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## INCREASED SPEED OF ANALYSIS IN DIRECTLY COUPLED GAS CHROMATOGRAPHY-MASS SPECTROMETRY SYSTEMS

### II. ADVANTAGES OF VACUUM OUTLET OPERATION OF THICK-FILM CAPILLARY COLUMNS

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#### SUMMARY

It is shown that direct insertion of the end of a capillary column into the ion source of a mass spectrometer increases the speed of analysis compared with atmospheric outlet conditions. This applies to thin-film columns, as reported previously [C. A. Cramers, G. J. Scherpenzeel and P. A. Leclercq, *J. Chromatogr.*, 203 (1981) 207], as well as to the thick-film capillaries treated in this paper.

For thick-film columns the negative effect of diffusion in the stationary liquid phase on the speed of analysis, via an increased minimal plate height and a decreased optimal gas velocity, is more than compensated for by the effects of vacuum outlet operation.

The gas chromatographic-mass spectrometric (GC-MS) coupling of capillary columns directly inserted into the ion source possesses the favourable properties of full sample transfer, no catalysis or adsorption in an interface and increased speed of analysis. Thick-film columns offer in addition a considerably increased sample capacity. The resolution of low-boiling compounds is enhanced and adsorption on the column wall is masked by the thicker film.

Further, thick-film columns are less demanding with respect to instrument specifications such as speed of sampling, time constants and noise levels of detection and registration systems. The conclusion is that the best GC-MS interface appears to be no interface at all but rather direct insertion of the column end into the ion source.

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#### INTRODUCTION

Operation of *thin-film* wall-coated open-tubular (WCOT) columns under vacuum outlet conditions has many advantages over normal operation at atmospheric outlet pressure. One advantage is an increase in speed of analysis. The reduction in analysis time was shown to increase strongly with lower (sub-atmospheric) optimal inlet pressures without a significant decrease in column efficiency<sup>1</sup>. This effect of vacuum outlet operation has been shown theoretically and verified experimentally

for WCOT columns where the resistance towards mass transfer in the stationary liquid phase is negligible compared with that in the mobile phase, *i.e.*, for capillaries with relatively thin liquid films<sup>1</sup>.

*Thick-film* WCOT columns have higher sample capacities, show less adsorption and facilitate injection. However, the analysis time required for a given separation problem is much longer than that with a thin-film column. This is true even when the capacity ratios are kept constant, implying that the thick-film column must be operated at a 20–30°K higher temperature. The reasons are the increase in the minimal plate height and the decrease in the optimal gas velocity owing to the influence of mass transfer in the liquid phase. These drawbacks often preclude the practical use of thick-film columns.

The increase in speed of analysis obtained with thin-film columns under vacuum outlet conditions led us to investigate the properties of thick-film capillaries under similar conditions. A theoretical treatment of the optimal gas chromatographic conditions for thick-film columns is very complicated. A direct comparison of vacuum vs. atmospheric outlet pressure operation of these columns is difficult. In this paper, vacuum outlet operation of thick-film columns is compared with atmospheric outlet pressure operation of thin-film columns.

#### THEORETICAL

Band broadening in capillary columns is satisfactorily described by the Golay equation as extended to situations of appreciable pressure drop by Giddings and co-workers<sup>2–5</sup>. Taking into account the decompression effect as described by these workers, the measured or apparent plate height equation for a capillary with uniformly distributed liquid film is

$$H = \left[ \frac{B_o}{v_o} + C_{m,o} v_o \right] f_1 + C_s v_o f_2 \quad (1)$$

This equation describes the effect of pressure gradient on the observed plate height,  $H$ . Defining  $P = P_i/P_o$  as the ratio of inlet to outlet pressures, the following symbols are used in eqn. 1:

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

(Giddings correction factor), where  $f_1 = 1$  for  $P = 1$  and  $f_1 = 9/8$  for  $P \rightarrow \infty$ , and

