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CHROMATOGRAPHIC CHARACTERIZATION OF POROUS POLYMER ADSORBENTS IN A TRAPPING COLUMN FOR TRACE ORGANIC VAPOR POLLUTANTS IN AIR

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SUMMARY

The validity of the extrapolation method generally used for estimating the adsorption capacity of porous polymer adsorbents has been examined for Porapak Q, Tenax GC and Chromosorbs 101, 102 and 103, with halogenated hydrocarbons (chloroform, carbon tetrachloride and 1,1,1-trichloroethane) as test compounds. Gas chromatographic determination of the retention volumes of these compounds on the polymer stationary phases showed a deviation from the values obtained by the extrapolation method.

INTRODUCTION

The use of sampling tubes packed with porous polymer adsorbents, *e.g.*, Porapak Q, Tenax GC or Chromosorb 101, 102 or 103, offers an excellent means for trapping organic pollutants present at sub-ppm levels in air¹⁻⁴. A known volume of air is passed through the sampling tube at a controlled flow-rate and at ambient temperature, and the organic pollutants collected on the adsorbent are thermally desorbed directly into a gas chromatograph for analysis.

To extend the usefulness of this method, the effects of air flow-rate, pollutant concentration and other parameters have been investigated. One of the most important of these parameters is the estimated column capacity, *i.e.*, the sampled air volume at which the compound being collected begins to elute from the sampling tube. This capacity is dependent on the retention time of the compound being adsorbed at ambient temperature using the adsorbent as stationary phase.

Because such retention times are long, an extrapolation method is normally used in the gas chromatographic determination of column capacity. This method consists of estimating the retention volume at ambient temperature by linear extrapolation of retention volumes determined at higher temperatures⁵. In this work, the validity of such extrapolation has been examined for the widely used adsorbents Porapak Q, Tenax GC and Chromosorbs 101, 102 and 103, with halogenated hydrocarbons (CHCl₃, CCl₄ and CH₂Cl₂) as test compounds.

EXPERIMENTAL

Reagents

Analytical-grade halogenated hydrocarbons (CHCl_3 , CCl_4 and CH_2Cl_2) were used without further purification. The porous polymer adsorbents Porapak Q (50–80 mesh), Tenax GC (60–80 mesh) and Chromosorb 101, 102 and 103 (60–80 mesh) were purchased from Waters Assoc. (Milford, Mass., U.S.A.), AKZO Research Laboratories (Arnhem, The Netherlands) and Johns-Manville Co. Ltd. (Denver, Colo., U.S.A.), respectively.

Chromatographic conditions

The instrument used was a Yanagimoto gas chromatograph (Model G-80) equipped with a 10-mCi ^{63}Ni electron-capture detector (ECD). The stainless-steel tube (16 cm \times 3 mm I.D. \times 4 mm O.D.) was packed with adsorbent (10 cm) between glass-wool plugs, and the column was conditioned for 2 h at 240 °C in a stream of nitrogen (25 ml/min).

Sample preparation

A dilute vapor sample of each halogenated hydrocarbon was prepared by injecting the liquid sample (CHCl_3 0.9 μl ; CCl_4 2.0 μl ; CH_2Cl_2 2.2 μl) into a previously evacuated glass flask (1 l) equipped with a rubber serum cap and then allowing the liquid to vaporize. The pressure in the glass flask was restored to atmospheric level by introducing dry air. A 5- or 50-ml portion of the sample gas in this flask was injected into a second dilution flask to yield a vapor sample of concentration suitable for ECD detection (CHCl_3 10^{-9} – 10^{-8} g; CCl_4 10^{-11} – 10^{-5} g; CH_2Cl_2 10^{-10} – 10^{-9} g in 0.8–8 μl of the gas injected into the chromatograph).

RESULTS AND DISCUSSION

A trapping tube packed with solid adsorbent can be regarded as a chromatographic column operated with the constant-concentration mixture. As the solid adsorbent until the volume of gas passing through the column becomes equal to the retention volume of the substance at the given temperature, the maximum sample volume (V) is given by the following equation (see ref. 6):

$$V = V_R - (w/2) \quad (1)$$

where V_R is the retention volume and $w/2$ represents the peak width at half-height; w is related to the number of theoretical plates (N) by the expression

$$N = 16(V_R/w)^2 \quad (2)$$

By combining eqns. 1 and 2, one deduces that

$$V = V_R (1 - 2/\sqrt{N}) \quad (3)$$

To determine the maximum sample volume (V) from eqn. 3, it is necessary to know V_R and to estimate N for the substance at the trapping temperature.

