CHROM. 6065

DECOMPOSITION OF FLUOROSILICONE STATIONARY PHASES IN SOLUTION

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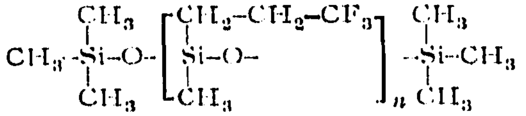
SUMMARY

The fluorosilicone stationary phases SP-2401, OV-210, and QF-1 (FS-1265) readily decompose in acetone solution. This decomposition may be catalyzed by residual catalyst and/or the glass surface of the container. Solution decomposition may be prevented by choosing a solvent that is a poorer promoter than acetone or by using a strong acid ion-exchange resin to stabilize the acetone solution.

INTRODUCTION

Organo-substituted polysiloxanes are widely used as stationary phases in gas–liquid chromatography. However, little information about structure, chemical composition, molecular weight distribution, and chemical and thermal stability of the commonly used silicone stationary phases has been provided.

Poly(methyl-3,3,3-trifluoropropyl)siloxanes (TFPM) (*e.g.*, QF-1 or FS-1265, OV-210, and SP-2401) have been among the most popular silicone stationary phases. The use of these materials for the gas chromatographic analysis of steroids, pesticides, and a wide variety of other materials is well documented in the published literature. These materials may all be represented by the general formula:



$$CH_3-\overset{CH_3}{\underset{CH_3}{Si}}-O-\left[\overset{CH_2-CH_2-CF_3}{\underset{CH_3}{Si}}-O-\right]_n-\overset{CH_3}{\underset{CH_3}{Si}}-CH_3$$

that is, a trimethylsilyl end blocked poly(methyl-3,3,3-trifluoropropyl)siloxane.

Although OV-210 and QF-1 have been widely used, there have been two common complaints associated with their use as stationary phases. First, column packings using OV-210 or QF-1 generally do not produce columns of high efficiency; 500 theoretical plates per foot for a packed column has been considered good efficiency. Secondly, the inability to reproduce retention parameters and column efficiency from one batch of packing to another has been a common complaint.

A poly(methyl-3,3,3-trifluoropropyl)siloxane stationary phase (SP-2401) that produces column packings of significantly higher efficiency than OV-210 and QF-1 has been introduced. Six-foot columns giving efficiencies of 800 theoretical plates per foot for cholesterol and 1040 theoretical plates per foot for mannitol have been described in advertising literature[1]. The second problem, that of being able to reproduce column packings, may result from decomposition of the stationary phase in solution.

DECOMPOSITION OF POLY(METHYL-3,3,3-TRIFLUOROPROPYL)SILOXANE IN ACETONE SOLUTION

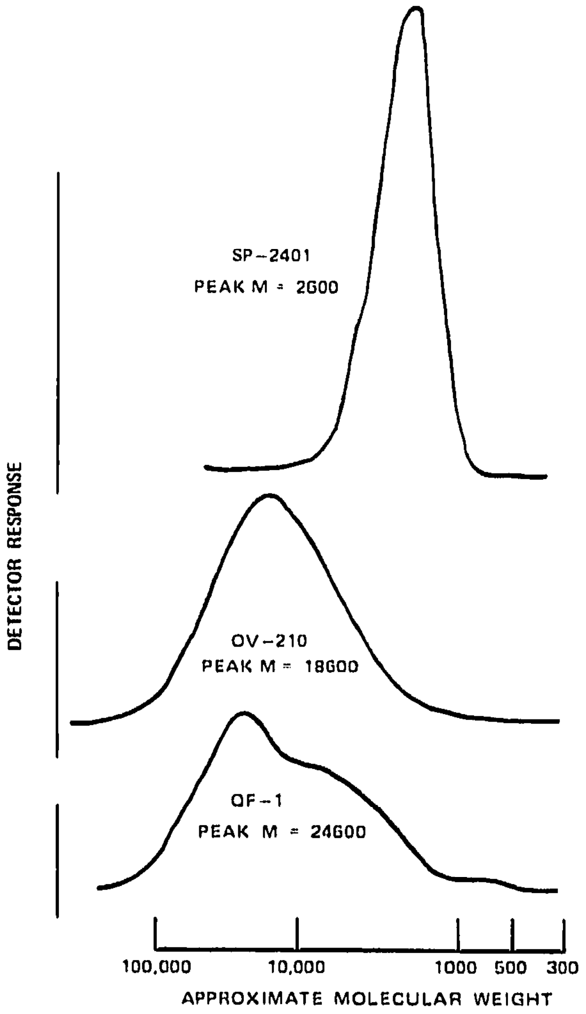
In most situations, the major suppliers of chromatography materials have recommended acetone as the solvent of choice for these stationary phases. It is a little known fact that acetone is an excellent promoter of the decomposition of these materials. The decomposition products are of low enough molecular weight to be readily eluted from the gas chromatographic column. The use of soft glass containers to store acetone solutions of these materials further promotes this decomposition.

