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Short Communication

Prediction of the retention of polynuclear aromatic hydrocarbons in programmed-temperature gas chromatography

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ABSTRACT

A procedure based on curve-fitting techniques for the calculation of the retention data in linear programmed-temperature gas chromatography was applied in order to calculate the elution temperature of fifteen polycyclic aromatic hydrocarbons on a DB-5 capillary column. The linear programmed-temperature retention data were calculated with a BASIC program starting from isothermal retention times and the calculated values were compared with experimental data. For five different linear temperature programmes the accuracy expressed as fractional difference was always better than 1% in spite of the simplifications introduced in the calculation methods.

INTRODUCTION

Programmed-temperature gas chromatography (PTGC) is widely used for the analysis of environmental samples containing compounds with a wide range of boiling points owing to the advantage of decreasing the analysis time and improving the resolution for later eluting compounds. The prediction of the temperature-programmed retention time from isothermal retention data has been reported by several workers both using thermodynamic parameters or retention indices [1–19].

In a previous paper [20] it was shown that the method proposed by Said [21,22] can be applied without complex calculations for the prediction of retention data in different temperature-pro-

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grammed analyses. In this work, the retention times in linear PTGC of fifteen polynuclear aromatic hydrocarbons (PAHs) were calculated starting from data collected during different isothermal runs with the same column and were compared with experimental results.

The fundamental equation for temperature programming is

$$\frac{\mathrm{d}t}{t_R} = \frac{\mathrm{d}l}{L} \quad (1)$$

which when integrated gives

$$\int_0^{T_p} \frac{\mathrm{d}t}{t_R} = \int_0^{L} \frac{\mathrm{d}l}{L} \quad (2)$$

where L is the column length, $\mathrm{d}l$ is the distance travelled by the solute in time dt, t_R is the isothermal retention time of the same solute at absolute temperature T and T_p is the solute retention temperature.

The isothermal retention time, t_R, changes with temperature T according to

$$t_R = A + a\exp(b/T) \quad (3)$$

In eqn. 3 some simplifications are made [21]: a and b are constants and A is also a constant equal to the dead time. This means assuming that the mean gas velocity remains constant during the temperature programming. This assumption is not strictly valid [23] as the gas velocity should decrease with increasing temperature, but many instruments have a built-in system that automatically increases the inlet pressure in order to compensate for this effect and maintain a constant flow-rate. A is therefore approximately but not exactly equal to the dead time and can be defined as the mean dead time. With these simplifications, the three constants in eqn. 3 can be evaluated from three isothermal runs at different temperatures.

In linear PTGC, the column temperature is a linear function of the analysis time, t:

$$T = T_0 + rt \quad (4)$$

where T_0 is the absolute initial temperature and r is the programming rate in °C min^{-1}.

By substituting eqns. 4 and 3 in eqn. 2, we obtain

$$1 = \frac{1}{r}\int_{\vartheta_0}^{4} \frac{\mathrm{d}\vartheta}{A + a\exp[b/(273+\vartheta)]} \quad (5)$$

or

$$1 = \frac{1}{r}\int_{\vartheta_0}^{\vartheta_t} y(\vartheta)\,\mathrm{d}\vartheta \quad (6)$$

where y(6) is the inverse retention time function:

$$y(\vartheta) = \frac{1}{A + a\exp[b/(273+\vartheta)]} \quad (7)$$

and ϑ_0 and ϑ_t are inlet and outlet column temperatures in °C.

The resulting integration has no analytical solution and eqn. 6 can be solved with approximate or iterative methods. In this work we applied the method proposed by Said [22], which uses curve-fitting techniques to replace the inverse retention time function $y(\vartheta)$ by a function that can be integrated. It can be shown that the normal distribution integral gives the best fit to eqn. 7 up to a value from 50 to 70°C above the inflection point ϑ_i, which is the elution temperature range usually observed under experimental conditions. An exhaustive description of the theory can be found in Said's original work and our previous papers [20–22].

