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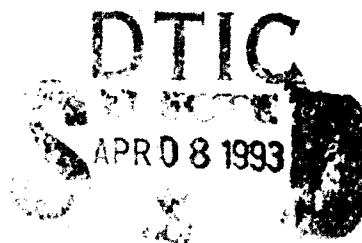
WL-TR-92-2053

AN INVESTIGATION OF RESOLUTION AS
ENCOUNTERED IN VARIOUS CHROMATOGRAPHIC
OPERATIONAL MODES



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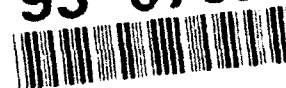
August 1992

FINAL REPORT FOR 01/01/91 - 04/30/92

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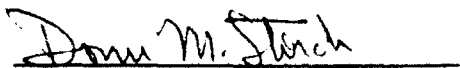
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REPORT DOCUMENTATION PAGE			Form Approved OMB No 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Service, Paperwork Reduction Project (0704-0188), Washington, DC 20503.				
1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE August 1992	3. REPORT TYPE AND DATES COVERED FINAL 01/01/91-04/30/92	
4. TITLE AND SUBTITLE AN INVESTIGATION OF RESOLUTION AS EN- COUNTERED IN VARIOUS CHROMATOGRAPHIC OPERATIONAL MODES			5. FUNDING NUMBERS C F33615-87-C-2714 PE 62204 PR 3048 TA 05 WU 24	
6. AUTHOR(S) Wayne A. Rubey				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) University of Dayton 300 College Park Dayton, Ohio 45469-0132			8. PERFORMING ORGANIZATION REPORT NUMBER UDR-TR-92-53	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Aero Propulsion and Power Directorate Wright Laboratory Air Force Materiel Command Wright-Patterson AFB, Ohio 45433-6563 WL/POSF, Attn: Anderson 513-255-3190			10. SPONSORING/MONITORING AGENCY REPORT NUMBER WL-TR-92-2053	
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution is unlimited			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) An investigation was performed relative to the generation of resolution in isothermal gas chromatography (ITGC), programmed-temperature gas chromatography (PTGC), and a newly evolving technique referred to as thermal gradient programmed gas chromatography (TGPGC). The generation of chromatographic resolution while using open tubular gas chromatographic columns was studied with respect to the influences of dispersion, selectivity, and solute partitioning. Experiments were subsequently conducted to simulate rapid whole column PTGC operation with lengthy open tubular columns. Close agreement between theory and actual generated resolution was obtained during this simulation activity. The major conclusion from this study was that a partition-ratio programming chromatographic operational mode, e.g., TGPGC, possesses considerable promise with respect to rapidly and effectively eluting solutes. Properly implemented TGPGC should be capable of operation whereby selectivity and partitioning are enacted in a near-optimum manner with respect to obtaining maximum useful resolution per unit time.				
14. SUBJECT TERMS Chromatography, Open tubular columns, thermal field programming, rapid analyses, and resolution			15. NUMBER OF PAGES 80	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT UL	

FOREWORD

This report was prepared by the Environmental Sciences Group within the Research Institute at the University of Dayton in Dayton, Ohio 45469-0132. The study reported herein was performed under Task No. 36 of Scholarly Research Program F33615-87-C-2714, which was funded by the Aero Propulsion Laboratory, Wright Laboratory, Wright-Patterson Air Force Base, Ohio 45433-6563. The Project Officer for this effort was Steven D. Anderson (WL/POSF). The experimental portion of this study was conducted during the summer and fall of 1991.

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ACKNOWLEDGMENTS

This investigation was conducted with the help and encouragement of several individuals. Steven Anderson, a research chemist with the Fuels Branch of the Aero Propulsion Laboratory, has enthusiastically encouraged research into advanced analytical chromatographic techniques. Within our immediate research group, Richard Striebich has been a tremendous help with respect to various facets of the TGPGC evolving technology. Also, contributions from and valuable discussions with Barry Dellinger, Dennis Gerdeman, and Lloyd Huff have clarified the approach and direction of this chromatography research. In addition to the above personnel, numerous chromatography researchers (from other organizations) have expressed an on-going interest in the TGPGC operational mode and have helped the author in centering attention upon the key aspects of the various chromatographic analytical techniques. The author is also indebted to Melissa Bertke and Diane Leach for their typing and assistance in preparing this technical report.

CONTENTS

<u>Section</u>		<u>Page</u>
	FOREWORD.....	iv
	ACKNOWLEDGMENTS.....	v
	FIGURES.....	vii
	TABLES.....	ix
1	INTRODUCTION.....	1
2	CHROMATOGRAPHIC RESOLUTION.....	3
	A. Chromatographic resolution expressions.....	3
	B. Chromatographic efficiency effects.....	7
	C. Relative retention aspects.....	7
	D. Influence of partition ratio.....	10
3	RESOLUTION IN VARIOUS GC MODES.....	14
	A. Isothermal gas chromatography.....	14
	B. Programmed-temperature gas chromatography.....	16
	C. Thermal gradient programmed gas chromatography.....	21
4	THEORETICAL ASPECTS AND EXPERIMENTAL APPROXIMATIONS OF RAPID PTGC BEHAVIORS.....	25
	A. Isothermal experiments approximating rapid PTGC behavior.....	2°
	B. Experimental data and results.....	30
	C. Discussions concerning experimental and theoretical observations.....	38
5	CONCLUSIONS.....	42
6	RECOMMENDATIONS.....	44
	REFERENCES.....	46
	APPENDICES.....	50
	A. Conditions for a temperature invariant plate height.....	50
	B. Temperature-sensitive factors and their influence upon ITGC resolution.....	53
	C. Optimum partition ratio.....	56
	D. Behavior of dissimilar open tubular columns in tandem assemblies.....	59
	E. Induced resolution loss as a function of distance for different size transfer tubes.....	64

FIGURES

		Page
1	The graphic measurement of chromatographic resolution. . . .	4
2	Experimentally measured α versus isothermal gas chromatographic temperature	9
3	Partition ratio variation with temperature	11
4	Variation of n-eicosane partitioning ratio with temperature . .	12
5	Relationship of partitioning term of resolution equation and the partition ratio	15
6	Resolution loss relationship as a function of increasing temperature	17
7	Anticipated selectivity behavior in PTGC operation	19
8	Anticipated partition ratio behavior in PTGC operation.	20
9	Comparison of retention ratio versus migration distance for various chromatography operational modes	22
10	Comparison of retention ratio versus migration time for various chromatography operational modes	23
11	Graphs of retention ratio versus relative distance	26
12	Graphing of partition ratio versus migration distance	27
13	The basic GC operating conditions.	31
14	Example copies of raw chromatograms	32
15	Measured resolution versus temperature for thin and thick film OTCs	36
16	Graphs of measured resolution and calculated theoretical behavior of n-tridecane/n-tetradecane pair for a tandem column assembly	37
17	Resolution versus temperature for n-tridecane/n-tetradecane pair	39
A-1	Measured HETP versus ITGC column temperature	52

B-1	Graph of E_{α}/E_k versus ITGC temperature	55
D-1	Sketch of incremental changes along column flowpath	60

TABLES

		Page
1	ACCEPTABLE PROGRAMMING RATES FOR WHOLE COLUMN PTGC OPERATION	18
2	ORIGINAL COLUMNS AND DIFFERENT TANDEM COLUMN ASSEMBLIES.....	29
3	MEASURED RETENTION PARAMETERS AT DIFFERENT COLUMN TEMPERATURES.....	33
4	MEASURED RESOLUTION AT DIFFERENT ISOTHERMAL TEMPERATURES	35

SECTION I

INTRODUCTION

This investigation was undertaken to more clearly understand and define the generation of analyte resolution as encountered in various gas chromatographic (GC) operational modes. Specifically, the GC modes investigated in this particular examination consist of: isothermal gas chromatography (ITGC), programmed-temperature gas chromatography (PTGC), and a new mode known as thermal gradient programmed gas chromatography (TGPGC).

Many of the resolution generation aspects associated with PTGC and TGPGC operation are not well-defined. Specifically, the descriptive behaviors associated with rapid separation forms of PTGC and TGPGC are lacking in detail and definitely need to be addressed further.

It is fortuitous that recent work in several of the non-gas chromatographic procedures have contributed to an increased general understanding of resolution generation in the various GC operational modes. Specifically, it has been found [1-4] that the techniques of gradient elution analysis (GEA), programmed multiple development (PMD), automated multiple development (AMD), and most recently, power programmed field strength in field-flow fractionation (FFF), have much to offer relative to comprehending and more fully describing the generation of resolution in various PTGC and TGPGC operational procedures.

An important observation was made recently concerning the objectives and working intentions [5,6] of the research team that performed the first PTGC separations. This *whole column* thermal programming technique (that is, PTGC) was originally intended [6] to be a procedure that was analogous to GEA operation in liquid chromatography. However, at this point in time, TGPGC is seen as a closer procedural analogy of the GEA methodology than is PTGC. This is an especially meaningful insight, and it is expected that a fuller understanding of chromatographic resolution generation in the TGPGC mode [7-10] will evolve from detailed re-examinations and further study of GEA and related procedures.

The desired goal of much of our gas chromatographic research is to develop an analytical capability for rapidly separating complicated organic mixtures which contain constituents that differ significantly in boiling point or molecular weight. Because of the wide volatility range (see the discussion of the general elution problem in references 11 and 12), it is necessary to perform some form of thermal-field programming to accomplish these GC separations in a useful time frame. Both PTGC and TGPGC do this. However, TGPGC invokes a form of partition-ratio programming which is quite similar in effect to that which occurs [11,13] in GEA. It is this form of k -programming (along with various other attributes of TGPGC) that beneficially impacts the rapid generation of resolution with this especially common type of GC sample, i.e., many constituents and a wide volatility range.

This present study is a brief investigation. A more detailed and comprehensive investigation of resolution as encountered in the various GC modes will be performed in the future.

SECTION 2

CHROMATOGRAPHIC RESOLUTION

Resolution measurements and characterizations have been developed for each of the various types [14] of chromatography, whether the technique involves solutes migrating through very high efficiency columns, or planar chromatographic migration through a variety of layers or particulate media. Closely related resolution characterizations [15] have also been applied in non-chromatographic separation techniques, e.g., in electrophoresis, sedimentation, field-flow fractionation, and various other disciplines of separation science.

A. Chromatographic Resolution Expressions

Throughout the history of elution chromatography, there have been many useful terms employed [16-19] for measuring and characterizing separation behavior that is to some extent related to resolution. Some of these terms are: the effective plate number, the separation factor, the resolving power, the trennzahl (or separation number), the theoretical peak capacity, etc. There have also been many proposed expressions for *chromatographic resolution*, and several of these resolution expressions [19-27] were quite helpful during the early development years of elution chromatography.

The most widely used expression that describes resolution in terms of fundamental chromatographic parameters is that introduced by Purnell [23]. This expression has been discussed and revised somewhat [12,28-32] by various later workers.

The resolution of two adjacent solute-concentration profiles can be graphically measured and expressed as

$$R_{ij} = \frac{2(t_j - t_i)}{w_i + w_j} = R_s \quad , \quad (1)$$

where t_j is the elution time of the j th concentration-zone centroid, t_i corresponds to the i th zone, while w_i and w_j represent the 4σ axial spread (expressed here in time-based units) of the i and j respective zones. This relationship (and measurement method) is shown graphically in Figure 1. The t_m value (i.e., the time for the mobile phase to traverse the column length) is also graphically depicted in this figure.

In high-performance elution chromatography, the concentration profile of a well-behaved migrating solute zone can be assumed to approach a Gaussian distribution, i.e.,

$$y = \frac{1}{\sigma \sqrt{2\pi}} \exp \left(-\frac{x^2}{2\sigma^2} \right) \quad , \quad (2)$$

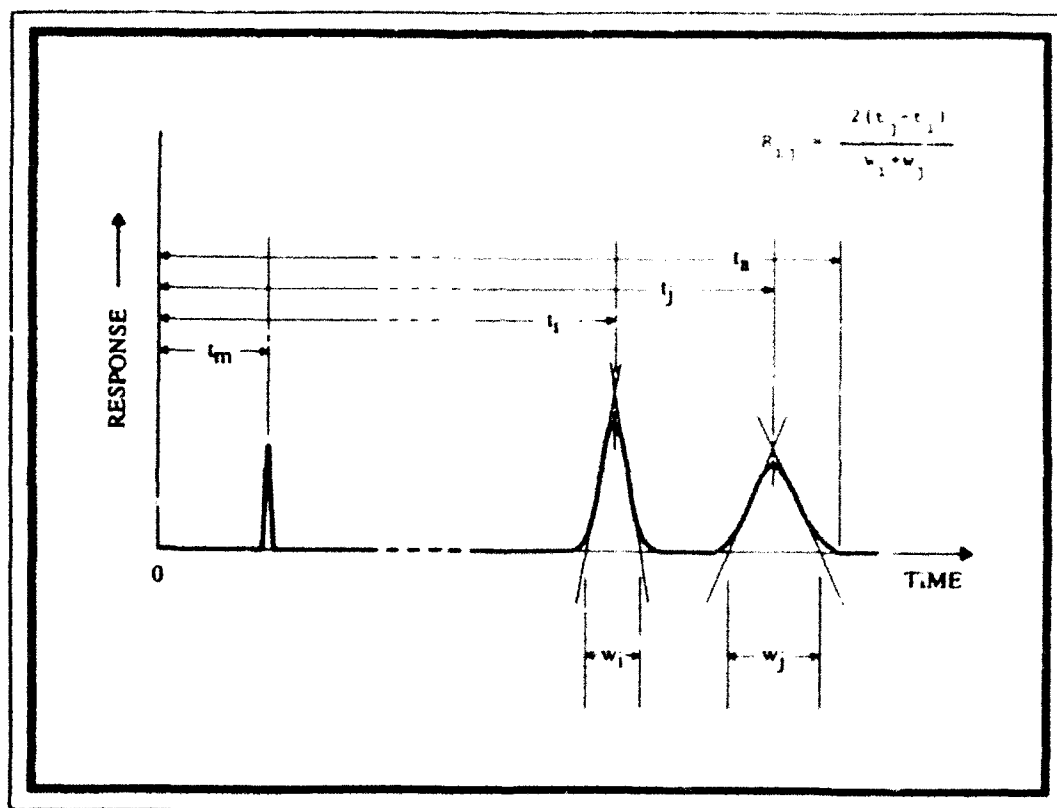


Figure 1. The graphic measurement of chromatographic resolution.

where x and y are the usual Cartesian coordinates, and σ is the profile standard deviation. Also, the number of theoretical plates [33] in ITGC operation can be written for the j th zone as

$$N_j = 16 \left(\frac{t_j}{w_j} \right)^2 = \frac{L}{\hat{H}_j} \quad (3)$$

where L is column length and $\hat{H}_j$ is experimentally measured plate height [34]. It is known that for a Gaussian profile the w_j value is equivalent to $4\sigma_j$.