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

(Martin–James correction factor), where  $f_2 = 1$  for  $P = 1$  and  $f_2 = 3/(2P)$  for  $P \rightarrow \infty$ .  $v_o$  is the linear velocity at the column outlet, related to the retention time,  $t_o$ , of an unretained component, column length,  $L$ ,  $f_2$  and the average carrier gas velocity,  $\bar{v}$ , as follows:

$$v_o = \frac{\bar{v}}{f_2} = \frac{L}{t_o f_2} \quad (4)$$

$$B_o = 2 D_{m,o} \quad (5a)$$

$$C_{m,o} = \frac{11 k^2 + 6 k + 1}{24(1 + k)^2} \cdot \frac{r^2}{D_{m,o}} \quad (5b)$$

$$C_s = \frac{2 k}{3(1 + k)^2} \cdot \frac{d_f^2}{D_s} \quad (5c)$$

$D_{m,o}$  is the diffusion coefficient of a component in the mobile phase at the column outlet pressure;  $D_s$  is the diffusion coefficient of a component in the stationary liquid phase;  $r$  is the column radius;  $k$  is the capacity ratio of a solute; and  $d_f$  is the film thickness.

The effect of operating at sub-atmospheric column outlet conditions is dependent on the relative magnitude of the  $C_m$  and  $C_s$  terms (describing the resistance to mass transfer in the gas and liquid phases, respectively).

#### *Optimal chromatographic conditions*

By differentiating eqn. 1 with respect to  $v_o$ , and setting the result equal to zero, the optimal value of  $v_o$  and the minimal value of  $H$  are found. This differentiation yields the following equations, describing the optimal gas chromatographic conditions<sup>5</sup>:

$$v_{o,opt} = \left[ \frac{B_o f_1}{C_{m,o} f_1 + C_s (f_2 + y_2)} \right]^{1/2} \quad (6)$$

$$H_{min} = [2 C_{m,o} f_1 + C_s (2 f_2 + y_2)] v_{o,opt} \quad (7)$$

where

$$y_2 = v_o \cdot \frac{\delta f_2}{\delta v_o} = f_2 (1 - f_2 P) \quad (8)$$

and  $y_2 = 0$  for  $P = 1$  and  $y_2 = -f_2/2 = -3/(4P)$  for  $P \rightarrow \infty$ .

For a given separation problem, the number of theoretical plates required,  $N$ , can be calculated using the well known resolution equation. The column length required,  $L$ , for optimal chromatographic conditions is determined by

$$L = N H_{min} \quad (9)$$

The retention time,  $t_R$ , of a given compound is given by

$$t_R = t_o (1 + k) \quad (10)$$

Combination of eqns. 4, 9 and 7 yields the following equation for  $t_o$  under optimal conditions:

$$t_o = \frac{L}{\bar{v}_{opt}} = \frac{N H_{min}}{v_{o,opt} f_2} = \frac{N}{f_2} [2 C_{m,o} f_1 + C_s (2 f_2 + y_2)] \quad (11)$$

#### *Vacuum outlet*

Under vacuum outlet conditions ( $P \rightarrow \infty$ ), eqns 2, 3 and 8 reduce to  $f_1 = 9/8$ ,  $f_2 = 3/(2 P)$  and  $y_2 = -f_2/2$ . Substitution of these factors in eqn. 11 gives

$$t_o = N \left[ \frac{9}{8} \cdot \frac{C_{m,o}}{f_2} + \frac{3}{2} C_s \right] = \frac{3}{2} N [C_{m,o} P + C_s] \quad (12)$$

The average gas velocity,  $\bar{v}$ , through a capillary column is described by the Poiseuille equation:

$$\bar{v} = \frac{3}{32} \cdot \frac{r^2 P_o}{\eta L} \cdot \frac{(P^2 - 1)^2}{P^3 - 1} \quad (13)$$

where  $\eta$  is the dynamic viscosity of the carrier gas. If  $P \gg 1$ , eqn. 13 simplifies to

$$\bar{v}_{vac} = \frac{3}{32} \cdot \frac{r^2 P_i}{\eta L} \quad (14)$$

#### *Thin-film vs. thick-film columns (vacuum outlet)*

If  $C_{m,o} f_1 \gg C_s f_2$  (cf., eqn. 5), as with thin-film columns, and if  $P_i \gg P_o$  (vacuum outlet), eqn. 12 reduces to

$$t_{o,thin} = \frac{3}{2} N C_{m,o} P_{thin} \quad (15)$$

under optimal chromatographic conditions.

