

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Separation Science and Technology

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713708471>

## Stationary Spatial Temperature Gradient in Gas Chromatography

P. E. Duarte<sup>a</sup>; B. J. McCoy<sup>a</sup>

<sup>a</sup> Department of Chemical Engineering, University of California, Davis, California

**To cite this Article** Duarte, P. E. and McCoy, B. J.(1982) 'Stationary Spatial Temperature Gradient in Gas Chromatography', *Separation Science and Technology*, 17: 7, 879 – 896

**To link to this Article:** DOI: 10.1080/01496398208082101

**URL:** <http://dx.doi.org/10.1080/01496398208082101>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

## Stationary Spatial Temperature Gradient in Gas Chromatography

---

P. E. DUARTE and B. J. MCCOY

DEPARTMENT OF CHEMICAL ENGINEERING  
UNIVERSITY OF CALIFORNIA  
DAVIS, CALIFORNIA 95616

### Abstract

Imposing an increasing stationary temperature gradient along the length of a gas chromatographic column is proposed as a technique for improving separation. Side outlet ports with control valves would allow the process to have the same advantages of programmed temperature gas chromatography without the disadvantages of temperature transients. For a simple model of gas chromatography the analysis provides expressions for temporal moments at any point along the column as a function of the temperature gradient. Reduced retention times, sharpening of peaks, and higher symmetry are predicted due to increasing the temperature gradient. The relationship to chromathermography is discussed.

### INTRODUCTION

Because gas chromatography has grown to industrial scale over the last several years, one expects that gradient and programming techniques, successful at the bench level, may be important to the optimization of larger scale chromatographic processes. Programmed temperature gas chromatography (PTGC), for which temperature is uniform along the column but varying in time, has the disadvantage of long temperature transients for large diameter columns. Since temperature strongly affects the equilibrium of separation, it is of interest to study the possibility that the imposition of a temperature gradient along the column, constant in time, may have the advantages of PTGC without the disadvantages.

In PTGC the column temperature is increased with time so that more volatile solutes are eluted at low temperatures and less volatile solutes at higher temperatures at a later time. Thus resolution for lower molecular

weight components is kept high at low temperatures, and elution of high molecular weight components is speeded up by the higher temperatures.

To accomplish similar objectives, we propose that a steady-state temperature gradient, increasing from inlet to exit, be imposed on the column. The process might be called Temperature Gradient Gas Chromatography (TGGC). Outlets with automatic valves along the column allow more volatile components to be taken from the column outlets at shorter distances from the inlet, because they are best separated at the lower temperatures. At these outlets the less volatile components are still too closely spaced, so they are taken off farther downstream where temperature is higher and where they move faster. Thus we have the benefits of PTGC without the problems associated with transient heat transfer effects in large-scale equipment.

In what follows we provide a theoretical analysis of the proposed process, with calculations of solute retention time (first temporal moment), band spreading (second central moment), and skewness (third central moment) as functions of temperature gradient and column properties. The resolution of output pulses corresponding to the compounds of a homologous series are presented for a linear spatial temperature gradient. Similar to an earlier study of PTGC (1), this study employs a simple model of gas-liquid partition chromatography that accounts for axial dispersion and partitioning, but ignores details of intraparticle and liquid diffusion. As in the earlier work on PTGC, we have assumed the pressure drop and temperature gradient in the column have a negligible effect on velocity. A numerical procedure is suggested for accounting for these effects.

The proposal method, TGGC, is not simply the limit as movement ceases for the process known as chromathermography. In chromathermography a heated region of the column is caused to move forward along the column. As is shown in our analysis, a motionless decreasing gradient has qualitatively different behavior from the increasing gradient proposed here. However, the present analysis, with a negative temperature gradient, does provide a theoretical explanation for the distribution of solute bands in chromathermography.

## THEORY: LINEAR GRADIENT

The differential equation for the chosen model of gas-liquid partition chromatography (2) is

$$\alpha(1 + k)\partial c/\partial t + v_0\partial c/\partial z - D_0\partial^2 c/\partial z^2 = 0 \quad (1)$$

which describes the partitioning, flow, and longitudinal dispersion of the solute in the column. The initial and boundary conditions are

$$c(z, 0) = 0 \quad (2)$$

$$c(z_0, t) = c_0(t) \quad (3)$$

$$c(\infty, t) = \text{finite} \quad (4)$$

The point  $z_0$  is any position in the column. In the Laplace domain the solution is

$$\bar{c}(z) = \bar{c}_0 \exp(\lambda z) \quad (5)$$

where

$$\lambda = (v_0/2D_0)\{1 - [1 + 4\alpha(1 + k)D_0s/v_0^2]^{1/2}\} \quad (6)$$

This solution is a generating function for temporal moments of the concentration at any position in the column,

$$m_n(z) = \lim_{s \rightarrow 0} (-1)^n d^n \bar{c}(z) / ds^n \quad (7)$$

from which we find expressions for the normalized first moment, second central moment, and third central moment, respectively,

