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PRACTICAL APPROACH TO THE THEORY OF LINEAR PROGRAMMED-TEMPERATURE GAS CHROMATOGRAPHY WITH PARTICULAR REFERENCE TO THE ANALYSIS OF AROMATIC HYDROCARBONS

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SUMMARY

A simplified method for the calculation of retention characteristics in linear programmed-temperature gas chromatography has been evolved. The effects of initial temperature and programming rate on these characteristics and on column performance can be calculated, including optimum conditions for the elution of components during the programme and to ensure a linear relationship between retention time and boiling point. Linearity is important in simulated distillation and in achieving an even distribution of error in peak measurement. The theory is substantiated by experimental results using a packed, a capillary and two PLOT columns.

INTRODUCTION

Theories of linear programmed-temperature gas chromatography (LPTGC) developed by Giddings¹⁻³, Habgood and Harris⁴⁻⁶, Rowan⁷⁻⁹ and others¹⁰⁻¹² are generally based on a fairly rigorous treatment of the operative variables. The use of these theories in practical optimization usually involves an iterative procedure which requires computing facilities. A graphical method has also been used¹³. There are also numerous methods for the calculation of retention indices by empirical or semi-empirical methods¹⁴⁻¹⁹.

Most of these earlier contributions form part of the general groundwork of chromatographic theory. Nevertheless, most analysts prefer to employ empirical methods for the choice of their programming variables, which can result in a considerable waste of operating time, with unnecessary losses in resolution and accuracy. Hence, there is a need for a simplified method of predicting approximate retention characteristics from the operative variables which is of practical interest to the analyst.

In isothermal GC the relationship between retention time and boiling point for compounds of a similar chemical type is logarithmic, resulting in a rapid increase in retention time and peak width even for samples with narrow boiling ranges. This has a deleterious effect on the distribution of error in peak measurement and hence on the overall accuracy of the analysis. LPTGC tends to oppose this logarithmic dependence and, under certain conditions, the relationship becomes linear, with only

a slow increase in peak width with increasing retention time. A linear relationship between retention time and boiling point is particularly advantageous in simulated distillation where boiling ranges are calculated from the peak retention times and an even distribution of error is desirable. Thus, for a particular sample type, we need to know the following:

- (a) the column parameters best suited to the purpose required;
- (b) the effects of the initial temperature and programming rate on the retention characteristics and resolution of the components;
- (c) the optimum initial temperature and programming rate to give a linear relationship between retention time and boiling point and to ensure that all the components emerge before the end of the temperature programme.

The prediction of these properties forms the major part of this paper and is based upon several simplifying assumptions that have been found to be tenable in practice. The only preliminary measurements necessary are at least two isothermal retention times of one or more typical components of the type of sample to be tested.

EXPERIMENTAL

All measurements were carried out using a Pye 104, Model 24, temperature-programmed gas chromatograph with flame-ionization detection (Pye-Unicam, Cambridge, Great Britain). Retention times were obtained from the print-out record of a Kemtronix Supergrator 1 computing integrator [Kemtronix (UK), Berkshire, Great Britain]. Retention temperatures were calculated from the retention times and set programming rates and so experimental values for these are subject to instrumental error. Isothermal temperatures, however, were measured thermometrically. Carrier gas flow-rates were pressure controlled by diaphragm-operated needle valves (Negretti and Zambra, Bucks, Great Britain). These were set at a suitable level for the particular column so as to maintain a constant pressure difference across the column.

Three different column types were employed. Packed columns were prepared conventionally, using stainless steel as the column material. The glass capillary column was purchased ready coated (Phase Separations, Connahs Quay, Great Britain) and the PLOT columns were of the type previously described by one of the authors^{20,21}.

THEORETICAL

In LPTGC, the zone accelerates as it travels along the column in a manner that depends on the initial temperature, T_1 , and the programming rate, r . Suppose the zone centre travels dx cm in dt min; then,

$$dt = \frac{dx}{u_x} (1 + k'_T) \quad (1)$$

where

- k'_T = partition ratio of the solute at temperature T ($^{\circ}\text{K}$);
- u_x = linear gas velocity at point x .

But

$$k'_T = K_T/\beta \quad (2)$$

where

K_T = partition coefficient of solute at temperature T ($^{\circ}\text{K}$);

β = column phase ratio

$$= \frac{\text{column hold-up volume}}{\text{volume of stationary phase in column}}$$

Substituting eqn. 2 into eqn. 1, we obtain

$$dt = \frac{dx}{u_x} (1 + K_T/\beta) \quad (3)$$

K_T is given by the thermodynamic relationship

$$K_T = a \exp(\Delta H_s/RT) \quad (4)$$

where

ΔH_s = molar heat of solution of the solute in the stationary phase at the column temperature T (expressed as a positive value);

R = the ideal gas constant;

a = constant for a given solute.

$$R \ln a = \Delta S_T$$

where ΔS_T is the molar entropy of solution at the column temperature. Therefore,

$$dt = \frac{dx}{u_x} \left(1 + \frac{a}{\beta} \exp(\Delta H_s/RT) \right) \quad (5)$$

In isothermal operation, T is constant, and if we define the mean carrier gas velocity as

$$\bar{u} = L/t_0$$

where L = column length, and t_0 = hold-up time, then the retention time is given by

$$t_R = \frac{aL}{\beta \bar{u}} \exp(\Delta H_s/RT) + t_0 \quad (6)$$

In LPTGC, T is not constant but varies linearly according to the programme. Hence

$$T = T_1 + rt \quad (7)$$

where

T_1 = initial programme temperature ($^{\circ}\text{K}$);

r = programming rate ($^{\circ}\text{C}/\text{min}$);

t = time from injection (min).

