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## INFLUENCE OF DIFFERENT CARRIER GASES AND TEMPERATURES ON THE OVERALL PERFORMANCE OF A PACKED COLUMN

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### SUMMARY

Using the carrier gases hydrogen, helium and nitrogen, the minimal plate height, the optimal flow-rate for this height and the corresponding pressure drop required for a 2-m column containing 10% of silicone oil on an 80-100-mesh support were determined at 50°, 100° and 150°. In order to evaluate the overall performance under the particular conditions, the column quality,  $Q$ , was calculated from the number of plates, the retention time and the pressure drop. It is found from these  $Q$  values that, for the column used, at temperatures above 70° hydrogen gives the largest number of plates in a fixed time under a restricted column input pressure, whereas at temperatures below 70° nitrogen is the most suitable carrier gas. With helium, the performances obtained under all conditions were poorer than those with hydrogen or nitrogen. The minimal plate height and flow-rate depend exponentially on the diffusion coefficient in the carrier gas.

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### INTRODUCTION

The carrier gas and the column temperature influence the performance of a packed gas chromatographic column in diverse ways: the different rate of diffusion of the sample components in the carrier gas, which is expressed by the diffusion coefficients,  $D_{pg}$ , results in different minimal plate heights,  $h_{min}$ , and different flow-rates,  $u_{min}$ , for the maximal separation efficiency of the column. The viscosity,  $\eta$ , of the carrier gas determines the pressure drop,  $\Delta P$ , which is necessary to set up a flow-rate  $u$ .

The viscosity and the diffusion coefficient are temperature dependent. Some selected values are listed in Table I.

The influence of the diffusion coefficient on the separation efficiency and the optimal flow-rate is given by the Van Deemter equation:

$$h = 2\lambda d_p + \frac{2\gamma D_{pg}}{u_0} + \frac{k'^2 d_p^2 u_0}{(1+k')^2 D_{pg}} + \frac{2}{3} \cdot \frac{k'}{(1+k')^2} \cdot \frac{d_p^2 \bar{u}}{D_1}$$

If it is assumed that  $u = \bar{u} = u_0$ , this equation is simplified to  $h = A + B/u + C_1 u$ .

TABLE I

DIFFUSION COEFFICIENTS<sup>1</sup>,  $D_{DC}$  ( $\text{cm}^2 \text{sec}^{-1}$ ), OF *n*-OCTANE AND VISCOSITIES<sup>2</sup>,  $\eta$  ( $\mu\text{P}$ ), FOR SOME CARRIER GASES

Carrier gas	$D_{DC}$ (30°)	$\eta$		
		50°	100°	150°
H <sub>2</sub>	0.277	94	103	112
He	0.248	208	229	249
N <sub>2</sub>	0.0726	188	208	227
Ar	0.0587	242	271	296
CO <sub>2</sub>	0.0589*	162	185	207

\* Estimated.

$B$  is proportional to the diffusion coefficient in the carrier gas, whilst

$$C_g = \frac{d_p^2}{D_{DC}} \cdot f(k')$$

is inversely proportional to  $D_{DC}$ . Large values of the diffusion coefficient increase  $B$  and thus  $h$ , but decrease  $C_g$  and  $h$ . The equations for the minimal plate height,  $h_{\min}$ , and the corresponding flow-rate,  $u_{\min}$ , are

$$h_{\min} = A + 2 \sqrt{B(C_g + C_1)}$$

$$u_{\min} = \sqrt{B/(C_g + C_1)}$$

For columns in which  $C_g \gg C_1$ , as with capillary columns,  $h_{\min}$  is independent of the diffusion coefficient, whilst  $u_{\min}$  is proportional to the diffusion coefficient and the particle diameter:

$$[u_{\min} = f(d_p D_{DC})]_{C_g \gg C_1}$$

For columns in which  $C_g \ll C_1$ , for example highly loaded supports with a large particle diameter,  $h_{\min}$  is dependent on the diffusion coefficient in the carrier gas, whilst  $u_{\min}$  is then dependent only on  $\sqrt{D_{DC}}$ . A thorough experimental study of these phenomena was carried out by Bohemen and Purnell in 1961<sup>3,4</sup>.

