1	29.7	2.50	0.041
15	0.025	1.95×10^{-5}	17.98	82.2	75.4	17.3	4.4	0.042

^a Restrictor permeability $B_o = d_c^2/32$ [22].

^b Parameter Λ according Eq. (1) (see Section 2).

^c Optimal data from corresponding Van Deemter plot.

^d Minimum cannot be observed on Van Deemter plot within the pressure range studied.

2. Experimental

2.1. Preparation of monolithic capillary column

A 45 cm long, 0.10 mm inner diameter quartz capillary was used for the preparation of monolithic capillary column using procedure described elsewhere [20]. Composition of polymerization mixture used for column preparation was 38% (v/v) divinylbenzene, 62% (v/v) porogen (mixture of dodecanol/toluene = 92/8) and 1% (mass) of azo-bis(iso-butyrionitrile) as initiator. Polymerization was carried out at a temperature of 75 °C for 1 h.

2.2. Chromatographic measurements

Experiments with open capillary columns were performed using GC-Chromarograph LKhM-8MD (Moscow, Russia) and a 30 m long, 0.245 mm I.D. open capillary column Zebtron by Phenomenex (USA). The inner surface of capillary was coated with a 0.25 μ m thick liquid film of polydimethylsiloxane SE-30.

All experiments with monolithic capillary column and high pressure separations using the open capillary column were performed on GC-device GC-17A produced by Shimadzu (Japan) and modified for work under high pressure as described by us earlier [21]. Separations were carried out under isothermal conditions (90 °C for open capillary column and 80 °C for monolithic capillary column). Other conditions were: carrier gas helium, temperature of injector 200 °C, FID detection with both devices LKhM-8MD and GC-17A, and solutes *n*-decane (open capillary column) and *n*-butane (monolithic capillary column).

Restrictors were used to achieve increased pressures at column outlet. Characteristics of restrictors are shown in Table 1. Each restrictor was calibrated to read the pressure at the connection point between restrictor and column outlet p_m . Theoretical relationship between the inlet column pressure p_i , the outlet restrictor pressure $p_{o,r}$ and the pressure at the connection point p_m is well known [21]:

$$\Lambda = \frac{S_2 B_{o2} L_1}{S_1 B_{o1} L_2} \quad \text{with} \quad p_m = \sqrt{\frac{p_i^2 + \Lambda p_{o,r}^2}{1 + \Lambda}} \quad (1)$$

where subscripts 1 and 2 relate to the column and to the restrictor, respectively, L is the length of the column and the restrictor, B_o is the permeability of the column and the restrictor, and S is the cross-sectional area of the column and the restrictor available for carrier gas. Λ can be easily calculated for open capillaries accounting for $B_o = d_c^2/32$ [22] and $S = \pi d_c^2/4$ where d_c is the tube diameter. However, for monolithic columns both S and B_o must be measured experimentally. For this reason we have calibrated restrictors according Eq. (1). T-connector was inserted between the column end and the restrictor and the pressure at the connection point was measured using electronic pressure sensor from Bronkhost (Holland). Five to eight experimental points were collected for each restrictor allowing calculation of Λ with an accuracy of not less than 5%. Values of Λ are collected in Table 1.

2.3. Data collection and mathematical treatment

Chromatographic data were collected using chromatographic software Ecochrom, ver. 2 (Boissoft, Russia). Mathematical treatment of the data was performed with software Origin 8 and Maple 12.

3. Results and discussion

Van Deemter relationship in a format presented by Giddings [2] and refined by Cramers et al. [23] can be written for a packed column in gas chromatography as:

$$H = A_j'' + \frac{B_j''}{u_o} + C_{Mj}'' u_o + C_{Sj}'' u_o^2 \quad (2)$$

with A , B , C_M and C_S being constants [22] representing the plate height contribution for the eddy diffusion, for the axial diffusion, for the mobile phase, and for the stationary phase resistance to mass transfer, respectively.

