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Novel approach for the prediction of retention times in operating parameter programmed gas–liquid chromatography with capillary columns

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Abstract

A novel approach has been established to predict the retention time in operating parameter programmed gas–liquid chromatography with capillary columns through the use of numerical calculation, which can be applied to multi-ramp programs for column temperature and/or carrier gas pressure at the column inlet. The results show that a better or, at least similar accuracy, can be achieved for the prediction of retention time in temperature-programmed gas chromatography with the approach reported herein, than that obtained with Curvers' approach, which has been widely utilized up to now. Our established procedure is particularly suitable for those operating conditions containing an inlet pressure program. In addition, the prediction of resolution under temperature-programmed conditions from the trajectory of the solute band moving in the column, column efficiency and other operating parameters is discussed. © 1998 Elsevier Science B.V.

Keywords: Retention prediction

1. Introduction

Capillary gas–liquid chromatography (CGC) is nowadays universally used for the analysis of various complex mixtures containing compounds with a broad range of boiling points and/or polarities. The column temperature is an important operating parameter for adjusting retention times in gas chromatography. An increase in temperature of 20°C to 30°C probably results in a two- to three-fold decrease in retention time. In general, isothermal or temperature-programmed modes can be utilized to perform the analysis of a specified sample. As commercial instruments for temperature-programmed CGC (TPCGC)

become readily available, more and more analytical approaches were developed for use with TPCGC. TPCGC has the advantage of decreasing the analysis time required and providing improved resolution [1]. TPCGC can also be proven to be of higher sensitivity than isothermal CGC even if the same resolution is acquired. In fact, TPCGC is the most suitable mode in preliminary experiments during the developing of analytical method for analysis of an unknown sample, as will be discussed in a forthcoming paper.

Sometimes, in order to reduce analysis time the adjustment of column temperature will result in unsatisfactory resolution. Pressure programming in CGC (PPCGC) is now staging a comeback in a more suitable form. An increase in pressure can still reduce the maximum column temperature required

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for an analysis, but it can also be used routinely to maintain near-optimum chromatographic conditions throughout a temperature program. In addition, pressure programming can be used to improve conditions for both injection and detection. As advances have been made in commercially available instrumentation, pressure programming can now be easily, inexpensively and repeatedly controlled electronically. This technique is gradually being accepted and applied by chromatographers.

With the aim of optimization of GC separation and confirmation of eluting components, the prediction of retention values in TPCGC from isothermal data (including retention times and Kovats' retention index) has been carried out by many authors using different methods [2–13]. Factually, the methods proposed by Curvers [2] and by Akporhonor [6] have widely been applied. Castello et al. [14] compared several methods. Bautz et al. [15] also presented a method based upon an approximation similar to the linear solvent strength model for gradient HPLC, which was used to predict retention time under various column temperature conditions from data in two linear temperature-programmed modes. So far empirical methods suggested by several authors [3–5] have rarely been used to predict chromatographic characteristics in TPCGC. Garcia et al. [16] predicted and compared retention times and retention indices of solutes with various polarities on four unequally polar stationary phases with seven different predicting methods. Wright et al. [17] and Gerbino et al. [18] predicted retention values in either single-column or serially linked capillary column systems in TPCGC with the equation of Curvers. An important approach has been suggested by Nogare [12] and by Cavalli [13] based on the algorithm used in the numerical solution of differential equations, which allows the calculation of retention times under various complicated program conditions.

In this paper, we shall discuss the prediction of the retention time in temperature and/or pressure programming modes.

2. Theory

The velocity ($u_i(x,t)$) of solute i moving in a

column can be expressed with the following equation:

$$u_i(x,t) \equiv \left(\frac{dx}{dt} \right)_i = \frac{u(x,t)}{1 + k'_i(T(t))} \quad (1)$$

where x is the distance of the solute band from the column inlet, $T(t)$ is column temperature (K) at time t , $u(x,t)$ is the linear velocity of carrier gas at position x and at time t , and $k'_i(T(t))$ is the capacity factor of solute i at temperature of $T(t)$. Generally, the capacity factor at temperature T ($k'_i(T)$) is correlated with T as follows:

$$\log k'_i(T) = -\frac{\Delta H_i}{R \cdot T} + \frac{\Delta S_i}{R} - \log \beta \quad (2)$$

where β is the phase ratio of the column used (the volume of gas phase divided by the volume of liquid phase), R is universal gas constant, and ΔH_i and ΔS_i are enthalpy and entropy of solute i in the retention process, respectively. According to the Darcy theorem for capillary columns the $u(x,t)$ under temperature-programmed and/or programmed-pressure conditions is given by:

$$u(x,t) \equiv \frac{dx}{dt} = -\frac{d_c^2}{32\eta(T(t))} \cdot \frac{\partial p'(x,t)}{\partial x} \quad (3)$$

where d_c is the diameter of column, $\eta(T(t))$ is the viscosity of carrier gas at temperature $T(t)$, and $p'(x,t)$ is the carrier gas pressure at position x and at time t . Let $x = \phi \cdot L$, we have:

$$\begin{aligned} \frac{dx}{dt} &= L \frac{d\phi}{dt} = -\frac{d_c^2}{32L\eta(T(t))} \cdot \frac{\partial p'(L \cdot \phi, t)}{\partial \phi} \\ &\equiv -\frac{d_c^2}{32L\eta(T(t))} \cdot \frac{\partial p(\phi, t)}{\partial \phi} \end{aligned} \quad (4)$$

where L is the length of column and ϕ is that fraction of x found in L and its value always varies from zero to one. Based on the continuity equation of fluid, derived from the principle of conservation of mass, and the state equation for an ideal gas, as well as Eq. (4), the variation of pressure of carrier gas in a capillary chromatographic column during temperature and inlet pressure programming can be described with:

$$\left\{ \begin{aligned} \frac{\partial}{\partial \phi} \left(p(\phi, t) \cdot \frac{\partial p(\phi, t)}{\partial \phi} \right) \Psi(T(t)) &= \left(\frac{\partial p(\phi, t)}{\partial t} - \frac{p(\phi, t)}{T(t)} \cdot \frac{dT(t)}{dT} \right) \\ p(\phi, t) &= p_i(t) \\ p(1, t) &= p_o \\ \frac{\partial^2 [p(\phi, t)]^2}{\partial \phi^2} \Big|_{\phi=0} &= 0 \end{aligned} \right. \quad (5)$$

