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NEW PERSPECTIVES IN CAPILLARY CHROMATOGRAPHY[a]

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SUMMARY

A coating procedure for preparing fused-silica capillary columns with graphitized carbon black, modified with a liquid stationary phase, is described. This yields reproducible results in terms of column efficiency, separation power and retention parameters. The factors that affect the final results are discussed and some analytical applications are reported.

INTRODUCTION

For several years, our group has been investigating the preparation of fused-silica capillary columns with the inner walls coated with graphitized carbon black and treated with suitable amounts of liquid stationary phases[1,2], in an attempt to enhance the selectivity of capillary columns by using the peculiar stationary phases yielded by gas–liquid–solid chromatography (GLSC)[3]. Faster analysis is also obtained with these capillary columns.

In a previous paper[1] we reported a method for the preparation of GLSC capillary columns, based on making a slurry of graphitized carbon black and the liquid phase to be used, in a suitable solvent [generally pentane–dichloromethane (1:1, v/v)]. The column is then filled with the slurry, closed at one end and the solvent is evaporated slowly from the other end by keeping the column in a water-bath at a temperature higher than the boiling point of the solvent mixture.

Although good results were obtained with the preparation and use of such columns and the theoretical expectations concerning their properties were confirmed, many questions remained open, in particular those concerning reproducibility. The preparation of a good column is affected by several critical parameters: the dimensions of the carbon black particles; the surface area of the particular carbon black used; the concentration of the slurry, both in carbon black and the liquid phase; and the final amount of stationary phase on the carbon black surface. These parameters also influence each other, so that the final result is the best compromise among them.

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In this paper, we present a method of preparation intended to obtain good column reproducibility. The influence of the carbon black concentration on different columns is shown and some applications to environmental analysis are reported.

EXPERIMENTAL

Preparation of the slurry and coating

The carbon black (Carbopack B or F, obtained from Supelco, Bellefonte, PA, U.S.A.) is first crushed and sieved to less than 200 mesh. In order to use the full power of the sonicator (Model 450; Branson, Danbury, CT, U.S.A.), the material is dispersed in water, which is the best medium for sonication, and maximum power is maintained for 30 min. Then the water is evaporated and a suitable organic solvent (dichloromethane) is added to the dry material. By using water, a much higher subdivision of the carbon black particles is obtained, so that the slurry is more homogeneous. The mixture of the organic solvents and the carbon black is again sonicated for 15 min and a homogeneous slurry is again obtained. The column is then coated, following the procedure described previously[1], and after the solvent has completely evaporated the column is dried under a stream of nitrogen.

Adjusting the amount of stationary phase and column conditioning

The initial amount of stationary phase added to the slurry is usually greater than needed for optimum conditions of GLSC, so that, prior to conditioning, the column is again placed in a water-bath kept at 25°C and washed with the solvent previously used for the slurry. In this way, some of the stationary phase is washed out, and the percentage that remains in the column depends on the amount of solvent passed through the column. The column is then dried and conditioned overnight. The silica tubes were not specially treated before coating.

Chromatographic measurements

All analyses were performed with a Carlo Erba (Milan, Italy) Mega Series HRGC 5160 gas chromatograph, with flame ionization detection (FID) and using a split/splitless injector, and with a DANI (Monza, Italy) Model 6500 chromatograph, with electron-capture detection (ECD) and using a programmed-temperature vaporizer (PTV) injector. The heat of adsorption of *n*-pentane was measured for the isosteres by plotting capacity ratio (k') against reciprocal temperature. The separation factor, α, between *n*-heptanol and *n*-octane was measured using the corrected retention times. As the heptanol peak is tailed, care was taken always to inject the same amount of this compound for the sake of reproducibility. The peak maximum is considered as the retention time.

Hydrogen was used as carried gas with FID and nitrogen with ECD measurements.

RESULTS AND DISCUSSION

Determination of the surface coverage

Because of the coating procedure, the actual percentage of stationary phase on the carbon black cannot be established directly, because by micronizing the carbon

particles, the surface area is increased with respect to the accepted value of 90 m^2/g given for Carbopack B and 6 m^2/g for Carbopack F in the 40–120-mesh range. However, the surface coverage can be established from the inflection point of the curve obtained by plotting the heat of adsorption of *n*-pentane against the nominal percentage[3]. This experiment was carried out by preparing a series of packed columns, containing Carbopack B coated with various amounts of SP-1000 liquid phase, and the results are shown in Fig. 1a. The change in the retention volume ratio between an aliphatic saturated linear hydrocarbon (*n*-octane) and an aliphatic saturated linear alcohol of analogous molecular weight (*n*-heptanol) was also measured on the packed columns, giving Fig. 1b.