Because of the difficulty in determining the efficiency of a column at different temperatures independent of the solutes used, only a few, relatively old investigations are available on this subject<sup>5,6</sup>. The overall performance of packed gas chromatographic columns, in which the influence of the carrier gas on the diffusion and the viscosity is taken into account, has not been investigated hitherto with different carrier gases at different temperatures. Thus, recommendations as to which carrier gas facilitates the highest column performance are also contradictory<sup>7-11</sup>. A literature survey showed that the predominant opinion is that the gas with the lowest viscosity, that is, hydrogen, is the best carrier gas and the other gases give similar column performances.

*Overall performance of a chromatographic column*

The overall performance of a chromatographic column can be described by the column quality,  $Q$  (ref. 12). This value links the minimal effective plate height,  $H_{\min}$ , with the permeability,  $k_p$ , of the column and the viscosity,  $\eta$ , of the carrier gas. As the following derivation from the Carman-Kozeny equation<sup>2</sup> shows, a pressure correction factor,  $j'$ , must be introduced into the equation. The eqn. 1 used here for the column quality index:

$$Q = \frac{N^2}{t_R \Delta P j'} = (N/t_R) (N/\Delta P j') \quad (1)$$

gives the relationship between the achievable resolution,  $R = 2(t_2 - t_1)/(w_1 + w_2)$ , and the retention time or analysis time,  $t_R$ , of the second component and the available column input pressure,  $P_1$ , which is linked by the equation

$$\Delta P = P_1 - P_0$$

to the pressure drop,  $\Delta P$ , and the column outlet pressure,  $P_0$ .

$Q$  indicates how many effective plates,  $N$ , can be obtained with a pressure drop  $\Delta P$  in the total retention time  $t_R$ :

$$N = \sqrt{Q t_R \Delta P j'}$$

As the resolution,  $R$ , is directly proportional to the square root of the number of effective plates,  $Q$  also indicates the relationship between  $R$  achievable in time  $t_R$  with a pressure drop  $\Delta P$  for two solutes with a retention ratio  $r = t_2/t_1$ :

$$R = \frac{1}{4} \cdot \frac{r-1}{r} \sqrt{N}$$

$$R = \frac{1}{4} \cdot \frac{r-1}{r} \sqrt[4]{Q t_R \Delta P j'}$$

$Q$  is the product of the number of effective plates per retention time  $t_R$  and the number of actual plates per pressure drop, corrected by the pressure correction factor  $j'$  introduced by Halasz *et al.*<sup>13</sup> for the relationship between the flow-rate,  $\bar{u}$ , and the pressure drop,  $\Delta P$ . The relationship for  $\bar{u}$  is<sup>10</sup>

$$\bar{u} = \frac{k_p \Delta P j'}{\eta L} = \frac{L}{t_M} \quad (\text{cm/sec}) \quad (2)$$

With  $L = NH$  and  $t_M = t_R/(1 + k')$ , the equation for the column quality can be derived from this equation:

$$Q = \frac{N^2}{t_R \Delta P j'} = \frac{k_p}{\eta H^2 (1 + k')} = \frac{k_p (k' + 1)^4}{\eta h^2 k'^4 (k' + 1)} \quad (1a)$$

$Q$  is at its maximum at the flow-rate  $\bar{u}_{\min}$ , at which the minimum plate height,  $H_{\min}$ , is observed. For substances with different  $k'$  values, the highest column quality is found at  $k'$  values of about 4. The highest resolution between two peaks is then also obtained in this range.

With a pressure drop restricted to  $\Delta P_{\max}$ , the analysis time,  $t_R$ , for a defined

analysis problem with the necessary number of plates,  $N_{\text{req}}$ , is inversely proportional to the column quality of the column packing:

$$t_R = \frac{N_{\text{req}}^2}{\Delta P_{\text{max}} j' Q} \quad (3)$$

Thus, doubling  $Q$  enables the retention time to be halved.