To demonstrate this decomposition, 5 % (weight/volume) solutions of OV-210, QF-1, and SP-2401 in acetone were prepared. Portions of each of these solutions were stored for various time increments in glass bottles and polyethylene bottles. Portions of these solutions stabilized with Dowex 50W ion-exchange resin were stored in glass bottles for various lengths of time to study the decomposition rate of stabilized acetone solutions.

Several other solvent systems were considered. Chloroform, carbon tetrachloride, and dichloromethane were not found to be satisfactory solvents; these solvents either do not readily dissolve TFPM or else give very cloudy solutions. Tetrahydrofuran (THF) and ethyl acetate solutions (5 % weight/volume) of QF-1 and SP-2401 stored in glass bottles were also studied.

The data presented in this study were obtained using a Model 200 gel permeation chromatograph (Waters Associates, Inc., Framingham, Mass., U.S.A.). Stainless steel columns, 4 ft. × 3/8 in. O.D., packed with Styragel® of stated porosities 3×10^6 Å, 1.5×10^5 Å, 1×10^4 Å, 1×10^3 Å, and 5×10^2 Å were held at 25°. A THF flow-rate of 1 ml/min and differential refractometer detector were employed. The chromatographic system was calibrated using well-characterized fractions of TFPM[2]. Peak maximum elution volume (count number) for each standard was related to molecular weight using a semi-logarithmic plot. Because of the nonlinear relationship, standards covering the entire molecular weight range of interest must be used.

Fig. 1 shows gel permeation chromatograms for 5 % (weight/volume) solutions of QF-1 (FS-1265), OV-210, and SP-2401 in acetone for $t = 0$; that is, the samples were dissolved in acetone and injected immediately into the GPC. Fig. 2 shows the chromatograms for the same three solutions following storage in a glass bottle for 4 h. The chromatogram for QF-1 shows a peak at 350–1200 molecular weight units for the decomposition products of the polymer. From this chromatogram it is obvious that one cannot store QF-1/acetone solutions in glass bottles for even short periods of time without destroying a significant amount of the polymer. The chromatograms for OV-210 and SP-2401 also show peaks in the region of 350–1200 molecular weight units. Comparison of peak maxima and peak shapes of the QF-1 chromatograms in Figs. 1 and 2 indicates that the higher molecular weight components undergo decomposition at a faster rate than do the lower molecular weight