As the retention volume ratio is linearly related to the surface coverage, by measuring this ratio on the capillary column its surface coverage can be found by comparing the value obtained with those for the packed column.

In this way, the actual surface coverage (θ) of three capillary columns was calculated to be 0.6, which corresponds to about 2.2% for the packed columns. However, it should be understood that we do not know the percentage for the capillary column, as the surface area of the carbon black is not known for the reasons stated above.

In fact, the coverage obtained approximately corresponds to the maximum value of the heat of adsorption on the curve, where the maximum of the "lateral interactions" of the eluate with the stationary phase takes place. This corresponds to a maximum of the column selectivity for hydrocarbons. The surface coverage is ob-

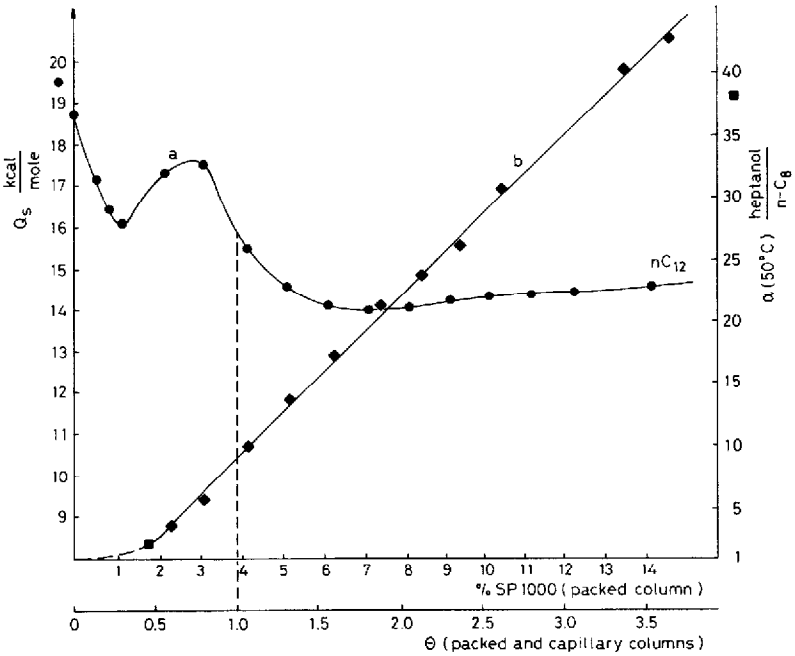

Fig. 1. Plots of (a) the chromatographic heat of adsorption and (b) separation factors against the surface coverage, θ, and the percentage (w/w) of liquid phase SP-1000 on Carbopack B.

tained by assinging a value of unity to the inflection point of the curve of the heat of adsorption[3,4]. Washing of the capillary column was carried out to such an extent on purpose, in order to obtain maximum selectivity for hydrocarbons.

This method seems to be the most convenient for establishing the extent of surface coverage by the stationary phase, as it is found from GC measurements and because measurements of the surface area with the Brunauer–Emmett–Teller (BET) method have only a relative meaning and may lead to different evaluations that have little significance for chromatographic purposes.

Column reproducibility

Once the optimum procedure had been established, we prepared three columns under the same conditions in order to test the reproducibility of the coating procedure. The results are summarized in Table I.

The reproducibility is very good in terms of the efficiency. The three columns show a maximum of 18 000 theoretical plates with respect to n-C_{12}. The same reproducibility is observed for the ratio of the retention volumes for an alcohol and a hydrocarbon of similar structure and molecular weight. The two compounds were chosen because the carbon black and the stationary phase have counteracting effects on polar and non-polar compounds. At zero surface coverage, the two compounds should have very similar retention volumes, as their polarizabilities are similar, as has been shown previously[3]. The retention of the polar compounds increases with increasing surface coverage by a polar stationary phase, such as SP-1000, whereas it decreases for the hydrocarbon. Hence, the ratio of the retention volumes is a very good index of the surface coverage by the stationary phase. Of course, this parameter is critical, and very small variations in the percentage of stationary phase may lead to considerable differences in the relative retentions. The three columns show a difference of about 10% in relative retention; it is our opinion that such a result is satisfactory and does not affect substantially the chromatographic characteristics of the columns.

