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Programmed-temperature gas chromatography

Comparative study of retention temperatures on four unequally polar stationary phases

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ABSTRACT

Retention temperatures (T_R) of a series of solutes on four packed columns coated with OV-105, PS-255, di-*n*-decyl phthalate and OV-275 were measured at different programming rates and compared with other T_R values calculated by some current equations, confirming that the equations of Curvers *et al.*, Krupčík *et al.* and Akporhonor *et al.* predict the retention temperatures closest to the observed T_R values. Programmed-temperature retention indices (PTRIs) calculated by cubic splines interpolation of both the experimental and some other calculated T_R values were also compared, taking the former as standard, the resulting PTRI values differing by only 2% for at least 90% of the solutes on the low-polarity stationary phases.

INTRODUCTION

Retention times and temperatures are the most important retention data in programmed-temperature gas chromatography (GC). This technique is advantageously used when dealing with analyses of complex mixtures. As in isothermal GC, the retention index of a given compound has to be calculated in order to identify it among the other peaks in a mixture.

The retention data available to a chromatographer have been chiefly obtained under isothermal conditions, and therefore it has always been an aim to utilize such data in order to interpret programmed-temperature information. Habgood and Harris [1], Grant and Hollis [2] and Curvers *et al.* [3] have shown the feasibility of predicting programmed-temperature retention data from data obtained at various isothermal temperatures. With a very similar formulation, Akporhonor *et al.* [4] calculated retention times at programmed temperatures from retention data obtained from isothermal chromatograms.

Early, empirical equations relating linearly retention temperatures (T_R) with an equivalent temperature were reported, for example, the equations of Giddings [5] and Guiochon [6] in the 1960s. In the 1980s, Lee and Taylor [7], Krupčík *et al.* [8] and Said [9] published other equations with which approaches to calculating programmed-temperature retention indices (PTRIs) could be made.

The objective of this work was to carry out a survey study of all of these retention temperatures for eleven *n*-alkane and fifteen non-*n*-alkane solutes using seventeen temperature programmes developed on four packed columns coated with both low- and high-polarity stationary phases. An empirical equation to calculate T_{eq} in terms of the logarithm of the

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measured retention time from chromatograms was also tested.

Comparisons were made both graphically, observing the ΔT_R differences between the observed and the equivalent/calculated T_R values of the distinct solutes *versus* their corresponding observed retention times, and also by calculating the variance of these differences.

The final aim of obtaining retention times (t_R) and T_R values at programmed temperatures for the above-mentioned solutes by applying directly the equations examined in this study was to be able to calculate at once their PTRIs, which cannot be determined by direct application of the Kováts [10] equation. The purpose of all of this is to reduce the need to obtain many programmed-temperature chromatograms.

Expressions such as those of Van den Dool and Kratz [11] and several others [12–17] have recently been reviewed and as a result of this study [18,19] it is noted that the cubic splines [20] interpolation offers the best results for the calculation of PTRIs and it is now preferred by many workers because it can be applied over broader retention temperature intervals.

PTRIs were obtained by interpolating the T_R values of fifteen non-*n*-alkane solutes for the seventeen afore-mentioned programmes and the differences between experimental PTRIs (using experimental T_R values) and calculated PTRIs (making use of T_R calculated by three equations) were calculated with the purpose of checking which equation yields T_R values closest to those measured from the chromatograms.

THEORY

It has been said that retention temperature is to programmed-temperature GC as retention time is to isothermal GC. Like the latter, retention temperature is in fact the peak fingerprint that enables the chromatographer to carry out its unequivocal identification in a mixture using temperature programming. Put more properly, the retention index is the parameter that finally leads to the achievement of the identification of a given peak and it is the main intention when programmed-temperature GC is undertaken.

If PTRI data are available, a solute in a mixture can be identified with temperature programming as easily as by using an isothermal temperature. On the other hand, it is more convenient to apply temperature programming because the peak separation is improved and peaks are eluted in a shorter time, are narrower and so can be measured better. If the temperature programme is simple, T_R values can be obtained directly from the chromatograms. Today, most chromatograms are measured with temperature programming.

If T_R values are unavailable, the use of equivalent or calculated temperatures may be of help in determining approximate PTRIs.

Equivalent temperatures (T_{eq})

The equivalent temperature is the retention temperature of a peak that would have the same retention time in a programmed-temperature run as it would in an isothermal run. Akporhonor *et al.* [21] distinguished between this temperature and another that they defined as that which would yield the same retention index in a programmed-temperature run as in an isothermal run. The two differ very little.

Calculated retention temperatures

There are three equations for determining T_R values from isothermal data: the equation of Curvers *et al.* [3], which calculates T_R values directly, the equation of Akporhonor *et al.* [4], which computes retention times, and the equation of Krupčík *et al.* [8], which involves retention temperatures of a standard *n*-alkane series.

The first two equations permit advantage to be taken of the enormous number of isothermal data that are available, although it is argued that the thermodynamic parameters of chromatographic peaks obtained from the isothermal capacity factors or retention times show some inaccuracies in their measurements owing to the very nature of the approach used in these treatments. This gives support to the argument that they are not as fine calculation methods as was at first thought [22]. Moreover, it is questioned whether *n*-alkanes may be used as reference solutes when one uses very polar phases [23].

On the other hand, the entropic term $\exp[(\Delta S/R)/\beta]$ (see eqn. 4 below) depends on the phase ratio, in the measurement of which some uncertainty exists, especially when packed columns are involved [24]. In addition, the enthalpic term also depends slightly on the phase ratio [21].

