

CHROM. 7231

EFFECT OF THE CARRIER GAS VELOCITY ON THE RETENTION VOLUME IN GAS CHROMATOGRAPHY ON PORAPAK SORBENTS

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SUMMARY

Specific retention volumes (V_g) at 150° of *n*-heptane on two different species of Porapak P, Porapak Q and Porapak Q coated with different loadings of silicone oil F-60 were measured at carrier gas flow velocities up to about 25 cm/sec. The same measurements were also carried out with Alusil and a 30% F60-Sterchamol packing for comparison. In a flow velocity region dominated by the interphase mass transfer (higher velocities), there was an apparent correlation between the extent of the flow velocity-induced fall in V_g and the magnitude of the mass transfer coefficient (C) with the uncoated Porapaks. Porapaks that had similar magnitudes of C (of the order of 10^{-3} sec) showed only a slight dependence of V_g on the flow velocity, but batches of Porapak P were found that had an extraordinarily high value of C (of the order of 10^{-1} sec) and, consequently, a sharp decrease in V_g occurred on increasing the flow velocity. The modification of Porapaks with a stationary liquid may lead to an increase in V_g on increasing the flow velocity.

INTRODUCTION

Concepts based on an idealized model of chromatography involving infinitely rapid equilibration of the solute between the phases imply that the retention volume of the solute is independent of the flow velocity of the mobile phase. Owing to the large phase interface area and the extremely short distances over which the solute has to diffuse during its transfer between the phases, encountered with most of the commonly employed chromatographic systems, real chromatographic situations approach very closely this idealized situation and usually no significant changes in retention volume are observed when flow velocity of the mobile phase is varied. However, a more rigorous approach to this problem^{1,2} reveals that there must generally be a deviation from real (stationary) equilibrium even in the centre of the zone under non-stationary chromatographic conditions. The direction of this deviation is always such as to reduce the chromatographic distribution coefficient in comparison with that at perfect equilibrium. Provided that the zone spreading is controlled by the interphase mass transfer rate, the extent of the deviation increases as the resistance to solute mass transfer and the flow velocity of the mobile phase increase. Hence, in a region of higher

flow velocities, an increase in the velocity will result in excessive shortening of the retention time and, consequently, a decrease in the retention volume.

In gas-liquid chromatography, the dependence of the peak maximum position on kinetic parameters, such as the diffusivity of the solute in the carrier gas and the rate of solute interphase mass transfer, was studied earlier³⁻⁵. Whereas the theoretical predictions based on a simplified model of solute mass transfer suggested that the relative shifts in the peak maximum should be approximately equal to the reciprocal number of plates in the column, the experimental results showed the actual shifts to be up to about 10 times as large as those predicted theoretically⁴. There is in the literature⁶ also a mention of a case in which the retention volume measured on Porapak P increases with increasing flow velocity. This phenomenon, of course, cannot be explained in terms of the above theoretical concepts.

This paper deals with these flow velocity effects in gas-solid systems, particularly those which involve porous organic polymers of the Porapak type as sorbents. This study was carried out simultaneously with an investigation of the solute mass transfer in the above systems⁷, and these two papers are closely related.

EXPERIMENTAL

A detailed description of the experiments has been presented in the related paper⁷, and only a brief summary of the experimental conditions is given here.

All the results presented in this paper refer to *n*-heptane as a model solute, chromatographed at 150° with helium as carrier gas on the following sorbents: Porapak P batches 550 and 411, Porapak Q batch 558, Porapak P 411 extracted with benzene and Porapak Q558 coated with 5, 30 and 50% (w/w) of silicone oil F60, and also Alusil (sodium aluminosilicate) and a GLC packing of 30% F60-Sterchamol. All the Porapaks were obtained from Waters Ass., Framingham, Mass., U.S.A., the F60 silicone oil from Carlo Erba, Milan, Italy, Alusil from Slovnaft, Bratislava, Czechoslovakia, and Sterchamol from Sterchamolwerke, Dortmund, G.F.R.

The measurements were carried out on a Chrom 2 gas chromatograph (Laboratory Instruments, Prague, Czechoslovakia) with flame ionization detection; a 50 cm long stainless-steel column of 3 mm I.D. was employed throughout. The flow velocity of the carrier gas was measured with a Mariotte flask at the column outlet.

Several microlitres of *n*-heptane vapour containing a trace amount of methane (dead retention time marker) were injected into the apparatus with a Zimmerman syringe (Zimmerman, Leipzig, G.D.R.). Small sample charges (about 5 μ l) at high sensitivity settings (1/5th-1/20th of the full instrument sensitivity) were applied, thus giving results that represent the linear parts of the sorption isotherms.

