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THE USE OF HIGH EFFICIENCY PACKED COLUMNS FOR GAS–SOLID CHROMATOGRAPHY

II. THE SEMI-PREPARATIVE SEPARATION OF ISOTOPIC MIXTURES *

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SUMMARY

High efficiency packed adsorption columns have been prepared with graphitized carbon black as adsorption medium. The influence of carrier gas, column design, packing characteristics, sample retention and size on column efficiency have been investigated. A HETP value of about 1 mm has been obtained for the 120-m column with methane when 0.5 c.c. s.t.p. of methane is injected.

The separation of CH_4 and CH_3D is shown using different column lengths.

The R^2/t ratio for this separation is of an order of magnitude greater than that found in the literature up to date. The implications of these results for a preparative separation of isotopes are discussed.

INTRODUCTION

Since the introduction of capillary columns by GOLAY in 1958[1], high resolution gas chromatography has been performed mainly with this type of column. However, because of the need of semi-preparative and preparative gas chromatography a good deal of work has been done in order to combine high resolution with high loading capacity.

SCOTT, in his classical work[2], has shown that about thirty thousand theoretical plates can be obtained with "high packed" columns. In a subsequent paper[3], the same author pointed out that resolution, capacity and speed of analysis are linked together in such a way that one can realize the optimum conditions for any two of these parameters, but only by sacrificing the third.

In this paper the first results of our efforts to construct semi-preparative columns for the separation of isotopes are reported: because of the very low separation factor of isotopes resolution must be regarded as the most important parameter. The problem can be summarized as the necessity to make gas chromatographic columns of about

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10^5 theoretical plates, with a reasonable analysis time and capacity. We have chosen CH_4–CH_3D as the test system for our columns because we have considerable experience with it[4] and it is relatively easy to separate this pair.

EXPERIMENTAL

Apparatus

A Carlo Erba ATC/f gas chromatograph equipped with a thermal conductivity detector was slightly modified for high pressure and low temperature work. Two different gas lines were used for the reference arm of the cell and the column inlet in order to avoid high pressure and low flow rate in the former. The carrier gas is purified of any condensable impurity by means of two traps containing molecular sieves, 5 Å; one was at room temperature and the other was maintained at the temperature of liquid nitrogen. The apparatus was also modified by connecting the column, fitted in a Dewar container, to the cell by means of two narrow copper tubings of negligible volume.

Column packing

Graphon, a partially graphitized carbon black, kindly supplied by Dr. W. R. SMITH (Cabot Corp., Billerica, Mass.) was used as packing material. The particle size was 40–60 mesh. Tailing of the peaks was eliminated by treating the adsorbent with a small amount of squalane (1°/₀₀ w/w). The columns were copper tube, 4 mm I.D., 6 mm O.D., made according to a previously described procedure[5].

Samples were injected by using gas tight and small cross section syringes; no particular difficulties were encountered up to a pressure of 15 kg/cm². A more sophisticated inlet system must be used for higher pressures.

RESULTS AND DISCUSSION

Column design and packing characteristics

The choice of column diameter, particle size and amount of squalane are ruled by the necessity of obtaining high efficiency, high permeability, a relatively fast analysis and a reasonable loading capacity. The most important of these parameters is efficiency, as pointed out earlier. The 40–60 mesh particle range assures a satisfactory value of HETP[6] together with a low packing density[7].

The 4 mm I.D. results in negligible dispersion of the chromatographic zone[8], and it lies in a rather flat zone of the plot of permeability *vs.* column diameter[9]. The retention times and the tailing of the peaks decrease sharply as the amount of squalane is increased; with as little as 0.1% peaks are obtained for *n*-butane at 55° and for methane at −78° without tailing.

The capacity ratio value for methane at this temperature is about 4; this permits a short analysis time together with satisfactory exploitation of the resolving power of the column.