If the relative retention, α , is expressed in measured time units as

$$\alpha = \frac{t_j - t_m}{t_i - t_m} \quad (4)$$

and if the partition ratio of the j th solute, i.e., k_j , is also expressed in time-measurable quantities according to

$$k_j = \frac{t_j - t_m}{t_m} \quad (5)$$

then from Equations 1, and 3 to 5, chromatographic resolution can be expressed as

$$R_s = \frac{\sqrt{N_j}}{4} \left(\frac{\alpha - 1}{\alpha} \right) \left(\frac{k_j}{1 + k_j} \right) \quad (6)$$

Equation 6 was originally derived [12,23] for ITGC conditions with the assumption that w_i was equal to w_j . A slightly refined version [28] of this R_s equation, which takes into consideration the case where w_i does not equal w_j , is presented as follows:

$$R_s = \frac{\sqrt{N_j}}{2 \left(1 + \frac{w_i}{w_j}\right)} \left(\frac{\alpha - 1}{\alpha}\right) \left(\frac{k_j}{1 + k_j}\right) \quad (7)$$

Even so, the resolution equation which will be used the most throughout this study is written simply as

$$R_s = \frac{\sqrt{\frac{L}{\hat{H}_j}}}{4} \left(\frac{\alpha - 1}{\alpha}\right) \left(\frac{k_j}{1 + k_j}\right) \quad (8)$$

There are two other versions of this basic ITGC resolution equation that need to be mentioned. Equation 8 can be written [29] in terms* of the retention ratio, R_r , as

$$R_s = \sqrt{\frac{L}{16 \hat{H}_j}} \left(\frac{\Delta R_r}{R_{r,i}}\right) \quad (9)$$

and for high-efficiency chromatography involving closely spaced zones, where it can be stipulated that $\hat{H}_j = \bar{H}_j$, the relationship and notation can be simplified to

$$R_s = \sqrt{\frac{L}{16 \bar{H}}} \left(\frac{\Delta R_r}{R_r}\right) \quad (10)$$

Also, an equation for *intracolumn* resolution can be stated as

$$R_s \Big|_z = \frac{\frac{\sqrt{z} \Delta R_r}{4 R_r}}{\left\{ \frac{1}{z} \int_0^z \left[\frac{\partial (\sigma_z)^2}{\partial z} \right] dz \right\}^{\frac{1}{2}}} \quad (11)$$

where z is axial distance along the ITGC column. An expression that is somewhat similar in form to Equation 11 can be descriptive in non-isothermal chromatographic situations.

* The retention ratio, R_r , is an updated version [27,29] of the retardation factor, R_F .

B. Chromatographic Efficiency Effects

The description of chromatographic efficiency is well-defined in gas-liquid chromatography (GLC) when performed using an open tubular column (OTC). The collective contributions of Golay [35], Giddings et al [36], Khan [37], and others [38-40], are such that an especially descriptive characterization of ITGC efficiency behavior is available for a single and uniform* OTC. As a result of this theoretical characterization, much is known, e.g., [30,41,42], about the operational effects of an OTC relative to: stationary film thickness, linear gas velocity, column internal pressure (and associated column lengths), the various physico-chemical factors consisting of gas and liquid diffusion coefficients, partition ratio, gas viscosity, etc., along with the physical size of an OTC, i.e., length and bore diameter.

With respect to the pertinent resolution equations (i.e., the graphic measurement expression, Equation 1, and the chromatographic fundamental expressions, Equations 5, 8 and 11), it is seen that ITGC column efficiency is a measured quantity that represents an average value [36] for the entire chromatographic column length. It will be shown later in this report that a slightly different apparent plate height [27,43] applies for coupled-column arrangements using dissimilar chromatographic members.

C. Relative Retention Aspects

Relative volatility for two adjacent solutes is expressed as α , and this factor appears in the second term of the resolution equation. Traditionally, this particular term is referred to as the *selectivity term*.

It is obvious from Equation 8 that to obtain a chromatographic separation, α must be greater than unity (if only slightly). Relative volatility, or relative retention, has been defined [33] as

$$\alpha = \frac{k_j}{k_i} = \frac{\Delta S_j}{\Delta S_i} \exp \left(\frac{\Delta H_j - \Delta H_i}{RT} \right) = \frac{\gamma_i P_i}{\gamma_j P_j} \quad (12)$$

where P_i and P_j are the saturation vapor pressures of the two components at column temperature T (in K units), γ_i and γ_j are the respective activity coefficients, ΔH_j and ΔH_i are the enthalpies of vaporization, and R is the gas constant. The ΔS values represent the

* A uniform OTC possesses a constant cross-sectional area and a fixed stationary-film thickness throughout the column length.

entropy portions of the free energies of vaporization for the two solutes. For similar molecules, their respective ΔS values are usually very close.

The variation in α with temperature is of interest in this study, and several parties [27,33,44,45] have investigated this behavior. It has been found that the α variation with temperature is strongly dependent upon the chemical nature of the solutes in question, as the change can be bidirectional, linear, nonlinear, and even represented by a power function. The situation is simplified considerably when the solutes are of the same homologous series. In such situations, the selectivity term of the resolution equation is temperature dependent and can be approximated over a suitable temperature range [27] as

$$\frac{\alpha - 1}{\alpha} = \frac{a}{T} - b \quad , \quad (13)$$

with

$$\frac{a}{T} > b \quad , \quad (14)$$

where a and b are inferred constants.

Certain experimental measurements help to clarify this thermal dependency situation, i.e., with respect to a pair of normal paraffin hydrocarbons and a hypothetical solute of a closely related chemical class. Figure 2 shows a graph of measured α versus ITGC temperature. These data were obtained using a special metal OTC that was 20.9-meters in length, by 0.28-mm bore, and contained a 0.25-micron film thickness of cross-linked 5 percent phenylmethyl polysiloxane. Hydrogen was used as a carrier gas.

The decline in α with increasing temperature that is depicted in Figure 2 can be considered as an average case for solute pairs that would be present in complicated mixtures [46-48]. Some solute pairs involving different classes of compounds would exhibit larger declines, while other pairs would show lesser changes of α with T , and even produce sign reversals.

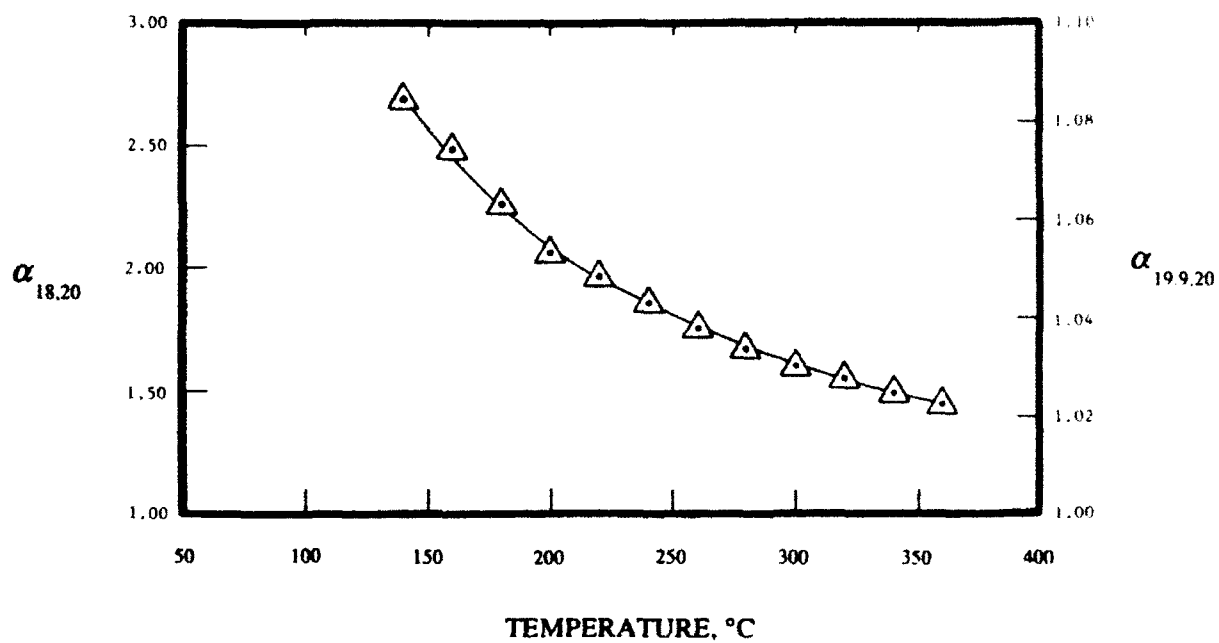


Figure 2. Experimentally measured α versus isothermal gas chromatographic temperature.

The sample used for this set of measurements was a series of n-alkanes dissolved in n-hexane (0.03 percent by volume). Typically, 0.1-microliters of this sample were split injected using a 1 to 60 ratio. The left-side ordinate in Figure 2 shows the α variation with temperature for the C18/C20 hydrocarbon pair. Practically any GC instrumental assembly could easily separate these two compounds, as the observed α values are large. Therefore, a right-side ordinate was constructed which describes α for a compound pair having approximately 1/20th the separation as that of the normal C18/C20 pair, and this latter referenced curve is more representative of a difficult separation of adjacent solutes. The first eluting compound of this difficult pair could hypothetically be a branched paraffin that consistently exhibits a fixed Kovat index of about 1990.

The number of theoretical plates required, N_r , for the separation of the difficult pair of compounds (right-side ordinate of Figure 2) can be calculated through a rearrangement of Equations 3 and 8, and is as follows:

$$N_r = 16 R_{ij}^2 \left(\frac{\alpha}{\alpha - 1} \right)^2 \left(\frac{k_j + 1}{k_j} \right)^2 \quad (15)$$

In the specified case where R_{ij} is unity and k_j is 2.0, it is seen from the α data of Figure 2 that at 140°C a calculated chromatographic efficiency of 6,000 plates is needed. However, for the same resolution value and some partition ratio at a 360°C operating temperature, 71,200 theoretical plates would be required.

Clearly, the α value for a solute pair is an important factor relative to GC resolution, and particularly so in situations of different or changing OTC temperature.

D. Influence of Partition Ratio

The last term of the resolution equation involves the partition ratio (specifically, that of the latter component of the solute pair). The effect of temperature on k is of key importance [49], and relevant experimental data have recently been obtained while using two different OTCs for separating n-alkanes. Figure 3 shows the k variation with isothermal temperature while using a 0.28-mm bore OTC having a 0.25-micron thickness of cross-linked 5 percent phenylmethyl polysiloxane phase. The plots shown here are for normal octadecane and normal eicosane. A wider ranging plot is shown in Figure 4 for n-eicosane. These latter data were obtained with a 12-m by 0.22-mm bore by 0.1- μ m d_f OTC of a similar stationary phase while using a hydrogen carrier at an average cross-sectional fluid velocity $\langle v_m \rangle$ of approximately 74 cm/s. Both of these graphs show the enormous change in k with temperature.

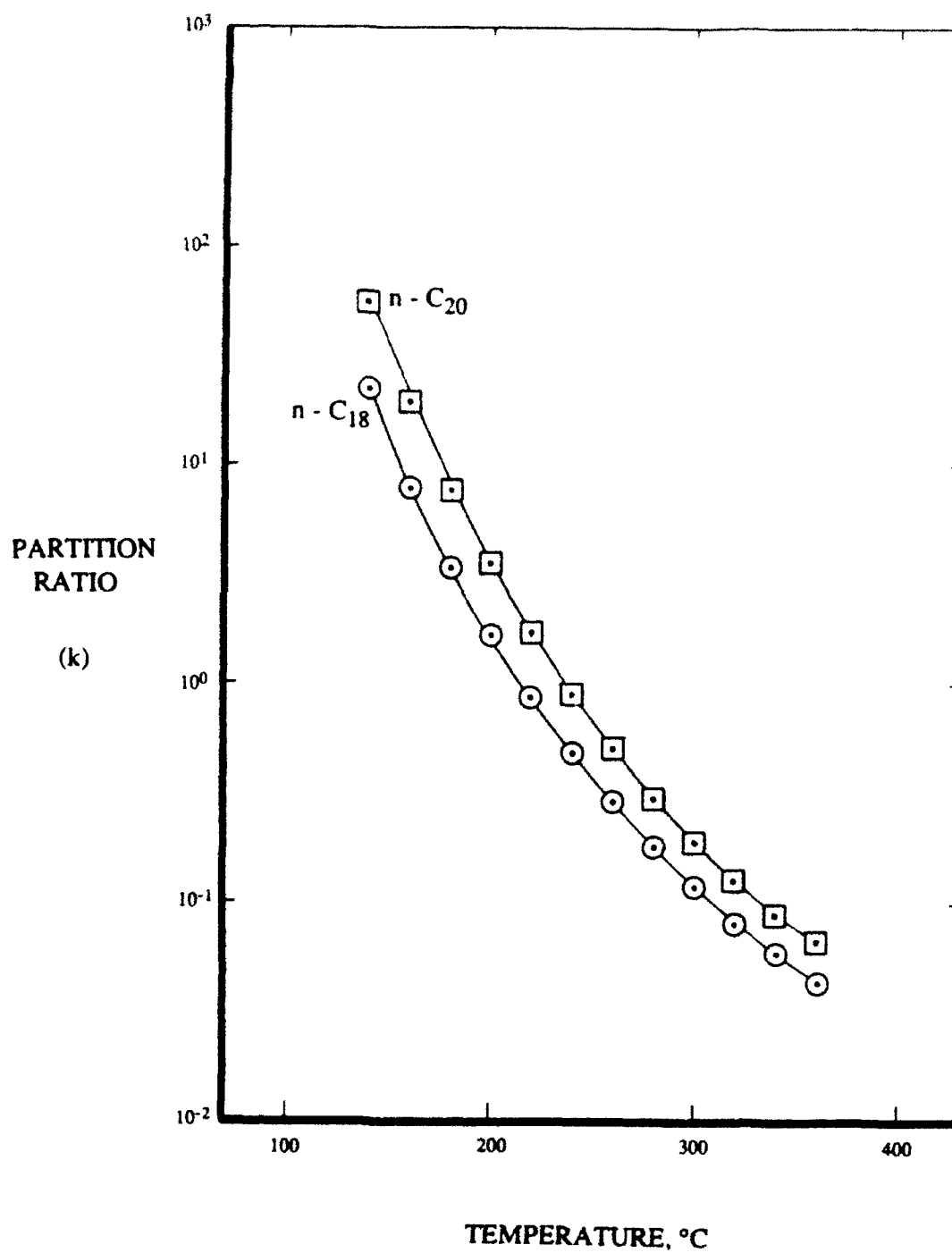


Figure 3. Partion ratio variation with temperature.

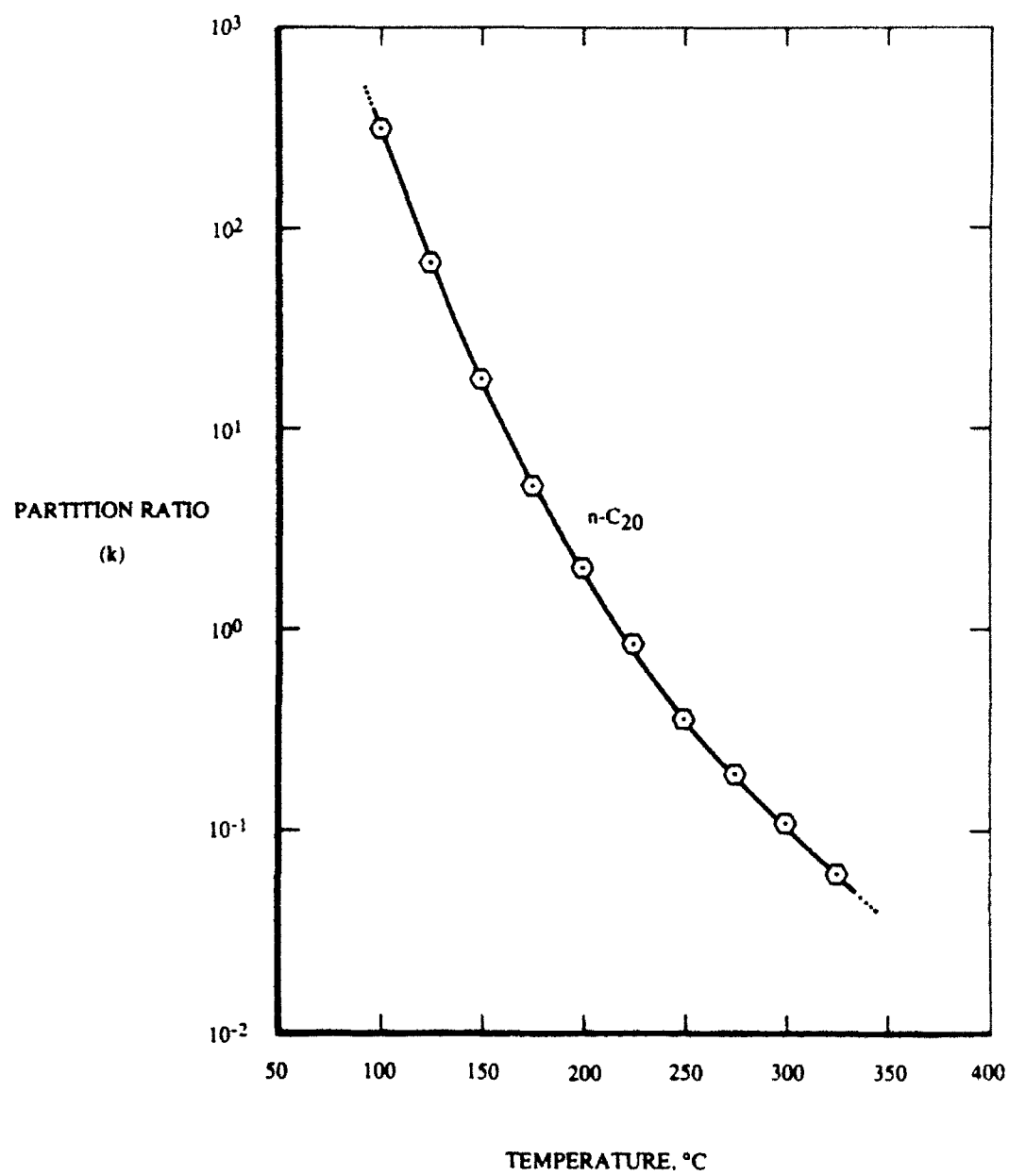


Figure 4. Variation of n -eicosane partition ratio with temperature.