Assume that the required plate number,  $N$ , is kept constant, implying that  $L_{thick} > L_{thin}$  (cf., eqns. 9 and 7). Assume further that  $C_{m,o}$  is kept constant (eqn. 5b), meaning that  $r^2/D_{m,o} = \text{constant}$ , and  $k_{thick} = k_{thin}$  [which in turn implies that the (longer) thick-film column be operated at a higher temperature than the thin-film column].

In the first instance it is assumed that for thick- and thin-film capillaries  $D_{m,o}$  has the same value, although the column temperature may differ 25°K. The same simplification is applied with respect to  $\eta$ . With these assumptions ( $N$ ,  $C_{m,o}$  constant), it follows from eqns. 12 and 15 that

$$\frac{t_{\text{thick}}}{t_{\text{thin}}} = \frac{P_{\text{thick}}}{P_{\text{thin}}} + \frac{C_s}{C_{m,o} P_{\text{thin}}} \quad (16)$$

where  $t$  stands for both  $t_o$  and  $t_R$  (cf., eqn. 10).

Under vacuum outlet conditions,  $P_o \approx \text{constant} \ll P_i$ . Also, for an ideal gas, both  $D_m$  and  $v$  vary inversely with pressure:

$$D_{m,o} P_o = D_{m,i} P_i = D_{m,1} P_1 \quad (17)$$

$D_{m,1}$  being the diffusion coefficient in the carrier gas at atmospheric pressure  $P_1$ . Hence  $C_{m,o}/P_o = C_{m,1}/P_1$  (cf., eqn. 5c), and eqn. 16 can be rewritten as

$$\frac{t_{\text{thick}}}{t_{\text{thin}}} = \frac{P_{i,\text{thick}}}{P_{i,\text{thin}}} + \frac{C_s P_1}{C_{m,1} P_{i,\text{thin}}} \quad (18)$$

If  $P \rightarrow \infty$ , it follows from eqns. 14, 9, 7, 6 and 4 that

$$P_i = \frac{32 \eta N H}{3 r^2} \cdot \bar{v} = A H \bar{v} = A H f_2 v_o$$

$$P_i = A [2 C_{m,o} f_1 + \frac{3}{2} C_s f_2] f_2 \cdot \frac{B_o f_1}{C_{m,o} f_1 + \frac{1}{2} C_s f_2} \quad (19)$$

where  $A = \text{constant}$  (if  $\eta$ ,  $N$  and  $r$  are constant). If  $C_{m,o} f_1 \gg C_s f_2$ , as for thin-film columns, eqn. 19 is reduced to

$$P_{i,\text{thin}} = 2A B_o f_1 f_{2,\text{thin}} \quad (20)$$

Assuming  $f_1 \rightarrow 9/8 = \text{constant}$ , division of eqn. 19 by eqn. 20 yields

$$\frac{P_{i,\text{thick}}}{P_{i,\text{thin}}} = \frac{2 C_{m,o} f_1 + \frac{3}{2} C_s f_{2,\text{thick}}}{2 [C_{m,o} f_1 + \frac{1}{2} C_s f_{2,\text{thick}}]} \cdot \frac{f_{2,\text{thick}}}{f_{2,\text{thin}}} \quad (21)$$

which gives

$$P_{i,\text{thin}} = P_{i,\text{thick}} \left[ \frac{(C_{m,1}/C_s) P_{i,\text{thick}}/P_1 + 2/3}{(C_{m,1}/C_s) P_{i,\text{thick}}/P_1 + 1} \right]^{1/2} \quad (22)$$