$$A = 2 \Lambda d_p \quad (3)$$

$$B = 2 \gamma D_M \quad (4)$$

$$C_M = \frac{\omega d_p^2}{D_M} \quad (5)$$

$$C_S = qk' \frac{d_f^2}{(k' + 1)^2} D_S \quad (6)$$

where λ , γ , ω and q are the other constants depending on the column quality, the packing structure, the properties of both stationary and mobile phases, etc., d_p is the particle diameter of the packing, d_f is the thickness of stationary liquid-phase layer, D_M and D_S are the solute diffusion coefficients in the mobile and the stationary phases under the column outlet pressure p_o , k' is the solute retention factor.

$$j'' = \frac{9(P^4 - 1)(P^2 - 1)}{8(P^3 - 1)^2} \quad (7)$$

is the correction factor, introduced by Giddings [2];

$$J_2^3 = \frac{3(P^2 - 1)}{2(P^3 - 1)} \quad (8)$$

is the correction factor, introduced by James and Martin [4].

$P = p_i/p_o$ is the relative pressure, u_o is the velocity of the carrier gas at column outlet.

Eq. (2) is also valid for an open capillary column with slightly different values of coefficients described by Golay [22,24]: $\lambda = 0$, $\gamma = 1$, $\omega = (1 + 6k' + 11k'^2)/(24(1 + k')^2)$ and $q = 1/6$.

As mentioned in Section 1, most of the researchers consider relative pressure P as the key parameter affecting column efficiency [2–10]. Therefore, it is reasonable to replace u_o in Eq. (2) with the relative pressure P . Linear velocity of the carrier gas at column outlet relates to the relative pressure through Darcy relationship [22]:

$$\Delta p \frac{P + 1}{2} = \frac{L\eta}{B_o} u_o \quad (9)$$

Substituting u_o from (9) into (2) results in:

$$H = A_1 \frac{(P^4 - 1)(P^2 - 1)}{(P^3 - 1)^2} + B_1 \frac{(P^4 - 1)(P - 1)^2}{(P^3 - 1)^2 \Delta^2} + C_{1M} \frac{(P^4 - 1)(P^2 - 1)^2 \Delta^2}{(P^3 - 1)^2 (P - 1)^2} + C_{1S} \frac{(P^2 - 1)^2 \Delta}{(P^3 - 1)(P - 1)} \quad (10)$$

where

$$A_1 = \frac{9}{4} \lambda d_p \quad (11)$$

$$B_1 = \frac{9L\eta\gamma\Omega}{2B_o} \quad (12)$$

$$C_{1M} = \frac{9B_o\omega d_p^2}{16L\eta\Omega} \quad (13)$$

$$C_{1S} = C_S \frac{3B_o}{4L\eta} \quad (14)$$

and Ω is the constant depending on the temperature, nature of the carrier gas and the solute properties. However, it is independent of column pressure.

Eq. (10) provides a relationship between HETP and relative column pressure and can be used to analyze experimental data. It is worth noting that Eq. (10) in contrast to Eq. (2) contains two independent variables and therefore minimization of HETP values requires not only optimization of the relative pressure P , but also of the pressure drop Δp . However, neither relative pressure, nor pressure drop are directly available for optimization. In contrast, inlet and outlet column pressures are good parameters for optimization of any GC system. Therefore, from practical point of view, it is reasonable to use p_i and p_o as independent variables. Corresponding

