A NOVEL TECHNIQUE FOR FILLING WIDE DIAMETER GAS CHROMATOGRAPHIC COLUMNS

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(First received August 31st, 1962)

(Modified February 27th, 1963)

INTRODUCTION

The low efficiencies found with large diameter columns are due mainly to the method of packing[1–4]. Various methods have been devised by which efficient columns can be produced, such as beating the column while adding the packing at a controlled rate, vibrating the column when filled and pouring the packing in without vibration. These methods are, however, not very reproducible.

We have based our methods of packing large diameter columns on the fluidization technique. The columns, which can be prepared by anybody, are efficient and reproducible. The time taken is not more than 10 min for a column, 1 m long, of any diameter.

For this present study, we have used stainless steel columns, 6 cm I.D. and 1 m long.

A gauge to support the packing is placed at the bottom of the column which is then filled with the chosen size of packing without any special precautions. The packing is fluidized for a few minutes by means of a stream of nitrogen fed into the column through a conical adaptor. When a steady fluidized state has been reached the nitrogen flow rate is gradually decreased until a fixed bed is obtained; the column is then ready for use and has the properties of a fixed bed.

EXPERIMENTAL

Test have been made under the following conditions:

Column. Stainless steel; I.D.: 6 cm; length: 1 m. Filling: Chromosorb P. Particle size: 30–40 mesh. Stationary phase: silicone oil DC 200 at 20 % by weight on the Chromosorb.

Carrier gas flow rate. 250 l/h of nitrogen.

Column temperature. 40°.

Vaporizer temperature. 85°.

Sample. 1–2 ml of a 50 % mixture by weight of pentane and hexane.

RESULTS

Reproducibility of column efficiency obtained by fluidization of the packing

For every test, the column was emptied, filled and fluidized. A survey of the results is given in Table I.

For injections of hexane of 0.022 ml/cm² of column cross sectional area, the fluidization technique produces columns with an efficiency of more than 300 plates/m, with a reproducibility of over 8%.

TABLE I

Test	*Density of packing g/ml*	*Efficiency in number of theoretical plates per m of column and calculated for hexane peak*
1	0.444	313
2	0.443	330
3	0.444	324
4	0.446	322
5	0.452	302
6	0.453	303

Effect of sample injection

A 6 cm I.D. column, 1 m long, can be injected with a sample of 10 ml of pentane–hexane mixture and still give an efficiency of 80 plates/m. Fig. 1 shows the chromatogram of a 1.2 ml and a 10 ml injection. It should be noted that the pronounced tail which appears on the hexane peak for the 10 ml injection is the second impurity.

In the present work, a 10 ml injection was the maximum, since by injecting larger quantities with a syringe, the injection time becomes too long and may affect the column behaviour.

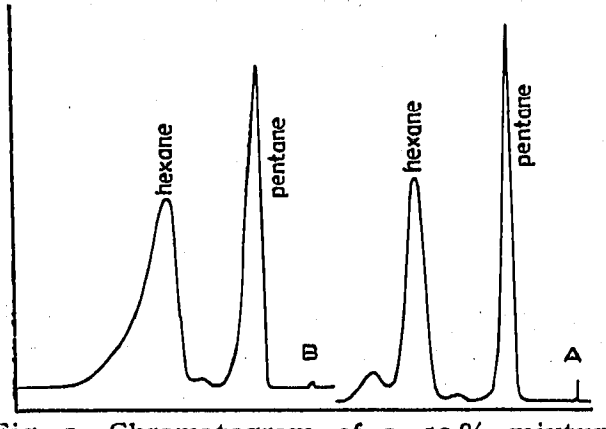

Fig. 1. Chromatogram of a 50% mixture (by weight) of pentane and hexane. Sample size: A = 1.2 ml; B = 10 ml.

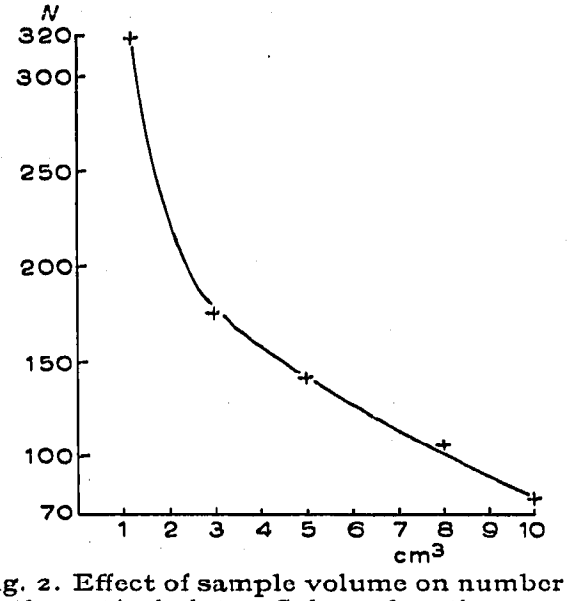

Fig. 2. Effect of sample volume on number of theoretical plates. Column length: 1 m.

