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EVALUATION OF GLASS CAPILLARY COLUMNS WITH DIFFERENT PRE-COATING LAYERS*

GIANCARLO GORETTI and ARNALDO LIBERTI

Istituto Chimica Analitica, Università Roma, Laboratorio Inquinamento Atmosferico C.N.R., Rome (Italy)

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SUMMARY

An evaluation is made of glass capillary columns pre-coated with dispersions of various materials (Silanox, Carbopack, Chromosorb, perlite and Porapak) and then coated with polyethylene glycol (PEG 20M) at various concentrations as stationary phase by analysing alkanes and alcohols in terms of the peak-asymmetry factor, separation factor and kinetic characteristics. Pre-coating with Silanox, Carbopack and Chromosorb yielded similar results, but with different amounts of stationary phase. Use of Carbopack for pre-coating offers the advantage that, according to the concentration of stationary phase, separation can be achieved by gas-liquid or gas-liquid-solid chromatography.

INTRODUCTION

Pre-coating of glass capillary columns is a well-established procedure for their preparation, and various techniques have been described. It has been shown recently that, by allowing a colloidal suspension of, *e.g.*, Chromosorb¹, Silanox² or graphitised carbon black³ to flow through a glass capillary, coating with these materials can be achieved.

Pre-coating seems to exert a twofold effect: it blocks active sites on the glass and it facilitates spreading of a uniform thin layer of the stationary phase. It seemed to us, however, that the pre-coating material might affect the chromatographic behaviour, and, in order to evaluate this effect, we have studied various pre-coating materials. By following the same operating procedure, columns with different pre-coatings and the same stationary phase have been prepared and evaluated in terms of peak asymmetry, separation factor and kinetic characteristics for various compounds. Although comparable results might be achieved with other pre-coatings by careful operation, it appears that Carbopack pre-coating offers certain advantages.

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EXPERIMENTAL

Suspensions of the pre-coating materials were made to flow through cleaned glass capillaries; procedures for obtaining suitable dispersions are described below.

Carbopack A

This material (Supelco, Bellefonte, Pa., U.S.A.) is a graphitised carbon black with a surface consisting mainly of graphite basal planes. A suspension was obtained by ultrasonic agitation (*ca.* 20 KHz) for *ca.* 40 min of 65 mg of the Carbopack in a mixture of carbon tetrachloride (20 ml) and dichloromethane (6 ml). This treatment yielded particles of size less than 0.1 μm . Two passes of *ca.* 5 ml of the suspension through the capillary in opposite directions were used.

Silanox 101

This material (Cabot, Billerica, Mass., U.S.A.) is described as a hydrophobic fumed silicon dioxide with a primary particle size of 7 nm that has been trimethylsilylated. A colloidal suspension was prepared by stirring 250 mg of Silanox with 20 ml of dichloromethane. Four passes of *ca.* 5 ml were made through the capillary, reversing the direction of flow each time.

Chromosorb P

This material (Johns-Manville, Denver, Colo., U.S.A.) is a calcined diatomaceous earth washed with acid and trimethylsilylated. It was crushed and mechanically ground for several hours, and a stable suspension was obtained by dispersing 250 mg in 20 ml of acetone. Four passes through the capillary, reversing the flow each time, were required to obtain uniform pre-coating.

Porapak Q

This material is a porous polymer derived from ethylbenzene cross-linked with divinylbenzene. A suspension was prepared by dispersing 250 mg of the mechanically ground material in 20 ml of acetone. The coarser fraction, which deposited after a short time, was removed, and the remaining stable suspension was passed through the capillary; four passes, with reversed flow, were required.

Perlite

This material is a natural volcanic glass (equivalent to rhyolite) that has been chemically purified; it was suspended in dichloromethane in the same way as for Porapak.

Column preparation

Glass capillary columns (10 m \times 0.4 mm I.D.) pre-coated as described above were coated by allowing a solution of polyethylene glycol (PEG 20M) at the selected concentration in dichloromethane to flow through them. The excess of solvent was removed by passage of a stream of nitrogen, and the columns were then conditioned in an oven at 140° for 12 h. The columns were used with a Carlo Erba Fractovap C 2101 apparatus.

