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PROPERTIES OF MICRO-PACKED COLUMNS AND OF POROUS-LAYER OPEN-TUBULAR COLUMNS WITH GRAPHITIZED THERMAL CARBON BLACK

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SUMMARY

The properties of porous-layer open-tubular (PLOT) columns and of so-called micro-packed columns with graphitized thermal carbon black not coated with a liquid phase were compared by means of characteristic parameters such as HETP, permeability, capacity ratio and the C term in the Van Deemter equation.

It was found that micro-packed columns with graphitized thermal carbon black are useful for efficient and rapid separations and for the determination of the retention data of low-boiling isomers.

INTRODUCTION

Gas adsorption chromatography with graphitized thermal carbon black (GTCB) using classical packed columns is suitable for the separation of structural and geometrical isomers that have only very small differences in their physical properties. Moreover, retention data obtained on GTCB not coated with a liquid phase together with semi-empirical calculations of adsorption energy give useful information for the identification of separated compounds. For the solution of difficult separation problems, it is desirable to improve the separating power of GTCB columns. From the theoretical point of view two types of columns are applicable: porous-layer open-tubular (PLOT) columns[1,2] and so-called micro-packed columns[3–8]. Their applicability in gas–solid chromatography (GSC) with unmodified GTCB was examined in this work.

EXPERIMENTAL

Preparation of micro-packed columns

For filling small-diameter glass tubes with GTCB particles we used a technique similar to that described for the preparation of classical packed columns[9] using a variable-speed electric motor as a vibrator. The treatment of the column with ultrasonic waves proposed by Cramers *et al.*[3] was unsuitable in this instance.

The connection of the columns to the injection and detection system of a

Varian instrument was achieved with Swagelok T-pieces modified as an inlet splitter and a make-up gas inlet, respectively.

Preparation of PLOT columns

The preparation of PLOT columns with GTCB was similar to the procedure described by Vidal-Madjar *et al.*[10] using ultrasonically stabilized suspensions of about 20% GTCB dust in a low-boiling alkyl halide and a home-made capillary drying oven after Jennings *et al.*[11]. In this manner we produce PLOT columns with a length of 10 m and a GTCB layer of 10–20 μm.

RESULTS AND DISCUSSION

Properties of micro-packed columns

Micro-packed columns with GTCB possess high efficiency and good permeability, as shown in Table I in which the experimental values for the permeability (*K*) of some typical micro-packed columns are compared with values calculated according the equation given by Kozeny-Carman[12] and by Halász[13].

TABLE I

EXPERIMENTAL AND CALCULATED PERMEABILITIES (*K*) AND MINIMAL HETP VALUES FOR TYPICAL MICRO-PACKED COLUMNS WITH GTCB

Carrier gas, hydrogen; column temperature, 120°; $HEPT_{min}$ determined for *n*-hexane.

Column		*Particle size (mm)*	$K_{exp.}$ ($cm^2 \times 10^{-7}$)	$K_{Koz.-Car.}$ ($cm^2 \times 10^{-7}$)	$K_{Halász}$ ($cm^2 \times 10^{-7}$)	$HETP_{min}$ *(mm)*
Length (m)	*I.D. (mm)*					
1.5	0.80	0.16–0.20	2.10	2.00	3.14	0.44
1.5	0.45	0.16–0.20	1.92	2.00	3.14	0.37
1.5	0.80	0.09–0.125	0.84	0.73	1.13	0.28
1.5	0.45	0.09–0.125	0.82	0.73	1.13	0.23
2.7	0.45	0.09–0.125	0.77	0.73	1.13	0.21
1.7	0.28	0.06–0.08	0.27	0.31	0.50	0.13

The measured values on vibrational packed columns agree well with the values calculated by the Kozeny-Carman equation, although in our work the pellets were not completely spherical and the ratio of particle diameter (d_p) to column diameter (d_c) was between 0.15 and 0.40 (see Figs. 1b and 1c). In agreement with the theory but contrary to the results of Rijks *et al.*[5], we found only a slight dependence of permeability on the column diameter. The *K* values calculated by the Halász equation are higher than the experimental values. Nevertheless, the Halász equation is helpful for estimating the permeability.

