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PRESSURE INDUCED TURBULENCE IN A PACKED GAS CHROMATOGRAPHIC COLUMN

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SUMMARY

HETP *versus* carrier gas flow velocity curves have been measured on a low liquid load packed column operated under two different mean absolute pressures within wide flow velocity limits, using hydrogen as the carrier gas. In the case of the higher column pressure, a fall-off of the HETP occurred at a certain velocity, indicating the onset of turbulence in the flow of the carrier gas, whereas the corresponding curve obtained at the lower pressure displayed all the characteristics of laminar flow. The extent of turbulence was checked by measuring the characteristics of the dynamics of flow under the corresponding conditions.

INTRODUCTION

The idea that the laminar flow was the only practical kind of mobile phase motion in a packed or open gas chromatographic column was at one time widely accepted. However, it was seen in further investigations[2–4] that turbulent flow may also occur in the column, especially with packed columns, under conditions not very remote from the conventional ones.

A typical consequence of the onset of turbulence is a fall-off of the HETP at higher carrier gas velocities. However, this effect can also be interpreted in terms of GIDDINGS' coupling theory[5], and it is difficult to separate the coupling and the turbulence contribution from each other in terms of chromatographic measurements alone.

A great deal of valuable information on the role of turbulence in chromatography can be gained from papers published on the dynamics of flow of fluids[6–8]; the above papers clearly indicate that it is in a transitory streamlined-to-turbulent flow regime, rather than in a streamlined one, that many gas chromatography experiments are carried out with packed columns.

The present paper shows the role of the mean absolute column pressure as a turbulence inducing factor. Initially, the aim of the experiments presented here was to verify the concepts on the effect of the column length and the mean absolute column pressure on the course of the HETP *versus* flow velocity curve under streamlined flow conditions[9,10]. In measurements on a low liquid load packed column of a given length, operated at two different column outlet pressures, *i.e.*, at two different levels of mean

absolute column pressure, it turned out that while the results obtained at the lower absolute pressure were as expected for the whole range of flow velocities employed, there was a marked fall-off of the HETP at higher velocities in the measurement at the higher column pressure. Since it was suspected that this phenomenon stemmed from turbulence in the column, additional measurements were carried out on the dynamics of the carrier gas flow under the corresponding conditions.

EXPERIMENTAL

The measurement was carried out with a conventional column packing, 3 wt. % dinonyl phthalate on Chromosorb P 60–80 mesh, prepared by the slurry technique. The support (Carlo Erba, Italy) was screened till free from fines, dried at 200° for 2 h, and then coated with the stationary liquid (Griffin & George Ltd., Great Britain), using dichloromethane as the solvent. The column was a 0.75 m long stainless steel tube of 3 mm inner diameter, filled with 2.70 g of the above packing. Hydrogen was used as the carrier gas and a thermal conductivity detector was employed. Hexane was used as the solute, the samples being introduced in the form of about 40 μl charges of saturated hexane vapours in hydrogen with traces of air; a Zimmermann syringe (Zimmermann, D.D.R.) was employed. The injection port, column, and detector were kept at 40°.

The measurements proper were carried out on a Becker Multigraph 409 (Becker Delft, The Netherlands) adapted for work at high column inlet pressures and adjustable column outlet pressures; a more detailed description of the instrumentation used can be found in a previous paper[9]. The chromatograms were recorded by a Servogor RE 512 recorder (Goerz Electro G.m.b.H., Austria).

RESULTS AND DISCUSSION

The results of the measurements were processed in such a way as to produce the graphs in Fig. 1. Curves 1 and 2 were obtained at pressures of 1 and 3 atm, respectively, at the column outlet. Curves 1′ and 2′ represent the $j(P_i^2 - P_o^2)/2P_o$ *versus* $\bar{u}$ dependences corresponding to curves 1 and 2; P_i and P_o stand for the column inlet and column outlet pressures and j denotes the James-Martin compressibility factor.

The mean carrier gas velocity related to the HETP, $\bar{u}$, was determined from the ratio of the column length and the hold-up time of the air peak maximum. The apparent HETP, $\bar{H}$, was calculated by dividing the column length by the number of theoretical plates determined from the expression[11] $5.54(b/\Delta b_{1/2})^2$ where b and $\Delta b_{1/2}$ denote the distance of the solute peak maximum from the start line in the chromatogram and the peak width at the peak mid-height, respectively.