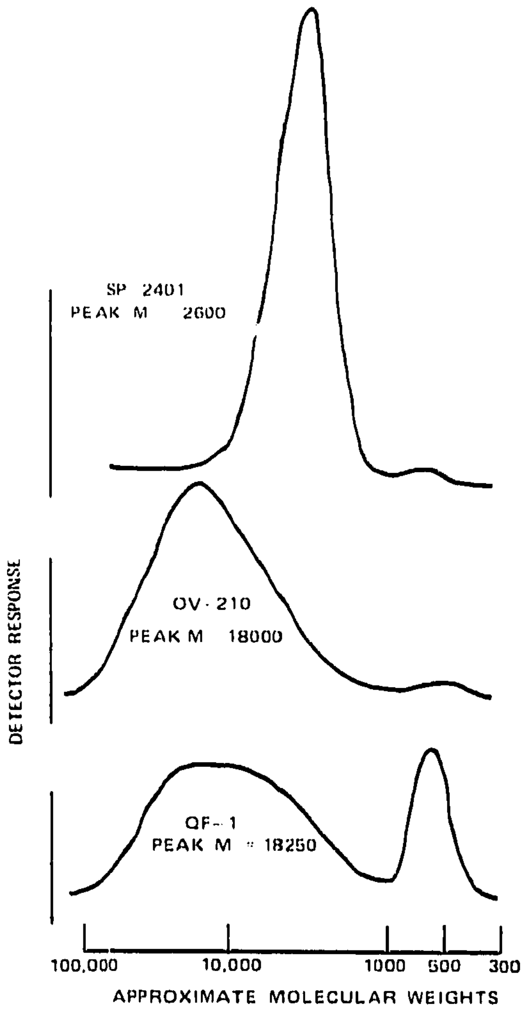


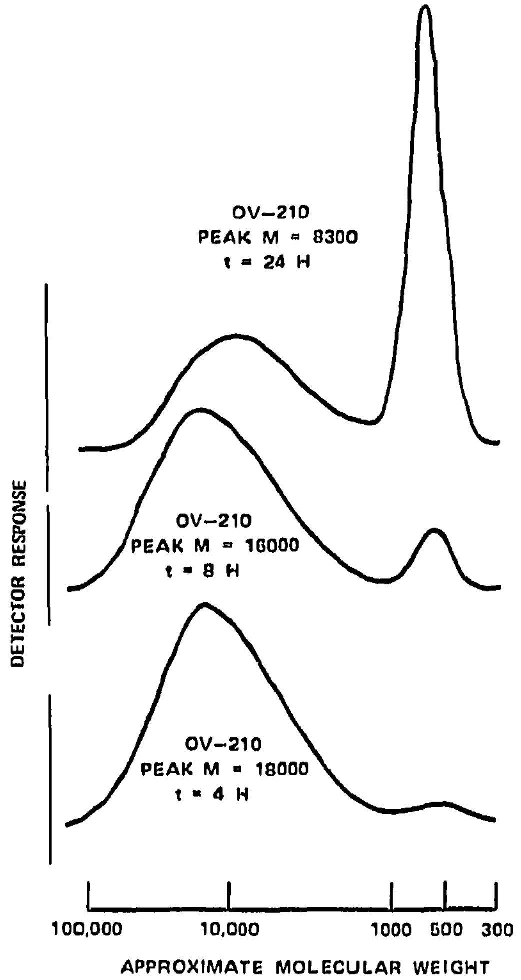
Fig. 1. Gel permeation chromatograms of 5% (weight/volume) QF-1, OV-210, and SP-2401/acetone solutions; *t* = 0.

Fig. 2. Gel permeation chromatograms of 5% QF-1, OV-210, and SP-2401/acetone solutions; *t* = 4-h storage in glass bottles.

components. This shift in peak maximum may also be readily observed in Fig. 3; the chromatograms shown in this figure illustrate the decomposition of OV-210 (in acetone solution) with time. One could not expect to produce a very good column if the stationary phase was dissolved one day and coated onto the support the following day.

Fig. 4 shows plots of percent unadjusted peak area attributed to the parent fluid *versus* time for the three phases. None of these stationary-phase solutions may be stored in a glass container over the weekend without significant decomposition of the polymer.

