Anal. Chem. **2000,** *72,* 591−598

Peak Capacity, Peak-Capacity Production Rate, and Boiling Point Resolution for Temperature-Programmed GC with Very High Programming Rates

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Recent advances in column heating technology have made possible very fast linear temperature programming for high-speed gas chromatography. A fused-silica capillary column is contained in a tubular metal jacket, which is resistively heated by a precision power supply. With very rapid column heating, the rate of peak-capacity production is significantly enhanced, but the total peak capacity and the boiling-point resolution (minimum boiling-point difference required for the separation of two nonpolar compounds on a nonpolar column) are reduced relative to more conventional heating rates used with convection-oven instruments. As temperature-programming rates increase, elution temperatures also increase with the result that retention may become insignificant prior to elution. This results in inefficient utilization of the downstream end of the column and causes a loss in the rate of peak-capacity production. The rate of peak-capacity production is increased by the use of shorter columns and higher carrier gas velocities. With high programming rates (100−600 °C/min), column lengths of 6−12 m and average linear carrier gas velocities in the 100−150 cm/s range are satisfactory. In this study, the rate of peak-capacity production, the total peak capacity, and the boiling point resolution are determined for C_{10}−C_{28} *n*-alkanes using 6−18 m long columns, 50−200 cm/s average carrier gas velocities, and 60−600 °C/min programming rates. It was found that with a 6-meter-long, 0.25-mm i.d. column programmed at a rate of 600 °C/min, a maximum peak-capacity production rate of 6.1 peaks/s was obtained. A total peak capacity of about 75 peaks was produced in a 37-s long separation spanning a boiling-point range from *n*-C_{10} (174 °C) to *n*-C_{28} (432 °C).

Temperature programming is essential for efficient GC analysis of mixtures containing a wide range of boiling points. Programming rates usually are empirically determined, and programs typically consist of one or more linear temperature ramps with isothermal intervals at the beginning and at the end of the separation.[1,2] Programming rates of a few degrees Celsius per minute are common, and methods using rates in excess of 20 °C/min are occasionally reported.[3,4] Laboratory GC instruments with conventional convection ovens typically have available maximum linear programming rates of about 50 °C/min. With some instruments, higher rates can be achieved at lower temperatures, but significant ramp curvature usually occurs at higher oven temperatures.[5,6]

Recent advances in high-speed GC[7,8] have led to significant reductions in separation times for isothermal GC. To obtain comparable reductions in separation time for mixtures containing a wide range of boiling points, higher programming rates are needed than can be obtained with convection ovens. Higher programming rates would be very useful for high-speed separations in a time frame of 10−150 s. In addition, for high-speed separations, the lengthy cool-down time of convection ovens will be the limiting factor determining sample throughput.

Until recently, oven design for laboratory GC instruments had not kept pace with advancements in other areas of GC instrumentation. A novel oven concept involving the resistive heating of a metal-clad fused silica column was described by Jain and Phillips[9] and by Hail and Yost.[10] Nonuniformaties in the cladding resulted in hot spots, which eventually led to destruction of the cladding. Practical methods for the high-speed heating of fused silica capillary columns were described by Rounbehler and Bedford.[11] These methods use resistance heating of a precision metal tube surrounding the column and have resulted in robust instruments for both field-portable[5] and laboratory[12] applications. Temperature control is achieved by sensing the electrical resistance of the metal column jacket or of a sensor wire contained

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(1) Harris, W. E.; Habgood, H. W. *Programmed Temperature Gas Chromatography*; Wiley: New York, 1966.
(2) Snow, N. H.; McNair, H. M. *J. Chromatogr. Sci.* **1992**, *30*, 271.
(3) Martos, P.; Pawliszyn, J. *Anal. Chem.* **1999**, *71*, 1513.
(4) Barshick, C.; Barshick, S.; Walsh, E.; Vance, M.; Britt, P. *Anal. Chem.* **1999**, *71*, 483.
(5) Ehrmann, E. U.; Dharmasema, H. P.; Carney, K.; Overton, E. B. *J. Chromatogr. Sci.* **1996**, *34*, 533.
(6) Leonard, C.; Grall, A.; Sacks, R. *Anal. Chem.* **1999**, *71*, 2123.
(7) Sacks, R.; Smith, H.; Nowak, M. *Anal. Chem.* **1998**, *70*, 29A.
(8) Smith, H.; Sacks, R. *Anal. Chem.***1998**, *70*, 4960.
(9) Jain, V.; Phillips, J. *J. Chromatogr. Sci.* **1995**, *33*, 55.
(10) Hail, M.; Yost, R. A. *Anal. Chem.* **1989**, *61*, 2410.
(11) Rounbehler, D.; Bedford, E. High-Speed Detection of Vapors of Specific Compounds. U.S. Patent 5,092,155, 1992.
(12) MacDonald, S. J.; Wheeler, D. *Int. Lab.* **1998**, *28*, 6.

10.1021/ac9911802 CCC: $19.00
Published on Web 12/23/1999

within the metal jacket. Typically, this measurement is made at a frequency of about 100 Hz and an electronic switch is used to connect the column jacket to a dc power supply as needed following every measurement cycle. This closed-loop control can obtain very linear temperature ramps even at very high programming rates.