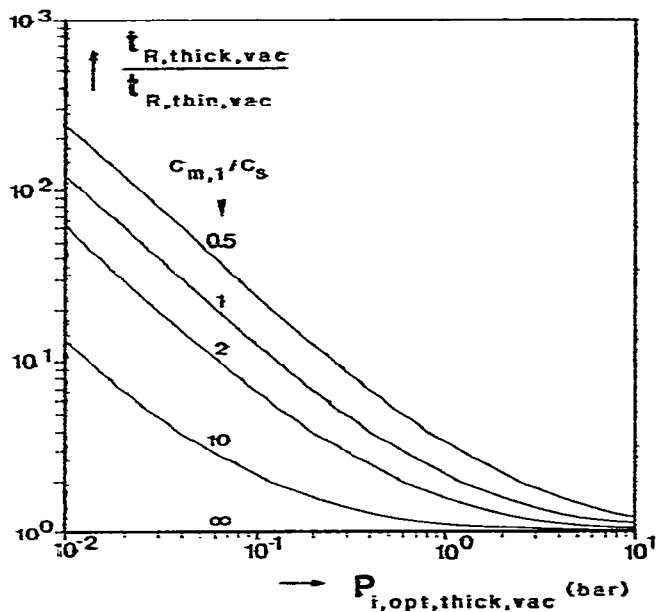


Fig. 1. Decrease in speed of analysis under optimal conditions by increasing influence of  $C_s$  (resistance to mass transfer in the liquid phase) as a function of the optimal inlet pressure,  $P_{i,opt,vac}$  with vacuum outlet operation.

The combined eqns. 18 and 22 fully describe the difference in behaviour between thin- and thick-film columns (for  $\eta$ ,  $N$  and  $C_{m,1}$  constant) under vacuum outlet conditions, in terms of  $C_{m,1}/C_s$  and optimal inlet pressures (Fig. 1).

#### *Comparison of thick-film vacuum outlet and thin-film atmospheric outlet pressure operation*

The gain,  $G_L$ , in optimal speed of analysis obtained by using a given thin-film column with the same carrier gas at constant temperature, under vacuum outlet conditions, compared with atmospheric outlet pressure operation, is given by<sup>1</sup>

$$G_L = \frac{\bar{v}_{i,thin,vac}}{\bar{v}_{i,thin,atm}} = \frac{(P_{i,thin,vac}^2 + P_1^2)^{3/2} - P_1^3}{P_{i,thin,vac}^3} \quad (23)$$

Theoretically, a decrease in column efficiency of up to 12.5% might be expected<sup>1</sup>. For a given separation problem, requiring  $N$  theoretical plates, therefore, the column should be 9/8 longer under vacuum outlet conditions. The gain in analysis time is therefore reduced to

$$G_N = \frac{8}{9} G_L \quad (24)$$

Using eqn. 4, the gain in retention time at  $P_o = 0$  compared with  $P_o = P_1$  for thin-film columns (under optimal chromatographic conditions, keeping  $\eta$ ,  $N$  and  $C_{m,1}$  constant) is therefore

$$\frac{t_{\text{thin,vac}}}{t_{\text{thin,atm}}} = \frac{1}{G_N} = \frac{9}{8 G_L} \tag{25}$$

A comparison of thick-film columns at  $P_0 = 0$  and thin-film columns at  $P_0 = P_1$  can now be made. Keeping the carrier gas, stationary phase,  $C_{m,1}$  and  $N$  constant ( $L$  and the temperature are different), the ratio of the retention times for optimal chromatographic conditions is

$$\frac{t_{\text{thick,vac}}}{t_{\text{thin,atm}}} = \frac{t_{\text{thick,vac}}}{t_{\text{thin,vac}}} \cdot \frac{t_{\text{thin,vac}}}{t_{\text{thin,atm}}} = \frac{t_{\text{thick,vac}}}{t_{\text{thin,vac}}} \cdot \frac{9}{8 G_L} \tag{26}$$

This ratio (eqn. 26) can be calculated using eqns. 18, 22 and 23 for different values of  $C_{m,1}/C_s$ . The results are plotted in Fig. 2.

EXPERIMENTAL

A 34 m × 0.40 mm I.D. glass capillary SE-30 column was prepared as described previously<sup>1</sup>. The film thickness was calculated to be 1.0 μm.