$$\mu'_1(z) - \mu'_1(z_0) = (z - z_0)f \quad (8)$$

$$\mu_2(z) - \mu_2(z_0) = (z - z_0)g \quad (9)$$

$$\mu_3(z) - \mu_3(z_0) = (z - z_0)h \quad (10)$$

where

$$f = \alpha(1 + k)/v_0 \quad (11)$$

$$g = 2D_0\alpha^2(1 + k)^2/v_0^3 \quad (12)$$

$$h = 12D_0^2\alpha^3(1 + k)^3/v_0^5 \quad (13)$$

Because the change of a moment is linear in  $z$ , we may write

$$\Delta\mu'_1 = f\Delta z \quad (14)$$

$$\Delta\mu_2 = g\Delta z \quad (15)$$

$$\Delta\mu_3 = h\Delta z \quad (16)$$

If the distance  $\Delta z = z - z_0$  is short enough that the temperature does not change significantly for TGGC, then the differential equations that result from letting  $\Delta z \rightarrow dz$  and  $\Delta\mu \rightarrow d\mu$  can be integrated to obtain

$$\mu'_1(z) = \mu'_1(0) + \int_0^z f(z) dz \quad (17)$$

$$\mu_2(z) = \mu_2(0) + \int_0^z g(z) dz \quad (18)$$

$$\mu_3(z) = \mu_3(0) + \int_0^z h(z) dz \quad (19)$$

Following Giddings' work (5) on PTGC, we write the temperature dependence of the partition ratio as

$$k = k_0 \exp(-\Delta H/RT) \quad (20)$$

With this expression substituted into Eqs. (11) to (13), the integrals of Eqs. (17) to (19) can be written without approximation for the linear temperature gradient  $T(z) = T_0 + \gamma z$  as

$$\mu'_1(L) = \frac{\alpha}{v_0} \left[ L + \frac{k_0}{\gamma} \frac{\Delta H}{R} G_1 \right] \quad (21)$$

$$\mu_2(L) - \mu_2(0) = \frac{2D_0\alpha^2}{v_0^3} \left[ L + \frac{2k_0}{\gamma} \frac{\Delta H}{R} (G_1 + k_0 G_2) \right] \quad (22)$$

$$\mu_3(L) - \mu_3(0) = \frac{12D_0^2\alpha^3}{v_0^5} \left[ L + \frac{3k_0}{\gamma} \frac{\Delta H}{R} (G_1 + 2k_0 G_2 + k_0^2 G_3) \right] \quad (23)$$

where

$$G_1 = \int_{x_0}^{x_R} X^{-2} e^X dX = \frac{e^{x_0}}{x_0} - \frac{e^{x_R}}{x_R} - Ei(x_0) + Ei(x_R) \quad (24)$$

$$G_2 = \frac{1}{2} \int_{X_0}^{X_R} X^{-2} e^{2X} dX = \frac{e^{2X_0}}{2X_0} - \frac{e^{2X_R}}{2X_R} - Ei(2X_0) + Ei(2X_R) \quad (25)$$

$$G_3 = \frac{1}{3} \int_{X_0}^{X_R} X^{-2} e^{3X} dX = \frac{e^{3X_0}}{3X_0} - \frac{e^{3X_R}}{X_R} - Ei(3X_0) + Ei(3X_R) \quad (26)$$

in terms of the tabulated (6) exponential integrals

$$-Ei(-x) = E_1(x) = \int_x^\infty t^{-1} e^{-t} dt; \quad x > 0 \quad (27)$$

In the preceding development the axial dispersion coefficient,  $D_0$ , has been assumed to be independent of temperature. As in the study (1) of PTGC, we examine the effect of allowing  $D_0(T)$  to vary as the first or second power of temperature. For

$$D_0 = \delta_1 T \quad (28)$$

we find

$$\begin{aligned} \mu_2(L) - \mu_2(0) &= \frac{2\delta_1 \alpha^2}{\gamma v_0^3} \left( \frac{\Delta H}{R} \right)^2 (-1) \\ &\times [G(0, 3) + 2k_0 G(1, 3) + k_0^2 G(2, 3)] \end{aligned} \quad (29)$$

and for

$$D_0 = \delta_2 T^2 \quad (30)$$

we find

$$\mu_2(L) - \mu_2(0) = \frac{2\delta_2 \alpha^2}{\gamma v_0^3} \left( \frac{\Delta H}{R} \right)^2 [G(0, 4) + 2k_0 G(1, 4) + 2k_0^2 G(2, 4)] \quad (31)$$

where the terms  $G(a, m)$  are given by

$$\begin{aligned} G(a, m) &= \int_{X_0}^{X_R} e^{aX} X^{-m} dX = \\ &= - \left[ \frac{1}{m-1} \frac{e^{aX}}{X^{m-1}} \right]_{X_0}^{X_R} + \frac{a}{m-1} G(a, m-1) \end{aligned} \quad (32)$$