The retention time for each halogenated hydrocarbon was determined by making a pulsed injection of the vaporized sample into the gas chromatographic column packed with the adsorbent.

Before each measurement, fresh adsorbent was conditioned at the appropriate temperature for 2 h in a stream of the carrier gas (nitrogen).

The oxygen peak of the air-containing sample gas was used as reference peak of a non-adsorbable gas to determine the net retention volume of the halogenated hydrocarbon. The corrected specific retention volume was calculated from the following equation (see ref. 7).

$$V_R = (t - t_o) \frac{273}{T_f} \cdot \frac{3}{2} \cdot \frac{(P_i/P_o)^2 - 1}{(P_i/P_o)^3 - 1} \cdot \frac{F}{W}$$

where t and t_o are the retention times (min) of the halogenated hydrocarbon and oxygen, respectively, T_f is room temperature ($^{\circ}\text{K}$), P_i and P_o are the pressures at the column inlet and outlet, respectively, F is the flow-rate of the carrier gas (ml/min) and W is the weight of adsorbent (g).

In the linear isotherm, the apparent equilibrium constant of adsorption (K) is given by

$$K = \frac{V_R}{RT}$$

where R is the gas constant and T is the column temperature ($^{\circ}\text{K}$) (ref. 8).

Thus, the linearity of an isotherm can be indirectly confirmed by the fact that the specific retention volume is independent of the partial pressure of the adsorbate.

In this work, the amount of vaporized sample injected into the gas chromatographic system was so selected that the relationship between V_R and sample volume was constant.

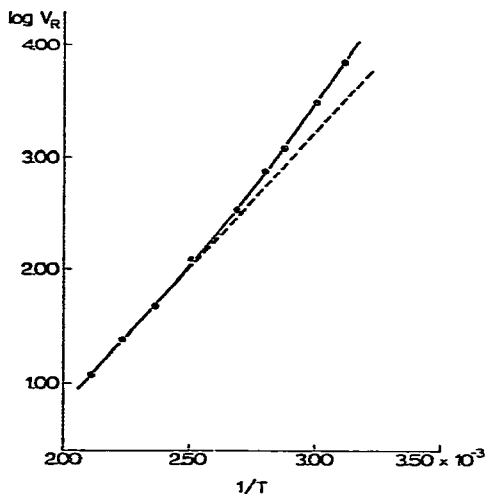


Fig. 1. Graph of $\log V_R$ vs. $1/T$ for CHCl_3 on Porapak Q.

