Short Communication

CHROM. 3791

Sandwiched capillary columns for gas chromatography

We use the term "sandwiched capillary columns" to describe columns made of any material, in which the fractionating medium is a thread inserted inside the capillary. Any material which is available in thread form may be used for this purpose; however, this research deals with glass capillaries in which carbon yarns have been sandwiched and with the evaluation of this new type of gas chromatographic column[1].

Experimental

A glass-drawing apparatus similar to the one developed by DESTY *et al.*[2] was modified to obtain glass capillaries of different internal diameters. A piece of carbon yarn was inserted into a length of glass tubing (2.2 mm I.D. and 2.6 mm O.D.); one end of the tube was heated until it was soft and pulled out to obtain an internal diameter of 0.4–0.5 mm, leaving the yarn hanging out. The stretched glass tubing was set into the apparatus and drawn out as usual (Fig. 1). While the spool of carbon yarn unwound continuously, the thread was sandwiched inside the glass capillary tubing. Columns of any length, in the form of spirals (diameter, 12 cm), may be obtained quite easily; their preparation is simple, and they give highly reproducible results, provided the surface of the yarn is not scratched when the glass tubing is drawn out.

Union Carbide carbon and graphite yarns designated WYB, WYD and VYB were used. WYB and WYD are two-ply yarns; they were washed several times with isopropyl alcohol to remove the lubricant and dried in an oven at 300°; they were unwound to obtain the one-ply yarn used in the preparation of these columns.

VYB, a one-ply yarn, was treated in the same way. The characteristics of these yarns, which consist of a bundle of filaments, are given in Table I.

The sandwiched columns were evaluated on a commercial apparatus (Fractovap., C. Erba, Milan), equipped with a flame ionization detector, by injecting a mixture of *n*-pentane, isopentane, and methane, using nitrogen as the elution gas; the volume of nitrogen used to elute methane was taken as the dead volume of the column.

Usually tailed peaks were obtained. However, if the eluting gas contained

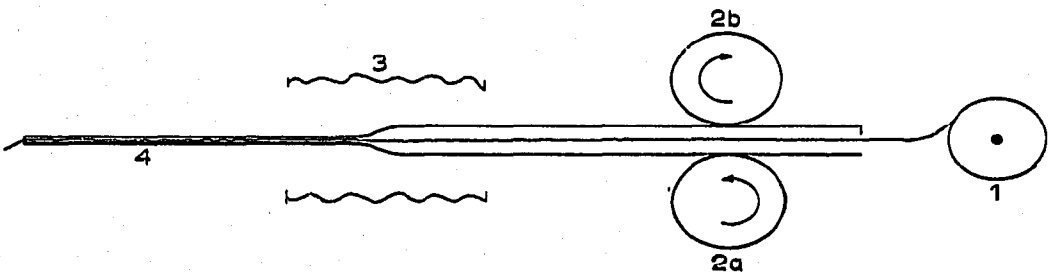

Fig. 1. Apparatus for the production of sandwiched columns. 1 = Spool of carbon yarn; 2 = feed rollers; 3 = electric furnace; 4 = carbon yarn sandwiched into glass capillary tubing.

TABLE I

CHARACTERISTICS OF CARBON AND GRAPHITE YARNS

Brand	*Type*	*Surface area*		*Filament size μ*
		m^2/g	m^2/m	
WYB	graphitized carbon black (2800°)	0.45	0.027	10
WYD	graphitized carbon black (2800°)	0.75	0.028	7.5
VYB	carbon fibres (1300°)	154	12.8	7.5

traces of compounds such as water or carbon disulphide, an improvement in the shape of the peaks was observed. As it has been found that also formic acid acts as an effective peak-tailing reducer, the elution gas was split into two streams, one of which was passed through a trap containing formic acid; the two streams were then combined. The temperature of the trap was changed in order to obtain symmetrical peaks; it was kept at 0° for a column temperature of 40°.

To obtain information on the behaviour of sandwiched columns, plots of the height equivalent to a theoretical plate *versus* velocity of the carrier gas were made for various hydrocarbons (Fig. 2). The minimum was obtained for quite a low velocity of the elution gas, and the efficiency of the column decreases with increasing flow rate. The values of the VAN DEEMTER equation of Fig. 2 are unsatisfactory, and occasionally negative values were obtained for the A term. The B and C values collected in Table II were obtained from the plot hU *versus* U^2 (Fig. 3), according to the equation:

$$h = \frac{B}{U} + CU$$

In the same table, experimental and calculated values for the minimum plate height, h, are reported.