The idea of deactivating the adsorbent with a liquid phase, and thus prevent tailing, was first described by EGGERTSEN *et al.*[10]. These authors used a 1.5% concentration to deactivate Pelletex carbon. In our case, however, the amount of squalane needed was about ten times less. This is due to the structure of graphitized carbon

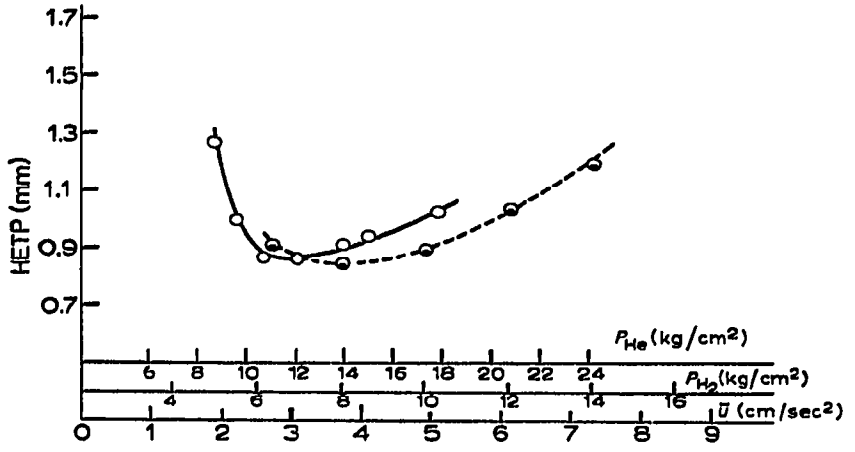

Fig. 1. HETP *vs.* $\bar{u}$ at −78° for CH_4. Column Graphon + 0.1% squalane, 4 mm I.D., 6 mm O.D., 60 m long. Carrier gases: ○ helium, ◒ hydrogen.

black, which is essentially a non-porous adsorbent with a few active sites mainly due to some cracks and cravices. The number of molecules of squalane, although much smaller than the monomolecular layer, does not essentially affect the adsorption process, but just block the few active sites.

Effect of the carrier gas

The most important problem was the limitation of the inlet pressure, so that only helium and hydrogen were considered as carrier gases; they also have a better thermal conductivity than other gases. Hydrogen gives the best results as can be clearly seen from the plots in Fig. 1, where the Van Deemter curves for methane at −78° are reported. The triple abscissa serves to show that the same linear gas velocity

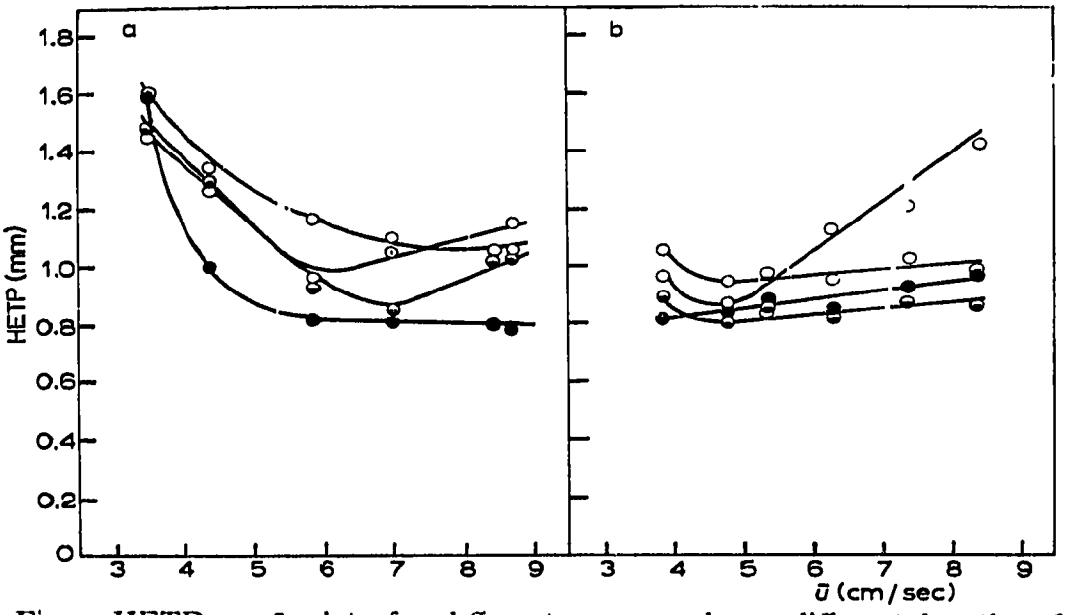

Fig. 2. HETP *vs.* $\bar{u}$ plots for different compounds on different lengths of column. (a) 15 m; (b) 60 m; T = 55°. Samples: ○ C_2H_4, ◒ C_2H_6; ○ C_3H_6; ● C_3H_8.