with

$$G(1, 2) = G_1 \quad (33)$$

and

$$G(2, 2) = 2G_2 \quad (34)$$

### DISCRETE STEP INCREASES OF TEMPERATURE

One method of establishing a stationary longitudinal profile in temperature is to raise the temperature in a number of discrete steps along the column. For equal length intervals, we let

$$\Delta z = L/n, \quad n = 1, 2, 3, \dots \quad (35)$$

and for equal temperature increments, the temperature is

$$T = T_0 + m\Delta T, \quad m = 0, 1, 2, \dots, n-1 \quad (36)$$

where  $\Delta T$  is the step increase in temperature chosen for the length intervals. The changes of the moments  $\Delta\mu'_1$ ,  $\Delta\mu_2$ ,  $\Delta\mu_3$  over distances  $\Delta z$  are given by Eqs. (14)–(16). Then the difference between the values of moments evaluated at either end of the column is simply given by the sum of the temporal moment expressions for each discrete step,

$$\mu'_1(L) = \frac{\alpha}{v_0} \sum_{m=0}^{n-1} \{1 + k_0 \exp[-\Delta H/R(T_0 + m\Delta T)]\} \Delta z \quad (37)$$

$$\mu_2(L) - \mu_2(0) = \frac{2D_0\alpha^2}{v_0^3} \sum_{m=0}^{n-1} \{1 + k_0 \exp[-\Delta H/R(T_0 + m\Delta T)]\}^2 \Delta z \quad (38)$$

$$\mu_3(L) - \mu_3(0) = \frac{12D_0\alpha^2}{v_0^5} \sum_{m=0}^{n-1} \{1 + k_0 \exp[-\Delta H/R(T_0 + m\Delta T)]\}^3 \Delta z \quad (39)$$

For infinitesimally small steps, i.e., when  $n \rightarrow \infty$  and  $\Delta z \rightarrow dz$ ,  $T_0 + m\Delta T$  becomes a smooth linear gradient in temperature, and Eqs. (37)–(39) can be reduced to Expressions (21)–(23).

The discrete step model suggests a procedure for considering the variation of gas velocity as a function of temperature, and the dependence of axial dispersion on velocity as well. If we assume  $v_0$  to vary with  $m$  because of its temperature dependence, then for the low pressure gas,

$$v_0(m) = [T(m)/T_0]v_0 = [1 + m\Delta T/T_0]v_0 \quad (40)$$

We continue to ignore the pressure drop along the column. The axial dispersion coefficient may be considered to vary with temperature because of the dependence of velocity, i.e.,

$$D_0(m) = D_0[v_0(m)] \quad (41)$$

Substituting Eqs. (40) and (41) into the moment expressions yields

$$\mu'_1(L) = \alpha \sum_{m=0}^{n-1} \frac{\{1 + k_0 \exp[-\Delta H/R(T_0 + m\Delta T)]\} \Delta z}{[1 + m(\Delta T/T_0)]v_0} \quad (42)$$

$$\mu_2(L) = \mu_2(0) + 2\alpha^2 \sum_{m=0}^{n-1} \frac{D_0[v_0(m)]\{1 + k_0 \exp[-\Delta H/R(T_0 + m\Delta T)]\}^2 \Delta z}{[1 + m\Delta T/T_0]^3 v_0^3} \quad (43)$$

The expressions provide the basis for a numerical calculation, easily programmed for computer, to analyze the more general case when  $v_0$  as well as  $D_0$  vary along the column because of the temperature gradient.

## EXPONENTIAL GRADIENT IN TEMPERATURE

We consider the time-independent exponential increase in temperature along the column to be given by

$$T(z) = T_0 \exp(\eta z) \quad (44)$$

changing the sign of  $\eta$  gives an exponential which decreases in temperature with distance. By substituting Eq. (44) into moment expressions and integrating, one obtains

$$\mu'_1(L) = (1 - k_0 H_1/\eta) \alpha / v_0 \quad (45)$$



$$\mu_2(L) = \mu_2(0) + \frac{2D_0\alpha^2}{v_0^3} \left[ L - \frac{2k_0}{\eta}(H_1 + k_0H_2/2) \right] \quad (46)$$

$$\mu_3(L) = \mu_3(0) + \frac{12D_0^2\alpha^3}{v_0^5} \left[ L - \frac{3k_0}{\eta} \left( H_1 + k_0H_2 + \frac{k_0^2}{3}H_3 \right) \right] \quad (47)$$

where

$$H_1 = Ei(X_0e^{-\eta L}) - Ei(X_0) \quad (48)$$

$$H_2 = Ei(2X_0e^{-\eta L}) - Ei(2X_0) \quad (49)$$

$$H_3 = Ei(3X_0e^{-\eta L}) - Ei(3X_0) \quad (50)$$

### EFFECT OF LINEAR GRADIENT IN TEMPERATURE ON MOMENTS

One of the main objectives of the present study is to establish the effect of the linear spatial gradient in temperature on moments. The influence of positive or negative gradient in temperature on the retention time given by  $\mu'_1(L)$ , on the band spreading between either end of the column,  $\mu_2$ , and on the band skewness,  $\mu_3$ , is made by changing the value of  $\gamma$ .