EXPERIMENTAL

The analyses were carried out using a Varian (Palo Alto, CA, USA) Model 3400 gas chromatograph, equipped with a standard flame ionization detector and a split-splitless injector. A narrow-bore DB-5 (5% phenyl-95% methylpolysiloxane bonded phase) silica column (J & W Scientific, Folsom, CA, USA) (30 m × 0.25 mm I.D.) with a film thickness of 0.25 μm was used. Standard solution of PAHs in dichloromethane at concentrations ranging between 0.1 and 0.5 g l^{-1} were injected (1 μl) with a microsyringe in the splitless mode. Highly purified nitrogen was used as the carrier gas at an average flow-rate of 3 ml min^{-1} into the column. The make-up gas dispatched to the detector was set in order to maintain constant flow-rate of 30 ml min^{-1} at the flame tip. The detector and injector temperatures were 300 and 250°C, respectively.

Five replicate isothermal runs were performed for each compound at temperatures ranging from 373 to 598 K, in order to obtain three values of retention time with a reasonable temperature interval. The temperatures of the isothermal runs used for each compound were chosen in order to approximate its elution temperature (see Table I). Programmed-temperature runs were carried out at a variety of combinations of initial temperature and oven heating rate. The assumption was made that the operator-set value matches exactly the actual temperature of the column oven; for the Varian 3000 series instruments this is true to within ±1.3°C. Calculations were performed with an IBM personal computer using a BASIC program [24].

RESULTS AND DISCUSSION

Five replicate isothermal runs were performed for each compound at three temperatures (Table I) in order to establish the reproducibility of retention data in isothermal analyses. The mean isothermal retention time, t_R, and overall standard deviation, a, are also given in Table I.

By using the equations described in the Introduction, the programmed-temperature retention times, t_p, were calculated for various initial temperatures and heating rates. The calculated (t_{pc}) and experimental (t_{pe}) values are compared in Table II. The percentage difference between the experimental and calculated values, A (%) = $100(t_{pe} - t_{pc})/t_{pc}$, is very small (<1%), notwithstanding the simplifications introduced above, showing the adequacy of a normal distribution integral to fit the inverse retention time function $y(\vartheta)$, giving an almost perfect fit to y(6) up to a 19 value from 50 to 70°C above the inflection point ϑ_i. The fifteen solutes examined elute from the column more than 50°C above ϑ_i, as shown in Table III.

As pointed out in the Introduction, the velocity of the carrier gas is temperature dependent: an increase in temperature increases the viscosity and the velocity of the carrier gas decreases proportionally in a chromatographic system having a constant inlet pressure. This results in a linear dependence of dead time on temperature, but this variation is relatively small when compared with the exponential variation of retention time with temperature. This effect is further reduced by the constant-flow regulator of the gas chromatograph used. Hence dead time can be replaced with the constant *A in* eqn. 3, where *A* is the mean dead time. Moreover, in eqn. 3 the thermodynamic terms $\beta \exp(\Delta S/R)$ and *-AH/R,* where β is the column phase ratio, AS is the molar entropy of solution, AH is the molar enthalpy of solution and *R* is the gas constant, are replaced with the constants a and b, respectively, but some deviation from linearity of the $\ln t_R$ *vs.* T^{-1} relationship is possible, owing to the variation of these thermodynamic characteristics with temperature [12,14,25]. As pointed out elsewhere [14], these variations do not have a great effect on the calculated retention values because the decrease in the enthalpy produces an increase in the entropy term owing to the correlation of AH and AS through the molar free energy of solution. The early-eluting solutes with a retention time very close to the dead time are more influenced by errors in evaluating the hold-up time and therefore would have less reliable isothermal data. Moreover, in the time corresponding to the dead time the solutes expand in the gas phase and are transported along the column; the distance travelled can be non-negligible for solutes showing a small retention time, particularly if high initial temperatures are used. In order to ensure greater accuracy, the three temperatures for evaluating the constants in eqn. 3 should cover the whole temperature range during temperature programming because a greater contribution to the difference between calculated and predicted retention times can be expected if the retention time of a compound significantly exceeds the upper limit of isothermal runs.

