MICRO-PACKED COLUMNS WITH GRAPHITIZED THERMAL CARBON BLACK

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Dedicated to Professor Dr J. Zýka on the occasion of his 60th birthday.

Two types of column were prepared, conventional packed and micro-packed with Sterling MT graphitized thermal carbon black (GTCB). Comparison demonstrated the advantages of the micro-packed column. The adsorption of C_5—C_{10} alkanes and C_4—C_{10} 1-alkenes was studied on these columns in the interval 448·15—488·15 K. The differential heats of adsorption were calculated by the linear regression method from the temperature dependence of the specific retention volumes and the usefulness of the micro-packed column for determination of adsorption thermodynamic quantities was evaluated on the basis of the results. The separation efficiency of the two columns was demonstrated on the separation of a mixture of the geometric isomers of tricyclododecane.

Although conventional packed columns have so far been used most widely, capillary columns are finding increasing use because of their high separation efficiency. The difficulty of preparing capillary columns, however, prevents broader utilization of their advantages in everyday practice. Consequently, micro-packed columns have begun to be tested. Their relatively easy preparation and the high efficiency of these columns permits it to be assumed that these columns will combine the advantages of conventional packed and capillary columns.

In the works published so far, micro-packed columns have been used in the GLC or GLSC systems[1-8]. Consequently, attention has been paid at our Department to the use of micro-packed columns with graphitized thermal carbon black (GTCB) in the GSC system. The properties of GTCB made these columns useful both for physico-chemical measurements (study of sorption and structural dependences) and for analytical purposes.

Micro-packed columns are defined as columns with an internal diameter less than one millimetre, where the ratio of the particle diameter to that of the column is between 0·1 and 0·3 and the packing density is comparable with conventional packed columns.

Compared with packed columns, micro-packed columns have a larger number of theoretical and effective plates and are characterized by a rather low pressure

gradient. They are economically attractive as their small volume permits the use of expensive packings.

Compared with capillary columns, any material can be used to prepare the column, columns with an arbitrary stationary phase, either polar or nonpolar, can be prepared, the pressure gradient is not too large, the properties of micro-packed columns are reproducible, direct sample injection does not involve problems and thus they can be used for quantitative analysis.

Their advantages have led to use of these columns, *e.g.*, for the separation of low boiling hydrocarbons[4,7], for analysis of complex mixtures of steroids[4], and for organic substances in water and atmospheric pollutants[5]. Bruner and coworkers[6,8] used a modified GTCB for separation of polar compounds.

This work was carried out in order to compare the properties of conventional packed and micro-packed columns with pure GTCB, both from the point of view of the separation efficiency and considering the precise measurement of thermodynamic adsorption quantities.

EXPERIMENTAL

Vapours of n-alkanes and 1-alkenes were used to measure the thermodynamic adsorption quantities. The separation properties of the columns were found using a mixture of tricyclododecanes formed by catalytic cyclization of cyclododecatrienes.

TABLE I
Characteristics of the columns prepared

Characteristic	Packed column	Micro-packed column
Material	glass	glass
Length, m	0·60	2·00
Internal diameter, mm	3	1
Adsorbent	GTCB Sterling MT	GTCB Sterling MT
Fraction, mm	0·25–0·30	0·09–0·12
Adsorbent mass, g	4·1280	1·1130
n_{ef}	285	315
$H_{ef,min}$, cm	0·211	0·063
$\bar{u}_{min}$, cm s^{-1}	4·86	2·76
$K \cdot 10^{-7}$, cm^2	2·31	0·50
k (n-heptane)	5·62	7·76
R_{ij} [a]	0·90	1·43

[a] Differentiation between two isomers of tricyclododecane.

The adsorption was carried out on Graphitized carbon black Sterling MT (Cabot Co., USA) with a well-defined surface area of 7·6 m^2/g.

The measurements were carried out on a Hewlett–Packard 5 700 A gas chromatograph with FID. The carrier gas was nitrogen with F_m for the conventional packed column of 23—25 ml . . min^{-1} and for the micro-packed column between 4·3 and 4·8 ml min^{-1}. The samples were injected as the saturated vapours in amounts of 0·5—1·5 μl (packed column) and 0·20—0·50 μl (micro-packed column) using Hamilton syringes.

Preparation of the micro-packed column. The column in the shape of a spiral was fixed in a holder, one end was sealed with glass wool and connected to a water pump. The other end was connected to a reservoir containing a selected GTCB fraction. The packing was deposited evenly through the whole column by reducing the pressure and lightly tapping the column walls with a rubber tube.

RESULTS AND DISCUSSION

The same measurements using the same adsorbates were carried out on both prepared columns. In the introductory experiments, the $H_{ef,min}$ and $\bar{u}_{min}$ values for heptane at 175°C were found for both columns and at $\bar{u}_{min}$ the permeability and capacity ratios for n-heptane were found (Table I).