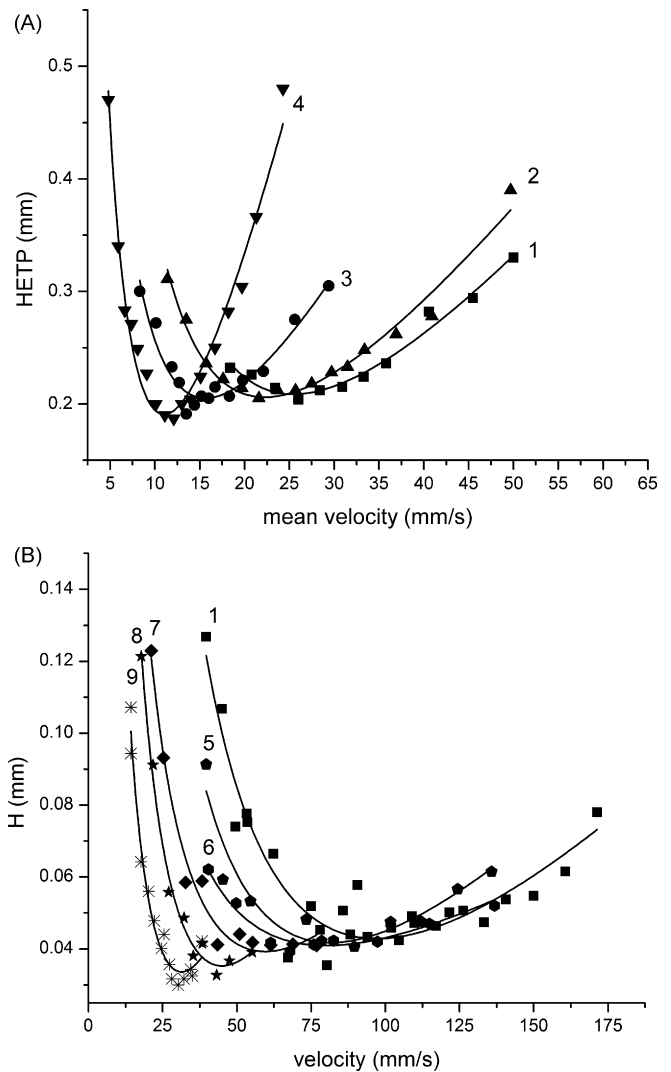


Fig. 1. Van Deemter plots for open (A) and monolithic (B) capillary columns, measured with and without restrictors: 1 (■) without restrictor, 2 (▲) restrictor 10 cm × 0.1 mm, 3 (●) restrictor 6 cm × 0.05 mm, 4 (▼) restrictor 18 cm × 0.05 mm, 5 (●) restrictor 14.8 cm × 0.025 mm, 6 (●) restrictor 50 cm × 0.025 mm, 7 (◆) restrictor 5 cm × 0.01 mm, 8 (★) restrictor 10 cm × 0.01 mm, 9 (★) restrictor 20 cm × 0.01 mm. Column and restrictor properties indicated in Table 1. Carrier gas is helium, temperature is 90 °C (open capillary) and 80 °C (monolithic capillary), solutes are *n*-decane (open capillary) and *n*-butane (monolithic capillary).

form of Eq. (10) is:

$$H = A_1 \frac{(p_i^4 - p_o^4)(p_i^2 - p_o^2)}{(p_i^3 - p_o^3)^2} + B_1 \frac{(p_i^4 - p_o^4)}{(p_i^3 - p_o^3)^2} + C_{1M} \frac{(p_i^4 - p_o^4)(p_i^2 - p_o^2)^2}{(p_i^3 - p_o^3)^2} + C_{1S} \frac{(p_i^2 - p_o^2)^2}{(p_i^3 - p_o^3)} \quad (15)$$

Experimental proof of Eq. (15) was demonstrated with measuring Van Deemter plots for open and monolithic capillary columns (see Sections 2.1 and 2.2) with and without restrictors. Fig. 1A and B show examples of Van Deemter plots measured for open and monolithic capillary columns. The main trends observed from the figures are:

- The higher the restrictor resistivity, the smaller the minimum HETP.