Upon inspection of the basic resolution equation (i.e., Equation 8), it is observed that changes in k can have a large influence upon resolution. In situations involving a large temperature change*, it is this third term of the resolution equation that is usually the most important. It is, therefore, beneficial to think of the partition ratio in terms of an effective value, that is, a k_e value that is either distance-averaged as

$$k_{e,z} = \frac{1}{L} \int_0^{z=L} k \, dz \quad , \quad (16)$$

or time-averaged as

$$k_{e,t} = \frac{1}{t} \int_{t_0}^t k \, dt \quad , \quad (17)$$

for a particular thermally varied chromatographic separation.

* It has been shown through a simple calculation [8] that a moderate molecular weight solute could experience a k change of 10^{10} during a broad-range PTGC analysis.

SECTION 3

RESOLUTION IN VARIOUS GC MODES

GLC theory is highly descriptive for isothermal operation. As stated earlier, OTC chromatographic efficiency is especially well-defined [35-40], and the roles of α and k are well-understood with respect to ITGC resolution [28,30,49].

The situation becomes complicated once there is departure beyond the isothermal GC condition. As an example, consider the behavior of the α value. For a given conventional isothermal GLC column, α is only dependent upon temperature, while in linear PTGC, the effective α value (i.e., α_e) is dependent upon the *whole column* temperature-programming rate, carrier velocity, and the time duration of any isothermal holds. In TGPGC operation, an effective α value is a function of no less than eight variables. Thus, the understanding of resolution simply from the standpoint of the α value becomes much more complicated when column related thermal changes are involved.

Before moving on, it is well to divide the basic chromatographic resolution equation into its customary three parts [12]. The first part is the efficiency portion, and here the desire is to obtain and maintain narrow migrating solute zones. The second part of the resolution expression is related to the difference in migration rates of the two solutes, while the third part involves the extent of solute partitioning between phases. Curiously, it is seen in Equation 8 that the first and third terms apply to the second solute zone, i.e., the j th solute, and that only the α value term (the second part of Equation 8) involves both solutes.

A. Isothermal Gas Chromatography

For well-behaved solutes that do not exhibit excessively large changes in diffusion coefficients (i.e., D_g or D_l) with temperature, it has been observed that column efficiency can remain almost temperature invariant (see Appendix A). Such a constancy in column efficiency requires a carefully selected carrier velocity. Even so, it is known that any residual change of a temperature-induced nature in column efficiency only impacts resolution (as evidenced in Equation 8) to a square-root extent.

The resolution loss associated with increased ITGC temperature as applied to a uniform OTC can be attributed primarily to changes in α and k values. As we have already seen, the α and k values for homologous solutes diminish with increased temperature. When k becomes small, (e.g., at the higher temperatures), it has been found that the partition ratio is by far the more sensitive factor (see Appendix B).

The impact of this partition-ratio variation upon $k/(1+k)$ is seen in Figure 5, and it is remembered from Equation 8 that $k/(1+k)$ is directly proportional to resolution. Consequently, if analysis time was not of concern, and a very long time was permitted for obtaining the separations, then a large k value could be selected. However, apart

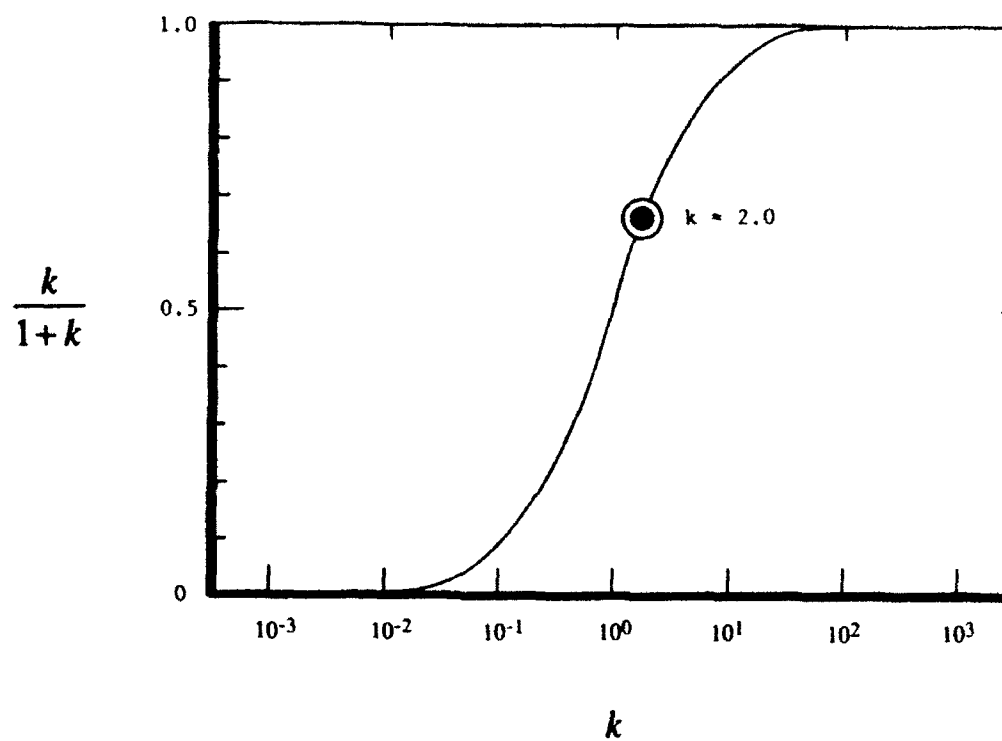


Figure 5. Relationship of partitioning term of resolution equation and the partition ratio.

from an inefficient use of analytical time, this would also produce highly diluted emerging solutes [11,12,30] and the accompanying need for increased chromatographic detection sensitivity.

Ideally, the most desirable achievement is the highest possible production of useful resolution (e.g., $R_s > 0.8$) in a given time [12,50]. To accomplish this task in ITGC, various studies [50-53] have shown that the desired partition ratio falls within the range of 1.5 to 3.0. However, for a single highly permeable and uniform OTC member, the optimum k value (Appendix C) is seen to be exactly 2. Although conducting chromatography with this k value would produce about 67 percent of the maximum attainable resolution, it should in theory provide the maximum analytical information per unit time. Keep in mind that the foregoing applies only for the ITGC mode of operation with fixed values of $\bar{H}_j$ and α . Nevertheless, it is quite probable that somewhat similar localized or effective k values would beneficially apply in the various operational modes where column temperature conditions are changing.

To illustrate the importance of T , k , and α relative to ITGC resolution, an example has been selected where: an OTC generates a constant 100,000 theoretical plates, α is initially 1.085, and column temperature changes from 140° to 360°C. With the use of Equation 8 and the data presented in Figures 2 and 3, it is seen in Figure 6 that a very large loss in resolution occurs as OTC temperature increases. Also, this loss in resolution is accentuated by the α value decline with temperature (observed previously in Figure 2).

B. Programmed-Temperature Gas Chromatography

To obtain high-resolution separations in PTGC while using a sizable length OTC, it is necessary to perform the thermal programming at a relatively low rate. Otherwise, a modest reduction in the selectivity term, $[(\alpha-1)/\alpha]_Z$, and a more severe loss in the partition-ratio term, $[k_j/(1+k_j)]_Z$, seriously diminishes the resultant resolution. The information presented in Table 1 shows the inverse relationship of column length and acceptable programming rate. Figures 7 and 8 are sketches which illustrate the predicted trend in behavior when *whole column* temperature programming is performed at progressively higher rates.

The selectivity curves in Figure 7 show the expected generalized PTGC behavior as contrasted to the fixed values of α (as encountered in ITGC operation). With respect to the partition-ratio curves roughly depicted in Figure 8, the localized or effective k values for various PTGC procedures are compared to a constant partition ratio of 2.0, which again would be indicative of an isothermal GC mode. It is also well to remember that the axial length of an individual migrating zone in PTGC operation continues to increase, and this axial spread is approximately proportional to the square-root of migration distance.

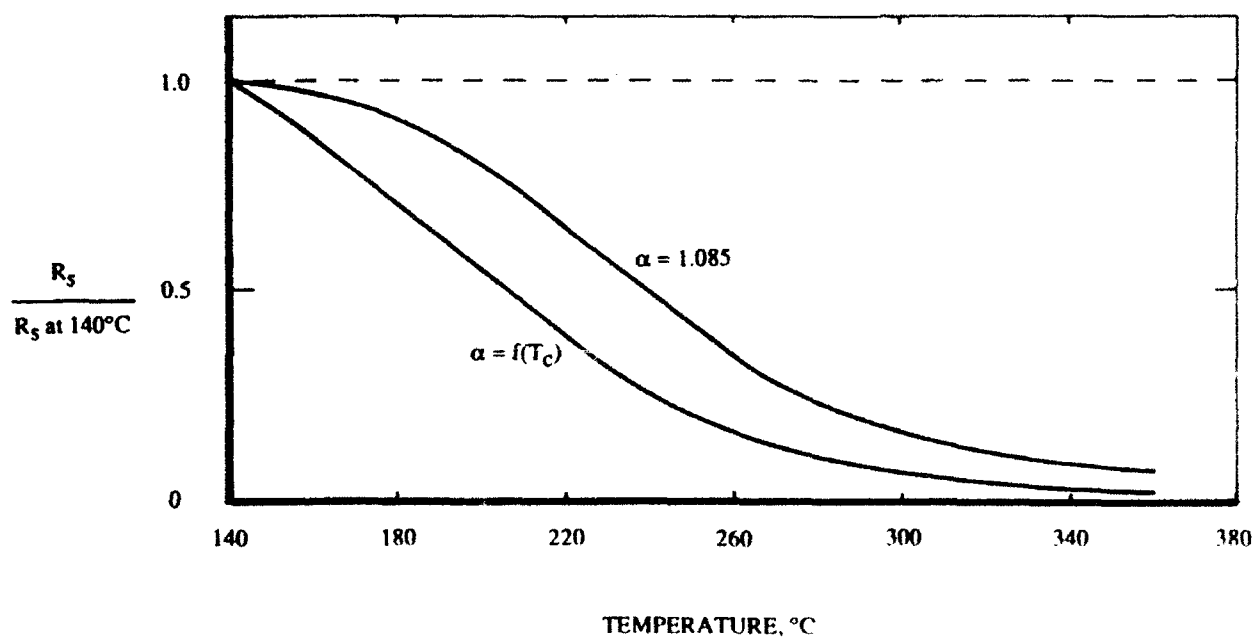


Figure 6. Resolution loss relationship as a function of increasing temperature.

TABLE 1

ACCEPTABLE* PROGRAMMING RATES
FOR WHOLE COLUMN PTGC OPERATION

OTC LENGTH	$\frac{dT_c}{dt}$
(meters)	(°C/min)
1	>50
2	50
5	30
10	15
25	6
50	2
100	1
200	<1

*without incurring significant R_s losses

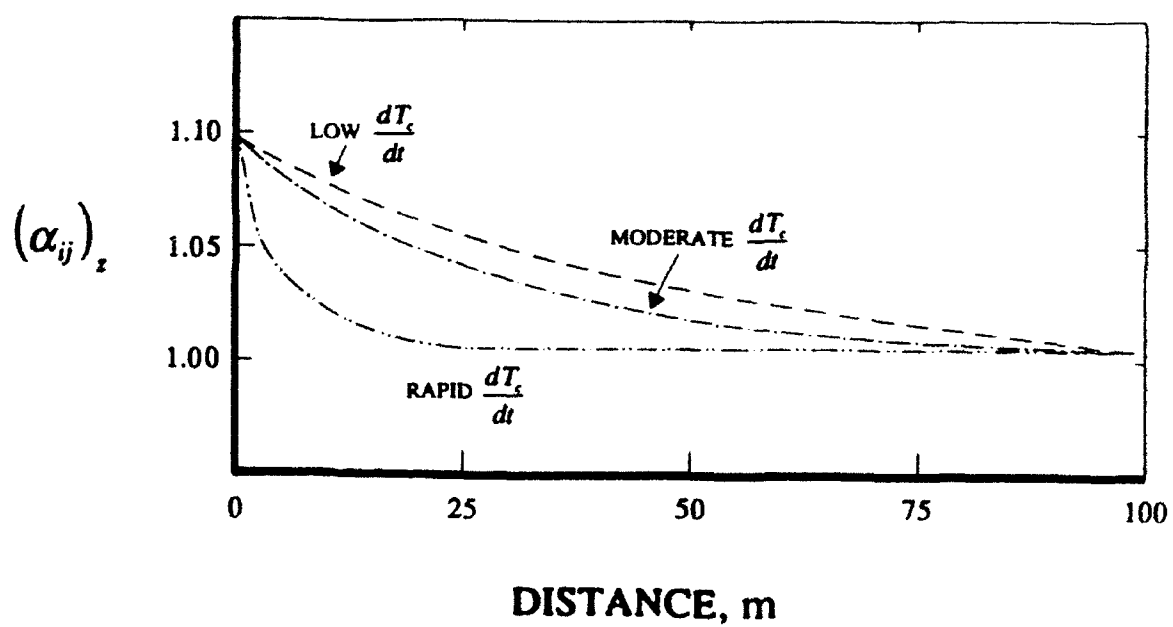


Figure 7. Anticipated selectivity behavior in PTGC operation.