Krupčík *et al.*'s equation calculates T_R values of non-*n*-alkane solutes from isothermal retention data for *n*-alkanes, that is, the isothermal retention index at a given temperature, thermal gradient of the retention index of the peak and the retention temperatures of the *n*-alkanes eluted before and after the solute under study.

Current equations

The seven expressions used in the calculations in this paper (Table I) are as follows:

(1) Equation of Giddings [5]:

$$T_{eq} = 0.92 T_R \qquad (1)$$

(2) Equation of Guiochon [6]:

$$T_{eq} = T_R - 20 \qquad (2)$$

(3) Equation of Lee and Taylor [7]:

$$T_{eq} = 2\, T_R T_0 / (T_R + T_0) \qquad (3)$$

where
T_{eq} = equivalent temperature (K);
T_0 = initial temperature (K);
T_R = measured retention temperature (K).

(4) Equation of Curvers *et al.* [3]:

$$r = \int_{T_0}^{T_R} dT / t_m(T) [1 + (a/\beta) \exp(\Delta H/RT)] \qquad (4)$$

where
$a = \exp(\Delta S/R)$ and $\Delta H/R$ are the entropic and enthalpic parameters;
r = programming rate;
$t_m(T)$ = hold-up time function.

TABLE I

RETENTION TEMPERATURE EQUATIONS

Workers	Eqn. No.	Year	Ref.
Giddings	1	1962	5
Guiochon	2	1964	6
Lee and Taylor	3	1982	7
Curvers *et al.*	4	1985	3
Krupčík *et al.*	5	1986	8
Said	6	1988	9
Akporhonor *et al.*	7	1989	4

(5) Equation of Krupčík *et al.* [8]:

$$T_{R,i} = \frac{[I(T_1) - 100\,Z - T_1(dI/dT)](T_{R,Z+1} - T_{R,Z}) + 100\,T}{100 - (dI/dT)(T_{R,Z+1} - T_{R,Z})} \qquad (5)$$

where
$T_{R,i}$ = retention temperature of compound i;
$I(T_1)$ = isothermal retention index at temperature T_1;
dI/dT = isothermal retention index gradient;
$T_{R,Z+1}$, $T_{R,Z}$ = retention temperatures of the $Z + 1$ and Z reference *n*-alkanes.

(6) Equation of Said [9]:

$$T_{eq} = (T_{Ri} - T_0)[\exp(-1.55\, \Delta t_p / t_{Ri})] + T_0 \qquad (6)$$

where
$\Delta t_p = t_{R,Z+1} - t_{R,Z}$;
$T_{R,i}$ = retention temperature of a solute i;
Δt_p = retention time differences of reference *n*-alkanes;
t_R = retention time of a solute i;
T_0 = initial temperature.

(6) Equation of Akporhonor *et al.* [4]:

$$1 = \int_0^{t_R} dt / t_m(T) \{1 + k_1 \exp[k_2/(T_0 + k_3 t)]\} \qquad (7)$$

where
$t_m(T)$ = hold-up time function;
$k_1 = \beta \exp(\Delta S/R)$ = entropic term;
$k_2 = -\Delta H/R$ = enthalpic term;
k_3 = programming heating rate;
$\beta = V_L/V_M$ = phase volume ratio.

(7) In addition to the above equations, the following empirical equation has been tried:

$$t_{eq} = 0.805 \log (T_R - T_0) \qquad (8)$$

where
T_R = retention temperature;
T_0 = temperature at which the programme starts;
t_{eq} = temperature expressed in °C.

EXPERIMENTAL

The columns used were 2 m × $\frac{1}{8}$ in. O.D. and 4 m × $\frac{1}{8}$ in. O.D. stainless-steel, packed with PS-255, OV-105, di-*n*-decyl phthalate and OV-275 stationary phases on Chromosorb W AW.

The solutes were C_5–C_{17} *n*-alkanes, the ten McReynolds' probes and acetone, cyclopentanone, toluene, *o*-xylene, ethyl acetate, *n*-octanol and dimethylaniline.

Isothermal temperatures used were 68, 79, 80, 90, 100, 110, 113, 120, 130, 140, 150 and 179°C. With temperature programming the initial temperatures were 50, 60, 70 and 80°C and the heating rates were 1, 1.5, 2, 3, 4, 6 and 10°C/min.

The chromatograph was a Perkin-Elmer Sigma 2 with a flame ionization detector. The oven temperature was monitored to within ±0.2°C. Minigrator and Varian 4270 electronic integrators were used. The carrier gas was nitrogen at a flow-rate of 10 ml/min.

RESULTS AND DISCUSSION

Experimental T_R values obtained directly from retention times obtained from programmed-temperature chromatograms via a linear programming temperature relationship have recently been reported [19]. The equivalent or calculated T_R values under the same conditions were obtained using eqns. 1–8.

Comparison of the two sets of T_R values was carried out in two manners, graphically, plotting the ΔT_R(exp. − eq.)/ΔT_R(exp. − calc.) *versus* the corresponding experimental retention times, and in terms of the variances of the same differences, $[\sum_{i=1}^{N} (\Delta T_R)^2]^{\frac{1}{2}}/(N-1)$, where N is the number of solutes. To compare all the different equations only retention temperatures of the non-*n*-alkanes were included in the plots, as same equations do not calculate *n*-alkane T_R values. For the calculation of the variances, data for all the solutes were taken.

ΔT_R difference curves

Fig. 1 shows the shapes of the difference curves, that is, the differences between the observed T_R values and the equivalent or calculated temperatures for solutes other than *n*-alkanes using all the equations. Five programmes were featured.

