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Gas chromatographic determination of isotopic molecules by means of open tubular thick layer graphitized carbon black columns*

High efficiency adsorption glass capillary columns may be obtained by replacing the smooth inner wall of a tubular column with a porous layer. This has been done by Mohnke and Saffert[1] and Bruner and Cartoni[2] by etching glass columns by various procedures. Halasz and Horvath[3] obtained adsorption packed capillary columns by filling the columns with a suspension of a very fine support material or by drawing out glass tubes, which were loosely filled with a selected solid of narrow mesh range.

This paper reports on a new type of capillary column, the "open tubular thick layer glass column", which combines the properties of the open tubular and of the packed columns, by using as adsorption material graphitized carbon black. These columns are very effective for separating several isotopic systems.

Experimental

Preparation of the open tubular thick layer graphitized carbon black glass capillary columns. A thin steel wire (0.2 mm diameter) was inserted into a glass tube (2.2 mm I.D. and 6.6 mm I.D.) and one end of it was pulled by hand so as to leave about 30 cm of the steel wire outside the glass tubing. The glass tubing was loosely packed with Sterling MT, a graphitized carbon black (kindly supplied by Dr. Smith of the Cabot Company) and transferred to a glass-tube drawing apparatus, made according to
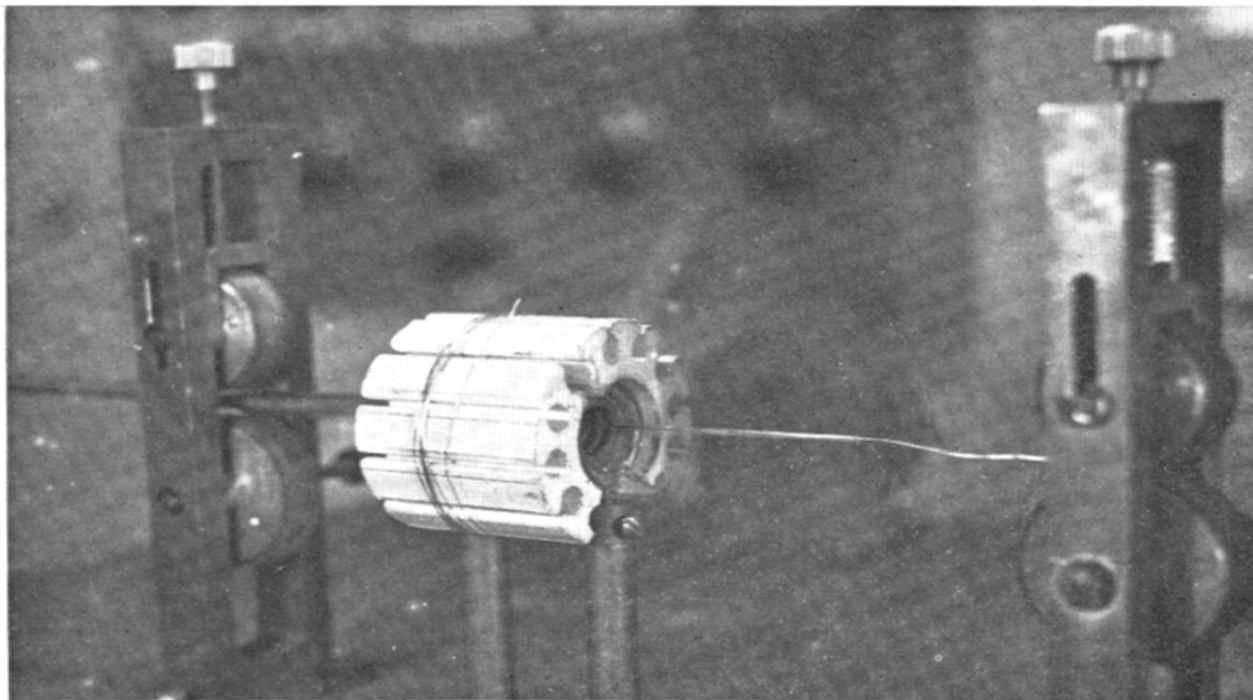

Fig. 1. Set-up for drawing-out the open tubular thick layer graphitized carbon black columns.

