

CHROM. 8519

GRADIENT TEMPERATURE PROGRAMMING OF SHORT CAPILLARY COLUMNS

DAVID C. FENIMORE

Texas Research Institute of Mental Sciences, Houston, Texas 77025 (U.S.A.)

SUMMARY

Rapid gas chromatographic separations are achieved by the application of temperature-programmed thermal gradients to a short (11 m) capillary column. The design of a column heater with individually controlled sections capable of rapid thermal transfer to the column is discussed. The separation of a test mixture of C₁₀-C₁₈ *n*-alkanes in 2.4 min with an average resolution of 6.5 is demonstrated.

INTRODUCTION

The application of moving thermal gradients to gas chromatographic processes was first reported in 1951 by Zhukhovitskii *et al.*¹, and concerned separations effected on columns of solid adsorbents by moving an oven along the longitudinal axis of the column from the inlet to the outlet. In 1963 Ohline and DeFord² described a similar technique applied to gas-liquid partition chromatography and demonstrated that a negative thermal gradient, *i.e.* a gradient with the higher temperature towards the inlet end of the column, moving in the direction of gas flow at a velocity less than that of the carrier gas will cause the solute mixture to separate with the components at predictable positions within the gradient. The more volatile components will move rapidly until the cooler portions of the gradient slow their movement while the less volatile compounds are held back in the regions of higher temperature. Movement of the gradient with the accompanying rise in temperature will cause the solute components to move with greater velocity until a steady state condition is reached where the components move at the same velocity as the oven producing the gradient. Each component is then eluted at a characteristic temperature of the gradient which is defined by the conditions of the operation. In addition, the gradient will tend to compress the chromatographic bands by retarding the leading edges while accelerating the trailing edges. This process, known as chromathermography, while showing considerable promise as a means of obtaining rapid separations, was not widely accepted because of the obvious technical difficulties involved in construction and control of the apparatus. Linear temperature programming, requiring relatively minor modifications of conventional column oven temperature control, became the method of choice for rapid analysis of mixtures having a wide range of volatility.

More recently Vergnaud and co-workers³⁻⁶ described applications of longi-

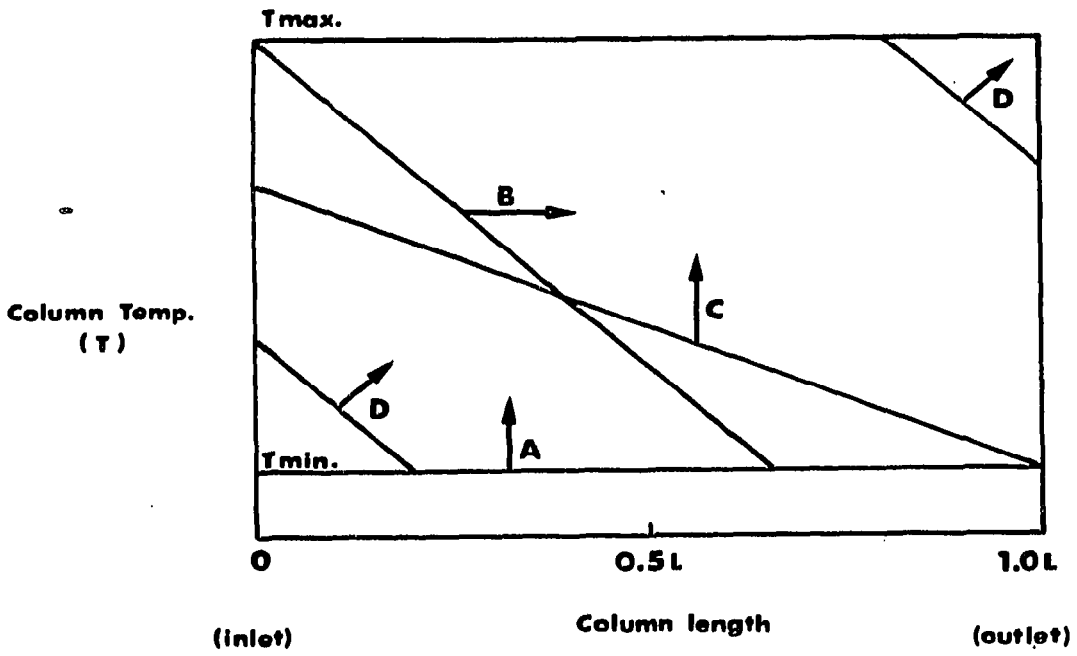


Fig. 1. Diagram of temperature programming operations: A = linear temperature programming; B = chromathermography; C = temperature programmed gradient; D = generalized gradient temperature programming.

