

CHROM. 17 640

## OPTIMIZING FLOW-RATES IN CAPILLARY GAS CHROMATOGRAPHY- MASS SPECTROMETRY

N. W. DAVIES

*Central Science Laboratory, University of Tasmania, P.O. Box 252C, Hobart, Tasmania 7001 (Australia)*  
(First received December 17th, 1984; revised manuscript received February 11th, 1985)

---

### SUMMARY

The effects of the type of gas chromatograph-mass spectrometer interface and the type of flow regulation on flow-rate requirements for optimum efficiency for both isothermal and temperature programmed analyses on capillary columns are examined. Equations and figures are presented which enable rapid selection of optimum parameters such as inlet pressure, average velocity and flow-rate for various situations.

---

### INTRODUCTION

The flow-rate of carrier gas is an important parameter in obtaining the maximum separation efficiency in capillary gas chromatographic (GC) analyses. Column efficiency is generally measured in terms of either the number of effective theoretical plates or the Trenzzahl number, a measure of the degree of separation of a pair of homologues<sup>1,2</sup>. A general review of gas flow in GC was presented by Guiochon<sup>3</sup>, and aspects relating to programmed temperature GC were discussed by Harris and Habgood<sup>4</sup>.

While the measured flow-rate at the column outlet can be used as a guide when installing capillary columns, the average carrier gas velocity is the parameter more directly related to column performance. For operation with atmospheric outlet pressure, such as is the case in most capillary GC, the optimum average velocity is relatively constant for different column lengths and internal diameters, depending principally on the type of carrier gas used. For columns between 0.2 and 0.5 mm I.D., typical quoted values are 25-30 cm/sec for helium and 45-50 cm/sec for hydrogen<sup>2,5,6</sup>.

Jennings and Adam<sup>7</sup> discussed the effects of the rate of temperature programming and carrier gas velocity on the speed of analysis and separation efficiency in capillary gas chromatography. Jones *et al.*<sup>8</sup> discussed an approach to optimizing performance in temperature programmed analyses in terms of both flow-rate and program rate. This article, however, did not note the direct relationship between column temperature and flow-rate that comes as a consequence of the type of flow regulation employed<sup>9</sup>.

Sellier and Guiochon<sup>10</sup> discussed the influence of the type of gas chromatography-mass spectrometry (GC-MS) coupling on column performance. Due to a limited pumping capacity they were not able to operate at the optimum flow-rate when using direct coupling, and this combined with the use of a very long capillary column led them to erroneously infer that column efficiency at a given average velocity was not affected by the column outlet pressure. Hatch and Parrish<sup>6</sup> subsequently showed that significantly higher average velocities were required when using direct coupling with its associated zero effective outlet pressure, and Cramers *et al.*<sup>5</sup> in a detailed analysis proved that it is the volume flow-rate that needs to remain the same for a given column to maintain optimum efficiency with variations in outlet pressure.

The following discussion reviews the effects on flow-rate requirements of the three principal forms of capillary GC-MS interface: direct coupling, open split and capillary leak. Equations and figures are presented enabling rapid determination of parameters such as optimum average velocity, dead time, flow-rate and inlet pressure for various situations. The effects on actual flow-rates of changes in column temperature with the two principal forms of flow regulation are examined in conjunction with the type of GC-MS interface employed.

#### EFFECT OF INTERFACE TYPE

##### *Direct coupling*

Cramers *et al.*<sup>5</sup> showed that column length and diameter had a very significant effect on the optimum average velocity when using directly coupled columns. Direct coupling in this context refers to situations in which the column is inserted right into the ion source, as well as when it is connected via a section of relatively high conductance tubing such that the column outlet pressure is still effectively zero. They showed that the optimum flow-rate from atmospheric outlet pressure studies can be used directly with vacuum outlet pressure to obtain the optimum efficiency. Optimum flow-rate for a particular temperature can be found from the following expression:

$$Q = \frac{\pi d^4 (P_i^2 - P_0^2)}{256\eta L} \quad (1)$$

using the optimum value for  $P_i = P_{i,\text{opt,atm}}$ , which in turn can be found from an iterative solution to Poiseuille's equation<sup>11</sup>:

$$\frac{(P_i^2 - P_0^2)^2}{(P_i^3 - P_0^3)} = \frac{128\eta L \bar{v}}{3d^2} \quad (2)$$

using  $\bar{v} = \bar{v}_{\text{opt,atm}}$ . Fig. 1 shows the result of this calculation for different column lengths for hydrogen (using  $\bar{v}_{\text{opt,atm}} = 50$  cm/sec) and helium (using  $\bar{v}_{\text{opt,atm}} = 25$  cm/sec) for three different diameter columns at 20°C. Where  $Q_{\text{opt}}$  is known, the flow-rate for directly coupled columns can be simply measured using the expression<sup>11</sup>:

$$Q = \frac{64\pi\eta L^3}{9t_a^2} \quad (3)$$

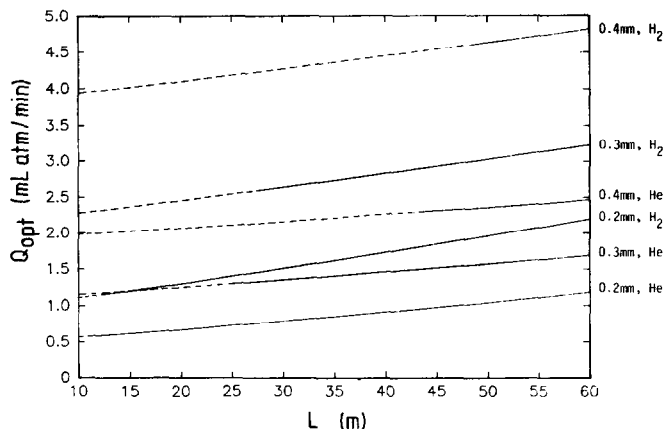


Fig. 1. Optimum flow-rates in ml/min at atmospheric pressure against column length for the internal column diameters and carrier gases indicated at 20°C. Dotted regions represent column lengths that will require sub-atmospheric inlet pressure when direct coupling is used. Values of 25 cm/sec for helium and 50 cm/sec for hydrogen as being the optimum average velocities with atmospheric outlet pressure operation have been used as the basis for calculations.

or alternatively, simply predict the optimum dead time,  $t_a = t_{a,opt,vac}$  from the rearrangement of eqn. 3:

$$t_{a,opt,vac} = \left( \frac{64\pi\eta L^3}{9Q_{opt}} \right)^{\frac{1}{2}} \quad (4)$$

The conversion factor for ml atm/min to S.I. units of  $m^3 Pa/sec$  is  $1.6885 \cdot 10^{-3}$ .

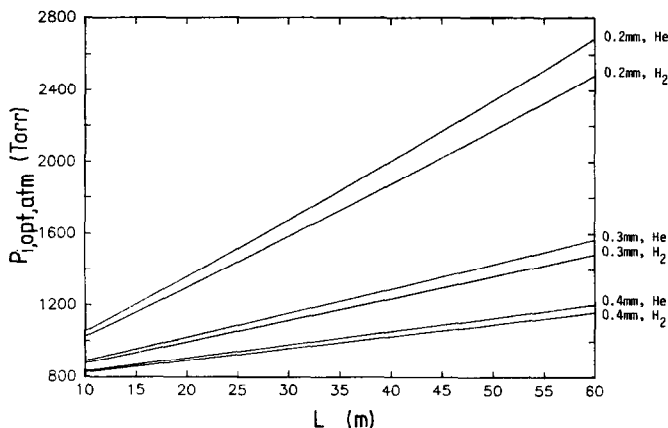


Fig. 2. Column inlet pressures required with atmospheric outlet pressure to generate the optimum flow-rates at 20°C in Fig. 1 for the lengths, internal diameters and carrier gases indicated.

The average velocity required with directly coupled columns is related to the optimum average velocity at atmospheric outlet pressure by the expression<sup>5</sup>:

$$\bar{v}_{\text{opt,vac}} = \bar{v}_{\text{opt,atm}} \cdot \frac{(P_{i,\text{opt,atm}}^3 - P_{\text{atm}}^3)}{(P_{i,\text{opt,atm}}^2 - P_{\text{atm}}^2)^{3/2}} \quad (5)$$

Figs. 3–5 illustrate the various parameters relating specifically to directly coupled columns versus column length for 3 different diameters and hydrogen and helium carrier gases at 20°C. Figs. 1 and 2 were obtained from eqns. 1 and 2 using ten different values for column length and constructing a curve of best fit. Fig. 4 was obtained from eqn. 5 for the same points, and Fig. 5 was obtained from  $t_a = L/\bar{v}$ . Fig. 3 was obtained from a rearrangement of eqn. 1, substituting  $P_0 = 0$  and  $Q = Q_{\text{opt}}$ :

$$P_i = \left( \frac{256\eta LQ}{\pi d^4} + P_0^2 \right)^{1/2} \quad (6)$$

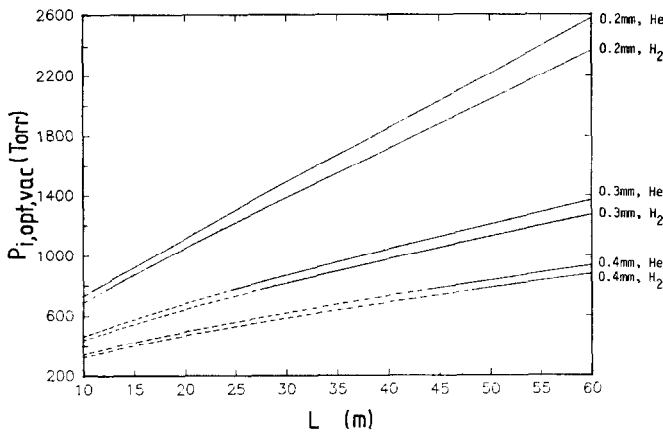


Fig. 3. Column inlet pressures required with vacuum outlet pressure (direct coupling) to generate the optimum flow-rates at 20°C in Fig. 1 for the lengths, internal diameters and carrier gases indicated. Dotted regions represent column lengths that will require sub-atmospheric inlet pressure.