Bristow and Knox<sup>14</sup> introduced a similar parameter, but with the number of theoretical plates,  $n$ . This performance parameter for liquid chromatography:

$$\pi = \frac{n^2}{t_R \Delta P} \quad (4)$$

leads, in gas chromatography at  $k' < 2$ , to excessively high values that are not directly related to the achievable resolution.

The performance index, PI, described by Golay<sup>15</sup> also contains, as shown by Halasz and Heine<sup>10</sup>, a term  $H_2 \eta / k_p$ . Because of the difficult theoretical considerations, the equation given by Golay has rarely been used in practice. In our experience, the column quality index,  $Q$ , defined in eqns. 1 and 1a is an excellent parameter for comparing support materials, columns and chromatographic methods, for investigating optimal analysis parameters and for the construction of high-performance columns.

## EXPERIMENTAL

The measurements were carried out with a commercially available gas chromatograph equipped with a flame-ionization detector and a pressure-controlled carrier gas supply. The 2-m stainless-steel column had an external diameter of 1/8 in.; the internal diameter was 2.1 mm. The column packing was 10% (w/w) of silicone oil DC 550 on Chromosorb W AW DMCS (80–100 mesh).

A gas sample with methane was used to determine the gas hold-up times.

The number of effective plates was determined at various temperatures using mixtures of  $n$ -alkanes. In order to determine the minimal plate heights,  $H_{\text{min}} = L/N$ , the flow-rate,  $\bar{u}_{\text{min}}$ , was sought at which the number of effective plates was greatest. The number of plates,  $N$ , and the separation number, TZ<sup>16,17</sup>, were calculated using eqns. 4 and 5 from the retention times  $t_R$  and the peak widths at half-height,  $b_{0.5}$ :

$$N = 5.54 \left( \frac{t_R - t_M}{b_{0.5}} \right)^2 \quad (5)$$

$$\text{TZ} = \frac{t_2 - t_1}{(b_{0.5})_1 + (b_{0.5})_2} - 1 \quad (6)$$

The separation efficiency was determined in each instance by interpolating graphically to a  $k'$  value of 4. The pairs of solutes listed in Table II were used for this purpose and these were then also used to calculate the separation numbers.

TABLE II

*n*-ALKANES USED TO MEASURE THE PLATE NUMBERS, AND THE  $k'$  VALUES AND RETENTION RATIOS ( $r$ ) OF THE ALKANES

Column temperature (°C)	<i>n</i> -Alkanes		
	$k'$	$k'$	$r$
50	Hexane 2.95	Heptane 7.29	2.48
100	Octane 3.20	Nonane 6.26	1.97
150	Decane 2.72	Undecane 4.54	1.68

## RESULTS

The results are shown in Table III and in the figures.

At a  $k'$  value of 4,  $h_{\min}$  and  $H_{\min}$  differ by the factor  $(k'/k' + 1)^2 = 0.64$ . The lowest plate height is always found with nitrogen or at the highest temperature. For the separation number, the highest values are obtained at the lowest temperature and with nitrogen as the carrier gas. The reason for this difference lies in the fact that the retention ratio,  $r$ , which contributes to the separation number, TZ, decreases with increasing temperature (see Table II).

$$\text{TZ} = \frac{t_2 - t_1}{(b_{0.s})_2 + (b_{0.s})_1} - 1 = 0.85 \cdot R_{n+1/n} - 1 \quad (7)$$

$$\text{TZ} = 0.21 (\ln r) \cdot \sqrt{N} - 1 \quad (7a)$$

As the temperature increases, the retention ratio,  $r$ , of the *n*-alkanes falls and reduces TZ, although  $N$  increases with increasing temperature.

The flow-rate,  $\bar{u}_{\min}$ , for the maximum performance of the column is lowest for nitrogen and, correspondingly, nitrogen also has the longest gas hold-up time,  $t_M$ .