RESULTS AND DISCUSSION

With all the sorbent materials studied, specific retention volumes⁸ were calculated from the results measured over a range of flow velocities of the carrier gas and plotted against the latter. The results obtained are presented in Figs. 1-10. The flow velocity of the carrier gas (v) is expressed in millilitres (at the column temperature and mean pressure) per second. As the porosities (ϵ) of the packings varied around a value of 0.8, the cross-section (φ_0) of the empty column being 0.0706 cm², a

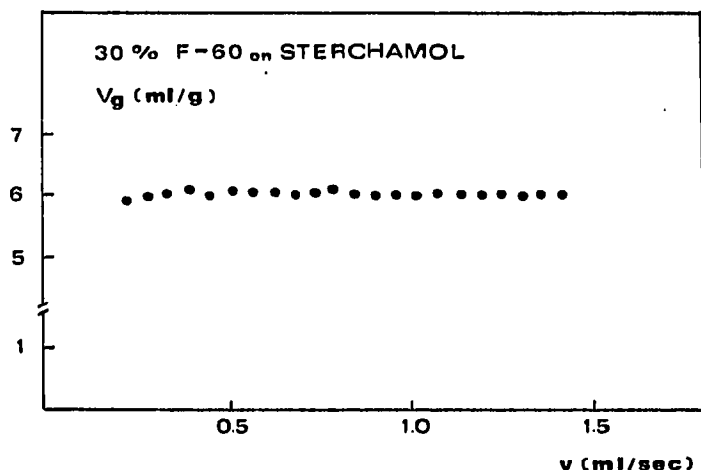


Fig. 1. Dependence of V_g on flow velocity for 30% F60 on Sterchamol.

volume flow velocity of 1 ml/sec corresponds to an average forward velocity (u) of about 18 cm/sec ($u = v/\epsilon\varphi_0$).

The F60–Sterchamol GLC packing (Fig. 1) shows a very slight decrease in V_g at both low and high flow velocities. When considering only the branch that descends in the direction towards higher velocities (dominant influence of the interphase mass transfer rate), the decrease in V_g is less than 1% of the average value. Both the course and the extent of the variations in V_g are in accordance with theory; the overall C coefficient (the sum of the sorbent and gas phase mass transfer coefficients) found⁷ for this system was 0.0058 sec.

Porapak P batch 550 (Fig. 2) displays a situation similar to that with F60–Sterchamol. Although the variations in V_g appear to be more pronounced, the fact that they occur at an appreciably higher V_g level makes them relatively less important. Also, with this sorbent ($C = 0.0028$ sec), the range of V_g variations does not exceed 1% of the average V_g value.

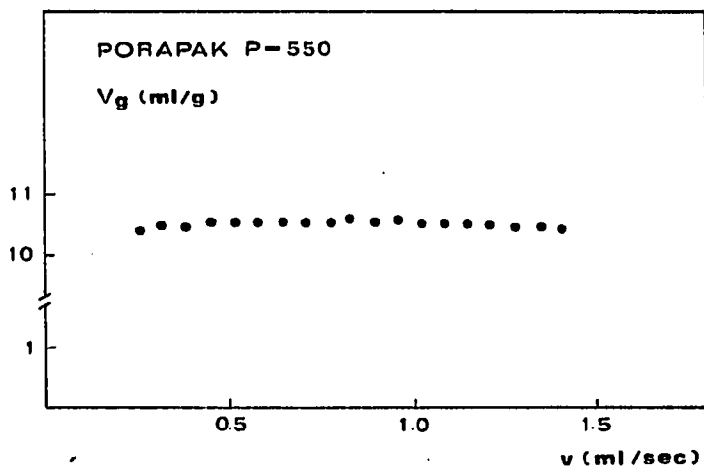


Fig. 2. Dependence of V_g on flow velocity for Porapak P batch 550.

