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Short communication

Programmed temperature gas chromatographic data from isothermal retention indices

Stephen J. Hawkes

Department of Chemistry, Oregon State University, Corvallis, OR 97331-4003, USA

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Abstract

Temperature programmed indices are calculated from isothermal indices. The slope b of the n -alkane log plot is used to avoid the need for retention times of the n -alkanes. Retention temperatures are obtained similarly.

Keywords: Retention indices; Programmed-temperature retention indices; Retention temperatures

1. Introduction

When a substance is to be identified from programmed-temperature retention data and the only published data are isothermal indices, one must be transformed to the other.

2. Retention temperatures

The increase in temperature during the program is the integral of the temperature increases experienced by the substance as it moves through each increment of column length. That is

$$T_r = T_0 + \int dT \quad (1)$$

It is shown in Appendix A that dT is given by

$$dT = \frac{r\{1 + (1/\beta)\exp[(\Delta H^\circ - T\Delta S^\circ)/RT]\}}{u_{\text{average}, T_0}(\eta_{T_0}/\eta)/j[1 + (P^2 - 1)(1 - z/L)]^{1/2}} dz \quad (2)$$

The mobile phase in this paper is helium; η_{T_0}/η is calculated using Hawkes' algorithm [1].

β changes slightly with temperature as the stationary phase expands: using the coefficient of expansion [2] gives

$$\beta = \beta_{T_0} / \{1 + 0.000925(T - T_0)\} \quad (3)$$

The temperature dependence of the slope b was calculated from the enthalpy and entropy data [3] for 2,4,4-trimethylpentene, 1-heptanol, isobutylbenzene and 1-tridecene in Curvers' table 7 and from their isothermal retention indices, using Eq. (5) below. This produced the equation:

$$b = -0.337 + 220/T \quad (4)$$

For other situations, equations for b have been reviewed by Takács' group [4].

ΔH° and ΔS° are related [5] to the two isothermal indices I_1 and I_2 at T_1 and T_2 by the equation¹

¹The derivation of Eq. (5) requires [4] the assumption that the free energy of partition of the n -alkane C_nH_{2n+2} is n times the free energy of partition of a methylene group $\Delta G_{CH_2}^\circ$. This approximation is justified by the accuracy of the predicted retention temperatures. When calculating I^T it is almost cancelled by the same assumption for the reference hydrocarbons.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = IbRT(\ln 10)/100 \quad (5)$$

Entering two retention indices I_1 and I_2 and the slopes of the log plot b_1 and b_2 at two temperatures T_1 and T_2 into Eq. (5) and then solving the two simultaneous equations that result, yields

$$\Delta H^\circ = -\frac{(I_1 b_1 - I_2 b_2)R \ln 10}{100(1/T_1 - 1/T_2)} \quad (6)$$

$$\Delta S^\circ = \frac{-I_1 b_1 R \ln 10}{100} + \frac{\Delta H^\circ}{T_1} \quad (7)$$

If I_1 is close to I_2 the calculated values of ΔH° and ΔS° will be imprecise but by fortunate coincidence this is exactly the case where the extrapolation is short and precision is unimportant.

Eq. (2) is then substituted into Eq. (1) and integrated by summation using the trapezoidal rule [6]. The step length was $L/10\,000$. It was found only 100 steps were necessary to get constant values of I within 0.01 unit, but 6000 were necessary to get retention temperatures that did not change by 0.1 K with still more steps.

All the values of T_R in Curvers' table 8 were recalculated using this integration. They differed from Curvers' experimental values in that table, by an average of 0.6 K with a standard deviation 0.4 K and a maximum deviation 3.0 K (for both 2-pentanone and 2,4,4-trimethylpentene-1, the two least retained substances in the collection). All of Curvers' values were used except those at 200°C which were outside the temperature program in all cases.

