

Minimum analysis time in capillary gas chromatography. Vacuum- versus atmospheric-outlet column operation

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Minimum Analysis Time in Capillary Gas Chromatography Vacuum- versus Atmospheric-Outlet Column Operation

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Summary

Previous studies on open tubular column operation at vacuum outlet vs. atmospheric outlet pressures focused on comparisons of given columns, or comparisons of columns with the same inner diameters. It was demonstrated that, for a given separation problem, vacuum outlet operation of columns with a constant i.d. always yields the shortest analysis times (under minimum plate height conditions).

In this paper, the comparison of vacuum vs. atmospheric outlet operation is broadened to columns with different dimensions. A general equation for the gain in speed of analysis by vacuum outlet operation of any column, as compared to atmospheric outlet operation of all possible open tubular columns with the same maximum plate number is presented. The resulting equation is further evaluated for thin film columns of different dimensions.

It appears that vacuum outlet operation is beneficial only, in terms of speed of analysis, if low maximum plate numbers are required. The gain in speed of analysis is more pronounced for wide-bore than for narrow-bore columns.

1 Introduction

The advantages of vacuum outlet over atmospheric outlet operation of open tubular columns have been demonstrated [1-5]. The theories presented thus far were limited to comparisons of columns with equal diameter, and to comparisons of thick-film [1] and thin-film [2,3] vacuum outlet with thin-film atmospheric outlet columns.

In this paper a theory is described, predicting instances where the use of (wide-bore) vacuum outlet columns results in shorter analysis times than the application of (narrow-bore) columns at atmospheric outlet pressure. Moreover, a general equation for the gain in speed of analysis by vacuum outlet operation is presented.

2 Theory

Under minimum plate height conditions, the retention time t_R of a solute in an open tubular column is given by [1]:

$$t_R = N(1+k) \left[2 C_m \frac{p_o}{p_a} \frac{f_1}{f_2} + C_s(3 - f_2 P) \right] \quad (1)$$

*Dedicated to Marcel Golay, the inventor of capillary gas chromatography, on the occasion of his 85th birthday.

where N is the maximum attainable plate number, k is the capacity ratio of the solute, p_i and p_o are the column (optimum) inlet and (fixed) outlet pressures, respectively, and P their ratio p_i/p_o , p_a is the atmospheric pressure, C_m and C_s are the non-equilibrium gas and liquid phase terms, respectively, and f_1 and f_2 represent the Giddings and James-Martin pressure drop correction factors:

$$f_1 = \frac{9}{8} \frac{(P^4 - 1)(P^2 - 1)}{(P^3 - 1)^2} \quad \text{with } 1 < f_1 < \frac{9}{8} \quad (2)$$

$$f_2 = \frac{3}{2} \frac{P^2 - 1}{P^3 - 1} \quad \text{with } 1 > f_2 > \frac{3}{2P} \quad (3)$$

Vacuum outlet operation of a given column under minimum plate height conditions always yields the shortest analysis times [1-4]:

$$t_{R,vac} = \frac{3}{2} N(1+k) \left[C_m \frac{p_i}{p_a} + C_s \right] \quad (4)$$

By operating a given column at vacuum outlet, the maximum attainable plate number is decreased. However, the column can be lengthened to compensate for this loss. If the required plate number, N , for a given separation problem is kept constant, the gain G_N in speed of analysis, by using a (longer) column at vacuum outlet, as compared to the same (but shorter) column, operated at atmospheric outlet (all other operational conditions being constant) follows from eqs (1) and (4):

$$G_N = \frac{2 \left[2 C_m \frac{p_o}{p_a} \frac{f_1}{f_2} + C_s(3 - f_2 P) \right]_{atm}}{3 \left[C_m \frac{p_i}{p_a} + C_s \right]_{vac}} \quad (5)$$

Interpretation of this equation is very complicated. Evaluation is possible only in boundary cases. For example for relatively thin film columns ($p_a C_s \ll p_i C_m$).

