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# USE OF PLURONIC F68 GLASS CAPILLARY COLUMNS FOR THE ANALYSIS OF ESSENTIAL OIL SAMPLES

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## SUMMARY

The molecular weight distribution (MWD) of the original and heat-treated Carbowax 20M and Pluronic F68 gas chromatographic stationary phases were determined by gel chromatography, and compared. The heat-induced changes in the MWD of Ploronic F68 were negligible compared with those in Carbowax 20M, even though the latter was heated to 30°C higher than Carbowax 20M. This finding supports previous observations concerning the superior stability of Pluronic phases in glass capillary columns. Glass capillaries coated with 0.25 $\mu$m Pluronic F68 were successfully used over a long period of time for essential oil analysis.

## INTRODUCTION

Effective quality control of batches of essential oils is impossible without high-resolution capillary gas chromatography (GC). Non-polar and medium- and high-polarity stationary phases have all been used for essential oil analysis, polyglycol-type materials, especially Carbowax 20M, being among the most frequently used. They suffer, however, from high bleeding rates and low maximum operating temperatures. Grob and Grob[1] found that Pluronic-type stationary phases were superior to other polyglycol phases with respect to both bleeding rate and maximum operating temperature. Therefore, a comparative investigation of the characteristics of Pluronic F68 and Carbowax 20M was initiated, and glass capillaries for essential oil analysis were prepared.

## EXPERIMENTAL

### *Apparatus*

A gel chromatograph consisting of an M6000 pump (Waters Assoc., Milford, MA, U.S.A.), a Rheodyne 7010 loop injection valve (Rheodyne, Berkeley, CA, U.S.A.), two *ca.* 500 Å and two *ca.* 10,000 Å nominal pore size $\mu$Styragel columns

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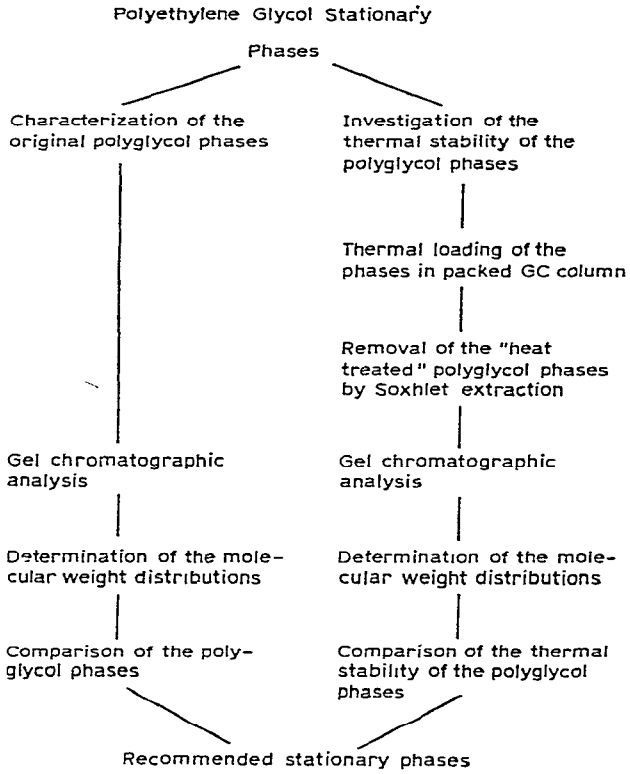


Fig. 1. Schematic diagram of the experimental procedure.

(30 cm × 3/8 in. O.D.) (Waters) connected in series, a Fresnel-type differential refractometer (Varian Aerograph, Walnut Creek, CA, U.S.A.) and a Varian A25 recorder was used. Analytical-reagent grade tetrahydrofuran (THF), filtered through a GF/F glass-fibre filter (Whatman, Clifton, NJ, U.S.A.) was used as the eluent.

GC separations were carried out on a Fractovap 2400P dual-column gas chromatograph (Carlo Erba, Milan, Italy).