The surface of the glass container provides a catalyst for this decomposition. Fig. 5 illustrates that 5% acetone solutions of OV-210 and SP-2401 may be stored in polyethylene containers for up to two weeks without significant polymer decomposition. The OV-210 does show a small peak in the 350–1200 molecular weight range for the decomposition products. No measurable amount of decomposition of SP-2401 could be observed. In contrast, QF-1 solutions could not be stored in polyethylene bottles for 24 h without significant decomposition occurring. These results most likely reflect the efforts of the manufacturers of OV-210 and SP-2401 to remove residual amounts of catalyst from these materials. That OV-210 decomposes in acetone solution slightly faster than SP-2401 may be due to the difference in molecular weights of the two materials.



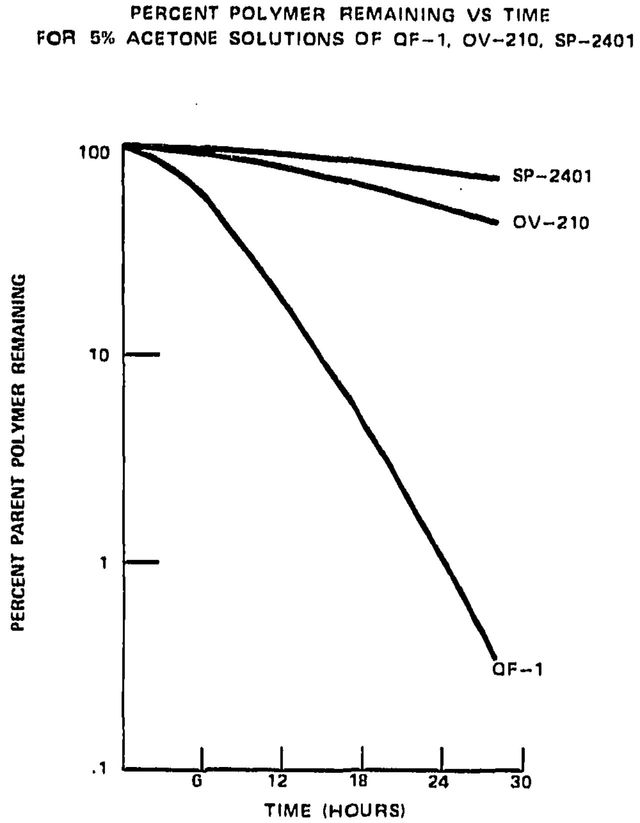


Fig. 3. Gel permeation chromatograms of 5% OV-210/acetone solution; t = 4-, 8-, and 24-h storage in a glass bottle.

Fig. 4. Semi-logarithmic plot of percent unadjusted peak area attributed to parent polymer *versus* time for 5% acetone solutions of QF-1, OV-210, and SP-2401.

STABILIZATION OF TFPM SOLUTIONS

Basically, there are two avenues of approach to prevent this decomposition of TFPM stationary phases in solution, *viz.* (a) to eliminate the catalysts and (b) to use a solvent that does not promote this decomposition.

The effects of the catalyst (residual catalyst from manufacture and the glass surface of the bottle or beaker) may be significantly reduced by keeping the TFPM/acetone solution in contact with Dowex 50W, a strongly acidic cation-exchange resin. Fig. 6 shows a gel permeation chromatogram for a QF-1/acetone solution stored in a glass bottle for four weeks. This solution was stabilized by adding the ion-exchange resin while the QF-1 was being dissolved; the amount of ion-exchange resin used in this experiment was 75% the weight of the TFPM polymer. No peak representing decomposition products in the range of 350–1200 molecular weight units is observed. SP-2401 and OV-210 acetone solutions may be stored in glass containers in a similar manner. Solutions stabilized with lesser amounts of resins (1%, 10%, and 50%) were studied; these solutions showed good stability for one to two weeks, but decomposition products appeared in the chromatograms of the solutions stored for longer periods of time.