EVALUATION OF COLUMNS

The evaluation of the columns was carried out by determining the peak asymmetry, the capacity ratio and the kinetic characteristics by examining a non-polar (eicosane) and a polar compound (octanol) on columns prepared with different amounts of the stationary phase PEG 20M.

The shape of the eluted peak gives an indication of interaction occurring in the elution process, and the asymmetry factor (A_s) was calculated for each peak as described previously³; Fig. 1 shows graphs of A_s vs. percentage of stationary phase in each column. Except for capillaries pre-coated with Silanox, the addition of small amounts of PEG definitely improved the peak shape, but, for each pre-coating material, a symmetrical peak was obtained only with a particular concentration of stationary phase.

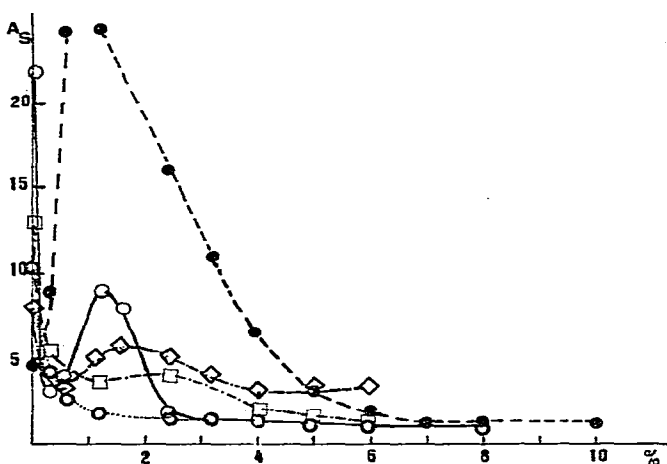


Fig. 1. Graphs showing variation in asymmetry factor (calculated from the octanol peak obtained at 60°) with concentration of PEG 20M for columns with different pre-coatings. —, Carbopack A; - - - -, Chromosorb P; ·····, Porapak; — — —, Silanox 101; ·····, perlite.

For Carbopack and perlite pre-coatings, this stage occurred at fairly low concentrations of stationary phase, whereas a higher concentration was needed with a Silanox pre-coating. When a small concentration of stationary phase was used, the peak was badly skewed, but, with a concentration of PEG of at least 8%, both polar and non-polar compounds yielded symmetrical peaks.

A similar trend is observed from graphs of capacity ratio, $K' [= (V - V_0)/V_0]$ vs. percentage of PEG (see Fig. 2). There is always a decrease in K' until a certain stationary phase concentration is reached, this concentration roughly corresponding to the concentration at which a symmetrical peak occurs. On further increasing the PEG concentration, K' rapidly increases. (It must be remembered that, as we used the dynamic process for preparing the capillary columns, the abscissa values do not indicate the true concentration of the stationary phase, but only that of the solution used for its application.)

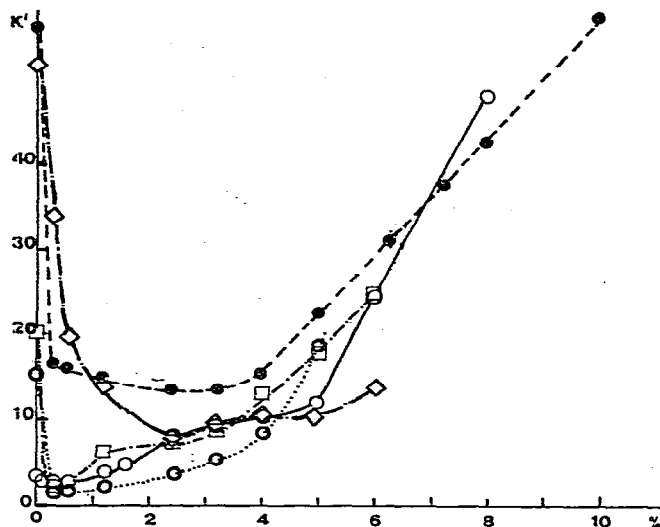


Fig. 2. Graphs showing variation in capacity ratio (calculated for octanol) with concentration of stationary phase for columns with different pre-coatings. Curve symbols as in Fig. 1.

