

Short communication

Retention simulation in gas chromatography

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Abstract

It is demonstrated that the differential equation (Model 1) describing a peak motion in GC process can be served as the general base for retention simulation. The integration equation (Model 2) is a special form of solution of the differential equation only in constant pressure mode. Both models are not analytically solvable in term of retention time, and numerical calculations based on standard algorithms (Ronge–Kutta algorithm for Model 1, Simpson algorithm for Model 2) have to be used. Simulation results show the existence of some difference between the models in pressure varying GC conditions. The difference usually varies from 0.01 to 0.15 min or more depending on the solutes, operating pressure and temperature conditions. A q index is proposed to correlate the model difference. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Retention simulation; Pressure program; Temperature programming; Mathematical modelling; Thermodynamic parameters; Gas chromatography

1. Introduction

The pressure and temperature operation mode in GC has experienced many changes since the invention of gas chromatography. Constant pressure and programmed temperature are the most popular mode used today. Programmed pressure function is available now in newly developed equipment, providing another variable to regulate the retention of a solute. Retention simulation under constant pressure has been well studied in the past [1–21]. Generally, both temperature and pressure (or flow) may be programmed in a GC process, thus tracing of a GC solute in this case is very important for the development of retention identification with the aid of modern gas chromatography, computer and some retention databases. Some related fundamental works have been achieved by a research group [22–24].

The discussions presented in this paper are mainly based on their works.

2. Pretreatment

The related equations and variables are rewritten in this part for convenience in the following demonstration and the numerical calculations. Based on the symbol definition in [22,25], we define $z = x/L$, x is the coordinate along the column axis, L is the column length, thus z is the unified column coordinate. P_z is defined as

$$P_z = \sqrt{P^2 - z \cdot (P^2 - 1)} \quad (1)$$

P is the relative pressure, and P_z the relative pressure at z . The Q in Ref. [22] can be expressed as

$Q = Pz \cdot j$, j is the compressibility correction factor (or James–Martin factor). The differential equation (referred to as Model 1) describing the motion of a solute becomes

$$\frac{dz}{dt} = \frac{1}{Pz \cdot j \cdot t_0 \cdot (1+k)} \quad (2)$$

Following the treatment in Ref. [24], the relation of k and T is expressed as

$$k = \frac{\alpha}{\beta} \cdot e^{-\frac{\Delta H_s}{R \cdot T}} \quad (3)$$

ΔH_s is the molar enthalpy, α the entropy factor, β the phase ratio of the column, R the gas constant. All of these are usually considered as constants in the simulation for a given solute and a column. With the aid of a reference condition of T^0 and P^0 , where the respected hold up time and James–Martin factor are t_0^0 , and j^0 , the t_0 at T and P conditions can be expressed as

$$t_0 = t_0^0 \cdot \frac{j^0}{j} \cdot \frac{P^{0^2} - 1}{P^2 - 1} \cdot \left(\frac{T}{T^0}\right)^N \quad (4)$$

For nitrogen carrier gas, N is 0.725. For a constant flow mode, as a special program pressure P can be expressed as a function of T as

$$P = \sqrt{1 + \left(\frac{T}{T^0}\right)^N \cdot (P^{0^2} - 1)} \quad (5)$$

Thus, the hold-up time in this mode can be obtained from Eqs. (5) and (4). The hold-up time *in constant flow mode* can also be expressed in terms of T and P as Eq. (6).

$$t_0 = t_0^0 \cdot \left(\frac{T}{T^0}\right)^{-(2+N)} \cdot \frac{P^3 - 1}{P^{0^3} - 1} \quad (6)$$

For a GC process in which both the temperature and pressure may be varying according to certain programs, the dependency of the variables in the equation can be expressed as follows

$$T = T(t)$$

$$P = P(t)$$

$$Pz = Pz(z, P) = Pz(z, t)$$

$$j = j(P) = j(t)$$

$$t_0 = t_0(T, P) = t_0(t)$$

$$k = k(T) = k(t)$$

As can be seen from the above relations, except Pz , all other variables can be expressed as functions of time t . Constant temperature and constant pressure process can be served as a special kind of program such that they keep constant as time develops. Although some variable transform can be made in the simulation, for example in terms of temperature, z and t are the actual variables to be worked on, and the corresponding temperature can be obtained according to a given temperature program.

The aim of the solution of the differential equation is to find $z = z(t)$ or $t = t(z)$ with $z = 0$ and $t = 0$ as an initial condition, which is meaningful in gas chromatography. The corresponding time at $z = 1$ is the retention time to be simulated.