Fig. 2 shows a practical example of the reproducibility of the columns. The characteristics of columns A, B, and C are the same and are reported in Table I. Some of the peaks show slight tailing, but the separations reported have no analytical

TABLE I

COMPARISON OF SOME PARAMETERS FOR THREE COLUMNS (A–C), PREPARED BY THE SAME PROCEDURE AND FOR A COLUMN WITH A HIGHER CONTENT OF CARBON BLACK IN THE SLURRY (D)

Column dimensions 7 m × 0.25 mm I.D.

Column	t_o *(s)*[a]	*Flow-rate (ml/min)*	k' *(140°C),* n-C_{12}	α *(90°C), n-heptanol/*n-C_8	H_{min} *(mm)*
A	18	1.5	49	3.8	0.40
B	18	1.5	52	3.8	0.38
C	18	1.5	56	3.7	0.40
D	18	1.5	125	4.0	0.40

[a] t_0 (dead time) = retention time of methane.

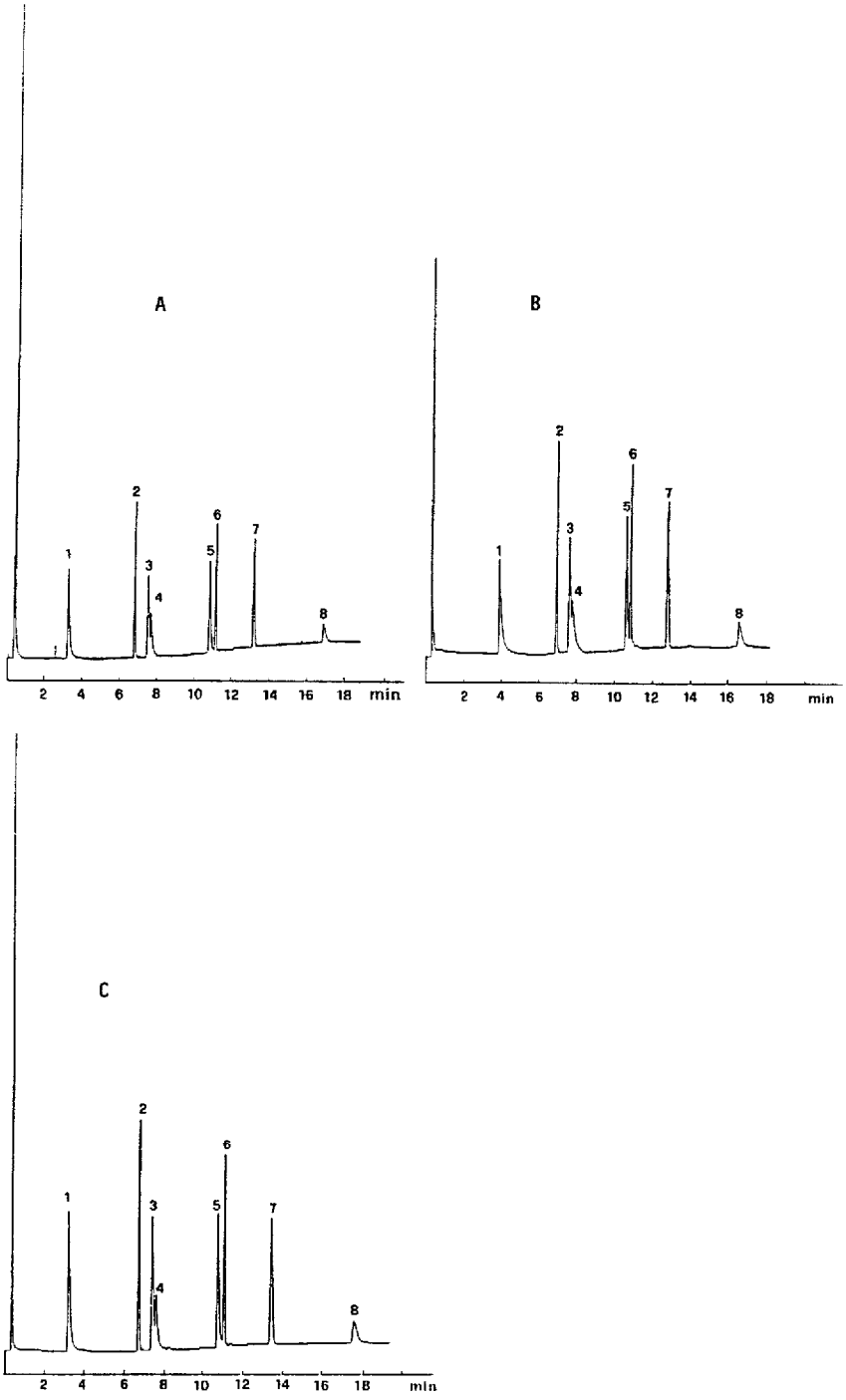

Fig. 2. Chromatograms showing the reproducibility of three columns (A, B and C) of the same length and diameter, coated by the same procedure and under identical conditions. Fused-silica capillary columns (7 m × 0.25 mm I.D.) coated by the procedure dexcribed in the text. 1 = 1, 2, 4-Trichlorobenzene; 2 = *n*-dodecane; 3 = 1-methylnaphthalene; 4 = 2-methylnaphthalene; 5 = 1,3-dimethylnaphthalene; 6 = *n*-tetradecane; 7 = *n*-pentadecane; 8 = hexachlorobenzene. Carrier gas, hydrogen; flow-rate, 1.5 ml/min at 140°C; temperature programme, 2 min at 140°C, then increased at 10°C/min to 240°C.

meaning, the mixture being made for the sake of comparison, not for solving actual analytical problems. A fourth column (D) was prepared with the same carbon black and the same stationary phase, but by changing the concentration of carbon black in the slurry while keeping the same ratio of the stationary phase to carbon black (30:1). The results are also given in Table I.

The data show that the column efficiency is very similar to the previous results, whereas a slight increase in the relative retentions of the alcohol and the hydrocarbon is observed. In contrast the retention of the n-C_{12} hydrocarbon increases substantially. This can only be explained by assuming that an increase in carbon black concentration in the slurry leads to a more extensive coating of the silica surface, whereas the surface coverage of the carbon black by the stationary phase is not affected to a large extent. In fact, the ratio of the SP-1000 to Carbopack B was kept unchanged for the three columns.