The minimal HETP values depend not only on the particle diameter but also on the column diameter. This could be explained by irregularities in packing and/or by random effects. From the fact that in these instances nearly the same permeability results, it follows that irregularities in the packing influence the efficiency to a greater extent than the permeability. This is also reflected by the plots of HETP values *versus*

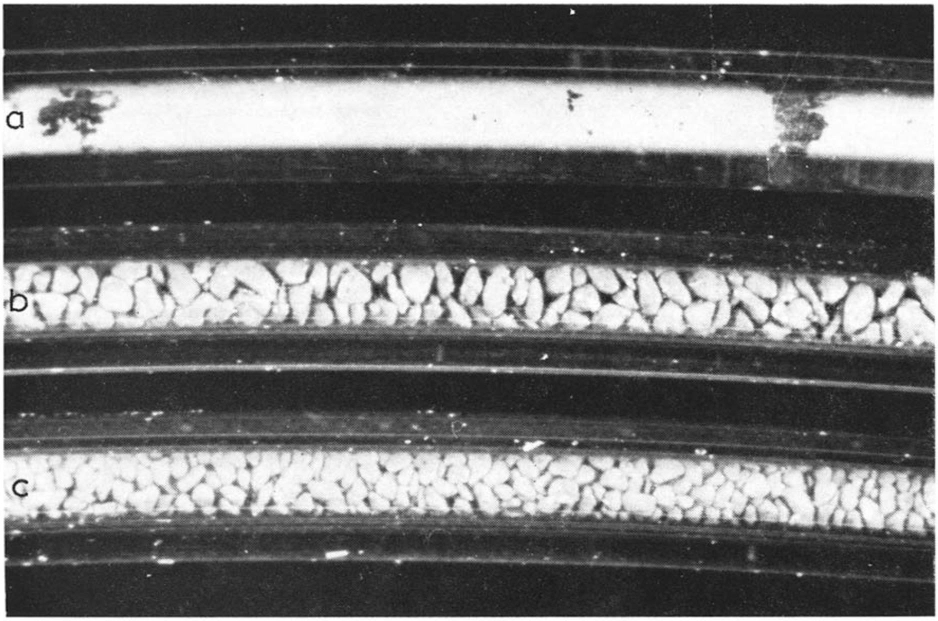

Fig. 1. Microphotographs of 0.45-mm I.D. columns filled with GTCB Sterling MT (Phase Separations, Solingen, G.F.R.). (a) PLOT column; (b) and (c) micro-packed columns with particle sizes of 0.16–0.20 and 0.09–0.12 mm, respectively.

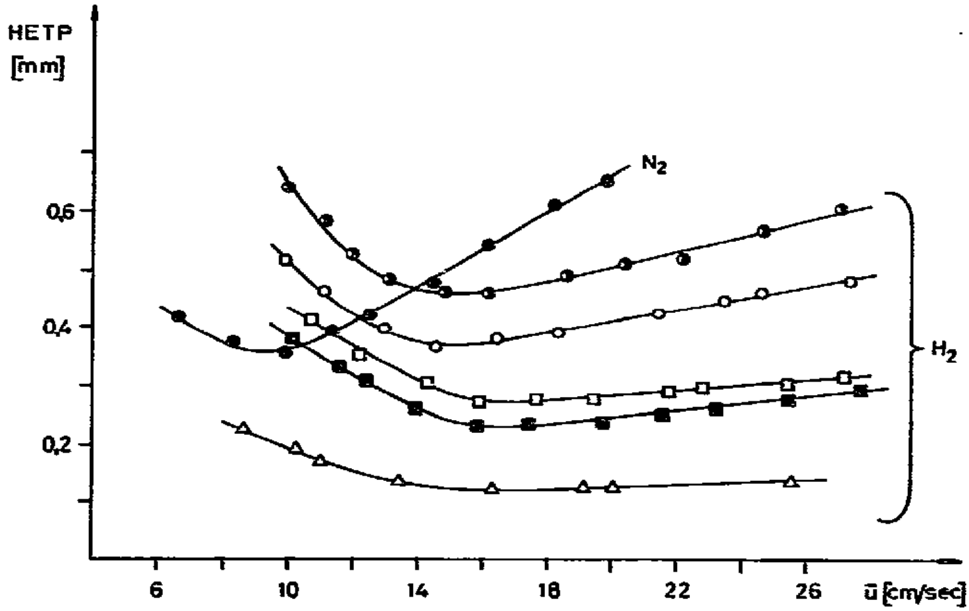

Fig. 2. Plots of HETP *versus* average linear gas velocity of the carrier gas measured for *n*-hexane ($k' \approx 19$) at 120° for different micro-packed columns. ●, ◐, Length = 1.5 m, I.D. = 0.8 mm, d_p = 0.16–0.20 mm; ○, length = 1.5 m, I.D. = 0.45 mm, d_p = 0.16–0.20 mm; □, length = 1.5 m, I.D. = 0.8 mm, d_p = 0.09–0.125 mm; ■, length = 1.5 m, I.D. = 0.45 mm, d_p = 0.09–0.125 mm; △, length = 1.7 m, I.D. = 0.28 mm, d_p = 0.06–0.08 mm.

average linear gas velocity for columns of different diameters with different particle sizes and different carrier gases (Fig. 2).