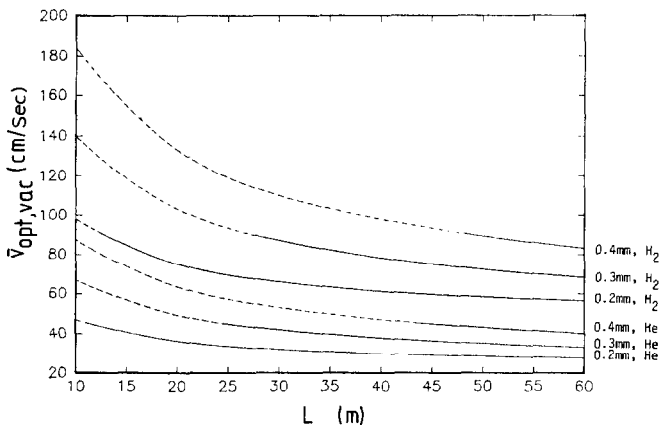


Fig. 4. Average carrier gas velocities required with vacuum outlet pressure (direct coupling) to generate the optimum flow-rates at 20°C in Fig. 1 for the lengths, diameters and carrier gases indicated. Dotted regions represent column lengths that will require sub-atmospheric inlet pressure.

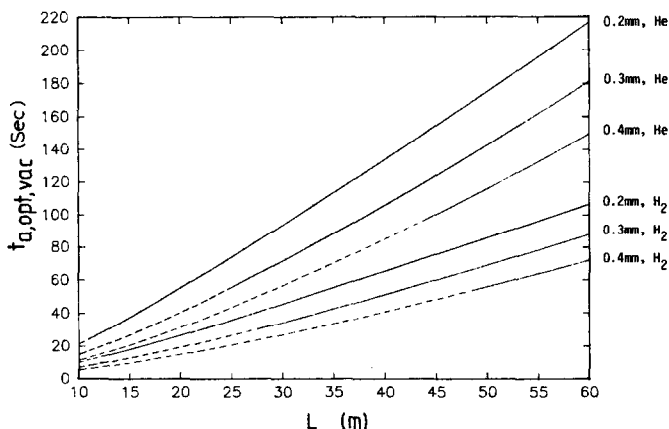


Fig. 5. Dead time required with vacuum outlet pressure (direct coupling) to generate the optimum flow-rates at 20°C in Fig. 1 for the lengths, internal diameters and carrier gases indicated. Dotted regions represent column lengths that will require sub-atmospheric inlet pressure.

The dotted region in each figure represents the column lengths for which sub-atmospheric inlet pressures would be required. Figs. 3–5 relate only to directly coupled columns with zero effective outlet pressure, while the dotted region in Fig. 1 refers to directly coupled columns as well, although the values for  $Q_{opt}$  are independent of the type of interface. While sub-atmospheric inlet pressures can be achieved readily enough, this naturally precludes the use of inlet splitting for injection. Column lengths and diameters can thus be quickly chosen by referring to the figures such that this situation does not arise.

#### *Open split*

In this interface, the pressure at the column outlet is maintained near 1 atmosphere, and hence the optimum average velocity will not differ from the values quoted for atmospheric outlet pressure.

#### *Capillary leak*

A third common type of interface incorporates a length of fine capillary tubing or other form of constriction between the end of the column and the mass spectrometer. This provides a substantial pressure drop so that a column is not exposed directly to the vacuum of the mass spectrometer, and yet all the sample is delivered to the ion source. This will result in atmospheric pressure at the column outlet for a specific flow-rate for each carrier gas, such that no change from normal atmospheric outlet operation is required. Even over the relatively wide range of flow-rates required to accommodate short, narrow bore columns up to long, wide bore columns, such as 0.5 to 3.0 ml atm/min for helium (Fig. 1), the difference in column outlet pressure remains less than a factor of 2 and the theoretical increase required in average velocity to maintain flow-rates is less than 30%.

For example an interface constructed of a 12-cm length of 0.1 mm internal diameter fused-silica tubing results in approximately 1 atmosphere outlet pressure when the optimum flow-rate (based on  $\bar{v}_{opt,atm} = 25$  cm/sec) of 2.5 ml atm/min of

helium is used for a 60 m × 0.4 mm column. A 20 m × 0.2 mm column with the optimum flow-rate of 0.7 ml atm/min of helium results in a calculated outlet pressure of around 400 Torr when used with same interface. The required inlet pressure can be found from eqn. 6, and from eqn. 2 the average velocity will need to be 31 cm/sec. This is an increase of only 25% over the atmospheric outlet pressure value, and almost within the normal quoted range.