The data necessary for assessing the character of carrier gas flow were obtained by measuring the volume flow rate at the column outlet, using a soap-bubble flowmeter. The flow rate was expressed for the mean pressure and temperature in the column, employing the relation $\bar{v} = P'v'Tj/P_oT'$ where v' is the volume flow rate as measured at pressure P' and temperature T' and T is the column temperature. In order to make the data directly comparable with the results of chromatographic measurement, the column void cross-section, a, was calculated from several pairs of

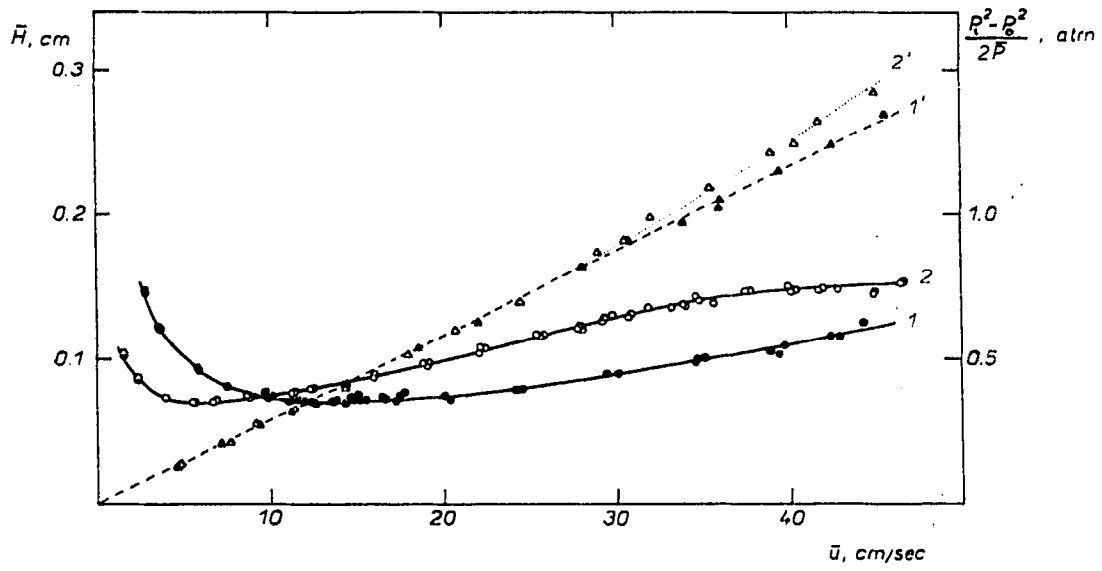

Fig. 1. $\bar{H}$–$\bar{u}$ curves and the corresponding $(P_i^2 - P_o^2)/2\bar{P}$ *versus* $\bar{u}$ plots obtained from the results measured for different levels of the mean absolute column pressure. Curves 1 and 2 correspond to P_o of 1 and 3 atm and P_i of within 1.08–2.36 and 3.02–4.45 atm, respectively, curves 1′ and 2′ have been constructed for the conditions corresponding to curves 1 and 2, respectively; P_i and P_o are the column inlet pressure and the column outlet pressure and $\bar{P}$ denotes the mean column pressure.

results determined at a lower flow velocity by means of the air peak hold-up time and the respective volume flow rate measured directly. Thus, the former relation could be rewritten to read $\bar{u} = P'v'Tj/P_oT'a$. The $\bar{u}$ values so obtained were plotted against the corresponding values of the parameter $j(P_i^2 - P_o^2)/2P_o$. It turned out that the $\bar{u}$ values determined by the above procedure were practically identical to the corresponding $\bar{u}$ values obtained by dividing the column length by the gas hold-up time also in the region of higher velocities. According to Darcy's law, the above plot should be a straight line as long as the flow is laminar, while a deviation from linearity should indicate the onset of turbulence.

Curve 1 in Fig. 1 displays a typical course for a low liquid load packing column, operated under streamlined carrier gas flow conditions, the latter being evidenced by the course of line 1′. With carrier gas velocities up to 28 cm/sec, the change in the course of the $\bar{H}$ *versus* $\bar{u}$ curve upon the rise of the column outlet pressure from 1 to 3 atm (curve 2) is quite in accordance with expectation[9]; the concurrence of lines 1′ and 2′ indicates that the flow also remains laminar under the elevated mean column pressure within the above flow velocity region. However, further increase in the flow velocity results in a flattening of the respective part of curve 2. The point of the HETP fall-off on curve 2 clearly coincides with the incipience of the deviation from linearity of curve 2′. Hence, the above point on curve 2 indubitably corresponds to the onset of turbulence in the column.

The above situation can be accounted for in terms of the modified Reynolds number[6], defined by $Re = 2\bar{u}'r_p d_m/\eta_m$ where $\bar{u}'$ is the actual carrier gas velocity within the packing bed, r_p is the radius of the packing particles, and d_m and η_m are the density and the viscosity coefficient of the carrier gas, respectively. As the carrier gas density rises with increasing pressure while the viscosity remains essentially

unchanged, the modified Reynolds number increases proportionally to the pressure at a given flow velocity.