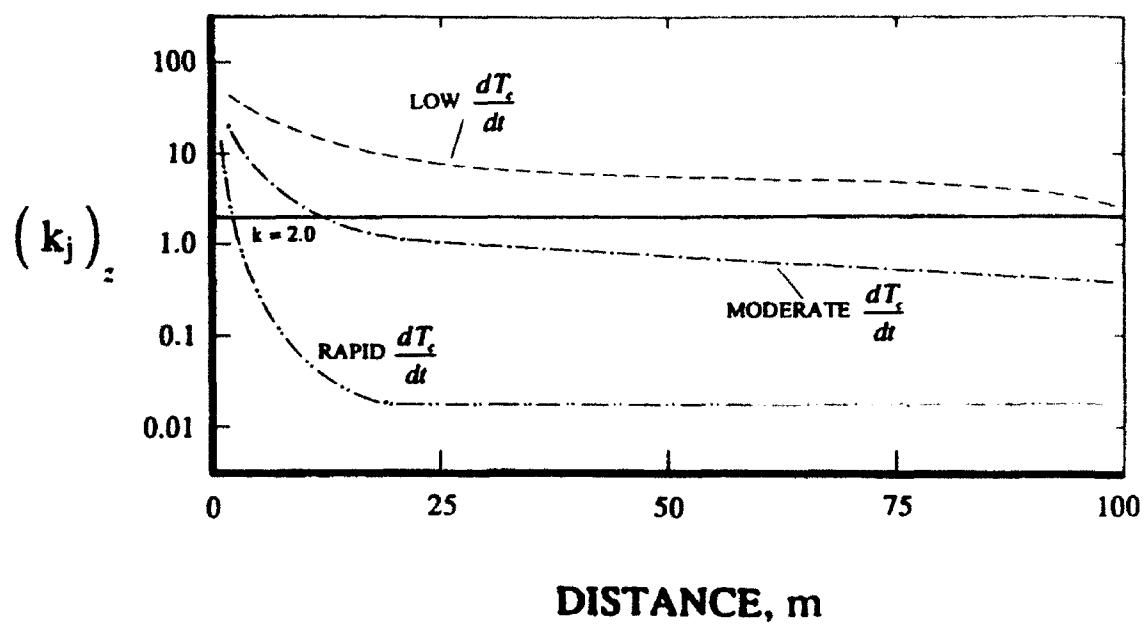


Figure 8. Anticipated partition ratio behavior in PTGC operation.

C. Thermal Gradient Programmed Gas Chromatography

The availability of a well-defined description of resolution for the family of TPGGC operational procedures is still some time in the future. There are many variables associated with such a description, as several more operational parameters are involved [7-10] with this mode of performing GC separations. Specifically, an almost unlimited variety of thermal fields can be applied to an OTC while using the TPGGC operational mode, and many of these procedures invoke [7,8,10] sharp band focusing at the column inlet. In addition, it is known that the axial length of a migrating zone can diminish [7,9,11,54-57] in this mode of operation, and by employing appropriate three-dimensional temperature surfaces [8-10], selectivity terms can feasibly be generated which approach constancy during the entire chromatographic passage. Also during a TPGGC program, a similar situation (i.e., approaching constancy) can develop along the column with respect to the localized partition ratio of individual solute zones. Comparable behavior [9] occurs in gradient elution analysis [1,11-13] which is considered as a desired solution to the "general elution problem" in liquid chromatography.

Another way of viewing and studying the differences in general behavior associated with ITGC, PTGC, and TPGGC is illustrated in Figure 9. Here the retention ratio, R_r , of the migrating solute [8,14,27,29] is graphed relative to column axial distance.* Also, through the use of the following expression:

$$t = \frac{1}{\langle v_m \rangle} \int_{z_1}^{z_2} \frac{dz}{R_r} \quad , \quad (18)$$

the R_r versus z functions can be re-plotted with respect to a time abscissa as seen in Figure 10**, and this provides a slightly different perspective of the same GC behavior.

The horizontal band shown in Figure 9 represents the region of desired operation for several operational procedures. The anticipated TPGGC behavior, with respect to R_r , is relatively distance invariant and remains chromatographically effective after a brief

* The retention ratio, or formerly the retardation factor in column chromatography, has a long history even though it contains a somewhat inverse terminology. Specifically, R_r varies from unity where there is no retention or retardation of a migrating solute, to zero where there is complete retention of a zone.

**The solid-line curves in Figures 9 and 10 apply for a long OTC that is highly permeable, i.e., Δp is assumed to be negligible. For a long OTC of narrow-bore construction (e.g., 100 m by 0.25 mm bore), the operational pressure drop will be at least several atmospheres. Therefore, the dashed-line curve in Figure 10 shows the corresponding behavior for the same rapid PTGC operation.

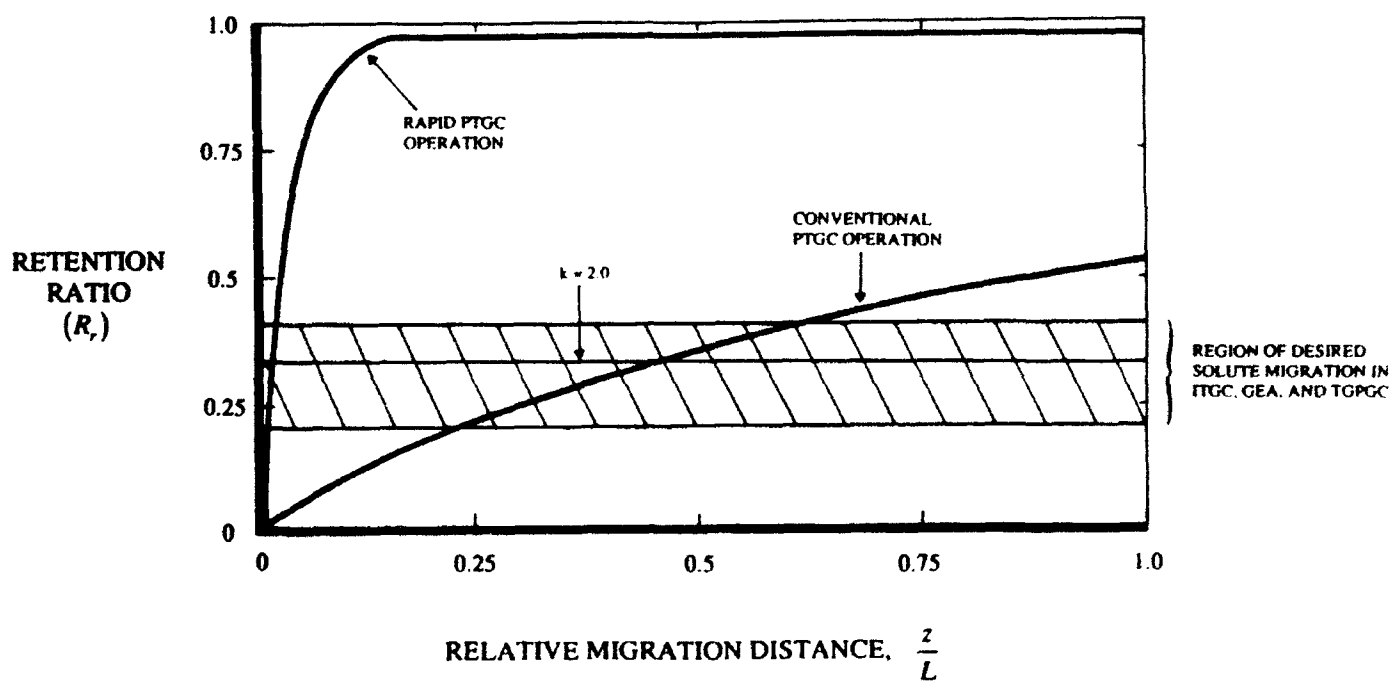


Figure 9. Comparison of retention ratio versus migration distance for various chromatography operational modes.

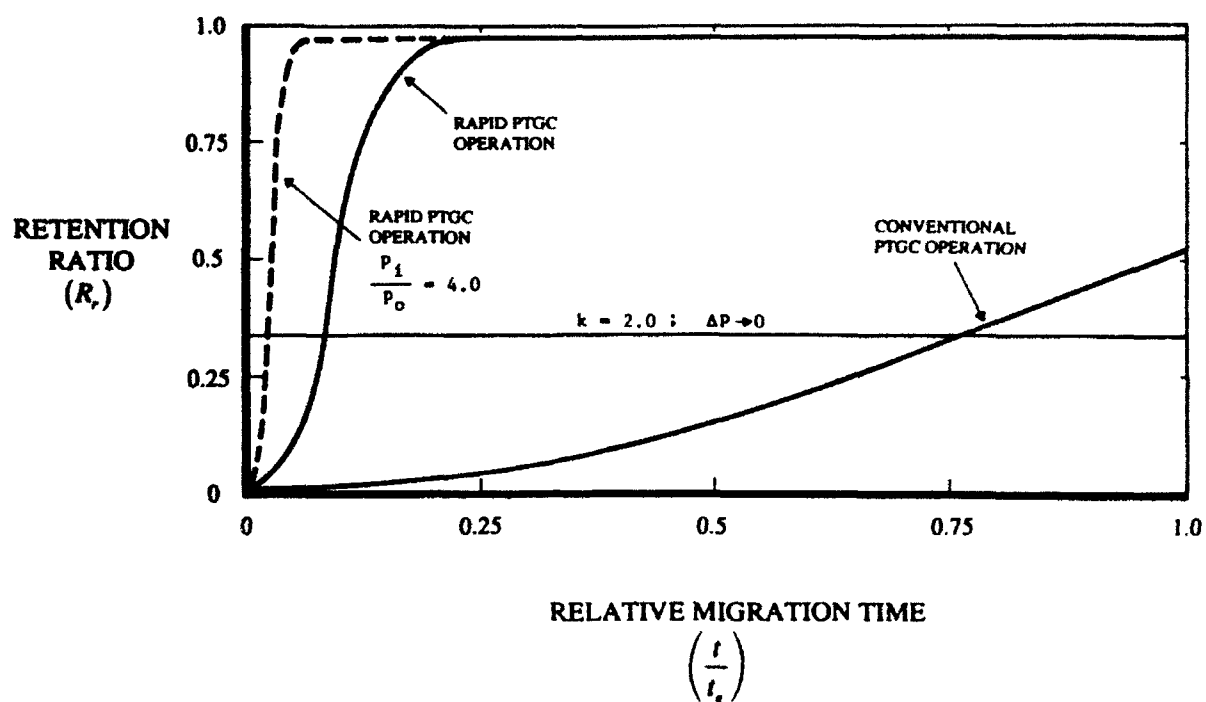


Figure 10. Comparison of retention ratio versus migration time for various chromatography operational modes.

initial solute reception and equilibration period. Such R_f versus distance (or time) behavior should be quite similar to that of GEA in HPLC. However, the sequentially faster rates of PTGC *whole column* temperature increase produce a sharply rising and large retention ratio. In those situations of very large dT_c/dt , the R_f value quickly approaches unity (i.e., a situation where there is an absence of solute/stationary-phase interactions) for the low and moderate molecular-weight solutes. This latter transport through the OTC is not chromatographically effective.

SECTION 4

THEORETICAL ASPECTS AND EXPERIMENTAL APPROXIMATIONS OF RAPID PTGC BEHAVIOR

A more detailed investigation of resolution generated in the various GC modes will surely be addressed in the future. Such a detailed study will undoubtedly take into account the enlightening aspects provided by a renewed inquiry into GEA operation and related [1,4,11-13] partition-ratio programming techniques.

Much of what has been stated thus far, e.g., in Section 3, concerning the resolution obtained with TGPGC and rapid PTGC can be considered (i.e., at this early point in time) to be of a hypothetical and an evolving speculative nature. Conversely, the description of resolution generated in the ITGC mode is theoretically and experimentally quite solid. Also, the well-defined behavior of the ITGC mode is readily demonstrable.

Two points need to be stressed at the present time. First, it seems quite likely that three-dimensional thermal fields, i.e., temperature surfaces [7,9], can be appropriately applied to a conductive OTC in a manner which produces effective and near-optimum α and k values as functions of migration distance or time. The second point that needs to be made (and experimentally demonstrated) concerns the magnitude of the α and k value changes which occur in rapid PTGC operation. In short, it needs to be clearly shown that the diminishing values of α and k are quantitatively the primary reasons for the severe resolution losses encountered in rapid *whole column* PTGC operation with lengthy OTCs.

Through the use of a tandem coupled-column assembly approach (see Appendix D), this rapid PTGC behavior can be experimentally approximated or simulated using the well-established contemporary ITGC technology. Basic chromatographic migration for both ITGC and PTGC can be viewed and studied by comparing the retention ratio of a particular solute zone with column axial distance. Figure 11 shows a graph of R_f versus relative distance, where the two solid-line curves depict single-ramp PTGC solute migration. In this figure, the curve for the rapid PTGC mode of operation would apply for a large programming rate (e.g., 100°C/min) subjected to a lengthy OTC. Correspondingly, the dotted step-function profile represents an ITGC simulation of the rapid PTGC behavior. This step-function profile can also be translated into a partition ratio versus distance relationship as shown in Figure 12. Also, as a distance-averaged effective partition ratio can be as stated in Equation 16, the equivalent $k_{e,z}$ for the step-function profile shown in Figure 12 would be

$$k_{e,z} = \frac{k_1 L_1 + k_2 L_2}{L_1 + L_2} \quad (19)$$

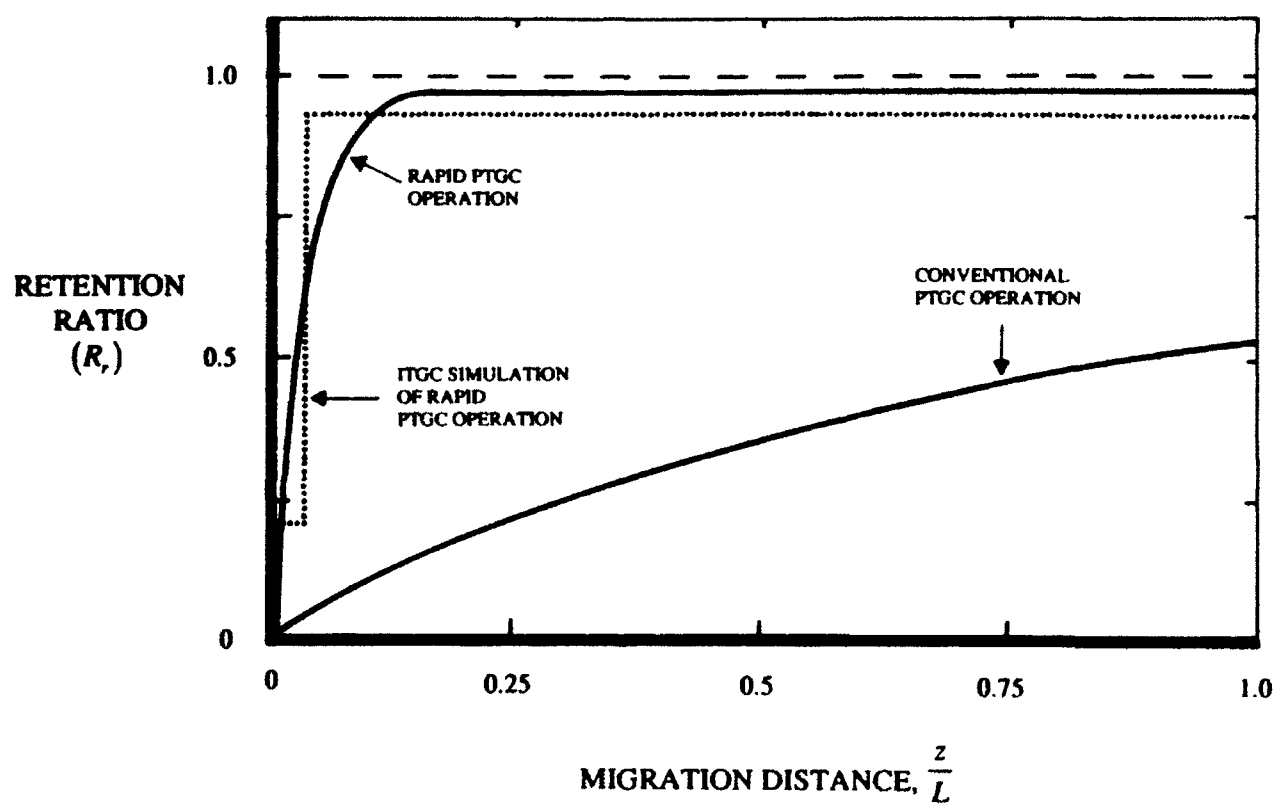


Figure 11. Graphs of retention ratio versus relative distance.