Differentiating eqn. 7 with respect to t we obtain

$$dT = r dt \quad (8)$$

which, on substituting into eqn. 5, gives

$$\frac{dT}{r} = \frac{dx}{u_x} \left(1 + \frac{a}{\beta} \exp(\Delta H_s/RT) \right) \quad (9)$$

Therefore

$$\int_{T_1}^{T_R} \left(\frac{dT}{1 + \frac{a}{\beta} \exp(\Delta H_s/RT)} \right) = r \int_0^L \frac{dx}{u_x} \quad (10)$$

where T_R ($^{\circ}\text{K}$) is the retention temperature of the solute, *i.e.*, the column temperature at which the peak maximum emerges.

To simplify the treatment, the following assumptions are made:

(a) the solute zone travels a negligible distance down the column when the air peak emerges, *i.e.*, the effect of the hold-up time can be neglected; and

(b) the mean gas velocity remains constant during the temperature programme and is replaced by \bar{u} , the mean velocity.

Clearly, (a) will not hold for rapidly eluted components and (b) is not strictly valid because of changes in the gas viscosity and thermal expansion. The effect of these changes depends on the method of gas flow control. Using a pressure controller the mass of gas supplied to the column decreases during the programme because of the increase in viscosity, but the effect of this on the linear velocity is largely compensated by the cubic expansion of the gas. With mass flow control the linear velocity increases during the programme because of its thermal expansion only and so a greater deviation from the theory can be expected. Hence we can state

$$\int_{T_1}^{T_R} \exp(-\Delta H_s/RT) dT = \frac{ar}{\beta \bar{u}} \int_0^L dx = \frac{raL}{\beta \bar{u}} \quad (11)$$

Thus the retention temperature, T_R , is dependent only on the column parameters L and β , the ratio of the operating variables r/\bar{u} and the thermodynamic constant a . An approximate solution to eqn. 11 is

$$\int_{T_1}^{T_R} \exp(-\Delta H_s/RT) dT = \left(\frac{RT^2 \exp(-\Delta H_s/RT)}{\Delta H_s} \right)_{T_1}^{T_R} \quad (12)$$

i.e.

$$\frac{R}{\Delta H_s} \left(\frac{T_R^2}{\exp(\Delta H_s/RT_R)} - \frac{T_1^2}{\exp(\Delta H_s/RT_1)} \right) = r \frac{aL}{\beta \bar{u}} \quad (13)$$

This equation is similar to that first derived by Giddings¹. T_R can be obtained from this expression by graphical means or by the use of a programmable calculator or

computer. However, this can be time consuming and may offer little advantage over the purely empirical method. Also, although T_1 , r , \bar{u} and L are all known or measurable parameters, values of ΔH_s , β and a are not usually available. However, they can be calculated from eqn. 6 after chromatographing the compounds concerned at two or three isothermal temperatures. Thus, for the particular column to be used,

$$\log(t_R - t_0) = \frac{\Delta H_s}{2.303 RT_R} + \log \frac{aL}{\beta\bar{u}} \quad (14)$$

Thus, plotting $\log(t_R - t_0)$ against $1/T_R$ gives a straight line of slope $\Delta H_s/2.303 R$ and intercept $\log(aL/\beta\bar{u})$.

Table I gives data derived from plots for a number of aromatic hydrocarbons chromatographed on a glass capillary column. These include values of ΔH_s and $\log aL/\beta\bar{u}$ calculated from the slopes and intercepts. The final column includes values for the ratio $\Delta H_s/T_B$, which approximates to the molar entropy of solution, ΔS_B , for the solute at its boiling point, T_B ($^{\circ}\text{K}$). The mean value of ΔS_B to the nearest integer is 21, which is close to the Trouton constant, given by $\Delta H_v/T_B$, where ΔH_v is the heat of vapourization at the boiling point. Thus, $\Delta H_s \approx \Delta H_v$ and the heat of mixing is virtually zero, *i.e.*, for aromatic hydrocarbons on SE-52 silicone the partition process approaches ideality. Little error will be made, therefore, by replacing ΔH_s by $21T_B$ for these compounds. For compounds that might be expected to have appreciable heats of mixing, ΔH_s will differ considerably from ΔH_v and the ratio $\Delta H_s/T_B$ will vary from the nominally ideal value of 21. Nevertheless, for chemically similar compounds, as in a homologous series $\log t_R$ is normally proportional to T_B , suggesting that $\Delta H_s/T_B$ is constant for the series but its numerical value is char-

TABLE I
DATA CALCULATED FROM ISOTHERMAL PLOTS

Compound	T_B ($^{\circ}\text{K}$)	Slope = $\Delta H_s/2.3R$	ΔH_s (cal/mole)	Intercept = $\log \phi^*$	ϕ^*	$\Delta H_s/T_B$ (cal/ $^{\circ}\text{K}\cdot\text{mole}$)
Benzene	353	1315	5.989	-4.20	$6.3 \cdot 10^{-5}$	17.0
Toluene	384	1500	6.831	-4.14	$7.3 \cdot 10^{-5}$	17.8
<i>p</i> -Xylene	412	1756	7.997	-4.55	$2.8 \cdot 10^{-5}$	19.4
Indene	456	2020	9.199	-4.75	$1.8 \cdot 10^{-5}$	20.2
Naphthalene	491	2135	9.723	-4.65	$2.2 \cdot 10^{-5}$	19.8
2-Methylnaphthalene	514	2283	10.397	-4.80	$1.6 \cdot 10^{-5}$	20.2
1-Methylnaphthalene	517	2390	10.884	-4.81	$1.6 \cdot 10^{-5}$	21.1
Biphenyl	528	2370	10.793	-4.84	$1.5 \cdot 10^{-5}$	20.4
Acenaphthene	550	2450	11.157	-4.81	$1.6 \cdot 10^{-5}$	20.3
Fluorene	571	2640	12.023	-5.05	$0.89 \cdot 10^{-5}$	21.1
Phenanthrene	611	2770	12.615	-5.02	$0.96 \cdot 10^{-5}$	20.6
Fluoranthene	655	3200	14.573	-5.50	$0.07 \cdot 10^{-5}$	22.2
Pyrene	666	3420	15.573	-5.90	$0.13 \cdot 10^{-5}$	23.4
Mean				-4.81**		20.8***

* $\phi = aL/\beta\bar{u}$.