2.1 Thin-Film Columns

Under minimum plate height conditions, the retention time of a solute in a thin-film open tubular column is given by [1]:

$$t_R = f(k) \frac{f_1 \bar{p}}{p_a D_{m,a}} d_c^2 N \quad (6)$$

where $D_{m,a}$ is the binary solute / carrier gas diffusivity at unit pressure p_a , $\bar{p} = p_o / f_2$ is the average column pressure, and d_c is the inner column diameter. The function of k is:

$$f(k) = \frac{11k^2 + 6k + 1}{48(k + 1)} \quad (7)$$

Vacuum outlet operation of a given thin-film column under minimum plate height conditions yields analysis times [1-4]:

$$t_{R,vac} = 9f(k) \left[\frac{2\eta}{p_a D_{m,a}} \right]^{1/2} d_c N^{3/2} \quad (8)$$

where η is the dynamic viscosity of the carrier gas.

The gain G_L in analysis time by operating a given thin-film column (length L and d_c constant) at vacuum outlet instead of atmospheric outlet follows from eqs (6) and (8):

$$G_L = \frac{t_{R,atm}}{t_{R,vac}} = \frac{d_c \bar{p}_{atm}}{8(2\eta p_a D_{m,a} N_{vac})^{1/2}} \quad (9)$$

where use was made of the relation $(N f_1)_{atm} = 9/8 N_{vac}$, as reported by C. A. Cramers *et al.* [3].

Eq. (9) shows that the gain is proportional to the column diameter and inversely proportional to the square root of the plate number. Therefore, vacuum outlet operation is particularly beneficial for short and wide-bore columns [1-2].

At the same time, however, both eqs (6) and (8) indicate that retention times decrease with smaller column diameters. The question arises when (wide-bore) vacuum-outlet columns are faster than (narrow-bore) columns operated at atmospheric outlet, while keeping N and k constant.

3 Results and Discussion

Using eqs (18) and (29) from Cramers *et al.* [1], eq. (9) can be elaborated to yield:

$$G_L = \frac{(A + 1)^{3/2} - 1}{A^{3/2}} \text{ with } A = \left[\frac{12}{d_c} \right]^2 \frac{2\eta D_{m,a} N_{vac}}{p_a} \quad (10)$$

Plots of G_L as function of N and d_c are given in **Figures 1** and **2** for different carrier gases.

G_N , the gain in analysis speed when keeping N constant under vacuum and atmospheric outlet conditions, is smaller than G_L . Under minimum plate height conditions G_N is maximum $(9/8)^{3/2}$ or 16.2% smaller than G_L , depending on the pressure drops [1]. Minimum time operation of the columns at gas velocities beyond the minimum plate height

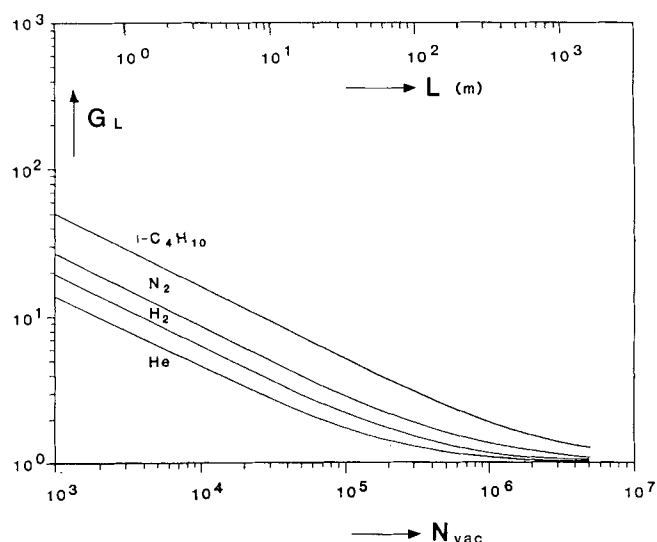


Figure 1

Gain in speed of analysis by operating given thin-film columns at vacuum outlet as compared to atmospheric outlet, as a function of the required plate number for four carrier gases. (Minimum plate height conditions; $d_c = 0.4$ mm, $n\text{-C}_{12}\text{H}_{26}$ at 400 K. The length axis is valid for $k = 2$.)