DESTY[3], as shown in Fig. 1. The other end of the steel wire was fastened to prevent the steel wire from being pulled into the glass capillary. The tube was drawn out at a ratio of 1:80. By means of this procedure a uniform thick layer of graphitized carbon black with an inner diameter of about 0.15 mm and outer diameter of about 0.7 mm is obtained.

This procedure seems to be of general application for the preparation of thick layers of any solid material in a glass capillary, providing the material does not undergo decomposition at the softening temperature of glass; the size of the packing material, however, seems to be a limiting factor.

Columns of various lengths are easily obtained and are employed as usual in a commercial apparatus (Fractovap C. Erba, Milan) equipped with a flame ionization detector. The behaviour of these columns has been checked by analyzing mixtures of various hydrocarbons. They have characteristics intermediate between the packed capillary and the open tubular columns.

Tailed peaks are usually obtained; to obtain symmetric peaks it has been found necessary to make the elution gas, nitrogen, bubble through a water trap: water vapour acts as an effective reducer of tailed peaks. As the support is a non-porous material it seems that the function of the water vapour is to eliminate the active sites due to the glass capillary.
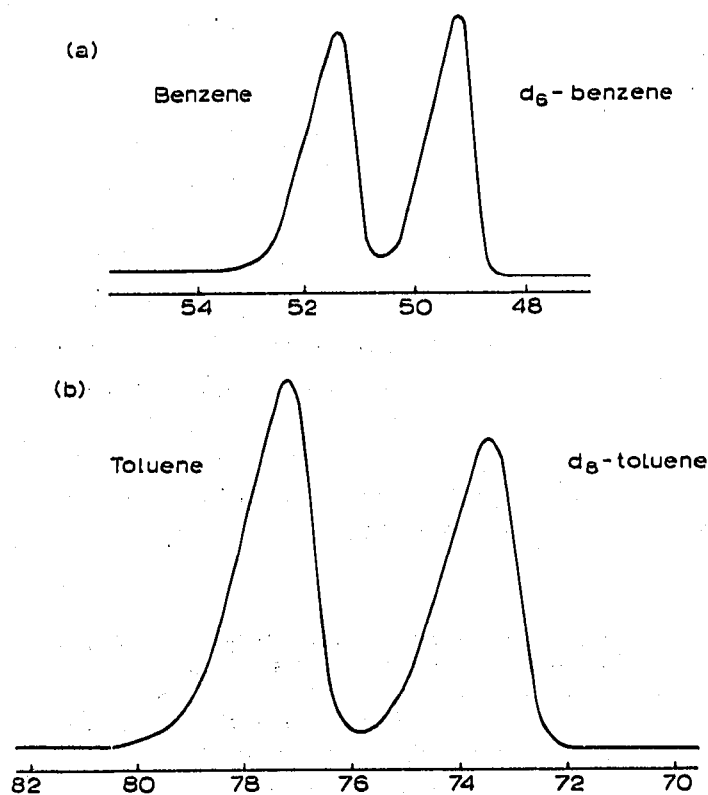

Fig. 2. Chromatographic separation on a 9.6 meter, 0.15 mm I.D. open tubular thick layer graphitized carbon black glass column of (a) C_6D_6–C_6H_6 T col. 69.5°C; P_{N_2} 1.75 atm., (b) C_7D_8–C_7H_8 T col. 98.4° C; P_{N_2} 1.9 atm.

An open tubular thick layer graphitized carbon black column was effective for the separation of the following isotopic species:

Benzene–deuterobenzene   (d_0-benzene)
Toluene–deuterotoluene   (d_8-toluene)
Acetone–deuteroacetone   (d_6-acetone)
Pyridine–deuteropyridine (d_5-pyridine).