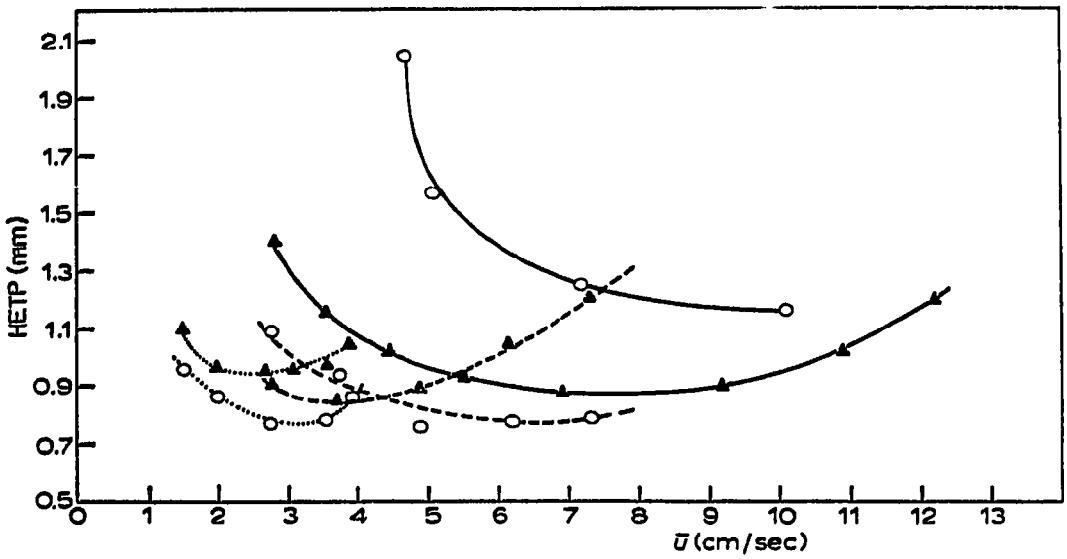

Fig. 3. HETP *vs.* $\bar{u}$ plots for columns of different length at −78°. - - - - - - 120 m, — — — — —, 60 m; ———, 15 m. Samples: ○ N_2; ▲ CH_4.

is reached with the two gases using quite different pressures. With hydrogen, the same average linear gas velocity is reached at a much lower pressure and $\bar{u}_{min}$ is shifted towards the higher velocities, improving the speed of analysis.

Effect of sample retention, column length and sample size on HETP.

Fig. 2 shows the Van Deemter curves for compounds of different retention at 55° relative on columns of different length. It should be noted that the constant C is larger for the unsaturated compounds than for the analogous saturated compounds.

The unsaturated hydrocarbons do in fact tail slightly, while perfectly symmetrical peaks are obtained for the alkanes. The same minimum HEPT is obtained on the two columns.

Fig. 3, in which the same plots are reported for methane and nitrogen at −78° for three columns of 15, 60, 120 m, respectively, is more interesting. The well retained peaks (methane) show about the same minimum HETP, while a noticeable decrease of HETP minimum with column length is observed for the more volatile material (nitrogen). The apparent decrease of HETP is however illusory because of the effect of the "dead time" on it.

Furthermore, the longer the column, the lower is the $\bar{u}_{min}$ value. This is explained by the fact that the diffusion effect decreases with the gas pressure so that for longer columns the B term of the Van Deemter curve becomes less important. The same effect has been observed by HALÀSZ *et al.*[11] who compared packed capillary columns of an order of magnitude shorter.

Fig. 4 shows the increase of n, the number of theoretical plates, and N, the number of effective theoretical plates[12], with increase in column length. The use of N is suggested by the low value (~ 4) of the capacity ratio for methane at −78° on our columns. Points are taken in the region of $\bar{u}_{min}$ in every case. A slight curvature is observed for long column lengths; this effect is probably due to the high inlet pressure, which causes the flow rate to be very high in the last part of the column.

