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MODEL DESCRIBING THE ROLE OF THE PRESSURE GRADIENT ON EFFICIENCY AND SPEED OF ANALYSIS IN CAPILLARY GAS CHROMATOGRAPHY

C. P. M. SCHUTJES*, P. A. LECLERCQ, J. A. RIJKS and C. A. CRAMERS

Eindhoven University of Technology, Laboratory of Instrumental Analysis, P.O. Box 513, 5600 MB Eindhoven (The Netherlands)

and

C. VIDAL-MADJAR and G. GUIOCHON

Ecole Polytechnique, Laboratoire de Chimie Analytique Physique, Route de Saclay, 91128 Palaiseau Cedex (France)

SUMMARY

Neglecting the term describing resistance to mass transfer in the stationary phase, the Golay plate height equation is rearranged in terms of the dimensionless parameters $\xi = H/H_{min}$ and $v = \bar{u}/\bar{u}_{opt}$. In the resulting model, two boundary cases can be distinguished: $P \approx 1$ and $P \gg 1$, P being the ratio of column inlet to column outlet pressure. The two expressions provide a clear insight in the increase in plate height which results from the use of average linear carrier gas velocities other than $\bar{u}_{opt}$. Hence the model is very helpful for optimization of the speed of analysis.

The validity of both boundary expressions was checked by comparing them with experimental plate height data. The data under conditions of $P \gg 1$ were obtained on a 60 m × 0.4 mm I.D. capillary column directly coupled to the ion source of a mass spectrometer, and on a 10 m × 55 μm I.D. capillary column operated at increased inlet pressure, using atmospheric outlet pressure. A 30 m × 0.4 mm I.D. column was tested using a flame ionization detector, with $P \approx 1$.

Excellent agreement was observed between the theoretical prediction and the experimental results.

INTRODUCTION

The speed of analysis in capillary gas chromatography can be considerably increased, without loss of resolution, by operating a standard capillary column of *ca.* 0.3 mm I.D. at vacuum outlet pressure[1] or by reducing the column inner diameter[2]. In recent publications[3–8] the practicality of these approaches, when using readily available modern equipment, has been convincingly demonstrated. Theoretical models were also presented, showing the increase in analysis speed obtained to be strongly dependent on the inlet-to-outlet-pressure ratio of the columns studied[6,7]. In these theories the carrier gas velocity was assumed to be set at $\bar{u}_{opt}$, for which the

column plate height is at a minimum value H_{min}. With standard capillary columns, however, carrier gas velocities larger than $\bar{u}_{opt}$ are required to attain the minimum analysis time[9,10]. An extension of the theoretical models therefore seems appropriate.

In this paper, the optimization of the carrier gas velocity is discussed using dimensionless quantities. Columns operated with small and with very large pressure gradients are treated.

THEORETICAL

Ettre and March[9] derived eqn. 1 for the analysis time, t_R, of a two-component mixture:

$$t_R = 16 \, R^2 \left(\frac{\alpha}{\alpha - 1} \right)^2 \frac{(k + 1)^3}{k^2} \frac{H}{\bar{u}} \tag{1}$$

where R is the resolution of both compounds, α is their relative retention, k is the capacity ratio of the last eluting compound, H is the column plate height and $\bar{u}$ is the average linear carrier gas velocity. The analysis time is seen to depend strongly on R. If rapid analysis is important, unnecessarily large values of R should neither be demanded nor accepted. In addition, the ratio of $H/\bar{u}$ should be minimized.

The plate height of a capillary column is a function of the carrier gas velocity, as given by the Golay equation[11]:

$$H = \left[\frac{B}{u_o} + C_g u_o \right] f_1 + C_s f_2 u_o \tag{2}$$

where B is a term describing longitudinal diffusion, C_g and C_s account for the resistance to mass transfer occurring in the gaseous phase and in the stationary phase, respectively, u_0 is the carrier gas velocity at the column outlet, and f_1 and f_2 are pressure correction factors:

$$f_1 = \frac{9}{8} \frac{(P^4 - 1)(P^2 - 1)}{(P^3 - 1)^2} \tag{3}$$

$$f_2 = \frac{3}{2} \frac{P^2 - 1}{P^3 - 1} \tag{4}$$

$$P = p_i/p_o \tag{5}$$

where p_i and p_o are the column inlet and outlet pressures.