The term  $\Delta P_j / \bar{u}_{\min} L$  is proportional, with a good degree of accuracy, to the tabulated viscosity of the carrier gases. Fig. 1 shows  $H_{\min}$  as a function of tempera-

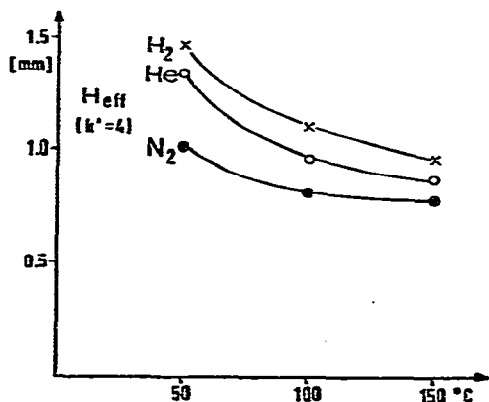


Fig. 1. Change of the minimal effective plate height  $H_{\min}$ , with temperature for various carrier gases, using a 2-m column with 10% DC 550 on Chromosorb W (80–100 mesh).

TABLE III

PERFORMANCE DATA FOR A 2-m COLUMN PACKED WITH 10% SILICONE OIL ON CHROMOSORB W AW DMCS (80-100 MESH)  
 Interpolated for an *n*-alkane component with  $k' = 4$ .

Parameter	50°			100°			150°		
	$H_2$	He	$N_2$	$H_2$	He	$N_2$	$H_2$	He	$N_2$
$h_{\min}$ (cm)	0.095	0.086	0.065	0.070	0.062	0.052	0.061	0.055	0.050
$H_{\min}$ (cm)	0.148	0.134	0.101	0.110	0.097	0.081	0.096	0.087	0.078
TZ	6.3	6.7	7.7	5.3	5.7	6.2	3.9	4.2	4.3
$\Delta P_{\min}$ (bar)	1.2	2.3	0.8	1.6	2.5	1.3	1.9	3.0	1.7
$J'$	0.956	0.914	0.973	0.939	0.907	0.952	0.927	0.892	0.935
$h_{\min}$ (cm/sec)	8.26	7.43	3.03	9.76	7.44	4.03	10.87	7.72	4.74
$t_M$ (sec)	24.2	26.9	66.1	20.5	26.8	49.6	18.4	25.9	42.2
$Q \cdot 10^{-3}$ (bar <sup>-1</sup> sec <sup>-1</sup> )	13.12	7.88	15.42	21.76	14.03	19.66	26.92	14.87	19.65
$u\Delta P/\sqrt{hL} \cdot 10^3$ (bar/cm <sup>2</sup> ·sec)	0.69	1.41	1.28	0.77	1.52	1.44	0.81	1.73	1.68
$r$		2.48			1.97			1.68	

ture for the various carrier gases. Fig. 2 shows the influence of temperature on the number of plates and the separation number. Fig. 3 shows the change in the flow-rate,  $\bar{u}_{min}$ , necessary for the maximal number of plates with temperature for various carrier gases.

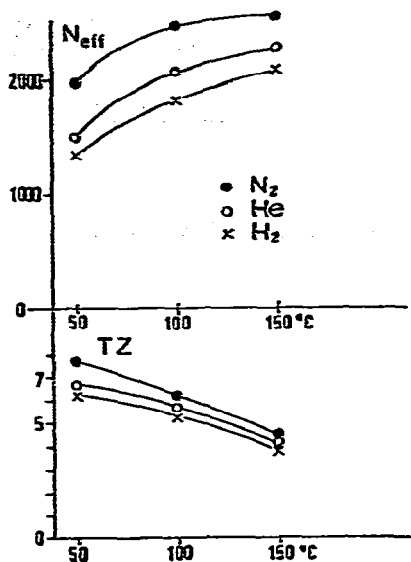


Fig. 2. Change of the separation number, TZ, and the number of effective plates,  $N$ , with temperature for various carrier gases. Column as in Fig. 1.

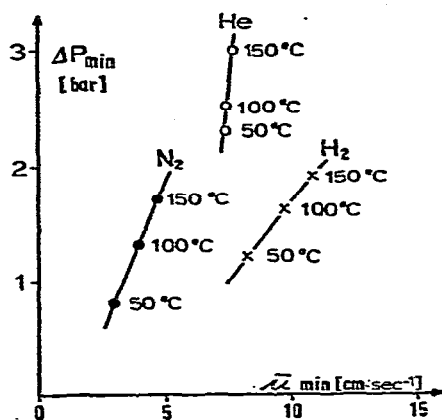


Fig. 3. Dependence of the optimal flow-rate,  $\bar{u}_{min}$ , on temperature for various carrier gases. Column as in Fig. 1.