where

$$\Psi(T(t)) = \frac{d_c^2}{32\eta(T(t))L^2}$$

The above partial differential equation is equivalent to:

$$p(\phi, t) = \left(\frac{2}{\Psi(T(t))} \right)^{1/2} \cdot \left\{ \frac{\partial}{\partial t} \int \left(\int p(\phi, t) d\phi \right) d\phi - \frac{1}{T(t)} \frac{dT(t)}{dt} \int \left(\int p(\phi, t) d\phi \right) d\phi + C \cdot \phi + D \right\}^{1/2} \quad (6)$$

and its initial condition. From the boundary conditions in Eq. (5), the constants *C* and *D* in Eq. (6) can be expressed with:

$$\left\{ \begin{aligned} D &= \frac{\Psi(T(t))}{2} [p_i(t)]^2 - \left\{ \frac{\partial}{\partial t} \left[\int \left(\int p(\phi, t) d\phi \right) d\phi \right] \right\} \Big|_{\phi=0} \\ &+ \left\{ \frac{1}{T(t)} \frac{dT(t)}{dt} \int \left(\int p(\phi, t) d\phi \right) d\phi \right\} \Big|_{\phi=0} \\ C &= \frac{\Psi(T(t))}{2} \{ p_o^2 - [p_i(t)]^2 \} - \frac{\partial}{\partial t} \left[\int_0^1 \left(\int p(\phi, t) d\phi \right) d\phi \right] \\ &+ \frac{1}{T(t)} \frac{dT(t)}{dt} \frac{\partial}{\partial t} \left[\int_0^1 \left(\int p(\phi, t) d\phi \right) d\phi \right] \end{aligned} \right. \quad (7)$$

Combining Eq. (4) with Eq. (6), we can thus get:

$$\frac{d\phi}{dt} = -\sqrt{\frac{\Psi(T(t))}{2}} \cdot \left[\frac{\partial}{\partial t} \left(\int p(\phi, t) d\phi \right) - \frac{1}{T(t)} \frac{dT(t)}{dt} \left(\int p(\phi, t) d\phi \right) + C \right] / \left[\frac{\partial}{\partial t} \int \left(\int p(\phi, t) d\phi \right) d\phi - \frac{1}{T(t)} \frac{dT(t)}{dt} \int \left(\int p(\phi, t) d\phi \right) d\phi + C \cdot \phi + D \right]^{1/2} \quad (8)$$

When inlet pressure, outlet pressure and temperature are separately kept constant p_{icp} , p_o and T , that is:

$$\left\{ \begin{aligned} \frac{\partial p(\phi, t)}{\partial t} &= 0 \\ \frac{dT(t)}{dt} &= 0 \end{aligned} \right.$$

Eq. (7) and Eq. (8) are simplified to:

$$\left\{ \begin{aligned} \frac{d\phi}{dt} &= -\frac{C \cdot \sqrt{\Psi(T)/2}}{\sqrt{C \cdot \phi + D}} \\ C &= \frac{\Psi(T)}{2} \cdot (p_o^2 - p_{icp}^2) \\ D &= \frac{\Psi(T)}{2} \cdot p_{icp}^2 \end{aligned} \right. \quad (9)$$

Through the integral of the above equation the corresponding holdup time $t_M(T)$ can be theoretically expressed with:

$$t_M(T) = \frac{4(p_{icp}^3 - p_o^3)}{3(p_{icp}^2 - p_o^2)^2 \Psi(T)} \quad (10)$$

At the same time, according to Ettre's suggestion [19] holdup time can be experimentally correlated with temperature T as:

$$t_M(T) = a + b \cdot T \quad (11)$$

where a and b are coefficients calculated from the linear regression. Combining Eq. (11) with Eq. (10), we have:

$$\Psi(T) = \frac{4}{3} \frac{p_{icp}^3 - p_o^3}{(p_{icp}^2 - p_o^2)^2} \frac{1}{a + b \cdot T} \quad (12)$$

By means of the determination of holdup times under constant inlet pressure p_{icp} and different isothermal conditions we can thus obtain the dependence of $\Psi(T)$ on temperature. Although the pressures p_{icp} and p_o appear in right side of Eq. (12), $\Psi(T)$ should not be affected by them as it is only concerned with d_c , L and $\eta(T)$ according to its definition in Eq. (5). Theoretically, $\Psi(T)$ can be also obtained through other means such as measurements of d_c , L and $\eta(T)$ instead of the procedure used above.

When temperature and/or pressure programming are used, from Eq. (1), Eq. (2), and Eq. (4) we can obtain the equation of velocity for solute i moving in a column under temperature and/or pressure programming conditions as follows:

$$\left(\frac{dx}{dt} \right)_i = \frac{L}{(1 + e^{-\frac{\Delta H_i}{R \cdot T(t)} + \frac{\Delta S_i}{R}} / \beta)} \cdot \frac{d\phi}{dt} \quad (13)$$

By rearrangement of Eq. (13), the following equation is obtained:

$$\left(\frac{dt}{d\phi}\right)_i = \left(1 + e^{-\frac{\Delta H_i}{R \cdot T(t)} + \frac{\Delta S_i}{R} / \beta}\right) \frac{d\phi}{dt} = t_i^*(\phi, t) \quad (14)$$

where $t_i^*(\phi, t)$ is the calculated retention time of solute i as it moves through the whole column with its velocity at time t and position ϕ . As variables ϕ and t cannot be separated in Eq. (14), it cannot be transformed to an equation expressed with a simple definite integral as proposed by Curvers or Akporhonor. Thus, here we must apply an alternative mathematical method. We divide the range of ϕ into n segments which means that the column is divided into n segments and the relative distance of a segment h to whole column length is computed with $h=1/n$ for all solutes. In accordance with the Euler approximation method we can easily compute $t_{k,j}$ of solute i as the band moves through the k th segment of column using the following equation:

$$t_{k,j} = \sum_{j=0}^{k-1} t_i^*(\phi_j, t_{j,i}) \cdot \frac{1}{n} \quad (15)$$

where

$$\phi_j = j/n + 1/n \quad (k = 1, 2, \dots, n - 1),$$

which has been developed and applied by Nogare [12] and by Cavalli [13]. However, only when the relationship of $d\phi/dt$ with t and ϕ is established to give an unequivocal expression of $t_i^*(\phi, t)$, can the above calculation of retention time be performed.