For columns operated with a small pressure gradient, the values of P, f_1 and f_2 are all *ca.* 1. When the pressure gradient is large, then $P \gg 1$. The factor f_1 now approaches its maximum value of 9/8, and f_2 is decreased inversely proportional to P:

$$f_2 \approx \frac{3}{2P} \qquad \text{when } P \gg 1 \tag{6}$$

The average carrier gas velocity and the column outlet velocity are related by[12]:

$$u_o = \bar{u}/f_2 \tag{7}$$

The value of u_o can also be calculated from Poiseuille's law:

$$u_o = \frac{d_c^2 p_o}{64 \eta L} (P^2 - 1) \tag{8}$$

where d_c is the column inner diameter, L is the column length and η is the dynamic viscosity of the carrier gas.

The contribution of the C_s term to the column plate height is usually less than 5%. In the following discussion this term is therefore neglected, so:

$$H = \left[\frac{B}{u_o} + C_s u_o \right] f_1 \tag{9}$$

Differentiation of this equation yields:

$$H_{min} = 2 f_1 (BC_s)^{\frac{1}{2}} \tag{10}$$

$$u_{o,opt} = (B/C_s)^{\frac{1}{2}} \tag{11}$$

$$B = \frac{H_{min} u_{o,opt}}{2 f_1} \tag{12}$$

$$C_s = \frac{H_{min}}{2 f_1 u_{o,opt}} \tag{13}$$

Combination of eqns. 9, 12 and 13 yields:

$$\frac{H}{H_{min}} = \frac{1}{2} \left[\frac{u_{o,opt}}{u_o} + \frac{u_o}{u_{o,opt}} \right] \tag{14}$$

If the parameters $\xi = H/H_{min}$ and $v = \bar{u}/\bar{u}_{opt}$ are defined, the plate height equation can be rewritten in a dimensionless form.

Using eqn. 7, it is found that:

$$\xi = \frac{1}{2} \left[\frac{f_2}{f_{2,opt}} \frac{1}{v} + \frac{f_{2,opt}}{f_2} v \right] \tag{15}$$

The value of $f_2/f_{2,opt}$ is determined by the column pressure gradient. Two boundary cases can be distinguished. Firstly, when $P \approx 1$: then f_2 and $f_{2,opt}$ are also approxi-

mately equal to 1. Secondly, when $P \gg 1$, then according to eqns. 6, 7 and 8, $f_2/f_{2,\mathrm{opt}}$ = $\bar{u}_{\mathrm{opt}}/\bar{u}$.
Consequently:

$$\xi = \frac{1}{2}\left[v + \frac{1}{v}\right] \text{ when } P \approx 1 \tag{16}$$

$$\xi = \frac{1}{2}\left[v^2 + \frac{1}{v^2}\right] \text{ when } P \gg 1 \tag{17}$$

It should be noted that these equations are valid for any carrier gas.

The ξ *versus* v curves described by eqns. 16 and 17 are illustrated in Fig. 1. A flat curve is predicted for columns operated with a small pressure gradient, as normally used in routine gas chromatography. Deviations of up to 20% relative to $\bar{u}_{\mathrm{opt}}$ affect the column plate height only to a negligible extent. From $v = 1$, the value of $H/H_{\min}$ increases slowly with $\bar{u}/\bar{u}_{\mathrm{opt}}$. When $v = 2$, $\xi = 1.25$. Thus, the plate height is increased by only 25% when the average carrier gas velocity is twice the optimum value. Consequently, when $P \approx 1$, the analysis time can be substantially decreased and a constant resolution maintained by increasing the carrier gas velocity above $\bar{u}_{\mathrm{opt}}$ while compensating for the loss of plates by increasing the column length proportionally to H. For values of v greater than 3, the ratio ξ/v approaches a constant value. Doubling of the carrier gas velocity thus results in a doubling of the plate height. The retention time then cannot be decreased further without loss of resolution.

For columns with a large pressure gradient, $P \gg 1$, $H/H_{\min}$ is predicted to vary approximately with the second power of $\bar{u}/\bar{u}_{\mathrm{opt}}$. The plate height is then raised by 25% when the value of v is increased from 1.00 to 1.41. The value of ξ is already doubled when v is increased to 1.93. Hence, columns for which $P \gg 1$ should always be operated at a carrier gas velocity close to $\bar{u}_{\mathrm{opt}}$. These columns require an accurate adjustment of the average carrier gas velocity. This is especially important when a temperature-programmed separation is to be performed, since $\bar{u}$ is then subjected to a gradual change during the analysis.
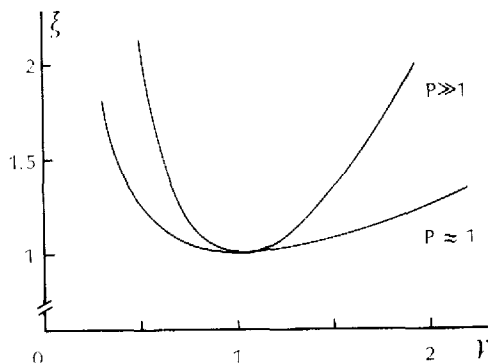

Fig. 1. Theoretical curves of $\xi = H/H_{\min}$ as a function of $v = \bar{u}/\bar{u}_{\mathrm{opt}}$ for capillary columns operated with a small ($P \approx 1$) and a large ($P \gg 1$) pressure gradient.

