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

### CAPILLARY COLUMNS AT SUB-ATMOSPHERIC OUTLET PRESSURES

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#### SUMMARY

A theoretical treatment of the optimum gas chromatographic conditions for open-tubular columns, operated at vacuum outlet pressures, is presented. Equations are given for the minimum plate height, the optimum linear gas velocity and the optimum inlet pressure. The maximum column efficiency was calculated to decrease by 12.5% at most, compared with atmospheric outlet conditions. The gain in speed of analysis obtained with vacuum outlet columns is dependent upon the nature of the carrier gas and increases strongly with lower (sub-atmospheric) optimum inlet pressures. The use of short and/or wide-bore columns can therefore be recommended.

Experimental results indicate the validity of the theory, although no loss in efficiency has been observed. The ultimate gas chromatography-mass spectrometry coupling device thus appears to be no device at all: the end of the column need only be inserted into the ion source of a mass spectrometer. In addition to the gain in speed of analysis, the many problems caused by wall effects and dead volumes in interface lines are avoided by this method. Moreover, the gas chromatographic peaks are narrower and thus higher, lowering detection limits.

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#### INTRODUCTION

The utility of integrated gas chromatography-mass spectrometry (GC-MS) systems is maximized when (glass) capillary columns are used. Apart from molecular separators as interfaces, there are basically two coupling devices: direct (closed) and open-split connections (see, for instance, refs. 1 and 2, respectively).

The direct connection has the obvious advantage of full sample transfer. If no restriction is used between the capillary column and the ion source, the column outlet is at a very low pressure. It is often claimed that a decreased outlet pressure has a deleterious effect on column efficiency. In practice<sup>3,4</sup>, up to 30% loss in optimum separation efficiency has been reported. Other workers reported no loss<sup>5,6</sup> or even improved resolution<sup>7</sup> with vacuum outlet pressures. On the other hand, the optimum gas velocity was found to be shifted to higher values<sup>3,4</sup>.

Although some attempts have been made to rationalize these (contradictory) findings<sup>3,4,16</sup>, no complete treatment of vacuum-outlet GC has been reported to date. In this paper it will be shown that operation of wall-coated open-tubular columns at vacuum outlet pressure has many advantages over operation at atmospheric outlet pressures.

## EXPERIMENTAL

A Duran 50 glass capillary (60 m × 0.40 mm I.D.) was leached with HCl, dehydrated and subsequently deactivated with benzyltriphenylphosphonium chloride<sup>8</sup>. The column was coated with SE-30 by a static procedure<sup>9</sup>. The film thickness was calculated to be 0.40 μm.

The column was operated isothermally at 400°K. In vacuum outlet GC-MS mode, the column was coupled directly to a Finnigan 4000 quadrupole mass spectrometer (Finnigan, Sunnyvale, CA, U.S.A.), via a glass-lined tube (40 cm × 0.4 mm I.D.) (GLT). The GLT was inserted as far as possible into the standard Finnigan 4000 GC-MS interface block. The column was connected to the other end of the GLT by a "graph-pack" coupling<sup>10</sup>. The GLT was maintained at 430°K. The mass spectrometer was used in the electron impact (EI) mode to monitor the current of alkyl fragment ions at  $m/z$  15 (helium carrier gas) or  $m/z$  43 (nitrogen), respectively. Chromatograms were recorded on a Leeds & Northrup Speedomax XL 681 A (Leeds & Northrup Italiana, Milan, Italy) fast pen recorder.

The column was subsequently divided into two parts each of 30 m length. One half was used to compare vacuum outlet with atmospheric outlet behaviour. In the latter case a Carlo Erba Fractovap 2900 gas chromatograph (Carlo Erba, Milan, Italy), equipped with a flame-ionization detector (FID) was employed. Sample splitters, with a splitting ratio of 1:200, were used as injector at 550°K throughout the experiments. Injections at sub-atmospheric inlet pressures were made by attaching a vacuum pump to the vent outlet of the splitter. The inlet pressure was regulated by a fine metering valve and measured with a Model FA 145 precision pressure gauge (Wallace & Tiernan, Günzburg/Do., G.F.R.).

