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## Note

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### Column packings for gas-liquid chromatography by coating the stationary phase, as a vapour, on the solid support using a fluidized-bed technique

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Uniform distribution of the stationary phase on the support surface is an important factor for column efficiency, but none of the methods of coating hitherto used in gas-liquid chromatography (GLC) ensures good uniformity of the liquid layer. Some improved techniques of coating have been suggested<sup>1,2</sup>.

In our previous paper<sup>3</sup>, we discussed the possibility of coating the stationary phase to the solid support in the vapour state. Coating in this instance was by adsorption, and it was possible thus to apply *ca.* 1-1.5% of stationary phase; the method was therefore suitable for preparing GLC columns with such loadings of stationary phase.

The work described here was an attempt to improve the vapour-state method of coating by making use of condensation effects and with a fluidized bed of support; thus we hoped to prepare packings with a higher percentage of stationary phase uniformly distributed on the support.

## EXPERIMENTAL

The packings studied were prepared by using the apparatus shown in Fig. 1. The coating was carried out in a large tube with a sintered-glass disc near its base; this tube was not heated externally. Pure dry nitrogen was used as carrier gas; the flow-rate and the temperature of the saturator depended on the stationary phase being coated and on the desired percentage of coating. The amount of stationary phase in all packings was determined by the evaporation method<sup>4</sup>.

The efficiency of each packing was studied with use of a Model Tswett 6 A gas chromatograph (USSR); the columns were 2 m long and of 3 mm I.D.

## RESULTS AND DISCUSSION

We found that it was difficult to obtain uniform coating of the stationary phase on the support. The condensation effect decreased from the inlet to the outlet of the tube containing the support, and a gradient appeared in the percentage of coating. Use of a temperature gradient along the support tube was without effect, and we found that non-uniformity of coating was best avoided by using a fluidized bed of

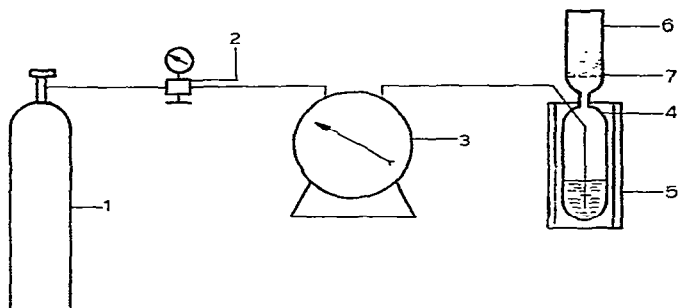


Fig. 1. Apparatus for coating. 1, Cylinder of nitrogen; 2, Pressure reducer; 3, Flow-meter; 4, Saturator; 5, Glass furnace; 6, Tube containing support; 7, Sintered-glass disc.

support. This we achieved by carrying out the coating at high flow-rates of carrier gas, and succeeded in attaining uniform coating.

First, it was necessary to establish the effects of some of the most important variables in the coating process, and the influence of carrier-gas flow-rate, temperature of the saturator and time of coating on the percentage of stationary phase are shown in Figs. 2, 3 and 4, respectively. The solid support in each instance was Sterchamol (grain size 0.2–0.3 mm), and the stationary phase was *n*-hexadecane. These figures show that the percentage of coating can be increased by optimising the conditions, particularly the temperature, but the scope for doing this is sometimes limited; stationary phases of high boiling points require high temperatures for coating, and thermal decomposition may then occur. Some idea of a suitable temperature for the saturator can be obtained from data for the maximum operating temperatures of the phases used in GLC columns; coating must be carried out at a temperature some 20–50° higher than the maximum operating temperature for the chosen stationary phase.

Fig. 2 also shows, that there is no advantage in increasing the carrier-gas flow-rate above 1300 ml/min. In our opinion, the best results are achieved by coating at as low a temperature as possible and with a moderate flow-rate, the desired percentage of coating being achieved by varying the duration of the coating process.

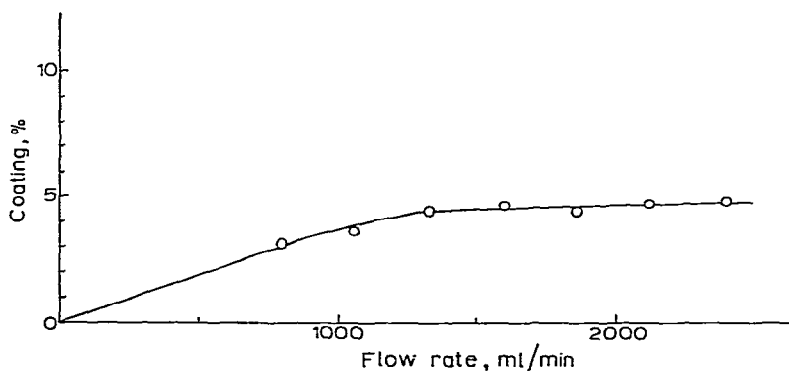


Fig. 2. Curve showing variation in percentage of coating with carrier-gas flow-rate. Temperature of saturator, 100°; time of coating, 15 min.