Temperature programming rates at least as high as 1000 °C/min are now commercially available. The upper temperature limit is about 350 °C or less for the most popular GC stationary phases. Thus, in extreme cases, it is possible that the temperature program will be completed before any of the mixture components have eluted from the column. That is, the temperature program can outrun the separation. Principal issues involved with high-speed, temperature-programmed GC include separation time, boiling-point range spanned by the chromatogram, and peak capacity. For isothermal GC, the height equivalent to a theoretical plate and the number of plates obtained during a separation are often used for evaluation of column efficiency and resolving power, respectively.[13] For temperature-programmed GC, the Trennzahl number (TZ), which is defined as the number of peaks that will fit between a consecutive pair of *n*-alkanes with a resolution of about 1.18, is frequently used for column performance evaluation.[14,15] Values of TZ give the local peak capacity at the specified resolution and in the specified region of the chromatogram.

The use of TZ was introduced in 1959[16] and was endorsed by Kaiser.[17] Grob and Grob[18] describe TZ as the only measure of separation efficiency that is compatible with temperature-programmed GC. Ettre[19] has studied TZ in detail, and he considers it an important advantage that TZ values can be used directly to express column efficiency under temperature-programmed conditions. The use of TZ is also convenient since it is measured as the ratio of the separation time interval for the two adjacent reference *n*-alkanes to the sum of their peak widths (full width at half-height).

Several other useful column performance characteristics can be obtained from TZ measurements. By summing TZ + 1 values for several adjacent pairs of normal alkanes, the total peak capacity can be computed for any portion of the chromatogram. If a TZ + 1 value is divided by the retention time interval for the corresponding *n*-alkanes, the rate at which peak capacity is produced (peaks/s) can be found for the corresponding region of the chromatogram. This describes column performance with respect to the utilization of time.[6] If the difference in boiling points ΔT_b for the corresponding *n*-alkanes is divided by TZ + 1, then the minimum boiling point difference between two compounds required for a separation with a resolution of 1.18 is obtained, assuming that differences in boiling point are entirely responsible for differences in retention. This is nearly the case for nonpolar solutes (alkanes) on a nonpolar column. The reciprocal of this value, $(TZ + 1)/\Delta T_b$, gives the boiling-point resolution, which may be useful in simulated distillation applications. The variation of TZ with average carbon number for a series of reference *n*-alkanes also is of considerable interest.[6,20]

Values of TZ as well as total peak capacity decrease with increasing temperature-programming rate.[6,20] This loss of peak capacity becomes more significant as component elution temperatures approach the component boiling points. This is explained by the decrease in column efficiency as component retention factors approach zero. With very fast temperature programming, the column hold-up time may be greater than the entire program duration. Here, the effects of programming rate, column length, and carrier gas flow rate are complex. In a recent study,[6] programming rates as high as 50 °C/min were used with columns as long as 25 m with only modest losses in peak capacity and boiling-point resolution relative to a programming rate of 20 °C/min. With a 24-m-long, 0.25-mm i.d. column and a 0.25-μm stationary-phase film thickness, a total peak capacity of about 300 peaks was obtained in a 300-s separation covering the boiling-point range from *n*-C_6 (68 °C) to *n*-C_{19} (330 °C).

For programming rates greater than about 50 °C/min, a significant decline in total peak capacity and boiling-point resolution with increasing programming rate is anticipated. In this study, linear temperature programming is explored in the range 60−600 °C/min. Detailed studies in this range have not been reported. The column length, average linear carrier gas velocity, and temperature-programming rate are considered as independent variables. The dependent variables considered are the separation time, boiling-point resolution, the rate of peak capacity production, and the total peak capacity produced in the boiling point range *n*-C_{10} (174 °C) to *n*-C_{28} (432 °C).

EXPERIMENTAL SECTION

Instrumentation. All chromatograms were obtained with a Thermedics model FLASH GC (Thermedics Detection, Inc., Chelmsford, MA). The instrument has two independently programmed column ovens and a utility oven. Each column is contained in a metal sheath, which is resistively heated. Column heating rates of over 1000 °C/min can be obtained. The utility oven is convection heated and is used to provide a heated zone for component connections.

Column heating is achieved by direct resistive heating of the metal sheath tube. A 96 V computer-controlled power supply is used. Every 13 ms, the heating current is interrupted, and the tube resistance is measured. An electronic switch is used to connect the sheath tube to the power supply for a 10-ms interval as needed to maintain the linear program.

Materials and Procedures. Both a 6-m-long and a 12-m-long nonpolar DB-1 column were used (Thermedics Detection, Inc, Chelmsford, MA). The columns were 0.25-mm i.d. and used 0.25-μm stationary-phase film thickness. For studies using an 18-m column length, the two columns were connected together in the utility oven. Connection was made with an all-glass union, and both column ovens were heated with the same temperature program.

