

Low temperature discontinuity of retention times with Carbowax 20M

Gas-liquid chromatography is being applied to the analysis of an ever widening range of materials. Complex mixtures of compounds whose boiling points vary widely may be analyzed by the use of programmed GLC. As a result, more stringent demands are being made on the performance of stationary phases with respect to temperature limits.

Carbowax 20M is a good general polar stationary phase. Because of problems associated with column bleeding, a considerable amount of information exists concerning the upper temperature limits of this material. However, little information is available on the behavior of Carbowax 20M at lower temperatures where the separation of volatile compounds is usually carried out. One commercial supplier of Carbowax 20M lists its minimum useable temperature at 50° while other suppliers list no minimum.

We have found that Carbowax 20M behaves quite differently above and below 60°, and that superior chromatograms are obtained above that temperature.

Experimental

A Perkin-Elmer* Model 800 dual column gas chromatograph with a flame ionization detector was used. The 10 ft. $\frac{1}{4}$ in. o.d. stainless steel column was packed with 30% by weight of Carbowax 20M on Gas Chrom P (60-80 mesh). Helium flow was 100 ml/min, injection port temperature was 235° and detector temperature 240°. Injections of 0.5 μ l of methanol, ethanol, acetone, and propionaldehyde were run isothermally at a series of temperatures from 30 to 120°.

Results

Fig. 1 illustrates the effect of column temperature on the retention time of four volatile compounds. From 30° to 58-60°, the retention times decrease with an increase in temperature as expected; however, at about 60° the retention times become as long as, or longer than, those observed at the initial low temperature. The maximum and minimum temperatures at which the retention values changed are the same for the four compounds tested. Since the compounds tested have different boiling points, the observed phenomenon was not a function of the boiling point of the solute. The effect of instrumental parameters was also ruled out by reproducing the results on an F and M* Model 609 single column gas chromatograph with a flame ionization detector, using a second 12 ft. $\frac{1}{4}$ in. o.d. copper column packed with 30% Carbowax 20M on Gas Chrom P (60-80 mesh). Since this anomalous behavior occurs in the range of the melting point of Carbowax 20M, it may be the result of the change from

* It is not implied the U.S.D.A. recommends the above company or its product to the exclusion of others in the same business.

the solid to the liquid phase. At temperatures below 58–60° separation of compounds may occur by gas–solid rather than gas–liquid chromatography.

It was also observed (Fig. 2) that at temperatures above 58–60° there is a sharpening of the eluting peak.

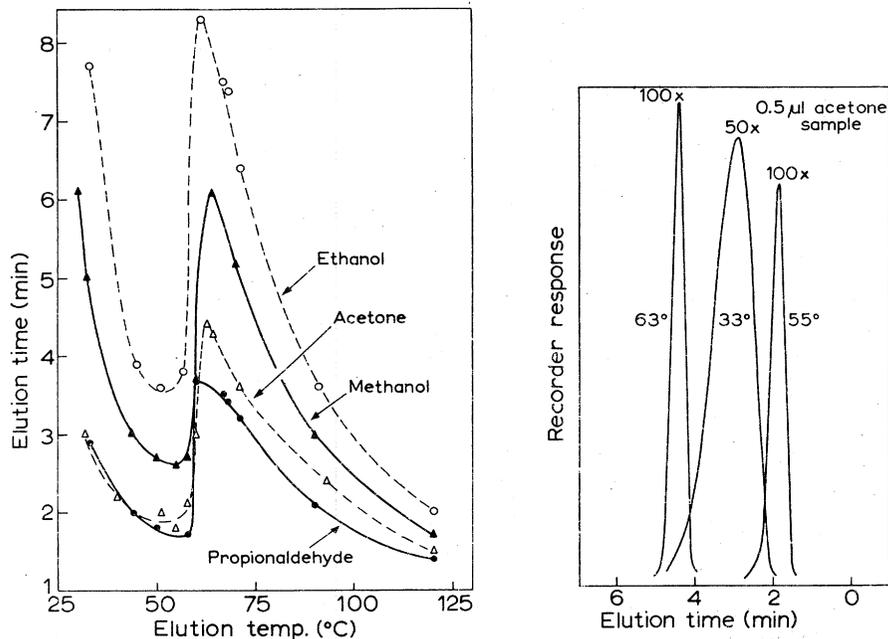


Fig. 1. Elution time discontinuity as a function of column temperature.

Fig. 2. Influence of column temperature on peak shape.

Thus, by proper selection of the elution temperature it is possible to obtain better resolution due to peak sharpening and to increase the retention time 2.0–2.5 fold within a 10° range. In the collection of volatiles, sharp peaks are often undesirable because the compound is in the collection trap for too short a time to allow condensation to take place. Use of temperatures below approximately 60° broadens the peak with the resulting increase in residence time in the trap.

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