** Omitting benzene, toluene, fluoranthene, and pyrene results because of extensive extrapolation involved.

*** Omitting benzene and toluene values.

acteristic of the class. Another important conclusion from the results in Table I is that the intercept remains sensibly constant, neglecting the results for the lowest and highest boiling compounds which would give inaccurate results because of the high degree of extrapolation involved. This implies a reasonably constant value of the thermodynamic constant a for compounds of similar chemical type.

Utilization of eqn. 13

Substituting the value $\Delta H_s = \Delta S_B T_B$ into eqn. 13, we have

$$\frac{R}{\Delta S_B T_B} \left(\frac{T_R^2}{\exp(\Delta S_B T_B / RT_R)} - \frac{T_1^2}{\exp(\Delta S_B T_B / RT_1)} \right) = r \cdot \frac{aL}{\beta \bar{u}} \quad (15)$$

In principle, this equation enables us to calculate the retention temperature for a known compound provided that we know its boiling point, the values of ΔS_B and a appropriate to the class, the column parameters L and β and the operating conditions T_1 , r and \bar{u} . For aromatic hydrocarbons chromatographed on non-polar phases such as silicone polymers, poly-*m*-phenoxylenes and Apiezon, one can reasonably expect ΔS_B to remain virtually constant at about 21. Hence, if we define the \varnothing value of the column as

$$\varnothing = aL/\beta \bar{u} \quad (16)$$

we can then determine the value of \varnothing from a single isothermal run, *i.e.*, from eqn. 14:

$$\log \varnothing = \log t'_R - \frac{21 T_B}{2.3 RT} \quad (17)$$

where $t'_R = (t_R - t_0)$, the adjusted retention time of the solute, measured from the air peak.

Eqn. 15 can be stated in the form

$$\frac{RT_R^2}{\Delta S_B T_B \exp(\Delta S_B T_B / RT_R)} = r\varnothing + \frac{RT_1^2}{\Delta S_B T_B \exp(\Delta S_B T_B / RT_1)} \quad (18)$$

$$= r\varnothing + f(T_1, T_B) \quad (19)$$

If T_1 is sufficiently small, $f(T_1, T_B)$ is small compared with $r\varnothing$, and therefore

$$T_R^2 \approx \frac{r\varnothing \Delta S_B T_B}{R} \exp(\Delta S_B T_B / RT_R) \quad (20)$$

i.e.

$$\frac{\Delta S_B T_B}{RT_R} = 2 \ln T_R - \ln T_B - \ln \frac{(\Delta S_B r \varnothing)}{R} \quad (21)$$

$$T_R = \frac{\Delta S_B}{R} - \frac{T_B}{\ln(\Delta S_B r \varnothing / R) + \ln(T_R^2 / T_B)} \quad (22)$$

Let $\theta_R = T_R/1000$ and $\theta_B = T_B/1000$

Then

$$\theta_R = \frac{\Delta S_B}{R} \cdot \frac{\theta_B}{[7 - \ln(\Delta S_B r \phi / R)] + \ln(\theta_R^2 / \theta_B)} \quad (23)$$

i.e.,

$$\theta_B = \frac{R}{\Delta S_B} \cdot [7 - \ln(\Delta S_B r \phi / R)] \cdot \theta_R + \frac{R}{\Delta S_B} \theta_R \ln(\theta_R^2 / \theta_B) \quad (24)$$

Practical values of θ_R lie in the range *ca.* 0.3–0.6, and values of θ_B are in the range 0.4–0.7. Thus $\ln(\theta_R^2 / \theta_B)$ is negative but decreases numerically with increasing values of θ_R . This term is almost exactly compensated for by the increasing value of θ_R and so the term $R\theta_R \ln(\theta_R^2 / \theta_B) / \Delta S_B$ remains sensibly constant. Thus, for a column operating under a fixed set of conditions:

$$\frac{R\theta_R}{\Delta S_B} \cdot \ln(\theta_R^2 / \theta_B) \text{ is constant} = C \quad (25)$$

Also, if we let

$$A = \frac{R[7 - \ln(\Delta S_B r \phi / R)]}{\Delta S_B} \quad (26)$$

then, from eqn. 24, we obtain

$$A\theta_R + C = \theta_B$$

i.e.

$$\theta_R = \frac{1}{A} \cdot \theta_B - \frac{C}{A} \quad (27)$$

or

$$T_R = \frac{1}{A} \cdot T_B - \frac{1000C}{A} \quad (28)$$

Hence, a plot of T_R versus T_B gives a straight line of slope $1/A$ and intercept $1000C/A$.