Sandwiched columns differ from conventionally packed columns, where the adsorbing material is randomly distributed, and from porous layer columns, where the adsorption takes place on the walls. In sandwiched columns the adsorbing medium is inserted in the columns in an orderly fashion, and since it is made of a bundle of filaments, a sandwiched capillary column may be regarded as a set of equal micro-capillaries, so that the multiple path term of the VAN DEEMTER equation is missing.

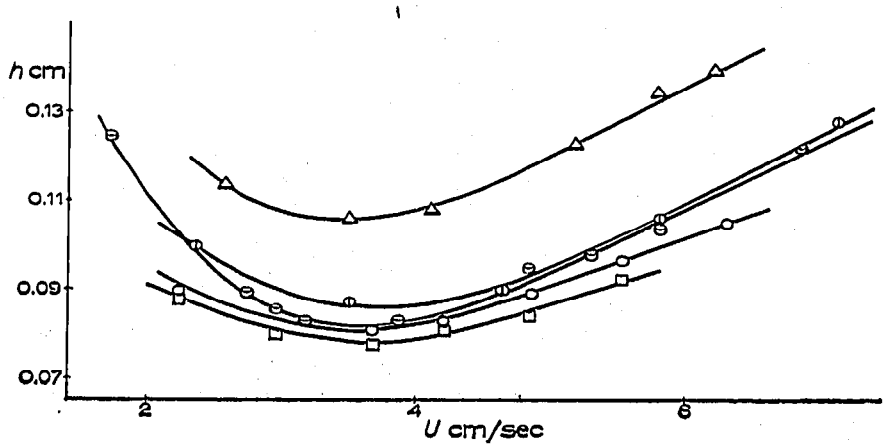

Fig. 2. Plots of HETP *vs.* linear velocity for various hydrocarbons on sandwiched columns of different internal diameters. □ = Isopentane, on 0.41 mm; ○ = pentane, on 0.41 mm; ⊙ = pentane, on 0.48 mm; ⊖ = pentane, on 0.44 mm; △ = heptane, on 0.41 mm.

TABLE II

VAN DEEMTER EQUATION CONSTANTS AND MINIMUM EXPERIMENTAL AND CALCULATED PLATE HEIGHT ON A WYD SANDWICHED COLUMN

	t (°C)	*I.D.* (*mm*)	*B* (cm^2/sec)	*C* (*sec*)	*h min* (*cm*)	
					exptl.	*calc.*
Isopentane	40	0.41	0.145	0.0095	0.078	0.0075
Pentane	40	0.41	0.130	0.0123	0.080	0.080
Pentane	40	0.44	0.130	0.0154	0.082	0.088
Pentane	40	0.48	0.130	0.0145	0.086	0.087
Heptane	60	0.41	0.120	0.0199	0.105	0.098

The B term has twice the value of the interdiffusion coefficient in the mobile phase, D_g, reported in the literature, as in an open tubular column, the labyrinth factor is equal to unity.

An examination of the VAN DEEMTER constants calculated for columns which had a different diameter shows that a better performance is obtained when the internal diameter is smaller. The same conclusion is reached by determining the pressure drop, Δp, necessary to obtain a specific separation within a certain time. As may be seen by considering the separation of isopentane–pentane shown in Fig. 3, Δp was plotted *versus* the time of analysis to obtain a resolution equal to 1.5. A smaller pressure drop and a shorter analysis time were found for the column with a smaller diameter.

Other data (capacity ratio, K'; performance index, P.I.; permeability, P) obtained for the separation of isopentane–pentane in sandwiched columns of various diameters are collected in Table III.

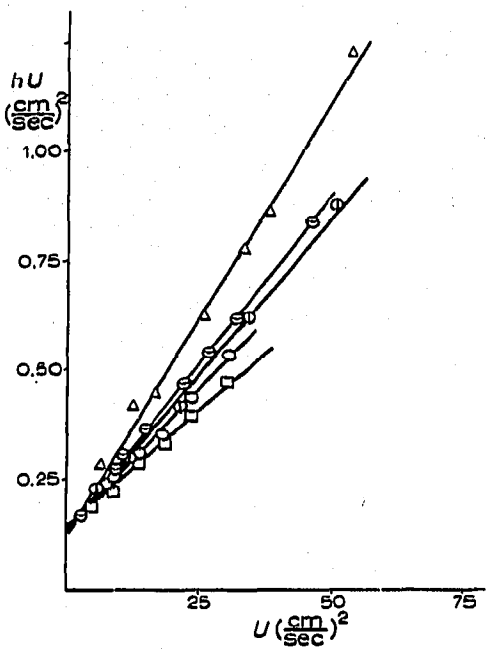

Fig. 3. Plot of hU *vs.* U^2 for the data of Fig. 2.

