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GAS CHROMATOGRAPHY WITH TEMPERATURE PROGRAMMING

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1. INTRODUCTION

The gas-chromatographic analysis of complicated mixtures of organic compounds, differing markedly in partition coefficients, almost always requires the application of a variable temperature. In fact, it is impossible to choose a constant temperature such that light and heavy components can be separated satisfactorily in the same analysis. If a low temperature is chosen, light components will be separated satisfactorily, but a long time will be required to analyse the heavy components. Furthermore, because of the considerable spreading of the peaks, the sensitivity of the chromatograph will be too low for the heavy components. At a high temperature the heavy components readily show up, but the retention time of the light components is so short that they cannot be separated even on a highly efficient column.

The problem has been solved by applying to the mixture to be separated either a moving temperature profile with a constant temperature gradient in the direction of flow of the carrier gas, or by varying the temperature simultaneously along the whole column.

The former method was proposed and developed by Zhukhovitskii and Turkel'taub together with their collaborators [1-5], and is termed stationary chromathermography. In this method the components of the mixture are distributed inside the column in such a way that the less volatile substances are located near the inlet, where the temperature is higher, and the more volatile substances near the outlet. The components remain practically stationary relative to the furnace producing the temperature gradient, and move towards the outlet from the column at the same speed as the furnace gradient. In the course of time the bands shrink and the mixture becomes enriched.

The other method, which has been called the programmed temperature method, was proposed by Griffiths et al. [6] Temperature programming permits the light components to escape at low temperatures, and the heavy components at high temperatures. In this way an acceptable retention time is obtained, together with quite narrow peaks for both light and heavy components.

At the present time the temperature programming method, which is simpler in practice, is predominantly used, and most of the papers have been devoted to it. Undoubtedly the stationary chromathermography method also shows promise, and will be developed in the future. The present paper discusses only the temperature programming method. A detailed description of stationary chromathermography can be found in two monographs [7,8].

The practice of temperature programming has developed greatly. A theory has been constructed which enables results for isothermal chromatography to be used to determine the retention temperature, ascertain the degree of component separation as a function of the operating conditions, and identify the components of a complex mixture.

Temperature programming is employed in the quantitative analysis of hydrocarbons, alcohols, ethers and esters, aliphatic acids, aromatic compounds, synthetic oils, etc.[9-16] Both packed and capillary columns are used. Several firms market instruments for chromatography with temperature programming.

Temperature programming in gas chromatography usually involves the use of linear programmes of the type

$$T = T_0 + rt \tag{1}$$

where T_0 is the initial temperature, r a parameter characterising the rate of change of temperature, and t the time. The choice of linear programmes is dictated primarily by the simplicity of producing them. But the most important reason is that linear programming enables reliable results to be obtained in the quantitative analysis of multicomponent mixtures. The peaks of components belonging to the same homologous series emerge at approximately equal intervals of time in a linear programme, while the resolution of the components is almost the same as under isothermal conditions. However, special forms of nonlinear programmes have several advantages, which will be discussed at the end of this paper.

2. DETERMINATION OF RETENTION TEMPERATURE AND TIME IN LINEAR PROGRAMMING

Underlying the theory of programmed-temperature gas chromatography is a simple equation obtained by several workers[17-20]. If a chromatographic peak traverses a path dl at a speed v in time dt, we have the differential equation

$$dl = v\,dt. \tag{2}$$

At constant temperature Eqn. (2) can be integrated to give

$$L = vt_R \tag{3}$$

where L is the length of the column and t_R the retention time of the peak. On the other hand, the retention time can be expressed in terms of the retention volume V_R and the speed of the carrier gas u:

$$t_R = \frac{V_R}{u}. \tag{4}$$

At any temperature the speed v of the peak at a given instant is

$$v = \frac{uL}{V_R} \tag{5}$$

(if u and V_R are measured at the same mean pressure in the column or at the pressure at the outlet). Substituting from Eqn. (5) in (2), we obtain

$$dl = \frac{uL}{V_R}\,dt. \tag{6}$$

Integration of Eqn. (6) yields

$$\int_0^{t_R} \frac{u\,dt}{V_R} = 1. \tag{7}$$

If the temperature is assumed to vary linearly with time as in Eqn. (1), we find that Eqn. (7) becomes