Some chromatograms are shown in Figs. 2 and 3. The column, which has a permeability value of 11×10^{-7} cm^2, has a length of 9.6 m. It permits the realisation of a complete separation for the hydrocarbons and a partial separation for pyridine and acetone. Table I shows (at the indicated temperature) the measured separation factors, α; the capacity ratio, K'; and the number of theoretical plates, n. The corresponding column length, L, and the analysis time to obtain a resolution, $R = 1.5$, have been calculated from these values.
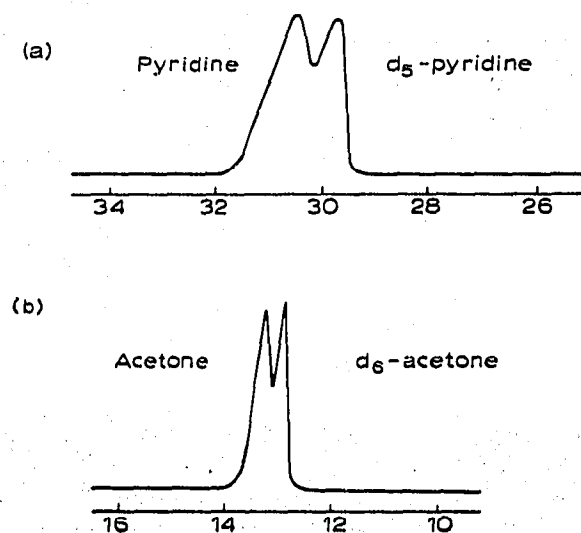

Fig. 3. Chromatographic separation as in Fig. 2 of: (a) C_5D_5N–C_5H_5N, T col. 87.5° C; P_{N_2} 1.25 atm; (b) C_3D_6O–C_3H_6O; T col. 52.8° C; P_{N_2} 1.20 atm.

These figures indicate that the efficiency of these columns for the separation of isotopic systems is much greater than with other partition and adsorption capillary columns[5].

Chromatograms have been run at various temperatures and in all cases an inverse isotopic effect has been observed, the heavier species being always eluted first. The logarithm of the relative retention volumes has been plotted versus $1/T$ (Fig. 4)

TABLE I

EXPERIMENTAL SEPARATION FACTORS, CAPACITY RATIOS, NUMBER OF THEORETICAL PLATES, ON A 9.6 m COLUMN, COLUMN LENGTH AND ANALYSIS TIME TO OBTAIN A COMPLETE SEPARATION

System	T (°K)	α	K'	n theor.	L (m)	t (min)
Acetone–deuteroacetone	325.0	1.042	2.0	12,000	38.3	52.6
Pyridine–deuteropyridine	360.0	1.030	10.7	12,000	40.7	94.6
Benzene–deuterobenzene	330.4	1.050	32.0	17,000	7.7	65.8
Toluene–deuterotoluene	360.2	1.056	37.7	16,000	8.1	111.4

to obtain the differences of enthalpy and entropy changes, which have been collected in Table II.

Comparison of these data with the chromatographic values obtained on partition and other adsorption columns seems to indicate that the high value of the separation factor obtained on these columns is mainly attributable to an entropy effect.

TABLE II

DIFFERENCES OF ENTHALPY AND ENTROPY CHANGES OF ISOTOPIC SYSTEMS

System	ΔH (cal·mol^{-1})	ΔS (e.u. × 10^2)
d$_6$ Benzene–benzene	—34.78	— 1.62
d$_8$ Toluene–toluene	—30.30	+ 1.24
d$_6$ Acetone–acetone	—74.80	—14.72
d$_5$ Pyridine–pyridine	—58.31	—10.88

Discussion

The open tubular thick layer graphitized carbon black columns, developed in this investigation, have been found quite effective for the separation of isotopic systems as they combine the properties of packed capillary columns and open tubular columns.