It is worth noting that scanning electron microscope photographs of the inner surface of the coated capillary show that the carbon black particles cover only 50% of the silica surface. This introduces a third variable into the column characteristics that should be taken into account for obtaining a more or less retentive layer while maintaining a very similar selectivity. We think this parameter is extremely important and is a peculiar feature of this type of column. In fact, making a comparison with the thickness of the liquid film in conventional GLC capillary columns, an increase in the film thickness produces the same effect as the increase in the surface coating of our columns. This is possible because the silica surface is not completely coated. Other-

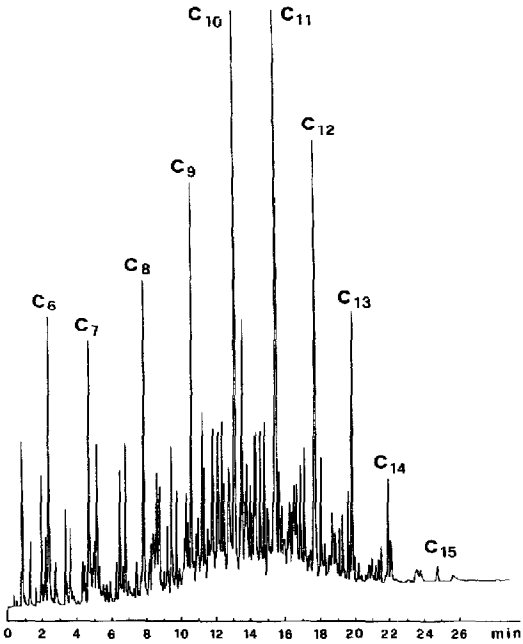

Fig. 3. Chromatogram of a virgin naphtha (80–250°C). Column D (see text). Carrier gas, hydrogen; flow-rate, 1.5 ml/min at 35°C; temperature programme, 35°C for 1 min, then increased at 12°C/min to 240°C.

wise, the thickness of an adsorptive layer does not affect the retention, which in this instance is due only to the surface phenomena.

We realize that the absorbent–stationary phase–silica surface system is very complex and that the retention mechanism may be different from that for classical packed columns with liquid-modified graphitized carbon. However, from the values and the behaviour of the heat of adsorption, measured with the capillary column, it can be concluded that the silica surface contributes to retention to a very minor extent and may only be responsible for some peak tailing of polar compounds. This is worth investigating, and some surface treatment prior to coating may be useful in eliminating irreversible adsorption phenomena due to the silica active sites.