*n*-Dodecane, having a capacity ratio of  $k = 2$  at 400°K, was injected as vapour. The carrier gas velocities were measured using methane (helium carrier gas), or propane (nitrogen), injected simultaneously with *n*-dodecane.

## THEORETICAL DISCUSSION

Band broadening in capillary columns is satisfactorily described by the Golay equation<sup>11</sup> extended to situations of appreciable pressure drop by Giddings and co-workers<sup>12,13</sup>. Taking into account the decompression effect as described by these authors, the expression for the measured or apparent plate height for a uniformly distributed liquid film, is:

$$H = \left[ 2 \frac{D_{m,o}}{v_o} + \frac{11k^2 + 6k + 1}{24(1+k)^2} \cdot \frac{r^2 v_o}{D_{m,o}} \right] f_1 + \frac{k^3}{6(1+k)^2} \cdot \frac{r^2}{K^2 D_s} v_o f_2 \quad (1)$$

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 pressure

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

where  $f_1 = 1$  for  $P = 1$ , and  $f_1 = 9/8$  for  $P \rightarrow \infty$

$$f_2 = \frac{3}{2} \frac{P^2 - 1}{P^3 - 1} \text{ (Martin-James correction factor)} \quad (3)$$

where  $f_2 = 1$  for  $P = 1$ , and  $f_2 = 3/(2P)$  for  $P \rightarrow \infty$ .

In eqn. 1 the following symbols are used:

$D_{m,o}$  is the diffusion coefficient of a component in the mobile phase at column outlet pressure.

$v_o$  is the linear velocity at the column outlet, and is 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:

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

$D_s$  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 is equal to  $K \cdot \beta$ .

$K$  is the partition coefficient of a solute.

$\beta$  is the volume ratio of the stationary and mobile phases,  $V_s/V_m$ .

Eqn. 1 can be written in a simplified form:

$$H = \left[ \frac{B_o}{v_o} + C_{m,o} v_o \right] f_1 + C_s v_o f_2 \quad (5)$$

The effect of operating at sub-atmospheric column outlet pressures 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). A treatment including the  $C_s$  term will be given in a forthcoming paper.

### Assumptions

In a first approximation it will be assumed that  $C_s$  is negligible compared to  $C_m$ . At the same time  $P \gg 1$ , if no restriction is used at the outlet of the column directly connected to the ion source of a mass spectrometer. The effect of these assumptions will be treated systematically.

### Optimum chromatographic conditions

By differentiating eqn. 5 or eqn. 1 with respect to  $v_o$ , and setting the result equal to zero, the optimum value of  $v_o$  and the minimum value of  $H$  are found. It has been shown<sup>14</sup> that, if  $C_m \gg C_s$ , this differentiation yields the following equations describing the optimum GC conditions

$$v_{o,opt} = \sqrt{\frac{B_o}{C_{m,o}}} = 4 \frac{D_{m,o}}{r} \sqrt{\frac{3(1+k)^2}{11k^2 + 6k + 1}} \quad (6)$$

and using eqn. 4:

$$\bar{v}_{\text{opt}} = \frac{4D_{\text{m.o}}}{r} f_{2,\text{opt}} \sqrt{\frac{3(1+k)^2}{11k^2 + 6k + 1}} \quad (7)$$

$$H_{\text{min}} = 2f_{1,\text{opt}} \sqrt{B_0 C_{\text{m.o}}} = f_{1,\text{opt}} r \sqrt{\frac{11k^2 + 6k + 1}{3(1+k)^2}} \quad (8)$$