It is impossible to obtain an exact functional solution of $p(\phi, t)$ from Eq. (5) directly. Even obtaining a numerical solution is also very difficult under temperature and/or inlet pressure programming conditions, but we are still able to deduce valuable conclusions on the basis of some assumptive and approximate operations.

Substituting Eq. (7) into Eq. (8) and then rewriting it as:

$$\begin{aligned} \frac{d\phi}{dt} = & -\sqrt{\frac{\Psi(T(t))}{2}} \cdot \left[\frac{\Psi(T(t))}{2} [p_o^2 - (p_i(t))^2] \right. \\ & \left. + \frac{\partial U(\phi, t)}{\partial t} - \frac{1}{T(t)} \frac{dT(t)}{dT} U(\phi, t) \right] / \\ & \left[\frac{\Psi(T(t))}{2} \{ [p_o^2 - (p_i(t))^2] \cdot \phi + (p_i(t))^2 \} \right. \\ & \left. + \frac{\partial V(\phi, t)}{\partial t} - \frac{1}{T(t)} \frac{dT(t)}{dT} V(\phi, t) \right]^{1/2} \quad (16) \end{aligned}$$

where

$$\begin{cases} U(\phi, t) = \int p(\phi, t) d\phi - \int_0^1 \left(\int p(\phi, t) d\phi \right) d\phi \\ V(\phi, t) = \int_0^\phi \left(\int p(\phi, t) d\phi \right) d\phi - \phi \cdot \int_0^1 \left(\int p(\phi, t) d\phi \right) d\phi \end{cases} \quad (17)$$

As the contributions of the items containing $U(\phi, t)$ and $V(\phi, t)$ in Eq. (16) are generally very small in comparison with the contribution of other items where the programming rates of pressure and temperature are not very high, Eq. (16) can be approximately processed as:

$$\frac{d\phi}{dt} \approx \frac{\Psi(T(t)) [(p_i(t))^2 - p_o^2]}{2 \cdot \sqrt{[p_o^2 - (p_i(t))^2] \cdot \phi + (p_i(t))^2}} \quad (18)$$

In Eq. (18), the pressure $p(\phi, t)$ is changed to $p^*(\phi, t)$:

$$p^*(\phi, t) = \sqrt{[p_i(t)]^2 - [(p_i(t))^2 - p_o^2] \phi} \quad (19)$$

Suppose that at any time t the distribution of pressure of carrier gas in the column is in equilibrium, Eq. (19) can also be obtained, and here the valid conditions of this assumption can be thus observed theoretically.

In fact, carrier gas cannot reach equilibrium at any given time but it can do so very quickly during temperature and/or inlet pressure programming. Therefore, we suggest a trial and error function as:

$$p(\phi, t) = p^*(\phi, t) + A(\phi, t) \cdot (\phi - \phi^2) \cdot t \quad (20)$$

Eq. (20) can always satisfy initial and regional conditions of the above partial differential. Therefore, when discussing $p(\phi, t)$ through Eq. (20) we need not consider limited conditions. Where linear programs are used, i.e.,

$$\begin{cases} p_i(t) = p_{i_o} + r_p \cdot t \\ T(t) = T_o + r_T \cdot t \end{cases} \quad (21)$$

combining Eq. (20) with Eq. (19) and Eq. (21) and then substituting Eq. (20) into Eq. (5) and ignoring those items containing $[A(\phi, t)]^2$ as well as differential of $A(\phi, t)$, we can approximately formulate a semi-empirical equation as:

$$A(\phi, t) = \frac{-(p_{io} + r_p \cdot t) \cdot r_p \cdot (1 - \phi) \cdot (p^*(\phi, t))^{-2} + r_T / T(t)}{(\phi - \phi^2) \cdot (p^*(\phi, t))^{-1} + 1.5 \cdot t \cdot (a + b \cdot T(t)) \cdot (p_{icp}^2 - p_0^2)^2 / (p_{icp}^3 - p_0^3)} \quad (22)$$

The second item in Eq. (20) conduces to a slight decrease of $p(\phi, t)$ parting from $p^*(\phi, t)$ during pressure programming, which is contrary to what occurs during temperature programming. That is intuitively reasonable. However, whether the approximation used is accurate enough to be accepted can be only examined through experimental results since it is very difficult to evaluate the validity of this approximation from mathematical theory for the above partial differential equation.

By the combination of Eq. (14) with Eq. (19), Eq. (20) and Eq. (22), $t_i^*(\phi, t)$ is thus obtained. Although $t_i^*(\phi, t)$ is rather complex in appearance, the calculation is very easily performed using a simple computer program. The linear programming modes are discussed above, but it can still be applied to multi-ramp modes assuming the carrier gas is in equilibrium at the moment when operating parameters in the program run are at their turning point. Certainly, if it was possible to establish a more accurate approximate function of $p(\phi, t)$, increasingly accurate predicted results may be obtained.

3. Experimental

Gas chromatographic experiments were carried out on HP 5890II gas chromatograph equipped with electron pressure control valve (EPC) and a flame ionization detector. HP 3365 Chemstation was used to record chromatograms. Detector and injector temperatures were maintained at 250°C. Helium was used as the carrier gas and column inlet pressure was kept constant at 20 or 25 psi unless operated in pressure programming mode. Retention times were determined at isothermal conditions (for OV-101 60°C, 100°C, 130°C, 160°C, and 200°C, respectively, and for Carbowax 20M with 10°C intervals from 70°C to 150°C, as well as 85°C). The related programs of temperature and pressure used in the following prediction of retention time are shown in Table 1. The zero value of EPC was carefully adjusted and the inlet pressure was also examined with a precise pressure gauge. The pressure of the carrier gas at the column outlet was set at 1 atm. Methane was used to determine the holdup time (t_M). Two fused silica capillary columns (30 m × 0.25 mm), which were separately coated with OV-101 and Carbowax 20M in this laboratory were used. All

Table 1
Programs for temperature and pressure used in the prediction of retention time