The mobile phase moves forward only in the interparticle space and is stagnant within the intraparticle voids. As the intraparticle void volume is accessible by diffusion, the velocity determined from the air peak hold-up time is lower than the actual flow velocity by the factor of the interparticle-to-total void volume ratio. Since the interparticle and intraparticle void volumes are approximately equal with low liquid load Chromosorb P[12], we shall assume that $\bar{u}' = 2\bar{u}$ in our case. The particle size of the 60–80 mesh support corresponds to an average particle radius of 0.0107 cm, and the viscosity coefficient of hydrogen amounts to about 0.92×10^{-4} Poise at 40°. The critical point on curve 2, corresponding to a $\bar{u}$ value of 28 cm/sec, corresponds to a mean absolute column pressure of 3.42 atm, *i.e.*, to a carrier gas density of 2.66×10^{-4} g/cm^3. For curve 1, the same velocity gives a pressure and density of 1.46 atm and 1.14 g/cm^3, respectively. Hence, the Reynolds numbers corresponding to the points given by $\bar{u} = 28$ cm/sec ($\bar{u}' = 56$ cm/sec) on curves 1 and 2 as well as 1′ and 2′ amount to 3.42 and 1.46, respectively. This is in good agreement with ERGUN's findings[6] indicating that turbulence begins at a Reynolds number of about 3 in packed columns.

The transitory laminar-to-turbulent flow region is very large, being completely turbulent[6] at a Reynolds number as large as about 3000, so that there are wide limits in which a fall of the steepness of the ascending branch of an $\bar{H}$–$\bar{u}$ curve may come about upon increasing the mean absolute column pressure. In this respect, the raising of the absolute column pressure under laminar and under turbulent flow conditions will result in opposite effects. This situation may be demonstrated by comparing the results obtained by measurements under streamlined flow conditions using H_2 carrier gas[9] with the results arrived at by HALÁSZ *et al.*[13] who worked with N_2 carrier gas. Owing to the density of nitrogen being more than one order higher than that of hydrogen and the viscosity only about twice that of hydrogen, the measurements by the latter authors were probably carried out within the above transitory region with respect to the higher flow velocities; the courses of their experimental points show a definite tendency towards domed curvature of the ascending branches of the $\bar{H}$–$\bar{u}$ curves measured at 4.0 and 6.0 atm outlet pressures, especially if less weight is given to the last three points of the 6.0 atm curve.

In open columns, turbulence begins at much higher Reynolds numbers. That is why the results of the measurements by HAZELDEAN AND SCOTT[14], also performed under elevated mean absolute column pressures, obey the concepts of the laminar carrier gas flow.

CONCLUSIONS

The raising of the mean absolute pressure in a gas chromatographic column by increasing the column outlet pressure leads to the onset of turbulence in the carrier gas flow. With a packed column, the turbulence becomes apparent at a modified Reynolds number value of about 3, which is in conformity with the conclusions reported by KNOX[3] for measurements in a different system.

The laminarity or the extent of turbulence of flow is indicated by the course of the $j(P_i^2 - P_o^2)/2P_o$ *versus* $\bar{u}$ plot; the incipience of the deviation from linearity

coincides with that of a fall-off of the HETP on the corresponding $\bar{H}$–$\bar{u}$ curve.

The conflicting findings with respect to the pressure dependence of the course of the ascending branch of the HETP *versus* flow velocity curve are probably due to the turbulence. The high propensity of the carrier gas flow towards pressure induced turbulence in packed columns may be a complicating factor in the determination of the gas phase and liquid phase mass transfer resistance coefficients by methods based on HETP measurements with gases of different density[15].

It also seems questionable as to what extent specific retention volumes remain independent of the carrier gas flow rate when measured under turbulent flow conditions and calculated using the James-Martin compressibility factor.

REFERENCES

1 J. H. PURNELL, *Gas Chromatography*, John Wiley, New York, London, 1962, p. 58.
2 J. C. STERNBERG AND R. E. POULSON, *Anal. Chem.*, 36 (1964) 1492.
3 J. H. KNOX, *Anal. Chem.*, 38 (1966) 253.
4 V. PRETORIUS AND T. W. SMUTS, *Anal. Chem.*, 38 (1966) 274.
5 J. C. GIDDINGS AND R. A. ROBISON, *Anal. Chem.*, 34 (1962) 885.
6 S. ERGUN, *Chem. Eng. Prog.*, 48 (1952) 89.
7 G. TAYLOR, *Proc. Roy. Soc. Ser. A*, 233 (1954) 446.
8 R. ARIS, *Proc. Roy. Soc., Ser. A*, 253 (1956) 67.
9 J. NOVÁK AND P. BOČEK, *J. Chromatog.*, 52 (1970) 1.
10 J. NOVÁK, *J. Chromatog.*, 50 (1970) 385.
11 J. H. PURNELL, *Gas Chromatography*, John Wiley, New York, London, 1962, p. 104.
12 J. M. HARPER AND E. G. HAMMOND, *Anal. Chem.*, 37 (1965) 490.
13 I. HALÁSZ, G. DEININGER AND H.-O. GERLACH, *J. Chromatog.*, 35 (1968) 1.
14 G. S. F. HAZELDEAN AND R. P. W. SCOTT, *J. Inst. Petrol.*, 48 (1962) 380.
15 J. C. GIDDINGS AND P. D. SCHETTLER, *Anal. Chem.*, 36 (1964) 1483.