$$\int_{T_0}^{T} \frac{u}{r}\,\frac{dT}{V_R} = 1. \tag{8}$$

If there is a controlled rate of flow, and this rate is independent of temperature, it follows from Eqn. (8) that

$$\int_{T_0}^{T} \frac{dT}{V_R} = \frac{r}{u}. \tag{9}$$

Eqn. (9) is the starting point for further analysis. It is interesting in that the integral on the left-hand side is the same for all components and columns: it is determined solely by the rate r at which the temperature rises and the speed u of the carrier gas.

The retention volume V_R should be corrected for expansion of the carrier gas. Correction factors, which depend on the pressure gradient in the column, have been given in Ref. 21.

The corrected retention volume can be written

$$V_R = V_m + V_R' \tag{10}$$

where V_m is the retention volume of the gas peak, and

$$V_R' = Ae^{\frac{\Delta H}{R_0 T}}. \tag{11}$$

Eqn. (11) gives the temperature dependence of the retention volume. Here ΔH is the heat of dissolution, R_0 the universal gas constant, T the absolute temperature, and A a constant independent of temperature.

Eqn. (9) can be generalised by making it independent of column length for a column of a given type[22]. On multiplying both sides of this equation by m, the quantity of liquid phase present in the column, we obtain

$$\int_{T_0}^{T} \frac{dT}{V_{Rg}} = \frac{r}{F} \tag{12}$$

where $V_{Rg} = V_g + V_m/m$ is the retention volume per unit mass of the liquid phase, and $F = u/m$ is the speed of the carrier gas per unit mass of the liquid phase.

If, in particular, the length of the column is doubled, while the speed u of the carrier gas remains unchanged, F will be halved, and the retention temperature, i.e. the temperature at which a peak appears, will be given by

$$\int_{T_0}^{T} \frac{dT}{V_{Rg}} = \frac{2r}{F}. \tag{13}$$

But if, at the same time as the column length is doubled, r is halved or u is doubled, the retention temperature will be unchanged.

Eqn. (7) and hence Eqn. (9) can be simplified by postulating that the speed of a peak due to a component is small at $T \simeq T_0$, and that heating is started at the instant of appearance of the carrier-gas peak. We then have

$$\int_{t_a}^{t_R} \frac{u}{V_R'}\,dt = 1 \tag{14}$$

and

$$\int_{T_a}^{T_R} \frac{dT}{V_R'} = \frac{r}{u}, \tag{15}$$

in which t_a is the retention time for the carrier-gas peak, T_a is its retention temperature, and V_R' is defined by Eqn. (11). Rowan considers[20] that Eqn. (15) is accurate, but actually this is not so. If the retention volume of the carrier-gas peak is large (e.g. in a capillary column), the error will be considerable.

Eqn. (9) has several times been tested experimentally. For example, Rowan[20] made a careful comparison of theoretical values of the retention temperature with experimental results. From Eqns. (15) and (11) he obtains for the elution temperature of the components the expression

$$\frac{rAR_0}{u\Delta H}=\int_{\Phi_1}^{\Phi_2}-\frac{e^{-\Phi}}{\Phi^2}d\Phi \qquad (16)$$

where

$$\Phi=\frac{\Delta H}{R_0T},\ \Phi_1=\frac{\Delta H}{R_0T_a},\ \text{and}\ \Phi_2=\frac{\Delta H}{R_0T_R}. \qquad (17)$$

Integration by parts yields

$$\frac{rAR_0}{u\Delta H}=\left[\frac{e^{-\Phi_2}}{\Phi_2}-\frac{e^{-\Phi_1}}{\Phi_1}+\int_{\Phi_1}^{\Phi_2}\frac{e^{-\Phi}}{\Phi}d\Phi\right]=f(\Phi_1-\Phi_2;\Phi_1) \qquad (18)$$

in which all quantities other than Φ_2 and hence T_R are known (A and ΔH are determined from isothermal data). The paper contains tables, compiled by the author, of values of the function f for various values of $\Phi_1-\Phi_2$ and Φ_1. By plotting graphs of this function $f(\Phi_1-\Phi_2,\Phi_1)$, it is easy to determine Φ_2 and T_R for known values of A, ΔH, r, and u. The good agreement with experiment justifies the use of Eqn. (15) as starting point for further calculations.