It should be noted that the accuracy of the predicted retention values is fair over the whole range of the programmed-temperature runs, notwithstanding the fact that the isothermal retention times were not measured for all the compounds at the same temperature and in the same isothermal runs. This is important from both the theoretical and practical points of view. It is in fact almost impossible to achieve the elution of all the analyte compounds with a

TABLE I

EXPERIMENTAL MEAN VALUES (n = 5) OF ISOTHERMAL RETENTION TIME, t_R (mitt), AND STANDARD DEVIATION, σ, ON A NARROW-BORE DB-5 COLUMN (30 m x 0.25 mm I.D.) WITH NITROGEN AS CARRIER GAS

Compound	373 K		398 K		423 K		448K		473 K		498 K		523 K		548 K		573 K		598 K	
	t_R	$\sigma \cdot 10^3$	t_R	$\sigma \cdot 10^3$	t_R	$\sigma \cdot 10^3$	t_R	$\sigma \cdot 10^3$	t_R	$\sigma \cdot 10^3$	t_R	$\sigma \cdot 10^3$	t_R	$\sigma \cdot 10^3$	t_R	$\sigma \cdot 10^3$	t_R	$\sigma \cdot 10^3$	t_R	$\sigma \cdot 10^3$
Naphthalene	6.334	4.8	3.586	4.8	2.612	4.0														
Acenaphthylene			9.616	14.0	5.098	11.0	3.328	9.0												
Acenaphthene					5.620	0.0	3.548	4.0	2.730	0.0										
Fluorene					7.762	7.0	4.442	6.0	3.130	6.0										
Phenanthrene									4.510	0.0	3.254	4.8	2.702	4.0						
Anthracene									4.620	9.8	3.308	7.4	2.132	6.4						
Fluoranthene									8.644	19.0	5.140	8.0	3.636	13.0						
Pyrene									9.966	8.1	5.742	8.9	3.922	7.2						
Benzo[*a*]anthracene											11.140	8.9	6.482	17.0	4.380	8.9				
Chrysene													6.630	10.0	4.444	23.0	3.452	18.0		
Benzo[*b*]fluoranthene													1.632	8.2	6.846	26.0	4.656	23.0		
Benzo[*k*]fluoranthene													1.840	22.0	6.894	19.0	4.664	19.0		
Benzo[*a*]pyrene															7.894	34.0	5.266	4.1	**3.902**	24.0
Dibenzo[*a*,*h*]anthracene															13.156	56.0	7.586	90.0	5.096	26.0
Benzo[*ghi*]perylene															14.746	89.0	8.538	94.0	5.626	92.0

TABLE II

COMPARISON OF EXPERIMENTAL, t_{pe}, AND CALCULATED, t_{pc}, MEAN VALUES OF RETENTION TIMES (mitt) FOR DIFFERENT TEMPERATURE PROGRAMMES

$A\ (\%) = 100(t_{pe} - t_{pc})/t_{pc}$.

