Permeability and preparation of micropacked columns

Permeability and Preparation of Micropacked Columns

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Summary

A simple procedure for preparing packed columns with an internal diameter of 0.6–0.8 mm and up to 15 m long is described. Theoretical plate numbers of the order 40,000 at capacity ratios > 4 can be obtained at moderate inlet pressures. Special attention is given to the permeability of packed capillaries and micropacked columns. Some examples are given of separations obtained with micropacked columns.

Introduction

It is now recognized that a particular separation problem not only requires an optimal stationary phase and an optimal column temperature, but may also require an optimal column type.

In most practical cases, however, the choice of column type is not made specifically to ensure a rapid separation of a given mixture or to give the required information but because the column is at hand and fits the apparatus. It cannot be expected that this is the optimal solution. Although most of the present column types can be prepared by skilled technicians without much difficulty, they require quite different technological procedures. It seems that when someone has succeeded in preparing good columns of a given type with reproducible properties, he is afraid to turn to another type that will require new trials and involve new difficulties.

False rumors concerning instability, short life and irreproducibility of some column types and the lack of instruments suited for their application can be considered as serious obstacles to overcoming practical difficulties. Therefore it will be interesting to study the possibilities and limitations of packed capillary [1–3] and micropacked columns [4, 5] because they link the two conventional column types: open tubular columns and packed columns.

In this paper we will discuss one of these intermediate column types: the micropacked columns.

The preparation of these columns, which combine to a large extent the advantages of packed and open tubular columns will be discussed in detail.

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Because of its fundamental significance for the preparation of micropacked columns, in this paper special attention is paid to the permeability of the column.

Column Permeability

The permeability is a very important property of a gas chromatographic column because of its direct and indirect influence on a number of separation factors. It sets a practical maximum for the column length i. e. the maximum separating power of a column type. It plays an important role in the final value of the retention time. Unfortunately it is not mentioned very often.

Integrating the Darcy equation, which is valid at low flow velocities and for ideal carrier gases normally encountered in gas chromatography [6] it follows that:

$$u_0 = \frac{\kappa p_0}{2\eta L}(P^2 - 1).$$

The permeability (κ) of the column can be obtained by plotting the column outlet flow-rate, u_0 (cm sec^{-1}), versus the corresponding values of $P^2 - 1$ (dyne cm^{-2}). P is the ratio of the column inlet pressure (p_i) and the column outlet pressure (p_0). The viscosity (η) depends only upon the carrier gas.

Theoretically the permeability of open tubular columns only depends on its diameter. In practice the permeability is somewhat less (10–30 %) than the theoretical value, $r_c^2/8$ [7], probably for reasons of roughness of the column wall and irregularities in the column diameter.

According to the Kozeny-Carman equation [3] the permeability of packed and packed capillary columns may be increased by an increase in particle size (d_p) or a decrease in packing density.

$$\kappa = \frac{d_p^2}{180} \cdot \frac{\epsilon^3}{1-\epsilon^2}$$

The porosity ϵ is the complementary value of the packing density. It is defined as the ratio of the mobile gas space and the column volume. This equation which applies to the case of smooth spherical particles can be extended to non spherical materials by introducing a suitable apparent particle diameter.

Permeabilities determined by the Kozeny-Carman equation and the integrated Darcy equation for micropacked columns of different internal diameter are in good agreement for d_p/d_c ratios less than 0.25, as shown in Table 1

The permeability of packed capillary columns and micropacked columns is compared with the permeability of

Table 1. Permeability of micropacked columns according to the Kozeny-Carman equation and the integrated Darcy equation.

d_c mm	d_p/d_c	ϵ	κ (Kozeny-Carman) $cm^2 \times 10^7$	κ (Darcy) $cm^2 \times 10^7$
0.6	0.28	0.59	5.0	3.1
0.7	0.24	0.50	2.7	2.7
0.8	0.21	0.51	2.8	3.0

packed and open tubular columns in Fig. 1. Comparing plots 2 and 4 for packed capillary columns and 3 and 5 for micropacked columns it can be concluded that for a constant particle diameter range the permeability decreases with an increasing column diameter. *Guiochon* [8] has shown that for packed capillary columns having a constant internal diameter, the permeability decreases with decreasing particle diameter range. In both cases the permeability decreases with decreasing d_p/d_c ratio.