Generally the differences in column outlet pressure in these cases can be ignored, and the normal atmospheric outlet pressure optimum average velocities can be used with little or no observable change in separation efficiency.

To calculate the length of a piece of capillary necessary to give atmospheric outlet pressure when constructing a capillary leak interface the following expression can be used:

$$L = \frac{\pi d^4 P_{\text{atm}}^2}{256 \eta Q_{\text{opt}}} \quad (7)$$

where  $L$  and  $d$  are the length and diameter of the interface tubing.

#### EFFECT OF TEMPERATURE PROGRAMMING

The following discussion points out the various changes that occur in flow-rates and average velocities as a consequence of changing column temperature after a flow-rate has been set with either constant pressure drop or "flow control". The influence that the type of GC-MS interface has on these changes is examined.

The theoretical optimum average velocity,  $\bar{v}_{\text{opt}}$ , increases slightly as temperature rises, due to the dependence, in the Van Deemter equation, of  $\bar{v}_{\text{opt}}$  on the diffusion coefficient in the gas, and to some extent, liquid phases<sup>3</sup>. For the purposes of this discussion  $\bar{v}_{\text{opt}}$  is not considered as varying with temperature, and also any changes in the column dimensions with increased temperature are ignored.

#### *Isobaric pressure control*

"Isobaric" refers to those systems in which the inlet pressure is set to a fixed value and hence a constant pressure drop is maintained throughout a temperature programmed analysis<sup>12</sup>. In these cases, the average carrier gas velocity and flow-rate at the column outlet,  $Q$ , will fall such that a value at a higher temperature will be related to a value at a lower temperature by the factor  $\eta_1/\eta_2$ , where  $\eta_1$  and  $\eta_2$  are carrier gas viscosities at the lower and higher temperatures respectively. This follows directly from Poiseuille's equation for average carrier gas velocity:

$$\bar{v} = \frac{(P_1^2 - P_0^2)^2 3d^2}{(P_1^3 - P_0^3) 128 \eta L} \quad (8)$$

and from eqn. 1 describing flow-rate. This effect is illustrated in Fig. 6a. The flow-rate that would be measured at room temperature outside the column oven must be adjusted for the temperature difference:

$$Q_{\text{end}} = \frac{\eta_1 T_1}{\eta_2 T_2} \cdot Q_1 \quad (9)$$

where  $Q_1$  is the flow-rate at the temperature corresponding to  $\eta_1$ , and  $Q_{\text{end}}$  is the measured flow-rate at room temperature corresponding to a column temperature  $T_2$  with a carrier gas viscosity  $\eta_2$ .

Fig. 6b shows the effect of column temperature on  $Q_{\text{end}}$  relative to the value at 20°C.

With isobaric pressure control, there is no difference in the relative effects of direct coupling or open split interfaces, and the column length, diameter, flow-rate and carrier gas also have no effect on these relationships.

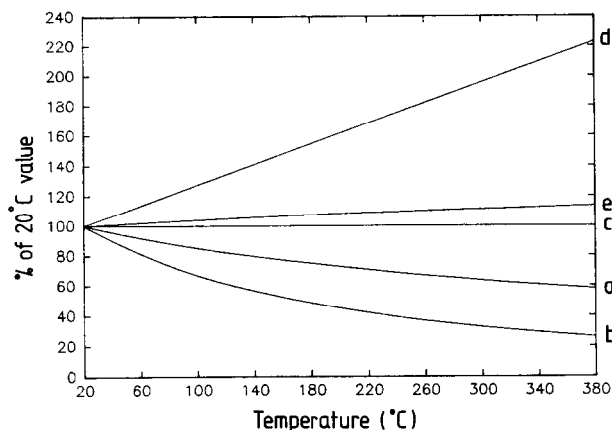


Fig. 6. Effects of temperature programming on various parameters after flow-rate has been set for different flow control and GC-MS interface combinations. The vertical axis shows the values as a percentage of any initial value at 20°C. (a)  $Q, Q_{\text{av}}$  and  $\bar{v}$  with isobaric pressure control and any interface. (b)  $Q_{\text{end}}$  with isobaric pressure control and any interface. (c)  $Q_{\text{end}}$  with mass flow control and any interface. (d)  $Q$  with mass flow control and any interface. (e)  $Q_{\text{av}}$  and  $\bar{v}$  with mass flow control and direct coupling.

For example a 25 m × 0.2 mm column programmed from 20°C to 200°C with an initial average velocity of 25 cm/sec using helium has  $Q = Q_{\text{end}} = 0.73$  ml atm/min at 20°C from eqns. 1 and 2. The average flow-rate, as defined by the ratio of column volume to dead time is 0.47 ml/min. At 200°C the average velocity will be:

$$\begin{aligned} \bar{v} &= \frac{(1.941 \cdot 10^{-5})}{(2.672 \cdot 10^{-5})} \cdot 25 \text{ cm/sec} \\ &= 18.2 \text{ cm/sec} \end{aligned}$$

$Q = 0.53$  ml atm/min,  $Q_{\text{end}} = (293/473) \cdot 0.53 = 0.33$  ml atm/min,  $Q_{\text{av}} = 0.34$  ml/min.