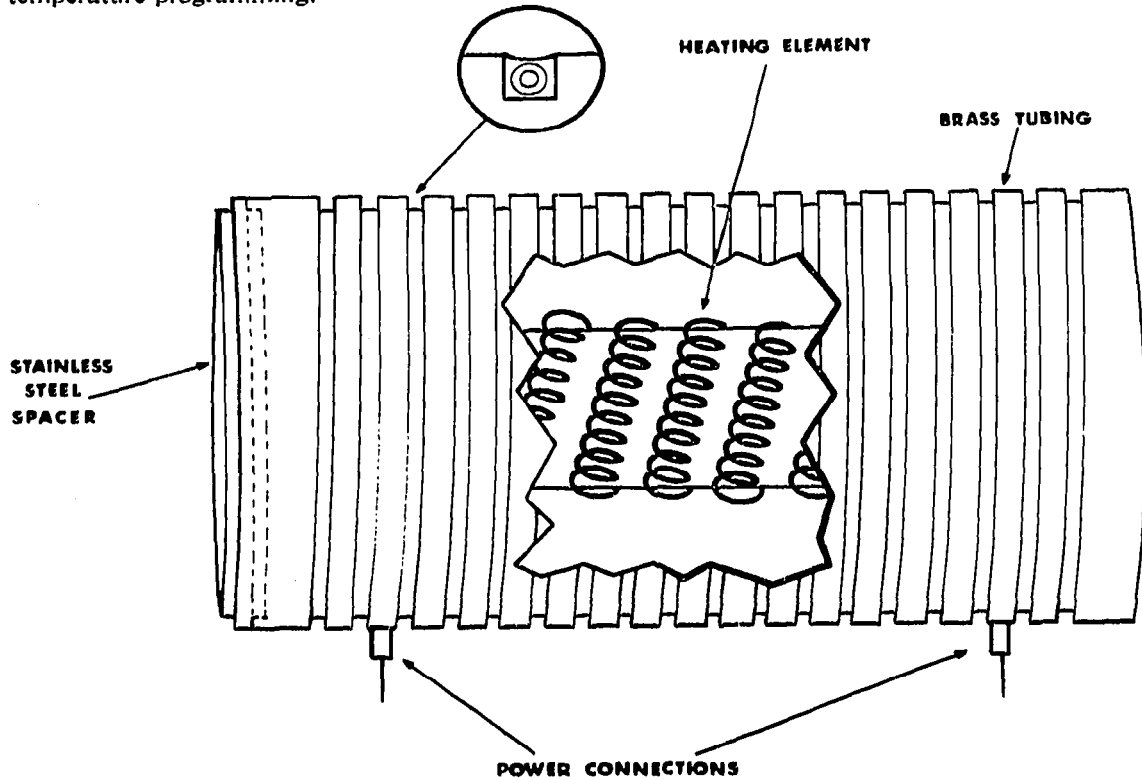


Fig. 2. Section of column heating system. Inset shows capillary column imbedded in silicone gum.

tudinal thermal gradients which differ from the moving oven gradient of chromatography. In their studies electrically insulated resistance heating wire was coiled around a stainless-steel packed column with the number of coils per unit length varied in such a way as to produce a linear thermal gradient. A number of options were then available with respect to the mode by which the gradient could be applied to chromatographic separations: the column could be operated with a constant, stationary gradient or with the slope of the gradient varying with time; the constant gradient could be combined with temperature programming; or temperature programming could be combined with a programmed gradient. The authors derived relationships by which the retention times of selected compounds were calculated from the known operating parameters and demonstrated that the combination of temperature programming and a longitudinal thermal gradient yielded shorter retention times than did temperature programming alone. Moreover, it was shown that as the gradient was made more steep, the decrease in retention times of higher boiling compounds was greater than that of the more volatile components, again suggesting decreased analysis time for mixtures having a wide volatility range.

All of the above studies were performed using conventional packed gas chromatographic columns. In view of the high column efficiencies and rapid analysis time attainable with short capillary columns^{7,8} and the higher rate of transfer of thermal energy to capillary columns than can usually be achieved with packed columns, the combination of programmed thermal gradients with capillary columns offered intriguing possibilities for extremely fast gas chromatographic analysis.