Obviously, the errors given by the Giddings, Guiochon and Lee and Taylor straight lines are large, of the order of 20°C (as a reference, the Guiochon parallel straight line at 20°C has been drawn in the plots). The difference between the Giddings and Lee and Taylor lines is the greater slope of the latter.

Considering the other equations, the ΔT_R differences are clearly curves and it is observed that only minor errors result when the equations of Curvers *et al.* and Krupčik *et al.* are applied.

When the equations of Akporhonor *et al.* and Said are used, errors lying between the above and those deduced from the reference Guiochon equation line are obtained.

With regard to OV-275, it can be said that the Lee and Taylor straight line represents smaller errors than for less polar phases. Moreover, all the errors are smaller for the polar OV-275. The same tendency was observed with other programme run.

With respect to the *n*-alkanes the same results are obtained, *i.e.*, the least errors are produced by the retention temperatures calculated with the equations of Curvers *et al.* and Akporhonor *et al.* and large errors are observed for the equivalent temperature empirical straight lines.

Therefore, it seems hat the equivalent temperatures are grosser approximations than the calculated temperatures.

Curvers et al. and Akporhonor et al. ΔT_R curves

An example of the differences between the T_R values calculated using eqns. 7 and 4 and the experimental temperatures is shown in Fig. 2A and B. Fig. 2A shows that in every case the points that represent the errors which result on applying Akporhonor *et al.*'s equation in the calculation of the T_R values of solutes other than *n*-alkanes fall more or less on the curve that contains these errors (the terms "error" and "difference" are used indistinctly) computed for the T_R values of the standard *n*-alkane homologues. With OV-275 all the lines occur at smaller differences values than for the other stationary phases. The only major disagreement is observed with the more polar solutes such as *n*-octanol and cyclopentanone using the more polar stationary phase, OV-275.

Fig. 2B depicts the error curves provided by the Curvers *et al.* equation. The situation is very similar. The *n*-alkane error points fall on curves and around them are located the corresponding error points deduced for the other solutes.

Again, it becomes evident that both the nearly non-polar OV-105 and PS-255 and the low-polarity di-*n*-decyl phthalate stationary phases behave in a different way to the polar OV-275 phase with respect to the way in which the differences between the