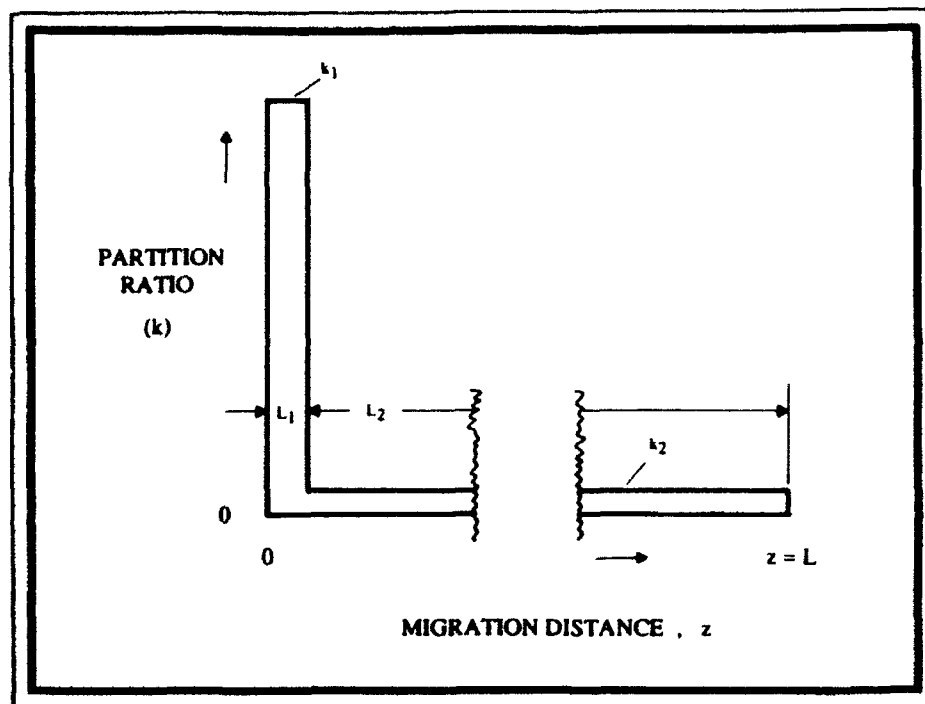


Figure 12. Graphing of partition ratio versus migration distance.

This experimental approach (or simulation procedure) utilizes basically two* well-defined low-pressure drop OTCs. GC operational characteristics of each individual column can be determined through various laboratory measurements, and these OTCs differ primarily in column length and in the thickness of the stationary-phase film. As each laboratory examination is conducted under a specific set of different ITGC conditions, the resolution produced by each individual column and each of the various coupled-column arrangements can be determined. It is then possible to chromatographically simulate with different serial-column assemblies the behavior produced by various rapid PTGC procedures. Measured resultant resolution values produced by these isothermal tandem assemblies can then be compared to calculated resolution, which is obtained from the previously determined characteristics of the individual OTC members.

A. Isothermal Experiments Approximating Rapid PTGC Behavior

Two different types of tubular members were used in this experimental work. They were both megabore fused silica OTCs, however the uniform stationary-phase film thickness, d_f , differed by a factor of approximately 16, i.e., one OTC contained a 0.17-micron film thickness (a GC measured effective value), while the other contained the same stationary phase, but as a moderately thick layer of 2.65-microns.

These very wide-bore OTCs (0.53-mm ID) were specifically selected so that existing pressure drops across the individual columns, or tandem arrangements, would be negligible. Thus, localized chromatographic efficiency would not be influenced [35,43,58] by any in-column mobile-phase pressure effects.

Both original OTCs were examined with respect to their $\bar{H}$ versus $\langle v_m \rangle$ behavior, optimum linear gas velocity, and measured partition ratios for n-tridecane and n-tetradecane at various isothermal temperatures. After obtaining the performance characteristics data for the thin-film megabore OTC, this column was left intact. The other OTC, i.e., the thick-film column, was characterized with respect to its ITGC performance, and then different lengths of this uniform and large d_f OTC were cut to size. Three different tandem arrangements were subsequently assembled using press-tight connections, and the specific information describing the original columns and different tandem column assemblies are presented in Table 2.

Each two-member column assembly was subjected to typical ITGC examinations using a dilute mixture of n-tridecane and n-tetradecane in either methane gas or n-hexadecane. These tests were conducted at different isothermal temperatures. The basic

* Multimember OTC tandem arrangements involving three or more columns could conceivably be assembled to more closely follow the smooth R_F rise associated with rapid PTGC. This would require numerous short OTC segments that contained markedly different film thicknesses. However, as discussed in Section 4.C, the use of such a multi-step function would not alter or enhance further the validity of the simulation procedure.

TABLE 2

ORIGINAL COLUMNS AND DIFFERENT TANDEM COLUMN ASSEMBLIES

Column Designation	Dimensions and Description
Thin-Film OTC	14.3 m Length by 0.53 mm Bore by 0.17 μm Film Thickness of 5% Phenylmethyl Polysiloxane
Thick-Film OTC	8.5 m Length by 0.53 mm Bore by 2.65 μm Film Thickness of 5% Phenylmethyl Polysiloxane
Coupled Column Assembly #1	0.92 m Thick-Film Segment Followed by the 14.3 m Thin-Film OTC
Coupled Column Assembly #2	0.46 m Thick-Film Segment Followed by the 14.3 m Thin-Film OTC
Coupled Column Assembly #3	0.23 m Thick-Film Segment Followed by the 14.3 m Thin-Film OTC

GC conditions are shown in Figure 13, while example copies of some of the raw chromatograms obtained during these examinations are seen in Figure 14.

B. Experimental Data and Results

Gas-phase or liquid samples were quickly inserted (<1 s) into the splitter injector of the chromatograph, and in every case symmetric elution zones were produced for the solutes of interest. When the output data from liquid injected samples were compared to the highly dilute gas-phase sample injections, it was clear that solute overloading was not occurring, and that the same GC efficiency was generated regardless of whether the solutes were contained in methane gas or in n-hexadecane.

The detailed dimensions of the original columns listed in Table 2 allowed the phase ratio, β , to be calculated according to

$$\beta = \frac{V_g}{V_l} = \frac{(r - d_f)^2}{r^2 - (r - d_f)^2} \quad , \quad (20)$$

where V_g and V_l are column gas-phase and liquid-phase volumes, respectively, and r is (in this situation) the radius of the uncoated tubing bore. It is then seen that the ratio of β values for the thin-film column relative to the thick-film OTC was 15.81.

The measured partition ratios for n-tridecane and n-tetradecane are presented in Table 3, which also lists the average α value for this pair of solutes at different isothermal temperatures. These data apply for the thick-film OTC, and again the same trend (α declining with increasing T) is observed as was seen earlier in Figure 2. Also, the average α values shown in Table 3 correspond very closely to those obtained with the thin-film OTC at the respective temperatures. This was as expected from the well-established and time-tested ITGC theory. Agreement to within experimental error was also found for the thin-film column partition ratios and the following relationship:

$$k_{j,2} = \frac{\beta_1}{\beta_2} k_{j,1} \quad , \quad (21)$$

where subscript 1 applies for the thick-film OTC and subscript 2 denotes the thin-film OTC. As these OTCs were static coated [59], it could be safely assumed the 2.65-micron stationary-phase film thickness would not vary to any appreciable extent as a function of column distance. Accordingly, different segment lengths of this assumed uniform thick-film column were subsequently used in preparing the various coupled-column assemblies.

GAS CHROMATOGRAPHIC CONDITIONS

Instrument HP-5890A
 Analyst W. Rubey
 Date 11/9/91
 Column:
 type and description WCOTC
 tubing material Fused Silica
 tubing length Noted m
 tubing inside diameter 0.53 mm
 Stationary phase 5% Phenylmethyl Polysiloxane
 film thickness Noted μ m
 Carrier gas Hydrogen
 inlet pressure ~1.05 abs atmo
 linear velocity ~25 cm sec⁻¹
 outlet flow ~3 cm³ min⁻¹
 Detector:
 type HFID
 range -
 attenuation Noted
 Detector gas flows:
 hydrogen 30 cm³ min⁻¹
 air 350 cm³ min⁻¹
 column outlet supplement 25 cm³ min⁻¹
 Output signal recording:
 full scale read out 1.0 mv
 chart advance rate Noted cm min⁻¹
 Sample:
 description n-Tridecane and n-Tetradecane
 solvent n-Hexadecane
 concentration in solvent ~1.0%
 injection sample size 0.02 μ l
 split ratio ~1 to 60
 Temperatures:
 injector 270 °C
 column:
 initial 190 °C
 initial hold - min
 final - °C
 program rate - °C min⁻¹
 detector 280 °C

Figure 13. The basic GC operating conditions.

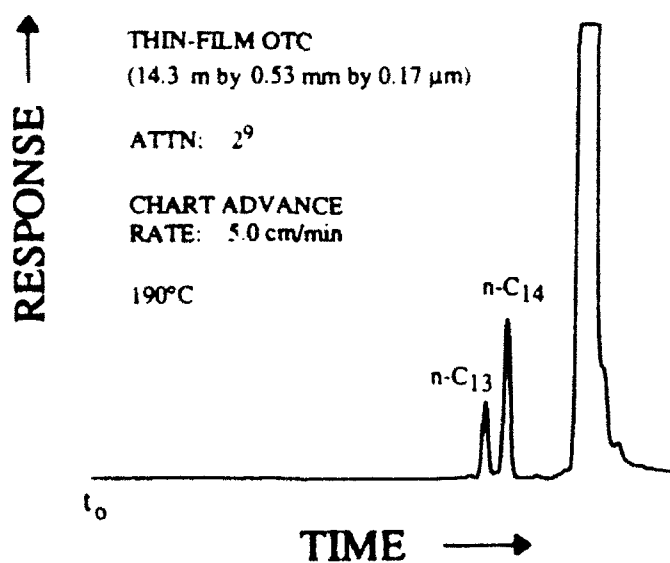
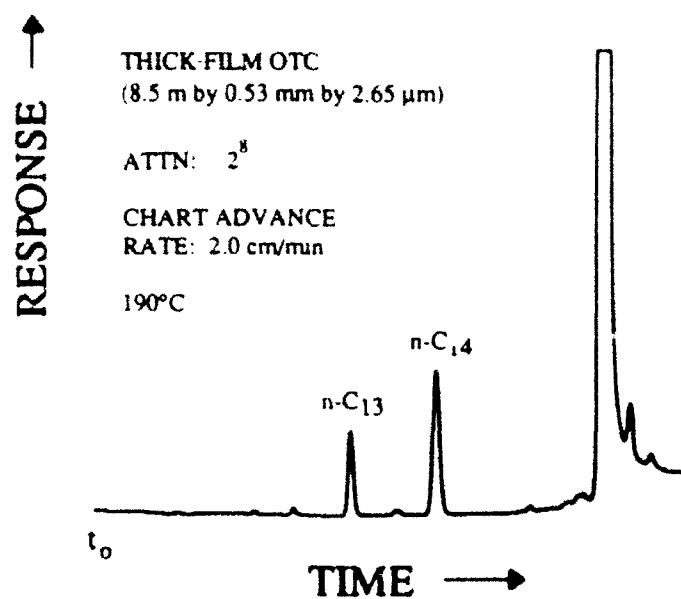


Figure 14. Example copies of raw chromatograms.

TABLE 3

MEASURED RETENTION PARAMETERS* AT DIFFERENT COLUMN
TEMPERATURES

T, °C	$k_{n-C_{13}}$	$k_{n-C_{14}}$	$\alpha_{13,14}$
100	38.5	72.0	1.870
140	9.0	15.5	1.722
150	6.4	10.5	1.641
160	4.7	7.5	1.596
180	2.6	4.0	1.538
190	2.00	2.95	1.475
200	1.55	2.25	1.452
210	1.20	1.72	1.433
220	0.98	1.37	1.398

* Average values obtained with 2.65 μm d_f OTC.

Table 4 shows the measured resolution obtained at different isothermal temperatures while using the five columns, or column assemblies, described previously in Table 2. Plots of measured resolution versus temperature for the original thin-film and thick-film OTCs are shown in Figure 15. Resolution was measured in accordance with the graphic procedure defined by Equation 1, although for closely spaced zones, a slightly revised graphical procedure [60] was used, i.e.,

$$R_s = \frac{t_j - t_i}{1.70 \bar{w}(\frac{h}{2})} \quad , \quad (22)$$

where the average of zone widths at half-height is

$$\bar{w}(\frac{h}{2}) = \frac{1}{2} \left\{ [w(\frac{h}{2})_i] + [w(\frac{h}{2})_j] \right\} \quad . \quad (23)$$

The behavior of the couple-column assembly consisting of the 0.92-m thick-film inlet member, followed by the 14.3-m thin-film OTC, was of special interest relative to rapid PTGC simulation. In this tandem-column assembly (coupled OTC assembly No. 1), the short inlet member contained the same amount of retentive phase as the downstream member, although it represented only 6 percent of the coupled flowpath total length.

Figure 16 shows graphs of measured resolution and calculated theoretical behavior for this tandem-column assembly. The description of theoretical resolution versus temperature for this couple-column assembly was obtained from the following equation:

$$R_s = \frac{\sqrt{\frac{L}{\hat{H}_s}}}{4} \left(\frac{\alpha - 1}{\alpha} \right) \left(\frac{\bar{k}_j}{1 + \bar{k}_j} \right) \quad , \quad (24)$$

which relies upon both previously measured and calculated GC parameters, e.g., α and

$$\bar{k}_j = \left[2 \frac{\beta_1}{\beta_2} k_j \right]_{2.65 \text{ } \mu\text{m OTC}} \quad , \quad (25)$$

TABLE 4
MEASURED RESOLUTION AT DIFFERENT ISOTHERMAL TEMPERATURES*

T, °C	Thin-film OTC 14.3 m by 0.53 mm with $d_f = 0.17\mu\text{m}$	Thick-film OTC 8.5 m by 0.53 mm with $d_f = 2.65\mu\text{m}$	Coupled OTC Assembly #1 0.92 m of thick-film OTC + thin-film OTC	Coupled OTC Assembly #2 0.46 m of thick-film OTC + thin-film OTC	Coupled OTC Assembly #3 0.23 m of thick-film OTC + thin-film OTC
100	15.4	16.4	10.5	11.2	10.8
140	7.7	12.4	7.0	6.5	6.4
150	6.1	---	6.0	5.6	5.4
160	4.3	10.4	---	4.1	4.1
180	2.2	8.2	3.9	2.4	2.5
190	1.67	7.5	---	2.1	2.0
200	1.21	6.5	2.2	1.44	1.32
210	1.01	5.6	1.54	1.18	1.02
220	0.67	4.7	1.29	0.98	0.77
230	---	3.9	---	---	---
240	---	3.0	---	---	---

* R_s data for n-tridecane/n-tetradecane pair.