It is fair to omit a temperature outside the range of the program knowing [3] that ΔH and ΔS are slightly temperature dependent, but in a practical situation an analyst may not have that luxury. So it is also fair to report that if the 200°C data is included the mean error is slightly less at 0.4 K but with a higher standard deviation 0.6 K and the same maximum error 3.0 K (for the same substances).

3. Extrapolating from isothermal retention indices to programmed-temperature retention indices

The programmed retention index I^T is usually defined by

$$I^T = 100n + \frac{100(T_R - T_{R(n)})}{T_{R(n+1)} - T_{R(n)}}$$

T_R for the hydrocarbons is obtained using Eq. (1) as before but replacing $\Delta H^\circ - T\Delta S^\circ$ in Eq. (2) with $IbRT(\ln 10)/100$ from Eq. (5) and putting $I = 100n$. So

$$dT_{Cn} = \frac{r\{1 + (1/\beta)\exp(nb \ln 10)\}}{u_{\text{outlet}}(\eta/\eta_{T_0})^j [1 + (P^2 - 1)(1 - z/L)]^{1/2}} dz \quad (9)$$

The values of T_R for the sample and the reference hydrocarbons were obtained as before from the isothermal indices of Curvers et al and used to calculate the programmed retention index I^T . The mean deviation from all the experimental values in Curvers' table 8 ($I_{\text{expt}} - I_{\text{calc}}$) was 0.4 unit with a standard deviation 0.6 and a maximum deviation 3.9 (for diethylbenzene, extrapolating to the highest program rate used, 8 K/min).

As before, the data for 200°C were omitted because this temperature was outside the range of the program. Again it is fair to report that if these data are included then the mean deviation increases to 0.8 with standard deviation 1.4 and maximum deviation 7.8 (again for diethylbenzene at 8 K/min). Evidently it is best to use isothermal values as close to the actual program as possible.

4. Use with published indices

The routine described here could be hard-wired into the data control system of a gas chromatograph to provide direct comparison of experimental programmed indices with Sadtler's index [7] or other collections such as the ASTM collection [8] or McReynolds data [9].

Another interesting use would be as an internal check of consistency. The Sadtler index could be checked completely in a few minutes of computer time to detect inconsistency between the isothermal and programmed data. This would warn users to be wary of the few data found inconsistent in this way. Alternatively if such suspect data are found to be correct, there would be opportunity for research to explain the inconsistency.

5. Alternative method

A less successful approach is reported only to prevent others following the less successful road. Like the method described above it uses the slope of the log plot 'b' to circumvent the need for experimental data on the *n*-alkanes that is required by most other methods. The programmed index I^T is the length-averaged value of the isothermal index and is therefore given by

$$I^T = \frac{1}{L} \int_0^L I dz \quad (10)$$

Substituting for I from reference [5] yields

$$I^T = \frac{1}{L} \int_0^L \frac{100(\Delta H^\circ - T\Delta S^\circ)}{bRT \ln 10} dz \quad (11)$$

When this is integrated ignoring data at 200°C, the mean error is 0.2 unit, standard deviation 1.0 unit and maximum error 8.0 units. When the 200° data is included, the mean error rises to 2.4 units, standard deviation 2.6 units and maximum error 8.7 units.

6. Symbols

b	slope of the <i>n</i> -alkane log plot, δ (log corrected retention time)/ δ (carbon number)
dz	distance travelled by zone during the temperature interval dT
I	isothermal retention index
I^T	programmed temperature retention index
j	James-Martin compressibility factor, $3(P^2-1)/2(P^3-1)$
L	column length
n	carbon number
P	the ratio (inlet pressure/outlet pressure)
r	heating rate
R	gas constant
t_M	hold-up time = isothermal retention time of uretained substance
T	absolute temperature
T_0	initial temperature
T_R	final ('retention') temperature
$T_{R(n)}$	T_R for C_nH_{2n+2}
u	linear gas velocity

u_{average}	average linear gas velocity = L/t_M
z	distance traversed by zone from T_0 to T ($= \sum_{T_0}^T dz$)
β	volume of mobile phase/volume of stationary phase
η	viscosity of gas
η_{T_0}	viscosity of gas at T_0