In dealing with the changes of moments, we assume that the feed entering the column is a very thin pulse. Therefore,  $\mu'_1$  may be approximated by a delta function at  $t = 0$ . This assumption permits (1) the replacement of  $\Delta\mu'_1$ ,  $\Delta\mu_2$ , and  $\Delta\mu_3$  by  $\mu'_1(z)$ ,  $\mu_2(z)$ , and  $\mu_3(z)$ .

The parameters have been selected as follows. The initial temperature,  $T_0$ , is 300 K, and  $\Delta H = -6000$  cal/mol, corresponding to  $X_0 \approx 10$ . The ratio  $k_0$  is given the value 0.01, and  $\alpha = 0.4$ ,  $L = 200$  cm,  $D_0 = 0.1$  cm<sup>2</sup>/s. For the superficial velocity we assume a value of  $v_0 = 8$  cm/s. Choosing a value for the retention temperature,  $T_R$ , allows us to compute  $X_R$ . Once  $X_0$  and  $X_R$  are found, the values of  $G_1$ ,  $G_2$ , and  $G_3$  may be obtained by employing tabulations (6) for the exponential integrals. For  $\gamma = 0$ , the calculation of moments is performed by applying Eqs. (8)–(10). Figure 1 shows the results of the calculations for different positive values of  $\gamma$ .

As expected, the values of  $G_1$ ,  $G_2$ , and  $G_3$  are somewhat similar to those that were obtained (1) for the case of PTGC. It is interesting that as the temperature increases with distance, the terms containing  $X_R$  become negligible compared to the terms containing  $X_0$ . This leads to small

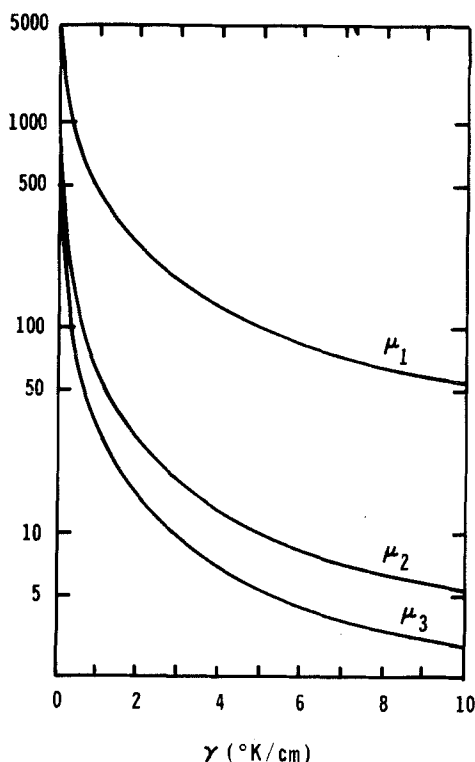


FIG. 1. Effect of an increasing linear temperature gradient on first, second, and third moments.

variations of  $G_1$  and to a relative constancy of  $G_2$  and  $G_3$  at high temperatures. Under these conditions the initial temperature,  $T_0$ , has a large effect. Consistent with the preceding observation, it is predictable that the retention time,  $\mu'_1(L)$ , becomes only slightly affected by the increase in temperature,  $T_R$ , when this reaches high values, and that the second and third moments,  $\mu_2$  and  $\mu_3$ , become almost inversely proportional to  $\gamma$ . Therefore the time of elution,  $\mu'_1(L)$ , for a component depends strongly on  $T_0$  for high gradients in temperature.

The effect of  $\gamma$  on the moments is shown in Fig. 1. In plotting the values of moments calculated by using Eqs. (21)–(23) as functions of  $\gamma$ , we followed the procedure proposed by Giddings (5) and extended by McCoy (1).

The effect of the temperature dependence of the axial dispersion coefficient,  $D_0(T)$ , was determined for the parameter values quoted before and with the quantities  $\delta_1$  and  $\delta_2$  obtained from Eqs. (76) and (93). For high

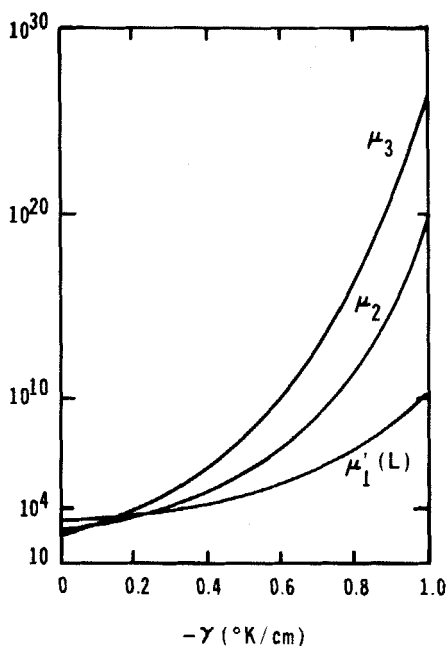


FIG. 2. Effect of a negative temperature gradient on first, second, and third moments.

values of  $\gamma$  (e.g.,  $\gamma = 5.0$ , which corresponds to  $T_R = 1300$  K), the increase of  $\mu_2$  was 8% for  $D_0 \propto T$  and 17% for  $D_0 \propto T_2$ . We have smaller deviations than those obtained for PTGC (1) because we did not make the approximation  $k \gg 1$ , which was made in Ref. 1.