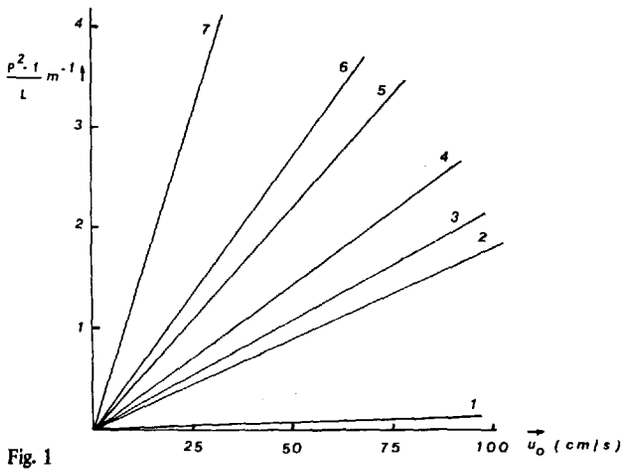

Fig. 1

• Plots of carrier gas outlet velocity u_0 vs. $\frac{p^2-1}{L}$ for various types of columns.

1. Open tubular column (i. d. 0.25 mm). 2 and 4. packed capillary columns, d_p = 100–125 µm, d_c = respectively 0.45 and 0.55 mm, support Chromosorb P. 3 and 5. micropacked columns, d_p = 140–160 µm, d_c = resp. 0.64 and 1.26 mm, support glass beads. 6 and 7. conventional packed columns, d_p = 200–250 µm, d_c = 4 mm, support glass beads and Chromosorb P respectively.

It seems that an optimal permeability will be obtained for packed capillary columns as well as for micropacked columns for a d_p/d_c ratio between 0.2 and 0.25.

From plots 6 and 7 it can be seen that the permeability for glass beads is better than for a porous support.

Comparison of Column Types

In another paper [5] the authors compared the properties of packed columns, open tubular columns and packed capillary columns. Attention was paid to, among others, plate number, speed of analysis, resolution, performance index, sample requirements (quantity and speed of introduction). It appears that open tubular columns are theoretically the most favourable ones. Packed capillaries according to *Halasz* and micropacked columns take an intermediate position.

In practice, however, there are many factors which do tip the scales in favour of packed columns, which are used in 90 % of cases. Open tubular columns are used in most other cases.

Micropacked Columns

Some years ago we succeeded in combining the advantages of conventional packed columns and to a large extent those of capillary columns in what we call micropacked columns [4, 5].

They can be defined as columns having an internal diameter less than 1 mm, a particle/column diameter ratio between 0.1 and 0.3 and a packing density comparable to conventional packed columns.

Micropacked columns have the following advantages:

- any support may be impregnated with any stationary phase in the desired quantity;
- packing may be prepared in large batches to insure reproducible properties;
- the pressure drop is not excessive;
- the number of theoretical and effective plates is high;
- direct injection presents no difficulties;
- economically attractive, the small column volume allows the use of expensive packings (e. g. Durapak, Corasil);
- any column material may be used.

Packing Material

The permeability of a packed column can be improved by a reduction of the internal diameter of the column as shown before.

For column diameters below 1 mm the introduction of packing material and the pressure drop are the limiting factors when the column length exceeds 3 to 4 m.

We have found that significant improvements are obtained if carefully sieved fractions of column material are used with particle sizes within 20 µm. The sieved support showed a markedly improvement in the regularity of packing. The regularity increases with decreasing particle size [4]. Large particles that might block the capillary during packing are removed. Elimination of the fines is achieved by suction under the sieves.