#### Flow controller

When flow-rate is regulated by a flow controller, a constant rate is maintained

through the controller regardless of any changes downstream such as in temperature or by installing a different column (Fig. 6c). However, the parameter that remains constant is  $Q_{\text{end}}$ , and hence changes to the actual flow-rate through the column occur whenever there is a change in temperature<sup>3</sup>. The flow-rate through the column will be:

$$Q = \frac{T_c}{T_r} \cdot Q_{\text{end}} \quad (10)$$

Thus in the example above the 0.73 ml atm/min becomes 1.00 ml atm/min at 200°C. Fig. 6d illustrates the effect on  $Q$  of changing column temperature with a flow controller in the line.

More relevant to the column performance, however, is the average velocity or average flow-rate. This effect will depend on the type of interface employed.

*Atmospheric outlet pressure (open split, capillary leak interfaces).* Average flow-rate,  $Q_{\text{av}}$ , can be found from  $Q$  from the following expression<sup>13</sup>:

$$\begin{aligned} Q_{\text{av}} &= Q \cdot \left[ \frac{3\left(\frac{P_i}{P_o}\right)^2 - 1}{2\left(\frac{P_i}{P_o}\right)^3 - 1} \right] \\ &= Q \cdot \frac{3(P_i^2 - P_o^2) P_o}{2(P_i^3 - P_o^3)} \end{aligned} \quad (11)$$

At a flow-rate  $Q_1$  at room temperature with  $P_i = P_1$ , the average flow-rate  $Q_{\text{av},1}$  will be

$$Q_{\text{av},1} = Q_1 \cdot \frac{3(P_1^2 - P_{\text{atm}}^2) P_{\text{atm}}}{2(P_1^3 - P_{\text{atm}}^3)}$$

At a column temperature  $T_c$  the flow-rate will be  $Q_2 = Q_1 \cdot T_c/T_r$  with an inlet pressure  $P_2$  when a flow controller exists in the line. The new average flow-rate  $Q_{\text{av},2}$  is now

$$Q_{\text{av},2} = Q_1 \cdot \frac{T_c}{T_r} \cdot \frac{3(P_2^2 - P_{\text{atm}}^2) P_{\text{atm}}}{2(P_2^3 - P_{\text{atm}}^3)}$$

and the ratio is therefore

$$\frac{Q_{\text{av},2}}{Q_{\text{av},1}} = \frac{T_c(P_2^2 - P_{\text{atm}}^2) (P_1^3 - P_{\text{atm}}^3)}{T_r(P_2^3 - P_{\text{atm}}^3) (P_1^2 - P_{\text{atm}}^2)} \quad (12)$$

$P_1$  and  $P_2$  can be calculated from eqn. 6 using the appropriate values for flow-rate and viscosity. Taking the example of the 25 m × 0.2 mm column using helium as



the carrier gas, programming from 20°C to 200°C with an initial average velocity of 25 cm/sec, corresponding to an initial flow-rate of 0.73 ml atm/min, from eqn. 6,  $P_1 = 1514$  Torr, and  $P_2$  at 200°C = 3319 Torr. From eqn. 12

$$\begin{aligned} \frac{Q_{av,2}}{Q_{av,1}} &= \frac{473}{293} \cdot 0.769 \\ &= 1.24 \end{aligned}$$

The factor increase in average velocity will be the same as this, since  $\bar{v} = Q_{av}/A$ . The percentage increases thus clearly depends on the actual flow-rate, the column length and column diameter, as  $P_i$  is related to all these. The lower the initial inlet pressure, the larger the percentage increase in average velocity with increasing temperature.

Fig. 7 shows the percentage increase in  $\bar{v}$  and  $Q_{av}$  with temperature for several situations relative to an initial value at 20°C. These are all much larger increases than the theoretical increase in  $\bar{v}_{opt}$  with increasing temperature.