Electron micrographs of columns pre-coated with Silanox or Carbo-pack and then coated with PEG 20M show no appreciable differences, distribution of the material being almost uniform in both; a more heterogeneous distribution was observed with the other pre-coating materials.

The evaluation of kinetic parameters obtained by plotting Van Deemter curves indicated very poor efficiency for columns pre-coated with perlite or Porapak, so that no further work was done with these columns. A low value for the minimum plate height was found for columns with other pre-coatings at a linear velocity of 5–7 cm/sec.

The efficiency of these columns was checked by examining the separation of members of homologous series of hydrocarbons and of alcohols. It was found useful to evaluate the separation in terms of the TZ value as defined by Ettre⁴:

$$TZ = \frac{t_{R(z+1)} - t_{R(z)}}{W_{b(z)} + W_{b(z+1)}} - 1$$

where t_R is the retention time and W_b is the peak width at the base.

In Fig. 3, the separation factor relative to various pairs of alkanes in the range C_{12} – C_{18} is plotted, together with the corresponding values of h_{min} and K' .

The columns showed similar behaviour, with a smaller separation factor for the column with the Chromosorb pre-coating; however, columns pre-coated with Silanox exhibited a rather high capacity ratio.

The advantage of using Carbo-pack or Chromosorb for pre-coating can be clearly seen from the graphs of TZ/t_R for various alkanes shown in Fig. 4; similar behaviour was observed for alcohols.

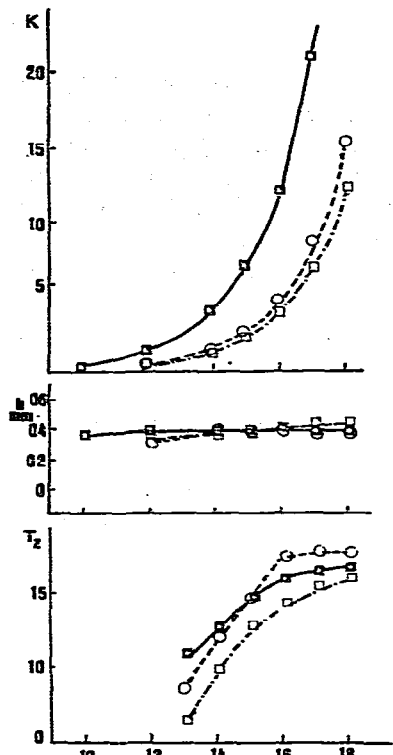


Fig. 3. Separation factor, minimum plate height and capacity ratio for a homogeneous series of hydrocarbons. Curve symbols as in Fig. 1.

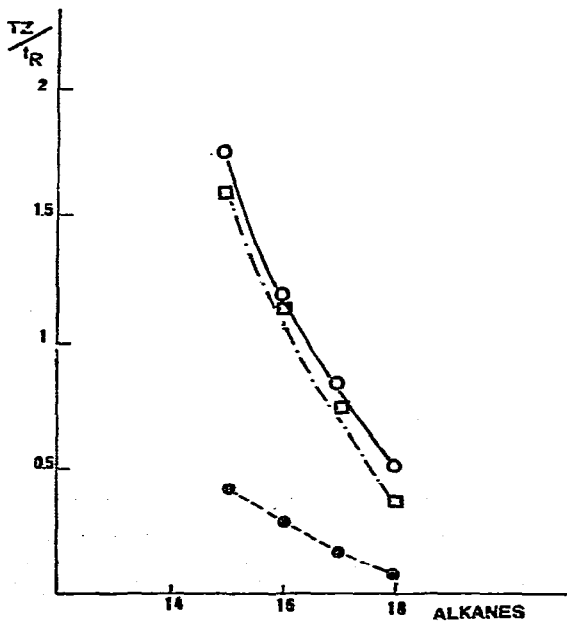


Fig. 4. Graphs showing variation in T_Z/t_R for hydrocarbons. Curve symbols as in Fig. 1.