Further, the retention times were measured for n-alkanes and 1-alkenes in the temperature range 175—215°C in five-degree intervals. The chromatographic peaks

TABLE II

Differential heats of adsorption ΔH of n-alkanes and 1-alkenes on GTCB in the temperature range 448·15—488·15 K

Hydrocarbon	ΔH, kJ/mol packed column	ΔH, kJ/mol micro-packed column	ΔH, kJ/mol published values
n-Pentane	34·19 ± 0·64[a]	38·38 ± 0·71	36·30 — 38·07
n-Hexane	39·20 ± 0·63	45·71 ± 0·60	41·10 — 46·86
n-Heptane	45·51 ± 0·59	50·57 ± 0·58	48·98 — 52·30
n-Octane	53·15 ± 0·76	57·98 ± 0·76	55·68 — 56·07
n-Nonane	58·12 ± 1·04	65·04 ± 1·00	61·13 — 61·92
n-Decane	65·58 ± 0·75	71·26 ± 0·82	67·40 — 69·87
1-Butene	27·61 ± 0·53	—	29·10 — 30·15
1-Hexene	34·49 ± 0·57	42·57 ± 0·54	38·25 — 41·87
1-Heptene	42·06 ± 0·72	47·37 ± 0·75	46·89
1-Octene	48·76 ± 0·65	53·92 ± 0·76	54·00
1-Nonene	54·11 ± 0·83	61·83 ± 0·66	59·45
1-Decene	59·65 ± 0·78	66·93 ± 0·57	64·06

[a] Standard deviation $n = 10$.

were sharp and symmetrical and the retention times were independent of the injected amount, indicating that the adsorption occurs in the linear part of the isotherm.

Table II lists the values of the heat of adsorption found on packed and micro-packed columns and compared with the heat of adsorption values found in the literature[9-14], measured either calorimetrically or by the GC method.

The sorption of substances on GTCB is dependent on the number of contacts

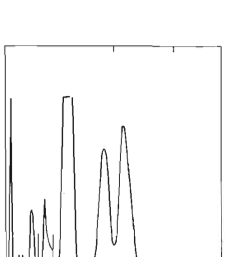

FIG. 1

Separation of a mixture of the geometric isomers of tricyclododecane on a packed column at a temperature of 215°C

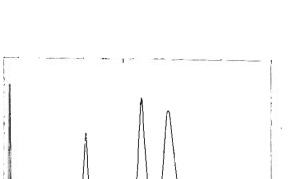

FIG. 2

Separation of a mixture of the geometric isomers of tricyclododecane on a micro-packed columns at a temperature of 215°C

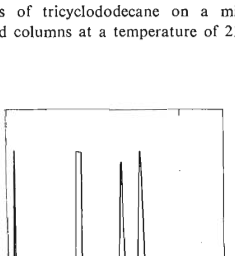

FIG. 3

Separation of a mixture of the geometric isomers of tricyclododecane on a micro-packed at a temperature of 240°C

of the force centres of the adsorbates with the surface. Various numbers of contacts with the best orientations of various molecules with respect to the GTCB surface leads to favourable conditions for separation of geometric isomers. An example of such a separation is the analysis of the geometric isomers of tricyclododecanes. This separation was carried out on both columns in the temperature interval 205–240°C. Figs 1 and 2 depict the chromatograms for separation of this mixture at a temperature of 215°C. The separation efficiency of the packed column decreased with increasing temperature, while the separation properties of the micro-packed column improved with increasing temperature, with shortening of the analysis time and an increase in the peak symmetry (Fig. 3).

In agreement with theoretical assumptions, it was found that the micro-packed column has far greater efficiency ($H_{ef} = 0{\cdot}063$ cm) but the other characteristics disagree with these assumptions. For the micro-packed column the $\bar{u}_{min}$ and K values are lower and the k values are higher than for the conventional column. Thus a very effective micro-packed column was prepared with a high load, at the cost of low permeability and the necessity of using a greater pressure gradient.

It follows from the values of the ratio $d_p/d_c = 0{\cdot}09-0{\cdot}12$ for the micro-packed column that the packing density was great, leading to the low permeability value. This fact also explains the higher value of the capacity ratio, as the overall surface of the adsorbent was large compared with the small size of the packing particles. This permitted direct injection of up to 0·1 μl of liquid sample, so that this column can also be used for quantitative purposes.

It is apparent from the chromatograms obtained in the measurements on the micro-packed column (Figs 2, 3) that the separation efficiency of this column makes it useful for analysis of impurities. The effective height of a theoretical plate for this column is even larger than H_{ef} for the PLOT column prepared by Guiochon and coworkers[15] packed with unmodified carbon black.

In the overall evaluation of various types of columns, a number of basic factors must be considered: means of preparation, the efficiency and the precision of the measurement of retention data. The PLOT column is the most tedious and difficult to prepare; this is far from compensated by the efficiency, while the preparation of micro-packed columns is as fast and simple as that of conventional packed columns. Micro-packed columns attain much higher efficiency than packed columns and, provided comparison with the published data is possible, have even greater efficiency than the PLOT columns. The precision of measurement of retention data on micro-packed columns is also better.

Because of these properties, it is suitable to use micro-packed columns both for physico-chemical measurements and for analytical purposes. It can be assumed that these properties will lead to ever broader use of micro-packed columns, especially in the analysis of complicated mixtures in which the components are present in very different concentrations, *e.g.* in environmental control.

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