7. Appendix

7.1. Derivation of Eq. (2)

The time δt to traverse the length δz is

$$\delta t = \frac{1+k}{u_{\text{local}}} \delta z \quad (12)$$

But $r \equiv \delta T / \delta t$ so

$$\delta T = \frac{r(1+k)}{u_{\text{local}}} \delta z \quad (13)$$

This must be expanded to show the temperature dependence of k and v .

$$k = K/\beta = (1/\beta) \exp[(\Delta H^\circ - T\Delta S^\circ)/RT] \quad (14)$$

where K is the partition coefficient

The velocity at any distance along the column is given by the textbook equation (see for example [10] Littlewood, equation 2.28)

$$\frac{u_{\text{local}}}{u_{\text{outlet}}} = \frac{1}{[1 + (P^2 - 1)(1 - z/L)]^{1/2}} \quad (15)$$

The data of Curvers et al gives the dead time t_M from which the average velocity $u_{\text{average}} = L/t_M$ can be obtained. This is related to u_{outlet} by the James-Martin [11] correction factor j

$$u_{\text{average}} = j u_{\text{outlet}} \quad (16)$$

$$j = 3(P^2 - 1)/2(P^3 - 1) \quad (17)$$

so that combining Eqs. (15–17) yields

$$u_{\text{local}} = \frac{u_{\text{average}}}{j[1 + (P^2 - 1)(1 - z/L)]^{1/2}} \quad (18)$$

But

$$u_{\text{average}} = u_{\text{average}, T_0} \eta_{T_0} / \eta \quad (19)$$

Combining Eqs. (18) and (19) gives

$$u_{\text{local}} = \frac{u_{\text{average}, T_0} \eta_{T_0} / \eta}{j[1 + (P^2 - 1)(1 - z/L)]^{1/2}} \quad (20)$$

Combining Eqs. (20,13,14) gives Eq. (2) as required.

A similar argument is used by Snijders et al [12], but is not correlated into a summary equation similar to Eq. (2).

References

- [1] S.J. Hawkes, *Chromatographia*, 37 (1993) 399.
- [2] J.M. Kong and S.J. Hawkes, *J. Chromatogr. Sci.*, 14 (1976) 279.
- [3] J. Curvers, J. Rijks, C. Cramers, K. Knauss, and P. Larson, *J. High Resolut. Chromatogr.*, 8 (1985) 611.
- [4] G. Tarján, Sz. Nyiredy, M. Györ, E.R. Lombosi, T.S. Lombosi, M.V. Budahegyi, S.Y. Mésáros and J.M. Takács, *J. Chromatogr.*, 472 (1989) 26–29.
- [5] S.J. Hawkes, *Chromatographia*, 25 (1988) 313.
- [6] S.M. Selby, *Standard Mathematical Tables*, CRC Press, Cleveland, OH, 16th ed., 1968.
- [7] The Sadtler Standard Gas Chromatography Retention Index Library, Sadtler Research Laboratories Division of Bio-Rad Laboratories, Philadelphia, PA, 1985.
- [8] O.E. Schupp and J.S. Lewis (Editors) in: *Compilation of Gas Chromatographic Data*, American Society for Testing and Materials, 1967.
- [9] W.O. McReynolds, *Gas Chromatographic Retention Data*, Preston Technical Abstracts Co., Evanston, IL, 1966.
- [10] A.B. Littlewood, *Gas Chromatography*, Academic Press, New York, 1970, p. 26.
- [11] A.T. James and A.J.P. Martin, *Biochem. J.*, 50 (1952) 679.
- [12] H. Snijders, H.-G. Janssen and C. Cramers, *J. Chromatogr. A*, 718 (1995) 339–355.