3. Demonstration

3.1. Solubility in constant pressure mode

For a constant pressure GC process, where P does not change by time, Pz depends only on z , and j become a constant, the differential Eq. (2) can be solved by variable separation and integration in the interested domain as Eq. (7)

$$\int_0^{t_R} \frac{1}{t_0(t) \cdot [1+k(t)]} dt = \int_0^1 Pz(z) \cdot j \cdot dz \quad (7)$$

It is easy to demonstrate that the value of the right part of Eq. (7) is 1 in a constant pressure mode, thus we have

$$\int_0^{t_R} \frac{1}{t_0 \cdot (1+k)} dt = 1 \quad (8)$$

This is the mathematical model widely used for retention simulation in the literature, and referred to as Model 2 in this paper. Most capillary gas chromatography works in this mode.

When the temperature is also kept constant, t_0 and

k become constants, thus we have the analytical solution of Eq. (8) as

$$t_R = t_0(1 + k) \quad (9)$$

This is the only analytical solution of the differential Eqs. (8) and (2) in terms of t_R .

Eq. (8) is only a solution in integrate equation form, not a final solution of the retention time, and numerical integration has to be applied to obtain the value of t_R .

3.2. Solubility in pressure varying mode

The original differential Eq. (2) can also be reformed as

$$Pz \cdot dz - \frac{1}{j \cdot t_0 \cdot (1 + k)} \cdot dt = 0 \quad (10)$$

to fit the general form of a typical ordinary differential Eq. (13), let

$$M(z,t) = Pz(z,t) \quad (11)$$

$$N(t) = -\frac{1}{j(t) \cdot t_0(t) \cdot [1 + k(t)]} \quad (12)$$

thus, Eq. (2) becomes

$$M(z,t)dz + N(t)dt = 0 \quad (13)$$

The sufficient and necessary condition to make the differential equation the exact differential and has the solution in the form of Eq. (15) is that Eq. (14) must be assured [26,27].

$$\frac{\partial M}{\partial t} = \frac{\partial N}{\partial z} \quad (14)$$

$$\int_0^z M(z,t)dz + \int_0^t N(t)dt = C \quad (15)$$

For the particular differential Eq. (10) we have

$$\frac{\partial N}{\partial z} = \frac{\partial}{\partial z} \left\{ -\frac{1}{j(t) \cdot t_0(t) \cdot [1 + k(t)]} \right\} = 0 \quad (16)$$

$$\frac{\partial M}{\partial t} = \frac{\partial Pz(z,t)}{\partial t} = \frac{(1-z) \cdot P(t)}{Pz(z,t)} \cdot P'(t) \quad (17)$$

The P and Pz will never be 0 in the chromatographically meaningful domain of $z[0,1]$ and $t[0,t_R]$.

So whether the condition Eq. (14) is applied exclusively depends on $P'(t)$. Eq. (17) will be 0 only when the P keeps constant in the whole process, rather than a part or at some points or vicinity of a point. And this can be served as a sufficient and necessary condition to make the differential Eq. (10) the exact differential. Thus, we will obtain the final solution in the form of Eq. (8).

In a pressure varying GC mode, where $P'(t)$ will not equal zero, Eq. (14) is not assured, thus no solution can be obtained. This conclusion is obvious from the above demonstration.

In one word, Model 1 and Model 2 are mathematically different. Model 1 is more general, while Model 2 is only a special solution of Model 1 in constant pressure GC mode.

4. Algorithms

As stated above, both the integration Eq. (8) and differential Eq. (2) are not analytically solvable in terms of t_R , numerical calculations have to be used [28]. In this paper, the constant step Ronge–Kutta algorithm is used for the numerical calculation of Model 1 in the range of $z[0,1]$, and the constant step Simpson integration algorithms are used for Model 2. In the integration of Model 2, the time margin is to be found until the integration value reached unity. In the Ronge–Kutta procedure, the initial condition of $z = 0$ and $t = 0$ is used, the corresponding t at $z = 1$ is the retention time to be simulated. These algorithms used in this paper are classical numerical procedures which can be found in numerical mathematics such as in Ref. [29,30]. An index q is defined as

$$q = \int_0^1 Pz(z,t) \cdot j(t)dz \quad (18)$$

this is the same as Eq. (18) in Ref. [24]. The q value can be obtained by trapezoid integration in the process of numerical calculation of the differential Eq. (2) by the Ronge–Kutta procedure.