Symbol	Temperature program	Pressure program
OV-101		
OVA	50°C → 2°C min ⁻¹ → 250°C	25 psi
OVB	60°C → 3°C min ⁻¹ → 250°C	25 psi
OVC	60°C → 5°C min ⁻¹ → 250°C	25 psi
OVD	60°C → 8°C min ⁻¹ → 250°C	25 psi
OVE	60°C → 10°C min ⁻¹ → 250°C	25 psi
OVF	60°C → 15°C min ⁻¹ → 250°C	25 psi
OVG	50°C (3 min) → 5°C min ⁻¹ → 80°C (5 min) → 2°C min ⁻¹ → 100°C (8 min) → 10°C min ⁻¹ → 160°C	25 psi
Carbowax 20M		
CWA	70°C → 2°C min ⁻¹ → 180°C	20 psi
CWB	80°C → 3°C min ⁻¹ → 180°C	20 psi
CWC	80°C → 5°C min ⁻¹ → 180°C	20 psi
CWD	80°C → 8°C min ⁻¹ → 180°C	20 psi
CWE	80°C → 10°C min ⁻¹ → 180°C	20 psi
CFW	80°C → 15°C min ⁻¹ → 180°C	20 psi
CWG	100°C	20 psi → 1 psi min ⁻¹ → 80 psi
CWH	100°C	20 psi → 2 psi min ⁻¹ → 80 psi
CWI	80°C → 3°C min ⁻¹ → 180°C	20 psi → 2 psi min ⁻¹ → 80 psi
CWJ	80°C → 5°C min ⁻¹ → 180°C	20 psi → 2 psi min ⁻¹ → 80 psi
CWK	80°C → 3°C min ⁻¹ → 180°C	20 psi → 1 psi min ⁻¹ → 80 psi

solutes appearing in this paper were analytical reagent grade. The values of retention time are given as the mean values of three determinations and their relative standard deviations were less than 0.2%. Resolution was calculated from retention time and halfpeak width as given by HP 3365 Chemstation. The calculation programs were written in Qbasic and run with an HP Vectra 486/33VL computer.

4. Results and discussion

When the inlet pressure was kept constant (i.e. $r_p=0$, and $p_{io}=25$ psi for OV-101 column and 20 psi for Carbowax 20M column) and the column was controlled isothermally (i.e. $r_T=0$), the retention time of some solutes and the corresponding holdup time on these two column systems were determined. From these data we can compute the coefficients a and b in Eq. (11) and the apparent thermodynamic parameters in Eq. (2) using least square regression. Certainly, it is impossible and unnecessary to isolate the phase ratio and entropy factors from regression coefficients in this work. Some equations modified from Eq. (2) were proposed in order to correlate capacity factors k' and temperature T more accurately or conveniently [20,21]. Our experiments showed that Eq. (2) is accurate only when the temperature range is not very wide. In this paper we use Eq. (23) in place of Eq. (2) in order to eliminate error from Eq. (2).

$$\log k'_i(T) = \frac{Z}{T^2} + \frac{W}{T} + G \quad (23)$$

where Z , W , G are regression coefficients. All the regression calculation with Eq. (23) showed that the correlation coefficients were above 0.9999 for OV-101 and also for Carbowax 20M excepting those of 2-butanone and n -decane on the latter phase, which were 0.999. We do not discuss these results in detail here as they are only used for numerical calculation. In this paper p_{icp} is equal to p_{io} , but such conditions are not compulsory. No extra parameters were used to predict retention time, except those regression coefficients and parameters described in the experimental section.

4.1. Prediction of retention time in temperature programmed mode

For capillary gas chromatography, constant flow is almost impossible to be realized with a mechanical valve but it is possible with EPC (in fact, the constant flow carried out with EPC corresponds to using pressure programming), therefore, the operation of constant pressure is the most important aspect of TPCGC. When inlet pressure is kept constant during a chromatographic run (i.e., $r_p=0$) Eq. (19) as well as Eq. (22) are simplified. The experimental data of retention time for various solutes with different temperature programs (see Table 1) are given in Table 2 (on OV-101) and Table 3 (on Carbowax 20M). Based on the two approaches separately proposed by us (abbreviated as "OUR") and by Curvers (abbreviated as "CVR") these data were precalculated from the isothermal data. The corresponding relative errors ($E\%$) are listed in Table 4 and Table 5. Here $E\%$ was computed according to:

$$E\% = \frac{t_R(\text{exp.}) - t_R(\text{cal.})}{t_R(\text{exp.})} \times 100 \quad (24)$$

From Table 4 and Table 5, we can see that nearly the same accuracy with these two approaches were given, but the accuracy with "OUR" appears somewhat better. And for multi-ramp temperature program there is no special difference from single-ramp one and good accuracy for prediction of retention time was realized with our procedure applying approaches either by Akporhonor et al. [6] (abbreviated as "AKP" in Table 4 and Table 5) or by us.

In general, the values of almost all of the data from prediction are smaller than those from the experimental determination and the errors increase as the rate of temperature programming increases. For this phenomenon non-equilibria of temperature and pressure are probably the main reason. The larger the r_T value is the more obviously the problem appears. With "OUR" although the non-equilibrium of pressure distribution has been considered, the non-equilibrium of temperature still exists and it more seriously affects on the accuracy of prediction of retention time in TPCGC. By supposing $A(\phi, t)=0$ (Eq. (22)) the completely same results can be

Table 2
Experimental retention time (min) for temperature programming on OV-101

No.	Compound	OVA	OVB	OVC	OVD	OVE	OVF	OVG
1	<i>n</i> -Octane	7.33	5.40	4.88	4.35	4.09	3.63	7.46
2	<i>n</i> -Nonane	12.40	8.69	7.34	6.16	5.64	4.77	11.31
3	<i>n</i> -Decane	18.98	13.00	10.30	8.21	7.34	5.99	17.52
4	<i>n</i> -Undecane	26.27	17.81	13.42	10.28	9.04	7.17	24.94
5	<i>n</i> -Dodecane	33.65	22.74	16.53	12.30	10.69	8.31	34.33
6	<i>n</i> -Tridecane	40.85	27.57	19.56	14.24	12.26	9.39	38.45
7	<i>n</i> -Tetradecane	47.75	32.24	22.44	16.09	13.76	10.42	41.93
8	2-Hexanone	6.13	4.62	4.25	3.86	3.66	3.31	6.41
9	2-Heptanone	10.66	7.58	6.53	5.59	5.16	4.43	9.96
10	2-Octanone	16.89	11.65	9.39	7.60	6.84	5.64	15.43
11	2-Nonane	24.10	16.41	15.53	9.71	8.58	6.86	22.70
12	2-Decanone	31.58	21.40	15.70	11.78	10.28	8.03	31.90
13	Toluene	5.70	4.38	4.07	3.73	3.55	3.23	6.00
14	Ethylbenzene	9.55	6.93	6.08	5.28	4.91	4.26	9.16
15	Isopropylbenzene	13.06	9.23	7.76	6.50	5.94	5.02	11.90
16	Propylbenzene	14.88	10.43	8.61	7.09	6.44	5.38	13.52
17	1,2,4-Trimethylbenzene	17.60	12.25	9.84	7.95	7.16	5.89	16.19
18	<i>sec</i> -Butylbenzene	18.76	13.00	10.37	8.31	7.45	6.10	17.35