Hydrogen carrier gas was purified with filters for water vapor, oxygen, and hydrocarbons. A split inlet was used with a split ratio

(13) Lipsky, S.; McMurray, W.; Hernandes, M.; Pursell, J.; Billeb, H. *J. Chromatogr. Sci.* **1980**, *18*, 1.
(14) Rooney, T. A.; Hartigan, M. J. *HRC & CC* **1980**, *3*, 416.
(15) Jennings, W.; Yabumoto, K. *HRC & CC* **1980**, *3*, 177.
(16) Turkeltaub, N.; Zuchowitsky, A. *Forthshriftsberichte Gas Chromatography 1959*; Aked-Verlag: Berlin, 1961.
(17) Kaiser, R. E. *Chromatographie in der Gasphase*, 2nd ed.; Bibliografisches Institut: Mannheim, 1966; Vol. 2.
(18) Grob, K., Jr.; Grob, K. *J. Chromatogr.* **1981**, *207*, 291.
(19) Ettre, L. A. *Chromatographia* **1975**, *80*, 291.
(20) Jones, L. A.; Kirby, S. L.; Garganta, C. L.; Gerig, T. M.; Mulik, J. D. *Anal. Chem.* **1983**, *55*, 1354.

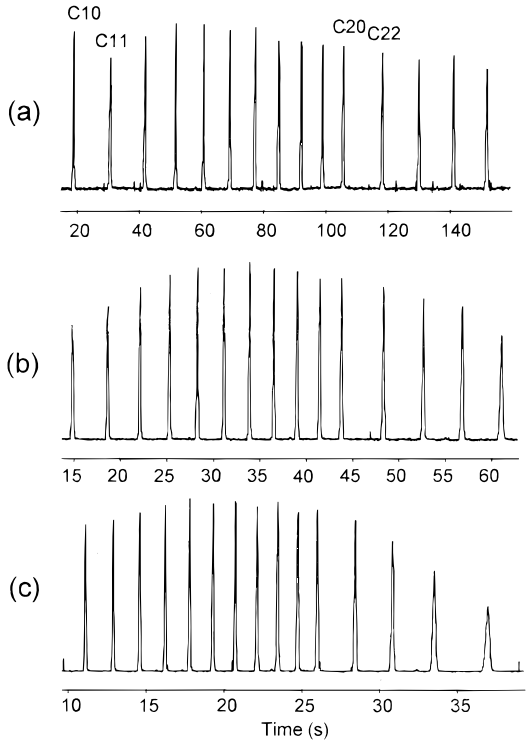

Figure 1. High-speed chromatograms of a C_{10}−C_{28} mixture of *n*-alkanes using a 6-m-long, 0.25-mm i.d. column with temperature programming rates of 100 (a), 300 (b), and 600 (c) °C/min.

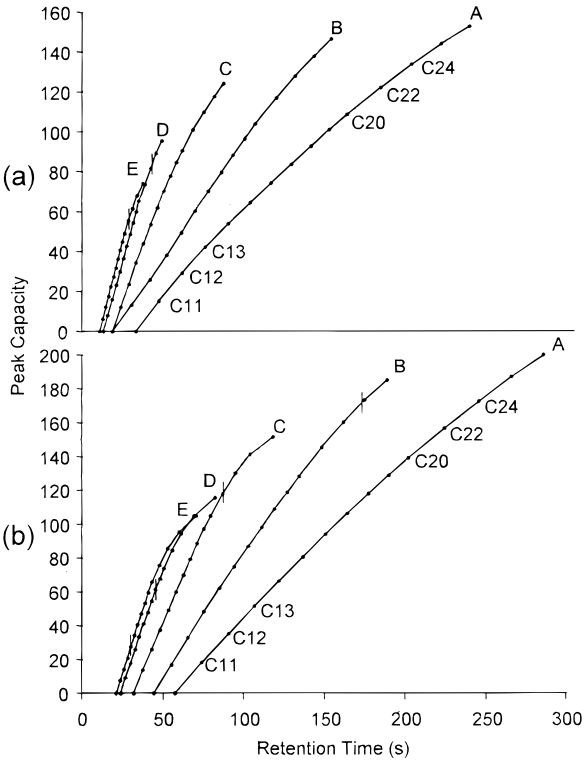

Figure 2. Cumulative peak capacity vs retention time plots for a 6-m-long, 0.25-mm i.d. column (a) and an 18-m-long, 0.25-mm i.d. column (b) using temperature programming rates of 60 (A), 100 (B), 200 (C), 400 (D), and 600 (E) °C/min. Vertical tick marks on the plots indicate the end of the temperature program.

of 20:1. The injector and flame ionization detector were both operated at a temperature of 250 °C. All measurements were made using a 100 Hz sampling rate. Chromatograms were recorded with the use of a Pentium-90 PC and a serial data port on the Flash GC instrument. Software provided with the GC instrument was used for data acquisition and instrument control. Data reduction and analysis were performed with Grams/32 Software (Galactic Industries, Inc.).

A test mixture was prepared which contained 420 ppm of each *n*-alkane in the range C_{10}−C_{20} plus C_{22}, C_{24}, C_{26}, and C_{28} using *n*-hexane as solvent. This mixture spans a boiling-point range from 174 to 432 °C. Injection size typically was 1.0 μL. The initial column temperature was 50 °C. The linear temperature ramp always began simultaneously with injection. When the column temperature reached 340 °C, it was held at this value until the last component eluted from the column.

