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Prediction of retention times in temperature-programmed multichromatography

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ABSTRACT

The calculation of retention times for temperature-programmed serially linked capillary gas chromatography columns is demonstrated. Equations are derived for the verification of operating conditions via two internal standards and for the precise calculation of the mid-point pressure required to obtain a given relative retentivity. The predicted retention times for 23 volatile organic compounds are compared to experimental results.

INTRODUCTION

In environment studies and other applications where the entire chromatogram is of interest there are several techniques to enhance gas chromatographic (GC) analyses beyond single-column isothermal operation. Among these, temperature programming has the advantage of decreasing the analysis time required for samples with a diverse range of compounds, while providing improved resolution for later-eluting compounds [1]. However, alteration of elution order is possible during temperature-programmed GC [2].

The prediction of GC retention as a function of temperature has taken two different approaches, one using thermodynamic parameters, and the other using retention indices. Both methods attempt to transport component retention data bases for a given stationary phase at isothermal temperatures into a temperature-programmed environment. A method for converting thermodynamic parameters to retention indices has been reported by Curvers *et al.* [3,4].

Harris and Habgood's summary [1] of their own work and that of others in the field of temperature-programmed gas chromatography includes derivations of the general equations for predicting temperature-programmed retention times from isothermally obtained thermodynamic parameters. Recent applications of the thermodynamic approach include the work of Dose [5] and Akporhonor *et al.* [6,7].

Another GC enhancement technique, mixed stationary phases, has been used to gain greater control of selectivity. Using selectivity-tuned serially coupled capillary columns, or multichromatography, there is no need for application-specific custom

blends of phases, nor do expensive columns have to be cut to achieve a desired phase ratio. Instead, fixed-length columns of different polarity are used, and the residence time in each column is adjusted by flow control. This permits rapid changes in experimental conditions during method development and use of the same column setup for diverse applications. Hinshaw and Ettre [8] have extensively reviewed multichromatography applications and theory.

Combining multichromatography with temperature programming holds the promise of simple changes in selectivity in conjunction with decreased analysis time. However, the number of variables present in this combination of techniques precludes effective optimization by experiment. The optimization of isothermal temperatures for serial columns in dual-oven chromatographs has been considered by several groups. Kaiser *et al.* [9] independently changed the temperature or flow in tandem capillary columns, and compared the resulting changes in selectivity. Mayfield and Chester [10] attempted to calculate optimum conditions for sequentially coupled columns with independent temperature control. Hinshaw and Ettre [11] did demonstrate the use of temperature programming to alter the selectivity of serial columns in a single oven, but did not attempt to predict retention times.

The object of this study was to demonstrate the prediction of gas chromatographic retention times using temperature-programmed multi-chromatography in commercially available, minimally modified, single-oven instruments. The thermodynamic approach to calculating retention times under temperature-programmed conditions was used in this project. Since both instruments used in the study control column flow by pressure regulation, the condition of constant inlet and outlet pressures fixed the form of the equation used to calculate temperature-programmed retention times. Only linear programs initiated upon injection were considered. In view of the observation that multi-step temperature programs can frequently be replaced by a single linear program [12] this does not seem overly restrictive.

EXPERIMENTAL

Chromatograms were obtained on Hewlett-Packard 5890 and Perkin-Elmer 8500 gas chromatographs. Instrumental differences in the experimental data were not significant. Both instruments used helium carrier gas and were equipped with dual injectors and a photoionization detector. For serial column operation the first column was joined to the second column with a low-dead-volume tee connector (Valco). The second injector, operated in split-injection mode to allow either addition or removal of carrier and regulate the mid-point pressure, was also connected to the tee.

Column head pressures were taken from the instrument injector gauges. Atmospheric pressure was determined with an aneroid barometer and used to correct gauge pressures to absolute pressure.

Compound mixtures were prepared as vapor phase static dilution bottles, 2 l, containing 6 μ l of liquid of each compound in the mixture [13].

Columns used were 30 m \times 0.32 mm I.D. fused-silica capillaries with 1.0 μ m bonded liquid-phase coatings of either cyanopropyl, phenyl, dimethylpolysiloxane (DB-624, proprietary phase ratio, J&W) or methylsilicone (DB-1, J&W).

Injections were performed in splitless mode using reagent-bottle headspace for individual compounds and static-dilution bottles for compound mixtures.