DISCUSSION

Use of a thin layer of Carbo-pack, Chromosorb or Silanox as pre-coating on the glass capillary gives chromatographic columns that yield comparable results. However, to obtain the same efficiency in terms of separation, only 6% of stationary phase is required when a Carbo-pack or Chromosorb pre-coating has been used, whereas for a Silanox pre-coating, 10% of stationary phase is needed. With a lower concentration of stationary phase, peaks are skewed because of interaction with the pre-coating material. Correspondingly, with pre-coating, the capacity ratio is higher and therefore the analysis time is longer. It appears that preparation of columns pre-coated with Silanox is more critical, and, because of the high capacity ratio, a short analysis time on such a column can be realised only when low-boiling compounds are analysed.

The improvement in peak shape and decrease in capacity ratio by addition of the stationary phase can be explained by the action of this phase, which can interact strongly with anomalous active sites on the surface. The more uniform the material used for pre-coating, the smaller is the amount of stationary phase required. In this respect, Carbo-pack has certain advantages over Silanox and Chromosorb, its highly regular structure playing an important role. By gradually increasing the concentration of stationary phase, an increase in surface coverage is obtained, and conditions varying from a complete monolayer to multi-layer adsorption can be attained.

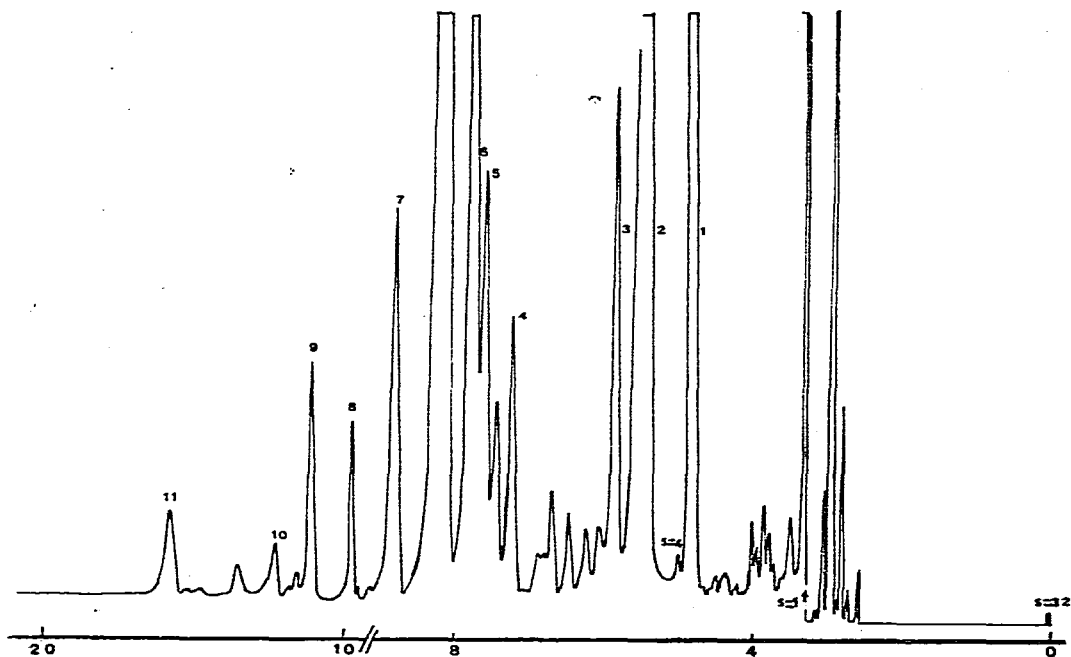


Fig. 5. Gas chromatogram of oxygenated terpenes of bergamot oil at 84° on a 23-m glass column pre-coated with Carbo-pack and de-activated with PEG. Peaks: 1 = linalol; 2 = linalyl acetate; 3 = terpenyl acetate; 4 = neral; 5 = α -terpineol; 6 = citronellyl acetate; 7 = geranial; 8 = neryl acetate; 9 = geranyl acetate; 10 = nerol; 11 = geraniol.