Trace amounts of oxygen and water were carefully removed from the carrier gas (nitrogen) by using Hydro-Purge and Dow Oxygen Scrubber gas filters (Applied Science, State College, PA, U.S.A.).

*Procedure*

The procedure followed is described in detail elsewhere[2,3] and is shown schematically in Fig. 1. Carbowax 20M and Pluronic F68 were dissolved in THF and and analysed by using the gel chromatograph. The molecular weight distributions corrected for band spreading and detector response were determined. Chromosorb W AW DMCS (60–80 mesh) was coated with 5% of Carbowax 20M and Pluronic F68, respectively, and 2 m × 4 mm I.D. glass columns were filled with the packings. After conditioning overnight at 200 and 220°C, respectively, the columns were subjected to 200 temperature programme cycles. The initial temperature and the programming rate were 60°C and 6°C/min, respectively. The upper temperature limit was 220°C

for Carbowax 20M and 250°C for Pluronic F68. After 200 cycles the packing was removed from the column and the stationary phase was removed by Soxhlet extraction with dichloromethane and concentrated under a stream of nitrogen. The stationary phases were redissolved in THF and analysed by gel chromatography. The molecular weight distributions were obtained and compared with each other and with those of the original stationary phases.

Capillary columns were prepared according to Grob *et al.*'s barium carbonate procedure[4]. The capillaries were coated by the static method using dichloromethane solutions of the stationary phases.

Bouquette essential oil samples were dissolved in methanol. The injection splitting ratio was 1:50. The chromatograms were obtained by temperature programming from 50 to 240°C at 3°C/min.

## RESULTS AND DISCUSSION

### *Comparison of the molecular weight distribution of Carbowax 20M and Pluronic F68*

The molecular weight distributions of the original stationary phases obtained with a polyethylene glycol calibration graph[2] are compared in Fig. 2. It can be seen that Carbowax 20M has a very wide distribution; the weight-average molecular weight, $\overline{M}_w$, is 14,070, the number-average molecular weight, $\overline{M}_n$, is 4770 and the polydispersity factor, $\alpha$, the ratio of the weight- and number-average molecular weights, is 2.95. On the other hand, the molecular weight distribution of Pluronic F68 is much narrower, with $\overline{M}_w = 6430$, $\overline{M}_n = 5700$ and $\alpha = 1.13$.

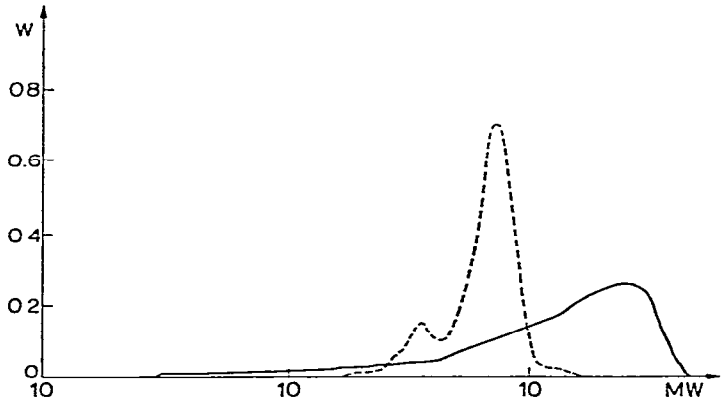


Fig. 2. Molecular weight distribution of the original Carbowax 20M (solid line) and Pluronic F68 (broken line).

These data indicate that Carbowax 20M contains significant amounts of both high- and low-molecular-weight components. It is known that polyethylene glycol molecules of widely different molecular weight have widely different polarity. Therefore, it can be expected that with the preferential loss of the low-molecular-weight components through bleeding during the life of the column, the polarity of the stationary phase will change. Pluronic F68, apart from a small amount of low-molecular-weight oligomers, is essentially a well defined polymer with a narrow molecular weight distribution and constant polarity characteristics. This implies that selective

bleeding, and consequently changes in the polarity of the stationary phase during its use, are less likely with Pluronic F68 than with Carbowax 20M. This indicates that, other factors being equal, Pluronic F68 would be a better stationary phase with respect to both the bleeding rate and the long-term stability of the polarity.