RESULTS AND DISCUSSION

The closed-loop heating control used in the instrument should obtain very good temperature-ramp linearity. Significant radial temperature gradients in the column are not likely since the column radius is small and the thermal conductivity of H_2 is relatively large. The wall of the fused silica columns used in this study is quite thin, thus providing relatively good thermal accommodation between the heated jacket and the column interior.[9]

Figure 1 shows chromatograms of the C_{10}−C_{28} *n*-alkane mixture using a 6-meter-long column at programming rates of 100 (a), 300 (b), and 600 (c) °C/min. For all chromatograms, the average linear carrier gas velocity was about 150 cm/s giving a column hold-up time of only about 4 s. Note that for a constant inlet pressure, the hold-up time increases slightly during the temperature program because of the increase in carrier-gas viscosity with increasing temperature. The greater peak spacing for the C_{20}−C_{28} range is largely because only even carbon numbers were present in the mixture.

For the 100 °C/min case, peak widths range from 0.40 s (full width at half height) for C_{10} to 0.64 s for C_{28}. The chromatogram is complete in about 140 s. For the 300 °C/min case, the peak width for C_{10} has decreased to 0.17 s and the separation time is about 62 s. When the programming rate is increased to 600 °C/min, the separation is complete in only 37 s. The C_{10} peak width is further reduced to only 0.084 s, but considerable relative broadening (0.29-s peak width for C_{28}) and some increase in relative peak separation is observed for the last few components.

Cumulative Peak Capacity. Figure 2 shows plots of cumulative peak capacity vs retention time for a 6-meter-long column (a) and an 18-meter-long column (b). Average carrier-gas velocity was about 150 cm/s. Each point on these plots gives the retention time of the corresponding *n*-alkane and the total peak capacity produced up to that point in the chromatogram. Peak capacity was determined for a resolution of 1.18 by computing the TZ values for all adjacent pairs of the *n*-alkane peaks.[14,15] Cumulative peak capacity is computed as the sum of (TZ + 1) values from the C_{10}−C_{11} interval up to the corresponding point on the plots. The plots labeled A−E are for linear programming rates of 60, 100, 200, 400, and 600 °C/min, respectively. In all cases, the initial column temperature was 50 °C and the program began at the time

of injection. At a final ramp temperature of 340 °C, the column was operated isothermally until the last component (n-C_{28}) eluted.

For the 60 °C/min case, the 6-meter-long column generates a peak capacity (C_{10}−C_{28}) of 152 peaks in about 236 s. When the programming rate is increased to 100 °C/min, the peak capacity is reduced only to 147 peaks, but the n-C_{28} retention time (total separation time) is reduced to less than 152 s. There is a steady decrease in cumulative peak capacity with increasing programming rate. However, the corresponding decrease in separation time is larger with the result that the separation becomes more efficient with respect to the utilization of time at the higher programming rates. For the 600 °C/min case, the cumulative peak capacity is 74 peaks and the separation time is only 37 s. This gives an average rate of peak-capacity production of 2.0 peaks/s.

The vertical tick marks on plots D and E of Figure 2a correspond to the end of the linear ramp and the beginning of the isothermal interval at 340 °C. For plots A−C, the chromatogram was complete prior to the end of the programming ramp. At the very high programming rates used in this study, the temperature program can outrun the separation with the result that the last mixture components elute under isothermal conditions. This degrades the rate of peak-capacity production and explains the increases in peak width and peak spacing observed for the last few peaks in Figure 1c.

In part b of Figure 2, the column length has been increased to 18 m giving a holdup time of about 12 s. All other conditions are the same as for part a. For the 60 °C/min case (plot A), an increase in column length from 6 to 18 m results in an increase in cumulative peak capacity (C_{10}−C_{28}) of 32% (152−200) and an increase in separation time of 21% (236−286 s). When the programming rate is increased to 600 °C/min, the 18-meter-long column generates a cumulative peak capacity of 105 peaks and a separation time of 71 s. The corresponding increases relative to the 6-meter column are 42% (74−105 peaks) and 92% (37−71 s). The larger relative increase in separation time with increasing column length at 600 °C/min relative to 60 °C/min shows that the average rate of peak-capacity production for the longer column is less that that of the shorter column at the very high programming rates.

Note the tick marks on plots B−E in Figure 2b. Again, these correspond to the points in the chromatograms where the linear temperature ramp is complete and isothermal operation at 340 °C begins. These marks occur much earlier in the corresponding chromatograms for the 18-m-long column. For the 600 °C/min case, the ramp ends just after the elution of C_{22} for the 6-m column and just after C_{14} for the 18-m column. Thus, for the 18-m column and a programming rate of 600 °C/min, most of the mixture components elute under isothermal conditions. This explains the relative increases in separation time and the increased degree of curvature in the plots of Figure 2b as the programming rate increases.

Column Length and Carrier-Gas Velocity Considerations. Figures 3 and 4 show cumulative peak capacity vs retention time for programming rates of 100 and 600 °C/min, respectively. For both figures, the upper set of plots (a) is for a 6-m column, the middle set (b) is for a 12-m column, and the lower set (c) is for an 18-m column. For each set, the plots labeled A−D are for average carrier gas velocities of 50, 100, 150, and 200 cm/s,