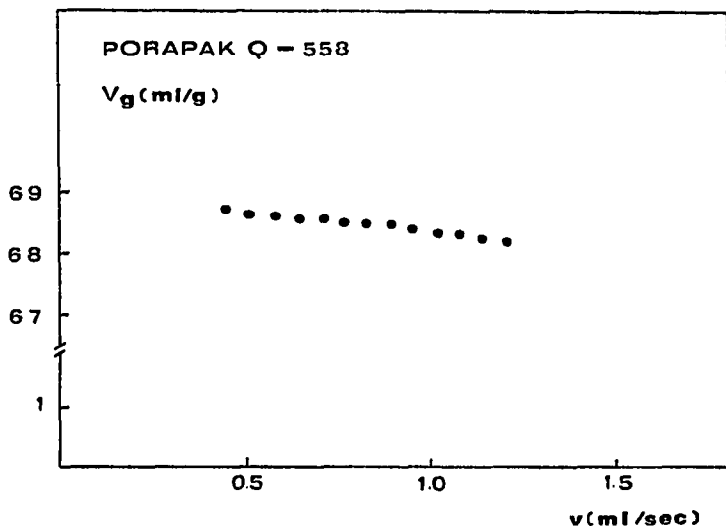


Fig. 3. Dependence of V_g on flow velocity for Porapak Q batch 558.

Fig. 3 shows the situation with Porapak Q batch 558 ($C = 0.0076$ sec). The decrease in V_g with increasing flow velocity is apparent in this instance, but, relative to the average V_g , the overall decrease is again only about 1%.

Porapak P batch 411 is a special case of this study (Fig. 4). This material displayed very bad separation properties (excessive peak broadening) and an extraordinarily large C coefficient (0.0780 sec). A decrease in V_g by more than 3% within the flow-velocity range shown in Fig. 4 is obviously due to the enormously high resistance of the sorbent phase to solute mass transfer. Extraction of this material with benzene for several hours (*cf.* Fig. 5) resulted in an even worse situation; the C

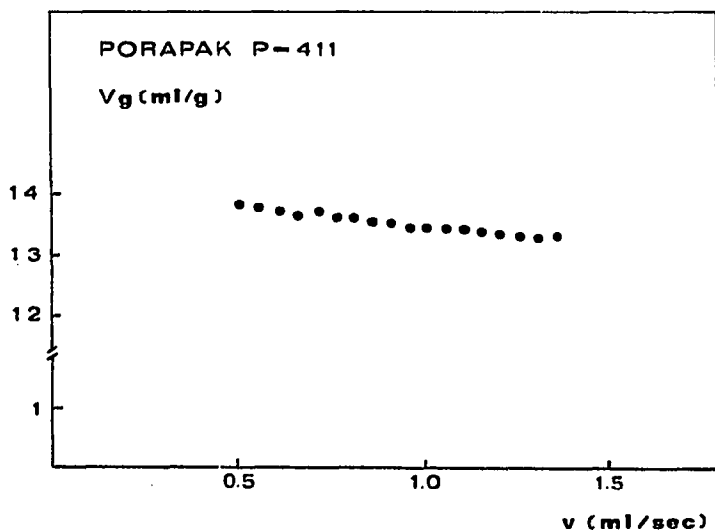


Fig. 4. Dependence of V_g on flow velocity for Porapak P batch 411.

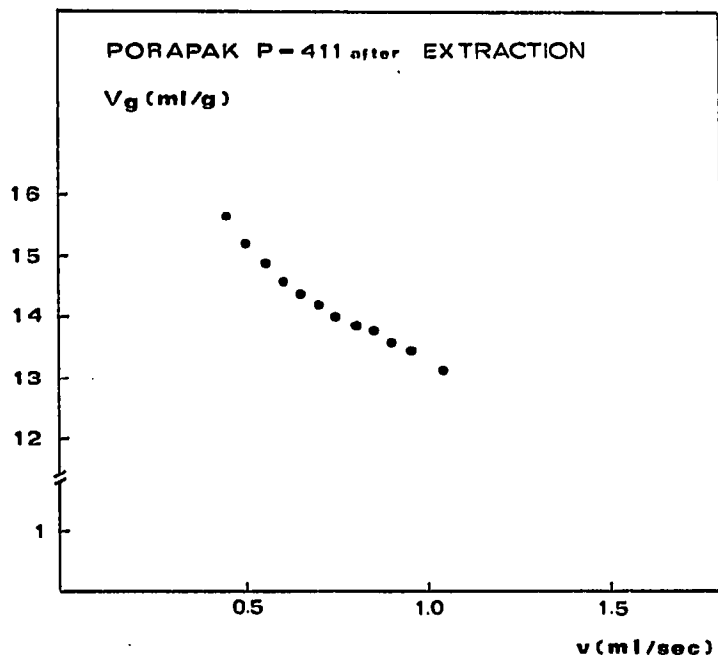


Fig. 5. Dependence of V_g on flow velocity for Porapak P batch 411 after extraction.

coefficient increased to a value of 0.16 sec, and the relative decrease in V_g reached about 14%, as measured over a flow velocity range of 0.5–1 ml/sec. It was thought at first that the high resistance to mass transfer was caused by liquid enclosed in the pores of the material, and the extraction was carried out in order to remove the liquid. However, it was found that no such liquid was present in the sorbent. The increase in the C coefficient brought about by the extraction was probably due to an unfavourable rearrangement of the geometry of the pores.