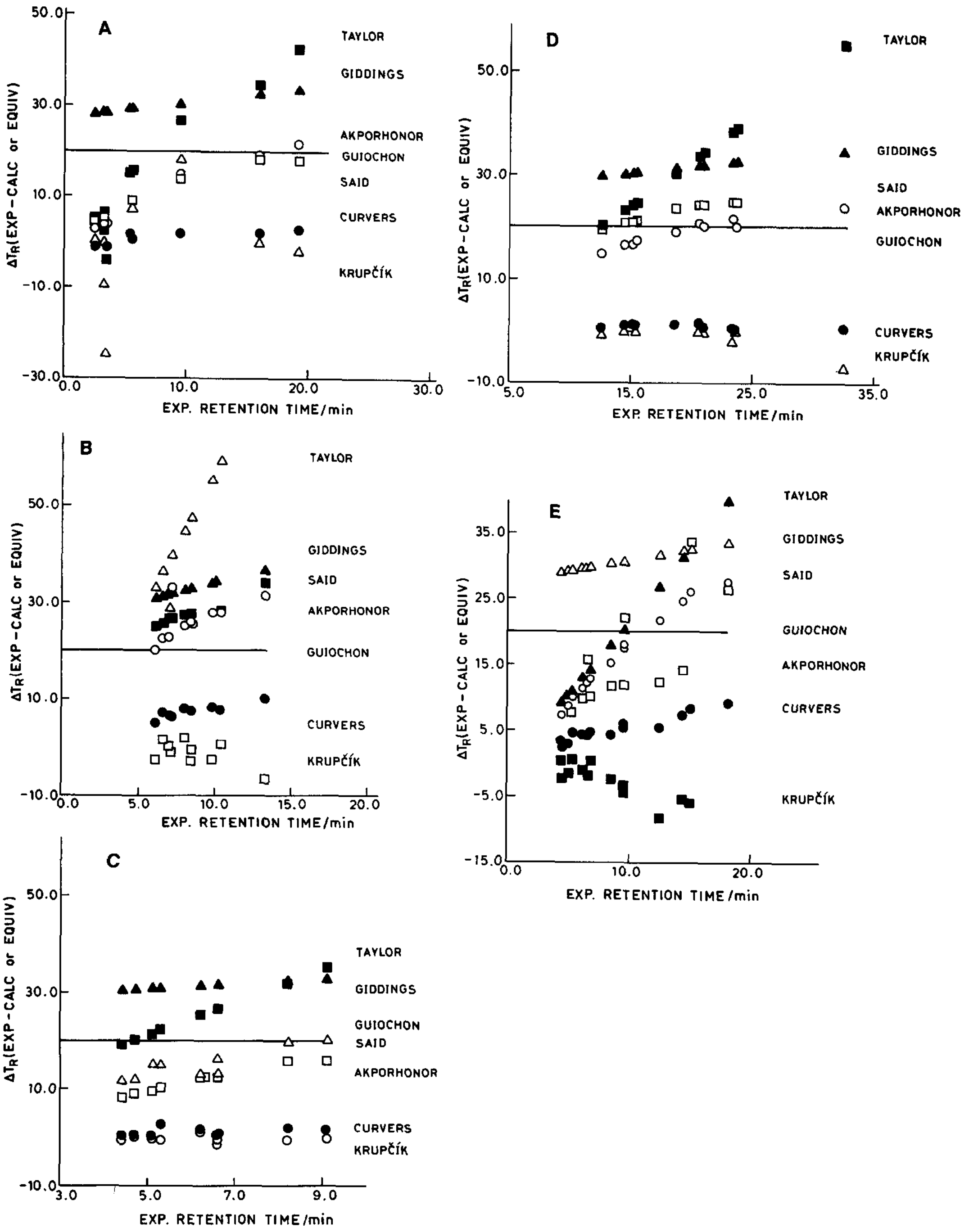

Fig. 1. Plots of ΔT_R(exp. − eq.) or ΔT_R(exp. − calc.) *vs.* the experimental retention times for solutes other than *n*-alkanes. Eqns. 1–8 were used in the calculations. Stationary phases and programmes: (A) PS-255, $T_0 = 70°C$, $r = 4°C/min$; (B) OV-105, $T_0 = 50°C$, $r = 10°C/min$; (C) OV-105, $T_0 = 80°C$, $r = 6°C/min$; (D) di-*n*-decyl phthalate, $T_0 = 60°C$, $r = 3°C/min$; (E) OV-275, $T_0 = 70°C$, $r = 4°C/min$.

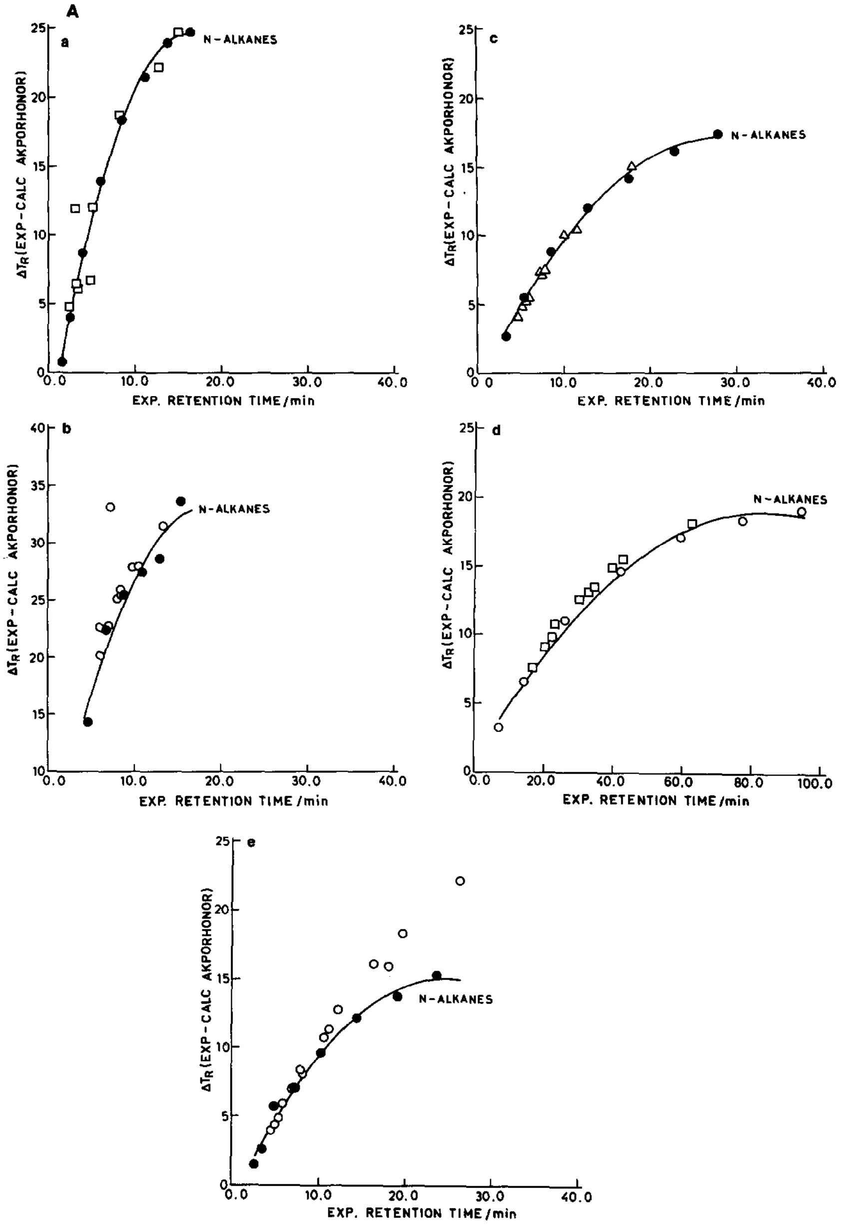
A
a
b
c
d
e
N-ALKANES
ΔTR(EXP-CALC AKPORHONOR)
EXP. RETENTION TIME/min
0.0
10.0
20.0
30.0
40.0
60.0
80.0
100.0
0
5
10
15
20
25
30
35
40

Fig. 2.