A comparison of columns with different particle sizes showed that the *C* term in the Van Deemter equation decreases as the particle diameter decreases. The *B* term decreases simultaneously because a decrease in particle size produces an increase in the pressure drop and thus a smaller diffusion coefficient. With decreasing particle size the minimal height equivalent to a theoretical plate also decreases, in accordance with eqn. 1 given by Huber *et al.*[14], provided that the diffusion coefficient of the components in the mobile phase is greater than the diffusion coefficient of the components in the GTCB particles. This assumption is confirmed by the very different slopes of the ascending part of the Van Deemter curve when hydrogen and nitrogen were used.

The usefulness of high-efficiency micro-packed columns with GTCB for the separation of low-boiling mixtures is shown in Figs. 3 and 4.

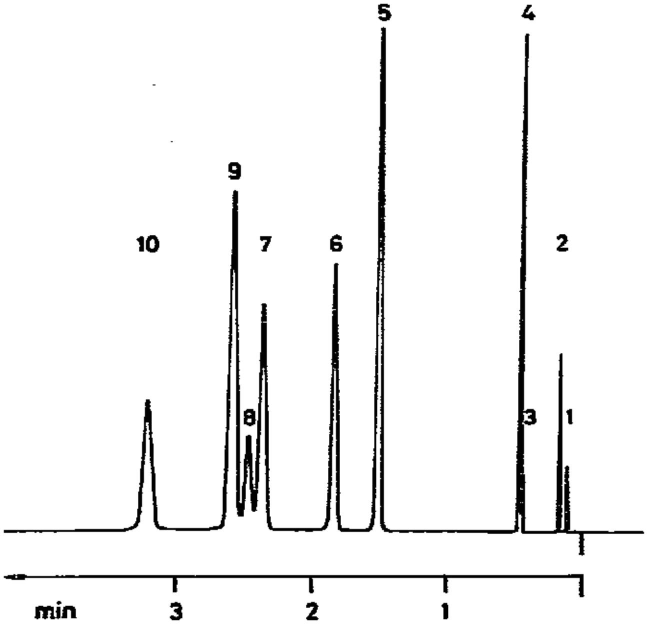

Fig. 3. Analysis of a mixture of gaseous hydrocarbons on a micro-packed column with GTCB. Column length, 1.7 m; I.D., 0.28 mm; GTCB, Sterling MT, particle size 0.06–0.08 mm; column temperature, 40°; carrier gas, hydrogen; inlet pressure, 7.2 bar. Peaks: 1 = methane; 2 = ethane; 3 = propene; 4 = propane; 5 = isobutane; 6 = 1-butene; 7 = isobutene; 8 = *n*-butane; 9 = *cis*-2-butene; 10 = *trans*-2-butene.

Properties of PLOT columns

The column efficiency expressed as the HETP (Table II) is unsatisfactory. The measured *C* term in the Van Deemter equation corresponds to the value obtained by Vidal-Madjar *et al.*[10], while the permeability is slightly poorer. Although the thickness of the GTCB layer is greater in our work, the *k'* values are not sufficient for a good separation of low-boiling mixtures.