Table 3
Experimental retention time (min) for temperature programming on Carbowax 20M

No.	Compound	CWA	CWB	CWC	CWD	CWE	CFW
1	<i>n</i> -Decane	5.50	4.42	4.18	3.90	3.75	3.48
2	<i>n</i> -Undecane	8.41	6.38	5.78	5.16	4.87	4.35
3	<i>n</i> -Dodecane	12.62	9.16	7.89	6.72	6.21	5.34
4	<i>n</i> -Tridecane	17.93	12.66	10.36	8.46	7.66	6.39
5	<i>n</i> -Tetradecane	23.99	16.68	13.05	10.27	9.16	7.49
6	<i>n</i> -Pentadecane	30.36	20.93	15.80	12.09	10.67	8.76
7	<i>n</i> -Hexadecane	36.71	25.19	18.49	13.95	12.39	10.33
8	2-Butanone	4.08	3.28	3.18	3.06	2.99	2.86
9	2-Pentanone	5.20	4.25	4.03	3.78	3.65	3.41
10	2-Hexanone	8.04	6.18	5.63	5.06	4.79	4.30
11	2,6-Dimethyl-4-heptanone	11.73	8.65	7.52	6.48	6.01	5.21
12	2-Heptanone	12.17	8.94	7.74	6.64	6.15	5.31
13	2-Nonanone	23.70	16.59	13.03	10.30	9.21	7.55
14	2-Decanone	30.27	20.98	15.87	12.19	10.79	8.89
15	2-Undecanone	36.90	25.44	18.69	14.17	12.63	10.57
16	1-Propanol	6.27	4.89	4.55	4.18	4.00	3.66
17	1-Butanol	9.87	7.28	6.45	5.65	5.27	4.63
18	1-Pentanol	14.92	10.61	8.88	7.40	6.76	5.73
19	1-Hexanol	20.84	14.53	11.55	9.24	8.30	6.82
20	2-Octanol	24.91	17.20	13.31	10.40	9.27	7.53
21	Cyclohexanol	24.03	16.81	13.16	10.40	9.27	7.61
22	1-Heptanol	27.22	18.78	14.34	11.11	9.83	8.01
23	1-Octanol	33.75	23.15	17.13	12.95	11.45	9.43
24	Di(<i>iso</i> -pentyl)ether	7.29	5.66	5.20	4.72	4.48	4.05
25	Ethylbenzene	10.11	7.66	6.81	5.99	5.60	4.94
26	Dipentyl ether	11.09	8.18	7.15	6.20	5.75	5.01
27	Methyl hexanoate	12.38	9.05	7.80	6.67	6.16	5.32
28	Cholorbenzene	14.15	10.38	8.85	7.49	6.88	5.89
29	Anisol	21.17	15.02	12.04	9.69	8.71	7.21

Table 4

Comparison of errors (%) from the prediction of retention time for temperature programming on OV-101 with these approaches proposed in [2] and [6]

No.	OVA		OVB		OVC		OVD		OVE		OVF		OVG	
	OUR	CVR	OUR	CVR	OUR	CVR	OUR	CVR	OUR	CVR	OUR	CVR	OUR	APK
1	0.03	0.11	0.65	0.74	0.94	1.13	1.40	1.65	1.52	1.83	1.96	2.40	0.39	0.38
2	0.36	0.43	0.83	0.92	1.01	1.16	1.41	1.62	1.56	1.83	1.95	2.33	0.63	0.74
3	0.86	0.91	1.35	1.43	1.25	1.38	1.61	1.79	1.74	1.97	2.07	2.42	0.91	0.99
4	0.56	0.60	0.97	1.03	0.92	1.02	1.25	1.41	1.40	1.60	1.77	2.06	0.68	0.66
5	0.07	0.11	0.52	0.58	0.62	0.71	1.02	1.15	1.19	1.36	1.60	1.85	0.17	0.19
6	0.29	0.33	0.65	0.69	0.83	0.91	1.05	1.17	1.21	1.36	1.62	1.85	0.59	0.45
7	0.19	0.28	0.60	0.64	0.82	0.89	1.01	1.12	1.18	1.32	1.59	1.81	0.64	0.70
8	-0.41	-0.33	0.43	0.54	0.61	0.78	1.17	1.42	1.36	1.69	1.82	2.27	-0.22	-0.28
9	-0.06	0.01	0.73	0.83	0.70	0.86	1.27	1.50	1.51	1.78	1.90	2.31	0.33	0.40
10	0.27	0.33	0.90	0.99	0.77	0.90	1.26	1.45	1.49	1.72	1.84	2.20	0.27	0.34
11	0.34	0.39	0.82	0.88	0.68	0.79	1.09	1.26	1.26	1.47	1.66	1.97	0.27	0.37
12	-0.33	-0.29	0.32	0.28	0.43	0.52	0.94	1.08	1.16	1.33	1.59	1.87	-0.75	-0.73
13	-0.56	-0.49	0.27	0.37	0.59	0.76	1.07	1.34	1.27	1.58	1.70	2.20	-0.42	-0.48
14	-0.48	-0.21	0.55	0.66	0.71	0.87	1.27	1.51	1.49	1.77	1.90	2.32	0.23	0.25
15	-0.03	0.04	0.71	0.81	0.81	0.95	1.31	1.52	1.52	1.78	1.93	2.31	0.72	0.36
16	0.03	0.09	0.75	0.83	0.80	0.84	1.30	1.49	1.49	1.76	1.90	2.27	0.14	0.27
17	-0.01	0.05	0.85	0.93	0.67	0.80	1.23	1.42	1.47	1.70	1.87	2.21	-0.03	0.06
18	0.17	0.20	0.82	0.89	0.79	0.91	1.26	1.44	1.44	1.68	1.85	2.20	0.13	0.25

obtained with those approaches used in this paper, which means that the effect of non-equilibrium of carrier gas during temperature programming on retention time could be corrected with our approach to some extent.