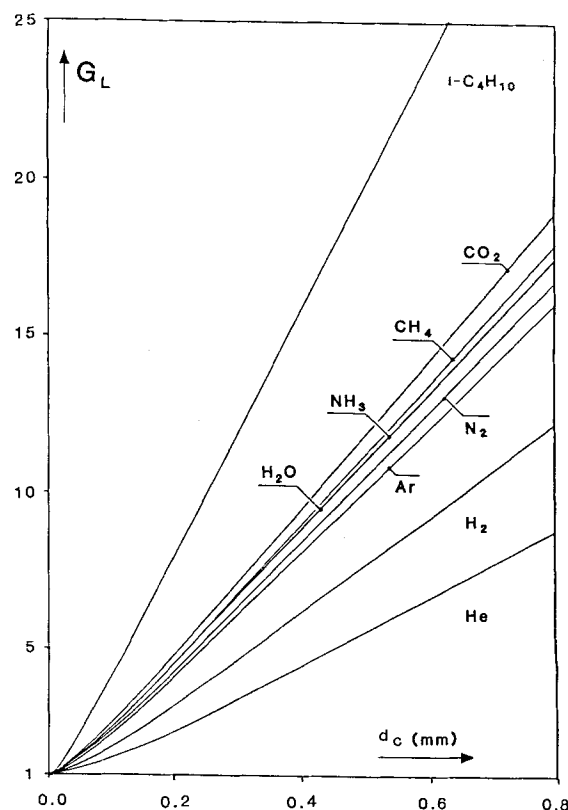


Figure 2

Gain in speed of analysis by vacuum outlet operation of a given thin-film column as compared to atmospheric outlet operation, as a function of the inner column diameter, for different carrier gases. ($N_{max} = 10^4$, other conditions as in Figure 1.)

velocity decreases G_L by a factor of 0.58 at most [5]. Overall, however, for columns with a given diameter, vacuum outlet operation always generates the highest number of plates per time unit, except for very high plate number columns, when G_N approaches unity (see Figure 1).

When comparing (thin-film) columns with different diameters for a given separation problem ($N_{\text{required}} = N_{\text{atm}} = N_{\text{vac}}$), the capacity ratio, k , is kept constant, i.e. the phase ratio of the columns and the separation temperature should be constant. Under these conditions, vacuum outlet is faster than atmospheric outlet operation whenever $t_{R,\text{atm}} > t_{R,\text{vac}}$ or, using eqs (6) and (8), whenever:

$$(f_1 \bar{p} d_c^2)_{\text{atm}} > 9 (2 \eta p_a D_{m,a} N)^{1/2} d_{c,\text{vac}} \quad (11)$$

under minimum plate height conditions.

This inequality was evaluated for SE-30 columns with a phase ratio of 250, "operated" at 400 K and atmospheric outlet pressure with hydrogen carrier gas ($\eta = 10.8 \mu\text{Pa}\cdot\text{s}$). Minimum plate height conditions were computed [4] for *n*-dodecane as the solute with $k = 2$. The diffusion coefficients in the gas and liquid phases were $D_{m,a} = 30.8 \text{ mm}^2/\text{s}$ and $D_s = 0.6 \times 10^{-3} \text{ mm}^2/\text{s}$, respectively. For N and $d_{c,\text{vac}}$ given, the column length and diameter, $d_{c,\text{atm}}$, were adapted iteratively until condition (11) was met.

The results are condensed in **Table 1** and **Figures 3** and **4**. The curves represent column diameters which yield equal analysis times at vacuum and atmospheric outlet pressures. The area to the right of the curves represents instances where vacuum outlet operation is faster. Likewise, atmospheric outlet columns with a diameter smaller than tabulated are faster than the corresponding vacuum outlet columns.