Substituting the value for θ_R in eqn. 27 into the logarithmic part of the C term in eqn. 25, we have (neglecting the squared term $C^2/A^2\theta_B^2$)

$$\ln(\theta_R^2 / \theta_B) \approx \frac{\theta_B}{A^2} - \frac{2C}{A} \quad (29)$$

A good approximation to this is

$$\ln(\theta_R^2 / \theta_B) \approx \ln(1.2\theta_B / A^2)$$

for the permissible range of values. Substituting this into eqn. 23, we obtain

$$\theta_R = \frac{\theta_B}{A + \frac{R}{\Delta S_B} \cdot \ln \frac{1.2\theta_B}{A^2}} \quad (30)$$

or

$$T_R = \frac{T_B}{A + \frac{2.3R}{\Delta S_B} \log \frac{1.2T_B}{1000 A^2}} \quad (31)$$

Substituting $\Delta S_B = 21$ and $R = 1.98$, we obtain, for aromatic hydrocarbons

$$T_R = \frac{T_B}{A + 0.22 \log (0.0012T_B/A^2)} \quad (32)$$

where $A = 0.44 - 0.22 \log r\phi$

RESULTS AND DISCUSSION

Eqn. 32 allows us to calculate T_R values, and hence retention times, from the boiling points of the components for different programming rates. The effects of changes in the important variables can also be evaluated, particularly the column and operating parameters embodied in the ϕ value, the programming rate r and the boiling point of the components, T_B . Referring also to eqn. 19, it can be seen that the linearity between T_B and T_R will be affected if $f(T_1, T_B)$ is not numerically insignificant in comparison with $r\phi$. In this event, the value of the right-hand side of the equation varies with T_B , which causes an increasing deviation from linearity with decreasing boiling point. Any of the other variables contained in the terms $f(T_1, T_B)$ or $r\phi$ will favour linearity if they cause a decrease in $f(T_1, T_B)$ relative to $r\phi$. Thus, high programming rates, long columns, low gas velocities and low phase ratios will tend to favour linearity of the T_R versus T_B relationship.

Fig. 1 gives theoretical plots of T_B versus T_R for aromatic hydrocarbons on the glass capillary column used earlier to obtain the results in Table I. The theoretical relationship is obviously linear and T_R increases with the programming rate. Fig. 2 gives the experimental plots for the same compounds. As predicted by the theory (see *Effect of initial temperature, T_1* , below), the initial temperature of 353°K is too high to attain linearity for the lowest boiling components indene and naphthalene except at the highest programming rate of 6 °C/min. All of the higher boiling members give linear plots at all of the programming rates used. A comparison between theoretical and retention temperatures, calculated from eqn. 32, and experimental values on four different columns is given in Table II. The agreement is generally excellent and within acceptable limits for most practical purposes.

Quantitative effects derived from theory

Effect of initial temperature, T_1 . As mentioned earlier, the initial temperature of the programme can affect the linearity of the T_B versus T_R relationship if it is too high for the particular column and conditions. An optimum value of T_1 can be defined for a mixture whose lowest boiling component is T_B (min), viz.,

$$f [T_1(\text{opt}), T_B(\text{min})] = \frac{r\phi}{10} \quad (33)$$

If the initial temperature is lower than $T_1(\text{opt})$, no significant increase in resolution will be obtained but the analysis time will be unnecessarily extended by

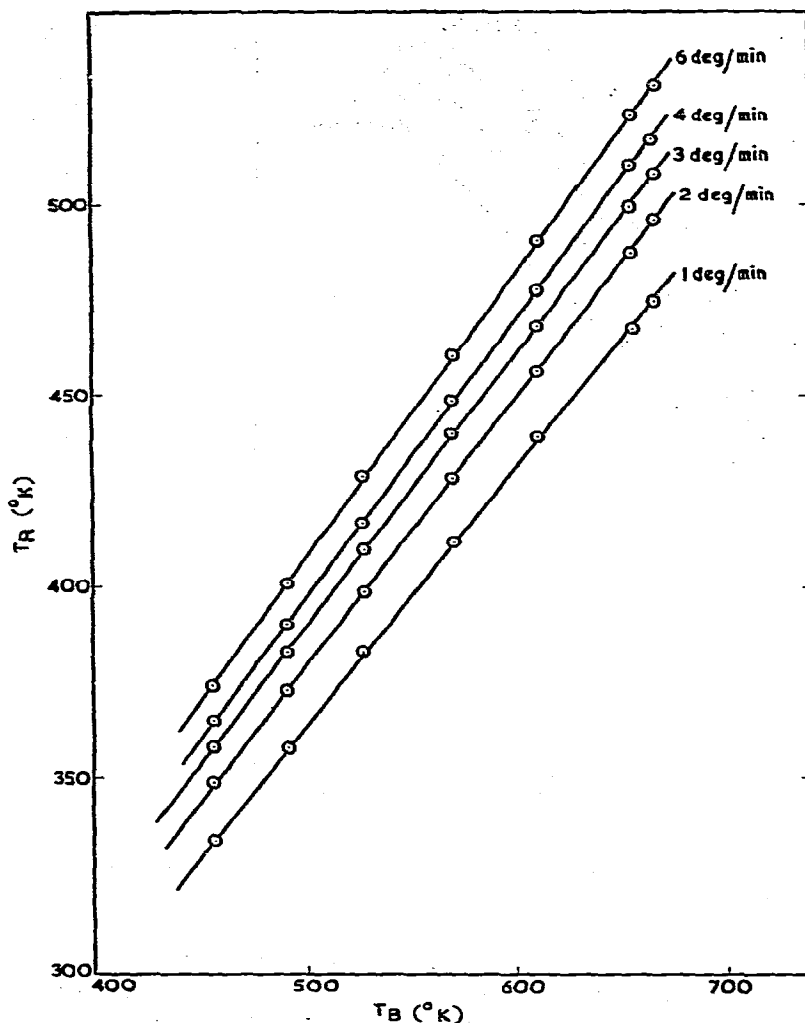


Fig. 1. Theoretical T_R versus T_B plots for glass capillary column ($\log \varnothing = -4.81$).