A fifth column was prepared with the more concentrated slurry, but this time the washing was omitted. This is important in order to understand the modifications induced by the solvent treatment. In fact, the retention time ratio between *n*-heptanol and *n*-octane is 56:1, which shows that the carbon surface is now covered by at least three or four monolayers of SP-1000. The column efficiency is also much lower, the minimum plate height (H_{min}) being *ca.* 1 mm.

The conclusion from these experiments is that, although a large amount of SP-1000 must be added to the slurry to make it stable, washing with the solvent is necessary to ensure both column reproducibility and better efficiency. Also, it has

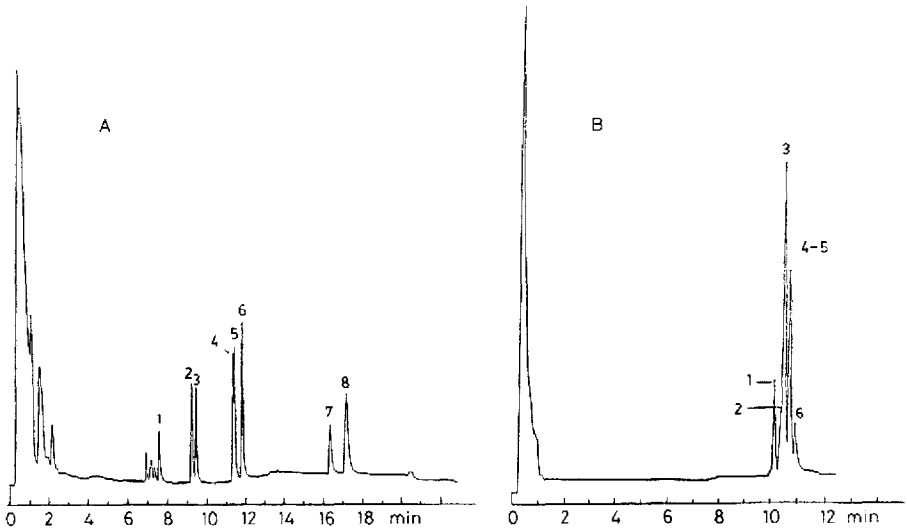

Fig. 4. (A) Separation of chlorodibenzodioxins and benzofurans. 1 = 2,3,7,8-Tetrachlorodibenzodioxin; 2 = 1,2,3,7,8-polychlorodibenzofuran; 3 = 1,2,3,7,8-polychlorodibenzodioxin; 4 = 1,2,3,6,7,8-hexachlorodibenzofuran; 5 = 1,2,3,6,7,8-hexachlorodibenzodioxin; 6 = 1,2,3,7,8,9-hexachlorodibenzodioxin; 7 = octachlorodibenzofuran; 8 = octachlorodibenzodioxin. Fused-silica capillary column (8 m × 0.25 mm I.D.); coating, Carbopack F + SP-1000; carrier gas, hydrogen; flow-rate, 1.5 ml/min at 150°C; temperature programme, 1.5 min at 150°C, then increased at 10°C/min to 280°C. (B) Separation of tetrachlorodibenzodioxin isomers: 1 = 1,4,7,8-tetrachlorodibenzodioxin; 2 = 1,2,3,4-tetrachlorodibenzodioxin; 3 = 1,2,3,7-tetrachlorodibenzodioxin; 4 = 1,2,7,8-tetrachlorodibenzodioxin; 5 = 1,2,3,8-tetrachlorodibenzodioxin; 6 = 2,3,7,8-tetrachlorodibenzodioxin. Fused-silica capillary column (8 m × 0.25 mm I.D.); coating, Carbopack F + SP-1000; carrier gas, hydrogen; flow-rate, 1.5 ml/min at 150°C; temperature programme, 1.5 min at 150°C, then increased at 8°C/min to 250°C.

been observed that, once the slurry has been prepared, it should be used within a short time. As time passes between preparation and use, the surface coverage by the stationary phase increases, probably because the graphitized carbon adsorbs some stationary phase from the solvent during storage. Hence, the time between preparation and use of the slurry is another parameter to be taken into account for column reproducibility.

