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# SUPEROX, A HIGH-TEMPERATURE STATIONARY PHASE IN GAS CHROMATOGRAPHY

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## SUMMARY

The possibilities of using a polyethylene glycol of molecular weight $4 \cdot 10^6$ (Superox-4) as a liquid phase in gas chromatography (GC) and glass capillary gas chromatography $(GC)^2$ have been evaluated. Superox-4 has two favourable characteristics: firstly, it can be used at very high temperatures in $(GC)^2$ (250–275° in continuous use and occasionally 300°) and in GC (300° in continuous use and occasionally 350°), and secondly, as a gum it adheres well to all types of glass. The polarity of Superox-4 is virtually the same as that of polyethylene glycol 20M.

## INTRODUCTION

Stability at high temperatures or the maximum allowable operating temperatures (MAOT) is a very important factor in the value of a gas chromatographic (GC) stationary phase. Much work on this aspect has been carried out and, as a result, several apolar and polar stationary phases, mostly polysiloxane phases, with high temperature stability have recently become available (for a review, see ref. 1).

Carbowax 20M, which is a unique phase as far as selectivity and polarity are concerned and which is used extensively, has the disadvantage of low and variable temperature stability. Another disadvantage is its source and even batch-to-batch variability.

For these reasons we have studied the use of a new polyethylene glycol polymer series, the Superox stationary phases, in GC and glass capillary gas chromatography $(GC)^2$. This paper presents the results and also a comparison between Carbowax 20M and Superoxes.

## EXPERIMENTAL

### *Stationary phases and coating procedures*

Carbowax 20M was obtained from Applied Science Labs. (State College, Pa., U.S.A.), Fluka (Buchs, Switzerland) and Union Carbide (New York, N.Y., U.S.A.). Superox-0.6 and Superox-4 were obtained from R.S.L. (Latem, Belgium); they are also available from Alltech (Arlington Heights, Ill., U.S.A.).

Superox* is a polyethylene glycol or polyoxirane obtained by polymerization under carefully controlled conditions with a small amount of catalyst, which afterwards is removed. Under these conditions a range of very high-molecular-weight polymers (up to $5 \cdot 10^6$) can be obtained. The polarities of all of these polymers are virtually the same.

Solubility diminishes and viscosity increases with increasing molecular weight: $\eta_{red}$ (0.1% in dichloromethane at 25°) for Carbowax 20M is 0.63, for Superox-0.6 it is 19.27 and for Superox-4 it is 39.25. This disadvantage related to viscosity is, however, offset by the thermal stability, which also increases with increasing molecular weight. We consider that this is not directly related to the higher molecular weight, but rather to the higher purity of the larger molecular weight polymers, less catalyst being used in their synthesis. For this reason a Superox of high molecular weight is preferred. The Romans expressed the figure 1,000,000 by the symbol $|\overline{X}|$, and therefore the name Superox-4 $|\overline{X}|$ (or Superox-4 for short) represents polyethylene glycol with a mean molecular weight of $4 \cdot 10^6$.

Superox-4 shows the typical characteristics of high-molecular-weight substances: it has an undefined melting point as the polymer is not really melting but rather softening.

Superox mixes with a number of solvents but the result is a gel rather than a solution. Up to 0.5% of Superox in methylene chloride can be used as a coating support material, but a large volume has to be used if heavy coating is required. Dynamic coating of capillary columns with Superox is not successful as the necessary concentrations cannot be reached; for very thin films, however, this technique is applicable. Solutions of 0.1–0.5% are used for the static coating of glass capillary columns. Filling the columns in the conventional manner using gas pressure is not practical. Even at very high pressures filling can take several hours and often results in columns that will not evaporate normally following the static coating procedure[2]. However, it is easy to fill the columns with a high-pressure reciprocating pump as used in high-performance liquid chromatography and takes typically 15–30 min with a pressure of about 10 kg/cm$^2$. The glass capillary is connected to the pump using two or three superposed GC septa; the last one has to be protected from the dichloromethane solvent with a PTFE thread. The columns are sealed by the stopper method[3]. Notwithstanding the high viscosity of the solutions, static coating evaporation proceeds normally.