For an ideal gas both  $D_{\text{m}}$  and  $v$  vary inversely with pressure or

$$D_{\text{m.o}} P_0 = D_{\text{m,i}} P_1 = D_{\text{m,1}} P_1 \quad (9)$$

$D_{\text{m,1}}$  being the diffusion coefficient in the carrier gas at atmospheric pressure  $P_1$ . For large values of  $P$  eqn. 7 together with eqns. 3 and 9 yields:

$$\bar{v}_{\text{opt,vac}} = \frac{6 D_{\text{m,1}} P_1}{P_{1,\text{opt,vac}} r} \sqrt{\frac{3(1+k)^2}{11k^2 + 6k + 1}} \quad (10)$$

Also if  $P \gg 1$  eqn. 8 can be rewritten as:

$$H_{\text{min,vac}} = \frac{9}{8} r \sqrt{\frac{11k^2 + 6k + 1}{3(1+k)^2}} \quad (11)$$

#### Gas velocity through the column

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

$$\bar{v} = \frac{3}{32} \frac{r^2 P_0}{\eta L} \frac{(P^2 - 1)^2}{P^3 - 1} \quad (12)$$

where  $\eta$  is the dynamic viscosity of the carrier gas. If  $P \gg 1$  eqn. 12 reduces to:

$$\bar{v}_{\text{vac}} = \frac{3}{32} \frac{r^2 P_i}{\eta L} \quad (13)$$

#### Optimum inlet pressure

For a given separation problem the number of required theoretical plates,  $N_{\text{req}}$ , can be calculated using the well known resolution equation. Under optimum chromatographic conditions, the length of the column,  $L$ , is given by eqn. 8:

$$L = N_{\text{req}} H_{\text{min}} = N_{\text{req}} f_{1,\text{opt}} r \sqrt{\frac{11k^2 + 6k + 1}{3(1+k)^2}} \quad (14)$$

Under sub-atmospheric outlet pressures (eqn. 11):

$$L = N_{\text{req}} H_{\text{min,vac}} = N_{\text{req}} \frac{9}{8} r \sqrt{\frac{11k^2 + 6k + 1}{3(1+k)^2}} \quad (15)$$

Using eqns. 7, 12 and 3, the inlet pressure,  $P_{1,\text{opt}}$ , can be calculated for a given separation problem assuming optimum chromatographic conditions. Thus,  $\bar{v}_{\text{Poiseuille}} = \bar{v}_{\text{opt,Golay-Giddings}}$  yields:

$$\frac{r^2 P_0}{\eta L} (P^2 - 1) = 64 \frac{D_{\text{m.o}}}{r} \sqrt{\frac{3(1+k)^2}{11k^2 + 6k + 1}} \quad (16)$$

Using eqns. 14 and 9, eqn. 16 yields:

$$P_{i,\text{opt}}^2 = \frac{64 P_1 N_{\text{req}} f_{1,\text{opt}} \eta D_{m,1}}{r^2} + P_o^2 \quad (17)$$

Under vacuum outlet pressure ( $P_o = 0$ ,  $P \gg 1$ ,  $f_1 = 9/8$ ) this reduces to:

$$P_{i,\text{opt,vac}}^2 = 72 P_1 N_{\text{req}} \eta D_{m,1} / r^2 \quad (18)$$

*Basic equations for vacuum outlet pressures ( $C_m \gg C_s$ )*

$$P_{i,\text{opt,vac}} = \sqrt{72 P_1} \sqrt{N_{\text{req}}} \sqrt{\eta D_{m,1}} / r \quad (19)$$

Knowing  $P_{i,\text{opt,vac}}$ , eqn. 10 can be rewritten as:

$$\bar{v}_{\text{opt,vac}} = \sqrt{\frac{P_1}{2}} \sqrt{\frac{1}{N_{\text{req}}}} \sqrt{\frac{3(1+k)^2}{11k^2 + 6k + 1}} \sqrt{\frac{D_{m,1}}{\eta}} \quad (20)$$

From eqns. 15 and 20 the retention time,  $t_R$ , for a given separation problem can be calculated under optimum conditions ( $P_i = P_{i,\text{opt,vac}}$ )

$$t_R = t_o(1+k) = (L/\bar{v}_{\text{opt}})(1+k) \quad (21)$$

and  $t_o$  is given by:

$$t_o = \frac{9}{8} \sqrt{\frac{2}{P_1}} N_{\text{req}}^{3/2} r \frac{11k^2 + 6k + 1}{3(1+k)^2} \sqrt{\frac{\eta}{D_{m,1}}} \quad (22)$$

*Comparison of atmospheric and vacuum outlet conditions*

For a given wall-coated capillary column operated at otherwise comparable conditions, the following relations can be deduced if  $C_s$  is negligible compared to  $C_m$ .