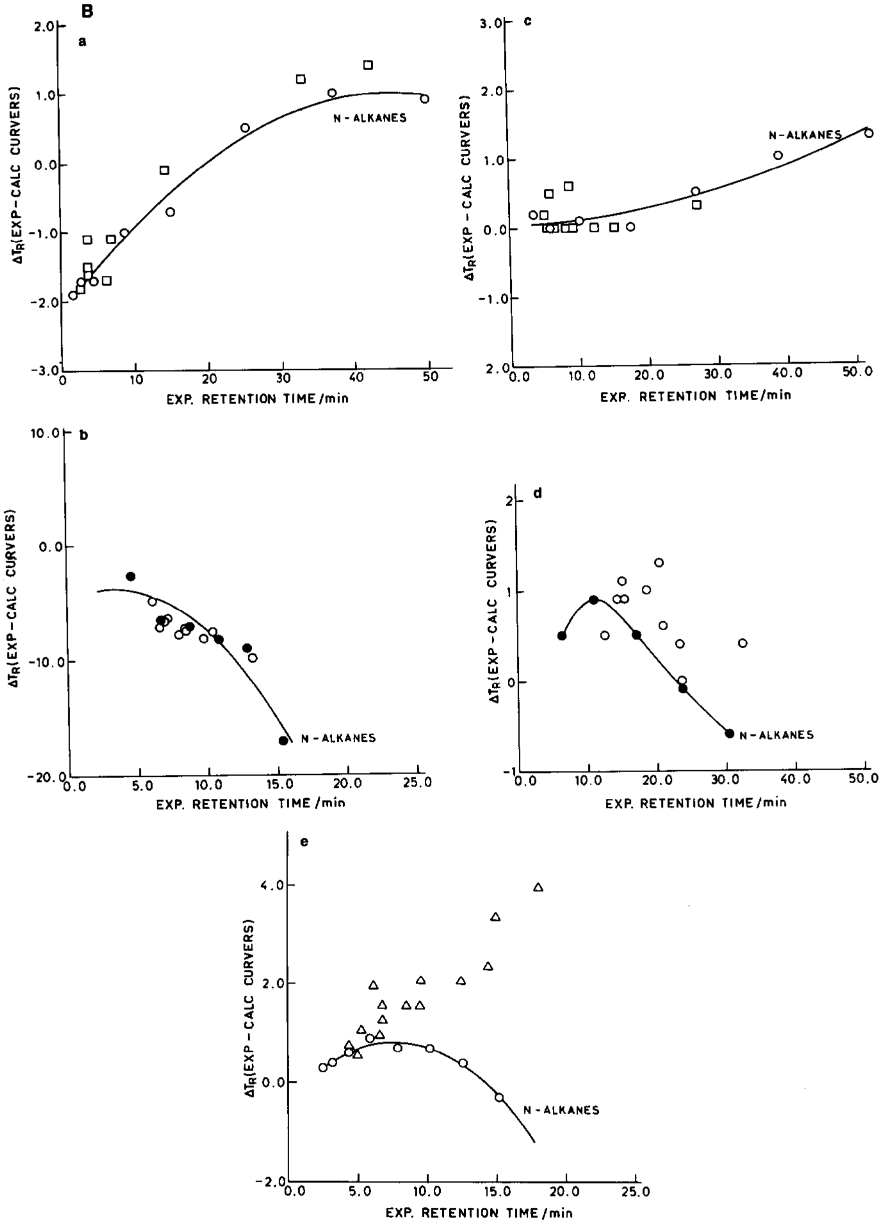

Fig. 2. (A) Plots of the errors of ΔT_R(exp. – calc. by eqn. 7) *vs.* experimental t_R values. All the solutes combined. Stationary phases and programmes: (a) PS-255, $T_0 = 70°C$, $r = 6°C/min$; (b) OV-105, $T_0 = 50°C$, $r = 10°C/min$; (c) OV-105, $T_0 = 80°C$, $r = 3°C/min$; (d) di-*n*-decyl phthalate, $T_0 = 60°C$, $r = 1°C/min$; (e) OV-275, $T_0 = 70°C$, $r = 2°C/min$. (B) Plots of the errors ΔT_R(exp. – calc. by eqn. 4) *vs.* experimental t_R values. All the solutes combined. Stationary phases and programmes: (a) PS-255, $T_0 = 70°C$, $r = 2°C/min$; (b) OV-105, $T_0 = 50°C$, $r = 10°C/min$; (c) OV-105, $T_0 = 80°C$, $r = 1°C/min$; (d) di-*n*-decyl phthalate, $T_0 = 60°C$, $r = 3°C/min$; (e) OV-275, $T_0 = 70°C$, $r = 4°C/min$.

measured and equivalent/calculated T_R values for both non-*n*-alkanes and *n*-alkanes lie close together for the former three phases; conversely, some dispersion of the T_R values for the non-*n*-alkane solutes with respect to the way in which the *n*-alkanes differences accumulate is observed with the strongly polar OV-275 stationary phase.

TABLE II

RETENTION TEMPERATURE DIFFERENCES FOR SEVERAL PROGRAMMES

Calculated variances for ΔT_R(exp. − eq.) or ΔT_R(exp. − calc.) according to eqns. 1–8. Solutes: *n*-alkanes, non-*n*-alkanes and all of the solutes combined.

Stationary phase	Eqn. No.	*n*-Alkanes	Non-*n*-alkanes	All solutes
PS-255 (T_0 = 70°C, r = 6°C/min)	1	12.7	11.4	7.9
	2	8.1	7.5	5.1
	3	12.6	10.1	7.5
	4	1.2	0.9	0.7
	5		5.2	5.2
	6		4.7	4.7
	7	6.8	5.4	1.3
	8	4.3	4.4	2.9
Di-*n*-decyl phthalate (T_0 = 60°C, r = 1.5°C/min)	1	11.9	10.5	8.0
	2	8.8	7.1	5.1
	3	7.5	8.4	7.0
	4	0.6	0.5	0.3
	5		0.4	0.4
	6		6.6	6.6
	7	4.5	5.5	2.1
	8	7.4	4.3	6.3
OV-105 (T_0 = 50°C, r = 2°C/min)	1	13.3	10.6	7.9
	2	8.8	7.1	5.1
	3	15.0	7.0	6.9
	4	0.8	0.9	0.6
	5		0.3	0.3
	6		5.7	5.7
	7	6.1	4.5	1.2
	8	13.2	11.9	8.3
OV-105 (T_0 = 80°C, r = 3°C/min)	1	14.0	10.6	7.9
	2	8.8	7.1	5.1
	3	11.8	4.8	5.2
	4	0.2	0.1	0.1
	5		1.8	1.8
	6		4.3	4.3
	7	5.3	3.0	1.8
	8	3.0	2.1	1.6
OV-275 (T_0 = 70°C, r = 4°C/min)	1	11.4	8.4	6.5
	2	7.5	5.5	4.2
	3	8.2	5.8	4.5
	4	0.8	1.5	1.0
	5		1.4	1.4
	6		2.8	2.8
	7	4.5	4.7	0.9
	8	4.3	2.9	2.3