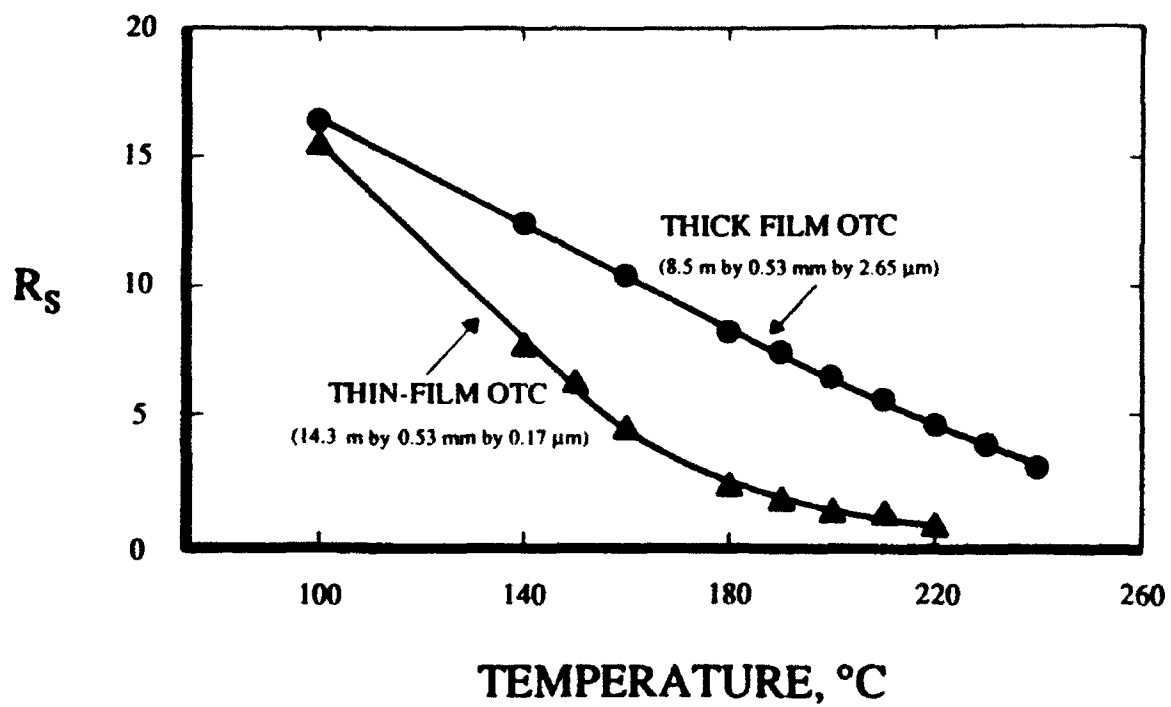


Figure 15. Measured resolution versus temperature for thin and thick film OTCs.

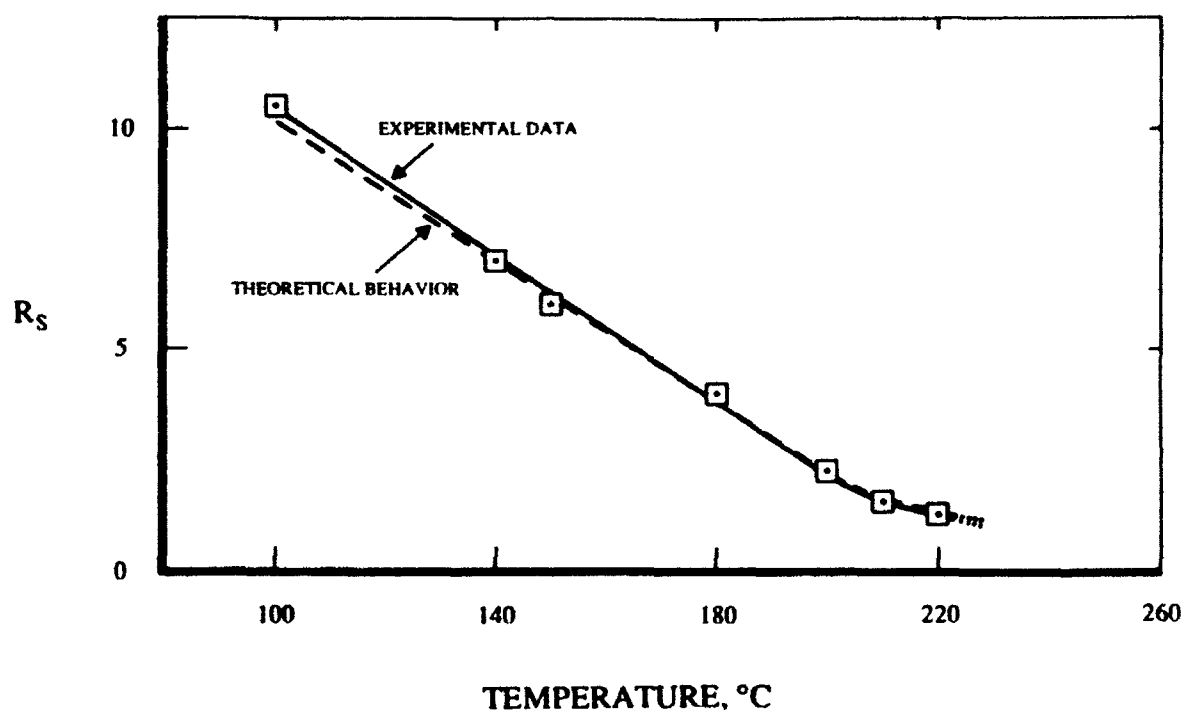


Figure 16. Graphs of measured resolution and calculated theoretical behavior of n-tridecane/n-tetradecane pair for a tandem column assembly.

and the coupled-column efficiency term (from Appendix D), which is written here as

$$\hat{H}_s = \frac{\frac{H_1 L_1}{L \left(\frac{\langle v_m \rangle}{1 + k_{j,1}} \right)^2} + \frac{H_2 (L - L_1)}{L \left(\frac{\langle v_m \rangle}{1 + k_{j,2}} \right)^2}}{\left[\frac{L_1}{L \left(\frac{\langle v_m \rangle}{1 + k_{j,1}} \right)} + \frac{L - L_1}{L \left(\frac{\langle v_m \rangle}{1 + k_{j,2}} \right)} \right]^2} \quad (26)$$

The various H_n values used in Equation 26 were calculated from the previous experimental data (those used in compiling Table 4) through a rearrangement of Equation 8, specifically,

$$H_n = \frac{L}{\left[4R_s \left(\frac{\alpha}{\alpha - 1} \right) \left(\frac{1 + k_j}{k_j} \right) \right]^2} \quad (27)$$

It was also of interest to compare the measured resolution generated by this same coupled-column assembly and the calculated resolution produced solely by the thick-film inlet member when operating separately. Therefore, the resolution for the isolated inlet member was calculated according to

$$R_s]_{L_a} = R_s]_{L_b} \sqrt{\frac{L_a}{L_b}} \quad (28)$$

where OTC length L_a corresponds to the 0.92-m inlet member, and L_b denotes the 8.5-m original thick-film OTC. The associated resolution values for L_b are those listed in Table 4. Figure 17 shows these plotted resolution versus ITGC temperature data.

C. Discussion Concerning Experimental and Theoretical Observations

Before discussing the experimental observations, which include the various GC results and associated theoretical aspects, it seems appropriate to become reacquainted with the intrinsic merits of the major instrumental component that is used in high-resolution gas chromatography. This is, of course, the open tubular separation column. Marcel Golay (the inventor of the OTC) often stated that the single most important attribute of an OTC was its high permeability. He emphasized and characterized this attribute through his studies with the performance index [33,35,49]. In essence, the OTC

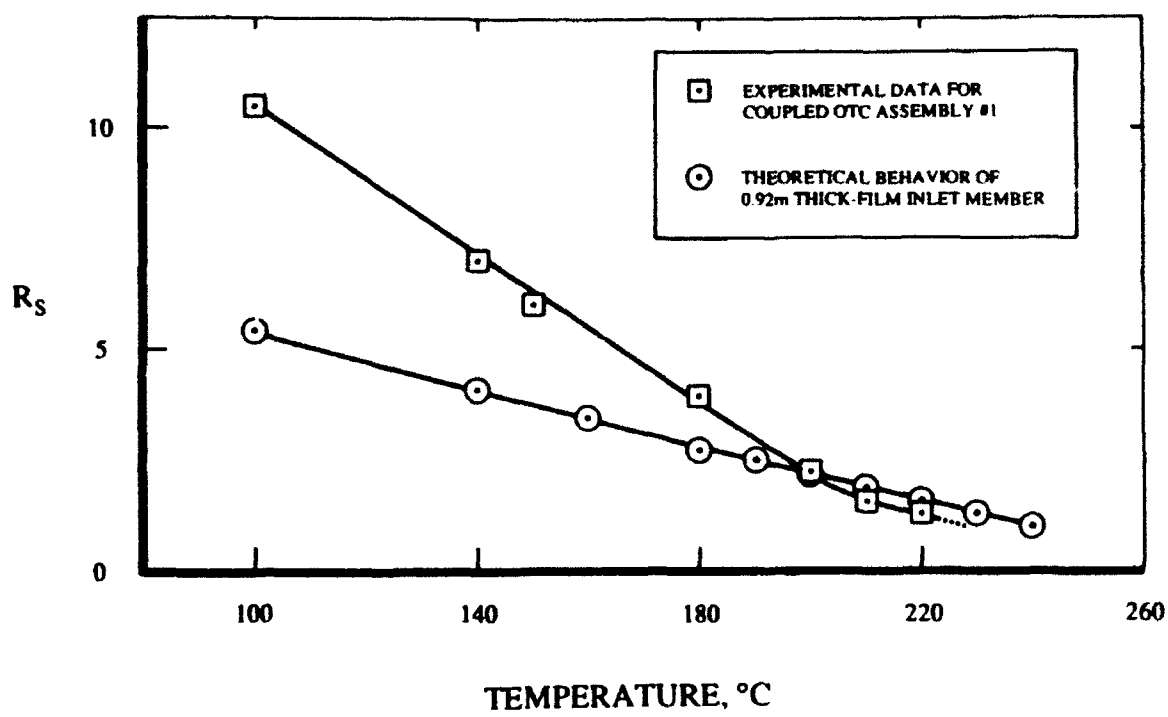


Figure 17. Resolution versus temperature for n-tridecane/n-tetradecane pair.

provides the gas chromatographer with a separation column which can produce high-efficiency separations with an acceptable amount of sample while not encountering excessively large pressure drops, even with lengthy chromatographic flowpaths. These practical attributes are very much in evidence today, that is, more than 35 years after the introduction [35] of the OTC. Modern OTCs range in bore size from approximately 50- up to almost 800-microns. Column lengths typically range from 5- to 150-meters in length, with a 30-meter OTC representing a very common separation column length.

It is obvious that the separation of complicated organic mixtures which differ significantly in solute molecular weight or volatility, cannot be accomplished by ITGC while using a single OTC. These separations require some form of OTC thermal programming. However, an operational disadvantage in conventional PTGC is encountered insofar as longer columns need to be programmed at exceedingly small rates (see again Table 1).

A very important question in GC technology still remains, and that is--"How can the spacial and temporal temperature of an OTC be best moved around to obtain optimal performance?" In this context optimal performance is referred to as -- maximum *useful* analytical resolution per unit time. For lengthy OTCs, it has been contended [9] that the technique of TGPGC is a more ideal procedure for obtaining optimal GC performance.

With the above discussion serving as an additional perspective and background, we can now proceed with the evaluation of the results of this study.

The decline of resolution with increasing ITGC column temperature is clearly shown in the data presented in Table 4 and in Figures 15 and 16. It is particularly noted in Figure 16 that there is good agreement between the experimental data and the theoretical behavior associated with coupled OTC assembly No. 1. Similar behaviors were seen for the coupled-column assemblies which used shorter inlet members, i.e., the 0.23- and 0.46-meter lengths of thick-film OTC. Although these resolution versus temperature data cover only a mild thermal range (not the extremes of temperature as represented by a -60° to + 450°C OTC program), it is anticipated that similar extrapolated behavior would occur over such an expanded thermal working range.

As already observed, calculated and measured resolution agreement for coupled-column assembly No. 1 was quite good; however, more importantly, the severe resolution loss which occurs with increasing ITGC temperature can be attributed to the significantly different GC behaviors taking place within the two different sections of the serial column assembly. This overall coupled column behavior is doubly important as it is a simulation of the activities occurring in very rapid PTGC. For example, it is seen from the data presented in Figures 16 and 17 that the short inlet member functioned appropriately and contributed a significant amount of chromatographic resolution. However, as the solute zones emerged from the thick-film OTC first member, the solute molecules experienced very little interaction thereafter with the stationary phase (especially at the higher temperature), and thus, their transport through the second member of the tandem assembly was chromatographically non-productive. As seen in Figure 17, this latter transport appears even to detract from the already obtained

intracolumn resolution. In other words, the downstream member was functioning as a transfer tube and not as a chromatographically effective separation column. Specifically, the k and $(\alpha-1)$ values for the high-temperature migration through the latter member were quite small. Therefore, for operation as depicted in Figure 11, it would seem that for lengthy OTCs that experience a very rapid excursion to a high temperature, it is possible for *intracolumn* resolution to crest and then diminish as a function of column length (e.g., transfer tube effect).

The data presented in Figures 16 and 17 indicate that the losses in α and k are the main factors for reduced resolution in rapid PTGC, as the resultant performance agrees with the established ITGC behavior for coupled-column assemblies. While obtaining the theoretical data presented in Figure 16, it was observed that although the $\bar{H}_S$ values are larger than the average of individual $\bar{H}$ values for the OTC members, the impact of this efficiency change upon resultant resolution was relatively insignificant.

Another point which needs to be discussed concerns what portion of the theoretical maximum resolution is usually attained in common practice while using conventional ITGC and PTGC modes of operation. In light of Equation 8, Figure 5, and the significant decline in average selectivity with temperature, it is probably fair to say that most practical GC separations are currently performed while using less than 50 percent of the maximum GC resolving capability that exists within the typical GC instrumental assembly. This practice is certainly justified, as it is most inefficient (timewise) to perform analytical separations at k values that are approaching 100 where, in theory, there should be 99 percent of the maximum resolution. In PTGC practice, effective k values are usually much lower than 10, and of course, the typical α value for a pair of solutes (on average) would be considerably less than that experienced at the significantly lower column temperature where k is approaching 100. Therefore, when we are targeting for a partition ratio of 1.5 to 4 for optimal solute zone migration (e.g., in ITGC, GEA, and TGPGC), it must be realized that we are probably losing half of the potential resolution that the particular chromatographic system is capable of generating. However, it must be remembered that the key goal is the generating of the maximum useful resolution per unit time, and not strictly maximum resolution.

It is important to note as shown in Figure 17, that most of the higher-temperature chromatographic resolution has been accomplished by the short inlet member. It matters little whether this chromatographic resolution was obtained by a close fitting multi-step function simulation arrangement or by a single moderately thick-film member (see Figures 11 and 12) that was efficiently functioning in the tandem column assembly. Either simulates the rapid PTGC behavior through the use of a dissimilar inlet member which is a small fractional length of the entire flowpath. The downstream member of such a tandem column assembly (with its thin film or large R_F) contributes very little to subsequent resolution. Indeed, operation at higher temperatures (as shown in Figure 17, and as discussed in Appendix E) indicates that lengthy migration at a relatively high retention ratio detracts from already obtained resolution.

SECTION 5

CONCLUSIONS

This study has produced several conclusions concerning the generation of chromatographic resolution while employing the ITGC, PTGC, and TGPGC modes of operation.

1. The analysis of relatively simple organic mixtures, which contain constituents that do not differ significantly in volatility, can be accomplished most readily by using ITGC. For such analytical situations, a large amount of resolution per unit time can be generated.
2. Organic mixtures which contain constituents that have significantly different volatilities obviously require some form of time-programmed GC thermal field variation.
3. It is widely accepted that for conventional temperature programming (i.e., PTGC operation), the longer the OTC, the lower the thermal programming rate must be. It has been observed that although very short OTCs can theoretically be programmed quite rapidly without a significant loss of resolution, it is necessary to resort to especially small programming rates with the longer OTCs, if resolution is not to be sacrificed. Indeed, it can be concluded that, for very long OTCs, fractional values of *whole column* programming rate ($<1^{\circ}\text{C}/\text{min}$) are needed; otherwise, the high-resolution and associated analytical merits provided by using lengthy OTCs are negated.
4. The major disadvantages associated with the required use of slow PTGC programming rates while using lengthy OTCs are that analysis times become quite long (i.e., time durations in hours), and the emerging solute zones are axially dispersed, and thus, low in mobile-phase concentration.
5. A factor analysis of the basic ITGC resolution relationship has produced the following three distinct findings:
 - (a) It has been determined that the dispersion effect, $f(\bar{H})$, can be almost insignificant with respect to its influence upon resolution at different column temperatures.
 - (b) The selectivity effect, $f(\alpha)$, for a homologous series of solutes was found to decrease by a factor of about 1.5 to 2 over an ITGC operational range of 100°C . Consequently, the selectivity effect does have a significant impact upon the loss of resolution with increasing temperature.