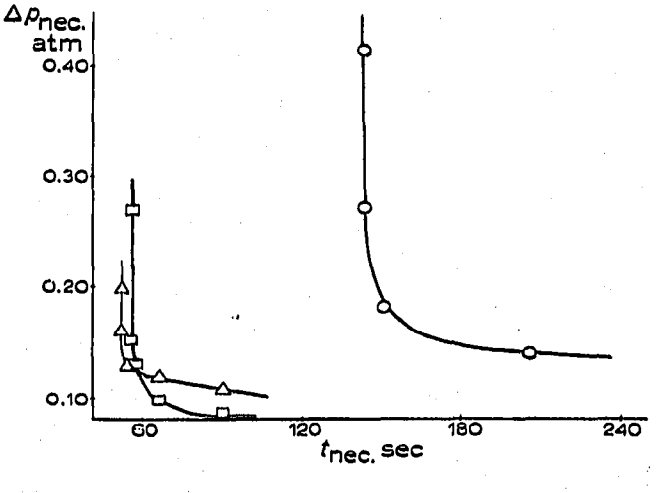

Fig. 4. Pressure drop *vs.* analysis time necessary to obtain complete resolution (R = 1.5) for a mixture of isopentane–pentane on columns having different internal diameters. ○ = 0.48 mm I.D.; □ = 0.44 mm I.D.; △ = 0.41 mm I.D.

TABLE III

COLUMN DATA AND PERFORMANCE INDICES AT 50°

Column		$\bar{K}$		*U min.* ($cm \cdot sec^{-1}$)	$P \cdot 10^7$ (cm^2)	*P.I.* (*poises*)
I.D. (*mm*)	*Length* (*m*)	*iso*-C_5	*n*-C_5			
0.48	6.0	0.21	0.3	3.6	27.9	55.4
0.44	4.3	0.49	0.8	3.2	10.5	88
0.41	4.8	0.51	0.83	3.5	8.3	91

TABLE IV

OPTIMAL COLUMN DATA AND PERFORMANCE PARAMETER

Length (*m*)	$Time_{nec.}$ (*sec*)	$\Delta p_{nec.}$ (*atm*)	*P.P.* (*atm/sec*)
6.4	143	0.271	38.7
1.5	57	0.133	7.55
1.2	54	0.129	6.9

The optimum values necessary to carry out the above separation ($R = 1.5$) are given in Table IV with the values of performance parameter, P.P., calculated according to the method of HALASZ[3].

These data clearly show that more satisfactory results in terms of column length, pressure drop and analysis time are obtained with the column of smaller diameter.

Specific gas permeability and other operational chromatographic parameters of sandwiched columns compare favourably with those of packed capillary columns.