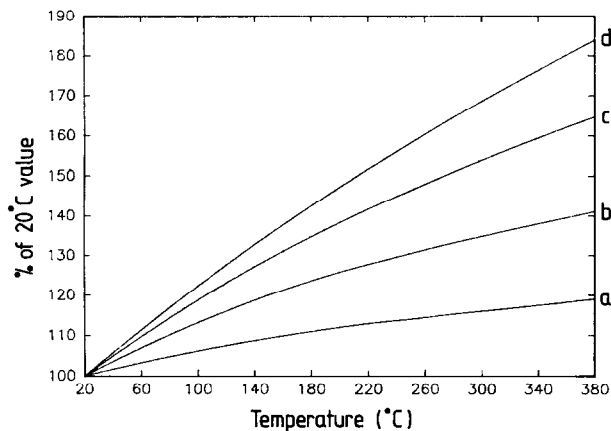


Fig. 7. Effects of temperature programming on  $Q_{av}$  and  $\bar{v}$  after flow-rate has been set with a mass flow controller and with atmospheric outlet pressure. The vertical axis shows the values as a percentage of the specific initial values at 20°C for the columns indicated. (a) 50 m  $\times$  0.2 mm with hydrogen as carrier gas, initial  $\bar{v} = 50$  cm/sec, initial  $Q_{av} = 0.94$  ml/min,  $Q_{end} = 2.0$  ml atm/min. (b) 25 m  $\times$  0.2 mm with hydrogen as carrier gas, initial  $\bar{v} = 50$  cm/sec, initial  $Q_{av} = 0.94$  ml/min,  $Q_{end} = 1.4$  ml atm/min. (c) 25 m  $\times$  0.3 mm with hydrogen as carrier gas, initial  $\bar{v} = 50$  cm/sec, initial  $Q_{av} = 2.12$  ml/min,  $Q_{end} = 2.5$  ml atm/min. (d) 25 m  $\times$  0.5 mm with helium as carrier gas, initial  $\bar{v} = 30$  cm/sec, initial  $Q_{av} = 3.53$  ml/min,  $Q_{end} = 4.0$  ml atm/min.

*Vacuum outlet pressure (direct coupling).* As  $P_0$  approaches zero in eqns. 11 and 12, the increase in average flow-rate can be seen to approach

$$\frac{Q_{av,2}}{Q_{av,1}} = \frac{T_c P_1}{T_r P_2} \quad (13)$$

However, this ratio can be found more simply without the use of inlet pressure terms. Since  $\bar{v} = L/t_a$ , substituting this and  $K = 64\pi L/9$  in eqn. 3 gives

$$Q_1 = K\eta_1 \bar{v}_1^2$$

and

$$Q_2 = K\eta_2\bar{v}_2^2$$

where  $\bar{v}_1$  and  $\bar{v}_2$  are the average velocities corresponding to  $Q_1$  and  $Q_2$ , respectively. Since  $Q_2 = Q_1 \cdot T_c/T_r$

$$\bar{v}_1 = \left( \frac{Q_1}{K\eta_1} \right)^{\frac{1}{2}}$$

$$\bar{v}_2 = \left( \frac{Q_1 T_c}{K\eta_2 T_r} \right)^{\frac{1}{2}}$$

Hence

$$\frac{\bar{v}_2}{\bar{v}_1} = \left( \frac{\eta_1 T_c}{\eta_2 T_r} \right)^{\frac{1}{2}} \quad (14)$$

In the example from above, a 25 m  $\times$  0.2 mm column programmed from 20°C to 200°C with helium directly coupled to a mass spectrometer will have an increase in velocity of

$$\frac{\bar{v}_2}{\bar{v}_1} = \left( \frac{1.941 \cdot 10^{-5} \cdot 473}{2.672 \cdot 10^{-5} \cdot 293} \right)^{\frac{1}{2}} = 1.083$$

This figure is again independent of flow-rate, column length, diameter and carrier gas. Fig. 6e illustrates the percentage increase in average velocity and average flow-rate when using directly coupled columns and a flow controller. It can be seen that only slight increases are encountered in this situation.

It should be noted that the changes in flow-rates with column temperature described represent the equilibrium state. This is approximated by relatively slow program rates, but at faster program rates the changes will be somewhat less than those specified due to the time taken for equilibrium to be reached.

#### EFFECTS OF HIGHER ISOTHERMAL TEMPERATURES

Figs. 1–5 presented optimum values of various parameters that correspond to flow-rates at 20°C that yield average velocities of 25 cm/sec and 50 cm/sec, respectively for helium and hydrogen with atmospheric outlet pressure. Higher temperature operation will change all these to some extent, with the degree of change depending on column length, diameter and carrier gas. Fig. 8 illustrates the changes for the specific example of a 25 m  $\times$  0.2 mm internal diameter column with helium as carrier gas. Higher values of  $Q$  will be necessary to maintain the same average velocities (Fig. 8a), which requires higher inlet pressures (Fig. 8b). The optimum flow-rate