- (c) It is the partitioning effect, $f(k)$, with its diminishing k value which most strongly causes the loss of chromatographic resolution in ITGC at the extreme high temperatures. Essentially, it is the dominant term with respect to resolution loss as a function of temperature.
6. When a lengthy column is subjected to a rapid PTGC program, it is seen that the vast majority of the column length cannot function in a chromatographically effective manner. The low and intermediate molecular-weight species will experience only gas-phase transport through the major portion of the flowpath, thus defeating the primary intent of using lengthy OTCs with their attendant high resolving capabilities.
 7. This study indicates that a better procedure for the heating (or thermal working) of a lengthy OTC is represented by the TGPGC mode of operation, wherein approximately constant retention ratio migration can be enacted throughout the entire chromatographic flowpath. This mode of operation addresses the "general elution problem" in a more economical and rapid analysis manner. TGPGC appears to possess the inherent properties for providing increased analytical information per unit time, when analyses are conducted with lengthy OTCs and the sample contains a complex and wide-molecular-weight range of constituents.
 8. For laboratories that work with relatively similar highly complex samples, multi-dimensional gas chromatography (MDGC) has much to offer. Therefore, it can be concluded that the conducting of MDGC analyses where separations are performed using sequenced TGPGC procedures should be especially promising.
 9. It is indicated that TGPGC analyses (while using long OTCs) can be conducted in relatively short analysis times, as the serious constraint of a very small thermal programming rate does not accompany the TGPGC operational mode. Therefore, the use of very long columns can be anticipated for future TGPGC operations.

SECTION 6

RECOMMENDATIONS

Several research and development activities are recommended as a consequence of this theoretical and experimental investigation. Currently, there is a growing desire within the gas chromatography community to obtain increased analytical information per unit time. Future analyses will undoubtedly be performed using long OTCs that operate over an extended thermal range. Accordingly, the following recommendations can be set forth to advance the analytical capability for expedient GC and GC-MS analyses of organic mixtures that contain constituents which cover a broad volatility range.

- The application of a partition-ratio programming technique, such as TGPGC, should receive serious consideration as an alternative operational mode. It can serve as a much needed rapid substitute analysis procedure for conventional programmed-temperature gas chromatography.
- An in-depth investigation needs to be conducted concerning the similar theoretical behaviors of GEA (that is, HPLC solvent programming) and k-programming in TGPGC. This study should cover the broad range of anticipated OTC dimensions.
- An aggressive program ought to be initiated where the major objective is to identify, and then evaluate, those instrumentally important factors in TGPGC. Also, another meaningful activity would be to establish which operational aspects are of minor or insignificant concern relative to implementing this new GC mode.
- A modular and versatile bench-scale TGPGC experimental apparatus should be constructed and continually updated so that actual operational information can be acquired with respect to the various detailed instrumental requirements and procedures needed for conducting TGPGC analyses.
- A design effort and companion testing program should be initiated for developing the key and unique components needed in a TGPGC system. Primary consideration should be given to the development of versatile column sheath assemblies and the associated control components needed for generating a variety of TGPGC temperature surfaces.

In addition to the above recommendations, a considerable amount of attention and forethought ought to be given to the activities that occur upstream of the TGPGC column assembly. Sample preparation processes and various instrumental inlet hardware aspects would need to be addressed. Likewise, considerable study and forethought needs to be directed at the components and operations that are downstream of the separation column. Specifically, attention and design reconsideration needs to be given to: detection devices,

associated electronics, data handling facets, and various instrumental hyphenated techniques.

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APPENDICES

Appendix A

Conditions for a Temperature Invariant Plate Height

As of this writing, the most thorough description of observed plate height for a gas-liquid chromatographic OTC which is functioning in an isothermal instrument [35-40], can be stated as

$$\begin{aligned} \hat{H}_j = & \frac{2D_g JG}{\langle v_m \rangle} + \frac{r^2(1 + 6k_j + 11k_j^2) \langle v_m \rangle G}{24 D_g J(1 + k_j)^2} + \\ & \frac{2k_j d_f^2 \langle v_m \rangle}{3D_l(1 + k_j)^2} + \frac{2k_j d_f \langle v_m \rangle}{k_d(1 + k_j)^2} + \frac{\tau_d^2 \langle v_m \rangle^2}{L(1 + k_j)^2} \end{aligned} \quad (A1)$$

where $\hat{H}_j$ is the observed plate height* for solute j , D_g is the gas-phase binary diffusion coefficient at column outlet pressure, J is the gas-phase compressibility correction factor, G is the Giddings decompression factor, $\langle v_m \rangle$ is the mobile-phase average velocity, r is the radius of the OTC, k_j is the partition ratio of solute j , d_f is the stationary-phase film thickness, D_l is the stationary-phase diffusion coefficient, k_d is the interfacial desorption rate constant, τ_d is the combined time-response constant, and L is the length of the OTC. The temperature-dependent variables appearing in Equation A1 are: D_g , k_j , J , G , $\langle v_m \rangle$, D_l , and k_d .

If sufficiently rapid injection and detection subsystems are used, and providing that d_f is quite small (or, better yet, that the phase ratio, β , is very large, e.g., >200), then the last three terms of Equation A1 can be neglected without introducing appreciable error. Also, if the OTC is assumed to be highly permeable, then J and G will approach unity and can thus be considered as inconsequential factors in this situation. The temperature-sensitive factors that still remain in the now simplified $\hat{H}_j$ expression are: D_g , k_j , and $\langle v_m \rangle$. Therefore, we can write

$$\frac{\partial \hat{H}_j}{\partial T} = \frac{\partial \hat{H}_j}{\partial D_g} \frac{\partial D_g}{\partial T} + \frac{\partial \hat{H}_j}{\partial \langle v_m \rangle} \frac{\partial \langle v_m \rangle}{\partial T} + \frac{\partial \hat{H}_j}{\partial k_j} \frac{\partial k_j}{\partial T} \quad (A2)$$

Upon examination of each term in Equation A2 under conditions where: 1) a solute is migrating through an ITGC thin-film and narrow-bore OTC, 2) with the use of a hydrogen carrier gas, 3) at a $\langle v_m \rangle$ which is slightly less than optimum, and 4) over a suitable test temperature range, it is found that the thermal-induced change in $\hat{H}_j$ can be

* This $\hat{H}_j$ expression does not address any surface adsorptive phenomena [61,62], or the recently described adsorptivity by Grob, et al. [63].

small (see as an example Figure A-1). Typically $\Delta \bar{H}_j$ is less than $0.1 \bar{H}_j$. Furthermore, the changes in $\bar{H}_j$ (at this selected carrier velocity) produced by an increasing D_g or k_j are positive, while negative changes in $\bar{H}_j$ are experienced for a larger value of $\langle v_m \rangle$.

Hence, a GC condition can be established where $\bar{H}_j$ remains almost constant over a broad range of ITGC temperature. This condition is facilitated by making an appropriate selection of $\langle v_m \rangle$.

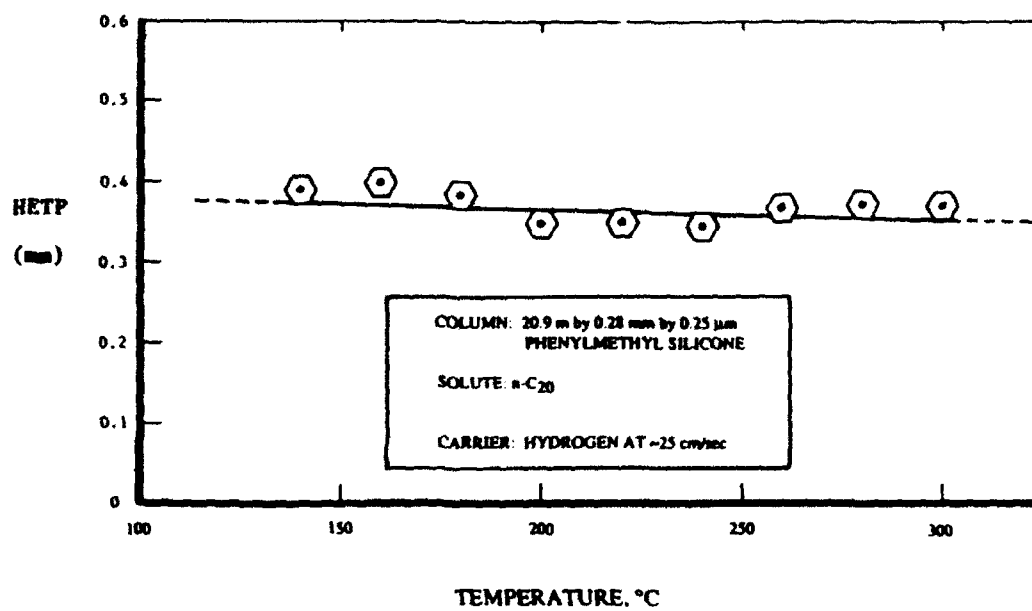


Figure A-1. Measured HETP versus ITGC column temperature.

Appendix B

Temperature-Sensitive Factors and Their Influence Upon ITGC Resolution

In ITGC operation, the *intracolumn* resolution of two adjacent solute zones has been equated as

$$R_s]_z = \frac{\sqrt{\frac{z}{\hat{H}_j}}}{4} \left(\frac{\alpha-1}{\alpha} \right) \left(\frac{k_j}{1+k_j} \right) = f(z, \hat{H}_j, \alpha, k_j) \quad (A3)$$

where the *j* subscript designates the latter of the two zones. For a uniform column of length *L*, an incremental change in resolution relative to ITGC temperature can therefore be expressed as

$$\frac{\Delta(R_s]_L)}{\Delta T} = \left(\frac{\partial R_s}{\partial \hat{H}_j} \right) \left(\frac{\Delta \hat{H}_j}{\Delta T} \right) + \left(\frac{\partial R_s}{\partial \alpha} \right) \left(\frac{\Delta \alpha}{\Delta T} \right) + \left(\frac{\partial R_s}{\partial k_j} \right) \left(\frac{\Delta k_j}{\Delta T} \right) \quad (A4)$$

Through appropriate carrier velocity selection, $\hat{H}_j$ can be such that it is essentially constant over substantial differences in ITGC column temperature (see Appendix A). Although α and k_j are carrier velocity invariant in ITGC, both of these factors are temperature dependent. Therefore, an incremental change in R_s can be expressed in simplified form as

$$\Delta R_s = \frac{\partial R_s}{\partial \alpha} \Delta \alpha + \frac{\partial R_s}{\partial k_j} \Delta k_j \quad (A5)$$

or

$$\Delta(R_s]_L) = \frac{\sqrt{\frac{L}{\hat{H}_j}}}{4} \left\{ \left(\frac{k_j}{1+k_j} \right) \left(\frac{\Delta \alpha}{\alpha^2} \right) + \left(\frac{\alpha-1}{\alpha} \right) \left[\frac{\Delta k_j}{(1+k_j)^2} \right] \right\} \quad (A6)$$

With the use of the experimental data presented in Figures 2 and 3, along with Equation A5, the relative influence of the α term (for solutes of the same chemical class) and the k_j term upon R_s can be compared over a significant temperature range. The relative effect of each term can be assessed using the following ratio

$$\frac{E_{\alpha}}{E_k} = \frac{\left(\frac{\alpha-1}{\alpha}\right)_T \left(\frac{k_j}{1+k_j}\right)_{T_0}}{\left(\frac{\alpha-1}{\alpha}\right)_{T_0} \left(\frac{k_j}{1+k_j}\right)_T} \quad (A7)$$

where T_0 is an initial reference temperature. Equation A7 permits the relative impact of the two terms upon R_s to be assessed with respect to ITGC operating temperature.

In practically every case involving PTGC and TGPGC operation, the distance-averaged partition ratio, i.e., $k_{e,z}$, is smaller than 10. Therefore, a graph of E_{α}/E_k versus temperature for the usual operating region where $k_j < 10$ has been constructed from the experimental data presented in Figures 2 and 3. This graph is shown in Figure B-1.

Thus, it is seen that with respect to resolution as expressed in Equation 8, the partition ratio is progressively the more sensitive factor as k_j diminishes. Furthermore, it is apparent from Figure B-1 that the partition-ratio term of the ITGC resolution equation is especially dominant (and even R_s limiting) when k_j becomes a small fractional value.

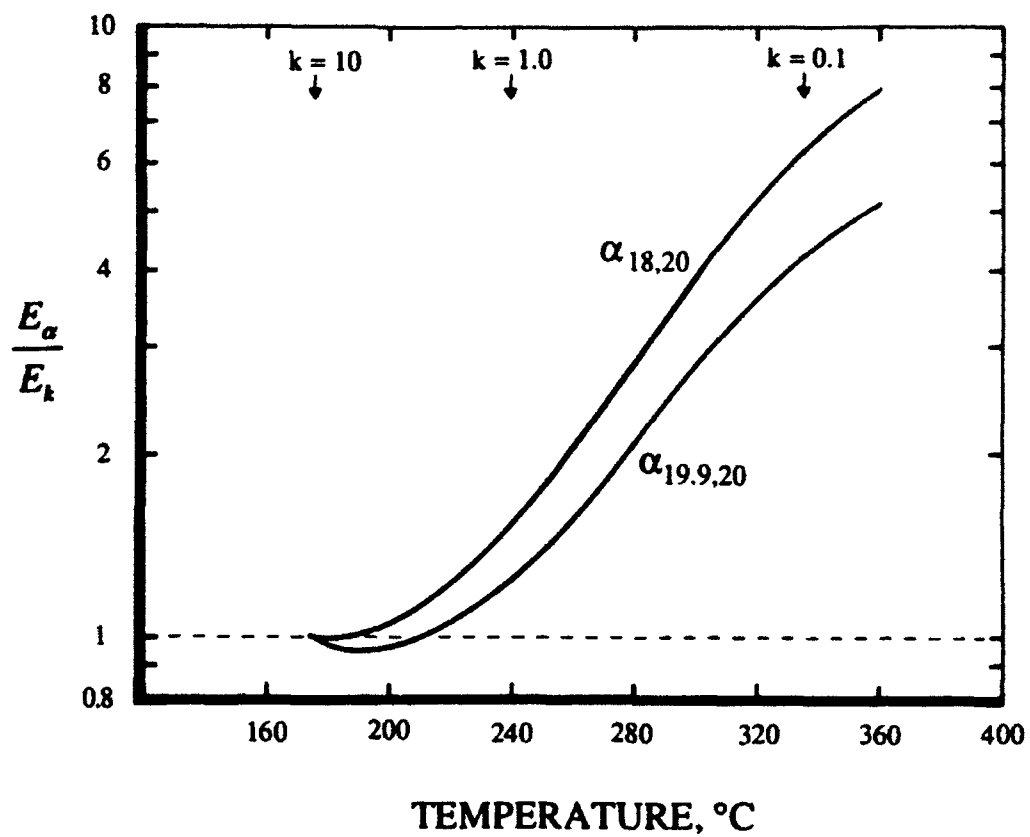


Figure B-1. Graph of E_α/E_k versus ITGC temperature.