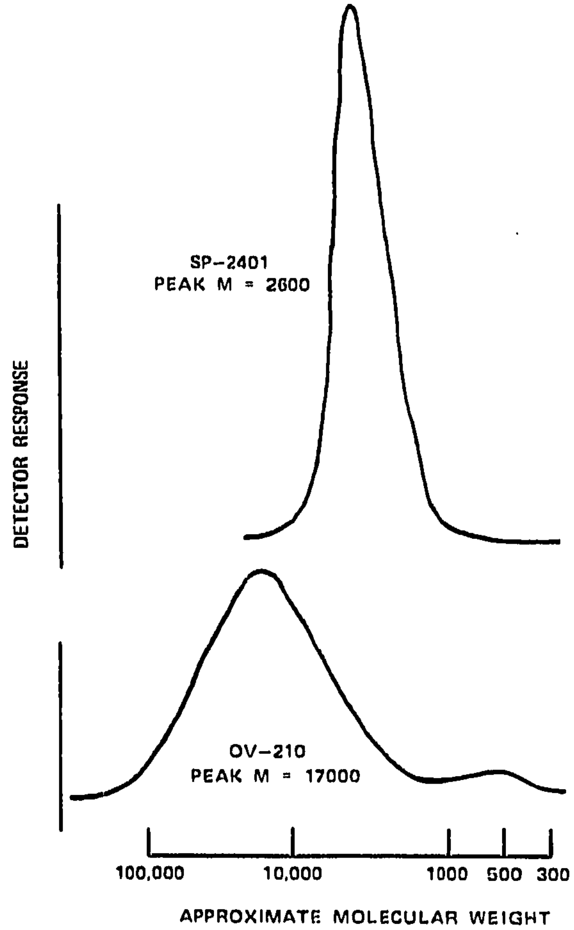


Fig. 5. Gel permeation chromatograms of 5% OV-210 and SP-2401/acetone solutions; *t* = 2-week storage in polyethylene bottles.

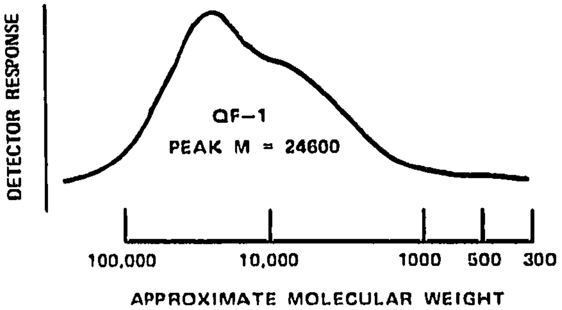
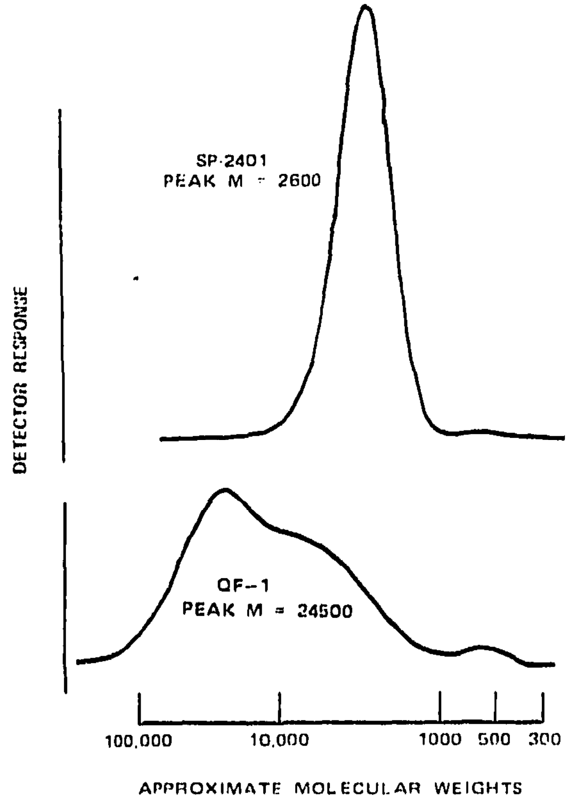


Fig. 6. Gel permeation chromatogram of 5% QF-1/acetone solution stabilized with Dowex 50W (75% weight of polymer); *t* = 4-week storage in a glass bottle.