The only analytical solution of Eq. (2) can be obtained as Eq. (9) in constant pressure and constant temperature GC mode, thus, this mode of GC can be used to test the performance of the algorithms, for

Table 1

Test of the algorithms by a constant pressure and constant temperature GC mode (thermodynamic data from Ref. [23])^a

Solute		Thermodynamic parameters		Eq. (8) (Model 2) Simpson integration algorithm			Eq. (2) (Model 1) Ronge–Kutta algorithm		Analytical solution
No.	Name	$-\Delta H_s/R$	$(\alpha/\beta) \times 10^6$	0.05 min step t_R	0.01 min step t_R	0.005 min step t_R	0.001 step t_R	The index q	t_R
1	<i>n</i> -Octane	4175	5.533	3.10	3.06	3.06	3.053239	1.000	3.053233
2	<i>p</i> -Xylene	4262	6.924	3.40	3.32	3.31	3.304248	1.000	3.304241
3	1,3,5- Trimethylbenzene	4661	4.417	3.90	3.82	3.81	3.809664	1.000	3.809658
4	1-Undecene	5313	1.729	5.00	5.00	4.99	4.988316	1.000	4.988303
5	Naphthalene	5107	4.623	6.50	6.44	6.44	6.430661	1.000	6.430640
6	<i>n</i> -Dodecane	5559	1.695	7.00	6.92	6.92	6.911489	1.000	6.911475
7	Tetradecane	5990	1.545	14.10	14.06	14.06	14.05250	1.000	14.05247
8	Hexadecane	6760	0.635	34.50	34.42	34.41	34.40947	1.000	34.40939

^a Note: nitrogen as carrier gas, $N=0.725$. Inlet pressure 1282 Torr, outlet pressure 770 Torr, hold up time 2.214 min, isothermal column temperature 130°C.

this is the only case we can obtain the accurate t_R which can be used as a standard to compare with. As can be seen in Table 1, when the 0.001 step of z is used in the Ronge–Kutta algorithm for Model 1, we can only find a difference of five digits after the decimal. And when the 0.005 min step is used in the Simpson algorithms for Model 2, the errors are no more than 0.01 min which is mainly from the condition loop of the Simpson integration procedure. Concerning the retention reproducibility level of the latest equipment, this level of accuracy of the algorithms is appropriate. The q value is also listed in the table, which is unity as can be predicted theoretically.

5. Numerical results and discussion

It is very necessary to make it clear if the Model 2 is explicitly applicable for a programmed pressure GC mode as demonstrated in Ref. [24]. This is very important for avoiding errors of mathematical model sources. Four typical pressure programs are simulated and the results are listed in Table 2. It can be seen that in the constant pressure mode (Program 2), as an extreme programmed pressure case, the maximum model difference was 0.01 min, which is mainly from the intercept error in the Simpson integration calculation. In the constant mass flow mode (in Program 1), as a special program of

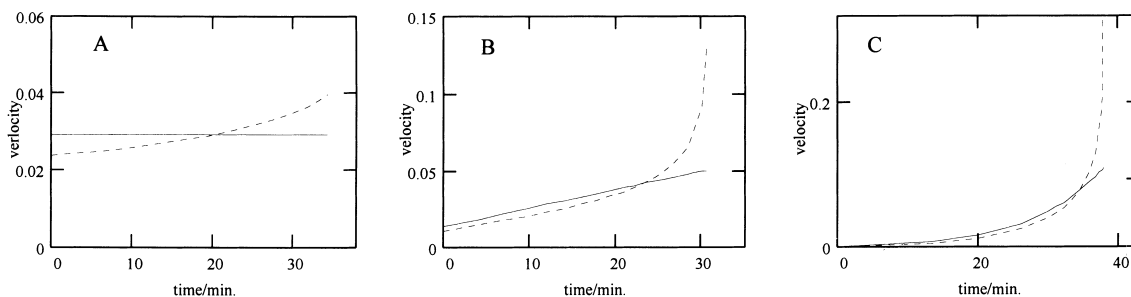


Fig. 1. Relation of unified local velocity (u) and unified average velocity (v) with time. Solid line for the average velocity, and dashed line for the local velocity, No. 8 solute: *n*-hexadecane. (A) Constant pressure and constant temperature mode, for detailed conditions see Table 1, Model difference 0.00 min; (B) programmed pressure and constant temperature mode, Program 4 in Table 2, Model difference 0.56 min; (C) programmed pressure and programmed temperature mode, Program 3 in Table 2, Model difference 0.11 min.

Table 2
Comparison of simulated retention times based on different models for different GC operating programs^a