Table 1

Columns with equal speed of analysis^a.

N	t_R (s)	Vacuum outlet		Atmospheric outlet		$\bar{p}\cdot f_1$ (kPa)
		d_c (μm)	L (m)	d_c (μm)	L (m)	
10^4	1.1	100	0.88	75	0.58	135
10^5	32.5	100	8.4	99	7.9	246
10^6	957	100	82.4	100	81.7	740
10^4	3.2	300	2.95	140	1.07	111
10^5	98.5	300	26.1	225	17.5	139
10^6	2981	300	251	290	231	263
10^4	5.2	500	4.3	185	1.4	107
10^5	163	500	45.5	310	23.7	122
10^6	5060	500	424	451	350	182

^a All data for minimum plate height conditions; *n*-C₁₂H₂₆ at 400 K and $k = 2$; hydrogen carrier gas.

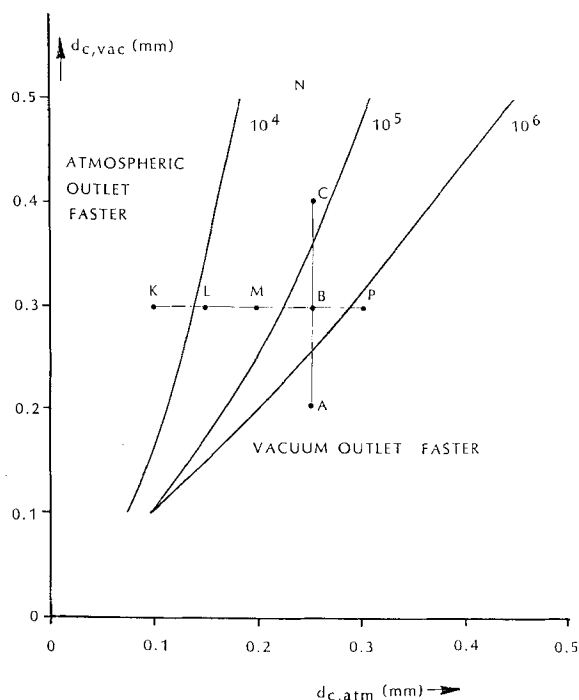


Figure 3

Diameters of thin-film vacuum outlet columns that give the same separation speed as atmospheric outlet columns as a function of the diameter of the latter, for various plate numbers. (Minimum plate height conditions; phase ratio 250; hydrogen carrier gas; *n*-C₁₂H₂₆ at 400 K and $k = 2$.)

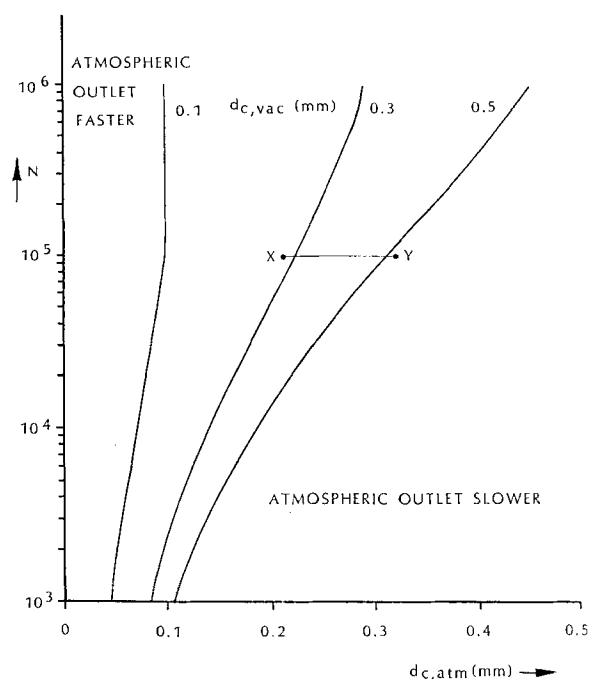


Figure 4

Plate numbers of columns which give equal speed of analysis in both vacuum or atmospheric outlet mode, as a function of the diameter of the atmospheric outlet column, for various vacuum outlet column diameters. (Conditions as in Fig. 3).