Measurements have been made[22] of retention volumes in a capillary column for 2,3,3- and 2,3,4-trimethylpentane as a function of temperature in isothermal processes. From these data, the integral

$$\int_{T_0}^{T}\frac{dT}{V_{Rg}} \qquad (19)$$

was evaluated as a function of T_R by numerical integration, and hence the retention temperature was calculated for various values of r/F (from 0 to 0.07 g cm^{-3}). Here, too, agreement between theoretical values and experimental results was good.

In both these[20,22] and other papers the calculated retention temperature was lower by several degrees than the experimental values, and this difference increases with increase in the rate of heating r of the column. Giddings has shown[23] that these errors are caused by a temperature gradient between the walls and the centre of the column. This gradient is due to thermal inertia, and the column therefore operates at lower temperatures than are assumed in the calculations. At the same time the temperature gradient inside the column causes additional spreading of the peaks, which somewhat impairs the separation of the mixture. Temperature distribution profiles in the column have been calculated[24] for various rates of heating.

Dal Nogare and Langlois[18] and Giddings[19] have attempted to calculate the velocity of the peak due to a component by means of the refined formula (11) for the retention volume, with the coefficient A evaluated as a function of the column parameters. The formulae obtained were extremely complicated. In particular, the linear relation between retention time and number of carbon atoms in molecules of a homologous series was shown only by numerical integration on a computer[18]. In order to obtain retention times or temperatures in these papers, the chief constants had to be determined empirically from isothermal chromatographic data, as in other papers[17,20,22]. A detailed account of this work[18,19] has been given in a review by Vigdergauz and Gol'bert[25]. Therefore we shall not discuss it further, especially as application of the simple formula (11) has been shown by several workers to yield good results.

Another paper by Rowan[26] mentions a method for determining the elution temperature of a component when the pressure remains constant at the outlet and the inlet of the column. The speed of the carrier gas then varies according to the law

$$u=\frac{M}{T}+N \qquad (20)$$

where M and N are constants. This paper contains tables and graphs for calculating the retention temperature T_R. In programmed-temperature gas chromatography, however, a constant flow of the carrier gas is usually established, not a constant pressure. It is not necessary, therefore, to discuss the paper[26] in detail.

3. THE EQUIVALENT TEMPERATURE

The so-called equivalent temperature T_γ —the constant temperature at which a peak is eluted in the same time as with the programmed temperature—is of considerable interest. It obviously lies between the limits $T_0<T_\gamma<T_R$. The concept of "equivalent temperature" was introduced by Giddings[27,28].

The time t for elution of a peak at a constant temperature T_γ is

$$t=\frac{V_{T_r}}{u} \qquad (21)$$

where V_{T_γ} is the retention volume at this temperature. On the other hand, the elution time of a peak with a programmed temperature is

$$t=\frac{T_R-T_0}{r}. \qquad (22)$$

Equating (21) and (22), we obtain

$$r=\frac{u(T_R-T_0)}{V_{T_r}}. \qquad (23)$$

Substitution for r in Eqn. (9), with the speed of the carrier gas assumed constant, yields the equation

$$\int_{T_0}^{T_R}\frac{dT}{V_R}=\frac{T_R-T_0}{V_{T_r}}, \qquad (24)$$

which relates T_R with T_γ, since V_{T_γ} depends on the latter temperature.

