Retention temperature in programmed temperature gas chromatography

Programmed temperature gas chromatography is now being used extensively for the separation of wide boiling-range mixtures, and several papers[1-4] have been published which deal with the relationship between retention time and column operating conditions for linear heating rates. One point which emerges from theoretical considerations[2] is that the retention temperature measured from the starting temperature is less dependent on heating rate than is retention time, provided that the ratio of fixed phase to moving phase capacity for the component is not too small (in which case the retention time is determined mainly by the dead volume of the column). This is supported by data which can be derived from published experimental results[3], but the logical step of replacing the chromatograph time axis by a temperature axis has not so far been reported.

In the present work a Moseley model 3S X-Y recorder was used and the column temperature, measured by a chromel–alumel thermocouple, was recorded on the X-axis. The normal detector signal was fed to the Y-axis, together with time interval pips derived from a synchronous motor–microswitch assembly for the simultaneous measurement of retention times. The 1/4 in. diameter columns was packed with 1/2 %
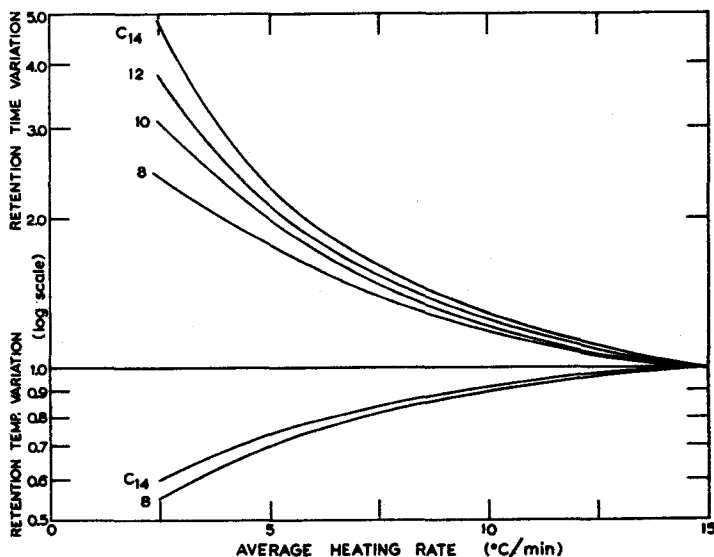

Fig. 1. Retention time (temp.) variation of C_8–C_{14} paraffins *versus* average heating rate.

Dow Corning silicone grease on 60–80 mesh glass beads, and could be cooled rapidly to room temperature by passing water through a copper coil wrapped around it. Representative results are shown in Fig. 1 for C_8–C_{14} paraffins, the retention time and temperature for each component being taken as 1.0 at the average heating rate

of 15 °C/min. Temperature changes are measured from the starting temperature of 20 °C, the retention temperature variation being defined as $t_v = \frac{t_n - 20}{t_{15} - 20}$ where t_n and t_{15} are the observed retention temperatures at heating rates of n °C/min and 15 °C/min respectively. Actual times (and temperatures) varied from 2.1 to 31 min (38 ° to 121 °C). It can be seen from the figure that, even at heating rates as low as a few degrees per minute, the retention temperature is less dependent on heating rate than is retention time. Moreover Fig. 1 shows that, with change in heating rate, there is a much greater overall change in the chromatogram on a time basis than on a temperature basis. The retention temperature is also relatively insensitive to change in carrier gas velocity[2].

It is thus seen that retention intervals for characterisation of components in a sample can be measured with greater reproducibility on a temperature basis than on a time basis. Conversely, a lower degree of control is required for retention temperature measurements than for retention time measurements, and retention data are more readily interchanged between different instruments. Moreover, the results obtained with non-linearly heated columns (as in the case of Fig. 1) are more readily correlated with linear programmed temperature data. The effect of heating rate on peak shape and resolution is also more readily seen on temperature axis chromatograms than on conventional time axis chromatograms since the lengths of the latter differ so much.

In the case of a linearly heated column, the temperature axis chromatogram will be identical with the time axis chromatogram (except for a scale factor). If the detector is temperature insensitive, and responds purely on a mass per unit time basis[5], the peak areas obtained from the chart can be used to measure component concentrations on the basis of isothermal detector calibration factors. However, all detectors so far devised appear to have some degree of temperature sensitivity. In the case of a non-linearly heated column, peak areas integrated with respect to time, rather than chart areas, must be used since equal intervals on the temperature axis do not represent equal time intervals.

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