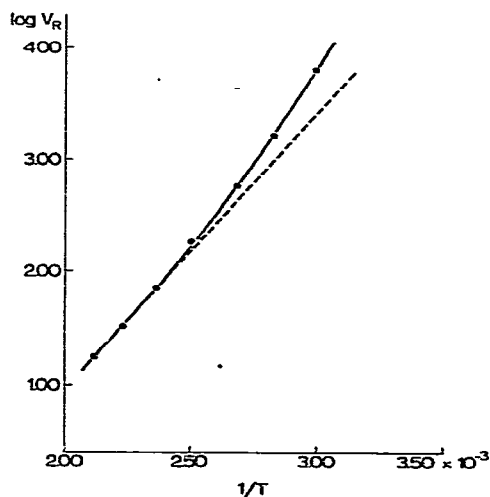
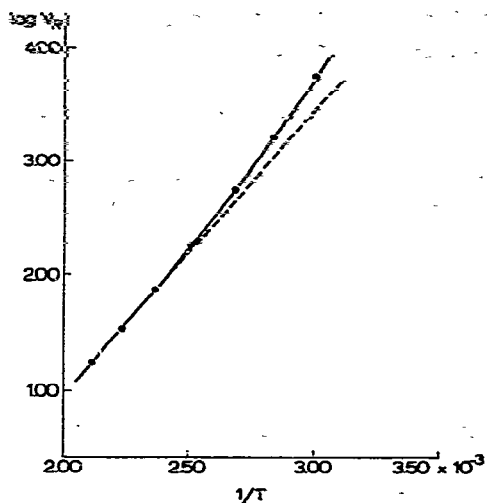
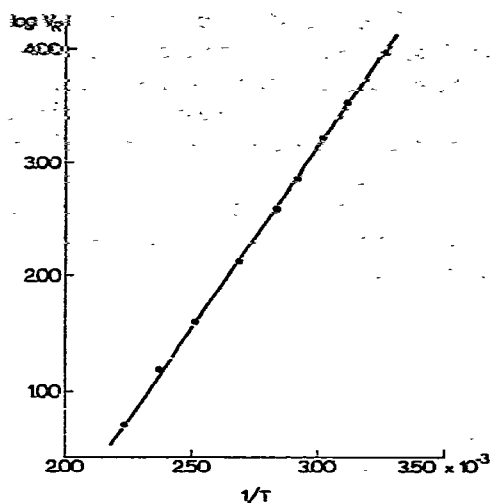
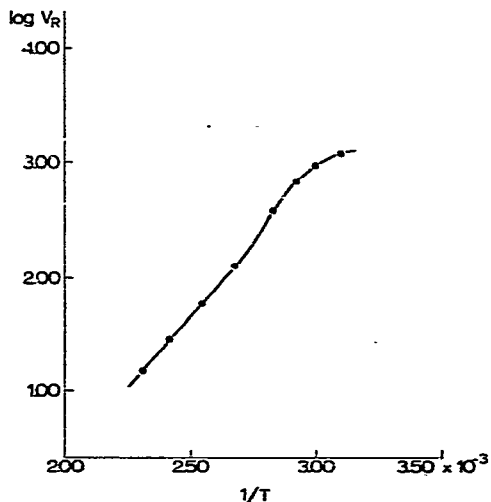
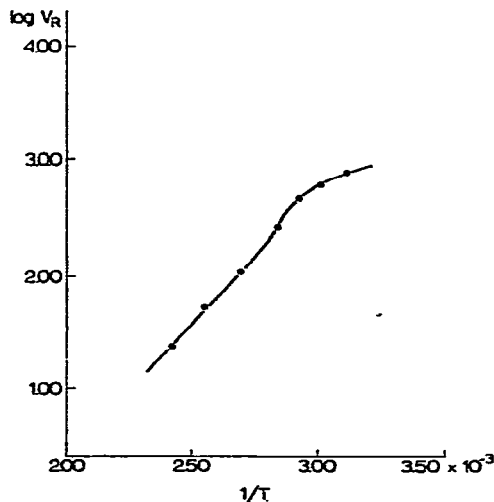


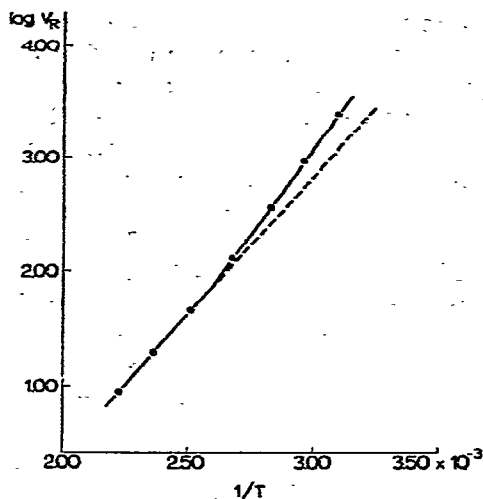
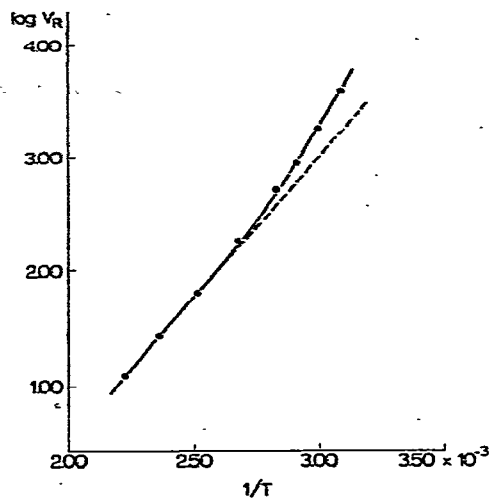
Fig. 2. Graph of $\log V_R$ vs. $1/T$ for CH_2Cl_2 on Porapak Q.