### EFFECT OF DECREASE IN TEMPERATURE

We may show the influence of cooling the column with distance by changing the sign of  $\gamma$ . With the previous procedure, values of moments have been computed, and shown an extraordinary increase of  $G_1$ ,  $G_2$ , and  $G_3$  for relatively small variations of  $\gamma$ . Moments, plotted in Fig. 2, are tremendously increased by lowering the temperature along the column. For this case the influence of  $T_0$  becomes rapidly negligible compared to that of  $T_R$ .

This effect is important in the process known as chromatography (2-4), where a gradient furnace is used to establish a temperature gradient decreasing down the column. Solutes entering the column distribute themselves along the temperature gradient according to their physical properties, mainly their equilibrium partition ratios. The large values of the first moments ensure that after an initial transient period the solute bands

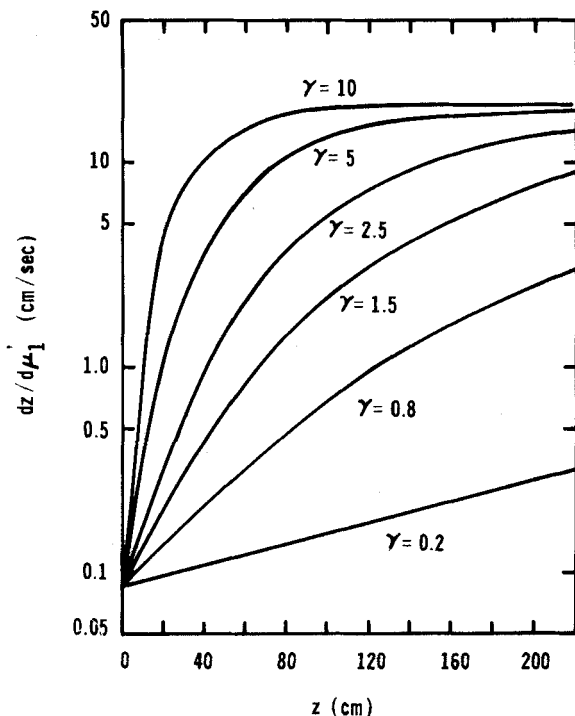


FIG. 3. Influence of temperature gradient on band velocity,  $dz/d\mu'_1$ , as a function of column length.

become essentially stationary but separated because of different values of  $k$  for different solutes. Then, movement of the gradient furnace toward the column outlet causes each band to move at the velocity of the furnace and to be separately eluted. However, in addition to the large value of the first moment, the second and third moments also increase dramatically with increased gradient (Fig. 2), leading to increased band overlapping and decreased resolution (2).

### VARIATIONS OF VELOCITY AND SECOND MOMENT WITH DISTANCE

It is interesting to determine the variation of the band velocity, given by  $dz/d\mu'_1$ , and the peak broadening effect, measured by  $\mu_2$  with distance,  $z$ , for different gradients in temperature. Calculations for  $dz/d\mu'_1$  and for  $\Delta\mu_2$  were performed by employing Eqs. (14) and (22) for several values of  $\gamma$  and  $z$ . The results are plotted in Figs. 3 and 4.

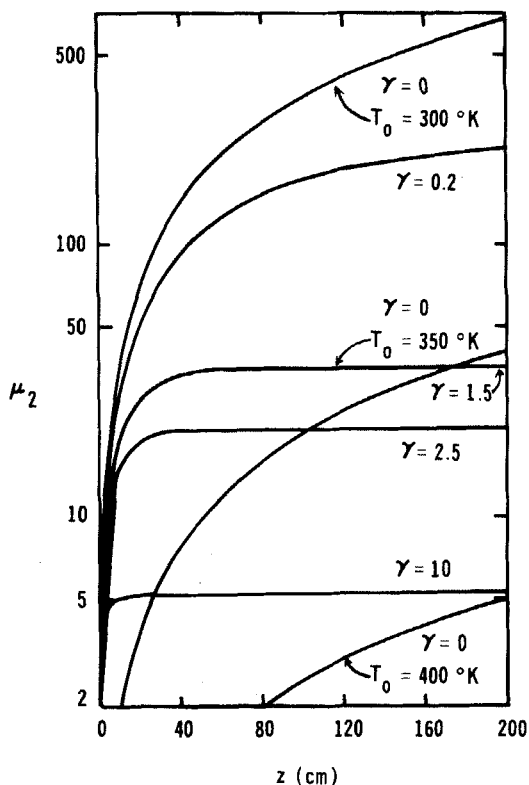


FIG. 4. Effect of an increase in  $\gamma$  on the second moment along the column.