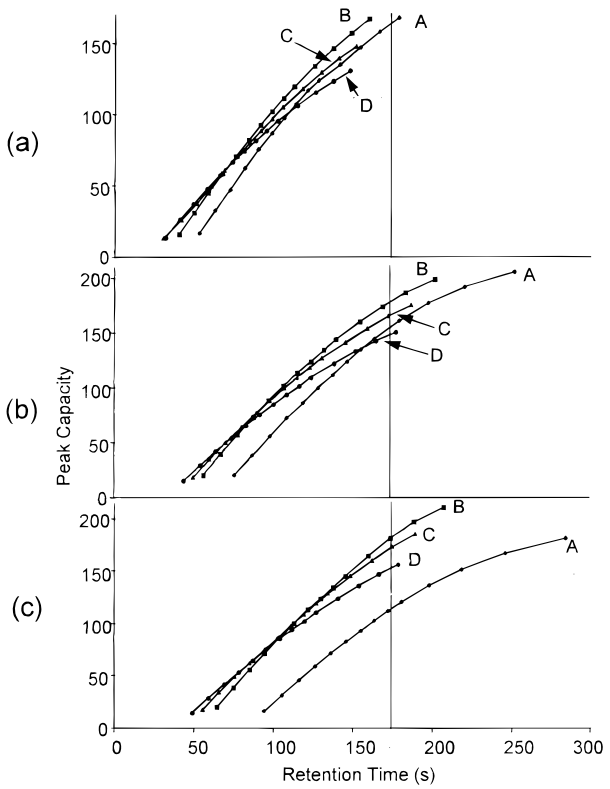

Figure 3. Cumulative peak capacity vs retention time plots for a 6-m-long column (a), a 12-m-long column (b) and an 18-m-long column (c) using a temperature programming rate of 100 °C/min. Plots A−D are for average carrier gas velocity values of 50, 100, 150, and 200 cm/s, respectively. Vertical lines indicate the end of the temperature program.

respectively. The vertical lines in the figures correspond to the end of the temperature ramp and the beginning of isothermal operation at 340 °C.

As expected, retention time for any specified component decreases steadily with increasing carrier-gas velocity, but in many cases, the decrease is remarkably small. For the 6-m column at a programming rate of 100 °C/min (Figure 3a), an increase in average gas velocity from 100 to 200 cm/s results in a decrease in retention time of C_{28} from about 160 to 145 s. The decrease in analysis time is less than 10%.

The use of 50-cm/s gas velocity is not justified for any of the conditions described in Figures 3 and 4. Only for the 6-m and the 12-m columns at a programming rate of 100 °C/min does the cumulative peak capacity (C_{10}−C_{28}) for the 50 cm/s gas velocity compare favorably with the other velocity values. As the column length increases and for the higher programming rate, the increased separation time and the reduced cumulative peak capacity for the 50 cm/s plots relative to the higher carrier-gas velocities become more significant.

The rate of peak-capacity production at any time in a chromatogram is equal to the slope of the corresponding plot in Figure 3 or 4. These slope values are given in Table 1 for the nearly linear regions of the plots corresponding to the early portions of the chromatograms. Values are found from linear regression analysis of the plots for the interval from n-C_{11} to n-C_{14}. For the 6-m column at a programming rate of 100 °C/min, the slope is greatest for the 50 cm/s case and only slightly smaller for the

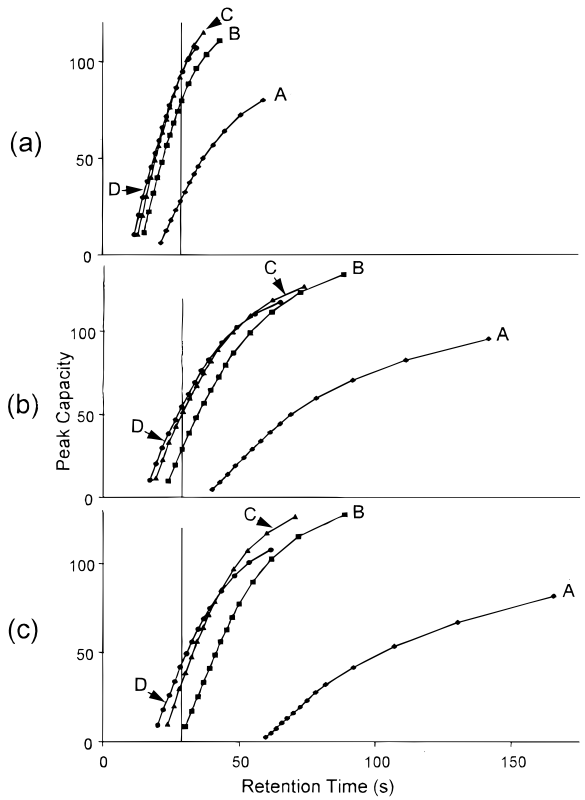

Figure 4. Cumulative peak capacity vs retention time plots for a 6-m-long column (a), a 12-m-long column (b) and an 18-m-long column (c) using a temperature programming rate of 600 °C/min. Plots A−D are for average carrier gas velocity values of 50, 100, 150, and 200 cm/s, respectively. Vertical lines indicate the end of the temperature program.

Table 1. Slopes of Cumulative Peak Capacity vs Retention Time Plots

	column length					
	6 m slopes		12 m slopes		18 m slopes	
u (cm/s)	at 100°/min	at 600°/min	at 100°/min	at 600°/min	at 100°/min	at 600°/min
50	1.59	3.10	1.58	1.69	1.33	1.30
100	1.57	5.67	1.69	3.78	1.70	3.82
150	1.21	6.10	1.52	4.27	1.50	4.48
200	1.32	5.74	1.32	4.07	1.33	3.85

100 cm/s case. For the longer columns at the 100 °C/min programming rate, an average-carrier-gas velocity of 100 cm/s results in the greatest rate of peak-capacity production. For the 600 °C/min programming rate, the slopes are largest for the 150 cm/s gas velocity for all three column lengths. The peak capacity production rate of over 6 peaks/s for the 6-m long column with a 600 °C/min programming rate and a gas velocity of 150 cm is noteworthy.