To find the approximate dependence of T_γ on T_R we shall neglect the retention volume of the gas peak, i.e. assume that $V_R\simeq V_R'$ and $V_{T_\gamma}\simeq V'_{T_\gamma}$. On then differentiating both sides of Eqn. (24) with respect to T_R, and making certain straightforward rearrangements, we obtain the differential equation

$$\exp\left\{-\frac{\Delta H}{R_0T_R}\left(1-\frac{T_R}{T_r}\right)\right\}=(T_R-T_0)\frac{\Delta H}{R_0T_r^2}\frac{dT_r}{dT_R}+1. \qquad (25)$$

An approximate solution of this equation with $T_0\simeq 300°K$ is

$$T_r\simeq\frac{T_R}{1+0.85\frac{R_0T_R}{\Delta H}}. \qquad (26)$$

With temperature programming the peak usually appears at $T_R\simeq T_k$, the boiling point of the component[29]. The value of the universal gas constant is $R_0\simeq 2$ cal deg^{-1}

mole^{-1}, and we also have the approximate value $\Delta H/T_k \simeq$ 23 cal deg^{-1} mole^{-1}. On the assumption that the boiling point of the component is $T_k \simeq 500$°K, we obtain

$$T_r \simeq 0.9T_R \tag{27}$$

whence

$$T_R \simeq T_r + 50. \tag{28}$$

The mean speed of a sample in a column with temperature programming approximately equals the speed of the sample at a constant temperature 50 deg lower than the temperature at which the peak appears with temperature programming.

4. SHARPNESS OF SEPARATION (RESOLUTION) OF COMPONENTS

The quality of the separation of two neighbouring peaks is usually represented by the expression

$$R = \frac{2(t_{R_2} - t_{R_1})}{W_1 + W_2} \tag{29}$$

where W_1 and W_2 are the widths of the peaks at the base, expressed in terms of time, while t_{R_2} and t_{R_1} are the retention times of the two peaks[22]. The formula (29) is used both in isothermal chromatography and with a programmed temperature. In the case of linear programming we have

$$t_{R_2} - t_{R_1} = \frac{T_{R_2} - T_{R_1}}{r}. \tag{30}$$

According to Habgood and Harris[17] the retention volume V_{T_r} for a peak at a constant temperature T_r and the peak width ΔV (retention volume of the peak) with a programmed temperature are linked by the relation

$$n = 16\left(\frac{V_{T_r}}{\Delta V}\right)^2, \tag{31}$$

in which n is the number of theoretical plates in the column, which defines its separating power[30]. The equivalent temperature defined by Eqn. (26) is to be taken[29] as T_r, not the elution temperature T_R of the peak with temperature programming.

With high rates of heating, when $T_R \gg T_0$, the peak widths remain practically constant at the programmed temperature. It has been shown[31] that the width of a peak is independent of the "previous history" of the warming up of the column.

Since

$$W_1 + W_2 = \frac{\Delta V_1 + \Delta V_2}{F} \tag{32}$$

we obtain from Eqn. (31) the formula†

$$W_1 + W_2 = \frac{4}{F\sqrt{n}}(V_{T_{r_1}} + V_{T_{r_2}}). \tag{33}$$

It is assumed here that the column has the same separating power for the two components.

It follows from Eqns. (29), (30), and (33) that

$$R = 2\frac{F}{r}\frac{T_{R_2} - T_{R_1}}{V_{T_{r_1}} + V_{T_{r_2}}} = R_i\frac{\sqrt{n}}{4}. \tag{34}$$

The quantity R_i is termed the intrinsic resolution. It is that part of the resolution which is independent of the separating power of the column and is determined by the thermodynamic properties of the components. In most cases R_i is a maximum at values of r/F lying within the range 0.001–0.1 g deg cm^{-3}.[32,33]

Experiment shows[15] that the intrinsic resolution R_i varies very little with F if the ratio r/F is maintained constant. This is not consistent with theoretical views, most likely because an isothermal retention volume is substituted in Eqn. (31). It is interesting that in general the intrinsic resolution varies little with r/F.

If we increase the column length L, while leaving the ratio r/F constant, the retention temperature remains unchanged. The resolution, however, increases as $L^{\frac{1}{2}}$, because $n^{\frac{1}{2}} \propto L^{\frac{1}{2}}$. When the input pressure far exceeds the output pressure, the former must be increased as $L^{\frac{1}{2}}$ for the ratio r/F to remain constant when the speed of the carrier gas is unchanged, while r should decrease as $L^{-\frac{3}{2}}$.[22] Consequently the emergence time of the peak (22) increases with $L^{\frac{3}{2}}$ under the above conditions, as in isothermal chromatography.