The column was operated isothermally at 422°K. Vacuum outlet GC-MS and atmospheric outlet experiments were carried out using the same equipment and conditions as reported for thin-film columns<sup>1</sup>.

*n*-Dodecane, having a capacity ratio of  $k = 2.0$  at 422°K, was introduced as vapour using split injection. The carrier gas velocities were measured using methane

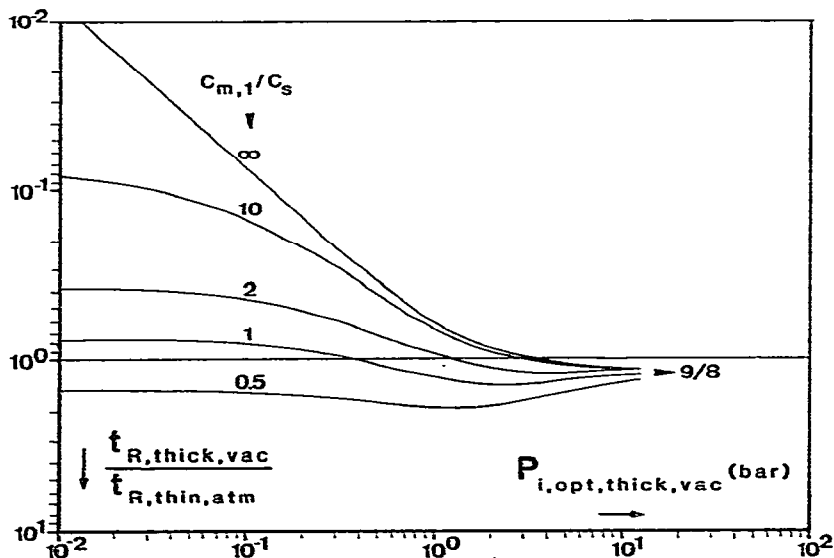


Fig. 2. Ratio of retention times under optimal conditions as a function of optimal inlet pressure.  $P_{i,opt,vac}$  Thick-film columns ( $C_s \neq 0$ ) operated under vacuum outlet and thin-film columns ( $C_s = 0$ ) under atmospheric outlet conditions.

TABLE I

DIFFUSION COEFFICIENTS, CARRIER GAS VISCOSITIES AND CALCULATED  $C_m$  AND  $C_s$  TERMSColumn I.D., 0.4 mm; SE-30 film thickness, 1  $\mu\text{m}$ ; all data for  $n\text{-C}_{12}\text{H}_{26}$  at 422°K (capacity ratio  $k = 2.0$ ).

Parameter	Helium	Nitrogen	Ref.
$D_{m,1}$ ( $\text{mm}^2/\text{sec}$ ) (= $0.5 B_1$ )	29.0	9.0	6
$D_s$ ( $\times 10^{-3}$ $\text{mm}^2/\text{sec}$ )	1.48	1.48	7
$\eta$ ( $\mu\text{Pa} \cdot \text{sec}$ )	24.8	23.7	6
$C_{m,1}$ (msec) (calc.)	0.36	1.17	
$C_s$ (msec) (calc.)	0.10	0.10	
$C_{m,1} C_s$ (calc.)	3.6	11.7	

TABLE II

COMPARISON OF DATA FOR TWO GLASS CAPILLARY SE-30 COLUMNS OPERATED UNDER OPTIMAL SEPARATION CONDITIONS AT VACUUM AND ATMOSPHERIC OUTLET PRESSURES

Column I.D., 0.4 mm; all data for  $n\text{-C}_{12}\text{H}_{26}$  at  $k = 2$ . Thick film column:  $L = 34$  m;  $d_f = 1.0$   $\mu\text{m}$ ; temperature = 422°K. Thin film column:  $L = 30$  m;  $d_f = 0.4$   $\mu\text{m}$ ; temperature = 400°K.