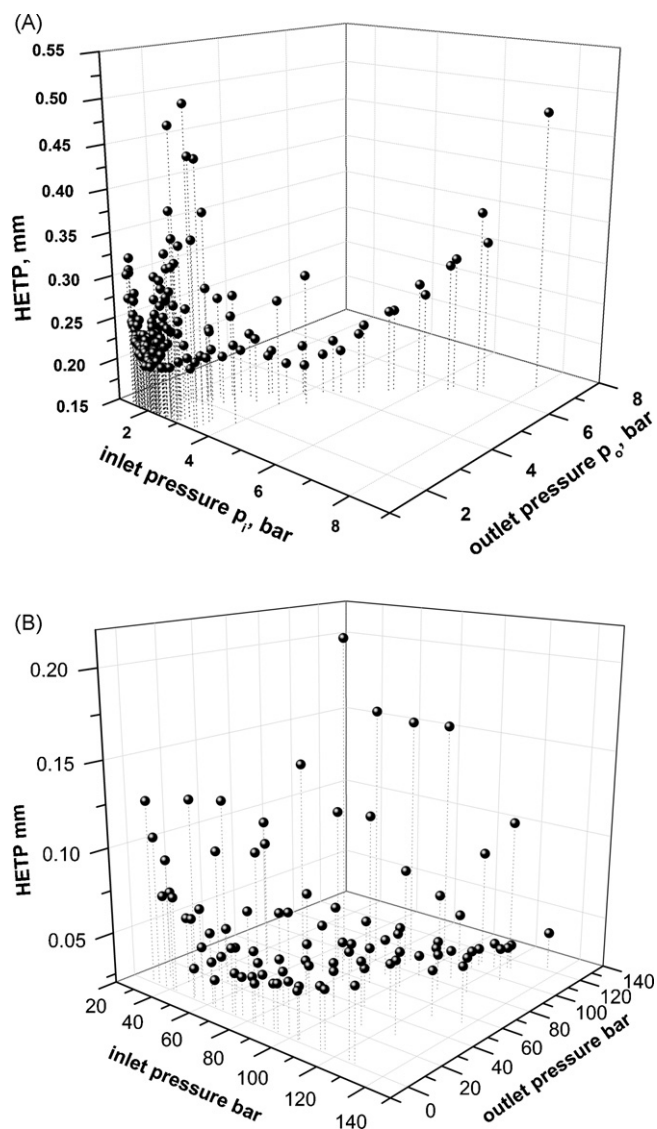


Fig. 2. Experimental data presenting HETP as a function of inlet and outlet column pressures for open (A) and monolithic (B) capillary columns. Measurement conditions as in Fig. 1.

- The higher the restrictor resistivity, the smaller the optimal carrier gas velocity.
- The higher restrictor resistivity, the narrower the Van Deemter plot due to an increase in C -terms (i.e. the sum of $C_M + C_S$).

The last trend is particularly expressed for open capillary columns. For example, C -term for the capillary column having restrictor $18 \text{ cm} \times 0.05 \text{ mm}$ is by factor 3 higher than that for the same column without restrictor.

In spite of the apparent similarity of all measured Van Deemter plots, the plots plotted for systems using restrictors are not identical with conventional ones. Conventional Van Deemter plots are measured under constant outlet pressure, i.e. at 1 bar. The outlet pressure changes with a change of inlet pressure for the column equipped with a restrictor. Relationship between the inlet and outlet column pressures is given by Eq. (1). Therefore, it is more reliable to present experimentally measured HETP values as a function of inlet and outlet column pressures (Fig. 2).

It can be seen from Fig. 2B that data obtained for monolithic capillary column are regularly distributed over the surface $p_i - p_o$ while experimental points for open capillary column are mainly