Compound	Initial temperature, ϑ_0 (°C), and programming rate, r (°C/min)														
	60 and 10			80 and 12.5			100 and 7.5			100 and 10			100 and 12.5		
	t_{pe}	t_{pc}	Δ (%)	t_{pe}	t_{pc}	Δ (%)	t_{pe}	t_{pc}	Δ (%)	t_{pe}	t_{pc}	Δ (%)	t_{pe}	t_{pc}	Δ (%)
Naphthalene	6.860	6.882	-0.32	4.792	4.819	-0.60	4.306	4.298	0.18	3.980	3.994	-0.35	3.760	3.357	0.08
Acenaphthylene	10.594	10.5%	-0.01	7.634	7.653	-0.24	7.882	7.872	0.12	6.896	6.892	0.05	6.200	6.205	-0.08
Acenaphthene	11.092	11.116	-0.21	8.014	8.048	-0.42	6.5%	6.563	-0.10	7.318	7.336	-0.24	6.5%	6.563	-0.10
Fluorene	12.318	12.335	-0.13	9.008	**9.028**	-0.22	9.912	9.908	0.04	8.498	a.474	0.28	7.498	7.501	-0.04
Phenanthrene	14.722	14.752	-0.20	10.928	10.971	-0.39	12.857	12.925	-0.52	10.762	10.794	-0.29	9.375	9.394	-0.20
Anthracene	14.894	14.872	0.14	11.056	11.069	-0.11	13.124	13.075	0.37	10.918	10.912	0.05	9.458	9.492	-0.36
Fluoranthene	17.720	17.715	0.02	13.376	13.378	-0.01	16.684	16.727	-0.26	13.690	13.721	-0.22	11.784	11.784	0.00
Pyrene	18.214	18.267	-0.29	13.776	13.832	-0.40	17.402	17.448	-0.26	14.342	14.277	0.45	12.186	12.238	-0.42
Benzo[*a*]anthracene	21.310	21.346	-0.17	16.302	16.325	-0.14	21.462	21.487	-0.11	17.302	17.347	-0.26	14.682	14.726	-0.29
Chrysene	21.458	21.466	-0.04	**16.406**	16.421	-0.09	21.620	21.648	-0.13	17.450	17.467	-0.09	14.812	14.822	-0.07
Benzo[*b*]fluoranthene	**23.926**	**23.942**	**-0.07**	**18.442**	**18.440**	**0.01**	**24.860**	**24.850**	**0.04**	**19.942**	**19.940**	**0.01**	**16.846**	**16.840**	**0.03**
Benzo[*k*]fluoranthene	**24.008**	**24.009**	**0.00**	**18.460**	**18.490**	**-0.16**	**24.992**	**24.964**	**0.11**	**20.124**	**20.010**	**0.56**	**16.902**	**16.891**	**0.06**
Benzo[*a*]pyrene	**24.662**	**24.505**	**0.47**	**18.984**	**18.928**	**-0.29**	**25.758**	**25.525**	**0.90**	**20.602**	**20.506**	**0.46**	**17.390**	**17.330**	**0.34**
Dibenzo[*a*,*h*]anthracene	**26.956**	**26.982**	**-0.09**	**20.964**	**20.890**	**0.35**	**28.802**	**28.882**	**-0.27**	**22.932**	**23.984**	**-0.22**	**19.378**	**19.298**	**0.41**
Benzo[*ghi*]perylene	**27.454**	**27.531**	**-0.28**	**21.442**	**21.375**	**-0.31**	**29.562**	**29.534**	**0.09**	**23.624**	**23.531**	**0.39**	**19.864**	**19.775**	**0.44**

TABLE III

CALCULATED INFLECTION POINT, ϑ_i (°C), OF THE SOLUTES AND COMPARISON BETWEEN EXPERIMENTAL, ϑ_e, AND CALCULATED, ϑ_c, ELUTION TEMPERATURES FOR DIFFERENT TEMPERATURE PROGRAMMES

$A\ (\%) = 100(\vartheta_e - \vartheta_c)/\vartheta_c$.