*Columns*

*Packed columns.* Glass columns (3 mm I.D.) were prepared by the evaporation method. The support was Chromosorb W HP (80–100 mesh) or Gas-Chrom Q (100–120 mesh). Superox-4 was coated on to this support from a 0.1–0.5% solution in dichloromethane.

*Capillary columns.* Soda-lime and borosilicate glass capillaries, drawn on a Hupe–Bush apparatus, were washed with dry methanol and freshly distilled dichloromethane. They were heated overnight with dry nitrogen at 250°.

Surface roughening of the glass, when required, was effected by etching with hydrochloric acid[4] or by deposition of sodium chloride dendrites for soda-lime glass[5]

* Superox is a trade-mark of R.S.L., Latem, Belgium.

and by whisker formation for borosilicate glass[6,7]. After the surface modification, the columns were dried overnight at 250° with a nitrogen flow of 5 ml/min prior to coating.

*Equipment*

GC analyses were performed on a Varian 3700 or 2100 gas chromatograph. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out on a DuPont 900 thermal analyser.

## RESULTS AND DISCUSSION

*Polarity and selectivity*

The similarity of the polarities and selectivities of Carbowax 20M and Superox-4 was established by comparison of the McReynolds standards. The absolute McReynolds constants for both phases are given in Table I. The difference of 23 units in the total value can be considered to be insignificant.

TABLE I

McREYNOLDS CONSTANTS

Temperature: 66.5°.

| *Compound* | *McReynolds constant** | | | |
|---|---|---|---|---|
| | $I^{C\ 20M}$ | $I^{S-4}$ | $\Delta I$ | $I^{*S-4}$ |
| Benzene | 954 | 951 | − 3 | 947 |
| 2-Pentanone | 981 | 978 | − 3 | 974 |
| Butanol | 1139 | 1184 | − 5 | 1132 |
| Pyridine | 1180 | 1171 | − 9 | 1167 |
| Nitropropane | 1211 | 1208 | − 3 | 1205 |
| Sum | 5465 | 5442 | −23 | 5425 |

* $I^{Carbowax\ 20M}$ on naked glass after conditioning at 100° for 2 h; $I^{Superox-4}$ on naked glass after conditioning at 100° for 2 h; $I^{*Superox-4}$ on NaCl dendrite surfaces after conditioning at 240° for 2 h.

The last column in Table I gives the values for a Superox-4 sodium chloride dendrite column after conditioning for 2 h at 240°. It can be seen that the polarity differs slightly with the conditioning temperature.

*Temperature limits (stability)*

The TGA of Carbowax 20M of different origins and of Superox-0.6 and Superox-4 showed only minor differences that are not in proportion to the large MAOT differences found in GC practice for these phases.

A better approach for establishing the MAOT value with TGA is obtained by isothermal runs over a definite period, *e.g.*, 100 min, using successive temperature increments of 25°. The materials are thus heated for 100 min at 150, 200, 225, 250 and 275°. After the run at 250°, Superox-4 lost only 0.2% of its weight, whereas the best Carbowax 20M had then already lost 2%. Conclusions about temperature stability are, however, best drawn from actual GC practice.

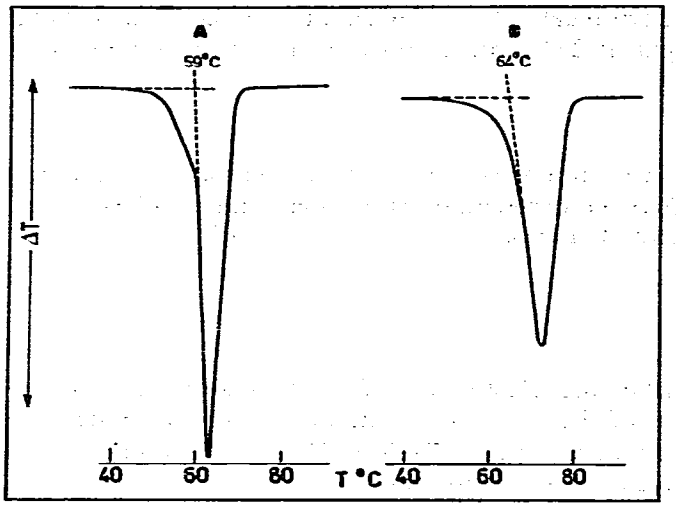


Fig. 1. DSC analysis of Carbowax 20M (A) and Superox-4 (B).