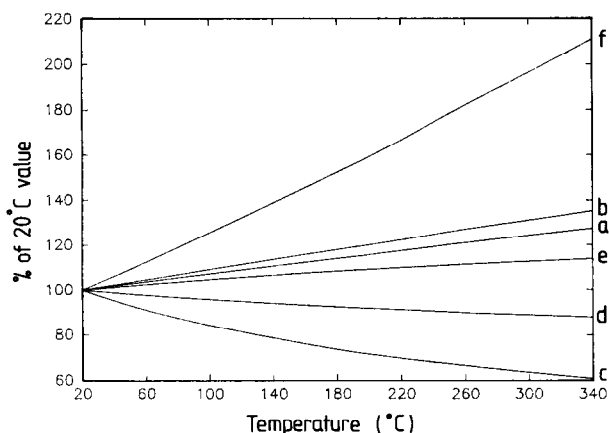


Fig. 8. Effects of increased isothermal temperature operation on optimum parameters for the specific case of a 25 m  $\times$  0.2 mm internal diameter column with helium as carrier gas. 25 cm/sec was used as the optimum average velocity for all temperatures with atmospheric outlet pressure. The vertical axis shows the values as a percentage of the specific initial values at 20°C. (a)  $Q_{opt}$ , initial value 0.73 ml atm/min; (b)  $P_{i,opt,atm}$ , initial value 1515 Torr; (c)  $Q_{end,opt}$ , initial value 0.73 ml atm/min; (d)  $\bar{v}_{opt,vac}$ , initial value 33.7 cm/sec; (e)  $t_{a,opt,vac}$ , initial value 74.2 sec; (f)  $Q_{end}$  set at 20°C and isobaric pressure control to give the optimum flow-rate at higher temperature, initial value 0.73 ml atm/min.

measured at room temperature (e.g. via a calibrated vacuum gauge) will fall (Fig. 8c). The optimum average velocity and dead time with vacuum outlet pressure will be the least affected (Fig. 8d and e). Fig. 8f illustrates the necessary increase in  $Q_{end}$  where this is set at room temperature with isobaric pressure control prior to establishing the column temperature.

#### PRACTICAL CONSIDERATIONS

The reduction in flow-rate and average velocity with rising temperature and isobaric flow control is a well known phenomenon. This can generally be compensated for in practice by setting flow-rates such that the optimum average velocity is achieved near the middle of the temperature range. *i.e.* set initial average velocity to  $\bar{v}_{opt} \cdot (\eta_m/\eta_s)$  where  $\eta_m$  and  $\eta_s$  are the carrier gas viscosities at the middle and start of the temperature range, respectively. This then maintains the flow-rate closer to the optimum value at all times.

With flow control and vacuum outlet pressure, average velocity is maintained very close to the starting value. Where flow control is used with atmospheric outlet pressure operation, significant increases in average velocity can occur with increases in temperature, particularly where wider bore columns are used.

From Fig. 7d, a 25 m  $\times$  0.5 mm column with an initial average velocity of 30 cm/sec at 20°C with atmospheric outlet pressure results in 50 cm/sec at 300°C. In these cases close to optimum average velocities would be maintained again if the middle of the temperature range was chosen to set flow-rates. In the above example, 30 cm/sec is required at 160°C. From eqn. 2,  $P_i = 942$  Torr; from eqn. 1  $Q = 3.97$  ml atm/min;  $Q_{end} = 2.68$  ml atm/min. Since a flow controller is employed, the latter is the value that will remain constant throughout the run. Since  $Q$  at 20°C is 2.68 ml

atm/min, from eqn. 6  $P_i$  at this temperature is 859 Torr, and the average velocity at 20°C will be, from eqn. 8, 21 cm/sec. A similar method yields an average velocity at 300°C of 43 cm/sec.

It can be seen from the above discussion the potential for significant discrepancy between actual and optimum flow-rates at higher temperatures during temperature programming unless the correct compromise flow-rate is set.

While average velocity can be determined and set accurately by the measurement of dead times, this can be time consuming where they are of the order of two or three minutes. The simplest method of assuring close to optimum flow-rates in capillary GC-MS systems which incorporate a backing pressure gauge is to calibrate the gauge against actual flow-rates at room temperature (in directly coupled systems eqn. 3 enables this to be simply done). The gauge is a measure of  $Q_{end}$ , and so actual flow-rates at the column temperature can be found by multiplying by  $T_c/T_r$ . Calcula-

TABLE I

FLOW-RATES CORRESPONDING TO AVERAGE VELOCITIES 25 cm/sec (FOR HELIUM) AND 50 cm/sec (FOR HYDROGEN), RESPECTIVELY, WITH AN OUTLET PRESSURE OF 1 atm FOR THE COLUMNS AND TEMPERATURES INDICATED

The optimum flow-rate values are independent of the type of interface used. A calibrated vacuum gauge should correspond approximately to  $Q_{end,opt}$  at the midpoint of a temperature programmed analysis. With mass flow control this will be the value of  $Q_{end}$  for the whole analysis, while with isobaric pressure control the value of  $Q_{end}$  in the last column (*i.e.* set to this value with the column at room temperature) will result in the appropriate  $Q_{end,opt}$  at the desired temperature.