In addition, although retention mechanism changes as temperature varies, which stems from the change of adsorption on gas-liquid surface, but in fact we did not observe a poor accuracy of prediction of retention time for *n*-alkanes on polar stationary liquid column by comparison of Table 5 with Table 4 and of *n*-alkanes with others in Table 5. We note that here the stationary liquid film is rather thick and adsorption may be insignificant.

4.2. Prediction of retention time in pressure programmed mode

Although pressure program almost improbably improves resolution, it can be used to reduce analysis time with the same resolution. As the carrier gas pressure at different position in column is very different, we cannot accurately precalculate retention time from the data at different constant pressure by following the example of temperature programming. Nevertheless, with “OUR” we can precalculate

retention time at pressure program from retention time under a condition of constant pressure, but here we still utilize *a*, *b* and thermodynamic parameters used in part 4.1. The results of prediction for two pressure programs (see Table 1) are shown in Table 6. Even though rather accurate results are displayed in Table 6 there is still small systematic error. In order to observe this systematic error clearly *E*% was plotted against retention time (shown in Fig. 1). From Fig. 1 we can observe that the longer retention time (t_R) is, the larger relative error (*E*%) will be and most of the $t_R(\text{cal.})$ are smaller than the $t_R(\text{exp.})$.

Sometimes, the retention time in pressure program needs to be transformed to one at constant pressure so that the structural information of related chromatographic peaks can be familiarly obtained from retention value, e.g., $t_R(T)$ at inlet pressure p_{icp} and corresponding temperature *T*, is calculated from:

$$\left(\frac{dt}{d\phi}\right)_i = -\frac{3t_R(T)(p_{\text{icp}}^2 - p_o^2)}{4(p_{\text{icp}}^3 - p_o^3)} \bigg/ \frac{\partial p(\phi, t)}{\partial \phi} \quad (25)$$

An iterative equation was developed as

$$[t_R(T)]_{m+1} = [t_R(T)]_m + t_R(\text{exp.}) - [t_R(\text{cal.})]_m \quad (26)$$

where $t_R(\text{exp.})$ is the experimental value of retention

Table 5

Comparison of errors (%) from prediction of retention time for temperature programming on Carbowax 20M with approaches by us and by Curvers

No.	CWA		CWB		CWC		CWD		CWE		CWF	
	OUR	CVR	OUR	CVR	OUR	CVR	OUR	CVR	OUR	CVR	OUR	CVR
1	1.18	1.25	0.23	0.34	0.60	0.81	0.92	1.26	1.15	1.52	1.58	2.16
2	0.97	1.06	0.34	0.47	0.78	0.97	1.12	1.43	1.38	1.75	1.86	2.54
3	0.78	0.86	0.44	0.56	0.94	1.10	1.32	1.59	1.60	1.92	2.10	2.58
4	0.61	0.68	0.47	0.57	0.98	1.14	1.38	1.62	1.66	1.95	2.21	2.63
5	0.51	0.59	0.52	0.81	1.05	1.19	1.43	1.64	1.70	1.95	2.28	2.83
6	0.48	0.53	0.55	0.64	1.11	1.23	1.48	1.65	1.78	2.06	2.21	2.88
7	0.47	0.51	0.59	0.66	1.11	1.22	1.51	1.76	1.69	2.08	2.04	2.70
8	1.04	1.14	-0.34	-0.18	-0.19	0.00	0.03	0.36	0.23	0.63	0.63	1.22
9	1.42	1.52	0.40	0.54	0.57	0.77	0.82	1.14	1.01	1.42	1.44	2.02
10	1.12	1.22	0.53	0.66	0.73	0.94	1.09	1.38	1.34	1.71	1.86	2.40
11	0.88	0.96	0.58	0.69	0.85	1.02	1.25	1.51	1.53	1.86	2.07	2.57
12	0.89	0.97	0.62	0.73	0.87	1.05	1.27	1.54	1.55	1.89	2.09	2.58
13	0.55	0.61	0.63	0.71	0.94	1.07	1.39	1.59	1.68	1.94	2.25	2.82
14	0.49	0.54	0.64	0.72	0.96	1.08	1.44	1.62	1.77	2.07	2.14	2.80
15	0.47	0.51	0.67	0.74	1.02	1.12	1.50	1.77	1.71	2.12	2.02	2.69
16	1.28	1.37	0.53	1.67	0.79	0.99	1.12	1.43	1.30	1.68	1.78	2.32
17	0.89	0.97	0.60	0.71	0.90	1.09	1.35	1.63	1.57	1.88	2.07	2.59
18	0.66	0.73	0.62	0.73	0.95	1.10	1.42	1.66	1.64	1.94	2.22	2.67
19	0.50	0.56	0.67	0.76	0.95	1.09	1.44	1.67	1.70	1.98	2.29	2.70
20	0.45	0.50	0.64	0.72	1.00	1.13	1.37	1.57	1.94	2.19	2.30	2.84
21	0.44	0.49	0.64	0.73	0.93	1.06	1.45	1.65	1.63	1.89	2.23	2.81
22	0.43	0.48	0.64	0.72	0.96	1.08	1.46	1.65	1.74	1.97	2.25	2.86
23	0.39	0.43	0.64	0.71	0.97	1.10	1.51	1.70	1.80	2.13	2.11	2.75
24	1.11	1.19	0.64	0.76	0.81	1.00	1.19	1.48	1.36	1.72	1.85	2.39
25	0.88	0.96	0.61	0.73	0.81	1.00	1.25	1.54	1.43	1.79	2.01	2.51
26	0.84	0.92	0.70	0.71	0.89	1.08	1.36	1.63	1.53	1.86	2.09	2.57
27	0.79	0.86	0.66	0.77	0.91	1.09	1.38	1.65	1.59	1.91	2.18	2.65
28	0.69	0.76	0.61	0.72	0.88	1.05	1.34	1.59	1.55	1.87	2.12	2.60
29	0.49	0.55	0.61	0.70	0.91	1.05	1.40	1.63	1.65	1.93	2.25	2.76

time in PPCGC, $[t_R(\text{cal.})]_m$ is the corresponding calculated value using the above approach when $t_R(T)$ is taken instead of $[t_R(T)]_m$ in Eq. (25). If $t_R(\text{exp.})$ is used as initial value of $[t_R(T)]_m$ and the calculation is circulated from Eq. (25), Eq. (15) to Eq. (26) the final results of $t_R(T)$ can be obtained. The predicted results at 100°C and 20 psi separately calculated from operating programs of CWG and CWH in Table 1 are listed in Table 7. The errors ($E\%$) of almost all of the compounds except several n -alkanes are less than 1%, which proves that our procedure to be accurate and useful.