The methods of heating the column and achieving the desired thermal gradient in this present study differ considerably from those mentioned above, as might be expected inasmuch as there are considerable differences in column length. Various techniques were considered including resistance heating of the metal column itself, liquid heating baths, air ovens, etc., but each of these was thought too difficult to control accurately or would not furnish thermal transfer to the column with sufficient speed. Consequently the heating system selected for this study consisted of individual heating sections in intimate contact with thin-walled capillary tubing. Although linear gradients were sacrificed for more easily controlled step gradients, the flexibility of such a system permitted ready selection of various operating modes. Each of the previously described gradient processes could be approximated with this heating system.

That all of these gradient processes are quite similar is illustrated in Fig. 1. Conventional linear temperature is shown as process A. Chromathermography employs an established thermal gradient moving along the length of the column as in B, and the combination of a constant gradient and temperature programming is shown as process C. If, however, the gradient chosen for the chromathermographic operation were to extend along the entire length of the column (and beyond) and if the upper and lower temperatures of the gradient were constrained by the limits shown as $T_{max.}$ and $T_{min.}$, movement of the gradient would be equivalent to the operation labelled D. Similarly, operation C can also be shown to be equivalent to D if the gradient is confined to the temperature limits. Thus, each operation is merely a special case of a gradient moving across an area defined by the column length and the temperature limits, and consequently could be included conveniently under the general description of gradient temperature programming (GTP) as differentiated from linear temperature programming (LTP).

EXPERIMENTAL

Column heaters: Sectional heaters were constructed from brass tubing of 4.45 cm O.D. and 0.32 cm wall thickness. Each section was 7.62 cm in length and a spiral groove was machined into the outer surface of the tube which would accept approximately 2.25 m of capillary tubing. Heat was supplied by a 475-W coiled nichrome element mounted on ceramic tubing coaxial to the brass tubing (Fig. 2). Five such heater sections were joined end to end and separated by stainless-steel spacers which provided some degree of thermal isolation.

Heating of the individual sections was regulated with proportional controllers (RFL Model 70-115, RFL Industries, Boonton, N.J., U.S.A.) utilizing temperature sensors fabricated from glass-bead-type thermistors (Fenwal Electronics, Framingham, Mass., U.S.A.). The temperature sensors were located in wells in the wall of the brass tubing and secured by short lengths of small-diameter brass tubing brazed to the surface of the column heaters. The temperature of each section was indicated by thermocouples in wells similar to those of the thermistor sensors.

Because of the inherent non-linearity of the thermistors used with this apparatus, column heater temperatures were pre-set by means of an array of variable resistors located on a separate control panel. Each heater could then be maintained at any of six temperatures determined by the value of a resistor selected by a rotary switch and a small 10×10 patchboard. Manipulating the circuits on the patchboard allowed either linear or gradient temperature programs. The temperatures selected for this study ranged from 80–180° in 20°-steps.

The column was 11 m. \times 0.50 mm I.D. \times 0.80 mm O.D. nickel-200 tubing (Handy & Harmon, Norristown, Pa., U.S.A.) prepared in the manner reported by Bertsch *et al.*⁹ and coated with Emolphor ON-870 (Supelco, Bellefonte, Pa., U.S.A.).

Sample introduction was made by means of a splitting injector (Hamilton, Reno, Nev., U.S.A.). A flame ionization detector (FID) (Antek, Houston, Texas, U.S.A.) provided the chromatographic signal. A diagram of the apparatus is shown in Fig. 3. In order to maximize thermal conductivity, the column was imbedded in silicone gum in the grooves of the heaters, as shown in the inset in Fig. 2, and silicone was similarly employed in the thermistor and thermocouple wells.

In addition to the usual carrier gas pressure regulator a low-pressure regulator was placed in the carrier gas line to permit accurate control of the very low inlet pressures necessitated by the short length of the capillary column. Nitrogen was employed as the carrier gas throughout the study.