The rate of decomposition of the TFPM stationary phases in solution may be significantly reduced by using a solvent that is a poorer promoter than acetone. Two common solvents, THF, b.p. $\approx$65°, and ethyl acetate, b.p. $\approx$77°, offer good alternatives to acetone. Fig. 7 shows the chromatograms for 5% solutions of QF-1 and SP-2401 in THF that had been stored in glass bottles for five days. QF-1 shows a small peak for some decomposition products; no decomposition products are observed for SP-2401. Fig. 8 illustrates the chromatograms for 5% QF-1 and

SP-2401 ethyl acetate solutions that have been stored in glass bottles for five days; no decomposition products can be observed for either stationary phase.

Thus, ethyl acetate appears to be a good alternative to acetone. If THF is used, however, care should be taken to ensure that the THF does not contain impurities; additives commonly added to stabilize THF can leave a residue on the packing.



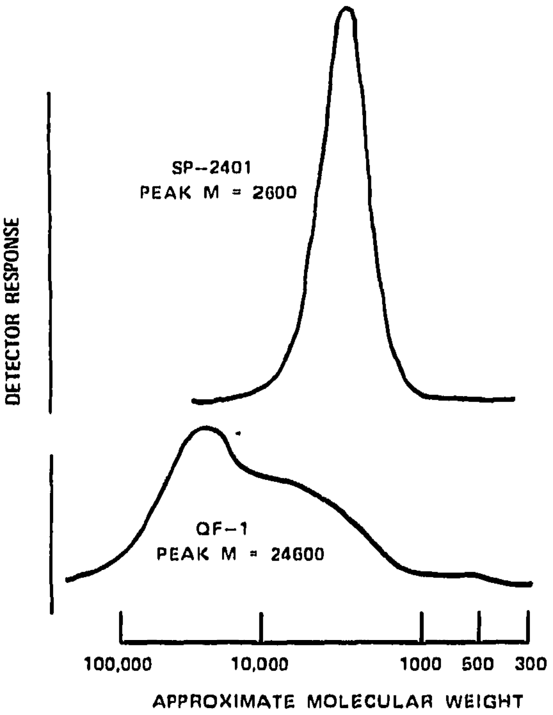


Fig. 7. Gel permeation chromatograms of 5% QF-1 and SP-2401/THF solutions; t = 5-day storage in glass bottles.

Fig. 8. Gel permeation chromatograms of 5% QF-1 and SP-2401/ethyl acetate solutions; t = 5-day storage in glass bottles.

SUMMARY OF CONCLUSIONS

The solution decomposition of QF-1, OV-210, and SP-2401 is promoted by acetone. THF and ethyl acetate are suitable solvents for these materials and do not promote the decomposition as readily as acetone; ethyl acetate is recommended.

The decomposition of QF-1 in acetone solution is catalyzed by residual catalyst in the polymer and by the glass surface of the container; SP-2401 and OV-210 decomposition in acetone solution is catalyzed by the glass surface of the container. Acetone solutions of these materials may be stabilized for storage of at least one month by addition of a strong acid ion-exchange resin such as Dowex 50W; an amount of resin equal to 0.75 times the weight of the polymer is recommended.

REFERENCES

1 SUPELCO, *Chromatography/Lipids*, Vol. 5, No. 6 (December, 1971).
2 R. R. BUCH, H. M. KLIMISCH AND O. K. JOHANNSON, *J. Polymer Sci.*, Part A-2, 7 (1969) 563.