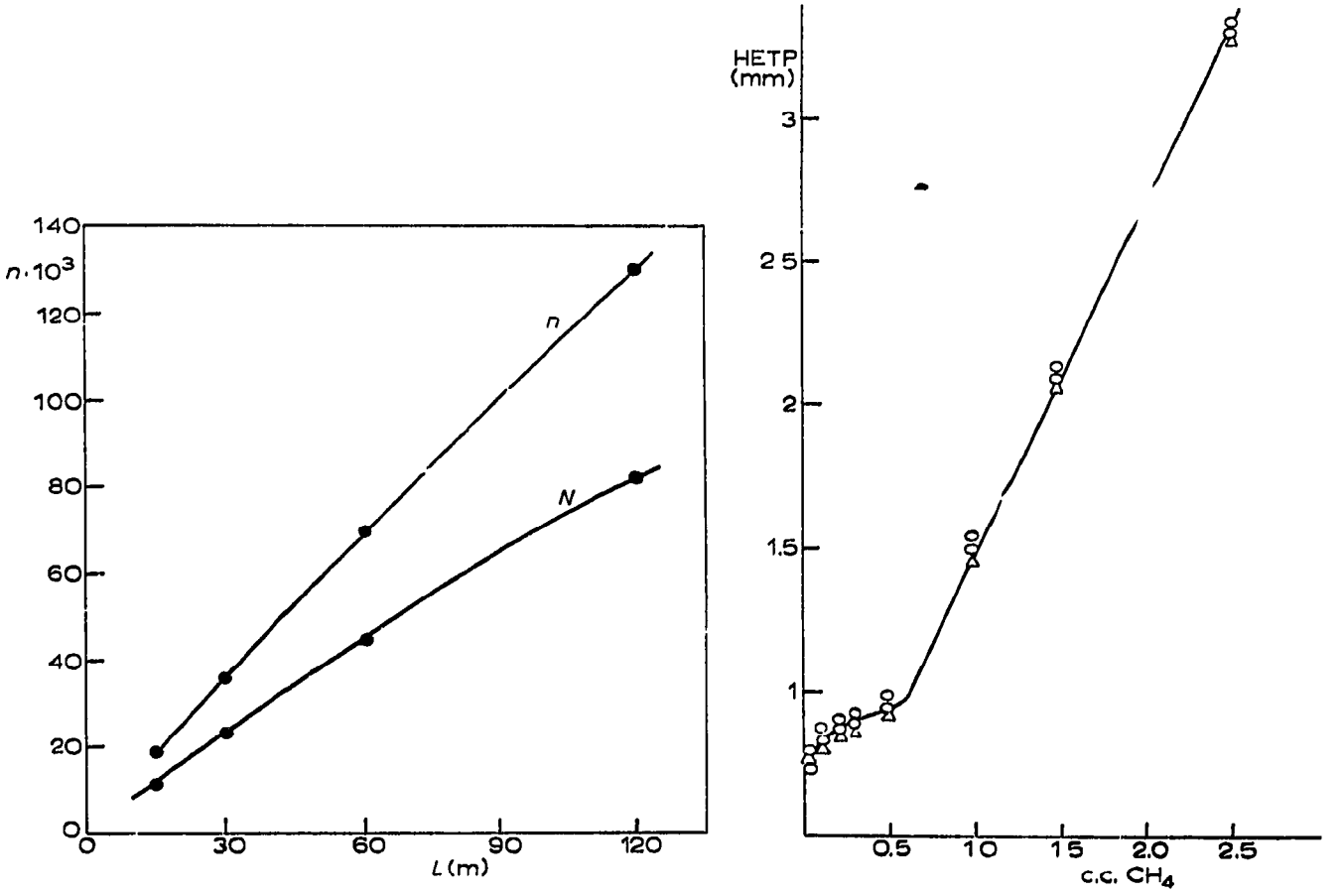

Fig. 4. Number of theoretical plates *(n)* and of effective theoretical plates *(N)* as a function of column length. Sample 0 5 c c CH_4; T = −78°

Fig. 5. HETP as a function of sample size Different dots refer to different columns, 15 m long each.