Programs No. of solute	Program 1				Program 2				Program 3				Program 4			
	t_{SM}	t_{RK}	q	$t_{SM}-t_{RK}$	t_{SM}	t_{RK}	q	$t_{SM}-t_{RK}$	t_{SM}	t_{RK}	q	$t_{SM}-t_{RK}$	t_{SM}	t_{RK}	q	$t_{SM}-t_{RK}$
1	6.21	6.19	0.997	0.02	4.60	4.59	1.000	0.01	5.10	5.05	0.989	0.05	2.86	2.84	0.993	0.02
2	7.78	7.76	0.996	0.02	6.04	6.03	1.000	0.01	6.52	6.45	0.986	0.07	3.20	3.17	0.992	0.03
3	10.58	10.55	0.994	0.03	8.87	8.87	1.000	0.00	9.53	9.43	0.983	0.10	3.91	3.87	0.991	0.04
4	13.60	13.56	0.992	0.04	12.56	12.56	1.000	0.00	14.96	14.83	0.981	0.13	5.59	5.52	0.987	0.07
5	14.87	14.83	0.991	0.04	13.97	13.97	1.000	0.00	17.48	17.33	0.981	0.15	7.18	7.09	0.985	0.09
6	15.46	15.42	0.991	0.04	14.71	14.71	1.000	0.00	19.55	19.40	0.981	0.15	7.99	7.88	0.984	0.11
7	18.25	18.21	0.992	0.04	17.88	17.88	1.000	0.00	28.07	27.93	0.984	0.14	15.35	15.09	0.976	0.26
8	20.81	20.78	0.993	0.03	20.78	20.77	1.000	0.01	38.08	37.92	0.988	0.11	31.21	30.65	0.972	0.56
Inlet pressure p_i^0	1277 Torr				1546 Torr				1282 Torr				1282 Torr			
Outlet pressure p_o^0	765 Torr				770 Torr				770 Torr				770 Torr			
Hold up time t_0^0	2.224 min				1.489 min				2.214 min				2.214 min			
Temperature program	50°C (2.5 min), 5°C/min to 80°C (0.5 min), 10°C/min to 250°C				50°C (2.5 min), 5°C/min to 80°C (0.5 min), 10°C/min to 250°C				50°C, 2°C/min to end				110°C isothermal			
Pressure program	Constant mass flow				Constant inlet pressure				1282 Torr, 51.715 Torr/min to end				1282 Torr, 51.715 Torr/min to end			

^a Note: the solutes and the respected thermodynamic parameters are the same as in Table 1. Carrier gas: nitrogen. Programs 1 and 2 are the same as Programs 2 and 5 in Table 3 of Ref. [23]. t_{SM} – the simulated retention time based on Model 2 by Simpson algorithm with step 0.005 min; t_{RK} – the simulated retention time based on Model 1 by Ronge–Kutta algorithm with step 0.001; q – the index as defined in Eq. (18). 1 Torr = 133.322 Pa.

pressure, the maximum difference of 0.04 min is found. In Program 3 where both pressure and temperature are programmed, a maximum difference of 0.15 min was found. A difference of 0.56 min is found in Program 4, the same pressure program as Program 3 but with constant temperature. These differences have exceeded the level of the calculation accuracy of 0.01 min, and this is the direct consequence of the use of Eq. (8) in the pressure varying mode, which coincides with the demonstration part.

We may also notice that the differences are accompanied with some extent of deviations of q value to unity. The maximum q deviation is 2.73% with a model difference of 0.56 min for *n*-hexadecane in Program 4. Though the q value correlates with model difference, the relation does not seem to be simple.

The local unified velocity (u) and average unified velocity (v) of a solute at a time t can be defined as below

$$u = \frac{1}{Pz \cdot j \cdot t_0 \cdot (1 + k)} \quad (19)$$

$$v = \frac{1}{t_0 \cdot (1 + k)} \quad (20)$$

Generally, both u and v change by time for a peak in a GC process, but the curves are different because of the $Pz \cdot j$ term. At the beginning, v is greater than u , as the solute approaches the end of the column, the curves intercross, and u increases more rapidly than v till to the end. Actually, the aim of the numerical simulation of retention time is to find the time such that the area underlying the curve is equal to unity, corresponding to $z = 1$. Although there are many ways to achieve this, the numerical solution is singular for a solute in a given temperature and pressure GC conditions. In a constant pressure GC mode, whether the temperature is constant or programmed, the change is compensated such that they reach the end at the same time (see Fig. 1A). This may be the special property of GC fluid dynamics mentioned in Ref. [24]. Although the compensation effect also occurs to some extent in non-constant pressure GC mode, a difference still exists as shown in Fig. 1B and C. Usually the difference is small, but sometimes this error may be comparable to ex-

perimental errors that deserve to be noticed as an error contribution from models.

6. Conclusions

Mainly four points can be drawn from the above investigations.

(1) The differential equation (Model 1) is the only general base of GC simulation in any pressure and temperature programming conditions, including constant pressure and/or constant temperature conditions.

(2) The integration equation (Model 2) is a special solution of the differential equation in constant pressure mode, and numerical solution has to be made to obtain the final solution of retention time. Retention time simulation can be achieved with this equation without theoretical approximation.

(3) Under the usual GC conditions, the difference between Model 1 and 2 is very small because of the compensation effect. Obvious differences may be found in some cases such as in slow temperature and rapid pressure changing GC conditions. Only approximate results could be obtained when the Model 2 is used for the pressure varying GC process.

(4) The deviation of the q value from unity can be served as an index of the model difference introduced in retention time simulation in specific operating conditions for a specific solute.

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