Parameter	Calculated or measured	Thick film				Thin film*	
		Helium		Nitrogen		Nitrogen	
		Vac.	Atm.	Vac.	Atm.	Vac.	Atm.
$\bar{v}_{\text{opt}}$ (mm/sec)	Calc. Meas.	497 435	258	288 265	106	301 287	117 116
$P_{i,\text{opt}}$ (bar)	Calc. Meas.	1.12 1.12	1.52	0.62 0.65	1.25	0.59 0.60	1.16 1.25
$t_0 = \frac{L}{\bar{v}}$ (sec)	Calc. Meas.	68.4 78	132	118.1 128	321	99.6 105	256.4 261
$H_{\text{min}}$ (mm)	Calc. Meas.	0.378 0.42	0.36	0.356 0.36	0.32	0.311 0.31	0.276 0.31
$N = \frac{L}{H}$ ( $\times 10^3$ )	Calc. Meas.	90.0 81.5	93.3	95.5 93.0	107.8	96.6 96.1	108.7 98.1

\* Data from ref. 1, corrected for observed values of  $D_{m,1}$  (ref. 6).(helium carrier gas) or propane (nitrogen carrier gas), injected simultaneously with  $n$ -dodecane.

## RESULTS AND DISCUSSION

The assumptions made in the theoretical treatment ( $N$ ,  $r$ ,  $k$ ,  $\eta$  and  $D_{m,1}$  constant) have consequences for the dimensions of the thick-film and thin-film columns to be compared, and for the operating conditions. Evidently the columns should have the same inner diameter and be operated with the same carrier gas. With increasing



TABLE III

PREDICTED AND MEASURED RATIOS OF OPTIMAL INLET PRESSURES AND ANALYSIS TIMES FOR THICK- AND THIN-FILM SE-30 COLUMNS

Carrier gas, N<sub>2</sub>; other conditions as in Table II.

Ratio	Measured from Table II	Calculated	
		From Table II	From eqns.*
$\frac{P_{i,thick,vac}}{P_{i,thin,vac}}$	1.08	1.06	1.04
$\frac{t_{thick,vac}}{t_{thin,vac}}$	1.22	1.19	1.36
$\frac{t_{thick,vac}}{t_{thin,atm}}$	0.49	0.46	0.59

\* Eqns. 22, 18 and 26, respectively, for  $C_{m,1}/C_s = 5$  (as observed).

film thickness, the thick-film column should be elongated and used at increased temperature compared with the thin-film column.

Under these conditions, the optimal inlet pressure, with vacuum outlet operation, increases with increasing film thickness, but is always less than  $\sqrt{3/2}$  times the optimal inlet pressure of the corresponding thin-film column (eqn. 22).

As expected (Fig. 1), the effect of a non-negligible  $C_s$  term increases the analysis time of a thick-film column with respect to a thin-film column ( $C_s = 0$ ), both operated under optimum vacuum outlet conditions. However, vacuum outlet operation of low-pressure-drop thick-film columns almost always yields even shorter analysis times than atmospheric outlet operation of thin-film columns (Fig. 2).

Optimal chromatographic conditions were calculated for the column under the experimental conditions using the data summarized in Table I. The calculated and experimental data are given in Table II. From Table II and eqns. 22, 18 and 26, the results given in Table III are obtained.

The measured and calculated data agree very well. Deviations can be accounted for by the fact that  $D_{m,1}$  and  $\eta$  differ for the two columns by approximately 10% and 4%, respectively, owing to the temperature difference of 22°K ( $D_{m,1} \approx T^{1.75}$  and  $\eta \approx T^{0.7}$ ;  $T$  in °K). Moreover,  $N$  was not entirely constant (Table II).

Further, there is some uncertainty in the value of the  $C_s$  term. On the one hand, its contribution cannot be entirely neglected with the thin-film column<sup>1</sup>. On the other hand, measured  $C_s$  values for the thick-film column were about double the calculated values (Table I and footnote to Table III). The accuracy of the term  $d_i^2/D_s$  (eqn. 5c) is therefore questionable.