*Minimum plate height (eqns. 11 and 8).*

$$\frac{H_{\text{min,vac}}}{H_{\text{min,atm}}} = \frac{f_{1,\text{opt,vac}}}{f_{1,\text{opt,atm}}} \quad (23)$$

$f_{1,\text{opt,vac}} = 9/8$  and  $f_{1,\text{opt,atm}}$  has a value between 1 ( $P_i = P_o$ ) and  $9/8$  ( $P_i \gg P_o$ ). Hence the loss in efficiency is 12.5% at most. From eqns. 23 and 14 the following expression is obtained

$$\frac{H_{\text{min,vac}}}{H_{\text{min,atm}}} = \frac{f_{1,\text{opt,vac}}}{f_{1,\text{opt,atm}}} = \frac{N_{\text{opt,atm}}}{N_{\text{opt,vac}}} \quad (24)$$

OR:

$$(Nf_1)_{\text{opt,vac}} = (Nf_1)_{\text{opt,atm}} \quad (25)$$

*Relation between optimum inlet pressures under atmospheric and vacuum outlet conditions.* Substituting eqn. 25 in eqns. 17 and 18 it readily follows:

$$P_{i,\text{opt,atm}}^2 = P_{i,\text{opt,vac}}^2 + P_1^2 \quad (26)$$

Gain ( $G$ ) in optimum carrier gas velocity by vacuum operation (eqn. 7).

$$G = \frac{\bar{v}_{\text{opt,vac}}}{\bar{v}_{\text{opt,atm}}} = \frac{D_{\text{m,o,vac}} f_{2,\text{opt,vac}}}{D_{\text{m,o,atm}} f_{2,\text{opt,atm}}} \quad (27)$$

Substituting the expression for  $f_2$  (eqn. 3) and using eqn. 9, the gain in speed of analysis is:

$$G = \frac{P_{i,\text{opt,atm}}^3 - P_1^3}{P_{i,\text{opt,vac}} (P_{i,\text{opt,atm}}^2 - P_1^2)} \quad (28)$$

Together with eqn. 26 this yields:

$$G = \frac{P_{i,\text{opt,atm}}^3 - P_1^3}{(P_{i,\text{opt,atm}}^2 - P_1^2)^{3/2}} = \frac{(P_{i,\text{opt,vac}}^2 + P_1^2)^{3/2} - P_1^3}{P_{i,\text{opt,vac}}^3} \quad (29)$$

In Fig. 1 a plot of  $G$  versus  $P_{i,\text{opt,vac}}$  is shown, stressing the importance of low optimum inlet pressures. The consequences of this will be discussed.

*Consequences for the pumping capacity of the mass spectrometer.* The carrier gas flow,  $Q$  (reduced to atmospheric pressure), is given by