$[T_1(\text{opt}) - T_1]/r$ min. If the initial temperature is higher than $T_1(\text{opt})$, then the linearity will suffer, as shown in Fig. 2 for the lower boiling components, and the resolution will decrease because the retention temperature is increased (see eqn. 43). Obviously, $T_1(\text{opt})$ is not critical and a latitude of about $\pm 10^\circ$ would normally be acceptable. The optimum initial temperature $T_1(\text{opt})$ can be calculated from an expression derived similarly to that for T_R , viz.,

$$T_1(\text{opt}) = \frac{T_B}{A' + 0.22 \log (0.0012T_B/A'^2)} \quad (34)$$

where $A' = 0.65 - 0.22 \log r \varnothing$ for aromatic hydrocarbons.

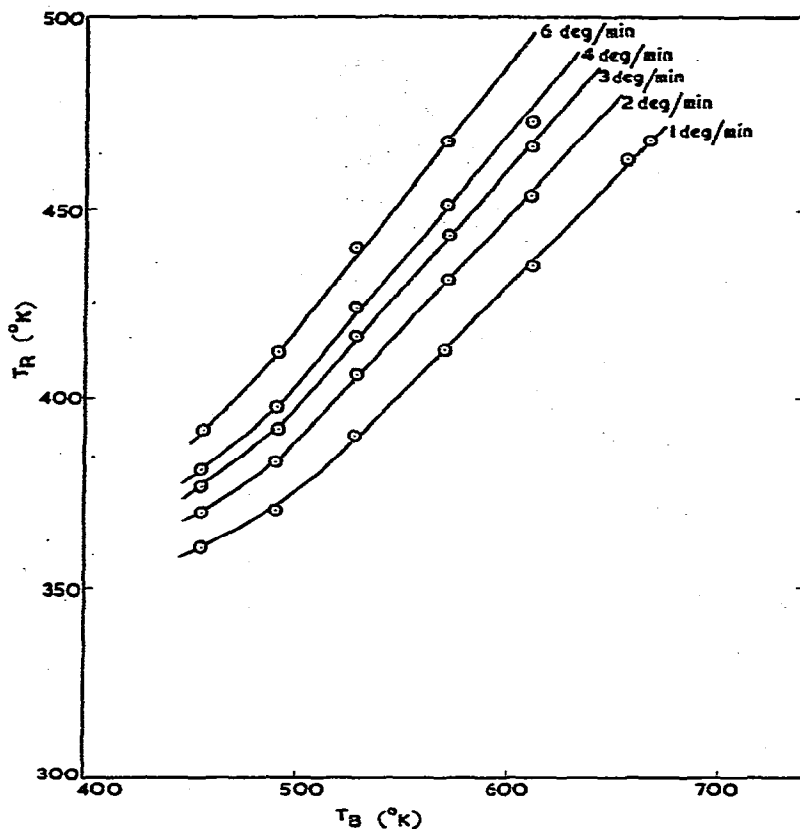


Fig. 2. Experimental T_R versus T_B plots for glass capillary column. Initial temperature, $T_1 = 353^\circ\text{K}$.

Table III shows some values calculated for the 25-m glass capillary column. The minimum practicable initial temperature is normally about 60°C (330°K), and so all of these compounds except indene and naphthalene can be eluted linearly at programming rates down to $1^\circ\text{C}/\text{min}$. Indene and naphthalene, however, would be expected to deviate from linearity at the lowest programming rates where $T_1 > T_1(\text{opt})$. This is confirmed by the experimental plots shown in Fig. 2. As the theory predicts, linearity is improved with increasing programming rate because the associated $T_1(\text{opt})$ value also increases. Fig. 3 shows experimental T_R versus T_B plots for the same column operated from various initial temperatures. There is, as predicted theoretically, an increasing deviation from linearity with increasing T_1 and when $T_1 = 413^\circ\text{K}$, as seen from Table III for the programming rate of $2^\circ\text{C}/\text{min}$, all chromatographed components are above their optimum T_1 values.

Choice of column. One of the main difficulties in LPTGC is the attainment of a sufficient separation between the lowest boiling components, particularly with relatively low-boiling mixtures. Capillary columns have high phase ratios, typically in the range 100–300, and so ϕ values tend to be lower than with packed columns, although the effect of high β values in eqn. 16 may be compensated for by their

TABLE II

COMPARISON BETWEEN THEORETICAL AND EXPERIMENTAL VALUES OF RETENTION TEMPERATURE ON DIFFERENT COLUMNS

Column 1: 25 m \times 0.25 mm I.D. glass capillary column coated with silicone SE-52. He carrier gas. $\Phi = 1.6 \cdot 10^{-5}$. $T_1 = 353$ °K.

Column 2: 3-m packed column, 6% silicone OV-101 on Chromosorb G. N₂ carrier gas. $\Phi = 3.5 \cdot 10^{-5}$. $T_1 = 343$ °K.

Column 3: 13-m PLOT column coated with Apiezon L. He carrier gas. $\Phi = 10^{-5}$. $T_1 = 373$ °K.

Column 4: 23-m PLOT column with silicone OV-101. He carrier gas. $\Phi = 1.6 \cdot 10^{-5}$. $T_1 = 343$ °K.