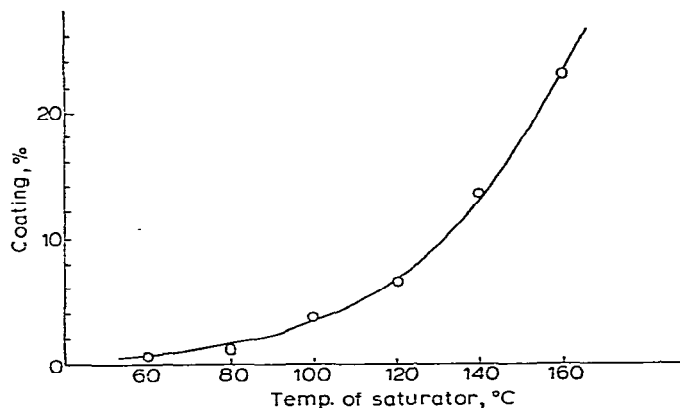


Fig. 3. Curve showing variation in percentage of coating with temperature of saturator. Carrier-gas flow-rate, 1060 ml/min; time of coating, 15 min.

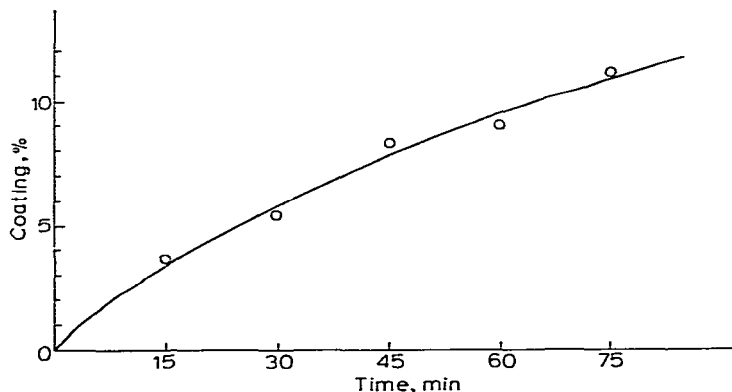


Fig. 4. Curve showing variation in percentage of coating with time. Temperature of saturator, 100°; carrier-gas flow-rate, 1060 ml/min.

#### Reproducibility of results

Reproducibility of coating was investigated by preparing six packings from Sterchamol and *n*-hexadecane at 100°, with a flow-rate of 1060 ml/min and a coating time of 15 min. For the six packings, the percentages of stationary phase were 3.4, 3.5, 3.6, 3.3, 3.8 and 3.8, respectively (mean 3.6).

The standard deviation for a single experiment is  $S = \pm 0.2\%$ , which, multiplied by Student's coefficient, gives at 95% probability a figure of  $\pm 0.5\%$ . Such reproducibility is good and is sufficient for normal GLC practice.

#### Examples of coating in the vapour state

Experiments with eight supports [Celite, Chromaton N, Chromosorb P, Chromosorb G, Sterchamol, Chromosorb P (silanized) and Chromosorb P (acid and alkali washed)] showed that neither the type of support nor its particle size significantly affected the percentage of coating. For instance, at 140°, a carrier-gas flow-

rate of 1325 ml/min, and a time of coating of 30 min, the amount of coating of dibutyl phthalate on the supports mentioned above was always between 5.5 and 6.5%.

In Table I are presented data for coating different stationary phases on Sterchamol, coating being for 30 min at a flow-rate of 1325 ml/min. The results show that stationary phases often used in GLC can be coated on the support without difficulty, bearing in mind that, by prolonging the coating time, it is possible to achieve higher percentages of coating.

TABLE I  
DATA FOR PREPARATION OF SOME PACKINGS

<i>Stationary phase</i>	<i>Temperature of coating, °C</i>	<i>Amount of stationary phase in packing, %</i>
Dinonyl phthalate	180	4.5
Squalane	200	2.8
Bis-(2-ethylhexyl) sebacate	220	4.4
Dibutyl tetrachlorophthalate	200	3.9
$\beta,\beta'$ -Oxydipropionitrile	160	4.7
1,2,3-Tris-(2-cyanoethoxy)propane	220	2.3
Polymethylsiloxane PMS-100	320	2.2

Six of the stationary phases listed in Table I are of medium volatility. Most phases of low volatility (*e.g.*, Apiezon, polyesters and silicones) are not individual compounds, but mixtures of high-molecular-weight products. Thus, in the conditions used for vapour-state coating, some fractionation is to be expected in accordance with the volatilities of these products.