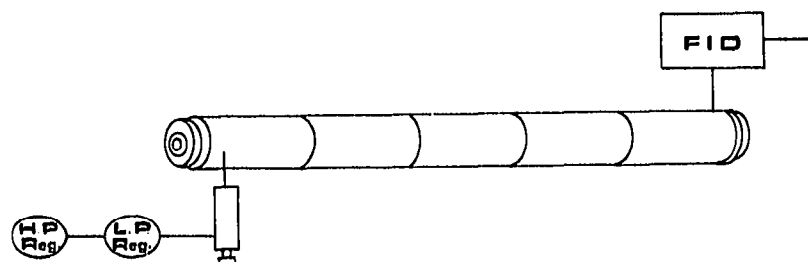


Fig. 3. Gradient temperature programmed chromatograph for short capillary columns. H. P. Reg. = High-pressure regulator; L. P. Reg. = low-pressure regulator.

RESULTS AND DISCUSSION

Testing of a column heater section with thermocouples to determine temperature at various points on the heater body indicated that heating rates of greater than $1^\circ/\text{sec}$ were possible and that the temperatures were relatively constant over the surface

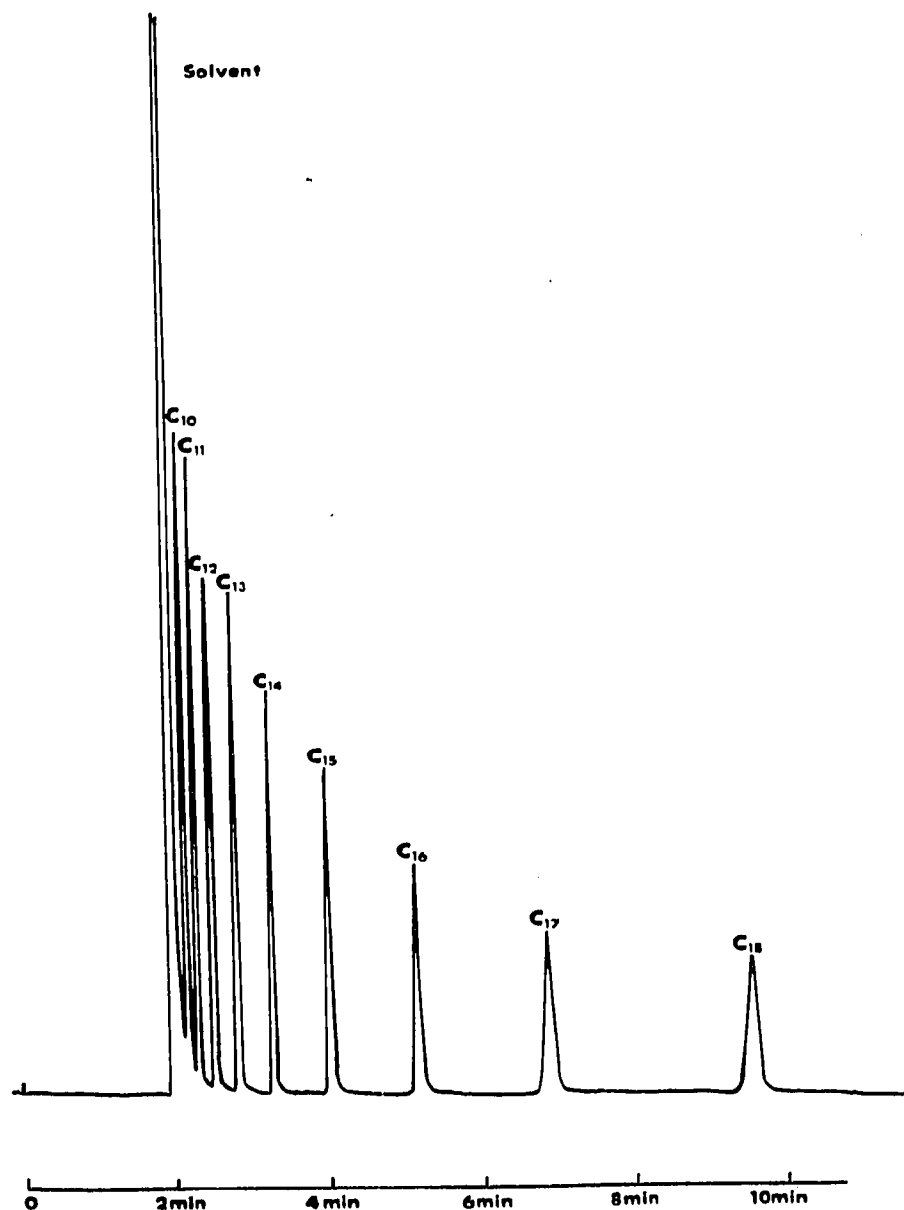


Fig. 4. Isothermal chromatogram of C₁₀-C₁₈ *n*-alkanes on 11-m capillary described in text. Column conditions: temperature, 160° ; flow-rate, 2.1 ml/min.

of the heater. When the heaters were joined together using the stainless-steel spacers, the step-like character of the gradient was modified by the thermal conductivity of the spacers but was still not sufficient to attain an ideal linear longitudinal gradient. This departure from the ideal together with the use of step programming rather than linear programming did not appear to detract substantially from the demonstrated performance of this GTP system.