Column	Compound	T_B (°K)	T_R at different programming rates									
			1°C/min		2°C/min		3°C/min		4°C/min		6°C/min	
			Theor.	Exp.	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.
1	Indene	456	334	361	349	370	358	377	365	381	374	392
	Naphthalene	491	358	371	373	383	383	392	390	398	401	412
	Biphenyl	528	383	390	399	406	410	417	417	424	429	410
	Fluorene	571	412	413	430	431	441	443	449	451	461	468
	Phenanthrene	611	439	435	457	454	469	467	478	473	491	iso
	Fluoranthene	655	468	463	488	iso*	500	iso	510	iso	523	iso
	Pyrene	666	475	468	496	iso	508	iso	517	iso	531	iso
2	Naphthalene	491	377	381	394	399	405	411	413	419		
	Fluorene	571	433	439	453	459	465	473	474	493		
	Anthracene	613	463	470	484	493	497	506	506	517		
	Pyrene	666	500	509	522	533	536	547	547	547		
	Chrysene	721	538	549	562	573	577	iso	588	iso		
3	Fluorene	571	414	421	423	437	443	453				
	Phenanthrene	611	440	445	457	465	477	485				
4	Naphthalene	491	364	375	381	391	391	397	399	403		
	Fluorene	571	418	425	439	447	451	451	455	459		
	Phenanthrene	611	445	448	467	469	478	475	487	483		
	Pyrene	666	483	481	505	505	517	514	523	iso		

* iso = eluted after completion of temperature programme.

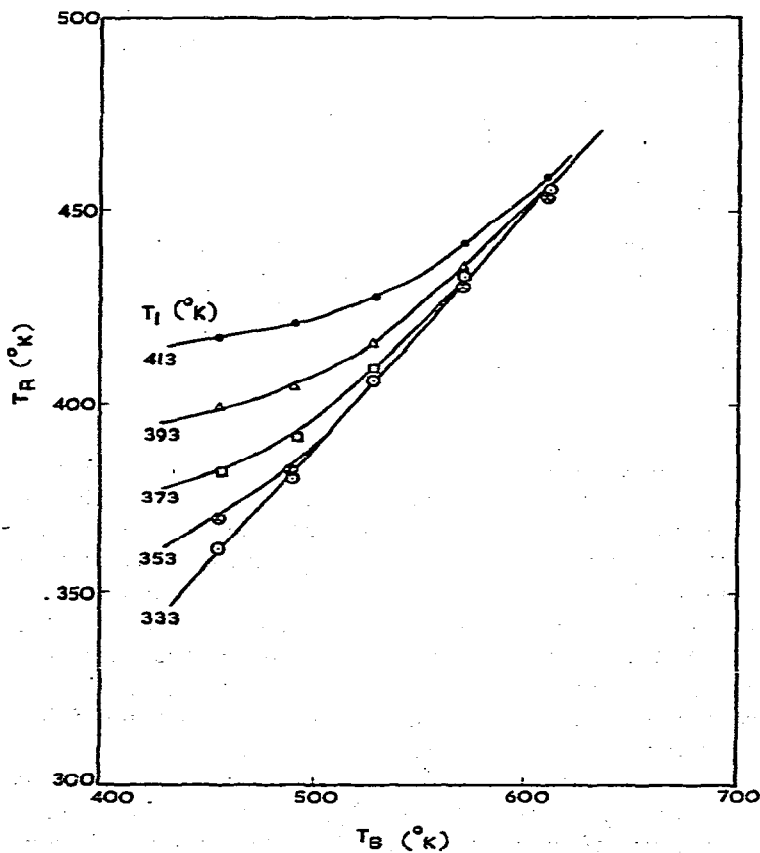
longer length. Hence the optimum initial temperature may be lower than with packed columns and may not be achievable for the lowest boiling components. Nevertheless, capillary columns are preferred for the detailed analysis of complex fractions where a high resolution is essential. The loss in resolution resulting from the non-linearity of the T_B versus T_R relationship is then amply compensated for by the very high efficiency of these columns. In this context, it is more important to ensure that the highest boiling components of the sample are eluted within the temperature programme. Thus, rapidly eluted peaks are easily measured by modern computing integrators but analytical accuracy will suffer for the higher boiling components if they "escape" the temperature programme and are eluted isothermally.

In simulated distillation the resolution between the components is usually less important than a linear relationship between T_B and T_R . Packed columns would normally be preferred here because of their intrinsically low phase ratios and consequently high Φ values. For low-boiling samples it may even be necessary to use a high stationary phase loading (say 10–20%) to ensure this linearity.

TABLE III

OPTIMUM INITIAL TEMPERATURES T_1 (opt) CALCULATED FOR AROMATIC HYDROCARBONS ON GLASS CAPILLARY COLUMN $\Phi = 1.6 \cdot 10^{-5}$.

Compound	T_B ($^{\circ}K$)	Programming rate ($^{\circ}C/min$)				
		1	2	3	4	6
Indene	456	292	304	311	316	324
Naphthalene	491	313	326	333	339	347
Biphenyl	528	336	349	357	363	371
Fluorene	571	361	375	384	390	399
Phenanthrene	611	385	400	409	416	425
Fluoranthene	655	411	427	436	443	454
Pyrene	666	417	433	392	393	394

Fig. 3. Experimental T_R versus T_B plots at different initial temperatures for glass capillary column. Programming rate = $2^{\circ}C/min$.

Effect of programming rate, r. In eqn. 32 the effect of programming rate, r , is described by the A term, which decreases numerically with increasing rate. This increases the retention temperature (see Figs. 1 and 2) which decreases the resolution, but the linearity of the T_B versus T_R relationship is improved because of the increase in $r\phi$ in comparison with $f(T_1, T_B)$ in eqn. 18.