Analytical applications

Although sandwiched columns are limited in use to materials available in

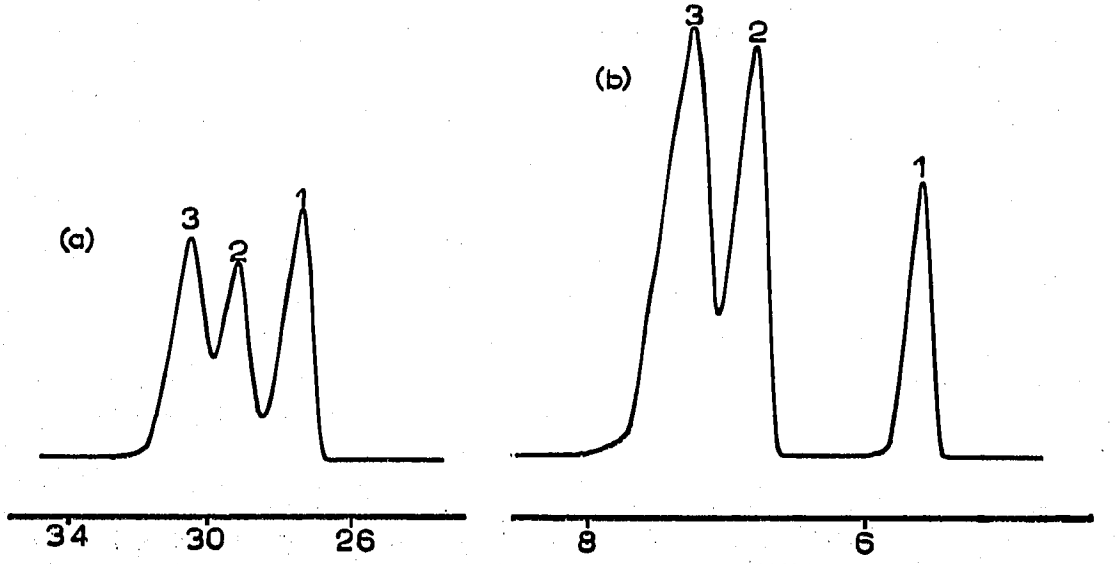

Fig. 5. Chromatogram of geometric isomers on a 10 m WYB sandwich column. (a) 1 = *m*-Xylene; 2 = *p*-xylene; 3 = *o*-xylene. Temperature = 124°; P_{N_2} = 0.8 atm. (b) 1 = *o*-Cresol; 2 = *m*-cresol; 3 = *p*-cresol. Temperature = 164°; P_{N_2} = 0.8 atm.

thread form, a large number of analytical applications may be expected, according to the specific nature of the adsorption material selected. The use of inorganic threads permits, one to operate at fairly high temperatures, and different results may be obtained if the surface area of the medium is modified. For example, gaseous hydrocarbons are separated above 100° on carbon yarn with a large surface area, whereas when the surface is small, separation occurs below room temperature.

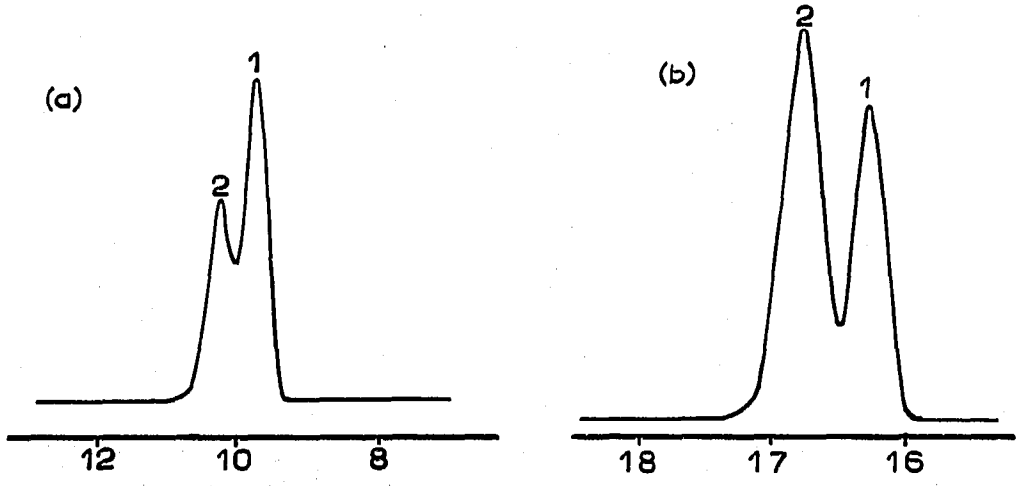

Fig. 6. Chromatogram of isotopic molecules. (a) 1 = d_6-Ethane; 2 = ethane. 10 m VYB sandwich column. Temperature = 115°; P_{N_2} = 1 atm. (b) 1 = d-cyclohexane; 2 = cyclohexane. 10 m WYB sandwich column; Temperature = 20°; P_{N_2} = 0.5 atm.

This research was limited to the use of graphitized carbon yarn and to carbon yarn, and examples of separations are described. The former is specifically used for the separation of polar compounds and geometric isomers, the latter, because of its high surface area, for the separation of permanent gases and volatile hydrocarbons at a fairly high temperature. Fig. 5 reports the separation of a mixture of geometric isomers on a WYB sandwich column. Fig. 6 shows the separation of isotopic pairs consisting of hydrocarbons and their deuterated homologues: ethane–deuteroethane and cyclohexane–deuterocyclohexane; the former is separated on a VYB (154 m^2/g) at 115°, and the latter on a WYB column (0.45 m^2/g) at 20°. One of the more interesting features of sandwiched columns is the reproducibility of results when columns of the same geometric properties are used.

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