Fig. 3. Graph of $\log V_R$ vs. $1/T$ for CCl_4 on Porapak Q.Fig. 4. Graph of $\log V_R$ vs. $1/T$ for CHCl_3 on Tenax GC.

The retention volume at the trapping temperature is usually obtained by linear extrapolation of the graph of $\log V_R$ vs. $1/T$ determined at temperatures higher than the trapping temperature.

Since the adsorbing capacity of the adsorbent bed is influenced by many parameters, *e.g.*, the physical character of the adsorbent, the sorption mechanism, the packing density and the degree of solute affinity, use of the extrapolation method poses problems in the estimation of the practical column capacity.

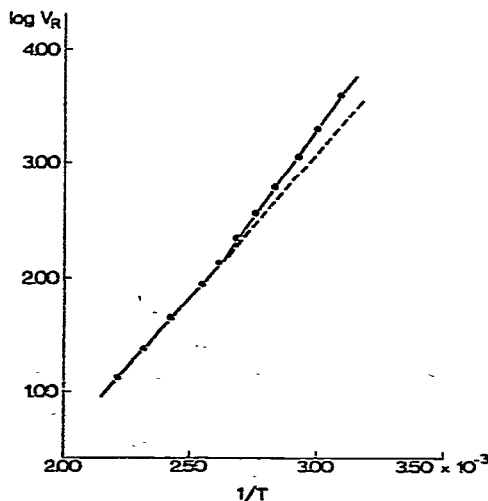
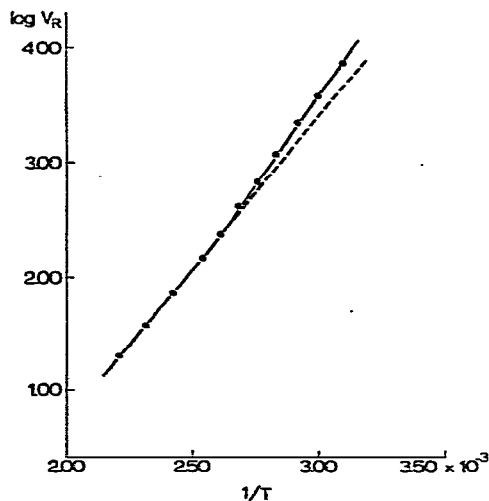
Fig. 5. Graph of $\log V_R$ vs. $1/T$ for CCl_4 on Tenax GC.Fig. 6. Graph of $\log V_R$ vs. $1/T$ for CH_2Cl_2 on Tenax GC.

Fig. 7. Graph of $\log V_R$ vs. $1/T$ for CHCl_3 on Chromosorb 101.Fig. 8. Graph of $\log V_R$ vs. $1/T$ for CCl_4 on Chromosorb 101.

In this work, the validity of the extrapolation method was examined by comparing the retention volumes calculated for lower temperature by use of the linear extrapolation method with the values obtained by gas chromatographic analysis at low temperature.

The measurements of retention volume were carried out on a short column (10 cm \times 3 mm I.D.) to give reasonable retention times (*ca.* 0.1–60 min) in the chromatographic procedure over a temperature range from 50 to 200 °C.

As shown in Figs. 1, 2 and 3, at lower temperature range (50–100 °C), graphs

Fig. 9. Graph of $\log V_R$ vs. $1/T$ for CHCl_3 on Chromosorb 102.Fig. 10. Graph of $\log V_R$ vs. $1/T$ for CCl_4 on Chromosorb 102.

of $\log V_R$ vs. $1/T$ for CHCl_3 , CH_2Cl_2 , and CCl_4 on the Porapak Q column deviated from the extrapolating line derived from the values at higher temperatures (100–200 °C). In the lower temperature range, retention times on Porapak Q were longer than the values expected from those obtained in the higher temperature range. This indicates that the column capacities of Porapak Q for all the halocarbons tested are greater than those derived by calculating the retention volume at low temperature by extrapolation of the graph of $\log V_R$ vs. $1/T$ plots for the higher temperature range.