*Thermal stability of Carbowax 20M and Pluronic F68*

The molecular weight distribution curves of the original stationary phases and the heat-treated phases (after 200 temperature programme cycles, Soxhlet extraction and concentration) are compared in Figs. 3 and 4 for Carbowax 20M and Pluronic F68, respectively. It can be seen that the low-molecular-weight fraction of the heat-treated Carbowax 20M is greater than that of the original stationary phase. The average molecular weights of the heat-treated phase are $\overline{M}_w = 10{,}600$, $\overline{M}_n = 2500$ and $\alpha = 4.24$. Hence, the stationary phase removed from the packing after 200 temperature programme cycles differs significantly from the original one ($\alpha = 4.24$ and 2.95, respectively).

However, Pluronic F68, although programmed to a temperature 30°C higher than Carbowax 20M, suffered a much smaller change. There was a slight increase in both the low- and high-molecular-weight fractions. The average molecular weights of heat-treated Pluronic F68 are $\overline{M}_w = 7250$, $\overline{M}_n = 5560$ and $\alpha = 1.30$. Even heat-

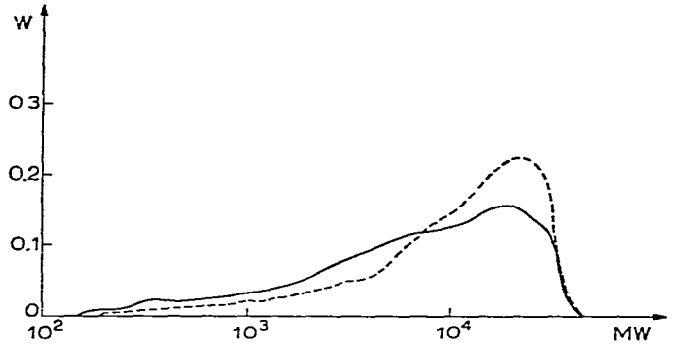


Fig. 3. Molecular weight distribution of Carbowax 20M before (broken line) and after heat treatment (solid line).

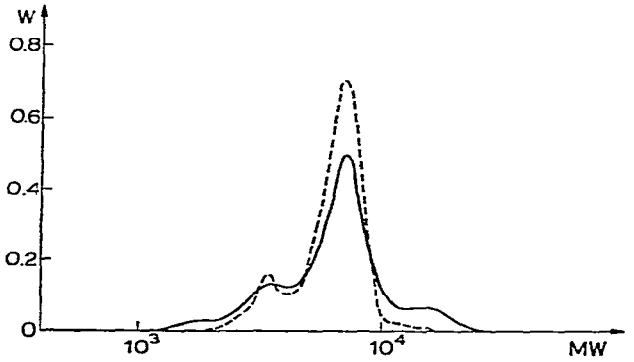


Fig. 4. Molecular weight distribution of Pluronic F68 before (broken line) and after heat treatment (solid line).

treated Pluronic F68 can be considered to be a polymer of narrow molecular weight distribution with well defined polarity characteristics.

On the basis of previous observations regarding the favourable bleeding characteristics of glass capillaries coated with Pluronic stationary phases[1], the higher bleeding rates of Carbowax 20M capillaries[5] and the data presented above, Pluronic F68 is the preferred stationary phase for high-resolution, stable glass capillary columns.