The band velocity shows an increment along the column as  $\gamma$  increases (Fig. 3); for high values of  $\gamma$  the velocity increases rapidly in the first sections of the column and appears to remain almost constant in the farther region of the column. On the other hand, velocity shows a small change for low values of  $\gamma$ . The explanation for this behavior is that as  $\gamma$  and  $z$  reach high values, i.e., at the final section of a column with a large gradient the partition ratio becomes negligible and affects insignificantly  $dz/d\mu_1'$ . Since a gradual increase in velocity along the column is desired, this kind of approach may provide a method to optimize the distance-dependent velocity for a specific gradient in temperature.

In Fig. 4 we have plotted  $\mu_2$  as a function of  $z$  for different  $T_R$ . These are curves corresponding to variations of  $\mu_2$  for different  $\gamma$  with  $T_0 = 300$  K, and curves representing changes of  $\mu_2$  for isothermal processes at  $T_0 = 300, 350$ , and  $400$  K. We observe that for isothermal operations the band spreading of

the peak increases as it traverses the column. The explanation for this is that for constant  $T$ , according to Eq. (37),  $g(z)$  remains constant; therefore,  $\Delta\mu_2$  only changes with increments of  $z$ . On the other hand, for the linear gradient case, in general  $\Delta\mu_2$  decreases as  $\gamma$  increases. It is interesting that only for small  $\gamma$  does  $\Delta\mu_2$  change progressively along  $z$ . Above certain values of  $\gamma$ , i.e.,  $\gamma \geq 1.5$ ,  $\Delta\mu_2$  increases in small ranges of  $z$  at the first section of the column, but remains nearly constant in the rest of the column. We may explain this behavior by analyzing the expression for  $\Delta\mu_2$ . For a specific value of  $\gamma$ , when a certain temperature is reached, the terms containing  $X_R$  become negligible; therefore, the terms involving  $X_0$ , i.e., the initial temperature,  $T_0$ , become the dominant ones, and  $\Delta\mu_2$  does not change significantly for increases of  $z$ .

Qualitatively, as previously mentioned, the band velocity increases as  $\gamma$  increases; therefore, for higher values of  $\gamma$  each peak traverses the column in less time. Since the retention time becomes small, the absorption as described by  $k$  is greatly reduced. But absorption is the principal broadening effect and consequently an increase in temperature leads to the sharpening of the pulse. This effect on  $\mu_2$  had been observed in previous work (2) for PTGC. Physically, the constancy of  $\mu_2$  for high values of  $\gamma$  may be attributed to the disappearance of phase partitioning at high temperature. Eventually, all solutes tend to remain in the gas phase when the temperature is sufficiently high.

### RETENTION TIMES AND RESOLUTION FOR DIFFERENT SPATIAL GRADIENTS IN TEMPERATURE

Because gas-liquid chromatography has become a full-scale industrial unit operation, we are interested in the application of our temperature-gradient processes to a suitable specific problem. We have chosen a mixture of four members of the  $n$ -alkane homologous series, i.e., from  $n = 17$  to  $n = 20$  carbon atoms, in order to analyze the retention time and the resolution by using the results of our model. Properties of these paraffins came from standard references (7, 8). Diffusivities,  $D_{BC}$  and  $D_{CD}$ , were calculated by using the Chapman-Enskog formula (7). For  $T = 600$  K and  $P = 1$  atm, an "average" axial dispersion coefficient,  $D_0 = 0.160$ , was obtained by using a graph for the correlation (9)  $v_0 d_p / \alpha D$  versus  $D_0 / D$ . We used the typical values  $L = 200$  cm,  $d_p = 0.2$  mm, and  $\alpha = 0.4$ . Since the optimum operating temperature of the column will be around the boiling point of the most abundant compound (10), we arbitrarily took an inlet temperature,  $T_0 = 590$  K. Since values for optimum velocity range from 3 to 10 cm/s, we selected  $v_0 = 4$  cm/s. Following a procedure indicated by Giddings (10), we calculated  $k_0 = 0.0005$ .

For the case of linear spatial gradient in temperature, first and second moments were computed by following the previous procedure. Two different gradients were considered,  $\gamma = 0.2$  and  $\gamma = 0.5$ , which correspond to  $T_R = 630$  K and  $T_R = 690$  K. For the case of step increase in distance-dependent temperature, the calculations for the moments gave results substantially the same as for the linear gradient. An increase in temperature for all cases gave lower retention times and consequent sharpening of the peaks. By comparing the isothermal process to the linear gradient case we found that for  $\gamma = 0.5$ , the time of elution was reduced by one-half of that achieved isothermally at  $T_0 = 590$  K. However, the peaks of isothermal operation at  $T_0 = 640$  K (which corresponds to the average temperature between  $T_0 = 590$  K and  $T_R = 690$  K, or  $\gamma = 0.5$ ) presented times of elution and spreading similar to those obtained by the linear gradient process of  $\gamma = 0.5$ . Furthermore, at higher temperatures the isothermal process may achieve a good separation at a temperature lower than the average one for the linear gradient.