As shown in Fig. 4, the graph of $\log V_R$ vs. $1/T$ plots for CHCl_3 on Tenax GC were linear over the full temperature range (50–200 °C), but for CH_2Cl_2 and CCl_4 , deviations from the extrapolated values were observed at temperatures below 70 °C (see Figs. 5 and 6). The retention times of CH_2Cl_2 and CCl_4 on Tenax GC were shorter than those expected from the value for CHCl_3 on Tenax GC, the peaks of these halocarbons appearing immediately after the air peak; thus, Tenax GC showed a lower affinity for CH_2Cl_2 and CCl_4 than for CHCl_3 .

The graphs for CHCl_3 and CCl_4 on Chromosorb 101 and 102 were similar to those of CHCl_3 , CH_2Cl_2 and CCl_4 on Porapak Q (see Figs. 7 to 12).

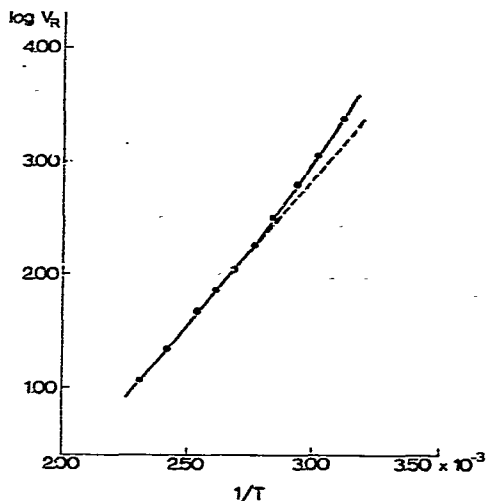


Fig. 11. Graph of $\log V_R$ vs. $1/T$ for CHCl_3 on Chromosorb 103.

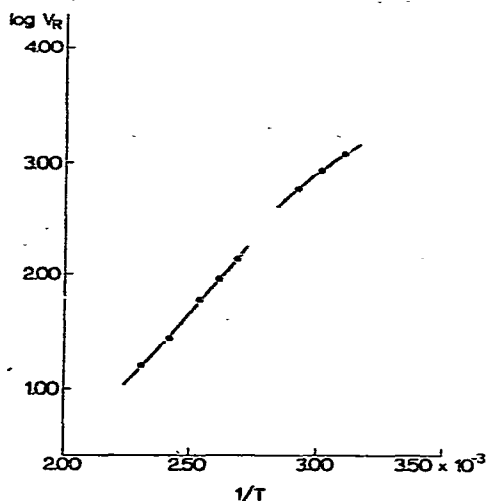


Fig. 12. Graph of $\log V_R$ vs. $1/T$ for CCl_4 on Chromosorb 103.

CONCLUSION

The affinity of adsorbates for adsorbents influences the column capacity of the adsorbent in certain adsorbate-adsorbent combinations, and the estimated column capacity of a porous polymer trapping tube calculated from the retention volume at the lower temperature obtained by the extrapolation method deviates from the true value.

REFERENCES

- 1 F. W. Williams and M. E. Umstead, *Anal. Chem.*, 40 (1968) 2232.
- 2 J. W. Russell, *Environ. Sci. Technol.*, 9 (1975) 1175.
- 3 E. D. Pellizzari, B. H. Carpenter, J. E. Bunch and E. Sawicki, *Environ. Sci. Technol.*, 9 (1975) 556.
- 4 E. D. Pellizzari, J. E. Bunch, B. H. Carpenter and E. Sawicki, *Environ. Sci. Technol.*, 9 (1975) 552.
- 5 L. D. Butler and M. F. Burke, *J. Chromatogr. Sci.*, 14 (1976) 117.
- 6 A. Raymond and G. Guiochon, *J. Chromatogr. Sci.*, 13 (1975) 173.
- 7 A. B. Littlewood, *Gas Chromatography, Principles, Techniques and Applications*, Academic Press, New York, 1962.
- 8 J. J. Van Deemter, F. J. Zuideker and A. Klinkenberg, *Chem. Eng. Sci.*, 5 (1956) 271.