Instead of sieving, flotation or sedimentation may be used. It may be expected that these techniques yield a very narrow range of particle sizes. It was also found that the specified mesh size ranges of commercial supports were smaller than those resulted from the sieving.

Preparation of Micropacked Columns

For the packing of micropacked columns a special technique is required. The empty column, provided with straight ends is placed in an ultrasonic bath filled with water as shown in Fig. 2. One end of the column is plugged with 1–2 cm of silanized glass wool and connected to a vacuum pump. The other end of the column is inserted in a vertical

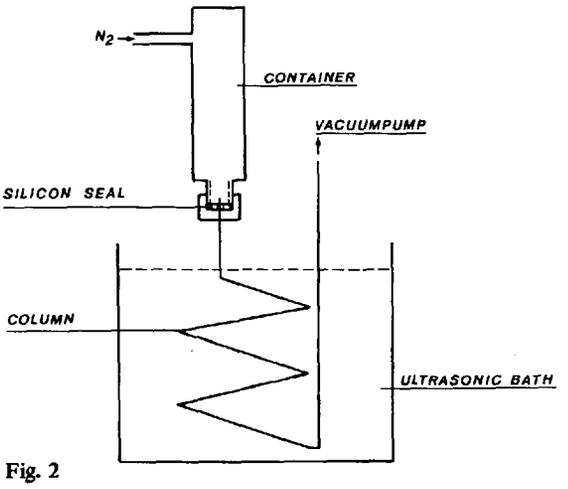

Fig. 2

● Equipment for filling micropacked columns

cylindrical container and sealed by a silicone rubber septum. It is essential that the axis of the coil is vertical.

The packing material is introduced into the container which is connected to a pressure line of inert gas. The ends of the column and the container are above the water level. The packing is continuously transported into the column by a gradual increase of the pressure drop across the column. To obtain a continuous stream of particles to the column inlet a hand vibrator is held on the surface of the container. The final inlet pressure which depends on the kind of column material will not exceed 6 atm for columns up to 15 m.

With glass columns the packing can be followed visually. In the case of metal columns packing up to a constant weight should be carried out.

The time required for the packing of the column will be between 1 and 4 min per m of column length.

The lower value applies to glass beads and the higher value to porous supports. The reproducibility of packing density is excellent for both glass and metal columns [4]. After filling, the column inlet is plugged with 1–2 cm of silanized glass wool. If it is more convenient for the connection of the column to the instrument the straight pieces can be cut off. Both column ends must be plugged again in this case.

For highly loaded supports (20–30 % of stationary phase) the packing procedure may be complicated because of clogging of the particles at the column inlet. This problem can be solved by a reduction of the inlet pressure for a short while. The particle stream in the column will be reversed during this time.

