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Note

Prediction of retention times in temperature-programmed gas–solid and gas–liquid chromatography

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Gas–solid (GSC) and gas–liquid chromatography (GLC) make use of differential sorption and partitioning principles, respectively, for the separation of components in a mixture. Temperature-programmed GC is a well established and commonly used method in which the separation is enhanced by slow changes in the column temperature during elution. Several reviews[1,2] have appeared dealing with the theoretical aspects of GC. Equations for predicting the retention times during temperature programming in GLC have been developed based on partition principles[3–5] and other thermodynamic properties[2]. Similar equations have also been developed for predicting retention times in GSC[6] based on differential adsorptions of solutes.

A difference will always exist between the oven and column temperatures during temperature programming, owing to the finite time taken by the column and the packing material to become heated to the oven temperature. This temperature difference will depend on the column dimensions and on the thermal properties of the packing material. This important aspect has been ignored by the previous workers, except for one paper[7] in which the effect of small changes in temperature on GC retention volumes was studied. In this paper, equations are developed for predicting retention times during temperature programming in GSC and GLC, taking into account the difference between the column and the oven temperatures, and the predictions are compared with experimental values.

THEORY

Based on the theory of partitioning of a solute in two phases, Porter *et al.*[5] derived an equation connecting the retention volume with the column temperature in GLC:

$$\frac{\ln (V-V_r)}{T} = \frac{\theta}{T} + \ln B \tag{1}$$

where V and V_r are the retention volumes of the sample and air, respectively, T is the column temperature (in K) and θ and B are constants. θ is directly proportional to the difference between the heat of vaporization of the solute and the excess partial heat of solution of the solute in the solvent. If u is the carrier gas velocity (in cm^3/min) measured at the ambient temperature T_{a}, eqn. 1 reduces to[4]

$$\frac{BT_{\mathrm{a}}}{u} = \int_{t_{\mathrm{a}}}^{t_{\mathrm{p}}} \mathrm{e}^{-\theta/T}\,\mathrm{d}t \tag{2}$$

where t_{a} and t_{f} are retention times (in minutes) of the air and the sample peaks, respectively. During temperature programming, the column temperature varies as

$$T = at + T_{\mathrm{in}} \tag{3}$$

where a is the oven heating rate (in K/min) and T_{in} the initial oven temperature (in K). Eqn. 2 can be integrated numerically to obtain t_{f} if all the operating conditions and constants are known.

In GSC, the equation for the retention volume is[6]

$$\ln (V - V_{\mathrm{r}}) = \frac{\theta'}{T} + \ln B' \tag{4}$$

Where θ' and B' are proportional to the heat and entropy of adsorption of the solute on the solid surface, respectively. This equation reduces to

$$\frac{B'}{u} = \int_{t_{\mathrm{a}}}^{t_{\mathrm{p}}} \mathrm{e}^{-\theta'/T}\,\mathrm{d}t \tag{5}$$

By experimentally determining the retention volumes at two column temperatures under isothermal conditions, the constants θ and B in eqn. 1 for GLC and θ' and B' in eqn. 4 for GSC can be estimated. In these equations the changes in carrier gas flow-rate due to the pressure drop along the column are neglected.

During temperature programming, the oven temperature increases linearly, whereas the column temperature generally is lower owing to the heat capacity of the packing material. The column and oven temperatures are related by the following partial differential equation:

$$\frac{\partial v}{\partial t} = k\left(\frac{\partial v}{\partial r^2} + \frac{1}{r}\cdot\frac{\partial v}{\partial r}\right) \tag{6}$$

where $v = (T_{\mathrm{o}} - T)/(T_{\mathrm{o}} - T_{\mathrm{in}})$. The boundary and initial conditions are given as $v = 0$ at $r = R$ (column radius): $\partial v/\partial r = 0$ at $r = 0$ and $v = 1$ at $t = 0$. k is the thermal diffusivity of the packing material (in cm^2/min). The solution of this equation is[8]

$$v = \sum_{n=1}^{\infty} A_n J_0(\alpha_n r)\mathrm{e}^{-k\alpha_n^2 t} \tag{7}$$

and

$$A_n = \frac{2}{R^2 J_1{}^2 (R\alpha_n)} \int_0^R r\, J_0 (r\alpha_n)\, \mathrm{d}r \tag{8}$$

α_n is the root of

$$J_0 (R\alpha_n) = 0 \tag{9}$$

and J_o is the Bessel function of order zero and the first kind. The roots of the Bessel function can be found in standard books on differential calculus. Substituting eqn. 8 in eqn. 7, we obtain

$$v = \frac{2}{R} \sum_{n=1}^{\infty} \mathrm{e}^{-k\alpha_n^2 t} \cdot \frac{J_o (r\alpha_n)}{\alpha_n J_1(R\alpha_n)} \tag{10}$$