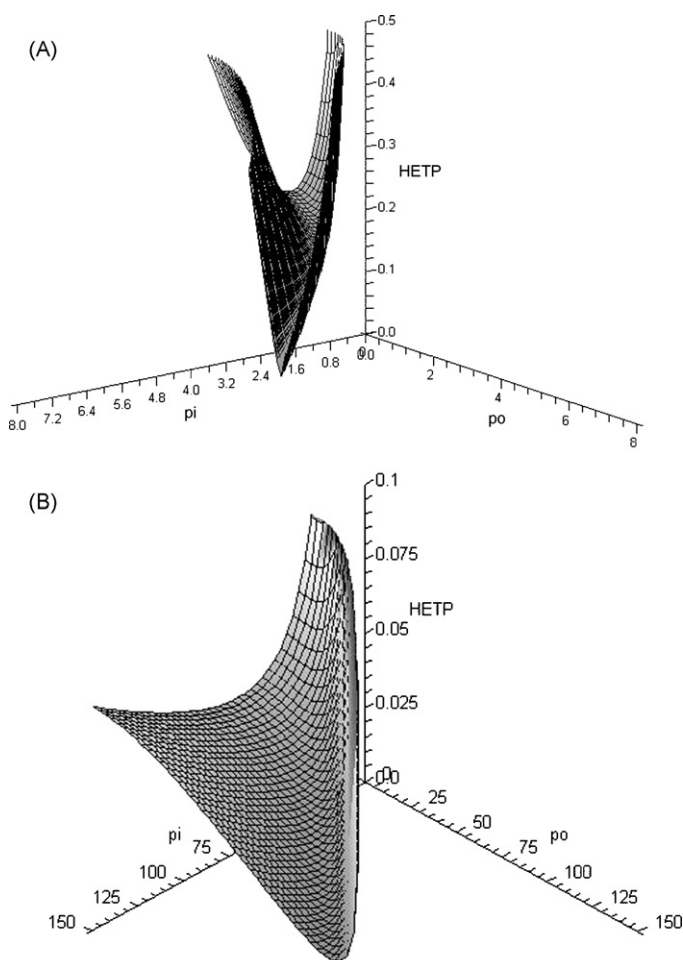


Fig. 3. Fitting experimental points presented in Fig. 2 by relationship (15) evaluating a dependence of HETP on inlet and outlet column pressures for open (A) and monolithic (B) columns.

situated in the range of low inlet column pressures. This is due to the much smaller flow resistance of open tubular column compared to that of monolithic column.

To elucidate the effect of inlet and outlet column pressures on HETP, the experimental points were fitted using Eq. (15). The fitting procedure resulted in creation of corresponding surfaces (Fig. 3A and B) and evaluation of coefficients A_1 , B_1 , C_{1M} and C_{1S} presented in Table 2. Parameter A_1 appears to be close to 0 for both columns, B_1 is for monolithic column larger than for open capillary column, and both C_1 terms are larger for open capillary column. However, an interpretation of these parameters is not as simple as interpretation of their counterparts in classical Van Deemter relationship. B_1 , C_{1M} and C_{1S} terms include column permeability (see Eqs. (12)–(14)). Permeability of open capillary column is by four decimal orders larger than that of its monolithic counterpart. This may be a reason for significant difference between parameter values observed for monolithic and open capillary columns.

The surfaces depicted in Fig. 3A and B look like a bended valley. The smallest HETP values are situated at the bottom of the valleys. However, it is difficult to evaluate changes in minimal HETP values from these plots. They can be observed more distinctly on the projection of the surfaces onto the plane $p_i - p_o$ (Fig. 4).

The projection map for open capillary column is shown in Fig. 4A. The smallest HETP values are located at the right upper corner of the graph where inlet and outlet pressures have their maximal values (Fig. 4A). HETP values in this area are extremely sensitive to variations in p_i and p_o . Even small deviations from the optimal pressure

Table 2
Parameters of Eq. (15) obtained by fitting of experimental points.

Column	A_1 mm	B_1 mm bar ²	C_{1M} mm/bar ²	C_{1S} mm/bar
Monolithic	0.014 ± 0.005	68 ± 4	$(6 \pm 10) \times 10^{-7}$	$(3 \pm 1) \times 10^{-4}$
Open tubular	0.01 ± 0.01	0.33 ± 0.02	0.027 ± 0.002	0.030 ± 0.007

parameters cause significant increase in plate height. For example, HETP of open capillary column is 0.183 mm at $p_i = 9.30$ bar and $p_o = 9.09$ bar and it increases to 0.353 mm, i.e. by factor of 2, when the outlet pressure increases to 9.24 bar, i.e. by 1.6% only.

The projection map for monolithic capillary column (Fig. 4B) demonstrates in general the same features described for open capillary column. The minimal HETP values are observed when the inlet and outlet pressures achieve their maximal values. However the minimal HETPs are less sensitive to small variations in inlet and outlet pressures compared to the open capillary column. Thus e.g., HETP of monolithic column increases by 0.6% (from 0.0344