Since the intrinsic separation is almost independent of F for identical values of the ratio r/F, it is advisable to operate with values of F for which R_i is a maximum with the given r.

The effect of r on the retention time resembles the effect of temperature in isothermal chromatography. The time for elution of the peak decreases with increase in r, approaching a limiting value. Correspondingly, the resolution diminishes somewhat with increase in r, as is immediately evident from the formula (34).

The number of theoretical plates defined by Eqn. (31) may differ markedly from the corresponding number for a constant temperature. Attempts[17,34] to calculate the number of theoretical plates as a function of the column parameters with temperature programming did not yield results showing good agreement with experiment.

It is found experimentally that, with a programmed temperature, the number of theoretical plates varies with r at a fixed rate of flow, diminishing with increase in r. In the case of temperature programming the resolving power is more difficult to predict than in an isothermal process, where it is proportional to $n^{\frac{1}{2}}$. The resolution of components varies both with the number of plates and with R_i, which depends on r/F.

In conclusion it must be emphasised that experiment shows[22] that the resolution which can be achieved with temperature programming is almost the same as, and sometimes even better than, in isothermal chromatography. If, however, the time available for the analysis has been specified, programming the temperature ensures a sharper separation than does the isothermal process, as Zhukhovitskii and Turkel'taub have shown (Ref. 7, p. 150). Furthermore, the enrichment of the components of the mixture, which is associated with the narrowing of the chromatographic peaks in temperature programming, enhances the sensitivity of the instrument, which is extremely important in the analysis of microsamples[31].

5. RETENTION INDEX

The retention index was introduced by Kováts[35,36] as a measure of the retention of a component which would vary

† Here and subsequently we are dealing with specific retention volumes, i.e. volumes per unit mass of the liquid phase.

little with the operating conditions of a separating column or its packing. Consequently the retention index can conveniently be used for the identification of the components of a complicated mixture.

In the case of isothermal chromatography the introduction of the retention index is based on a linear variation in the logarithm of the retention volume V_R' with the number of carbon atoms in unbranched-chain hydrocarbons. The retention index varies very slightly—and linearly—with temperature.

In the case of a programmed temperature, introduction of the retention index is based on an approximately linear dependence of the retention temperature on the number of carbon atoms. The retention index is then by definition

$$I = 100\,\frac{T_R(x) - T_R(z)}{T_R(z+1) - T_R(z)} + 100\,z \qquad (35)$$

where $T_R(x)$, $T_R(z)$, and $T_R(z+1)$ are the retention temperatures of the test compound and of hydrocarbon components containing z and $z+1$ carbon atoms. If the relation between the retention temperature and the number of carbon atoms in the molecules were strictly linear, the retention index would simply equal the number of carbon atoms multiplied by 100. Since, however, this relation will not be exactly linear, the index will not coincide with this product, although in several cases it will be close to the latter. The formula (35) for the retention index is convenient, as it can be evaluated directly from a chromatogram without any preliminary calculations.

The retention index (35) is usually equal to the index for the isothermal process conducted at the equivalent temperature[37].

It is significant that, as experiment shows with a programmed temperature, the retention index varies little over quite a wide range—variation in the initial temperature T_0 and in the rate r of rise in temperature—of operating conditions. If, therefore, a component has once been reliably identified, and its retention index is known, unknown components in a complicated mixture can be identified by measuring their retention indices by means of the chromatogram. A detailed examination has been made[38] of the temperature dependence of the retention index both with temperature programming and in isothermal chromatography.

It is difficult to use the retention temperature T_R directly for purposes of identification, since Eqn. (9) cannot be solved explicitly for constant ΔH, which characterises the component. Values of T_R, however, vary markedly with the operating conditions of the chromatographic column.

6. NON-LINEAR TEMPERATURE PROGRAMMING

The application of linear temperature programming, which has been discussed in the preceding paragraphs, involves certain difficulties. The chief of these is the impossibility of obtaining the retention time (or, what amounts to the same, the retention temperature) in a simple analytical form[8]. Recourse must be had either to numerical integration or even to the use of tables of special functions. Further, the coefficient r, representing the rate of change of temperature, cannot, for technical reasons, be varied continuously. Consequently, in order to obtain different rates of change of temperature, a set of programmes must be used.