Fig. 4 shows the main results, viz., the influence of temperature and carrier gas on the overall performance of the column examined, measured by the column quality index,  $Q$ . Whilst at 50° the highest  $Q$  value is obtained with nitrogen, hydrogen is the most suitable carrier gas for high performance at 100° and 150°.

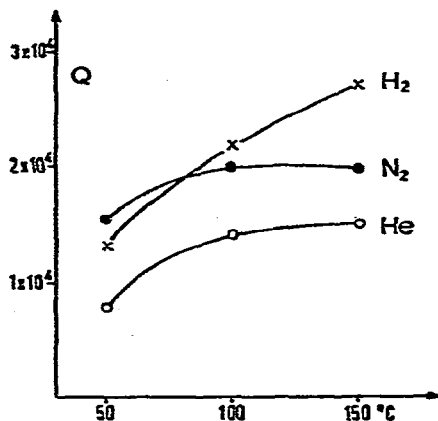


Fig. 4. Influence of temperature on the overall performance of the column tested for various carrier gases.

*Dependence of  $H_{min}$  and  $u_{min}$  on the diffusion coefficient*

For the minimal plate heights,  $H_{min}$ , and optimal flow-rates,  $\bar{u}_{min}$ , measured at 50°, there is a good correlation with the diffusion coefficients at 30°, which are shown in Table I, and the following equations apply:

$$H_{min} = A_1 D^{n_H} = 0.20 D^{0.26} \quad (8)$$

$$\bar{u}_{min} = A_2 D^{n_u} = 21.1 D^{0.74} \quad (9)$$

Table IV compares the plate heights measured at 50° and calculated according to eqns. 8 and 9.

TABLE IV

$H_{min}$  AND  $\bar{u}_{min}$  VALUES MEASURED AT 50° AND CALCULATED FROM THE DIFFUSION COEFFICIENTS IN TABLE I

Carrier gas	$\bar{u}_{min}$ (cm/sec)		$H_{min}$ (cm)	
	Measured	Calculated	Measured	Calculated
H <sub>2</sub>	8.26	8.12	0.148	0.143
He	7.43	7.48	0.134	0.139
N <sub>2</sub>	3.03	3.01	0.101	0.101

A significant feature of this correlation is that the sum of the exponents of the diffusion coefficient,  $n_H + n_u$ , is 1.

Thus, the observed dependence of the plate height and of the flow-rate on the diffusion coefficient assumes a midway position between the extreme cases of  $C_g \gg C_l$  and  $C_g \ll C_l$ , which have already been dealt with. For these cases also, as shown in the introduction, it is to be expected that  $n_H + n_u = 1$ , as Table V shows.

TABLE V

DEPENDENCE OF  $H_{min}$  AND  $\bar{u}_{min}$  ON THE DIFFUSION COEFFICIENT FOR THE COLUMN TESTED AND FOR THE CASES OF  $C_g \gg C_l$  AND  $C_g \ll C_l$

	Case					
	$C_g \gg C_l$	$n$	2-m column, 50°, 10% DC 550	$n$	$C_g \ll C_l$	$n$
$H_{min}$ is proportional*	$D^0$	0	$D^{0.26}$	0.26	$\sqrt{D}$	0.5
$\bar{u}_{min}$ is proportional	$D^1$	1	$D^{0.74}$	0.74	$\sqrt{D}$	0.5
$n_H + n_u$		1		1.00		1

\* If the eddy diffusion term  $A$  can be neglected.

There is thus a proven relationship between the minimum plate height,  $H_{min}$ , and the diffusion coefficient,  $D_{pg}$ , in the carrier gas and between the optimum flow-rate,  $\bar{u}_{min}$ , and the diffusion coefficient,  $D_{pg}$ , in the carrier gas.