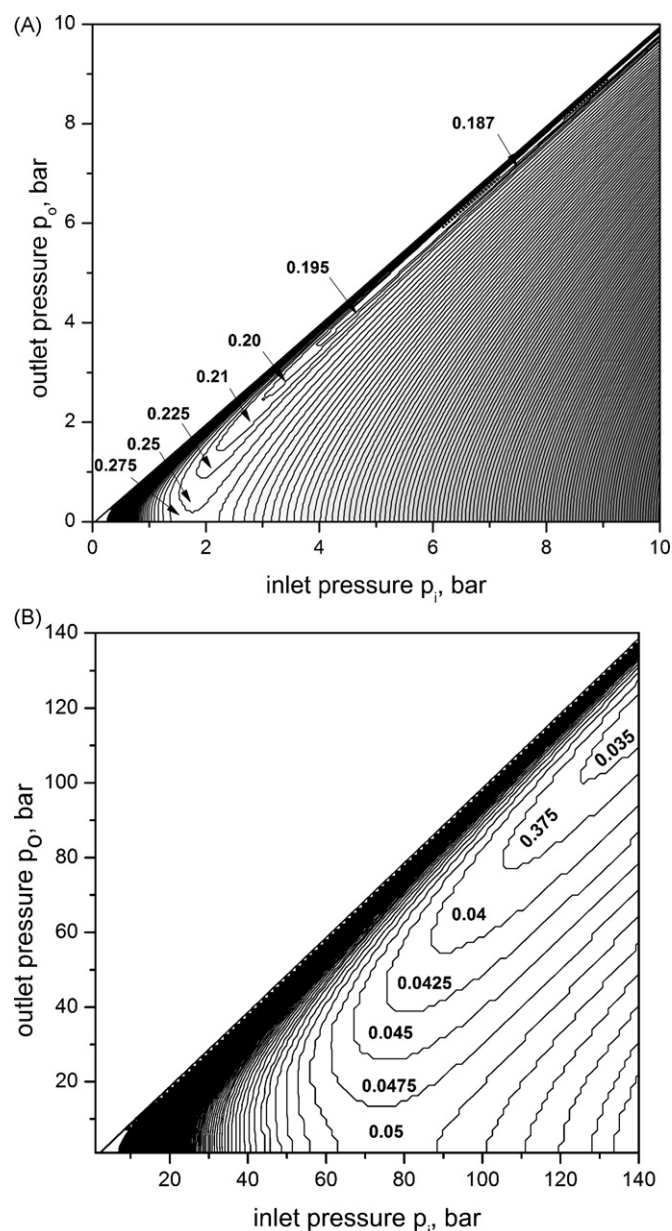


Fig. 4. Map projection of the dependence of HETP on inlet and outlet column pressures (presented in Fig. 3) for open (A) and monolithic (B) capillary columns.

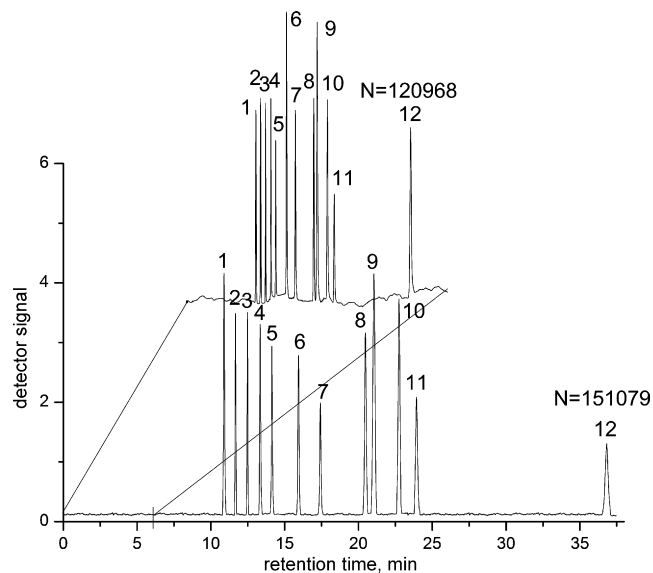


Fig. 5. Separation of hydrocarbons test-mixture on open capillary column. Carrier gas is helium; column temperature is 90 °C; solutes are (1) methane, (2) *n*-pentane, (3) *n*-hexane, (4) benzene, (5) *n*-heptane, (6) toluene, (7) *n*-octane, (9) (*m*+*p*)-xylene, (10) *o*-xylene, (11) *n*-nonane, (12) *n*-decane. Upper chromatogram obtained without restrictor, p_i 1.9 bar, p_o 1 bar, P 1.9, Δ 0.9 bar, u_{opt} 32 cm/s. Low chromatogram obtained with restrictor 14.8 cm \times 0.025 mm, p_i 14.8 bar, p_o 14.6 bar, P 1.01, Δ 0.2 bar, u_{opt} 4.6 cm/s.