$$Q = \pi r^2 \bar{v} (\bar{P}/P_1) \quad (30)$$

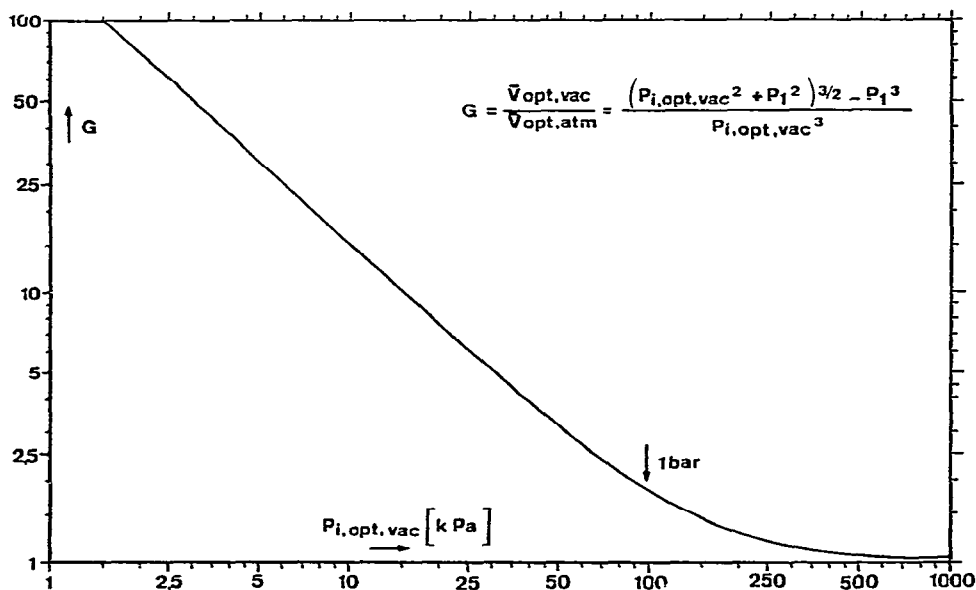


Fig. 1. Gain in speed of analysis ( $G$ ) by vacuum outlet operation as a function of the optimum inlet pressure ( $P_{i,\text{opt,vac}}$ ).

where  $\bar{P}$  is the average column pressure. Therefore, using eqn. 27:

$$\frac{Q_{\text{opt,vac}}}{Q_{\text{opt,atm}}} = \frac{\bar{v}_{\text{opt,vac}}}{\bar{v}_{\text{opt,atm}}} \cdot \frac{\bar{P}_{\text{opt,vac}}}{\bar{P}_{\text{opt,atm}}} = G \cdot \frac{\bar{P}_{\text{opt,vac}}}{\bar{P}_{\text{opt,atm}}} \quad (31)$$

Because (cf., eqn. 3):

$$\bar{P} = P_o/f_2 \quad (32)$$

$$\bar{P}_{\text{opt,vac}} = 2/3 P_{\text{i,opt,vac}}$$

$$\bar{P}_{\text{opt,atm}} = \frac{2}{3} \frac{P_{\text{i,opt,atm}}^3 - P_1^3}{P_{\text{i,opt,atm}}^2 - P_1^2}$$

Thus (cf., eqn. 28):

$$\frac{\bar{P}_{\text{opt,vac}}}{\bar{P}_{\text{opt,atm}}} = \frac{1}{G}$$

Consequently:

$$Q_{\text{opt,vac}} = Q_{\text{opt,atm}} \quad (33)$$

Notwithstanding the shorter analysis time under vacuum operation, the pump capacity of the mass spectrometer can remain the same.

### Discussion

A given separation problem requires  $N_{\text{req}}$  theoretical plates at a certain fixed value of  $k$ . If furthermore  $P \gg 1$ ,  $C_m \gg C_s$  and the column is operated under optimum conditions (at optimum inlet pressure,  $P_{\text{i,opt,vac}}$ ), then the following conclusions can be drawn (pressures expressed in bar).

(1) The minimum plate height,  $H_{\text{min}}$  (eqns. 8, 11 and 23), is independent of the carrier gas and, except for a factor of 9/8, independent of the outlet pressure of the column. The minimum plate height is proportional to  $r$ , and a function of  $k$ . The same conclusions are valid for the required column length  $L = NH$  (eqns. 14 and 15).