Analytical applications

In Fig. 3 the chromatogram of a virgin naphtha, obtained on the fourth column (D), made with a more concentrated slurry, is shown. The analysis was performed in 22 min. The complexity of the mixture in terms of number of peaks and separation power is analogous to that obtained with a much longer column by GLC. This is due to the ability of GLSC columns with carbon black coated with a polar stationary phase, to separate hydrocarbon isomers.

Fig. 4A shows the separation of some chlorodibenzodioxins and chlorodibenzofurans. This separation was obtained with a column only 8 m long, coated with Carbopack F covered by SP-1000. In Fig. 4B the same column was used with the specific purpose of separating the isomers of tetrachlorodibenzodioxins. It is interesting that, owing to the selectivity of this particular column, a separation analogous to

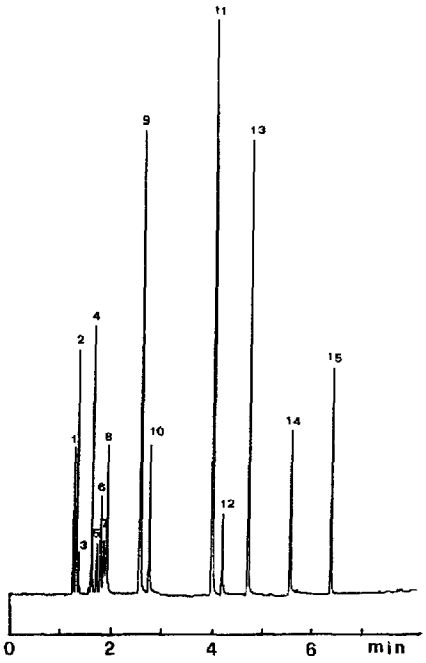

Fig. 5. Separation of some chlorinated priority pollutants. 1 = Dichloromethane; 2 = *trans*-1,2-dichloroethylene; 3 = 1,1,1-trichloroethane; 4 = carbon tetrachloride; 5 = bromochloromethane; 6 = chloroform; 7 = trichloroethylene; 8 = bromochloromethane; 9 = *cis*-1,3-dichloropropene; 10 = 1,1,2-trichloroethane; 11 = tetrachloroethylene; 12 = dibromochloromethane; 13 = bromoform; 14 = 1,4-dichlorobutane; 15 = 1,1,2,2-tetrachloroethane. Fused-silica capillary column (20 m × 0.25 mm I.D.), coated with Carbopack B + SP-1000; temperature programme, 2 min at 30°C, then increased at 20°C/min to 120°C.

that obtained with a 60-m capillary column of the standard GLC type was obtained with an 8-m column within 12 min.

In Fig. 5 the separation of some halogenated low-molecular-weight compounds of environmental interest is shown. Very fast analysis is obtained.

CONCLUSIONS

The results help to clarify the mechanism of operation of capillary columns coated with liquid-modified cabron black. We have now found a reproducible method of preparing such columns, and their chromatographic properties can be predicted as a function of the various parameters investigated. As has been pointed out, a better performance for polar compounds should be obtained by appropriate treatment of the silica surface. Different stationary phases should be tested according to preliminary experiments performed previously. We believe that much more work is needed to exploit fully the analytical potential of these columns, which have the advantage that they couple a high selectivity with the high efficiency typical of capillary columns. As a final consideration, we think that previous attempts to obtain capillary columns coated with carbon black[5,6] remained interesting experiments but were not exploited further because of the difficulties encountered reproducing the results. Reproducibility depends on many parameters that need to be considered, especially those which mutually interact.

REFERENCES

1 F. Bruner, G. Crescentini, F. Mangani, P. Palma and M. Xiang, *J. Chromatogr.*, 399 (1987) 87.
2 F. Bruner, G. Crescentini, F. Mangani and M. Xiang, *Ann. Chim. (Rome)*, 77 (1987) 745.
3 F. Bruner, P. Ciccioli, G. Crescentini and M. T. Pistolesi, *Anal. Chem.*, 45 (1973) 1851.
4 G. Crescentini, F. Mangani, A. R. Mastriogiacomo and P. Palma, *J. Chromatogr.*, 392 (1987) 83.
5 C. Vidal Madjar, S. Bekassy, M. F. Gonnord, P. Arpino and G. Guiochon, *Anal. Chem.*, 49 (1977) 768.
6 G. Goretti, A. Liberti and G. Pili, *J. High. Resolut. Chromatogr. Chromatogr. Commun.*, 9 (1978) 143.