As in the case of the column tested here the column quality,  $Q$ , for a constant  $k'$  value and a constant permeability  $k_p$ , is dependent only on the product  $\eta H^2$ , according to eqn. 1a, the parameter

$$\eta H^2 = \eta A_1^2 D^{2n_H}$$

determines  $Q$ . In order to ascertain the influence of the carrier gas on the column quality, we therefore calculated the product  $\eta D^{2n_H}$  in the range  $0 < n_H < 0.5$  from



the diffusion coefficients at 30° and viscosities at 50°. Fig. 5 shows the influence of  $n_H$  on the product  $\eta D^{2n}$ . Accordingly, in the range of small  $n$  values (capillary columns), hydrogen is the carrier gas with which the maximal column qualities can be achieved, whilst when  $n > 0.25$  nitrogen, argon or carbon dioxide is to be preferred. The diffusion coefficient of carbon dioxide used for the calculation is only an estimated value, so that the dependence in respect of carbon dioxide which is shown in Table V and Fig. 5 still requires experimental confirmation.

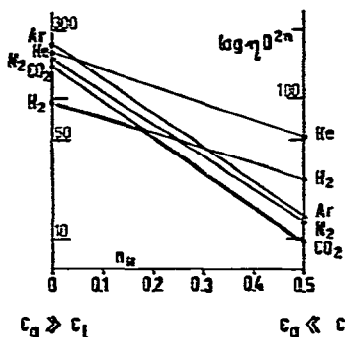


Fig. 5. Dependence of the product  $\eta D^{2n}$ , which is characteristic of the overall performance of the column, on  $n_H$  in the range between  $C_g \gg C_i$  and  $C_g \ll C_i$ . Low values for  $\eta D^{2n}$  give high column qualities,  $Q$ .

## CONCLUSIONS

The following conclusions can be drawn from the measurement results and calculations.

With hydrogen, as the carrier gas that has the lowest viscosity, the overall performance of a gas chromatographic column is greatest when  $C_g \gg C_i$  and  $n_H = 0$ , as, for example, with capillary columns.  $H_{min}$  is then independent of the carrier gas.

When  $C_g \ll C_i$ , as with more highly loaded packed columns,  $H_{min}$  is dependent on the carrier gas. Then, at least at low temperatures, the overall performance is better with a carrier gas of higher molecular weight which has a low diffusion coefficient,  $D_{pg}$ , for the sample component in the carrier gas.

In the range between these extreme cases, the use of nitrogen, argon or carbon dioxide can result in higher overall performances, as has been found for the column tested.

The dependence of  $H_{min}$  on the carrier gas falls as the temperature increases and, correspondingly, hydrogen is then the more suitable carrier gas.

Other relationships, which still have to be tested experimentally, apply in the case of columns that are used not at the maximum of the separation efficiency but with a flow-rate higher than  $\bar{u}_{min}$ .

## SYMBOLS

- $A$  Eddy diffusion term
- $A_1, A_2$  Constants
- $B$  Diffusion term
- $b_{0.5}$  Peak width at half-height

$C_2$	Gas phase diffusion term
$C_1$	Liquid diffusion term
$D$	Diffusion constant
$D_{\text{PG}}$	Diffusion constant in the carrier gas
$D_1$	Diffusion constant in the stationary liquid
$h$	Theoretical plate height
$h_{\text{min}}$	Minimal theoretical plate height
$H$	Actual plate height
$H_{\text{min}}$	Minimal actual plate height
$j'$	Pressure correction factor
$k'$	Capacity factor
$k_p$	Column permeability
$L$	Column length
$N$	Number of actual plates
$N_{\text{req}}$	Required number of actual plates
$n_H, n_a$	Exponents of diffusion coefficient
$\Delta P$	Pressure drop
$P_1, P_0$	Inlet and outlet pressure, respectively
$Q$	Column quality index
$R$	Resolution
$i_R, i_2, i_1$	Retention time
$t_M$	Gas hold-up time
$u$	Flow-rate
$\bar{u}$	Average flow-rate
$u_0$	Flow-rate at the end of the column
$\bar{u}_{\text{min}}$	Flow-rate for the minimal plate height
$\lambda, \gamma$	Constants in the Van Deemter equation
$\eta$	Viscosity

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