However, in order to evaluate the vapour-state method of coating for a low-volatility stationary phase, we carried out some experiments with polymethylsiloxane PMS-100, which has an average molecular weight of 5000 and is recommended for use at up to 300°. As shown in Table I, this phase also was coated on the support at a useful level, particularly if we take into consideration that columns for high-temperature GLC are "low loaded".

#### *Efficiency of packings obtained by vapour-state coating*

The efficiency of packings prepared as described here is higher than that of packings prepared by the usual wet method. Figs. 5, 6 and 7 show Van Deemter functions for cyclohexane, benzene and acetone, respectively, at 70°, measured with packings of dibutyl phthalate on Sterchamol. One of the packings was prepared by coating 10.7% of stationary phase in the vapour state and the other by coating 11.2% of the phase in solution. It can be seen that the HETP for the packing prepared in the vapour phase is some 20–30% lower than that for the other packing. The corresponding Van Deemter curves are almost parallel over the entire range of flow-rates tested.

The following conclusions can be drawn from our results: (1) our proposed vapour-phase method of coating, based on condensation, offers the possibility of

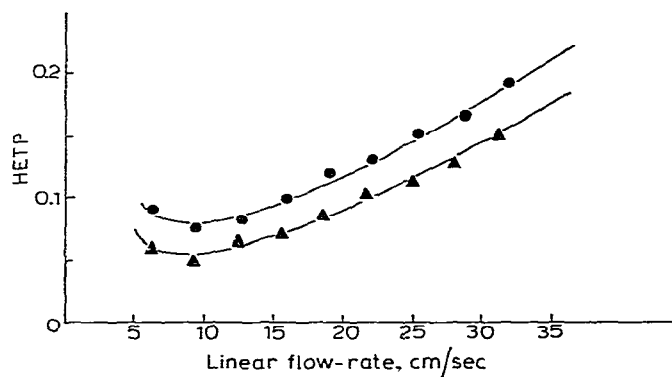


Fig. 5. Curves showing variation in HETP for cyclohexane with linear carrier-gas flow-rate. ▲, Vapour-phase coating; ●, coating in solution.

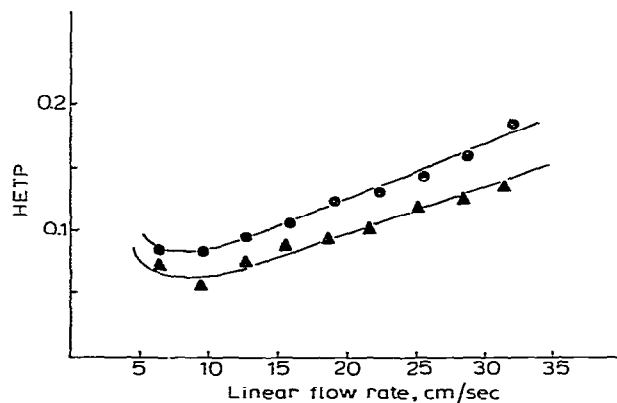


Fig. 6. Curves showing variation in HETP for benzene with linear flow-rate. Symbols as for Fig. 5.

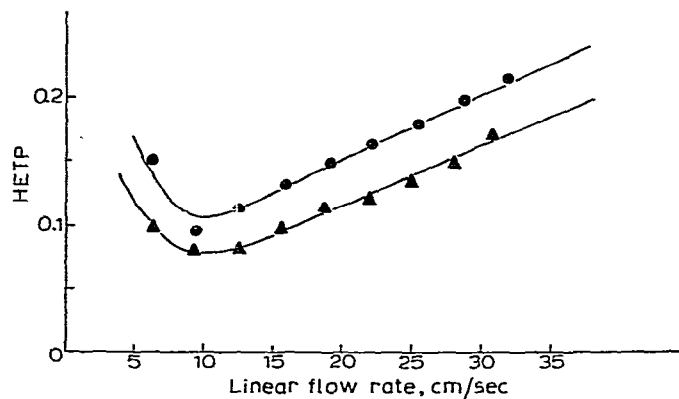


Fig. 7. Curves showing variation in HETP for acetone with linear flow-rate. Symbols as in Fig. 5.

preparing column packings having higher efficiencies than packings prepared in solution; (2) use of a fluidized bed of support ensures uniformity of coating; and (3) no solvent is necessary, so that the layer coated on the support is of high purity.

The method described above might be of use in practical GLC in the cases, when a higher efficiency or an absence of solvent are desirable.

#### REFERENCES

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