The choice of programming rate for a particular application will depend on the time available for the analysis and the highest boiling component of the mixture. Very low programming rates will give long analysis times and may give a non-linear relationship between retention time and boiling point, with an uneven distribution of peak measurement accuracy. Conversely, high programming rates may cause the high-boiling end of the sample to elute after the programme has finished, and so they will give wider peaks than those eluted during the programme. Table IV gives the theoretical maximum values of the programming rate necessary to elute aromatic

TABLE IV

THEORETICAL MAXIMUM PROGRAMMING RATES NECESSARY TO ELUTE HIGH-BOILING HYDROCARBONS DURING THE PROGRAMME FOR COLUMN 1

Maximum temperature		Compound	T_B ($^{\circ}\text{K}$)	Maximum programme rate, r ($^{\circ}\text{C}/\text{min}$)
$^{\circ}\text{C}$	$^{\circ}\text{K}$			
200	473	Biphenyl	528	20
		Fluorene	571	10
		Phenanthrene	611	4
		Fluoranthene	655	1
300	573	Fluoranthene	655	23
		Chrysene	721	6

hydrocarbons during the programme for column 1, assuming the maximum permissible temperatures of 200°C and 300°C , respectively. These values were calculated from eqn. 32 by putting $T_R = 473^{\circ}\text{K}$ and 573°K , and using a programmable calculator to solve the equation for r . Generally, for wide boiling range mixtures, the programming rate should be set at this highest permissible value unless the resolution between certain of the components is less than necessary for their separate measurement. In this event a lower rate may be expedient. For relatively low-boiling samples the maximum theoretical rate may be impracticably high and here, also, a lower rate should be employed commensurate with the degree of resolution required and the analysis time to be allowed. Appropriate values can be calculated from eqn. 32.

Analysis time, t_R . The analysis time in LPTGC is given by

$$t_R = \frac{T_R - T_1}{r}$$

where t_R is the retention time of the highest boiling component. Thus, increasing the programming rate will decrease t_R but not in inverse proportion to r because of the increase in T_R . This is illustrated by Fig. 4 which gives theoretical plots for the glass capillary column. Table V gives retention time data for the four columns described in Table II and similarly compares theoretical and experimental values.

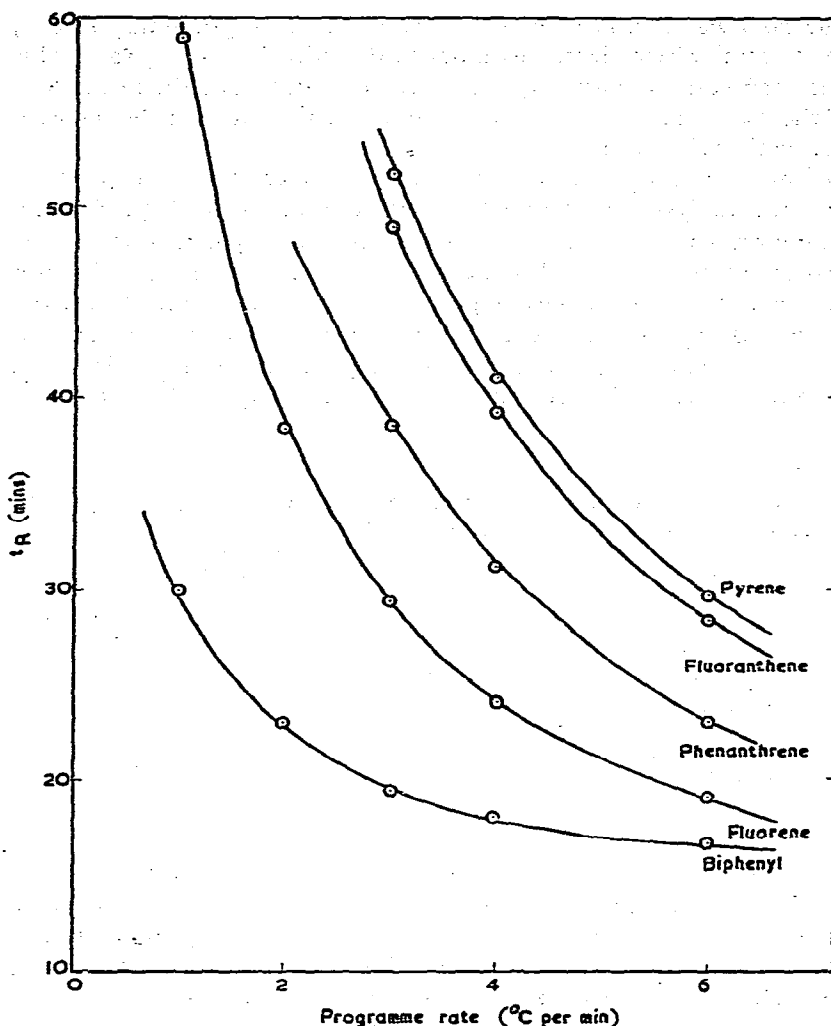


Fig. 4. Effect of programming rate on elution time (theoretical). Glass capillary column (see text for conditions).

The comparison is generally very good except for indene and naphthalene on column I, particularly at the lower programming rates. This is because the theoretical value assumed T_1 to be below the optimum value. In fact, as shown earlier by Fig. 2, these components deviate from linearity on this column at the lower rates because the initial temperature of 353°K is significantly higher than the optimum values for these compounds.