By selecting the appropriate programming sequence it was possible to condition the capillary column by means of a temperature programmed positive thermal gradient, *i.e.* one in which the outlet temperature is maintained higher than the inlet temperature. Whether or not this treatment was superior to the usual linear temperature programmed conditioning can only be a matter of conjecture at this point, but the column was found to have an efficiency of *ca.* 15,000 theoretical plates for *n*-tetradecane at a temperature of 100° and a carrier gas flow-rate of 2.1 ml/min. This value would then correspond to less than 0.8 mm height equivalent to a theoretical plate (HETP), a respectable value for 0.5 mm I.D. tubing, but still greater than the HETP

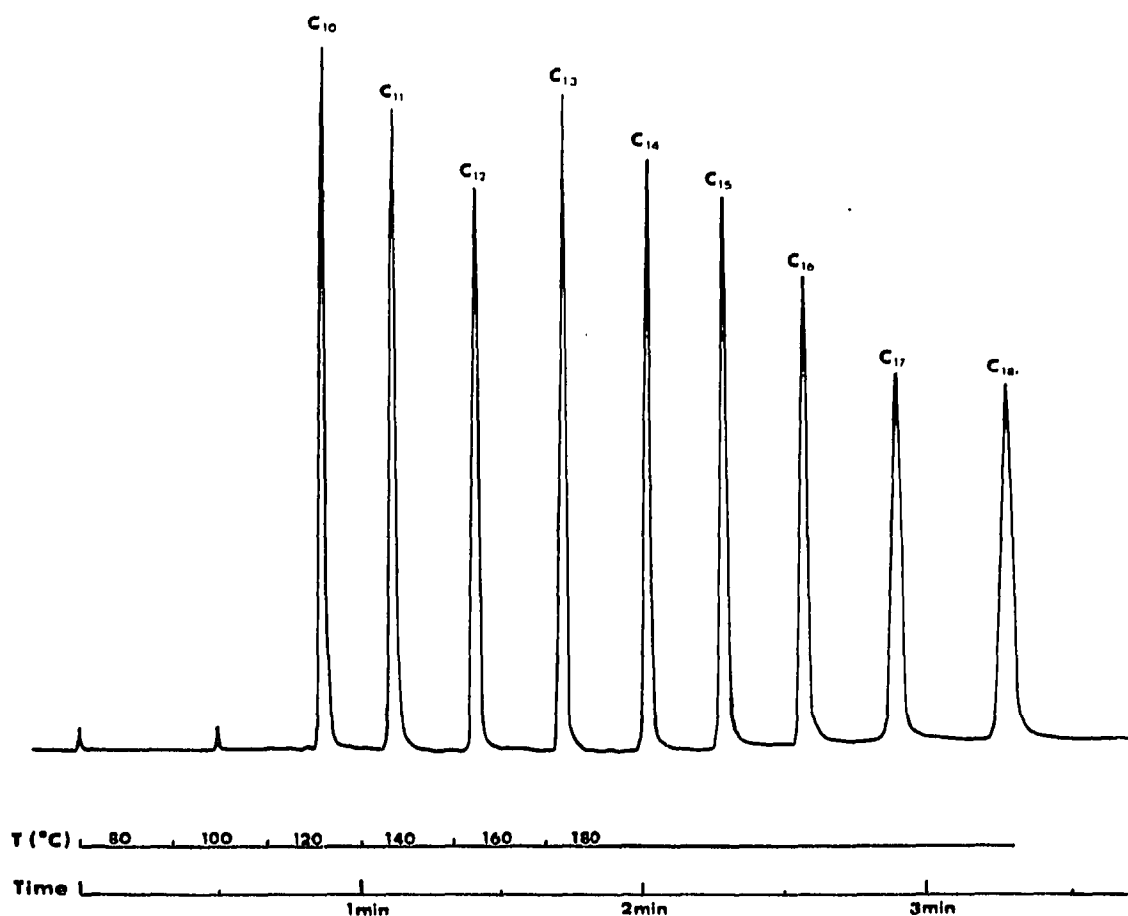


Fig. 5. Linear temperature programmed chromatogram of *n*-alkanes on the same column as in Fig. 4. Carrier gas flow-rate, 10 ml/min.

values reported by Grob and Grob¹⁰ for short capillary columns of somewhat smaller I.D. A chromatogram of the test mixture obtained under isothermal conditions is shown in Fig. 4.