A first inspection of Table 1 and Figures 3 and 4 shows that the difference between vacuum and atmospheric outlet operation decreases with increasing plate numbers. This trivial effect is more pronounced for narrow-bore columns: the curve corresponding to $N = 10^6$ in Figure 3 coincides with the bisector of the axes for column diameters up to about 0.2 mm, and the $d_{c,vac} = 0.1$ mm curve in Figure 4 approaches the asymptotic value of $d_{c,atm} = 0.1$ mm already at a plate number of about 10^5 . Similar conclusions can be drawn from Table 1.

Further interpretation of the figures is best explained with the aid of some examples. Consider line A-C in Figure 3, which represents 0.25 mm i.d. columns operated at atmospheric outlet pressure. Comparison of these columns with vacuum outlet columns shows that the latter are faster if $d_{c,vac} < 0.3$ mm for $N = 10^5$ (point B) and < 0.2 mm for $N = 10^6$ (point A). On the other hand, atmospheric outlet operation is faster than vacuum outlet if $d_{c,vac} > 0.4$ mm for $N = 10^5$ (point C) and > 0.3 mm for $N = 10^6$ (point B).

Compare 0.3 mm i.d. vacuum outlet columns (line K-P in Figure 3) with atmospheric outlet columns. Atmospheric outlet columns are slower, if $d_{c,atm} > 0.15$ (L), 0.25 (B) and 0.30 mm (P), for 10^4 , 10^5 and 10^6 plates, respectively.

However, atmospheric outlet operation is faster whenever $d_{c,atm} < 0.10$ (K), 0.20 (M) and 0.25 mm (B) for $N = 10^4$, 10^5 and 10^6 , respectively.

Compare columns with 10^5 plates (line X-Y in Figure 4). A 0.32 mm i.d. column, operated at atmospheric outlet pressure (point Y), is slower than vacuum outlet columns with an i.d. of less than 0.5 mm. But a 0.21 mm i.d. column at atmospheric outlet pressure (point X) is faster than vacuum outlet columns wider than 0.3 mm.

4 Conclusion

In this paper wall-coated open tubular columns with different dimensions, but with constant maximum plate numbers, are compared.

Vacuum-outlet columns always yield analysis times shorter than atmospheric-outlet columns, as long as the inner diameter of the former is smaller than, or equal to, that of the latter. The gain in speed of analysis by vacuum-outlet operation is reduced by decreasing column diameters and increasing maximum plate numbers. For example, for columns with 10^5 plates the gain becomes negligible for column diameters smaller than 0.1 mm.

Vacuum-outlet operation of columns with a diameter larger than atmospheric-outlet columns can still be beneficial, but only for wide-bore columns with relatively low maximum plate numbers. In these instances, the gain in analysis times is only marginal, all the more so because low-pressure-drop (atmospheric-outlet) columns can be operated advantageously at gas velocities beyond the optimum ones, while vacuum-outlet columns require optimal velocity tuning [5].

The application of high maximum-plate-number (long narrow-bore) columns at vacuum outlet does not increase the attainable speed of analysis, and is advantageous only if secondary factors are important. Apart from trivial advantages as in combined gas chromatography mass spectrometry (GC/MS) [1,3], these factors might aim at the reduction of effective detector dead volumes (hot wire, electron capture [6], and light pipes for Fourier transform infrared spectrometry).

Obviously, the choice between application of wide-bore or narrow-bore columns can also be governed by considerations other than striving for minimum time operation. *E.g.*, large column working ranges, and detectability of low minimum analyte concentrations, require the use of wide-bore columns [7]. However, narrow-bore thin-film columns are recommended whenever detectable amounts have to be minimized [7].

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