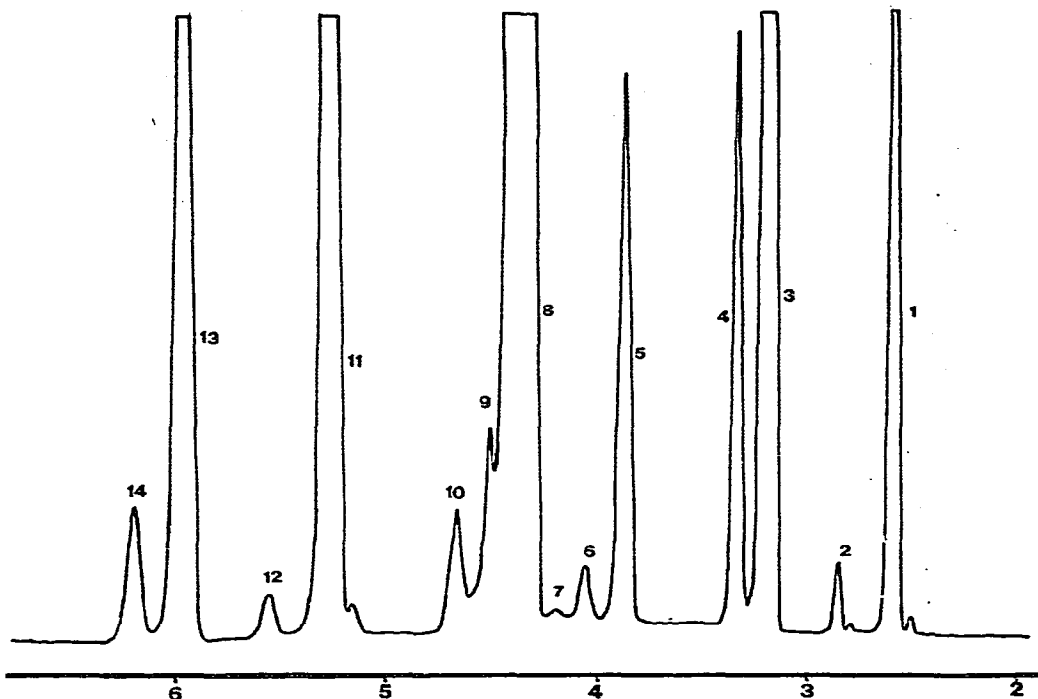


Fig. 6. Gas chromatogram of bergamot terpenes at 64° on a column pre-coated with Carbowack and with 8% of PEG as stationary phase. Peaks: 1 = α -pinene; 2 = camphene; 3 = β -pinene; 4 = sabinene; 5 = myrcene; 6 = α -terpinene; 7 = 1,4-cineole; 8 = limonene; 9 = β -phellandrene; 10 = 1,8-cineole; 11 = γ -terpinene; 12 = *cis*-ocimene; 13 = *p*-cymene; 14 = terpinolene.

The versatility of columns pre-coated with Carbowack was demonstrated by the analysis of some complex mixtures, in which use was made of gas-liquid-solid chromatography (GLSC) or gas-liquid chromatography (GLC)⁵.

Fig. 5 shows the separation of oxygenated terpenes from a bergamot oil at 84° on a 23-m column coated with Carbowack de-activated with PEG, which has a low degree of surface coverage. The influence of the carbon surface in the chromatographic process predominates, so that separation occurs mainly on the basis of differences in polarisability, *i.e.*, by GLSC.

The fractionation of terpene hydrocarbons shown in Fig. 6 was performed with a similar column, but with a higher concentration (8%) of PEG and at 64° . The high selectivity of this column when performing difficult separations by GLC can easily be seen.

These examples indicate that it is possible to prepare "tailor-made" glass capillary columns as well as packed columns by adjusting the liquid-solid ratio to yield the best fractionation of a particular mixture.

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