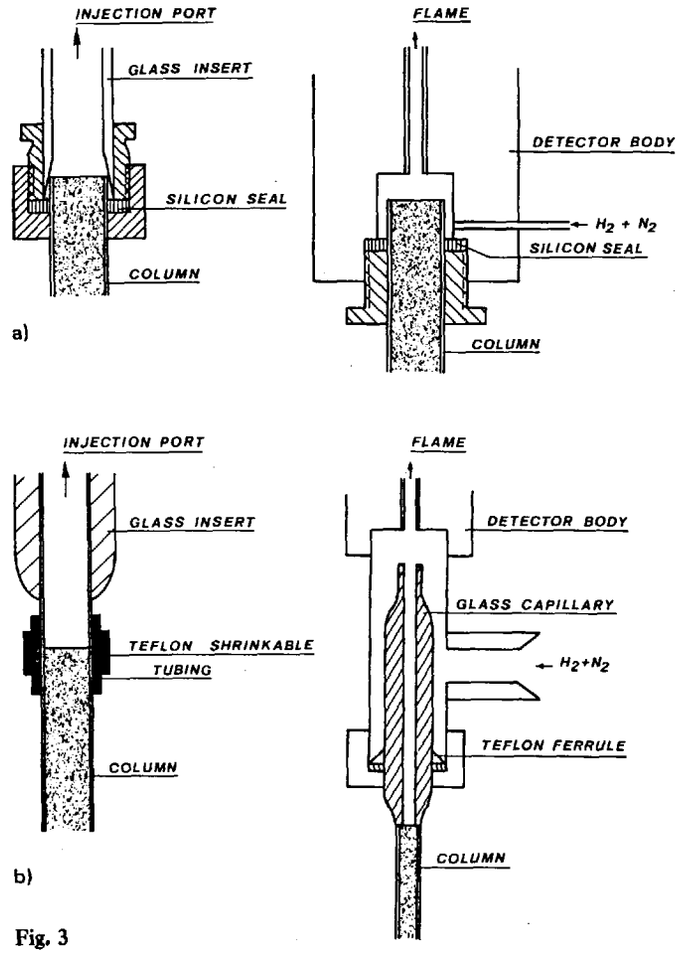

Fig. 3

● Connections of micropacked columns to injection and detection systems of commercial instruments.

Connection of the Columns to the Injection and Detection System of Commercial Instruments

The connection of micropacked columns to the injection and detection system of commercial instruments can be effected in different ways. The connections described by *Schomburg* [9] for open tubular columns and *Halasz* and *Heine* [3] for packed capillary columns, can also be used for micropacked columns. In our laboratory two different connections have been used up to now. In both systems a purge gas is supplied at the column outlet to minimize the effective dead volume between column and detector. The construction of both the systems is schematically given in Fig. 3.

In the first system (a) the inlet part is provided with a glass insert tube with an internal diameter equal to the column inside diameter (normally 0.8 mm). The column connection side of this tube is wider and conically shaped. The column is inserted about 2 mm into the cone and the seal is made with a silicone rubber ring.

The outlet of the column protrudes into the hydrogen (mixed with nitrogen) stream for the FID detector so that the effective dead volume between column and detector is very small.

In the second system (b) the insert tube of the inlet system is drawn out to match the outside diameter of the column. The column is connected to this insert tube by double teflon shrinkable tubing.

At the detection end the column is connected to a glass rod (o. d. = 6.3 mm, i. d. = 0.3 mm) which is also drawn out at both ends to match the outside diameter of the column (normally 1.2 mm). The glass rod is connected to the detector as shown in Fig. 3b. The seal is made of

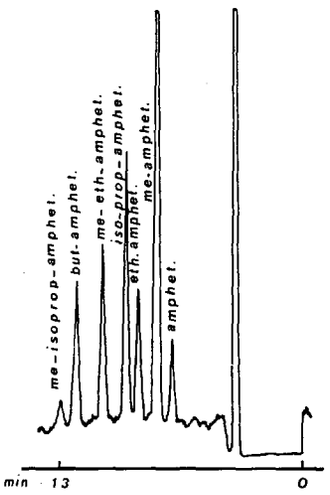

Fig. 4

- Analysis of amphetamines with micropacked column. Chromosorb W-AW/5 % KOH/10 % OV 101, 180–200 μm, L = 10 m, I.D. = 0.8 mm, T = 150 °C, P_i = 4.0 atm., $n_{opt.}$ (at 4.0 atm.) = 25,000.

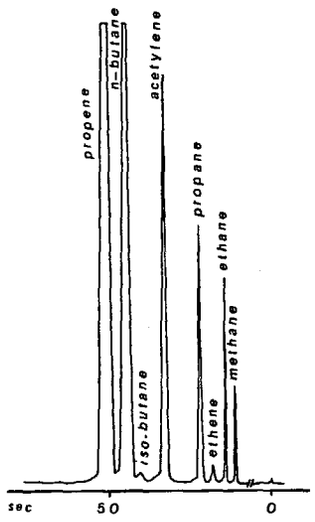

Fig. 5

- Fast separation of hydrocarbons (C1–C4) with micropacked column, Porasil C/phenylisocyanate, 180–200 μm, L = 0.5 m, I.D. 0.8 mm, T = 70 °C.

a normal $\frac{1}{4}$ in. teflon ferrule, Swagelok type. In this system also a purge gas (nitrogen) is used to overcome the dead volume problem.