Resolution in LPTGC

In gas chromatography, resolution is defined as

$$R = \frac{\text{time (or distance) between peak maxima}}{\text{mean peak width (in similar units)}} \quad (35)$$

TABLE V
COMPARISON OF THEORETICAL AND EXPERIMENTAL RETENTION TIMES IN LPTGC FOR FOUR DIFFERENT COLUMNS

Column*	Compound	T_B (°K)	t_r (min) at different programming rates									
			1°C/min		2°C/min		3°C/min		4°C/min		6°C/min	
			Theor.	Exp.	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.
1	Indene	456	-20	8	-2	8.5	1.7	8.0	7.0	3.5	3.5	6.5
	Naphthalene	491	5.0	18	11	15	10	13	9.3	11	8.0	9.8
	Biphenyl	528	30	37	23	27	19	21	16	18	13	15
	Fluorene	571	59	60	39	39	29	30	24	25	18	19
	Phenanthrene	611	86	82	52	51	39	38	31	30	23	iso
	Fluoranthene	655	115	iso**	68	iso	49	iso	39	iso	28	iso
2	Pyrene	666	122	iso	72	iso	52	iso	41	iso	30	iso
	Naphthalene	491	34	38	26	28	21	23	18	19		
	Fluorene	571	90	96	55	58	41	43	33	38		
	Anthracene	613	120	127	71	75	51	54	41	44		
	Pyrene	666	157	166	90	95	64	68	51	54		
	Chrysene	721	195	206	105	115	78	iso	61	iso		
3	Fluorene	571	41	48	25	32	18	20				
	Phenanthrene	621	67	72	42	46	26	28				
4	Naphthalene	491	21	32	19	24	16	18	14	15		
	Fluorene	571	75	82	48	52	36	36	28	29		
	Phenanthrene	611	102	105	62	64	45	44	36	35		
	Pyrene	666	140	138	81	81	58	57	45	iso		

* See Table II.

** iso = eluted after completion of temperature programme.

This equation is independent of the chromatographic conditions provided that the peaks are approximately Gaussian in shape.

If we assume that the column efficiency n remains constant, then all solute zones will occupy the same length in the column when they reach the exit. Thus, if z_0 is the concentration zone length at column exit,

$$z_0 = 4L/\sqrt{n} \tag{36}$$

The actual peak width, p_w , on the chromatogram is given by

$$p_w = z_0 \left/ \frac{dx}{dt} \right. \tag{37}$$

where dx/dt is the zone velocity at the point of emergence i.e.,

$$p_w = \frac{4L}{\sqrt{n} \cdot \frac{dx}{dt}} \text{ min} \tag{38}$$

But

$$\frac{dx}{dt} = \frac{\beta u_0}{a} \exp(-\Delta H_s/RT_R)$$

(from eqn. 5, neglecting dead volume), where u_0 = carrier gas velocity at column exit.

Therefore,

$$p_w = \frac{4Laj}{\bar{u}\sqrt{n}} \exp(\Delta H_s/RT_R) \quad (39)$$

where j = Martin compressibility factor. From eqn. 15 (neglecting T_1 term):

$$\frac{aL}{\beta\bar{u}} \exp(\Delta S_B T_B/RT_R) = \frac{RT_R^2}{\Delta S_B T_B r} \quad (40)$$

Substituting eqn. 40 into eqn. 39, we obtain

$$p_w = \frac{4RT_R^2 j}{\Delta S_B \sqrt{n} T_B r} \quad (41)$$

Thus, from eqn. 35 and substituting $R = 1.98$ and $\Delta S_B = 21$:

$$R = \frac{2.63 \Delta t_R r T_B(\text{mean}) \sqrt{n_{Av}}}{j T_R^2(\text{mean})} \quad (42)$$

or

$$R = \frac{2.63 \Delta T_R T_B(\text{mean}) \sqrt{n_{Av}}}{j T_R^2(\text{mean})} \quad (43)$$

where

n_{Av} = mean column efficiency;

Δt_R = difference in retention times (min);

ΔT_R = difference in retention temperatures;

$T_R(\text{mean})$ = mean retention temperature of the two components;

$T_B(\text{mean})$ = mean boiling point of the two components.

Thus, resolution is inversely proportional to the square of the absolute retention temperature. Table VI gives theoretical values of the resolution expected between anthracene and phenanthrene for the glass capillary column at different programming rates. Increasing the programme rate is seen to adversely affect the resolution because of the increasing retention temperature. Experimental values are included for comparison.

TABLE VI

THEORETICAL AND EXPERIMENTAL VALUES OF RESOLUTION BETWEEN ANTHRACENE AND PHENANTHRENE IN LPTGC

Programming rate, r ($^{\circ}\text{C}/\text{min}$)	Resolution, R	
	Theory	Experimental
1	1.84	1.79
2	1.78	1.72
3	1.72	1.59
4	1.68	1.52

CONCLUSIONS

Aromatic hydrocarbons have been shown to give a linear relationship between retention time and boiling point in LPTGC provided that the initial temperature is sufficiently low and the programming rate is suitably chosen. An optimum initial temperature for a particular boiling range can be calculated from eqn. 32, as can the maximum programming rate that will ensure elution of the entire sample within the programme. The only preliminary information required to apply the equations is the ΔS_B value for the chemical class and the \emptyset value for the column and its operating conditions. Both are derived from $\log t_R$ versus $1/T_c$ plots (where T_c = column temperature) for typical components of the sample at at least two isothermal temperatures. The calculations have been shown to apply to packed, capillary and PLOT columns for aromatic hydrocarbons. Under linear elution conditions the retention temperature increases with (a) boiling point, (b) programming rate, (c) \emptyset value of the column, and any factor which increases the retention temperature will decrease the resolution according to eqn. 43. However, the analysis time decreases with increasing programming rate, as shown in Table IV, and so in practice a compromise between resolution and analysis time must be made.

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