At low carrier-gas velocities, the temperature change of the column during an interval equal to the holdup time may be very large, particularly for the 600 °C/min programming rate. Table 2 lists the holdup times and the corresponding temperature changes for programming rates of 100 and 600 °C/min and using the three different column lengths and the four values of average-carrier-

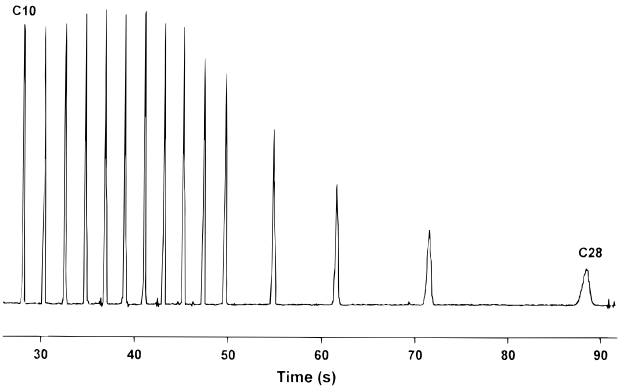

Figure 5. Chromatogram of a C_{10}−C_{28} mixture of *n*-alkanes using a 12-m-long, 0.25-mm i.d. column with a temperature programming rate of 600 °C/min. The temperature program is complete before the elution of C_{11}.

gas velocity. For the most extreme case (18-m column, 50 cm/s gas velocity), the holdup time is 36 s, and for the 600 °C/min programming rate, the column temperature changes by the full ramp interval of 290 °C in less than the holdup time. Under these conditions, all mixture components elute in the isothermal interval following completion of the temperature program. Even at a carrier-gas velocity of 100 cm/s, only the first component (C_{10}) elutes from the 18-m column before completion of the temperature ramp when the 600 °C/min programming rate is used. This is clear from Plot A in Figure 4c where the vertical line indicating completion of the temperature ramp occurs before elution of C_{11}. The chromatogram for this case is shown in Figure 5. The nearly equal spacing and the relatively constant peak widths of components C_{10}−C_{20} appear, typical of a temperature-programmed chromatogram, but all components that elute after C_{10} have the same elution temperature of 340 °C. From the data in Table 2 and the plots in Figures 3 and 4, it appears that the column temperature change during an interval equal to the holdup time should not exceed about 20−25 °C in order to have most components elute during the temperature ramp.

When the temperature change of the column is large in a time interval equal to the holdup time, retention factors may fall to very low values before elution of the corresponding components. When this occurs, the downstream portion of the column contributes little additional separation but continues to cause band broadening, due to the parabolic carrier-gas flow profile as well as axial diffusion. Thus, component separation occurs primarily before completion of the ramp, and the resulting pattern of component bands continues to migrate through the rest of the column with all such components having migration velocities only slightly lower than the carrier-gas velocity. This represents inefficient use of the column, and the cumulative peak capacity as well as the rate of peak-capacity production is reduced. For components C_{20}−C_{28}, significant retention occurs even at the 340 °C final temperature, and thus peak separation and peak width increase during this portion of the chromatogram.

The decrease in the rate of peak-capacity production (slopes in Figures 3 and 4) with an average carrier gas velocity of 200 cm/s relative to values with gas velocities of 150 or 100 cm/s is due to significantly reduced column efficiency. This occurs as the average carrier gas velocity is increased to well above the optimal

Table 2. Holdup Times and Column Temperature Changes for the Holdup Time Intervals

	column length								
	6 m			12 m			18 m		
		ΔT, °C during holdup			ΔT, °C during holdup			ΔT, °C during holdup	
u (cm/s)	holdup (s)	at 100°/min	at 600°/min	holdup (s)	at 100°/min	at 600°/min	holdup (s)	at 100°/min	at 600°/min
50	12	20	120	24	40	240	36	60	290*
100	6	10	60	12	20	120	18	30	180
150	4	6.4	40	8	13	80	12	20	120
200	3	5	30	6	10	60	9	15	90