Inasmuch as the object of this study was to attempt rapid separations and to ascertain whether GTP offered any advantage over LTP, a comparison was made using a mixture of *n*-alkanes from decane to octadecane. Conditions were chosen so that the peaks would be eluted in a fairly linear fashion with a maximum rate of temperature rise and with a carrier gas flow-rate greater than optimum but selected for rapid elution of the test mixture. The results of this comparison are illustrated by the chromatograms in Figs. 5 and 6. Both chromatograms show excellent separation of the individual peaks, but the retention time of *n*-octadecane in the LTP chromato-

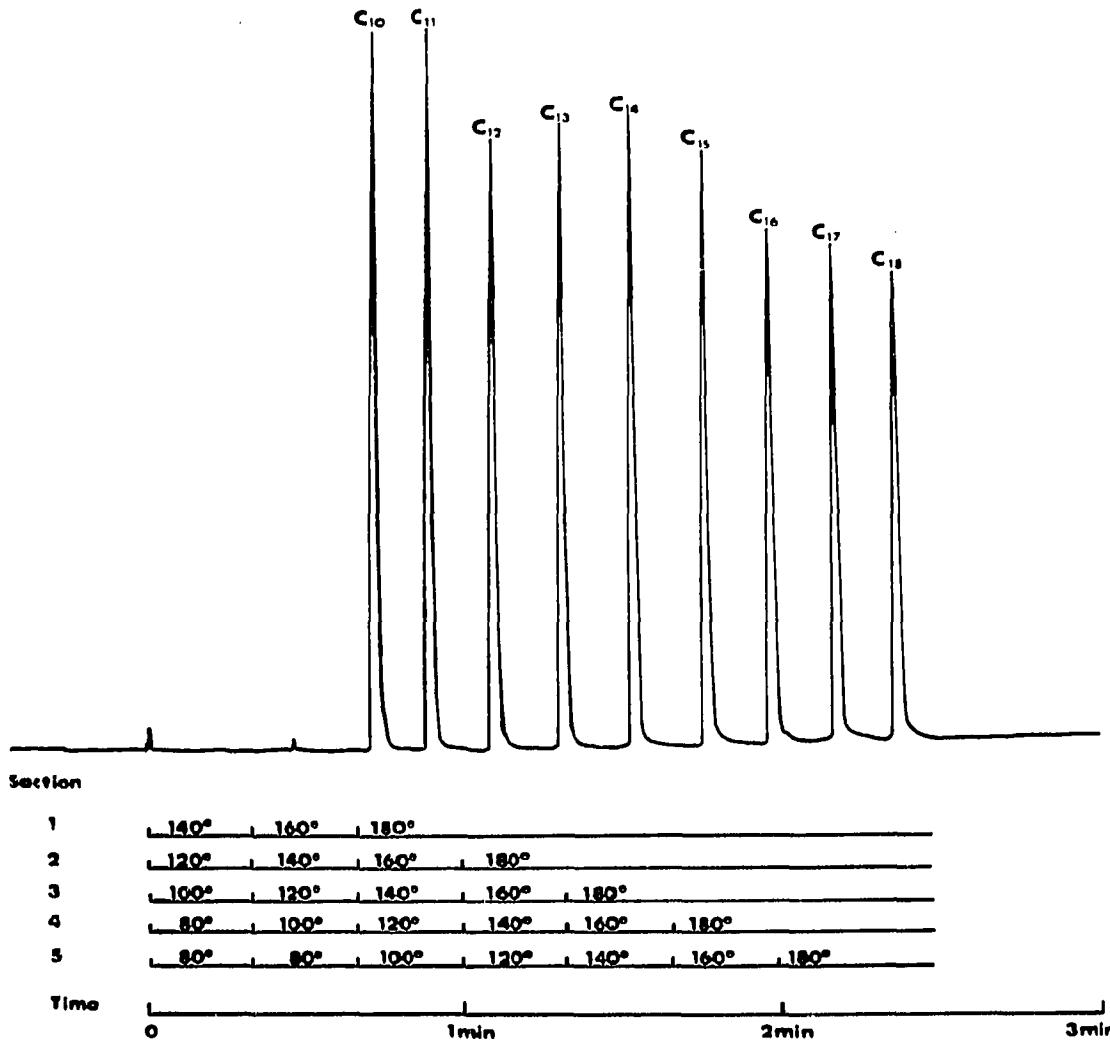


Fig. 6. Gradient temperature programmed chromatogram of *n*-alkanes as indicated. Heater section 1 is closest to column inlet.