Fig. 2 shows the number of theoretical plates plotted against the size of the sample injected. The curve has the appearance of part of a hyperbola.

DISCUSSION

The phenomena of fluidization have been studied by LEVA[5] and REBOUX[6]. The main properties of a fluidized bed may be summarized briefly as follows.

It is known that the pressure drop of a fluidized bed is equal to the weight of solid particles per unit cross-sectional area. Thus the pressure drop/flow diagram shows that the fluidizing point is reached at the point B corresponding to P/S in Fig. 3. With increasing fluid velocity, the pressure drop reaches a maximum and then decreases to a stable point, which has the same value as point B and is also equal to P/S.

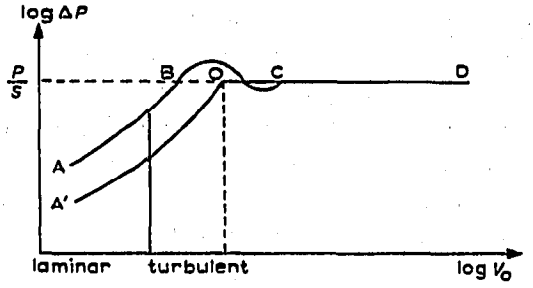

Fig. 3. Pressure drop/flow diagram according to REBOUX.

If we reverse this operation, *i.e.* start from the stable fluidized state at the point D and reduce the fluid velocity, then the pressure drop follows a new curve DOA' which has the same slope as the first but lower pressure drop values. If the fluid velocity is now increased the curve A'OD is produced but the expansion of the fixed bed occurs as soon as the value P/S is reached and there is no maximum value as in curve ABC.

The following properties distinguish an initial fixed bed and a fixed bed after fluidization:

(1) The onset of fluidization in an initial fixed bed is an unstable phenomenon and is non-reversible.

(2) The fixed bed after fluidization has reproducible reversible properties. The voidage Em, required for the onset of fluidization is termed the "minimum fluid voidage" and its value is higher than for an ordinary fixed bed—in this state the particles are touching.

The consequences of such a theoretically perfect filling for large diameter, preparative gas chromatographic columns are as follows:

(a) Because of the uniform compactness, the carrier gas profile inside the column must show a minimum concavity from the walls to the centre.

(b) The minimum compactness of the packing increases the radial diffusion. This property has a direct effect on the constant A of the Van Deemter equation[7]. The constant A depends upon the packing of the column and its value is $A = 2 \lambda dp$, where dp is the particle diameter, and λ the measure of packing irregularities.

(c) The time taken to fill a column is definitely reduced and, in addition, the long time required to reach the desired temperature, due to the temperature gradient between the walls and the centre of the column, may be reduced. In a fluidized bed the heat transfer is at a maximum because of the large heat exchange area between the gas phase and the solid, and the turbulence of the gas and the particles. Since the temperature inside the fluidized bed is homogeneous, the preparation of the column may also be improved by fluidizing the column inside the chromatograph with carrier gas preheated to the required temperature.

CONCLUSION

The technique of fluidization has many advantages for preparative columns and provides an answer to the problem of preparing large diameter columns.

The advantages are:

(i) Preparation of the column is independent of the operator's skill.

(ii) The technique involved is very rapid.

(iii) The columns thus prepared are efficient.

(iv) The efficiency of such columns is reproducible.

(v) Finally, the column may be brought into operation more quickly by fluidizing the packing with carrier gas preheated to the required temperature.

If the technique of fluidization is applied to columns of still larger diameter, it is possible to foresee the use of preparative gas chromatography on a more important scale, perhaps reaching the size of semi-industrial separation equipment.

ACKNOWLEDGEMENTS

The author expresses his thanks to Dr. C. L. A. HARBOURN (Research Centre, B.P., Sunbury-on-Thames) for translating this paper into English and to Mr. G. PALLAS, his assistant, who so patiently repacked the columns so many times.

SUMMARY

The fluidization technique provides a solution to the problem of filling wide diameter columns used in preparative gas chromatography.

The density of a packing after fluidization is uniform both in the direction of the column and across the diameter. When applied to preparative gas chromatographic columns, this feature of fluidization offers the possibility of obtaining a gas profile with the minimum of concavity.

The average efficiency of a 6 cm I.D. column filled in this way is 315 plates per metre when 1.2 ml of a mixture of equal parts by weight of pentane and hexane is injected.

The preparation of the columns is quick and reproducible with a performance independent of the operator.

Since with a fluidized bed, heat transfer is at a maximum, the setting up of a column can be made more rapid by using carrier gas heated to the desired temperature for fluidizing the packing.

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