If $\bar{T}_{av}$ is the average column temperature, then

$$\begin{aligned} \frac{T_o - \bar{T}_{av}}{T_o - T_{in}} &= \frac{2}{R^2} \int_0^R r\, v\, \mathrm{d}r \\ &= \frac{4}{R^2} \sum_{n=1}^{\infty} \frac{1}{\alpha_n^2} \cdot \mathrm{e}^{-k\alpha_n^2 t} \end{aligned} \tag{11}$$

If

$$T_o = T_{in} + at$$

and

$$\bar{T}_{av} = T_{in} + a't \tag{12}$$

then from eqn. 11,

$$a' = a\left(1 - \frac{4}{R^2} \sum_{n=1}^{\infty} \frac{1}{\alpha_n{}^2} \cdot \mathrm{e}^{-k\alpha_n^2 t}\right) \tag{13}$$

It can be seen from eqn. 13 that the apparent column heating rate, a', is less than the oven heating rate, a, and depends on the column radius, thermal diffusivity of the packing and time.

An increase in the column diameter or heating rate increases the difference between T_o and $\bar{T}_{av}$, whereas an increase in the thermal diffusivity, k, reduces the difference. The time at which this difference is maximal can also be calculated by differentiating eqn. 11 with respect to t and equating the resulting function to zero to give

$$t_{\mathrm{m}} = \sum_{n=1}^{\infty} \frac{1}{R\alpha_n^2} \tag{14}$$

EXPERIMENTAL

In order to verify the equations derived above for predicting retention times during temperature programming, four columns of different types were chosen, as follows: (1) 7 ft. × $\frac{1}{4}$ in. I.D. stainless-steel column packed with Porapak Q, 100–120 mesh (k = 0.0025 cm^2/min); (2) 2.1 m × $\frac{1}{4}$ in. I.D. stainless-steel column packed with 10% Carbowax 20M + 2% potassium hydroxide on 80–100-mesh Chromosorb W HP (k = 0.0001 cm^2/min); (3) 10 ft. × 1/8 in. I.D. stainless-steel column packed with Porapak Q, 80–100 mesh (k = 0.0025 cm^2/min); (4) 2 m × 1/8 in. I.D. stainless-steel column packed with 8.9% TEPA + 1.1% potassium hydroxide on 80–100-mesh Porapak Q (k = 0.00018 cm^2/min). Porapak Q (columns 1 and 3) represents the gas–solid system and Carbowax 20M (column 2) and TEPA (column 4) the gas–liquid system. A Pye Unicam Model 204 gas chromatograph with a thermal conductivity detector was used. The injection port and the detector temperature were set at 200 and 150°C, respectively. Helium was used as the carrier gas at a flow-rate of 30 cm^3/min.

The different solutes considered were methanol, ethanol, *n*-propanol, isopropanol, *n*-butanol, isobutanol, *sec.*-butanol and *tert.*-butanol. The retention times at several isothermal temperatures for each solute on the various columns were determined independently. For each solute, the constants θ and B in GLC and θ' and B' in GSC were determined from the appropriate equations. The oven was set to the desired initial temperature and temperature programming was initiated as soon as the liquid was injected into the column. The retention time at which the sample eluted out was noted. The heating rates used were 2, 4 and 8 K/min.

RESULTS AND DISCUSSION

The elution times were also calculated theoretically by two methods. In the first method (method 1), the retention time was calculated from eqn. 2 or 5, depending

TABLE I

COMPARISON OF OBSERVED AND CALCULATED ELUTION TIMES (min) AT A HEATING RATE OF 2 K/min

Solute	*Column 1*			*Column 2*			*Column 3*		
	Observed	*Method 1*	*Method 2*	*Observed*	*Method 1*	*Method 2*	*Observed*	*Method 1*	*Method 2*
Methanol	3.3	4.04	3.3	2.7	2.9	2.75	10.0	8.4	9.9
Ethanol	6.3	6.14	6.53	2.7	3.0	2.8	16.0	13.8	16.2
n-Propanol	23.2	22.2	23.15	3.1	3.5	3.1	27.1	23.9	27.0
n-Butanol	35.6	34.7	35.68	7.3	9.0	7.6	38.6	34.5	37.15

TABLE II

AVERAGE ABSOLUTE ERRORS (%) BY METHODS 1 AND 2

Column No.	*Method 1*	*Method 2*
1	4.0	2.6
2	10.8	2.5
3	5.7	1.3
4	13.1	4.0

on whether the system used was GLC or GSC, respectively. In the second method (method 2), the column temperature ($\bar{T}_{av}$) was calculated using eqn. 11 and substituted into the appropriate equation to obtain the elution time (here T is taken to be equal to $\bar{T}_{av}$).

Table I compares the retention time predictions by both methods with the experimentally observed values for the four solutes and three columns. In all instances the prediction by method 2 was closer to the true value. The average absolute errors [where error = 100 · (experimental – calculated)/experimental] determined by the two methods for all four columns are presented in Table II. The averages were evaluated from 24 experiments carried out at three heating rates and with eight solutes. It can be seen that method 2 consistently gave a smaller percentage error (three to four times smaller) than method 1. When the predictions were made by method 1, the error for GSC was less than that for GLC, because the thermal diffusivity of the packing in GLC is very small.

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