The minimum operating temperature follows from the DSC analysis (Fig. 1) and from our practical experience.

The low-temperature limit is taken as the tangential intercept with the baseline (64° for Superox-4 and 59° for Carbowax 20M). This value for Superox-4 is in agreement with the experimental results. Below this limit, peak broadening and a decrease in column efficiency are observed.

*Superox in GC and (GC)*[2]

*Packed columns.* For high-temperature analysis, columns packed with 1% Superox-4 on Gas-Chrom Q (100–120 mesh) provide the best stability and separating power. Fig. 2 shows the analysis of cholesteryl esters on a 0.5-m 1% Superox-4 column at 275°. The column was conditioned at 300° for 6 h. In an attempt to separate triglycerides, the same column was used at temperatures up to 350°, but we did not succeed in eluting these polar substances. After this high-temperature treatment, the efficiency of the column was still good. A 3% column separated squalane and squalene in 23 sec at 300° and was used to analyse free sterols at 275° and pentacyclic diacetates and diketones at 250°.

*Capillary columns, (GC)*[2]. Carbowax 20M coatings on untreated glass capillary columns usually give satisfactory results only up to 180°; even then on prolonged use breaking of the film and droplet formation are soon observed. The fixation power of sodium chloride crystalline and dendritic surfaces allows a temperature of 220° to be used, while on whisker surfaces a temperature of 240° for even longer times is possible if the surface has been properly deactivated[7]. These data depend on the origin (batch) of the Carbowax. The temperature stability of Superox-4 is also dependent on the surface characteristic of the column.

On an untreated glass surface, temperature limits of 240° are attainable. Even with a film thickness of 0.4 $\mu$m, soda-lime glass columns are slightly alkaline (tailing of nitropropane) and borosilicate glass columns slightly acidic (tailing of pyridine).

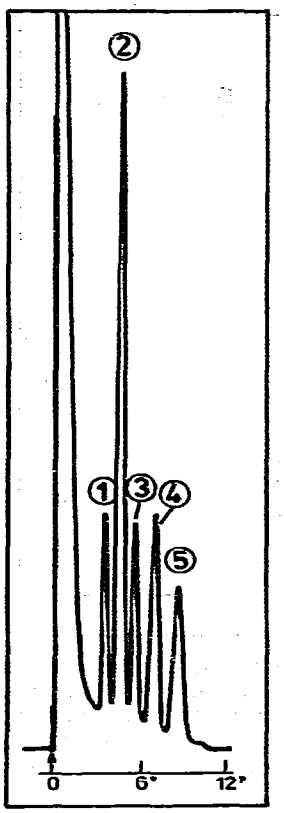


Fig. 2. Separation of cholesteryl esters on a 0.5 m × 3 mm I.D. glass column packed with 1% Superox-4 on Gas-Chrom Q (100–120 mesh). Temperatures: column, 275°; injector and detector, 350°. Carrier gas (hydrogen) flow-rate: 20 ml/min. Peaks: 1 = cholesteryl myristate; 2 = cholesteryl pentadecanoate; 3 = cholesteryl palmitate; 4 = cholesteryl heptadecanoate; 5 = cholesteryl stearate.

The activity of borosilicate glass can be suppressed by deactivation with nitrogen, hydroxyl-containing compounds[7]. Fig. 3a illustrates the efficiency and inertness of a Superox-4 wide-bore capillary column that was deactivated with N-cyclohexyl-3-azetidinol (CHAZ). Pyridine and nitropropane, the alkaline and acidic compounds of the McReynolds standards, are eluted without adsorption. Fig. 3b shows the analysis of the McReynolds standards after conditioning the column at 310° for 8 h. The plate number is reduced from 1650 to 300 plates/m. This decrease in efficiency is caused by droplet formation of the film. Note, however, that the activity of the column is still acceptable.

On a sodium chloride-modified capillary column, a temperature of 250° can be used without any deterioration. The film stability and column durability at 250° of a Superox-4 dendritic column were followed for several weeks and no decrease in column efficiency was observed.