4.3. Prediction of the retention times under both temperature and pressure programmed conditions

With the approach proposed in this paper, it is also

easy to predict retention values under both temperature and pressure program conditions. Some predicted results are listed in Table 8. The relative error $E\%$ is about 1.5%, and we think that this is acceptable for the prediction of separation.

4.4. Trajectory of solute band moving in column

Sometimes, chromatographers are interested not only in predicting retention time but also in understanding the behaviour of solute band moving in column so as to optimize separation system as well as to simulate chromatographic process. According to the approach suggested by Nogare [12] and Cavalli [13] simulated computation can be achieved. Here we describe the trajectory of solute band when the gradient of pressure in column is considered

Table 6

Prediction of retention time for inlet pressure programming and isothermal operations on Carbowax 20M with our approach

No.	CWG		CWH	
	$t_R(\text{exp.})$	$E\%$	$t_R(\text{exp.})$	$E\%$
1	3.31	-0.17	3.10	-0.05
2	4.58	-0.14	4.22	0.07
3	6.69	0.00	6.02	0.32
4	10.07	0.25	8.81	0.64
5	15.29	0.44	13.00	0.92
6	23.08	0.66	19.05	1.17
7	34.21	0.98	27.48	1.39
8	2.63	-0.56	2.49	-0.51
9	3.22	-0.11	3.02	-0.02
10	4.47	-0.01	4.12	0.17
11	6.30	0.16	5.69	0.40
12	6.54	0.18	5.89	0.44
13	15.05	0.69	12.79	1.03
14	22.82	0.97	18.82	1.31
15	34.07	1.24	27.34	1.54
16	3.56	-0.13	3.32	-0.05
17	5.18	0.10	4.73	0.27
18	7.96	0.36	7.08	0.62
19	12.35	0.73	10.65	1.01
20	16.34	0.91	13.80	1.22
21	15.43	0.91	13.08	1.18
22	19.06	1.03	15.92	1.34
23	28.97	1.30	23.50	1.60
24	4.10	-0.09	3.79	0.11
25	5.58	0.07	5.08	0.33
26	5.90	0.14	5.35	0.39
27	6.60	0.18	5.95	0.47
28	7.82	0.31	6.96	0.62
29	12.81	0.62	11.01	0.99

Table 7

Prediction of retention time for constant pressure from data at pressure programmed and isothermal operations on Carbowax 20M

No.	$t_R(T_o)$	$E\%$ (CWG)	$E\%$ (CWH)
1	3.59	-0.16	-0.24
2	5.12	-0.19	0.44
3	7.81	-0.34	-0.72
4	12.53	-0.61	-1.14
5	20.86	-0.92	-1.63
6	35.46	-1.32	-2.14
7	60.71	-1.85	-2.60
8	2.81	-0.31	-0.35
9	3.48	-0.33	-0.45
10	4.97	-0.43	-0.65
11	7.27	-0.60	0.26
12	7.57	-0.64	0.20
13	20.37	-1.26	-0.68
14	34.80	-1.67	-1.26
15	60.19	-2.13	-1.87
16	3.87	-0.35	0.67
17	5.83	-0.56	0.38
18	9.49	-0.82	0.00
19	15.94	-1.25	-0.54
20	22.56	-1.49	-0.92
21	20.96	-1.52	-0.87
22	27.45	-1.69	-1.17
23	47.93	-2.17	-1.83
24	4.51	-0.46	0.47
25	6.33	-0.61	0.25
26	6.75	-0.63	0.22
27	7.66	-0.70	0.12
28	9.29	-0.82	-0.04
29	16.67	-1.20	-0.61

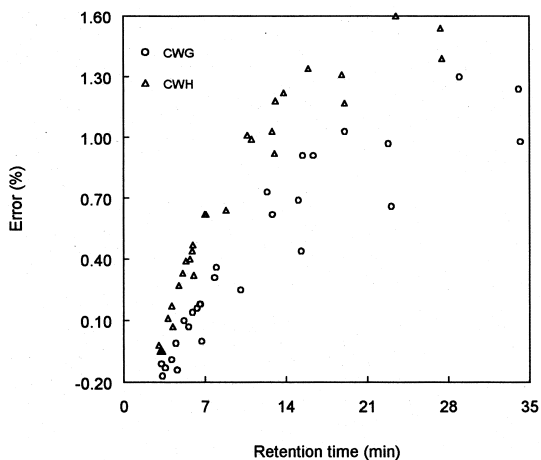


Fig. 1. The relationship of $E\%$ in PPCGC with retention time.

during temperature and/or pressure programming. With such a numerical procedure the trajectory of solute band moving in column can be easily acquired while retention time is re-calculated. As an example, Fig. 2 describes the relation between position and the time taken for required solutes (listed in Table 2) to get to that position during multi-ramp temperature programming. According to Fig. 2 for the solute strongly retained, the time on the initial column segments mainly contributes to the total retention time but only very slightly contributes to resolution. Therefore, the longer the retention time is, the less the resolution is improved through reduction of initial column temperature.

With our approach, resolution can be predicted from the trajectory of the moving solute band. The effect of operating parameters and the properties of

Table 8

Prediction of retention time for temperature and inlet pressure programming on Carbowax 20M with our approach