Column	Carrier gas	Temperature (°C)	$Q_{opt}$ (ml atm/min)	$Q_{end,opt}$ (ml atm/min)	$Q_{end,20°C}$ (ml atm/min)
25 m × 0.2 mm	H <sub>2</sub>	100	1.50	1.18	1.76
	H <sub>2</sub>	200	1.61	1.00	2.22
	H <sub>2</sub>	300	1.72	0.88	2.71
	He	100	0.78	0.62	0.92
	He	200	0.84	0.52	1.16
	He	300	0.91	0.46	1.43
25 m × 0.3 mm	H <sub>2</sub>	100	2.59	2.03	3.05
	H <sub>2</sub>	200	2.67	1.66	3.69
	H <sub>2</sub>	300	2.77	1.43	4.37
	He	100	1.35	1.06	1.59
	He	200	1.40	0.87	1.93
	He	300	1.46	0.75	2.30
50 m × 0.2 mm	H <sub>2</sub>	100	2.17	1.70	2.55
	H <sub>2</sub>	200	2.42	1.50	3.33
	H <sub>2</sub>	300	2.68	1.37	4.23
	He	100	1.13	0.88	1.33
	He	200	1.27	0.79	1.74
	He	300	1.41	0.72	2.23
50 m × 0.3 mm	H <sub>2</sub>	100	3.21	2.52	3.77
	H <sub>2</sub>	200	3.43	2.12	4.73
	H <sub>2</sub>	300	3.65	1.87	5.76
	He	100	1.67	1.31	1.96
	He	200	1.80	1.12	2.48
	He	300	1.92	0.98	3.03

lation of  $Q_{\text{opt}}$  at the midpoint of a temperature program, and hence  $Q_{\text{end,opt}}$ , enables flow-rates to be set correctly by the use of the backing pressure gauge. In the case of isobaric pressure control, the value of  $Q_{\text{end}}$  with the column at room temperature that will yield the appropriate  $Q_{\text{end,opt}}$  at the midpoint of the temperature program is the relevant parameter when installing a column.

Table I summarizes some typical values of  $Q_{\text{opt}}$ ,  $Q_{\text{end,opt}}$  and  $Q_{\text{end}}$  set at 20°C with isobaric pressure control to yield the optimum flow-rate at the specified temperatures.

## SYMBOLS

$Q$	flow-rate measured at atmospheric pressure and column temperature
$d$	internal column diameter
$P_i$	column inlet pressure
$P_o$	column outlet pressure
$\eta$	carrier gas viscosity
$L$	column length
$\bar{v}$	average carrier gas velocity
$t_a$	dead time, the retention time of an unretarded peak
$t_{a,\text{opt,vac}}$	optimum value of $t_a$ with zero outlet pressure
$Q_{\text{opt}}$	optimum value of $Q$
$\bar{v}_{\text{opt,vac}}$	optimum value of $\bar{v}$ with zero outlet pressure
$\bar{v}_{\text{opt,atm}}$	optimum value of $\bar{v}$ with atmospheric outlet pressure
$P_{i,\text{opt,atm}}$	optimum value of $P_i$ with atmospheric outlet pressure
$P_{i,\text{opt,vac}}$	optimum value of $P_i$ with zero outlet pressure
$P_{\text{atm}}$	atmospheric pressure
$T_r$	room temperature in Kelvin
$T_c$	column temperature in Kelvin
$Q_{\text{end}}$	flow-rate measured at atmospheric pressure and room temperature
$A$	internal cross-sectional area of the column
$Q_{\text{av}}$	average flow-rate ( $= AL/t_a$ )
$Q_{\text{end,opt}}$	optimum value of $Q_{\text{end}}$
$\bar{v}_{\text{opt}}$	optimum value of $\bar{v}$

## REFERENCES

- 1 R. E. Kaiser, *Z. Anal. Chem.*, 189 (1961) 1.
- 2 K. Grob, Jr. and K. Grob, *J. Chromatogr.*, 207 (1981) 291.
- 3 G. Guiochon, *Chromatogr. Rev.*, 8 (1966) 1.
- 4 W. E. Harris and H. W. Habgood, *Programmed Temperature GC*, Wiley, New York, 1966.
- 5 C. A. Cramers, G. J. Scherpenzeel and P. A. Leclercq, *J. Chromatogr.*, 203 (1981) 207.
- 6 F. W. Hatch and M. E. Parrish, *Anal. Chem.*, 50 (1978) 1164.
- 7 W. G. Jennings and S. Adam, *Anal. Biochem.*, 69 (1975) 61.
- 8 L. A. Jones, S. L. Kirby, C. L. Garganta, T. M. Gerig and J. D. Mulik, *Anal. Chem.*, 55 (1983) 1354.
- 9 N. W. Davies, *Anal. Chem.*, 56 (1984) 2600.
- 10 N. Sellier and G. Guiochon, *J. Chromatogr. Sci.*, 8 (1970) 147.
- 11 N. W. Davies, *Anal. Chem.*, 56 (1984) 2618.
- 12 A. Zlatkis, D. C. Fenimore, L. S. Ettre and J. E. Purcell, *J. Gas Chromatogr.*, March (1965) 75.
- 13 A. T. James and A. J. P. Martin, *Analyst (London)*, 77 (1942) 679.