Forecasting Retention Times in Temperature-Programmed Gas Chromatography: Experimental Verification of the Hypothesis on Compound Behavior

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Abstract

The hypothesis of a theoretical "slicing" of the column in temperature-programmed gas chromatography for the accurate forecasting of retention time is tested by actually "slicing" a column. Calculated and observed retention times in relation to the column length are in good agreement.

Introduction

In a previous work (1), an easy and accurate method was described for the calculation of retention times in temperature-programmed gas chromatography (TPGC). This method is based on a theoretical "slicing" of the column; each "slice", or element, is considered to be under isothermal conditions and at a temperature inferior to that of the following slice. In this paper, we attempted to confirm this hypothesis by the actual "slicing" of a column.

Theory

It has been established (1) that the retention time of a compound in TPGC, t_R, may be calculated from a small set of isothermal data:

$$t_R = t_{[n]} = \sum_{i=1}^{n} \frac{t_0}{n}\left(1 + e^{\frac{a}{\theta\left(t_{[i-1]}\right)} + b}\right) \qquad \text{Eq 1}$$

where t_0 is the dead time, n is the number of elements, and $\theta(t_{[i-1]})$ is the oven temperature when the solute enters the i^{th} element at time $t_{[i-1]}$. a and b are thermodynamic parameters (2):

$$a = \frac{-\Delta H^0}{R} \qquad \text{Eq 2}$$

$$b = \frac{\Delta S^0}{R} + \ln\frac{V_S}{V_M} \qquad \text{Eq 3}$$

ΔH^0 and ΔS^0 are, respectively, the variation of standard enthalpy and entropy of transfer of the solute from mobile to stationary phases. V_S and V_M are the volumes of these phases (ΔH^0 and ΔS^0 are considered to be constant over the studied temperature range). a and b are easily determined experimentally from the linear regression of the retention factor of the compound, k, against the temperature of the oven (3):

$$\ln k = \frac{a}{\theta} + b \qquad \text{Eq 4}$$

Therefore, a small set of isothermal data, for determining the dead time and thermodynamic parameters of a compound, can be used to calculate the retention time of the compound over a wide range of nonisothermal conditions.

Experimental

Apparatus

A Delsi Di-200 gas chromatograph with a flame ionization detector was used with a Spirawax column (50 m × 0.32-mm i.d., 0.15-µm film thickness) from Spiral (Dijon, France). Nitrogen was the carrier gas, and the outlet flow rate was maintained at about 2 mL/min^{-1}. Injector and detector temperatures were set at 240°C. The split ratio was set at 5:1.

To eliminate the solvent peak, which would have caused problems with the shortening of the column, a solid-phase microextraction (SPME) device from Supelco (Bellefonte, PA) was used (7-µm polydimethyl siloxane coating). The solute was adsorbed onto the SPME coating from an aqueous solution for 15 min without stirring and then thermally desorbed in the chromatograph injection chamber. A 1% guaïacol aqueous solution was used. Injections were repeated three times, and the variations were typically less than $^2/_{100}$ of a minute.

Isothermal experiment

An initial set of isothermal experiments was carried out as described elsewhere (1) to determine the thermodynamic parameters of guaïacol and dead time.

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Temperature program and "slicing"

The oven was programmed to go from 140°C to 200°C at a rate of 10°C/min. After an initial measurement of the retention time of the guaïacol, the column was shortened by cutting off lengths of 1–2 m at a time. After each cut, the column was allowed to reach thermal equilibrium, the dead time was adjusted, and the guaïacol retention time was measured again.

Dead time adjustment

The term t_0/n in Equation 1 is used with the supposition that the carrier gas velocity is approximately constant all along the column, because t_0/n represents the time taken by the gas to pass through column elements of equal length. This is, of course an approximation, as was stated in the previous article (1). The flow velocity in element i can be expressed as:

$$\bar{u} = \frac{\Delta P_{i-1,i} \times J_{i-1,i}}{L \times \eta} \times \frac{r_c^2}{8} \qquad \text{Eq 5}$$

where

$$J_{i-1,i} = \frac{3}{4} \times \frac{\left(P_{i-1,i}^2 - 1\right)\left(P_{i-1,i} + 1\right)}{\left(P_{i-1,i}^3 - 1\right)} \qquad \text{Eq 6}$$

$$P_{i-1,i} = P_{i-1} / P_i \quad \text{and} \quad \Delta P_{i-1,i} = P_{i-1} - P_i$$

where η is the carrier gas viscosity, and $P_{(i-1)}$ and P_i are, respectively, the pressure at the entry and at the end of element i. Even if the gradient of pressure were linear along the column, the term $J_{i-1,i}$ is not constant. Moreover, the viscosity of gases varies with the temperature and pressure. Therefore, the velocity of the carrier gas is not constant throughout the chromatographic process.