(2) The optimum inlet pressure,  $P_{\text{i,opt,vac}}$  (eqn. 19), is proportional to  $1/r$ ,  $\sqrt{N_{\text{req}}}$  and  $\sqrt{\eta D_{\text{m,1}}}$ . From Table I it can be seen that  $P_{\text{i,opt,vac}}$  has a low value for isobutane, but higher values for the carrier gases helium and hydrogen. For a given column a simple relation holds between the optimum inlet pressures under vacuum and atmospheric outlet pressures (eqn. 26):

$$P_{\text{i,opt,vac}}^2 = P_{\text{i,opt,atm}}^2 - 1$$

(3) The optimum average carrier gas velocity under vacuum outlet pressures,  $\bar{v}_{\text{opt,vac}}$  (eqn. 20), is independent of  $r$ , but proportional to  $1/\sqrt{N_{\text{req}}}$  and  $\sqrt{D_{\text{m,1}}/\eta}$ . The smallest analysis time is obtained with hydrogen as the carrier gas (Table I).

(4) Comparing  $P_o = 0$  and  $P_o = 1$  bar for a given column at constant experi-

TABLE I

INFLUENCE OF DIFFERENT CARRIER GASES ON OPTIMUM PARAMETERS CALCULATED FOR  $n\text{-C}_{12}\text{H}_{26}$  AT 400°K AND 1 BAR

Carrier gas	$\eta$ at 400° K ( $\mu\text{P}$ )	$D_{m,1}$ * ( $\text{cm}^2/\text{sec}$ )	$\sqrt{\eta D_{m,1}}$	$\sqrt{\frac{\eta}{D_{m,1}}}$	$G = \frac{\bar{v}_{\text{opt,vac}}^{**}}{\bar{v}_{\text{opt,atm}}}$
Hydrogen	109	0.377	6.41	17.0	5.6
Helium	235	0.304	8.45	27.8	4.3
Water	136	0.119	4.02	33.8	8.8
Ammonia	138	0.119	4.05	34.0	8.8
Methane	140	0.111	3.94	35.6	9.0
Isobutane	100?	0.05	2.2	45	16.0
Nitrogen	219	0.092	4.49	48.8	7.9
Carbon dioxide	198	0.070	3.73	53.1	9.5
Argon	285	0.081	4.79	59.3	7.4
Determining for			$P_{i,\text{opt,vac}}$	$t_{R,\text{vac}}$	

\* Calculated according to ref. 15.

\*\* At  $N = 10^4$  and  $r = 0.2$  mm.

mental conditions, it appears that vacuum operation always leads to a higher optimum carrier gas velocity. The ratio of optimum gas velocities is given by eqn. 29:

$$G = \frac{(P_{i,\text{opt,vac}}^2 + 1)^{3/2} - 1}{P_{i,\text{opt,vac}}^3}$$

This ratio, indicating the gain in the speed of analysis, increases strongly for lower inlet pressures ( $P_{i,\text{opt,vac}} < 1$  bar), approaching  $3/(2 P_{i,\text{opt,vac}})$ . Lower inlet pressures means in practical terms the use of wide bore and/or shorter columns. In Table I, values of  $G$  for different carrier gases are given for a 0.4 mm I.D. column having 10,000 theoretical plates. Using the chemical ionization reagent gases methane, isobutane or ammonia as carrier gases, the gain in speed of analysis is even higher than obtained with nitrogen. If more theoretical plates are required, the consequence is an increase in  $P_{i,\text{opt,vac}}$ , and a decrease in  $G$  (Fig. 1).

(5) Vacuum outlet operation results in narrower and thus higher peaks for a given amount of sample and therefore improves detection limits.

## RESULTS AND CONCLUSIONS

Experimental results indicate the validity of the theory. The obtained data are summarized in Table II and Fig. 2.

As predicted by theory, under vacuum conditions no significant difference in plate number is found between the carrier gases nitrogen and helium. Comparing the experimental results for the 30 m column, operated with nitrogen at  $P_o = 0$  and  $P_o = 1$  bar, respectively, no evidence is found for a loss in plate number by a factor  $f_1 = 9/8$ . The difference between  $N_{\text{calc.}}$  and  $N_{\text{meas.}}$  under atmospheric outlet pressures is probably due to the contribution of the  $C_s$  term from the Golay-Giddings equation.