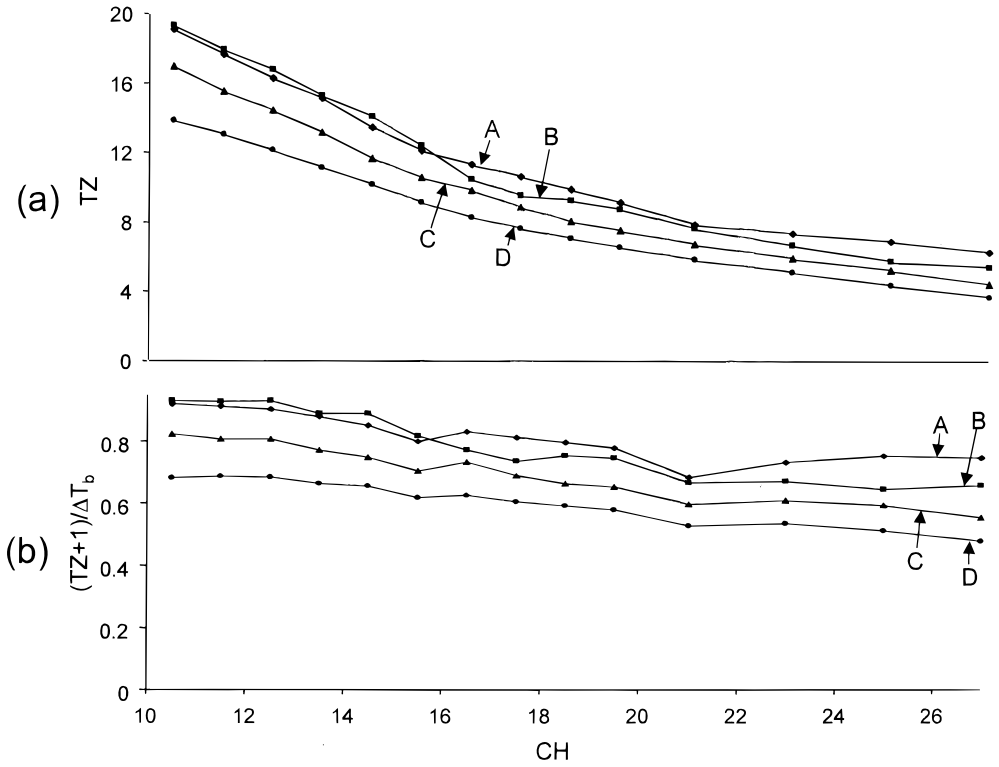

Figure 6. Plots of Trennzahl number (TZ) (a) and the ratio of TZ + 1 to the boiling-point interval for the corresponding two *n*-alkane reference components [(TZ + 1)/ΔT_b] (b) vs average carbon number (CH) for a 12-m-long column with a temperature programming rate of 100 °C/min. Plots A−D are for average carrier gas velocity values of 50, 100, 150, and 200 cm/s, respectively.

value. Thus, the optimal carrier gas velocity for high-speed, temperature-programmed GC is a compromise between two factors. First, there is the steady loss in column efficiency with increasing average carrier-gas velocity above the optimal value. Second, there are decreases in elution temperatures with attendant increases in stationary-phase interaction when components are driven off the column more rapidly.

Boiling-Point Resolution. Figure 6 shows plots of the TZ value versus average carbon number (CH) (a) and the ratio of TZ + 1 to the boiling-point difference ΔT_b for the corresponding two *n*-alkane peaks vs CH (b) using a temperature-programming rate of 100 °C/min. For example, a point at CH = 16.5 corresponds to the TZ or (TZ + 1)/ΔT_b value for the C_{16}−C_{17} retention interval. A 12-m-long column was used at average carrier gas velocities of 50 (Plot A), 100 (B), 150 (C), and 200 (D) cm/s.

The general decrease in TZ values with increasing average carbon number has been discussed,[6,14,15,20] and is attributed to the decrease in retention time difference for adjacent homologues with increasing molecular weight and with increasing column temperature. For most of the boiling-point range explored here, TZ values decrease with increasing carrier gas velocity. This is a result of reduced column efficiency at the higher carrier gas velocities.

While TZ values are used frequently as a measure of peak capacity for temperature-programmed GC, more direct information about boiling-point resolution is found from the ratio of the TZ + 1 value to the boiling-point difference between the reference compounds. The reciprocal of the (TZ + 1)/ΔT_b values gives the minimum boiling point difference between two compounds required for a separation with a resolution of 1.18 assuming that differences in boiling point are entirely responsible for differences in retention. This is nearly the case for nonpolar solutes (alkanes) on a nonpolar column.

The (TZ + 1)/ΔT_b plots in Figure 6b show the same general trends as the TZ plots except that they are flatter and show somewhat greater differences with respect to the differences in carrier gas velocity. For the 50 cm/s case (plot A), values increase slightly for CH values greater than about 20 because the corresponding sample components elute after completion of the