The resolution between two peaks,  $A$  and  $B$ , is defined by

$$R_S = \frac{\mu'_{1B} - \mu'_{1A}}{\sqrt{\mu_{2B}} + \sqrt{\mu_{2A}}} \quad (51)$$

with  $R_S \geq 2$  indicating satisfactory separation between  $A$  and  $B$ . The resolutions between  $C_{18}H_{38}$  and  $C_{19}H_{40}$ ,  $R_{S(BC)}$ , and between  $C_{19}H_{40}$  and  $C_{20}H_{42}$ ,  $R_{S(CD)}$ , have been calculated for different temperatures for the isothermal and gradient processes and have been plotted in Figs. 5 and 6. The resolution for isothermal operation decreases rapidly as the temperature increases and falls down nearly to zero when the column is operated at high temperatures (Fig. 5). For the gradient case the resolution decreases gradually with  $\gamma$ , but remains above good values of  $R_S$  for very high spatial gradients in temperature (Fig. 6). According to our results, we can infer that isothermal operation may achieve separations with retention times and resolution similar to those that can be achieved by using TGGC processes. Although there seems to be no distinct advantage to operating an ordinary chromatographic column of a given length with a spatial gradient as compared with its isothermal operation, one can propose a configuration which would provide the same benefits as PTGC. In PTGC more volatile components are eluted from the column at lower temperatures, and less volatile components are eluted from the column at a later time. Thus resolution for lower molecular weight components is kept high at low temperatures, and elution of high molecular weight components is speeded up by the higher temperatures. To accomplish the same objectives we propose that columns for TGGC processes may be modified by adding

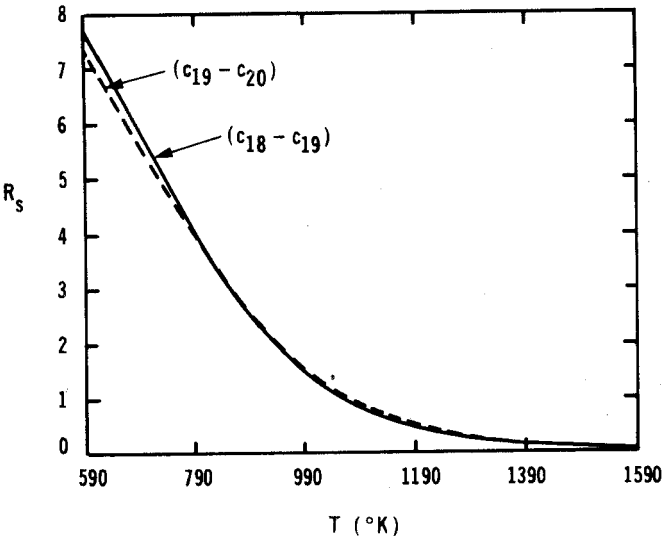


FIG. 5. Effect of column temperature on resolution for an isothermal process.

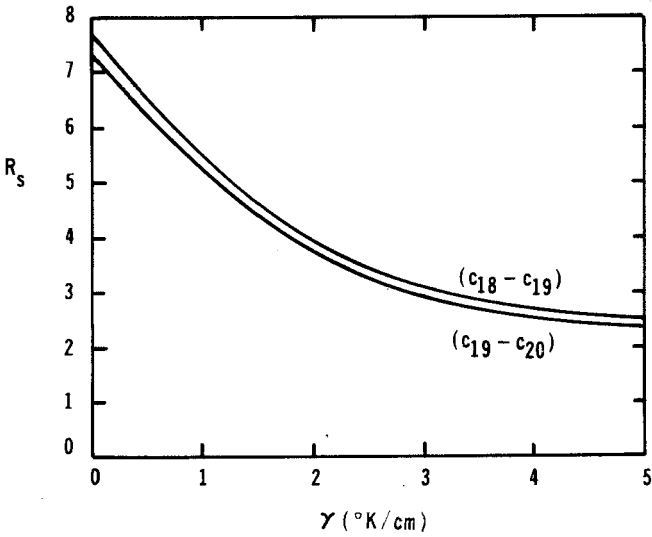


FIG. 6. Effect of temperature gradient on resolution for a linear gradient in temperature.



outlets along the length of the column. All the outlets have valves that allow them to be closed off or on at will. Then the procedure for TGGC processes that is analogous to PTGC is as follows: more volatile components are taken from the column outlets at shorter distances from the inlet because they are best separated at the lower temperatures. At these outlets less volatile components are still too closely spaced, so they are taken off farther downstream where temperature is higher and where they move faster. Thus we have the benefits of PTGC without the problems associated with transient effects of heat transfer in large-scale equipment.

## CONCLUSIONS

The stationary spatial gradient in temperature has been proposed as a method for improving separation in chromatographic processes. In the present work we compare retention times, broadening effects, and resolution for such processes to those of isothermal chromatography.