Calculated and experimental values of  $P_{i,\text{opt}}$ ,  $\bar{v}_{\text{opt}}$  and  $N$  agree very well. The



TABLE II

COMPARISON OF DATA FOR A SE-30 GLASS CAPILLARY COLUMN, OPERATED AT OPTIMUM SEPARATION CONDITIONS AT VACUUM AND ATMOSPHERIC OUTLET PRESSURES, RESPECTIVELY

Column diameter, 0.4 mm I.D.; film thickness, 0.4  $\mu\text{m}$ . All data for  $n\text{-C}_{12}\text{H}_{26}$  at 400°K (capacity ratio  $k = 2$ ).

		$P_o = 0, L = 60\text{ m}$			$P_o = 0, L = 30\text{ m}$	$P_o = 1\text{ bar}, L = 30\text{ m}$
		Hydrogen	Helium	Nitrogen	Nitrogen	Nitrogen
$P_{1,\text{opt}}$ (bar)	calc.	1.22	1.60	0.85	0.60	1.16
	meas.	—	1.55	0.80	0.60	1.25
$\bar{v}_{\text{opt}}$ (cm/sec)	calc.	66	40	23	32	11.7
	meas.	—	36	21	29	11.6
$t_R$ (sec)	calc.	279	456	798	282	783
	meas.	—	495	879	327	933
$N (\times 10^3)$	calc.	190	190	190	95	107
	meas.	—	177	180	96	98
$G = \frac{\bar{v}_{\text{opt,vac}}}{\bar{v}_{\text{opt,atm}}}$	calc.	1.6	1.4	2.1	2.7	
	meas.	—	—	—	2.5	

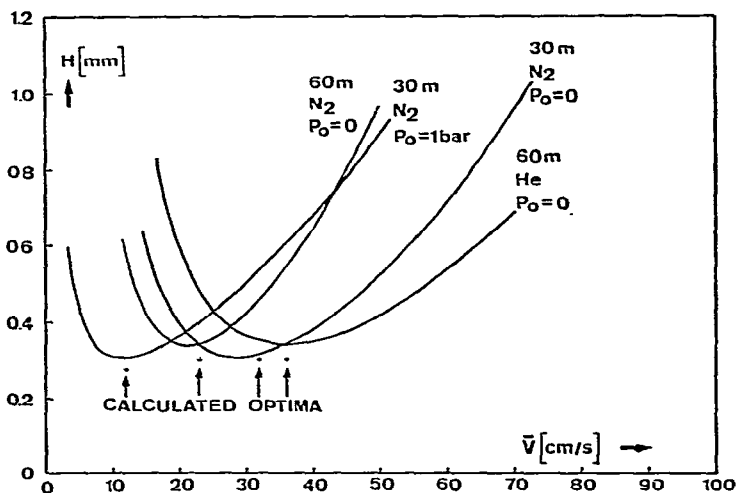


Fig. 2. Measured  $H$  vs.  $\bar{v}$  curves (computer fitted) for a SE-30 glass capillary column (0.4 mm I.D.). Column length,  $L$ , carrier gas and column outlet pressure as indicated. Data were obtained with  $n\text{-C}_{12}\text{H}_{26}$  at 400°K ( $k = 2$ ).

results obtained with the 30 m column at  $P_o = 0$  demonstrate a gain in analysis time of a factor 2.5, as predicted by theory. The derived equations show that much larger "gain" factors can be obtained for chemical ionization reagent gases such as isobutane (*cf.*, Table I). The optimum volume flow (reduced to 1 bar) to the mass spectrometer is unaffected. From the constancy of  $N$  and the increase of the optimum linear carrier gas velocity, it appears that the peak width is decreased under vacuum outlet pres-

tures. The effect is an improvement in detection limits for both concentration and mass-flow detectors.

The advantageous effects described above hold for WCOT columns where the resistance towards mass transfer in the liquid phase is negligible compared to that in the gas phase. This is valid for capillaries with uniformly distributed thin liquid films, but also for wide-bore columns with thick films. The latter have higher sample capacities, show less adsorption and facilitate injection.

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