Variance of retention temperature errors

To know which equations yield retention temperatures closest to the experimental values, the error ΔT_R(exp. − eq.) or ΔT_R(exp. − calc.) variances for all the solutes over all the seventeen programmes run were calculated according to eqns. 1–8.

Variances for *n*-alkanes and the other solutes for five programmes can be compared in Table II. The first column gives the equation used and the other three columns give the variance values for the *n*-alkanes, the non-*n*-alkanes and all of the solutes combined.

In all instances the *n*-alkane variances show the highest values. Also, it is apparent that the lowest variance values result from applying eqns. 4, 7 and 5 when all the solutes are considered. Clearly larger values are associated with eqns. 1 and 3, in agreement with Fig. 1.

A more general review of the variance behaviour for all the solutes with the seventeen programmes executed is shown in Table III. Eqn. 2 is the standard straight line in the plots in Fig. 1 and logically yields the same value irrespective of the rate being considered. It is observed that the variance increases with increase in the rate of heating and that eqns. 4, 7 and 5 yield low values of the variance. According to Akporhonor *et al.* [21], their equation works well for capillary columns but does not seem to perform as well for packed columns, maybe because it is difficult and erratic to measure β [24] and this parameter takes part in the formulation (see eqn. 7) affecting the entropic term which, on the other hand, depends on the phase ratio, two aspects that must be accounted for. Said's equation (eqn. 6), the empirical equation proposed on this paper and the equations of Guiochon, Lee and Taylor and Giddings give increasingly larger variances.

Table IV is intended to give an overall view of the performance of these equations and the extent to which they can be used to obtain approximate retention temperatures without having to measure any programmed-temperature chromatograms. The values given represent the averages of the variances in Table III for all the heating rates for each stationary phase and for each equation, all of them referred to the value of the variance corresponding to eqn. 2. For instance, considering PS-255, $1.49 = (1/4)[7.3 + 7.5 + 7.7 + 7.9]/5.1$, and so on. Table IV indicates that for every stationary phase the smallest values result when the equations of Curvers *et al.*, Akporhonor *et al.* and Krupčík *et al.* are used to calculate the T_R values. The three least suitable equations are those of Giddings, Guiochon and Lee and Taylor, and eqns. 6 (Said) and 8 are located in the middle of the eight. The bottom row in Table IV gives the results of adding the figures for the four stationary phases for each equation, and corroborates the above conclusion for the four stationary phases separately. It should be remembered that eqns. 5 and 6 do not calculate retention temperatures for *n*-alkanes.

Retention indices error

It seems widely accepted that the retention indices closest to the true values are the PTRIs calculated by cubic splines interpolation of experimental retention temperatures of the *n*-alkanes in ref. 20, as becomes evident on observing the T_R *vs.* Z curves for these solutes where excellent cubic splines fits are obtained [18,19].

In this work, a comparison was made between the cubic splines PTRIs computed for the above T_R values and for those calculated via eqns. 4, 7 and 8. Table V shows these values for some programmes.

The relative errors of the retention indices were calculated for all the non-*n*-alkane solutes and mean values for each equation all over the programmes were also evaluated, as shown in Table VI. Again it can be seen how much better the Curvers *et al.* equation performs compared with the other two.

The number of solutes with errors up to 2%, the value usually accepted, is included in Table VII, expressed as a percentage of solutes with respect to the total of all the programmes run. It is seen that the three approaches behave in the same way when the low-polarity stationary phases are considered, but less successfully for the high-polarity OV-275. PTRI determinations giving errors >2%, say about 2–5%, were as follows: six cases with PS-255 (ethyl acetate and pyridine were the solutes involved), three determinations with OV-105 (solute 2-pentanone) and no cases with di-*n*-decyl phthalate. With OV-275 the situation is worse, about ten solutes giving errors >2% when eqns. 4 and 8 are used and almost twice this number when eqn. 7 is used to obtain the retention temperatures. 1-Iodobutane, cyclopentanone, *n*-octanol, pyridine, 2-pentanone, 1-nitropropane and *n*-butanol are, among others,