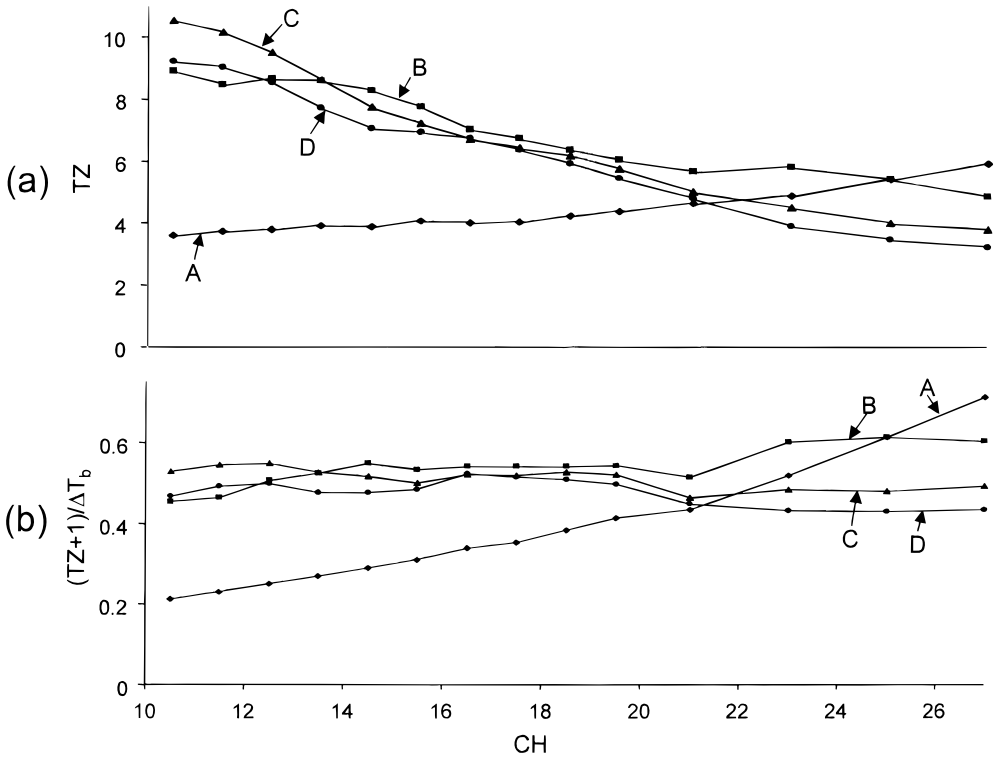

Figure 7. Plots of Trennzahl number (TZ) (a) and the ratio of TZ + 1 to the boiling-point interval for the corresponding two *n*-alkane reference components [(TZ + 1)/ΔT_b] (b) vs average carbon number (CH) for a 12-m-long column with a temperature programming rate of 600 °C/min. Plots A−D are for average carrier gas velocity values of 50, 100, 150, and 200 cm/s, respectively.

temperature ramp and have significant retention at the highest temperature of 340 °C (isothermal separation conditions).

Figure 7 shows plots similar to those in Figure 6 except for the case of a 600 °C/min programming rate. With the exception of the plot for 50 cm/s (A), the TZ values for the 600 °C/min rate are about half as large as the values for the 100 °C/min rate, but the separation time is more than cut in half at the higher programming rate. Note, for plot A, the temperature ramp is complete in only 29 s and the first peak (C_{10}) does not elute until about 40 s [see plot A, Figure 4b]. In this case, the TZ value increases steadily with increasing CH. Note that for the very high programming rate used here, most components elute after completion of the program for all carrier-gas velocity values considered here. This gives the separations more isothermal character, and the 100 cm/s average carrier-gas velocity gives the largest TZ values for CH values greater than about 17.

For average-carrier-gas-velocity values of 100, 150, and 200 cm/s, the (TZ + 1)/ΔT_b plots are remarkably flat with values in the 0.4−0.5 peaks/°C range over most of the boiling-point range considered here. For a carrier-gas velocity of 50 cm/s (A), the boiling point resolution is very poor for the lower boiling-point components but increases steadily with increasing CH value. Again note that at this carrier-gas velocity, all components elute well after completion of the temperature program, and only components C_{20}−C_{28} have significant retention at the final isothermal temperature of 340 °C. This results in boiling-point resolution more characteristic of an isothermal separation for the higher boiling-point compounds.

CONCLUSIONS

Fast temperature programming using columns contained in resistively heated metal tubes is very attractive for high-speed GC separations of wide-boiling-point range mixtures. With a 600 °C/min temperature ramp rate and a 6-m-long column, the boiling point range from *n*-C_{10} to *n*-C_{28} can be eluted in less than 40 s with a total peak capacity (resolution = 1.18) of about 75 peaks. Higher peak-capacity values are obtained with lower programming rates, but the increase is small for programming rates less than about 100 °C/min.

For the largest programming rate investigated here, the rate of peak-capacity production can be very large (>6 peaks/s) for the 6-m-long column. Thus, very high efficiency is achieved with respect to the utilization of time. For high programming rates, higher average-carrier-gas velocities are preferred, especially for the longer columns. Higher gas velocity results in lower elution temperatures and smaller column temperature changes on the time scale of the column holdup time. This provides greater interaction of the sample with the downstream end of the column (larger retention factors), and thus the column is used more efficiently. Future studies will explore the use of microbore columns (0.1-mm i.d.). In addition to greater efficiency, these columns have larger optimal-carrier-gas velocity values. This will allow the use of higher gas velocities with smaller losses in efficiency.

The use of columns longer than about 6 m does not appear to offer significant advantages for the very high programming rates, since the increases in peak capacity are very small relative to the increases in separation time. At very high programming rates,

the temperature program can outrun the separation. This results in a lower rate of peak-capacity production than could be achieved with a shorter column. To exploit programming rates greater than the values used in this study, columns less than 6 m in length are recommended.

On-column focusing appears to be very effective in the studies reported here, since elution peak widths as small as 0.084 s were observed at a programming rate of 600 °C/min. However, the *n*-hexane solvent has a boiling point of about 68 °C, which is significantly greater than the initial column temperature of 50 °C. Thus, some solvent-effect focusing may have occurred. For elution times less than about 60 s, the observed elution peak widths may be significantly increased by the injection plug width. In this case, boiling-point resolution and peak-capacity production rate may be further increased by the use of an inlet which produces narrower injection plugs.

ACKNOWLEDGMENT

The authors gratefully acknowledge Thermedics Detection, Inc. for the use of the Flash GC instrument.

Received for review October 13, 1999. Accepted November 8, 1999.

AC9911802