Appendix C

Optimum Partition Ratio

The usual ITGC equations for retention time, average mobile-phase velocity, and apparent plate height, i.e.,

$$t_r = t_m(1 + k_j) \quad , \quad (A8)$$

$$\langle v_m \rangle = \frac{L}{t_m} \quad , \quad (A9)$$

$$\hat{H}_j = \frac{L}{N_j} \quad , \quad (A10)$$

can be substituted into the basic resolution equation (specifically, Equation 8), which can then be written as

$$R_s = \frac{1}{4} \sqrt{\frac{t_r \langle v_m \rangle}{\hat{H}_j (1 + k_j)}} \left(\frac{\alpha - 1}{\alpha} \right) \left(\frac{k_j}{1 + k_j} \right) \quad , \quad (A11)$$

and by squaring and rearranging, we find

$$t_r = 16 R_s^2 \left(\frac{\hat{H}_j}{\langle v_m \rangle} \right) \left(\frac{\alpha}{\alpha - 1} \right)^2 \left[\frac{(1 + k_j)^3}{k_j^2} \right] \quad . \quad (A12)$$

Upon differentiation with respect to k_j , it is seen that

$$\frac{\partial t_r}{\partial k_j} = \frac{c_1}{k_j^4} \left\{ k_j^2 [3(1 + k_j)^2] - 2k_j(1 + k_j)^3 \right\} \quad , \quad (A13)$$

where

$$c_1 = 16 R_s^2 \left(\frac{\hat{H}_j}{\langle v_m \rangle} \right) \left(\frac{\alpha}{\alpha - 1} \right)^2 \quad . \quad (A14)$$

By setting

$$\frac{\partial t_r}{\partial k_j} = 0 \quad , \quad (A15)$$

and simplifying, we therefore find the smallest t_r required to deliver a specified R_s (for a given solute pair, with a fixed ITGC column) occurs when

$$k_j = 2.0 \quad . \quad (A16)$$

For a similar analysis where the maximum ITGC resolution in a fixed time is desired, Equation A11 can be written as

$$R_s = \sqrt{\frac{(v_m)t_r}{16 \hat{H}_j}} \left(\frac{\alpha - 1}{\alpha} \right) \left[\frac{k_j}{(1 + k_j)^{\frac{1}{2}}} \right] = c_2 \frac{k_j}{(1 + k_j)^{\frac{1}{2}}} \quad , \quad (A17)$$

and then

$$\frac{\partial R_s}{\partial k_j} = \frac{c_2 \left[(1 + k_j)^{\frac{1}{2}} - \frac{3k_j}{2} \sqrt{1 + k_j} \right]}{(1 + k_j)^3} \quad . \quad (A18)$$

By setting

$$\frac{\partial R_s}{\partial k_j} = 0 \quad , \quad (A19)$$

and simplifying, we again see that (for these negligible pressure drop GC column situations) the largest R_s generated in a fixed time is produced when

$$k_j = 2.0 \quad . \quad (A20)$$

It is therefore observed that when the desired objective is to obtain the maximum *useful* ITGC resolution in a given analysis time, i.e., R_s/t_a , we find that this occurs when the partition ratio is in the vicinity of 2.0 while using highly permeable OTCs. Upon recalling that

$$k = \frac{1 - R_r}{R_r} \quad . \quad (A21)$$

we also see that the optimum R_r is 1/3, and therefore if R_s/t_a is to be maximal, the desired axial velocity for the various migrating solutes should be

$$\langle v_s \rangle = \frac{\langle v_m \rangle}{3} \quad . \quad (A22)$$

where $\langle v_m \rangle$ likewise has been selected for best operation.

Appendix D

Behavior of Dissimilar Open Tubular Columns in Tandem Assemblies

The observed plate height, i.e., $\bar{H}$, for a nonuniform or coupled-column assembly which is functioning under isocratic LC or ITGC conditions has been studied and characterized by various investigators [27,43,64,65]. For such chromatographic flowpaths, the visualization and characterization of the basic zone dispersion process can be more readily facilitated through the use of an incremental column approach whereby the lengthy flowpath is finely divided into equal axial increments. Within each of these incremental OTC lengths, the chromatographic parameters are uniform. It also needs to be specified that throughout each increment the average carrier velocity is fixed and the stationary film thickness is also constant. However, adjacent increments may have different GC parameters.

The sketch shown in Figure D-1 helps to visualize the incremental changes occurring along the lengthy flowpath. Zone dispersion or the H value contributed for each OTC increment can be expressed as

$$H_i = (\Delta L)_i \frac{[\Delta(\sigma^2)]_i}{[(\Delta t)_i]^2} \quad , \quad (A23)$$

and the apparent or observed H for the total flowpath is obtained through appropriate summations of the L , σ , and t terms. Specifically, the total column length is the sum of the axial increments, or simply L . Likewise, the total elapsed time for a solute to migrate through the entire flowpath length would be the summation of the individual transport times through the various in-line increments. And thus, t^2 is written as

$$t^2 = \left[\sum_{i=1}^n (\Delta t)_i \right]^2 \quad . \quad (A24)$$

The total variance of an eluted solute zone however is expressed as the sum of the variance changes* contributed by each of the OTC increments, that is,

$$\sigma^2 = \sum_{i=1}^n [\Delta(\sigma^2)]_i \quad . \quad (A25)$$

* It is assumed that σ^2 at the inlet or origin is zero, i.e., a Dirac delta function is injected.

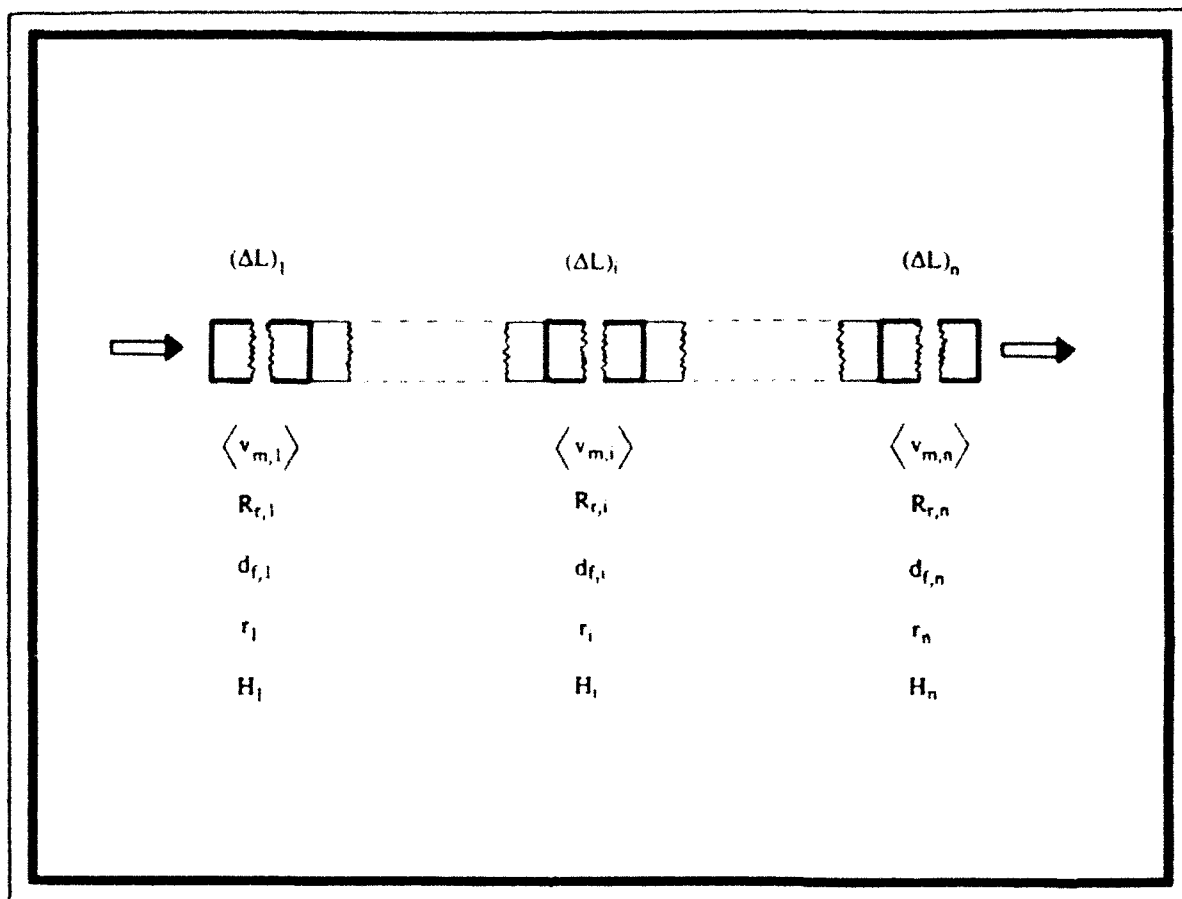


Figure D-1. Sketch of incremental changes along column flowpath.

The summation equation which represents observed H for the entire flowpath would then be written as

$$\hat{H} = L \frac{\sum_{i=1}^n [\Delta(\sigma^2)]_i}{\left[\sum_{i=1}^n (\Delta t)_i \right]^2} \quad (A26)$$

Furthermore, as for each axial increment,

$$\Delta t = \frac{\Delta L}{R_r \langle v_m \rangle} \quad (A27)$$

and

$$\Delta(\sigma^2) = \frac{H (\Delta t)^2}{\Delta L} \quad (A28)$$

then the above summation equation can be stated in terms of localized values of plate height, retention ratio, and average carrier velocity, that is,

$$\hat{H} = L \frac{\sum_{i=1}^n \frac{(\Delta L)_i H_i}{R_{r,i}^2 \langle v_{m,i} \rangle^2}}{\left(\sum_{i=1}^n \frac{(\Delta L)_i}{R_{r,i} \langle v_{m,i} \rangle} \right)^2} \quad (A29)$$

This latter expression applies for the discontinuous or step-like migration through finite increments. It can be rewritten in definite integral form where now it applies for smooth continuous flow through the nonuniform GC flowpath. Specifically, such an expression would be

$$\hat{H} = L \frac{\int_0^{z=L} \frac{H}{R_r^2 \langle v_m \rangle^2} dz}{\left(\int_0^{z=L} \frac{dz}{R_r \langle v_m \rangle} \right)^2} \quad (A30)$$

where

$$H \equiv \frac{\partial(\sigma_z)^2}{\partial z} \quad (A31)$$

Now, for a basic two-member tandem assembly

$$\hat{H} = \frac{\frac{H_1 L_1}{L(R_{r,1} \langle v_{m,1} \rangle)^2} + \frac{H_2 L_2}{L(R_{r,2} \langle v_{m,2} \rangle)^2}}{\left(\frac{L_1}{L R_{r,1} \langle v_{m,1} \rangle} + \frac{L_2}{L R_{r,2} \langle v_{m,2} \rangle} \right)^2} \quad (A32)$$

In the case where

$$\left. \begin{aligned} H_1 &= H_2 = H \\ v_{m,1} &= v_{m,2} = v_m \end{aligned} \right\} \quad (A33)$$

and

$$R_{r,1} = c R_{r,2} \quad (A34)$$

where the phase ratios, β_n , for the two column members are related as

$$c = \frac{\beta_1}{\beta_2} \quad (A35)$$

then Equation A32 can be rewritten as

$$\hat{H} = \frac{\frac{HL_1}{LR_{r,1}^2 \langle v_m \rangle^2} + \frac{H(L-L_1)}{L \langle v_m \rangle^2 \left(\frac{R_{r,1}}{c}\right)^2}}{\left[\frac{L_1}{L \langle v_m \rangle R_{r,1}} + \frac{L-L_1}{L \langle v_m \rangle \left(\frac{R_{r,1}}{c}\right)} \right]^2} \quad (A36)$$

which can be simplified to

$$\hat{H} = \frac{HL [L_1 + c^2 (L - L_1)]}{[L_1 + c (L - L_1)]^2} \quad (A37)$$

Equation A37 can also be expressed in relative terms, i.e., L_1/L , as

$$\hat{H} = H \frac{\frac{L_1}{L} (1 - c^2) + c^2}{\left[\frac{L_1}{L} (1 - c) + c \right]^2} \quad (A38)$$

Taking this further, it is seen that

$$\frac{d\hat{H}}{d\left(\frac{L_1}{L}\right)} = H \frac{\left[\frac{L_1}{L} (1 - c) + c \right] (1 - c^2) - \left[\frac{L_1}{L} (1 - c^2) + c^2 \right] (2 - 2c)}{\left[\frac{L_1}{L} (1 - c) + c \right]^3} \quad (A39)$$

and, under the conditions as stated in Equations A33 through A35, it is found that the maximum observed H for this basic two-member coupled-column assembly is

$$\hat{H}_{\max} = H \left(\frac{c}{4} + \frac{1}{4c} + \frac{1}{2} \right) \quad (A40)$$

Appendix E

Induced Resolution Loss as a Function of Distance for Different Size Transfer Tubes

The chromatographic model of plate height can by definition [15,34] be expressed in distance units as

$$\frac{\partial(\sigma_z)^2}{\partial z} \equiv H \quad . \quad (A41)$$

Then, for an axial segment of an actual column that possesses isothermal and relatively uniform properties,

$$d(\sigma_z)^2 = \hat{H} dz \quad , \quad (A42)$$

where $\hat{H}$ is the apparent plate height. Consider then the case of a dissimilar two-member tandem column assembly where the inlet OTC has a moderately thick film of stationary phase, while the same inside diameter outlet OTC possesses a very thin film. It is also stipulated that $\hat{H}$ is constant throughout the entire flowpath. In addition, this GLC column assembly is operating at its maximum temperature, i.e., $T_{c,m}$. The variance of the j th solute zone at the junction location z_2 can then be written as

$$(\sigma_z)_j^2 \Big|_{z_2} = \int_{z=0}^{z=z_2} \hat{H} dz = \hat{H}(z_2) \quad , \quad (A43)$$

and therefore, at further downstream locations

$$(\sigma_z)_j^2 \Big|_{z > z_2} = \hat{H}(z - z_2) + (\sigma_z)_j^2 \Big|_{z_2} \quad . \quad (A44)$$

ITGC resolution [28,42] can be equated as

$$R_{ij} = \frac{2(t_j - t_i)}{w_i + w_j} = R_s = \frac{2(\Delta z)_{ij}}{4\sigma_i + 4\sigma_j} \quad (A45)$$

and, under conditions of closely spaced solute zones where it can be assumed that $\sigma_i = \sigma_j$, then

$$R_s = \frac{2(\Delta z)}{8\sigma} = \frac{\Delta z}{4\sigma} \quad (A46)$$

With the column at the extreme elevated temperature of $T_{c,m}$, and in the case where within the thin-film downstream OTC

$$k_j \Big]_{T_{c,m}} \rightarrow 0 \quad (A47)$$

it is seen that the axial spacing between zones, i.e., $\Delta z]_{i,j}$, is essentially constant* over the remaining length of a highly permeable OTC. Then from Equations A44 and A46, R_s as a function of distance beyond z_2 can be written as

$$R_s \Big]_{z > z_2} = \frac{\Delta z]_{ij}}{4\sqrt{(\sigma_z)_j^2]_{z_2} + \hat{H}(z - z_2)}} \quad (A48)$$

Beyond z_2 (that is, the junction location), the change in R_s with distance is

* Although k_j will be quite small, e.g., 0.01 to 0.05 for low and moderate molecular weight solutes at a high $T_{c,max}$, respective values of $\Delta R_f/R_f$ will be even smaller. Therefore, the $\Delta z]_{i,j}$ constancy assumption is further strengthened.

$$\left. \frac{dR_s}{dz} \right]_{z > z_2} = - \frac{\Delta z \hat{H}}{8} \left\{ (\sigma_z)_j^2 \right]_{z_2} + \hat{H} (z - z_2) \right\}^{-\frac{3}{2}}, \quad (\text{A49})$$

and it is observed that this R_s loss is strongly dependent upon $\hat{H}$.

Zone dispersion for a situation where solute partitioning in an OTC is approaching zero can be simply stated [35] as

$$\frac{d(\sigma_z)^2}{dz} = \frac{2 D_g}{\langle v_m \rangle} + \frac{\langle v_m \rangle r^2}{24 D_g}, \quad (\text{A50})$$

and therefore the *intracolumn* R_s loss, that is,

$$\Delta R_s \Big|_{k \rightarrow 0} = R_s \Big|_{z_2} - R_s \Big|_{z=L}, \quad (\text{A51})$$

is dependent upon several variables. Specifically, for an OTC

$$\Delta R_s \Big|_{k \rightarrow 0} = f(D_g, \langle v_m \rangle, r, L, z_2, \Delta z) \quad (\text{A52})$$

As indicated by Equation A49, the R_s loss with distance is smaller as $\hat{H}$ or OTC bore size diminishes.