gram is 3.3 min while the same component emerges at 2.4 min in the GTP chromatogram. The resolution achieved with the two programs was comparable: the average resolution of LTP was 6.8 and that of GTP was 6.5, where resolution is defined as the ratio of distances between peak maxima to the average peak base width. When the individual peaks are compared with respect to resolution per unit time as shown in Table I, the GTP operation exhibits substantial improvement over LTP.

TABLE I
COMPARISON OF LINEAR AND GRADIENT TEMPERATURE PROGRAMMING
Conditions as shown in Figs. 5 and 6.

Carbon number of <i>n</i> -alkane	Retention time (min)		Resolution*		<i>R</i> /min	
	LTP	GTP	LTP	GTP	LTP	GTP
10	0.84	0.72				
11	1.08	0.90	7.1	6.7	6.5	7.5
12	1.39	1.10	7.6	7.4	5.5	6.7
13	1.69	1.32	7.8	7.7	4.6	5.8
14	1.99	1.55	7.2	7.7	3.6	5.0
15	2.27	1.77	6.3	6.8	2.8	3.9
16	2.55	1.98	6.1	5.7	2.4	2.9
17	2.86	2.18	6.2	5.4	2.1	2.4
18	3.26	2.38	6.3	4.8	1.9	2.0

* Resolution (*R*) defined as ratio of distance between peak maxima to average peak base width.

As stated previously, the primary purpose of investigating this particular mode of operation of a gas chromatograph was to improve the speed of analysis without sacrificing unduly the ability to separate the components of a mixture. This emphasis on rapid analysis was therefore a major influence on the choice of the short capillary column as the model for which this particular apparatus was designed. The application of GTP to longer capillary columns, however, should not be overlooked. Guermouche *et al.*⁵ examined the retention times of a series of *n*-alkanes as a function of column length when the magnitude of the thermal gradient, the rate of programming, and the inlet temperature are held constant. As the column length increases, the retention times of the higher alkanes also increase but much less quickly than the retention times of the lower homologs. Thus there is reason to believe that GTP of longer columns would provide greater resolution, as theory and experience would predict, but with less increase of total analysis time than might be expected.

Perhaps one of the most important considerations in the use of gradient temperature programming is the addition of yet another parameter to those currently employed in chromatographic separations. Future studies of this process will therefore be directed not only toward rapid analysis but will also explore separations which may yield to the variety of operating conditions provided by this technique.

REFERENCES

- 1 A. A. Zhukhovitskii, O. V. Zolotareva, V. A. Sokolov and N. M. Turkel'taub, *Dokl. Akad. Nauk SSSR*, 77 (1951) 453.

- 2 R. W. Ohline and D. D. DeFord, *Anal. Chem.*, 35 (1963) 227.
- 3 M. Fatscher and J.-M. Vergnaud, *J. Chromatogr.*, 47 (1970) 297.
- 4 M. Coudert and J.-M. Vergnaud, *J. Chromatogr.*, 54 (1971) 1.
- 5 M. H. Guermouche, M. Fatscher and J.-M. Vergnaud, *J. Chromatogr.*, 52 (1970) 9.
- 6 M. Coudert, J. Larrat and J.-M. Vergnaud, *J. Chromatogr.*, 58 (1971) 159.
- 7 L. S. Ettre, *Open Tubular Columns*, Plenum Press, New York, 1965, p. 127.
- 8 T. H. Gouw, I. M. Whittemore and R. E. Jentoft, *Anal. Chem.*, 42 (1970) 1394.
- 9 W. Bertsch, F. Shunbo, R. C. Chang and A. Zlatkis, *Chromatographia*, 7 (1974) 128.
- 10 K. Grob and G. Grob, *J. Chromatogr. Sci.*, 7 (1969) 515.