TABLE III

VARIANCES OF THE ΔT_R(exp. – eq.) OR ΔT_R(exp. – calc.) DIFFERENCES FOR ALL OF THE SOLUTES OVER THE 17 PROGRAMMES

Stationary phase	Eqn. No.	r (°C/min)			
		1	2	4	6
PS-255 ($T_0 = 70°C$)	1	7.3	7.5	7.7	7.9
	2[a]	5.1	5.1	5.1	5.1
	3	3.0	4.4	6.1	7.5
	4	0.3	0.3	0.4	0.7
	5	1.8	2.9	4.3	5.2
	6	2.4	3.2	4.2	4.7
	7	0.9	1.1	1.3	1.3
	8	6.7	3.9	2.7	2.9
		r (°C/min)			
		1.0	1.5	2.0	3.0
Di-*n*-decyl phthalate ($T_0 = 60°C$)	1	7.7	8.0	8.2	8.6
	2[a]	5.1	5.1	5.1	5.1
	3	6.2	7.0	7.9	9.2
	4	0.1	0.3	0.3	0.3
	5	1.3	0.4	0.5	0.9
	6	5.8	6.6	7.3	7.6
	7	2.1	2.1	2.4	2.8
	8	6.1	6.3	6.4	6.2
		r (°C/min)			
		2	6	10	
OV-105 ($T_0 = 50°C$)	1	7.5	7.5	8.2	
	2[a]	5.1	5.1	5.1	
	3	6.9	11.5	13.5	
	4	0.6	1.0	2.2	
	5	0.3	0.5	0.9	
	6	5.7	8.2	9.1	
	7	1.2	1.6	1.2	
	8	8.3	7.0	5.4	
		r (°C/min)			
		1	3	6	
OV-105 ($T_0 = 80°C$)	1	7.6	7.9	8.3	
	2[a]	5.1	5.1	5.1	
	3	2.7	5.2	8.5	
	4	0.1	0.1	0.4	
	5	0.1	1.8	0.3	
	6	2.3	4.3	5.9	
	7	1.2	1.8	2.2	
	8	4.5	1.6	2.7	

TABLE III *(continued)*

Stationary phase	Eqn. No.	r (°C/min)		
		1	2	4
OV-275 ($T_0 = 70$°C)	1	6.1	6.2	6.5
	2[a]	4.2	4.2	4.2
	3	2.0	3.1	4.5
	4	0.4	0.6	1.0
	5	0.3	1.0	1.4
	6	1.8	2.7	2.8
	7	0.6	0.7	0.9
	8	4.0	2.4	2.3

[a] Eqn. 2 is taken as a reference.

TABLE IV

RETENTION TEMPERATURE VARIANCES OF ΔT_R(exp. – eq.) OR ΔT_R(exp. – calc.) DIFFERENCES (OVERALL VIEW)

Stationary phase	T_R calculated by eqn.							
	1	2	3	4[a]	5[a]	6	7[a]	8
PS-255 (4 programmes)	1.49	1.0	1.02	0.08	0.69	0.71	0.23	0.80
OV-105 (6 programmes)	1.53	1.0	1.58	0.14	0.12	1.16	0.29	0.96
Di-*n*-decyl phthalate (4 programmes)	1.59	1.0	1.49	0.05	0.16	1.33	0.45	1.23
OV-275 (3 programmes)	1.49	1.0	0.76	0.16	0.21	0.58	0.17	0.69
All four stationary phases (17 programmes)	6.11	4.0	4.86	0.43	1.18	3.78	1.16	3.67

[a] The lowest values of the variance correspond to the eqns. 4, 5 and 7.

TABLE V

CUBIC SPLINES PROGRAMMED-TEMPERATURE RETENTION INDICES USING EXPERIMENTAL AND CALCULATED T_R VALUES FOR SEVERAL PROGRAMMES IN ACCORDANCE WITH EQNS. 4, 7 AND 8

Stationary phase	Solute	T_R (exp.)	T_R calculated from eqn.		
			4	7	8
OV-105 ($T_0 = 50$°C, $r = 6$°C/min)	Benzene	677	675	674	676
	n-Butanol	701	696	696	696
	2-Pentanone	716	717	720	716
	1-Nitropropane	780	782	783	777
	Pyridine	775	779	779	777
	2-Methyl-2-pentanol	765	761	764	760
	1-Iodobutane	839	835	832	836
	2-Octyne	875	875	875	876
	1,4-Dioxane	726	727	728	725
	cis-Hydrindane	1014	1011	1004	1011

(Continued on p. 214)

TABLE V *(continued)*

Stationary phase	Solute	T_R (exp.)	T_R calculated from eqn.		
			4	7	8
OV-105 (T_0 = 80°C, r = 6°C/min)	Benzene	679	681	681	683
	n-Butanol	694	694	695	695
	2-Pentanone	714	718	721	717
	1-Nitropropane	782	784	786	783
	Pyridine	780	784	783	783
	2-Methyl-2-pentanol	766	761	764	759
	1-Iodobutane	844	840	837	841
	2-Octyne	875	875	875	875
	1,4-Dioxane	727	729	731	727
	cis-Hydrindane	1017	1015	1007	1014
PS-255 (T_0 = 70°C, r = 4°C/min)	Ethyl acetate	602	605	563	605
	Benzene	659	661	657	655
	n-Butanol	658	658	661	655
	2-Pentanone	668	679	681	678
	Pyridine	749	738	739	740
	Toluene	757	759	757	760
	o-Xylene	886	882	882	885
	n-Octanol	1058	1062	1065	1061
	Dimethylaniline	1143	1146	1142	1146
Di-*n*-decyl phthalate (T_R = 60°C, r = 3°C/min)	Benzene	728	730	729	729
	n-Butanol	769	768	770	767
	2-Pentanone	759	759	759	759
	1-Nitropropane	858	856	854	856
	Pyridine	853	847	844	847
	2-Methyl-2-pentanol	823	820	820	820
	1-Iodobutane	894	892	886	891
	2-Octyne	898	897	899	897
	1,4-Dioxane	775	774	774	774
	cis-Hydrindane	1032	1032	1023	1032
OV-275 (T_0 = 70°C, r = 2°C/min)	Benzene	1125	1131	1128	1133
	n-Butanol	1307	1296	1287	1295
	2-Pentanone	1227	1213	1209	1212
	1-Nitropropane	1479	1482	1452	1483
	Pyridine	1442	1424	1400	1425
	2-Methyl-2-pentanol	1228	1218	1220	1218
	1-Iodobutane	1192	1182	1176	1183
	2-Octyne	1087	1085	1089	1084
OV-275 (T_0 = 70°C, r = 2°C/min)	1,4-Dioxane	1325	1314	1300	1314
	cis-Hydrindane	1145	1123	1117	1124
	Acetone	1103	1106	1100	1106
	Toluene	1204	1208	1209	1208
	o-Xylene	1349	1323	1309	1324
	Cyclopentanone	1511	1492	1459	1492
	n-Octanol	1661	1612	1575	1611