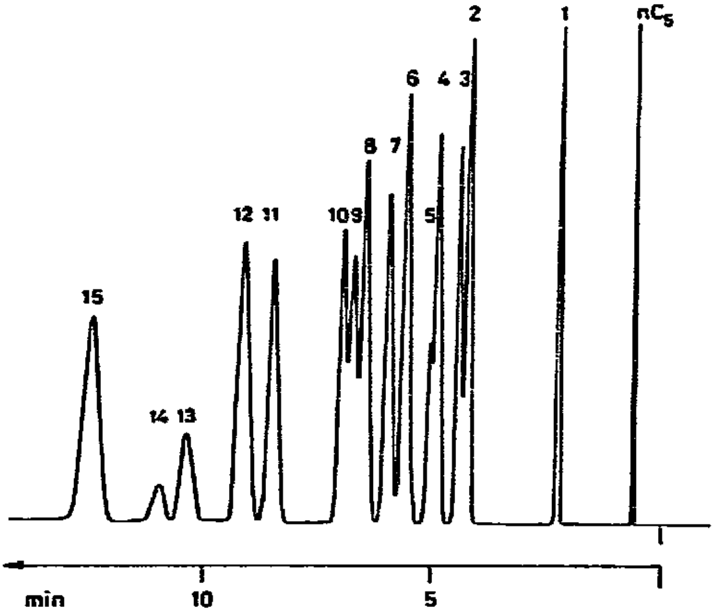

Fig. 4. Analysis of a mixture of isooctanes on a micro-packed column with GTCB. Column length, 2.7 m; I.D., 0.45 mm; GTCB, Sterling MT, particle size 0.09–0.125 mm; column temperature, 150°; carrier gas, hydrogen; inlet pressure, 5 bar. Peaks (with retention indices in parentheses): 1 = 2,2,3,3-tetramethylbutane (619); 2 = 2,2,3-trimethylpentane (676); 3 = 2,2,4-trimethylpentane (679); 4 = 3-methyl-3-ethylpentane (689); 5 = 2,3,4-trimethylpentane (691); 6 = 3,3-dimethylhexane (701); 7 = 2,2-dimethylhexane (706); 8 = 2,4-dimethylhexane (713); 9 and 10 = diastereomeric 3,4-dimethylhexane (716 and 719); 11 = 3-ethylhexane (737); 12 = 2,5-dimethylhexane (743); 13 = 4-methylheptane (754); 14 = 3-methylheptane (759); 15 = 2-methylheptane (770).

Moreover such columns exhibit some disadvantages:

(a) The preparation procedure is very time consuming.

(b) The reproducible production of a uniform layer is difficult. During the evaporation of the solvent some parts of the capillary column remain vacant (see Fig. 1a) or some GTCB particles break away and lead to obstructions.

(c) The retention characteristics of the GTCB can be changed by the suspension liquid. Trace amounts of thermal decomposition products of alkyl halides deposited on the surface of the GTCB and change their adsorption properties.

(d) The sample capacity is very low and high splitting ratios are necessary.

Comparison of different types of column

Table II compares some typical types of GTCB columns by means of the HETP, C term of the Van Deemter equation, optimal average linear gas velocity ($\bar{u}_{opt}$), inlet pressure for this velocity ($p_{i_{opt}}$), permeability (K), partition ratio for n-hexane (k'), resolution between n-hexane and 3-methylhexane (R) and gross retention time for the last peak, 3-methylhexane (t_{ms}). It can be seen that the micro-packed columns Nos. 2 and 3 exhibit good parameters. Their $HETP_{min}$ values are smaller than those of a packed and of a PLOT column. In addition the C term of column No. 3 is the smallest of all, thus permitting a much higher "working velocity" of carrier gas to be

TABLE II

COMPARISON OF DIFFERENT TYPES OF GTCB COLUMNS

Carrier gas, hydrogen; column temperature, 120° (40° for PLOT column).

No.	Type of column	Length (m)	I.D. (mm)	Particle size (mm)	$HETP_{min}$ (mm)	C ($sec \times 10^{-4}$)	$\bar{u}_{opt}$ (cm/sec)	$P_{i_{opt}}$ (bar)	K (10^{-7} cm^2)	k'	R	t_{ms} (min)
1	Packed	1.5	1.65	0.16–0.20	0.65	32	11.2	0.65	2.3	15.0	6.1	6.9
2	Micro-packed	1.5	0.80	0.16–0.20	0.44	15	15.5	1.20	2.1	16.8	7.7	5.9
3	Micro-packed	1.5	0.45	0.09–0.125	0.23	5	16.4	4.20	0.8	17.6	10.5	5.8
4	PLOT	10.0	0.45	—	1.20	13	26.5	0.24	141	7.1	8.1	9.6

applied without loss of resolution. This type of column is therefore very useful in the so-called high-speed GSC.

The partition ratio is nearly the same for classical packed and micro-packed columns. The resolution for micro-packed column No. 3 is 1.7 times higher than that obtained with the packed column with a shorter analysis time. Hence for the same resolution, the analysis time for a micro-packed column is much smaller. A drawback of this type of column may be the inlet pressure, which limited the column length by necessitating the use of a commercial instrument.

As mentioned above, the PLOT column has a poorer minimal HETP value than the micro-packed column, and even a significant increase in length does not compensate for this effect. With a longer analysis time the resolution obtained on the PLOT column is higher than that with columns Nos. 1 and 2, but lower than that of the micro-packed column No. 3*. The good permeability should allow the use of high "working velocities" at a low pressure drop. The limiting factor is, however, the relatively high *C* term in the Van Deemter equation.

CONCLUSIONS

The so-called micro-packed columns represent a good compromise in GSC with GTCB between resolution, analysis time and sample capacity. Particularly for the analysis of low-boiling mixtures they have certain advantages over PLOT columns: the preparation time is very short; $HETP_{min}$ is smaller; the *C* term in the Van Deemter equation is small; the resolution that can be obtained in a given time is better; the sample capacity is greater; and the unchanged adsorption properties of GTCB permit the precise and accurate determination of retention data.

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* The comparison is not quite exact, as the *k'* value of the peak in question is smaller on the PLOT column (the capacity ratio on the PLOT column was measured at a temperature that was 80° lower).