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Short communication

Extrapolating programmed gas chromatographic data from one set of conditions to another

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Abstract

Programmed temperature retention indices can be extrapolated from one set of conditions to another by a simple logarithmic relation. A similar relation for retention temperatures is less successful, but Giddings' approximation works well.

Keywords: Programmed-temperature gas chromatography; Retention indices; Temperature programming

1. Extrapolation of retention temperature or time

When an analyst wishes to compare a programmed chromatogram with published data for the same solutes that is produced on the same stationary phase but under different conditions, a method is needed to extrapolate data from one to the other. This problem is different from the one solved by Snijders et al. [1] who calculated programmed retention temperatures from isothermal retention indices and the retention times of the *n*-alkanes.

The problem is simplified by the fact that the retention time is a function [2] of rm/F where r =heating rate, m =mass of stationary phase, and F =volume flow-rate of mobile phase. Hence, these three can be considered together. Also, data on the effect of changing one can be used directly to show the effect of changing either of the other two.

2. Logarithmic extrapolation

$\log(rm/F)$ is nearly linear with $(1/T_0 - 1/T_R)$ and therefore with $1/T_R$, and the slope is nearly independent of the column or its conditions, except when $T_0 \Rightarrow T_R$. This relation is best seen in Harris and Habgood's figure 4.08 [2] which clarifies Rowan's original [3]. Then if T_{R1} and T_{R2} are known retention temperatures and T_{RX} is the value to be extrapolated, then it would be expected that

$$\frac{1/T_{RX} - 1/T_{R1}}{1/T_{R2} - 1/T_{R1}} = \frac{\log[(rm/F)_x / (rm/F)_1]}{\log[(rm/F)_2 / (rm/F)_1]} \quad (1)$$

In many practical problems, parts of the logarithmic expression will cancel. For example, if results on one column are to be compared, then the mass of stationary phase, m , remains constant, $m_x = m_1 = m_2$, and m disappears from the equation.

Eq. (1) was less successful than expected, as

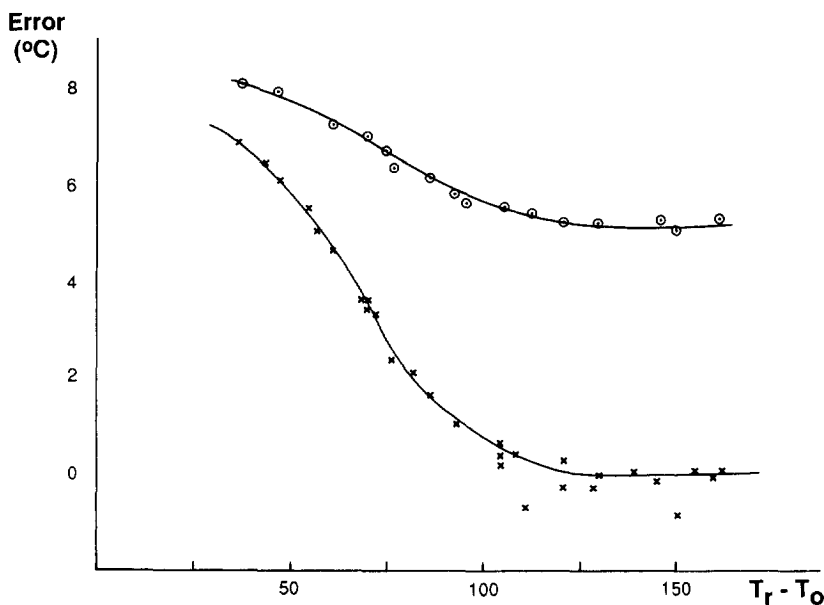


Fig. 1. Error in retention temperatures calculated from the logarithmic extrapolation and from Giddings' approximation. (○) logarithmic extrapolation; (×) Giddings' approximation.

shown in Fig. 1, so it was used only as a starting approximation for a re-entry procedure using Giddings' equation as described below.

3. More precise equation for T_R

Giddings [4] gives a relation which holds when the dead time is negligible, or equivalently when $T_R \gg T_0$. This may be re-arranged to

$$T_r = \frac{\Delta H/R}{\ln\{mr(\Delta H/RT_r + 0.85)^2/(F\rho_s\Delta H/R)\} - \Delta S/R} \quad (3)$$

Given two retention temperatures T_R under different conditions Eq. (3) may be solved iteratively for $\Delta H/R$ and $\Delta S/R$ and the value applied to solve the third set of conditions. The iteration converges in less than ten cycles using the following procedure.

4. Iterative procedure

To obtain approximate values of $\Delta H/R$ and $\Delta S/R$, the 0.85 in Eq. (3) is at first neglected. Eq. (3) then reduces to

$$-\Delta H/RT_r = \ln\{mr(\Delta H/RT_r + 0.85)^2/(F\rho_s\Delta H/R)\} - \Delta S/R \quad (4)$$

Two such equations for two values T_{R1} and T_{R2} and $(rm/F)_1$ and $(rm/F)_2$ are then simultaneously solved to give

$$\frac{\Delta H}{R} \approx \frac{2 \ln(T_{R1}/T_{R2}) - \ln[(rm/F)_1/(rm/F)_2]}{1/T_{R1} - 1/T_{R2}} \quad (5)$$

$$\Delta S/R \approx \ln(rm/F)_1 + \ln(\Delta H/R) - 2 \ln T_{R1} + \Delta H/RT_{R1} \quad (6)$$

The less inexact Eq. (3) is then used to give

$$-(\Delta H/R)(1/T_{R1} - 1/T_{R2}) = \ln[(rm/F)_1/(rm/F)_2] + 2 \ln[(\Delta H/RT_{R1} + 0.85)/(\Delta H/RT_{R2} + 0.85)] \quad (7)$$

The approximate value of $\Delta H/R$ is entered into the \ln terms on the right, and the equation is solved for the $\Delta H/R$ on the left. The new value of $\Delta H/R$ is then entered into the logarithmic terms and the equation is again solved for $\Delta H/R$, which is again entered into the logarithmic terms and so on until successive values of $\Delta H/R$ are negligibly different.