These disadvantages (mainly the first) can be eliminated by using a special type of non-linear programme[39]. By this means it is possible to obtain practically the same results as with the linear programme, but with a simple analytical expression for the elution time of various components of the mixture. Furthermore, the choice of different initial points on the programme is roughly equivalent to varying the rate of temperature rise in a linear programme.

If the temperature of the column varies with time according to the law

$$T = \frac{T_0}{1 - \beta t} \qquad (36)$$

where β is a constant defining the rate of temperature rise, we obtain from Eqns. (14) and (11) for the retention time t_R the simple expression

$$e^{\varepsilon t_R} = \varepsilon t_{0R} + e^{\varepsilon t_a} \qquad (37)$$

in which

$$\varepsilon = \frac{\Delta H \beta}{R_0 T_0} \qquad (38)$$

and

$$t_{0R} = \frac{A}{u}\, e^{\frac{\Delta H}{R_0 T_0}} \qquad (39)$$

is the retention time of the peak on chromatographing at a constant temperature. If the elution time t_a of the carrier-gas peak is short, taking logarithms in Eqn. (37) yields the following simple formula for the retention time

$$t_R = \frac{1}{\varepsilon} \ln(\varepsilon t_{0R} + 1). \qquad (40)$$

From Eqn. (40) it is easy to show that the condition of equal distances on the chromatogram between peaks due to successive members of a homologous series is approximately satisfied with the temperature programme (36), provided that the number of carbon atoms in the molecules is sufficiently large. This conclusion is supported by experiment. Retention times measured experimentally for normal alkanes agree well with Eqn. (40).

The above non-linear programme (36) is equivalent to a series of successive linear programmes having increasing values of r. But, since the resolution R is only slightly dependent on r, the resolution obtained with the non-linear programme will differ little from that obtained with a linear programme having $r \simeq \beta T_0$. Of course, the peaks due to heavy components will be rather less well resolved, since they appear at high effective values of r.

With non-linear programming it is possible to introduce a retention index just as with linear programming, but the retention temperature must be replaced by the retention time, since it is the latter which depends approximately linearly on the number of carbon atoms. The retention index can be defined

$$I = 100\,\frac{t_R(x) - t_R(z)}{t_R(z+1) - t_R(z)} + 100\,z \qquad (41)$$

where $t_R(x)$, $t_R(z)$, and $t_R(z+1)$ are the retention times of the test compound and of hydrocarbon components containing z and $z+1$ carbon atoms.

Nevertheless, the relation between the retention time and the parameter ϵ characterising the component is so simple that components can be identified directly from the retention time by means of Eqn. (40).

However, it is not always easy to carry out the isothermal experiment (e.g. with mixtures having a wide range of boiling points). A new method was therefore proposed for determining heats of dissolution ΔH and identifying components, based on the use of two non-linear programmes of the type (36) with different rates of temperature rise[40].

If two chromatograms are obtained with rates of temperature rise defined by the parameters β and $\beta' = \alpha\beta$ (where α is a number), the isothermal retention time t_{0R} of the component can be eliminated, and two equations of the type (40) used to obtain the simple expression

$$e^{\epsilon t_R} = \frac{1}{\alpha} e^{\alpha\epsilon t'_R} + e^{\epsilon t_a} - \frac{1}{\alpha} e^{\alpha\epsilon t'_a} \qquad (42)$$

for determining ϵ and hence ΔH, where t_R and t'_R are the retention times of the component for the different programmes, and t_a and t'_a those of the gas peak. It is easy to evaluate ϵ by the graphical solution of Eqn. (42).

Good results have been obtained in a test of this method of determining heats of dissolution using a mixture of primary alcohols, methyl ketones, and hydrocarbons. The heats of dissolution fitted satisfactorily on straight lines representing the homologous series, which permitted reliable identification of the components.

This method of identifying components has the advantage, in comparison with the method based on the retention index, that it does not in principle require a linear dependence of retention temperature on number of carbon atoms. Furthermore, from it an important physical quantity—the heat of dissolution—can be determined.

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