Fig. 4 shows an analysis of fatty acid methyl esters (FAME) at 250° on a Superox-4 sodium chloride dendrite column. The analysis is performed in less than

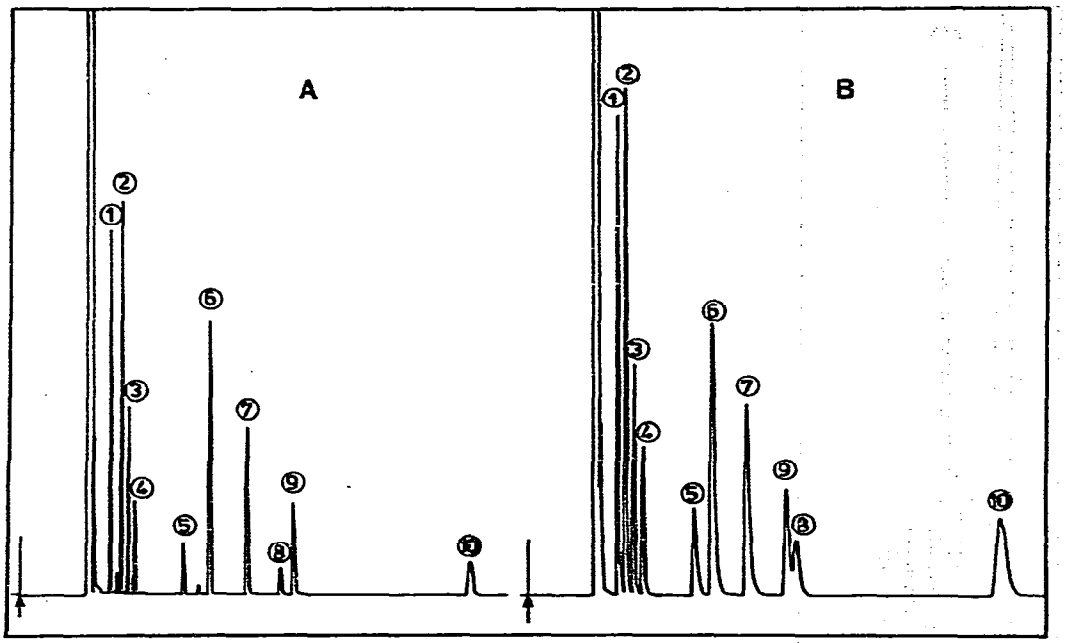


Fig. 3. Gas chromatogram of the McReynolds standards on a 40 m × 0.53 mm I.D. borosilicate glass capillary column, deactivated with N-cyclohexylazetidinol (CHAZ) and coated with Superox-4. Temperatures: column, 66°; injector and detector, 250°. Carrier gas (hydrogen) flow-rate: 4 ml/min. Peaks: 1 = nonane; 2 = benzene; 3 = 2-pentanone; 4 = decane; 5 = undecane; 6 = *n*-butanol; 7 = pyridine; 8 = dodecane; 9 = 1-nitropropane; 10 = tridecane. A, After conditioning at 240° for 1 h; B, after conditioning at 310° for 8 h.

2.20 min with a resolution between stearic and oleic acids of approximately 2. Sterols, vitamins $D_2$ and $D_3$ (Fig. 5) and methoxylamine-trimethylsilyl derivatives of steroids have also been successfully separated on Superox-4 capillary columns.

The highest temperature stability of Superox-4 in (GC)[2] was obtained on whisker surfaces deactivated with CHAZ. The capacity ratio ($k'$) of methyl linoleate and the resolution of methyl stearate and methyl oleate were measured at 200° after conditioning a whisker Superox-4 column at 250° for 8 h, 275° for 3 h and 300° for 3 h. The $k'$ value (7.33) remained constant. After conditioning at 300°, a slightly lower resolution of $C_{18}$ and $C_{18:1}$ was observed, caused by tailing of the compounds. On injecting the deactivating agent triethanolamine, the original resolution was regained and the column was still useful for the separation of hydrocarbons, ketones, esters and alcohols. With highly polar compounds such as pyridine, tailing was then observed. The main reason is the temperature stability of the deactivating agent (approximately 275°). High-temperature treatment will also increase the activity of Gas-Chrom Q and Chromosorb W HP supports.