Four iterations are usually sufficient. This value is then entered into Eq. (6) to obtain $\Delta S/R$.

These values of $\Delta H/R$ and $\Delta S/R$ are then entered into Eq. (3) which is solved for T_{R_x} using $(rm/F)_3$. A re-entry procedure is again needed because T_{R_3} appears in the \ln term on the right. A first approximation is obtained by assuming $1/T_R$ is linear with $\ln(rm/F)$ as shown earlier. This is entered into the logarithmic term on the right of Eq. (3), which is then solved for T_{R_x} . The new value of T_{R_x} is then entered into the \ln term, a new value of T_{R_x} is calculated, again entered into the \ln term and so on as before, until successive values of T_{R_x} are negligibly different. Four iterations are again usually sufficient.

This procedure can be performed tediously on a hand calculator in about half an hour. A computer is preferable.

5. Extrapolating retention indices I^p under two programs to a third program

The Sadtler Index [5] lists indices at $2^\circ/m$ and $8^\circ/m$ and these may differ by up to 30 units or may differ very little. If the analysis is performed at some other rate, then a method of extrapolation is needed. A simple linear extrapolation produces poor results, but this time a logarithmic extrapolation works well. A graduate student pointed out to me that my logical argument leading to this logarithmic relation contained a fallacy, so I offer it only as an empirical relation that works.

If two programmed indices are available they may be interpolated or extrapolated using the simple relations

$$\frac{I_x^p - I_1^p}{I_2^p - I_1^p} = \frac{\log[(rm/F)_x / (rm/F)_1]}{\log[(rm/F)_2 / (rm/F)_1]} = \frac{\log[(rd_r L \rho / d_c v)_x / (rd_r L \rho / d_c v)_1]}{\log[(rd_r L \rho / d_c v)_2 / (rd_r L \rho / d_c v)_2]} \quad (8)$$

As before, there will usually be several of the quantities in parentheses that remain constant and will cancel out of the equation.

This relation was tested on the data of Curvers et al. [6] using experimental values at $2^\circ/m$ and $4^\circ/m$ to calculate I^p at $8^\circ/m$ and compare the result with their experimental value at $8^\circ/m$. Agreement with

experiment was always within one unit. The mean deviation was +0.1 and the mean absolute deviation was 0.4. Even for the most volatile sample (2-pentanone, b.p. 102°C) where the approximations might be expected to fail, the deviation was only 0.2 unit.

6. Other units for rm/F

In open tubular columns, the amount of stationary phase is often specified as the film thickness d_f at room temperature. This is proportional to the mass, so it can replace m in Eq. (1) where masses appear as ratios, provided the column dimensions are otherwise identical. Otherwise, it must be replaced by $d_f L d_c \rho$ (neglecting π which cancels from the ratios) where L is the column length, d_c the column diameter, and ρ the density of the stationary phase. If the linear flow-rate v is given it must be transformed to the volume flow-rate $F \propto d_c^2 v$ (again neglecting π). With both of these corrections, rm/F may be replaced by $rd_r L \rho / d_c v$. Eq. (1) then becomes

$$\frac{1/T_{R_x} - 1/T_{R_1}}{1/T_{R_2} - 1/T_{R_1}} = \frac{\log[(rd_r L \rho / d_c v)_x / (rd_r L \rho / d_c v)_1]}{\log[(rd_r L \rho / d_c v)_2 / (rd_r L \rho / d_c v)_1]} \quad (2)$$

Again, some of these may be constant between the two columns and will cancel from the equation.

Two cases are important. If only one column is being considered, but the heating rate or flow-rate is changed, then the mass of stationary phase remains constant and $d_r L \rho / d_c$ will cancel. When two columns are considered, ρ can usually be cancelled because the density of the stationary phase ρ will not usually change significantly between the conditions of the two columns.

7. Using the Sadtler programmed indices

Sadtler gives data at $2^\circ/m$ and $8^\circ/m$. They also give the dimensions of the columns: 25 m long with film thickness $0.52 \mu\text{m}$ and internal diameter 0.31 mm. They do not specify a flow-rate. They provide one example of an isothermal chromatogram that shows a methane peak at 1.199 m at 140°C . This corresponds to 20.85 m/min or 34.75 cm/s or

0.0262 cm³/s. They do not say whether this is their routine flow-rate applicable to all their data, but in the absence of other information it is reasonable to assume that all their work was carried out at the same constant inlet pressure. In this case, their flow-rate will be inversely proportional to the viscosity of the gas. Since this was hydrogen, and the viscosity of hydrogen varies [7] with $T^{0.6967}$ and the published flow was at 423 K their isothermal flow-rate will be

$$F_T = (0.0262 \text{ cm}^3/\text{min}) (423/T)^{0.6967} \quad (9)$$

$$v_T = (34.75 \text{ cm/s}) (423/T)^{0.6967} \quad (10)$$

An analyst may therefore plug these into the equations above if he/she is prepared to rely on the assumption that the entire Sadtler Index was prepared using a constant (though unspecified) inlet pressure.

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