EXPERIMENTAL

The validity of eqns. 16 and 17 was verified using accurately measured $H = f(\bar{u})$ data which was not biased by extra-column peak broadening effects. All these data, together with the experimental conditions, have recently been published[5,7,8,13]. The data under conditions of $P \approx 1$ were obtained on a 30 m × 0.4 mm I.D. SE-30 column operated at atmospheric outlet pressure[7]. Inlet pressures of $p_{i,opt} = 1.49$ bar (abs) and 1.25 bar (abs) were observed when the column was operated at the optimum carrier gas velocity with helium and nitrogen, respectively.

The data under conditions of $P \gg 1$ were taken from vacuum outlet studies[7,8] on a 60 m × 0.4 mm I.D. column ($p_{i,opt} = 1.55$ bar with helium and 0.80 bar with nitrogen) and from plate height studies on a 10 m × 55.4 μm I.D. capillary column ($p_{i,opt} = 11.1$ bar with helium)[5].

Data obtained on a 24.7 m × 0.31 mm I.D. thick film column ($d_f = 2.0$ μm)[13], operated at atmospheric outlet pressure, with $p_{i,opt} = 1.53$ bar (abs) for helium and 1.20 bar for nitrogen, was used to study the effect of the C_s term.

RESULTS AND DISCUSSION

ξ versus v curves derived from data measured by Cramers et al.[7] and Leclercq et al.[8] for vacuum outlet gas chromatography are illustrated in Fig. 2. The vacuum outlet data were obtained at $P > 100$ and agreed well with the theoretical curve. The ξ values observed with atmospheric outlet pressure ($P \approx 1$) were slightly above the ξ values predicted by theory when v exceeded a value of 2. In this case column inlet pressures exceeding 2 bar (abs) were required, causing P to deviate significantly from 1.

A ξ versus v curve measured for n-dodecane ($k = 4$) on a 10 m × 55.4 μm I.D. fused-silica crosslinked OV-1 column[5], at atmospheric outlet pressure, is illustrated in Fig. 3. The sample was applied to the column with a "fluidic logic" injector[3,5], giving sample bands of 5-msec standard deviation. Column inlet pressures between 6 and 20 bar were employed, so the column was operated with a large
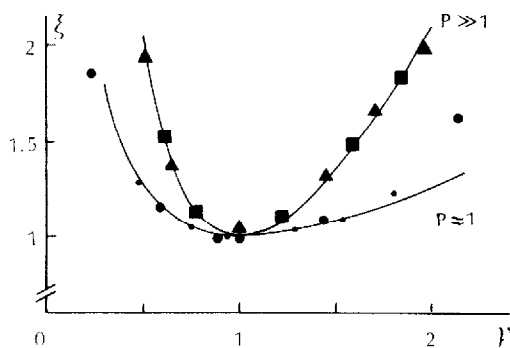

Fig. 2. ξ versus v curves measured for n-dodecane ($k = 2$) on a 30 m × 0.4 mm I.D. capillary column (●, ●) operated at atmospheric outlet pressure ($P \approx 1$) and on a 60 m × 0.4 mm I.D. column (▲, ■) operated at vacuum outlet pressure ($P \gg 1$). Carrier gases: ● and ■, nitrogen; ● and ▲, helium. The solid lines are theoretically predicted curves.
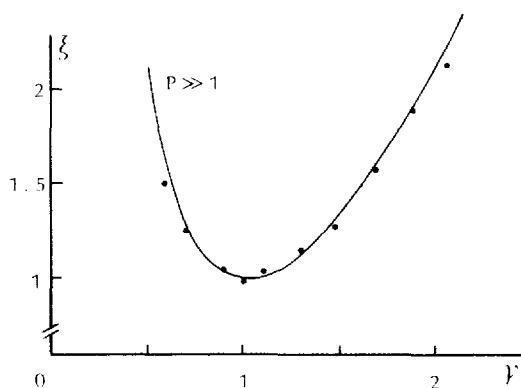
Fig. 3. ξ *versus* v curve measured for n-dodecane ($k = 4$) on a 10 m × 55.4 μm I.D. fused-silica column, with helium as the carrier gas. Column outlet pressure, 1 bar. The solid line is the theoretical curve for $P \gg 1$.

pressure gradient. The data obtained agreed very well with the curve predicted for $P \gg 1$.