These columns have a considerable amount of adsorbing material and the thickness of the layer may also be changed by using wires of different diameter in the column manufacture. They can be made to any length just as ordinary glass capillary
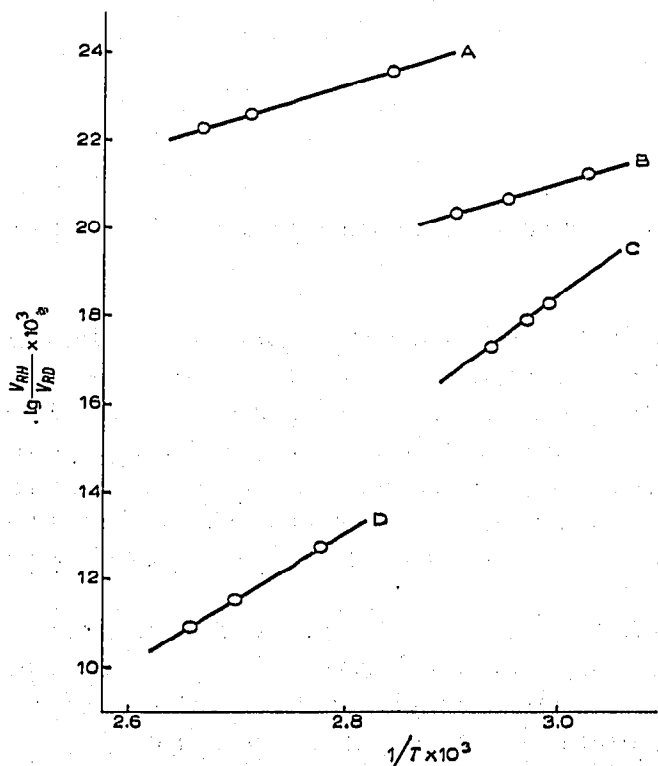

Fig. 4. Plots of logarithm × 10^3 of ratio of retention volumes *vs.* $1/T$ × 10^3 for: (A) toluene–deuterotoluene; (B) benzene–deuterobenzene; (C) acetone–deuteroacetone; (D) pyridine–deuteropyridine.

glass columns and can operate with a low pressure drop. These features therefore permit separations which are not feasible with other columns.

Graphitized carbon black is a thermally stable, inert, non-specific and non-porous adsorbent. Its use in gas–solid chromatography for the separation of some hydrocarbons from their deuterated homologues was pointed out by YASHIN[6].

The interaction energy on this material depends upon the geometrical structure of the molecules and of the adsorbent surface and on non-specific dispersion forces acting between them. It seems that the different sizes of hydrogen and deuterium and the greater mobility of the deuterium compounds should be the determining factors which affect the different adsorption of the isotopic molecules.

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Rapid method for calculating percentage recoveries of compounds from gas chromatograms

In studies on food flavours it is often desirable to know the efficiency of isolation of the volatile organic compounds responsible for a particular flavour. This is usually done by experiments on model systems where known amounts of compounds resembling the unknown in boiling point and other characteristics are added to the food, and are isolated by the appropriate technique. The percentage recoveries are often determined by comparing the peak heights of gas chromatograms of a standard solution of the compounds in an organic solvent with a chromatogram prepared with the isolated compounds.

Using this approach FORSS AND HOLLOWAY[1] have investigated the recoveries of added C_{2-10}n-alkan-1-ols and C_{3-12} alkan-2-ones from butter oil by molecular distillation and reduced pressure steam distillation. The yields were calculated by measuring the relative peak heights of the compounds in the gas chromatograms.

A more rapid and simpler method for the calculation involves the use of the graph illustrated in Fig. 1. The peak height on the standard chromatogram is measured with a pair of dividers. The point on the graph (B) where this distance (AB) corre-