Fig. 6 shows the dependence of V_g on the flow velocity measured on the in-

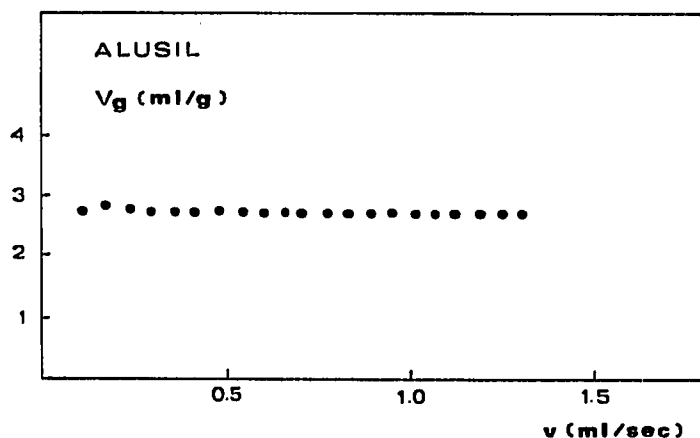


Fig. 6. Dependence of V_g on flow velocity for Alusil.

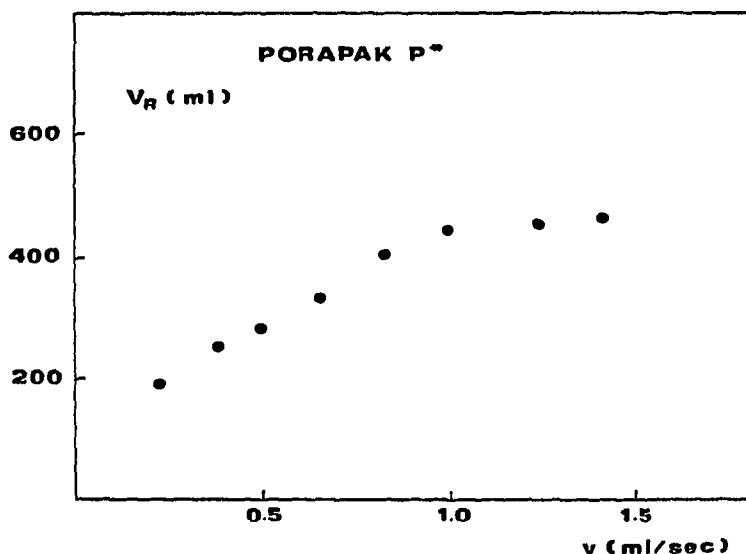


Fig. 7. Dependence of V_R on flow velocity for Porapak P* (ref. 6).

organic adsorbent Alusil ($C = 0.0044$ sec). Owing to the low V_R values, their changes on varying the flow velocity are imperceptible with this sorbent.

Fig. 7 is part of Fig. 1 presented in a *Becker Application Note*⁶, referring to *n*-hexane chromatographed on a Porapak P (designated by P* in this paper) at 150° with helium as carrier gas. Contrary to the situations found with the sorbents discussed above, the retention volume increases sharply on increasing the flow velocity. The nature of this phenomenon is unclear, but it is possible to bring about conditions under which the same effects occur. It was found that V_R measured on packings of Porapak Q coated with F60 silicone oil also increases when the flow rate of the carrier gas is increased. This is shown in Figs. 8–10, referring to Porapak Q 558 coated with

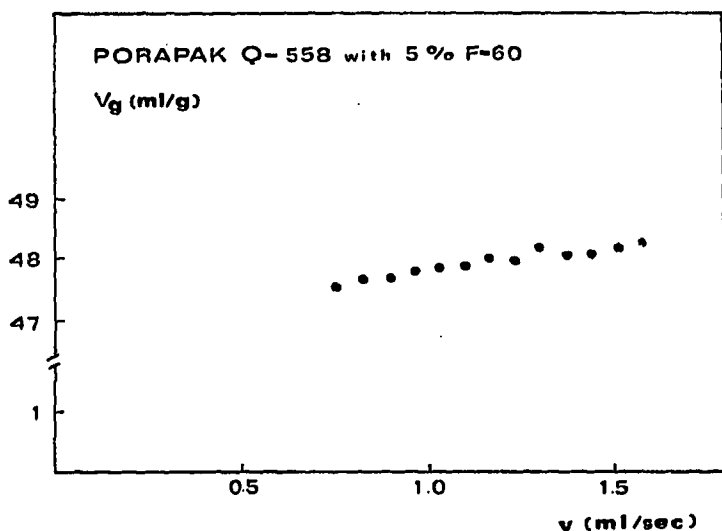


Fig. 8. Dependence of V_g on flow velocity for Porapak Q batch 558 coated with 5% F60.