Compound	ϑ_i	Initial temperature, ϑ_0 (°C), and programming rate, r (°C/min)													
		60 and 10			80 and 12.5			100 and 7.5			100 and 10			100 and 12.5		
		ϑ_e	ϑ_c	Δ (%)	ϑ_e	ϑ_c	Δ (%)	ϑ_e	ϑ_c	Δ (%)	ϑ_e	ϑ_c	Δ (%)	ϑ_e	ϑ_c	Δ (%)
Naphthalene	115.13	128.60	128.82	-0.17	139.90	140.25	-0.25	132.29	132.24	0.03	139.80	139.94	-0.10	147.00	**146.96**	0.03
Acenapthylene	154.38	165.94	165.97	-0.02	175.42	175.67	-0.14	159.04	159.11	-0.05	**168.96**	168.92	0.02	177.50	177.51	-0.04
Acenaphthene	158.92	170.92	171.16	-0.14	180.18	180.60	-0.28	162.99	163.41	-0.26	173.18	173.37	-0.11	181.95	182.04	-0.05
Fluorene	173.13	183.18	183.36	-0.10	192.60	192.85	-0.13	173.34	173.31	0.01	184.98	184.74	0.13	193.73	193.77	**−0.02**
Phenanthrene	195.19	207.22	207.53	-0.15	216.00	217.15	-0.25	**196.43**	**196.34**	0.04	207.62	207.95	-0.16	217.19	217.44	-0.12
Anthracene	**196.41**	**208.94**	208.71	0.11	218.20	218.37	-0.08	198.43	198.07	0.18	209.18	209.12	0.03	218.65	218.23	-0.19
Fluoranthene	226.74	237.20	237.10	0.05	247.20	247.23	-0.01	225.13	225.46	-0.15	236.90	237.22	-0.13	247.30	247.31	**0.00**
Pyrene	233.89	242.14	242.68	-0.22	252.20	252.91	-0.28	230.51	230.86	-0.15	243.52	242.77	0.27	252.32	252.98	-0.26
Benzo[*a*]anthracene	259.51	273.10	273.46	-0.13	284.07	283.77	0.10	261.00	261.15	-0.06	274.50	274.68	-0.06	283.53	284.08	-0.19
Chrysene	260.58	274.58	274.67	-0.03	285.08	285.27	-0.07	262.15	262.36	-0.08	273.02	273.48	-0.17	285.15	285.28	-0.05
Benzo[*b*]fluoranthene	290.63	299.26	299.40	-0.05	310.52	310.51	0.00	**286.45**	286.44	0.00	299.42	299.40	0.00	310.58	310.51	0.22
Benzo[*k*]fluoranthene	290.11	300.08	300.10	0.00	310.75	311.13	-0.12	287.44	287.23	0.07	301.24	300.10	0.56	311.28	311.13	0.05
Benzo[*a*]pyrene	307.97	306.22	305.05	0.38	317.30	316.62	0.21	293.18	291.44	0.59	306.02	305.06	0.31	317.37	316.63	0.23
Dibenzo[*a*,*h*]anthracene	315.50	329.56	329.85	-0.09	342.05	341.23	0.23	316.01	316.62	-0.19	329.32	329.85	-0.17	342.23	341.23	0.30
Benzo[*ghi*]perylene	320.10	334.54	335.31	0.23	348.02	347.19	0.24	312.72	321.51	0.06	336.24	335.31	0.28	348.30	347.19	0.32

single isothermal analysis; at low temperatures the retention time of high-boiling compounds is too long and the peak shapes (tailing or very wide) make correct measurement of retention times difficult unless large sample amounts are injected; at high temperatures, interference with the solvent peak tail and elution of many peaks within a very small interval impair the determination of early-eluting compounds.

The differences between the experimental and calculated values are also due to non-instantaneous cooling of the sample from the heated injector to the initial column temperature and to the temperature lag between the column and oven during programming. Probably this lag makes the greatest contribution because the difference between calculated and observed elution temperatures is always within ±1.3°C (see Table III), which represents the observed deviation between the set and actual temperatures of the column oven. The thermal mass of the capillary column and of its supporting cage is relatively small, but it may contribute further to the difference in the actual column temperature with respect to set oven values, mainly with high programming rates [26].

Notwithstanding these causes of error, the prediction of the retention times in the linear PTGC of complex mixtures of PAHs gives suitable results and can permit the identification of these compounds in environmental samples on the basis of retention data, without the need to perform a series of isothermal runs for each sample in order to identify compounds having a wide range of boiling points. By determining many standards, the flame ionization detection (FID) responses of PAHs were found to be very similar, as they are governed by their carbon content, which is fairly uniform for different compounds, and therefore they have very similar FID response factors (response/mass) [27]. Therefore, the identification on the basis of retention data and the similarity of response facilitate the determination of PAHs in environmental samples by reducing the number of standard mixtures required.

The method, which is easily applied with simple programming on personal computers, can also be used as an analogue of the Van Deemter plot for optimization of carrier flow-rate, to establish whether the column used can give a satisfactory resolution of closely eluting peaks. If the application of the equation with many PTGC parameters does not give a sufficient difference in retention times, this means that further experiments in order to improve the resolution by changing the analysis conditions will be useless, and that other solutions must be tried, such as the choice of longer columns, the use of stationary phases with greater polarity and the combination of different length of polar and non-polar columns.

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