*Application of Pluronic F68 capillaries to the analysis of Bouquette* essential oil concentrates*

Batches of Bouquette essential oil were analysed on a 0.25-$\mu$m Pluronic F68 capillary column, prepared according to Grob *et al.* barium carbonate method[4]. A sample chromatogram is shown in Fig. 5. Using an internal standard technique, five

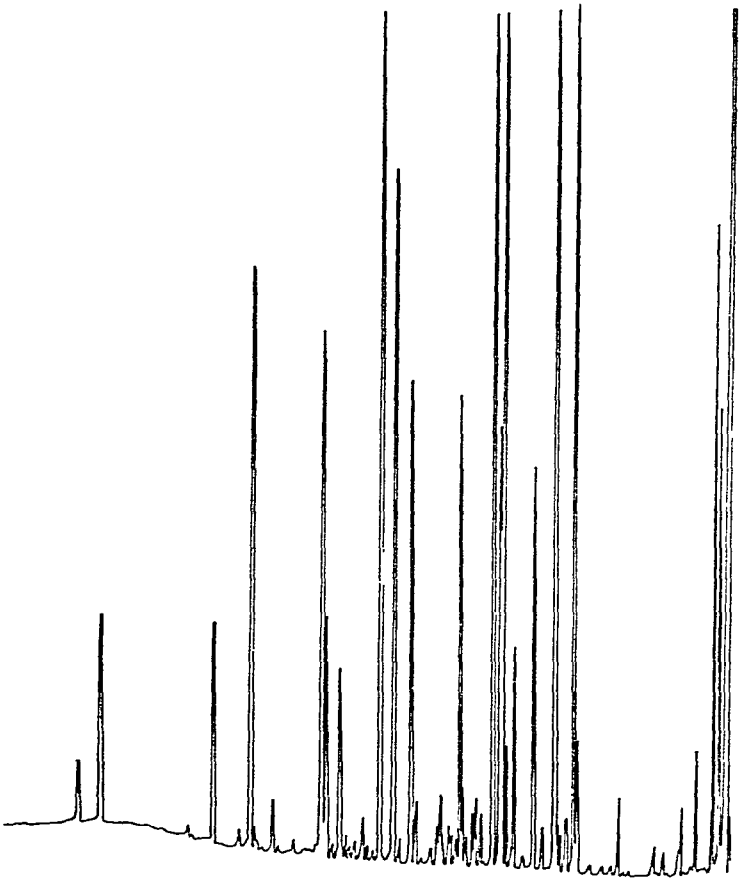

Fig. 5. Chromatogram of a Bouquette essential oil sample (batch No. 6716). Carrier gas, nitrogen; initial temperature 50°C; programming rate, 3°C/min; final temperature, 240°C; column, 40 m × 0.37 mm I.D. $BaCO_3$-treated Pyrex capillary coated with 0.25-$\mu$m Pluronic F68; sample volume injected, 1 $\mu$l; splitting ratio, 1:50.

* Bouquette is a proprietary material of Manefils (Le Bar sur Loup, France) and is used as a fragrance in cosmetical preparations.

groups of peaks can be identified that show varying peak heights, associated with odour problems in the sample. A detailed multi-dimensional GC and GC–MS study of the five groups of peaks is under way to establish the identity of the components.

The Pluronic F68 capillaries have been used over 18 months for the purpose of quality control of the batches of Bouquette essential oil. During this period no changes in the retention characteristics of the column have been observed.

## CONCLUSION

Gel permeation chromatography (GPC) has been used succesfully to select polyglycol-type stationary phases with a narrow molecular weight distribution, *i.e.*, phases that are composed mainly of molecules with closely similar polarities. Changes caused by thermal loading of the stationary phase in a GC column can be followed and compared through the molecular weight distribution determined by GPC. A method based on the determination of the molecular weight distributions of the original and heat-treated stationary phase has been developed to aid the selection of preferred high-performance stationary phases for GC.

The method was used to compare two polyglycol-type stationary phases, Carbowax 20M and Pluronic F68. The original molecular weight distribution of Pluronic F68 is much narrower than that of Carbowax 20M. The heat-induced changes in the molecular weight distribution of Pluronic F68 are negligible compared with those in Carbowax 20M. The polarity of the stationary phase is connected with its molecular weight distribution and therefore, other factors being equal, Pluronic F68 is to be preferred to Carbowax 20M for capillary GC purposes. The conclusions of this study can be used to explain the superiority of the Pluronic capillaries observed by Grob *et al.*[4].

## ACKNOWLEDGEMENT

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