The metal T-piece is a metal $\frac{1}{4}$ in. Swagelok T-piece which is modified at its upper end to fit the detector.

Some Examples of Separations with Micropacked Columns

Some examples of the use of micropacked columns are given in this paper. The application of these columns in petroleum chemistry and steroid analysis is given in references [4, 5].

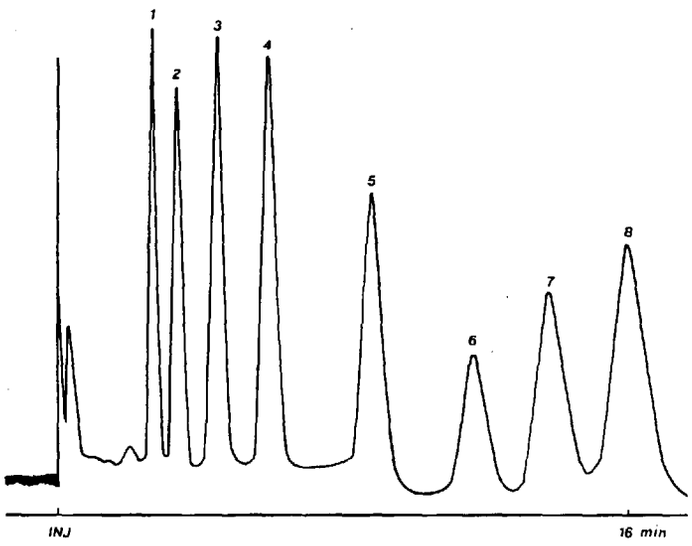

Fig. 6

- Analysis of mixture of barbiturates with micropacked column, Gaschrom Q/OV 17 (2 %), OV 225 (1 %), 180–200 μm, T = 200 °C, L = 0.8 m, I.D. = 0.8 mm, sample 100 μg per component, detector F.I.D., atten. 32 for comp. 1–4 and 16 for comp. 5–8. 1 = aprobarbital, 2 = amobarbital, 3 = secobarbital, 4 = hexobarbital, 5 = brallobarbital, 7 = heptobarbital, 8 = heptabarbital. Courtesy Dr. *O. Driessen*, Academic Hospital, Leiden, The Netherlands.

The separation of alkyl amphetamines with a micropacked OV 101 column is demonstrated in Fig. 4.

An example of a very fast analysis of low boiling hydrocarbons on Porasil C/phenyl isocyanate is given in Fig. 5. The separation of a number of barbiturates is given in Fig. 6.

References

[1] *Halasz, I.* and *Heine, E.*, Nature 194, 1971 (1962).
[2] *Halasz, I.* and *Heine, E.*, Anal. Chem. 37, 495 (1965).
[3] *Halasz, I.* and *Heine, E.*, "Advances in Chromatography" Vol. IV, p. 207.
[4] *Cramers, C. A., Rijks, J. A.*, and *Bocek, P.*, J. Chromatog. 65, 29 (1972).
[5] *Cramers, C. A., Rijks, J. A.*, and *Bocek, P.*, Clin. Chim. Acta 34, 159 (1971).
[6] *Guiochon, G.*, Chromatog. Rev. 8, 1 (1966).
[7] *Landault, C.* and *Guiochon, G.*, "Gas Chromatography 1964". *A. Goldup*, ed., Institute of Petroleum, London 1965.
[8] *Guiochon, G.*, "Advances in Chromatography", Vol. VIII.
[9] *Schomburg, G.* et al., "Advances in Chromatography 1974". *A. Zlatkis* and *L. S. Ettre*, ed., Chromatography Symposium Department of Chemistry, University of Houston, p. 73.