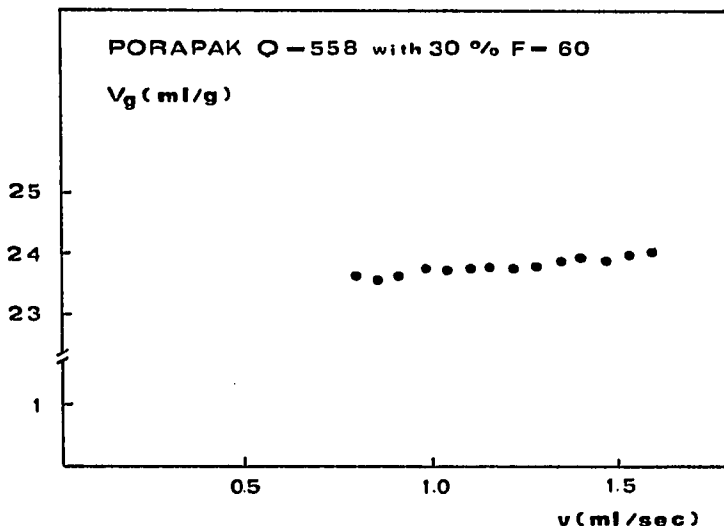


Fig. 9. Dependence of V_g on flow velocity for Porapak Q batch 558 coated with 30% F60.

5, 30 and 50% (w/w) of F60 silicone oil ($C = 0.0086, 0.0103$ and 0.020 sec), respectively. In spite of the fact that the C coefficients of the coated Porapak Q are larger than that of the unmodified Porapak, all the coated materials display a decreasing dependence of V_g versus v . It appears that the effects that cause V_g to increase on increasing the velocity are greater than the non-equilibrium effects in these instances. As the C coefficient increases on increasing the percentage of F60, the slope of the graph of V_g versus v decreases. Hence, although the nature of this phenomenon remains unexplained, it may be supposed that the situation presented in the *Becker Application Note* might be due to the presence of a small amount of a liquid in the Porapak employed.

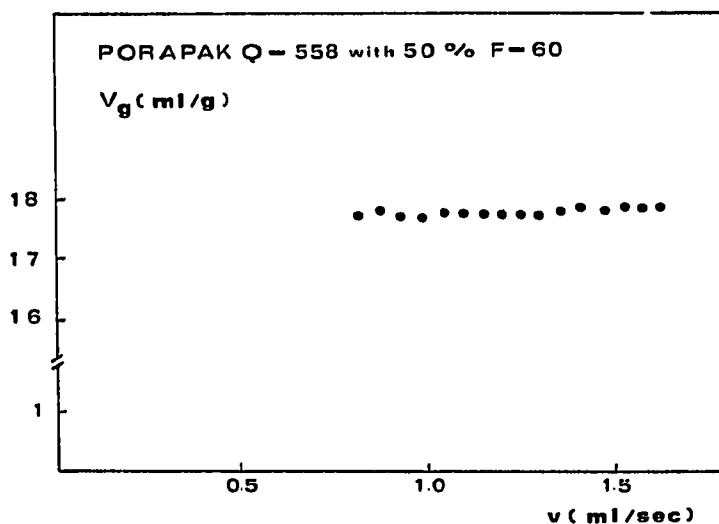


Fig. 10. Dependence of V_g on flow velocity for Porapak Q batch 558 coated with 50% F60.

CONCLUSIONS

The specific retention volumes of a given solute measured on porous Porapak polymers depend on the flow velocity of the carrier gas. Provided that the measurements are made in a flow velocity region of dominant influence of the interphase mass transfer rate, there is an apparent correlation between the extent of the decrease in V_g induced by the flow velocity and the magnitude of the overall coefficient of the resistance to mass transfer (C coefficient). In accordance with theory, the dependence of V_g on flow velocity is virtually insignificant with materials that have normal C coefficients (of the order of 10^{-3} sec).

With Porapak P, production batches occur that show an excessively large C coefficient (of the order of 10^{-1} sec) and, consequently, a sharp decrease in V_g on increasing the flow velocity.

Low contents of a stationary liquid deposited on the porous polymer sorbent may lead to an increase in V_g on increasing the flow velocity.

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