No.	CWI		CWJ		CWK	
	$t_R(\text{exp.})$	$E\%$	$t_R(\text{exp.})$	$E\%$	$t_R(\text{exp.})$	$E\%$
1	3.77	0.87	3.60	1.05	4.05	0.69
2	5.24	1.14	4.84	1.32	5.70	0.86
3	7.24	1.37	6.44	1.48	7.97	1.02
4	9.70	1.46	8.29	1.57	10.76	1.09
5	12.51	1.49	10.30	1.58	13.93	1.13
6	15.53	1.50	12.37	1.58	17.29	1.15
7	18.61	1.45	14.46	1.58	20.68	1.12
8	2.88	0.21	2.81	0.32	3.06	0.07
9	3.64	0.99	3.49	1.06	3.90	0.80
10	5.09	1.22	4.73	1.38	5.53	0.96
11	6.86	1.37	6.16	1.51	7.54	1.07
12	7.06	1.39	6.32	1.55	7.78	1.11
13	12.40	1.45	10.27	1.65	13.83	1.18
14	15.49	1.43	12.42	1.64	17.28	1.20
15	18.68	1.39	14.58	1.64	20.81	1.12
16	4.14	1.16	3.90	1.33	4.45	0.97
17	5.90	1.36	5.36	1.53	6.45	1.09
18	8.27	1.47	7.20	1.62	9.14	1.18
19	11.02	1.52	9.22	1.67	12.25	1.22
21	12.56	1.50	10.38	1.66	14.01	1.22
22	14.03	1.50	11.33	1.65	15.62	1.24
23	17.17	1.47	13.47	1.63	19.09	1.21
24	4.70	1.19	4.40	1.34	5.09	0.96
25	6.15	1.32	5.61	1.44	6.74	1.05
26	6.53	1.38	5.89	1.55	7.17	1.10
27	7.15	1.41	6.37	1.55	7.87	1.13
28	8.06	1.43	7.12	1.56	8.92	1.13
29	11.27	1.47	9.51	1.63	12.56	1.19

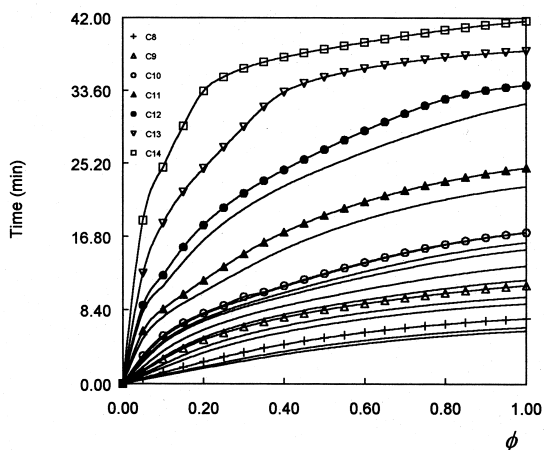


Fig. 2. Moving trajectory of solutes on OV 101 for column temperature programming with OVG.

solutes on column efficiency is ignored. In other words, the regional widths of solute band at the column outlet are regarded as the same for different solutes under differing operating conditions. The resolution is commonly computed with:

$$R_s = \frac{t_R(2) - t_R(1)}{\Delta W_{\frac{1}{2}}(2) + \Delta W_{\frac{1}{2}}(1)} \quad (27)$$

where $t_R(i)$ and $\Delta W_{\frac{1}{2}}(i)$ are the retention time and the half peak width for solute i in minutes, respectively. When R_s is computed from the solute moving trajectory, Eq. (28) is applied instead of Eq. (27):

$$R_s = \frac{0.319(p_{i0}^2 - p_o^2) \cdot p_o}{p_{i0}^3 - p_o^3} \cdot N^{\frac{1}{2}} \cdot (1 - \phi_2) \quad (28)$$

where N is the number of theoretical plates for the column, p_{i0} and p_o are pressure values of inlet and

outlet respectively when N is determined, and ϕ_2 is the position for solute 2 in the column as solute 1 just arrives at the outlet of the column. By using Eq. (28) and the method described above, the prediction of resolution is not difficult for any program of temperature and inlet pressure. Some resolution values for three solute pairs under different operating programs (see Table 1) were precalculated with Eq. (28) and are shown in Table 9. Here the column efficiency was 90 000 theoretical plates in total, tested with 1-heptanol at 100°C and 20 psi for p_{io} . These data show that our formula suggested to precalculate resolution from solute movement in a column for temperature-programmed CGC is reasonable. Obviously, it could not be applied, however, for operating parameter programs containing pressure programming as pressure strongly affects the column efficiency N . In addition, N is slightly concerned with the k' value, especially when k' is small. A more accurate precalculation of resolution may be performed if the effect of k' value on N is considered.

The solute band moves forward to the outlet of the column a little more slowly in the head of the column, when a correction for the effect of non-equilibrium of pressure distribution in TPCGC on retention time is made, more so than when the correction is not made and the reverse is true in the outlet part of the column. However, with pressure programming the situation is in contrast with that

found in TPCGC. We also noted that the difference between velocities of correcting pressure distribution in TPCGC and those obtained without correction was not very obvious for the strongly retained solute. The phenomena observed in calculations using our approach are easily intuitively understood, and we shall not illustrate them in detail here.

In a word, our procedure is more convenient and accurate for predicting retention times in OPPCGC. At the same time, the resolution in temperature-programmed CGC can be predicted from solute band moving trajectory in the column, column efficiency and other related parameters.

5. Conclusion

A novel approach has been established to predict retention time in operating parameter programmed gas-liquid chromatography with capillary columns by using numerical calculation, which can be applied to multi-ramp programs including column temperature and/or inlet pressure of carrier gas. Using this procedure the resolution is easily and accurately predicted from solute movement in column temperature-programmed CGC. However, it cannot be applied to pressure-programmed CGC because column efficiency is seriously affected by the velocity of carrier gas.

Table 9
Prediction of resolution from the trajectory of the solute band moving in the column on Carbowax 20M

Symbol	A			B			C		
	R_s (exp.)	R_s (cal.)	E%	R_s (exp.)	R_s (cal.)	E%	R_s (exp.)	R_s (cal.)	E%
CWA	2.72	2.87	-6	4.51	4.25	6	6.49	6.31	3
CWB	2.44	2.58	-6	2.71	2.62	3	4.66	4.59	2
CWC	2.30	2.40	-4	1.42	1.36	4	3.79	3.77	1
CWD	2.16	2.19	-1		0.11		2.81	2.83	-1
CWE	2.01	2.08	-3		0.43		2.30	2.33	-1
CWF	1.85	1.83	1	1.23	1.22	1	1.43	1.44	-1
CWG	2.33	2.62	-12	4.02	4.63	-15	3.38	3.73	-10
CWH	2.13	2.76	-30	3.66	4.95	-35	3.21	3.88	-21
CWI	2.22	3.09	-39	1.98	2.87	-45	4.46	5.42	-22
CWJ	2.14	2.87	-34	3.09	4.41	-43	3.70	4.56	-23
CWK	2.33	2.87	-23	3.04	3.73	-23	4.56	4.95	-9

Note A: 2,6-dimethyl-4-heptanone/2-heptanone; B: 2-octanol/cyclohexanol; C: ethylbenzene/di(pentyl)ether.

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