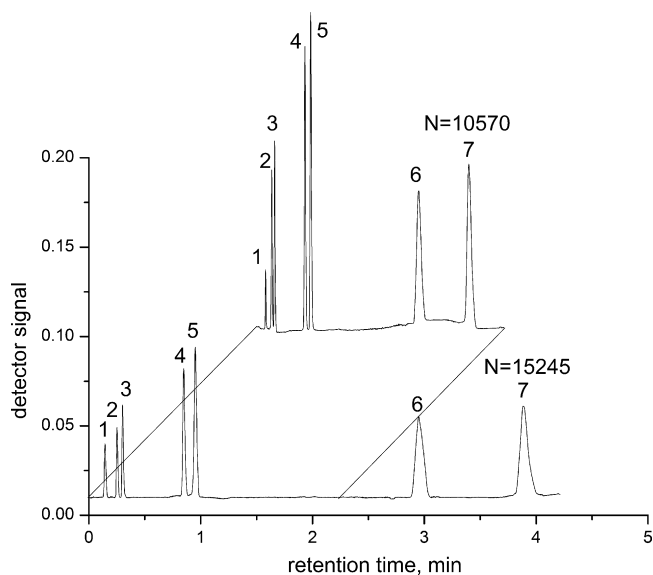


Fig. 6. Separation of light hydrocarbons test-mixture on monolithic capillary column. Carrier gas is helium; column temperature is 80 °C; solutes are: (1) methane, (2) ethene, (3) ethane, (4) propene, (5) propane, (6) 2-methylpropane, (7) *n*-butane. Upper chromatogram obtained without restrictor, p_i 76 bar, p_o 1 bar, P 76, Δ 75 bar, u_{opt} 9.4 cm/s. Low chromatogram obtained with restrictor 10 cm \times 0.01 mm, p_i 127 bar, p_o 103 bar, P 1.38, Δ 24 bar, u_{opt} 5.5 cm/s.

to 0.0346 mm) when outlet pressure increases from 108.9 bar to 111.7 bar (i.e. by 2.5%) keeping inlet pressure constant at 131.5 bar (see Fig. 4B).

It is interesting to compare the minimal HETPs predicted for the same column using both classical Van Deemter relationship and the extended model (Eq. (15)). Projection of conventional Van Deemter plot on plane $p_i - p_o$ is a straight line parallel to abscissa and starting at ordinate $p_o = 1$ bar (Fig. 4). The figure shows that the minimal HETPs acquired using classical Van Deemter plots are ca. 0.25 mm for open capillary column and ca. 0.05 mm for monolithic capillary column. The minimal HETP values predicted from Eq. (15) for the same columns are 0.187 and 0.036 mm correspondingly, i.e. by 30–40% lower.

Figs. 5 and 6 demonstrate experimental proof of the predictions. The upper chromatograms show separations achieved under conditions that are optimal according to conventional Van Deemter approach: the outlet pressure was set to atmospheric and the inlet pressure was adjusted to obtain the optimal flow rate. The chromatograms at the bottom were obtained under inlet and outlet

pressures optimized according to Eq. (15) (Fig. 4). An increase in column efficiency under elevated pressures was observed for both capillary and monolithic columns (Figs. 5 and 6) and the improvement observed coincide fairly well with the prediction of the theoretical model.

Changes in HETP with column pressure are in the literature commonly considered with respect to relative column pressure $P = p_i/p_o$ [2,3,5–10]. However, the same relative pressure P can be obtained using numerous combinations of inlet and outlet pressures. Therefore, one has to be careful using relative pressure P as a parameter affecting column efficiency. According to Eq. (10) relative pressure cannot be a single variable and the pressure drop over the column has to be used as a complementary parameter. The projection maps of the surfaces given by Eq. (10) are shown in Fig. 7A and B. The absolutely minimal HETP values are observed when relative pressure P approaches 1 and pressure drop approaches 0.