The observed decrease in the speed of analysis due to the influence of the thick film is even less than predicted by eqns. 18 and 26 (Table III). Previously<sup>1</sup>, no evidence was found for a decrease in plate number by a factor of  $f_1 = 9/8$  when operating a given thin-film column under vacuum outlet conditions compared with atmo-

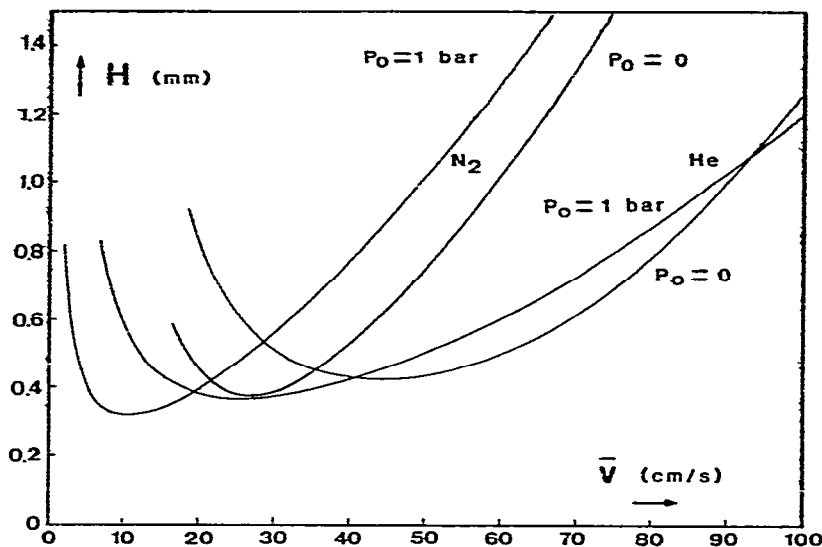


Fig. 3. Measured  $H$  versus  $\bar{v}$  curves (computer fitted) for a thick-film SE-30 glass capillary column (34 m  $\times$  0.4 mm I.D.; film thickness 1.0  $\mu\text{m}$ ). Carrier gases and outlet pressures as indicated. Data were obtained with  $n\text{-C}_{12}\text{H}_{26}$  at 422°K ( $k = 2$ ).

spheric outlet pressure conditions. This seems to be confirmed here. Deletion of this factor in eqns. 24–26 decreases the calculated ratio of retention times by 12.5%.

Vacuum outlet operation of capillary columns therefore always results in an increase in speed of analysis compared with normal use at atmospheric outlet pressure. This conclusion was drawn previously by Giddings<sup>4,8</sup>. This is valid, under optimal chromatographic conditions, for both thick- and thin-film<sup>1</sup> columns. The  $H$  versus  $\bar{v}$  curves in Fig. 3 demonstrate this effect. As with thin-film columns, the optimal inlet pressure and hence the gain factors of thick-film columns are dependent on the carrier gas (Table II and Fig. 3).

As can be seen from the theoretical curves in Fig. 2, the increase in speed of analysis is particularly pronounced for low-pressure-drop columns with sub-atmospheric optimal inlet pressures. The use of wide-bore and/or short columns is therefore recommended.

By combining the advantages of thick-film columns and vacuum outlet operation, the sample capacity of the GC–MS combination is considerably increased, as is the speed of analysis.

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#### NOTE ADDED IN PROOF

The factor of 8/9 in eqns. 24, 25 and 26 should be replaced by  $(f_{1,\text{atm}}/f_{1,\text{vac}})^{3/2}$ .

The power  $3/2$  originates from the fact that, if  $L_{vac}$  is elongated by  $9/8$  in order to maintain the required  $N$ ,  $P_{i,opt,vac}$  increases by  $\sqrt{9/8}^1$ . Eqn. 15 shows that  $t_{thin,vac}$  is proportional to  $L$  and  $P_i$  and hence to  $(9/8)^{3/2}$ . In practice  $f_{1,atm} > 1$  and  $(f_{1,atm}/f_{1,vac})^{3/2} \approx 8/9$  (specifically obtained for  $P_{i,opt,atm}/P_1 = 2.2$ ). Therefore Fig. 2 represents a realistic situation. In the worst case, *i.e.* for very low pressure drop columns,  $(f_{1,atm}/f_{1,vac})^{3/2} = (8/9)^{3/2} = 0.8380$ . See also the comments on  $f_1$  in the Results and discussion section.

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