These variations are complex, but in a previous work (1), the errors were not significant when the variations were neglected. It was decided to consider the gas velocity along the column as a constant. The column inlet pressure was set so that the dead time of the shortened column, $t_{0(l)}$, was a linear function of its length, l, and of the dead time of the whole column of length L (Figure 1):

$$t_{0(l)} = t_0 \times \frac{l}{L} \qquad \text{Eq 7}$$

Results and Discussion

The data obtained from the isothermal experiments (Table I) were used to set up a worksheet of an Excel spreadsheet as described in reference 1. The experimental retention times of the guaïacol for each column length were compared with those

Table I. Preliminary Experimental Data

Temperature (°C)	Retention time (min)
120	26.05
140	10.16
160	6.83
180	5.83
200	5.46
220	5.29
a	*b*
1188	–8.477

Table II. Experimental Data

Column length (mm)	Calculated t_0 (min)	Observed t_0 (min)	Calculated t_R (min)	Observed t_R (min)	Difference (%)
50510	5.06	5.06	6.41	6.44	0.528
48500	4.85	4.87	6.19	6.24	0.801
46510	4.65	4.64	5.97	5.93	-0.725
44520	4.45	4.47	5.76	5.78	0.398
42500	4.25	4.22	5.54	5.58	0.753
40510	4.05	4.04	5.32	5.27	-0.930
38510	3.85	3.82	5.10	5.06	-0.771
36520	3.65	3.68	4.88	4.87	-0.123
34510	3.45	3.48	4.65	4.65	-0.043
32500	3.25	3.28	4.43	4.45	0.517
30510	3.05	3.07	4.20	4.20	0.024
28500	2.85	2.85	3.97	3.99	0.526
26520	2.65	2.64	3.74	3.74	0.107
24510	2.45	2.44	3.50	3.48	-0.575
22500	2.25	2.23	3.26	3.25	-0.338
20510	2.05	2.06	3.02	3.01	-0.266
18520	1.85	1.84	2.77	2.75	-0.727
16500	1.65	1.65	2.52	2.51	-0.279
14520	1.45	1.43	2.26	2.23	-1.256
13500	1.35	1.34	2.13	2.14	0.701
12510	1.25	1.25	1.99	1.97	-1.066
11500	1.15	1.15	1.85	1.85	-0.216
10520	1.05	1.05	1.72	1.69	-1.479
9520	0.95	0.95	1.57	1.56	-0.897
8510	0.85	0.85	1.43	1.41	-1.348

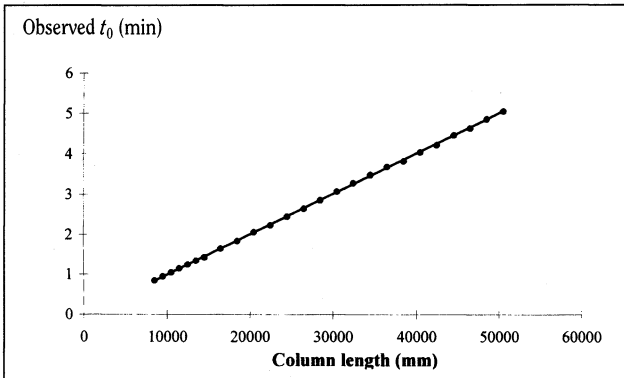

Figure 1. Plot of observed dead time versus column length.

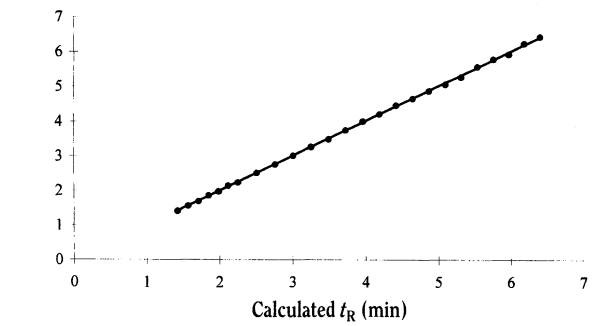

Figure 2. Plot of observed and calculated retention times.

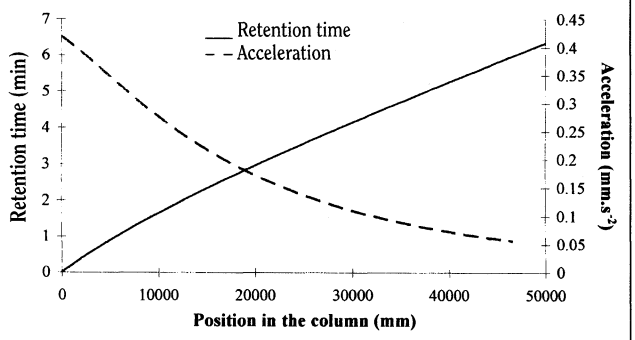

Figure 3. Plot of the retention time and acceleration of the compound versus the compound position in the column, according to Equation 1.

appearing in the worksheet for the equivalent position in the entire column. The results are in Table II.

Figure 2 shows the plot of experimental retention times versus calculated times. The parameters of the fitted line are: slope = 1.006 ± 0.003, intercept = –0.026 ± 0.013, and determination coefficient = 0.9997.

The correlation is excellent despite the approximation made on the carrier gas flow velocity. The variations of this velocity appear to be either small or compensated by the variation of another parameter. This will be investigated in further work.

Conclusion

This work shows that the step-by-step calculation of retention time (Equation 1) leads to an accurate description of the "trajectory" of the compound in the column under non-isothermal conditions (Figure 3).

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