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Note

Static coating method for glass capillary columns at elevated temperature

XIN BU AIJIN HUANG and YILIANG SUN*
Department of Chemistry, Peking University, Beijing (China)

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The static coating method for glass capillary columns at elevated temperature was first proposed by Kong and Lee[1] in 1983. With this innovation, the merits of high coating efficiency and ease of control of the film thickness of the stationary liquid to be coated were retained, and the process of solvent evaporation was significantly accelerated. These authors also found that the coating process using a mixed solvent instead of either of the individual solvent components could be considerably shortened[2].

This new coating method was further studied by Xu and Vermeulen[3,4] and they designated it as the 'free-release' static coating method. At elevated temperature, the bumping of the solution to be evaporated in the capillary is an acute problem, directly associated with the success or failure of the new method. So Xu suggested a degassing treatment, and connection of a damping column in series with the capillary. These measures are quite effective, but according to our experience are not sufficient and convenient.

We now describe additional work carried out in order to increase the rate of success of the new static coating method, especially to avoid the bumping effect during solvent evaporation. Also, a systematic study was undertaken to optimize the solvent which gives the fastest evaporation rate.

EXPERIMENTAL

Materials and equipment

The glass capillaries (0.2–0.4 mm I.D., 0.7–1.1 mm O.D.) were drawn from Type 95 borosilicate glass tube (Beijing Glass Factory) with a Shimadzu GDM-1B glass-drawing machine.

The stationary phases used were OV-101, OV-1 (Chrompack), OV-17 (Serva), PEG 20M (BDH), SE-30 and SE-54 (Chrompack). The solvents were *n*-pentane, acetone and dichloromethane.

A self-assembled thermostat (a direct heating type for easy observation, well-insulated with expansible polystyrene chips) heated at 75°C with a precision of ±0.05°C was used for static coating as well as for the study of the solvent optimization. The coated columns were conditioned and evaluated wit a Shimadzu GC 9A gas chromatograph equipped with a flame ionization detector.

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Coating procedure

The stationary phase solutions used in the experiment were passed through a Type 5 sintered glass funnel to remove particles of diameter larger than 1.5–2.5 μm and then degassed with an ultrasonic wave generator for 5–10 min. This solution was used to fill the column to be coated. Then both ends of the column were straightened and drawn into thinner capillaries in a small flame. One of the ends was sealed and the open end was used as a "damping column" to suppress bumping of the solution to be evaporated. The column was placed in the thermostat, keeping both ends above the surface of water. In the first few minutes after immersion of the column in the water-bath a thermal expansion of the solvent occurred. Then the evaporation process began smoothly. After the solvent had vaporized in two or three coils and the water-bath with the column in it had attained a steady state of thermal exchange, bumping occurred less often and the thinner outlet became unnecessary. It was broken off to accelerate the speed of vaporization.

RESULTS AND DISCUSSION

Some experimental artifices

(1) In the static coating procedure, bumping of the coating solution is more likely to occur when tiny gas bubbles and/or particulates are present. At elevated temperature, *e.g.*, at 75°C, as the solution is actually in a superheated state, the presence of such bubbles and particulates may lead to serious bumping phenomena. Therefore, it is necessary to remove the particulates and gas dissolved in the solution in the way proposed. With our method the concentration of the stationary phase solution can be kept virtually unchanged, which is very important for controlling the liquid film thickness in the column. Moreover, the bumping effect can be avoided as effectively by a restrictor outlet as by a damping column, proposed previously[3].

(2) The importance of controlling the precision, *i.e.*, the short-term temperature stability of the thermostat, should not be overlooked. Grob and Grob[5] first pointed out the importance of precise temperature control in their study on the conventional static coating technique. However, the effect of the precision of temperature control of the water-bath on the coating speed is more easily observable at elevated temperature than at ambient temperature, as at elevated temperature the movement of the meniscus of the solution is considerably faster. When the precision of the temperature is lowered to ± 0.08°C, the meniscus of the solution in the column retreats and stops intermittently. When the precision is further lowered to ± 0.1°C, the meniscus moves backwards and forwards intermittently leading to a serious decrease in coating speed and coating efficiency of the column. The movement of the meniscus in the column became uniform and steady only at a precision of ± 0.05°C.

Optimum binary solvent systems for static coating at elevated temperature

n-Pentane–acetone and *n*-pentane–dichloromethane were chosen to prepare the coating solution for various stationary phases and the evaporation behaviour of these solutions *versus* their compositions was investigated. The results are represented in Figs. 1, 2. It is interesting that even with the addition of a few tenths of one per cent of stationary phase in the binary solvent mixture, the evaporation behaviour of the solution is usually distinct from that of the solvent itself. In some cases, *e.g.*,