Fig. 5 shows the effect of sample size on HETP for three different columns packed with the same material. Efficiency is comparable with that of analytical columns up to 1 c.c. A value of HETP higher than 2 results in an unsatisfactory separation for the system CH_4–CH_3D even on the 120 m column. The most significant separations of CH_4–CH_3D, obtained on columns of different length at −78°, are reported in Fig. 6. The separation shown in (a) is remarkable for the short elution time and its resolution. It is useful for comparison with analogous separations obtained under different conditions, but it is of little interest for preparative purposes.

The separations obtained in (b) and (c) for the pair CH_4–CH_3D are for the 60 m and the 120 m columns. Chromatogram (c) can be compared with one previously reported[13] which was obtained at the temperature of liquid nitrogen with a column packed with powdered etched glass. The resolution is about the same but in the present case the analysis time has been reduced to about one half.

It should be noted that at −78° the "abnormal" isotope effect takes place but this is much lower as an absolute value than the "normal" one which occurs at −196°, so that the same resolution is only obtained with a much longer column.

A comparison of the efficiency of a given gas chromatographic separation can

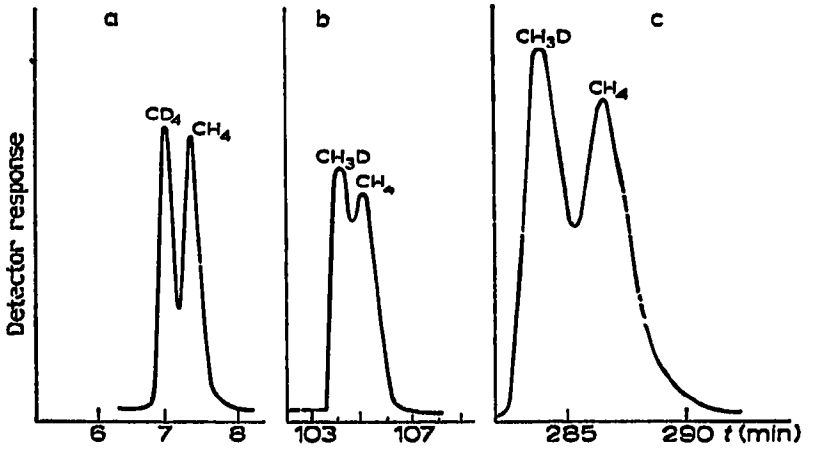

Fig. 6. Separation of isotopic systems on columns of different length. (a) CH_4–CD_4 on 15 m column; (b) CH_4–CH_3D on 60 m column; (c) CH_4–CH_3D on 120 m column. T = −78°. $\bar{u}_{min}$ in every case. Samples: 1 c.c. of mixture.

be made in terms of the factor R^2/t (ref. 14), where R is the resolution expressed in the usual way and t the analysis time. The results obtained by several authors are compared in Table I. The R^2/t value is much higher in the present work and this compensates the use of so long a column for the separation of CH_4–CH_3D.

Such results, which are promising for preparative applications, have been possible because of the peculiar characteristics of graphitized carbon black, the use of which allows one to make use of the selectivity of adsorption gas chromatography and the linearity of the gas–liquid chromatography isotherm. Furthermore, it is possible to adjust the retention volumes by simply changing the amount of liquid phase used.

TABLE I

MEAN R^2/t VALUES ON DIFFERENT ADSORPTION MEDIA FOR THE SYSTEM CH_4–CD_4 (PACKED COLUMNS)

Author	*Ref.*	*T (°C)*	*Adsorption medium*	*Column length (m)*	*R*	$R^2/t \times 10^4$ *(sec^{-1})*
GANT AND YANG	15	−3.5	High activity charcoal	15	1.0	0.9
ROWLAND *et al.*	16	20	Molecular sieves 5 Å	(recycling)	0.9	0.4
BRUNER *et al.*	13	−196	Etched glass	8	1.3	0.5
CZUBRYT *et al.*	17	−45	Porapak Q	30	1.3	5.7
POSSANZINI *et al.*	18	−78	Porapak Q	4	0.9	2 3
This work		−78	Modified graphitized carbon black	15	0 75	15.0

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