TABLE VI

MEAN VALUES OF THE PTRI ERRORS CALCULATED BY CUBIC SPLINES USING T_R VALUES CALCULATED BY EQNS. 4, 7 AND 8 OVER ALL THE PROGRAMMES

$$\text{Error} = \frac{\text{PTRI (exp.)} - \text{PTRI (calc.)}}{\text{PTRI (exp.)}} \times 100.$$

Stationary phase	Eqn. No.	*r* (°C/min)			
		1	2	4	6
PS-255 ($T_0 = 60$°C)	4	0.85	1.10	0.53	0.55
	7	1.27	1.79	1.27	1.29
	8	0.83	0.90	0.61	0.39
		r (°C/min)			
		2	6	10	
OV-105 ($T_0 = 50$°C)	4	0.32	0.33	0.31	
	7	0.32	0.45	0.45	
	8	0.54	0.29	0.27	
		r (°C/min)			
		1	3	6	
OV-105 ($T_0 = 80$°C)	4	0.56	0.62	0.32	
	7	0.68	0.85	0.50	
	8	0.80	0.58	0.32	
		r (°C/min)			
		1	1.5	2.0	3.0
Di-*n*-decyl phthalate ($T_0 = 60$°C)	4	0.37	0.34	0.45	0.21
	7	0.48	0.50	0.42	0.39
	8	0.56	0.36	0.45	0.21
		r (°C/min)			
		1	2	4	
OV-275 ($T_0 = 70$°C)	4	1.41	1.02	2.07	
	7	1.79	1.79	3.25	
	8	1.47	1.02	1.98	

the solutes with poorer PTRI predictions. The high-polarity of the OV-275 phase may be the cause of such unfavourable results. As has been pointed out, it is a poorly behaving phase because it uses the unsuitable *n*-alkanes with very low retention times, which may be a source of errors [23].

Of the three equations compared, eqn. 7 is the least reliable, with errors on various solutes being

TABLE VII

STATISTICS OF CUBIC SPLINES PTRI DETERMINATIONS FOR THE 15 NON-*n*-ALKANE SOLUTES ON THE FOUR COLUMNS OVER ALL THE 17 PROGRAMMES RUN

Stationary phase	% of solutes with error in PTRI ≤2%		
	T_R calculated by eqn.		
	4	7	8
PS-255	97	89	97
OV-105[a]	100	100	100
OV-105[b]	97	97	97
Di-*n*-decyl phthalate	100	100	100
OV-275	78	56	73

[a] $T_0 = 50°C$.
[b] $T_0 = 80°C$.

larger than the permitted 2%. A common factor here seems to be the solutes for which the retention index predictions are more erratic, that is, most of them are polar solutes chromatographed on a very polar stationary phase.

The result for ethyl acetate on PS-255, a nearly non-polar stationary phase, may be due to the fact that this peak has a low retention temperature approaching the abrupt zone of the cubic splines where errors become important. The same effect might occur with 2-pentanone. For pyridine, the error may be due to the fact that it is a tailed, broad and peculiar peak with a t_R that is difficult to measure.

Final hints

On comparing retention temperatures deduced from the published equations for both *n*-alkanes and other solutes and the retention indices of non-*n*-alkane solutes, some differences seem to arise depending on how polar the stationary phase under consideration is. The retention temperatures are better predicted with the low-polarity stationary phases than with OV-275, although for the latter the differences between the T_R values compared in this paper tend to smooth with respect to the other three much lesser polar stationary phases. On the other hand, retention indices (up to a 2% error) are reproduced with almost 100% accuracy for OV-105, PS-255 and di-*n*-decyl phthalate, whereas the prediction is much worse for OV-275. Hence the polarity of the stationary phase seems to be important for this kind of prediction, and the polarity of the solutes involved might also play an important role.

The least errors in the prediction of the retention temperatures are produced with the Curvers *et al.* and the Krupčík *et al.* equations; the Akporhonor *et al.* and Said equations follow with larger errors, but by far the largest errors result when using the early empirical equations of Giddings, Guiochon and Lee and Taylor.

When cubic splines retention indices are compared it is found that the equation of Curvers *et al.* again has a better performance than the other two compared.

Except for OV-275, the percentage of solutes for which the prediction is made with an error up to the tolerated 2% is 89–100% for T_R obtained with eqn. 7 and 97–100% for T_R obtained with eqns. 4 and 8.

It is apparent that the Akporhonor *et al.* equation works less well than the Curvers *et al.* equation, perhaps owing to the uncertainty in the measurement of the phase ratio, β, on packed columns.

For the polar stationary phase OV-275, there are various solutes for which predictions are made with errors $>2\%$, *e.g.*, the mean value of the error for a heating rate $r = 4°C/min$ is 3.25% (see Table VI). Consequently, none of the equations can be recommended for calculating retention indices on this type of phase.

For non-polar and low-polarity stationary phases it has been shown that one can calculate PTRIs by cubic splines interpolation of T_R values calculated by the treatments of Curvers *et al.* or Akporhonor *et al.* with fair agreement with the experimental values. This is very important as it permits one to operate with isothermal retention data, saving a lot of experimental work in many instances, which facilitates the identification of difficult peaks for complicated multi-component mixtures.

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