Based on data presented in Fig. 4 one can conclude that the highest column efficiency in GC is observed at increased inlet and outlet pressures and the increase must be achieved in such a way that relative column pressure approaches 1 and pressure drop 0. The drawback of this optimization procedure is that the optimal carrier gas velocity decreases at optimal pressure values (see Eq. (9)). Experimental support for this statement can be seen in Figs. 5 and 6. Duration of analysis under increased pressure at column outlet (figures at the bottom) is longer than separation time under atmospheric column outlet pressure (upper figures). This effect is stronger expressed for open capillary column than for monolith, probably, due to the smaller length of the latter. However, one can maintain analysis time shorter by variations in column temperature which has in GC little impact on column efficiency, but strong effect on solute retention.

4. Conclusions

Optimization of separation conditions is an important step in development of any separation method. Classical Van Deemter plot is a common tool used to optimize column performance. However, it does not provide single-valued solution because the same carrier gas velocity can be achieved using numerous combinations of inlet and outlet column pressures. We introduce extended form of Van Deemter relationship which includes inlet and outlet column pressures as independent variables. Graphical presentation of our extended relationship clearly indicates that column efficiency of both open and monolithic columns should significantly increase with an increase in inlet and outlet column pressures. Pressure variation must be performed in such a way that the relative pressure approaches 1 and the column pressure drop approaches 0. Carrier gas velocity under optimal pressure conditions then reduced and results in corresponding increase in the analysis time. This effect is smaller and the gain in efficiency is higher for monolithic columns than for open capillaries. Monolithic columns are operated under increased column pressures and optimization procedure described in this report represents a valuable tool enabling improvements in overall performance of monolithic column.

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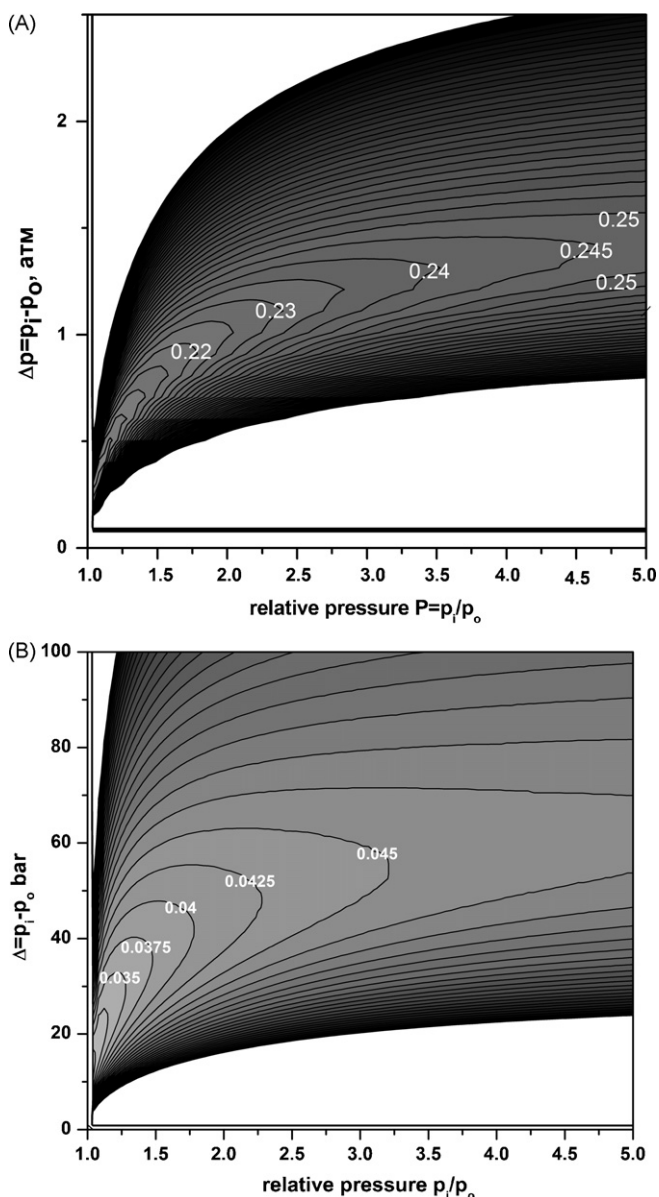


Fig. 7. Map projection of the dependence of HETP on relative pressure P and pressure drop over the column (Eq. (10)) for open (A) and monolithic (B) capillary columns.

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