The whisker Superox-4 capillary column used above was then conditioned at 325° for 5 h. The $k'$ value of methyl linoleate was decreased to 4.22 and the resolution of $C_{18}$ and $C_{18:1}$ was halved. Considering these data, the MAOT of Superox-4 on whisker surfaces is 300°.

The lifetime of a Superox-4 and also of a Carbowax 20M column is greatly

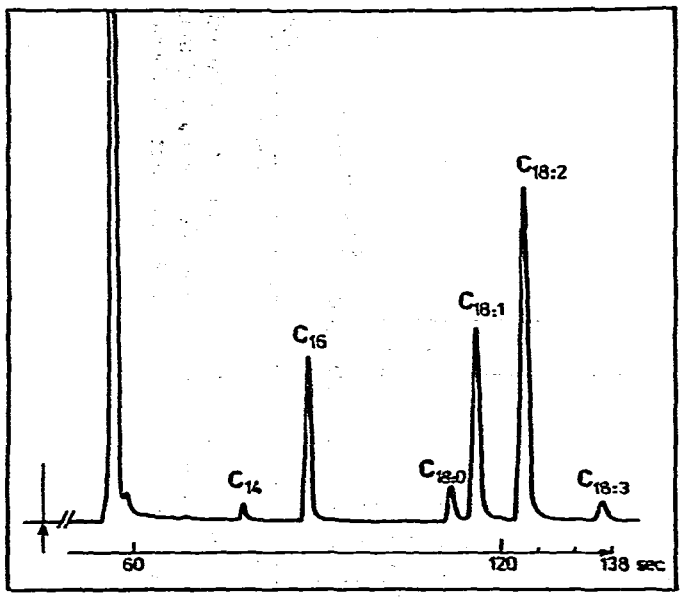


Fig. 4. FAME analysis on a 25 m × 0.5 mm I.D. NaCl dendrite column coated with Superox-4. Temperatures: column, injector and detector, 250°. Carrier gas (hydrogen) flow-rate: 5 ml/min.

influenced by the amount of water on the glass surface and the purity of the carrier gas. The physisorbed water on the glass surface was removed by heating the column overnight at 250° with a dry nitrogen flow of 5 ml/min. After this treatment both ends were sealed until coating was carried out.

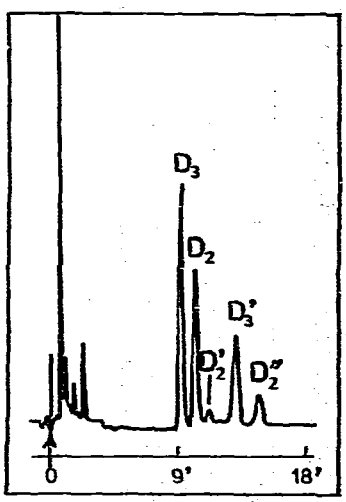


Fig. 5. Chromatogram of the mixture of vitamin $D_3$ and $D_2$ standards, which were apparently contaminated with $D_3'$ and $D_2'$ and $D_2''$, respectively; regular peak shape excludes thermal decomposition. Column: 7.5 m × 0.5 mm I.D. NaCl dendrite capillary coated with Superox-4. Column temperature: 250°. Solid-state injection; carrier gas (hydrogen) flow-rate, 4 ml/min.