These observations strongly support the validity of eqns. 16 and 17. To maximize the speed of analysis, columns with a small pressure gradient must be operated at a much higher value of $\bar{u}/\bar{u}_{opt}$ than columns with a large pressure gradient. Consequently, the effects of vacuum outlet operation and of a decreased column inner diameter on the speed of analysis will be over-estimated when a comparison with conventional chromatographic columns is made at carrier gas velocities equal to $\bar{u}_{opt}$.

Eqn. 1 indicates that $H/\bar{u}$, and hence ξ/v, must be minimized to obtain the lowest possible analysis time. For a given column, eqn. 1 shows that in this case $(H/\bar{u})_{min}$ is constant. Consequently, the value of $\bar{u}$ (or v) giving the optimum speed of analysis for a column can be easily obtained, by drawing a tangent to the experimentally measured H-$\bar{u}$ curve (or the ξ *vs.* curve) which also passes through the origin. The value of the (ξ/v) minimum can be calculated by rewriting eqn. 16 or 17, followed by differentiation, yielding:

$$(\xi/v)_{min} = 0.865 \text{ for } P \gg 1 \text{ and } v = \sqrt[3]{3} \tag{18}$$

$$(\xi/v)_{min} = 0.5 \text{ for } P \approx 1 \text{ and } v \rightarrow \infty \tag{19}$$

In practice, (ξ/v) is already very close to 0.5 at $v \geqslant 3$. Moreover, (ξ/v) will never be situated at "inifinite" values of v, since GC columns operated at very large carrier gas velocities necessarily will have a large pressure gradient. Usually, $(\xi/v)_{min}$ is attained at $v < 5$.

Let A_{opt} be the ratio of the retention times observed for two columns with a small and a large pressure gradient, respectively, both operated at their $\bar{u}_{opt}$ values. Using eqn. 1, the ratio of the retention times at the carrier gas velocities corresponding to $(\xi/v)_{min}$ can now be calculated:

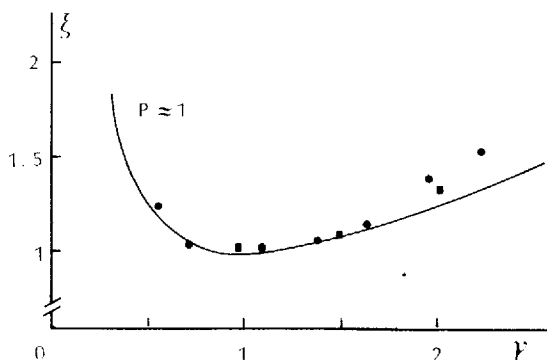$$\frac{t_{R,2}}{t_{R,1}} = A_{opt} \frac{(\xi/v)_{min,1}}{(\xi/v)_{min,2}} \tag{20}$$

Fig. 4. ξ versus ν curve measured for n-dodecane ($k = 6$) on a 24.7 m × 0.31 mm I.D. fused-silica thick film column ($d_f = 2.0$ μm). Carrier gases: ■, nitrogen; ●, helium. Column outlet pressure, 1 bar. The solid line is the theoretical curve for $P \approx 1$.

Now suppose that P approaches 1 for the column with the small pressure drop and that $P \gg 1$ for the column with the large pressure drop. Then:

$$\frac{t_{R,1}}{t_{R,2}} = A_{opt} \frac{0.50}{0.865} = 0.58 \, A_{opt} \tag{21}$$

In the most unfavourable situation ($P \approx 1$ *versus* $P \gg 1$), the true difference in the speed of analysis of the two columns thus is only 58% of the value found when both columns are compared at carrier gas velocities equal to $\bar{u}_{opt}$. The factor of 0.58, for instance, has to be applied when the effect of vacuum outlet operation on the analysis time is calculated according to ref. 7.

Eqns. 16 and 17 were derived assuming that the contribution of the C_s term to the plate height can be neglected. When this is not allowed, the equations describing the relationship between the reduced plate height and the reduced carrier gas velocity become complicated. The influence of the C_s term was therefore only studied experimentally, using data obtained for a 25 m × 0.31 mm I.D. thick film ($d_f = 2.0$ μm) column[13]. The ξ versus ν curve is illustrated in Fig. 4. A very good agreement with the theoretical curve for $P \approx 1$ is observed. The film thickness apparently has no influence on the $\xi = f(\nu)$ relationship, even though the value of $\bar{u}_{opt}$ itself is affected.

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