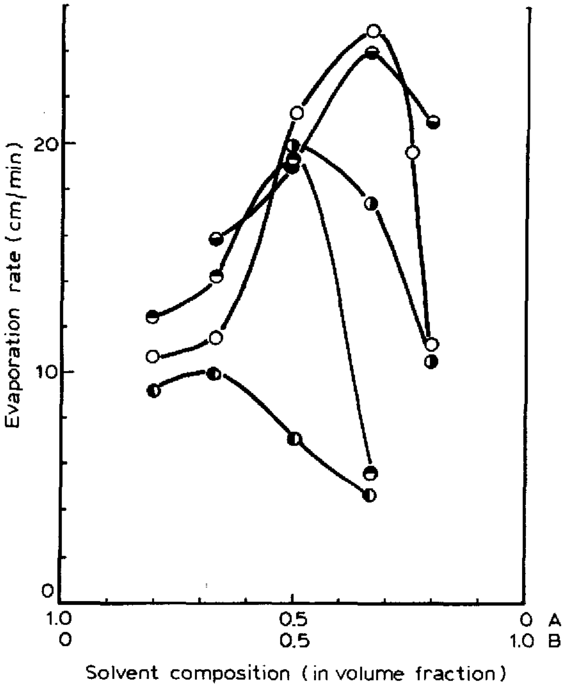

Fig. 1. Relationship between the coating rates of some stationary phase solutions and their compositions in *n*-pentane–dichloromethane. Column: 25 m × 0.22 mm (0.79 mm O.D.) glass capillary, 75 ± 0.05°C. A = *n*-pentane; B = dichloromethane. ○–○, Solvent; ◓–◓, OV-101; ◒–◒, OV-17; ◐–◐, OV-1; ◑–◑, PEG 20M. Stationary phases as 0.38% (v/v) solutions.

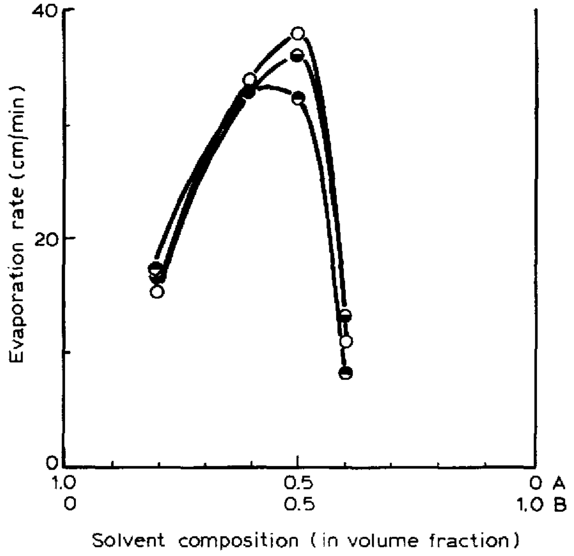

Fig. 2. Relationship between the coating rates of some stationary phase solutions and their composition in *n*-pentane–acetone. Column: 25 m × 0.21 mm (0.79 mm O.D.), glass capillary, 75 ± 0.05°C. A = *n*-pentane; B = acetone. ○–○, solvent; ◒–◒, OV-101; ◓–◓, OV-17. Stationary phases as 0.38% (v/v) solutions.

TABLE I

COATING TIME AND EFFICIENCY OF SOME COLUMNS COATED BY THE STATIC COATING METHOD AT 75 ± 0.05°C

Deactivation was performed according to Schomburg *et al.*[6] for the OV-101 column, and De Nijs *et al.*[7] for the PEG 20M column.

No.	*Stationary phase*	*Coating time (min)*	*L (m)*	*I.D. (mm)*	d_f *(μm)*	*k*	*n* (m^{-1})	*CE (%)*
1	OV-101	98	26.5	0.25	0.15	3.86	3500	71
2	OV-101	131	31.4	0.34	0.37	3.01	2700	71
3	OV-101	110	25.5	0.29	0.38	3.19	3695	75
4	OV-101	104	24.5	0.26	0.34	3.92	3853	71
5	OV-101	110	26.5	0.27	0.35	3.35	3910	84
6	PEG 20M	284	39.7	0.26	0.15	3.72	2330	49
7	PEG 20M	241	31.3	0.26	0.30	3.60	3050	64
8	PEG 20M	212	25.5	0.26	0.50	6.55	2930	63
9	PEG 20M	183	27.5	0.22	0.26	3.56	4240	75
10	PEG 20M	179	25.0	0.24	0.28	3.49	5192	99

OV-101 in Fig. 1, the optimum solvent composition shifts noticeably. The rate of evaporation of the solution becomes lower than that of the relevant pure solvent. On the contrary, within certain ranges, the rate of evaporation of the solution may be faster than that of the pure solvent. We are still unable to explain all these phenomena theoretically. The evaporation rate of the solvent also slightly depends on the concentration of stationary phase used in the range 0.24–0.8% (v/v). When a column of 0.25 mm I.D. is used, with the film thickness increasing from 0.15 to 0.5 μm, the evaporation rate decreases only by 14%. From a practical point of view, *n*-pentane–acetone (1:1, v/v) and *n*-pentane–dichloromethane (1:1, v/v) are recommended for OV-101 and PEG 20M respectively. Typical results on columns coated with these solvents at 75°C are given in Table I.

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REFERENCES

1 R. C. Kong and M. L. Lee, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 6 (1983) 319.
2 R. C. Kong and M. L. Lee, *Chromatographia,* 17 (1983) 451.
3 B. Xu and N. P. E. Vermeulen, *Chromatographia,* 18 (1984) 520.
4 B. Xu and N. P. E. Vermeulen, *Chromatographia,* 18 (1984) 642.
5 K. Grob and G. Grob, *J. Chromatogr.*, 123 (1976) 417.
6 G. Schomburg, H. Husmann and H. Borwitzky, *Chromatographia,* 12 (1979) 651.
7 R. C. M. de Nijs, J. J. Franken, R. P. M. Dooper, J. A. Rijks, H. J. J. M. de Ruwe and F. L. Schulting, *J. Chromatogr.*, 167 (1978) 231.