A simple model of gas-liquid partition chromatography is developed for the analysis of temperature gradient gas chromatography (TGGC) via the moment technique. Expressions for the first, second, and third moments are found for three TGGC chromatographic processes: linear gradient, step increase, and exponential gradient case. Integrations of the moments for the linear gradient case show results similar to those that have been obtained for programmed temperature gas chromatography (PTGC). Reduced retention times, sharpening of peaks, and higher symmetry are achieved by increasing the temperature gradient,  $\gamma$ . However, resolution of output peaks is decreased for TGGC as it is for PTGC and chromatography. The temperature dependence of the axial dispersion coefficient has an insignificant effect on second moment. The velocity of the pulse changes slowly along the column for small gradient,  $\gamma$ ; however, for high  $\gamma$  the velocity increases rapidly in earlier sections of the column and is almost constant in the farther regions of the column. In general, the spreading of the band,  $\mu_2$ , decreases as  $\gamma$  increases. For small values of  $\gamma$ ,  $\mu_2$  changes significantly with distance,  $z$ . However, for relatively high values of  $\gamma$ ,  $\mu_2$  increases rapidly in the first section of the column (small  $z$ ), and appears to be constant in the rest of the column. On the other hand, for the case of isothermal processes, the spreading of the peak increases with  $z$  for any temperature.

A comparison between isothermal chromatography and TGGC processes is shown for a homologous series of solutes. Such comparison shows that times of elution and resolution of isothermal processes may be quite similar to those obtained in TGGC processes if an appropriate temperature is chosen. However, if the TGGC column is fitted with outlet ports to selectively remove faster moving solutes, then the process should have

the same advantages as PTGC, without the disadvantages of temperature transients.

The model selected for this work is linear and does not include details about mass transfer. Some restrictions are imposed because of the assumptions made; therefore, some improvements in the analysis are possible. However, the results that are achieved seem to be provisionally satisfactory for our purpose of initiating discussion of this gas-liquid chromatography technique.

## SYMBOLS

$c$	space and time dependent solute concentration in the mobile phase
$c_0$	concentration of solute at $z = z_0$
$\bar{c}$	Laplace-transformed concentration of solute
$\bar{c}_0$	Laplace-transformed concentration of solute at column inlet
$D_0$	axial dispersion coefficient, $\text{cm}^2/\text{s}$
$d_p$	effective particle diameter, $\text{cm}$
$H$	enthalpy, $\text{cal/mol}$
$k$	partition ratio
$L$	column length, $\text{cm}$
$m_0$	$= \int_0^\infty c \, dt$ , unnormalized zeroth moment
$m_n$	$= \int_0^\infty t^n c \, dt$ , unnormalized $n$ th moment
$R$	gas constant
$R_s$	resolution
$s$	Laplace transform parameter, $\text{s}^{-1}$
$T$	absolute temperature, $^\circ\text{K}$
$T_0$	temperature at the inlet of the column, $^\circ\text{K}$
$T_R$	retention temperature, $^\circ\text{K}$
$t$	time, $\text{s}$
$v$	intrinsic velocity, $\text{cm/s}$
$v_0$	$= \alpha v$ , average (superficial) mobile phase velocity, $\text{cm/s}$
$X$	$= \Delta H/RT < 0$ , dimensionless parameter
$X_0$	$= \Delta H/RT_0 < 0$ , dimensionless parameter
$X_R$	$= \Delta H/RT_R < 0$ , dimensionless parameter
$z$	distance coordinate, $\text{cm}$
$z_0$	a position in the column, $\text{cm}$
$\gamma$	Spatial gradient in temperature, $^\circ\text{K/cm}$
$\alpha$	Fractional void space
$\mu'_n$	Normalized $n$ th moments, $\text{s}$
$\mu_n$	Normalized $n$ th central moments

## REFERENCES

1. B. J. McCoy, *Sep. Sci. Technol.*, **14**, 515 (1979).
2. S. Dal Nogare and R. S. Juvet, Jr., *Gas-Liquid Chromatography: Theory and Practice*, Wiley-Interscience, New York, 1962.
3. R. W. Ohline and D. D. Deford, *Anal. Chem.*, **35**, 227 (1963).
4. A. P. Tudge, *Can. J. Phys.*, **40**, 557 (1962).
5. J. C. Giddings, *J. Chromatogr.*, **4**, 11 (1960).
6. M. Abramowitz and J. A. Stegun, *Handbook of Mathematical Functions*, U.S. Government Printing Office, Washington, D.C., 1964, Chap 5.
7. R. B. Bird, W. C. Stewart, and E. N. Lightfoot, *Transport Phenomena*, Wiley, New York, 1960.
8. R. C. Reid, J. M. Prausnitz, and T. K. Sherwood, *The Properties of Gases and Liquids*, 3rd ed., McGraw-Hill, New York, 1977.
9. F. A. L. Dullien, *Porous Media: Fluid Transport and Pore Structure*, Academic, New York, 1979.
10. J. C. Giddings, in *Gas Chromatography*, Academic, New York, 1962, Chap. 5.

*Received by editor September 11, 1981*