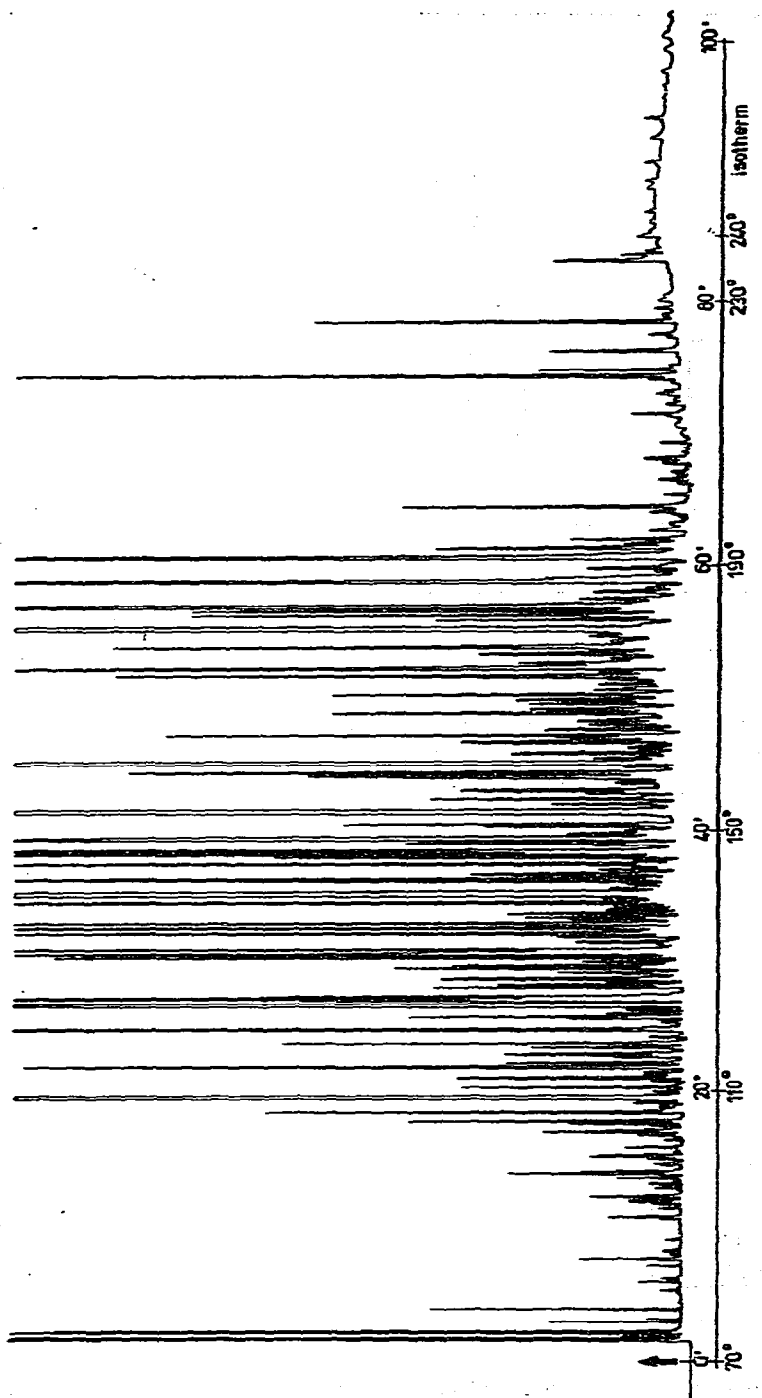


Fig. 6. Chromatogram of the oxygen fraction of black pepper essenial oil. Borosilicate capillary column, 40 m × 0.26 mm I.D., deactivated with N-cyclohexylazetidinol (CHAZ) and coated with Superox-4. Injection, 0.2 μl, split *ca.* 50:1 in an all-glass splitter. Temperature programmed from 70° to 240° at 2°/min; carrier gas (hydrogen) flow-rate, 1.5 ml/min Sensitivity setting: attenuation 1, range $10^{-11}$ (Varian 3700). Note the absence of baseline deviation at the end of the temperature programme.

The purity of the gas is very important. Trace amounts of oxygen and water cause decomposition of the polyethylene glycols (the column becomes brown) with an increasing loss of resolution. Nitrogen contains trace amounts of oxygen and water, which are not completely removed by a Drierite and BTS purge gas filter. The durability of the columns is considerably improved by using hydrogen (or helium) as the carrier gas.

Superox-4 capillary columns are particularly temperature stable for temperature-programmed analyses, as can be deduced from Fig. 6, which represents the analysis of the oxygen fraction of pepper essential oil. Although this chromatogram was recorded at high sensitivity, the baseline remained practically stable. Such temperature programming can be extended to 300° without damaging the column. Only after prolonged heating of the column at 300° is a decrease in efficiency observed. Bleeding of the stationary phase at elevated temperatures is very small. This makes Superox-4 also very useful for combined gas chromatography–mass spectrometry.

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