Column holdup time and flow measurements were taken at four or more temperatures separated by 20°C, 40–100°C for the DB-1 column, and 40–120°C for the DB-624 column. Holdup times were determined by the method of Grobler and Balizs [14] using a sequential mixture of normal alkanes, hexane through decane. The column dead volume at oven temperature was calculated for each temperature, and since the values should be indistinguishable over the temperature range investigated [1], the results were averaged.

PC-XT and PS-2/60 microcomputers were used for computations. The program used to calculate temperature-programmed retention times was written in FORTH with floating point arithmetic (Laboratory Microsystems, PC/FORTH 3.2). This program and supporting documentation will be uploaded to the Laboratory Microsystems and U.S. Environmental Protection Agency bulletin boards. All other calculations were performed with a spreadsheet program (Lotus Development).

RESULTS AND DISCUSSION

In this work several assumptions have been made, chief being that the column outlet at the detector is at atmospheric pressure and that there is no significant time lag between the oven temperature and column temperature. Experimentally, the study was restricted to columns of equal length, radii and phase thickness; the latter by chance. However, the approach should be valid for capillary columns of differing dimensions. A list of symbols used is given at the end of this article.

The mean flow in a capillary column is a function of column dimensions, pressure gradient across the column and carrier viscosity [1]:

$$F_T = j\pi r^4 (P_i^2 - P_o^2) / (16L\eta P_o) \quad (1)$$

where j , the pressure-gradient correction factor, is [15]:

$$j = \frac{3}{2} P_o (P_i^2 - P_o^2) / (P_i^3 - P_o^3) \quad (2)$$

Several expressions and approximations have been used to describe the relation between temperature and viscosity, η . In this work

$$\eta \propto T^{2/3} \quad (3)$$

has been used. The choice of 2/3 is a compromise between values used by others, *i.e.*, 0.647 [16], 0.6567 [17] and the commonly used 0.7 [1].

Combining eqns. 1 and 3, with consideration of thermal expansion, affords the expression-relating flows in a column under the same pressure conditions but at two different temperatures:

$$F_{T_1} = F_{T_2} (T_2/T_1)^{5/3} \quad (4)$$

Using the thermodynamic approach, the net retention volume of a compound on a column under isothermal conditions is given by the expression:

$$V_R^o - V_M^o = A e^{AH/RT} \quad (5)$$

The general equation for a single column with a linear temperature program in a pressure-controlled system, *i.e.*, with P_i and P_o constant, is [1]:

$$\frac{s}{F_{T_0}} = \int_{T_0}^{T_e} \frac{T_0^{5/3} dT}{T^{5/3} (Ae^{\Delta H/RT} + 273 V_M^{\circ T}/T)} \quad (6)$$

If F_{T_0} is replaced by F_{273} then:

$$\frac{s}{F_{273} \cdot 273^{5/3}} = \int_{T_0}^{T_e} \frac{dT}{T^{5/3} (Ae^{\Delta H/RT} + 273 V_M^{\circ T}/T)} \quad (7)$$

For a linear temperature program starting at the time of injection with an initial column temperature T_0 , the solution of eqn. 7 for T_e by numerical integration provides, via the program rate s , the elution time of a compound. To solve for the retention of a given compound, the required parameters are the holdup volume, the mean flow for the column and the thermodynamic parameters A and ΔH for the compound on that column. Eqns. 5 and 7 establish the basis for the calculation of retention times under either isothermal or linear temperature-programmed conditions.

Isothermal retention times at at least four temperatures were collected for a group of 23 compounds on two different capillary columns. These data form the basis data sets for each column. Column-dependent thermodynamic parameters were obtained for each compound by least-squares fit of the respective basis data sets to the logarithmic form of eqn. 5. The results are presented in Table I.

Correlation coefficients for the DB-1 column were generally better than 0.9994. Exceptions were the three earliest-eluting compounds and 1,4-dimethylbenzene, although their correlation coefficients were better than 0.996. When the parameters were used to calculate isothermal retention times for the four basis data sets the worst case provided an average absolute relative difference, $|t_{\text{calc}} - t_{\text{obs}}|/t_{\text{obs}}$, of 2.3%. For the worst case the greatest relative difference was 3.8% and the range was 7.1%. Best case values were 0.7, 4.5 and 5.2%, respectively.

For the DB-624 column all correlation coefficients were 0.9999. The isothermal worst-case absolute relative differences average was 2.2%, with a 3.0% maximum and a range of 2.2%. Corresponding best-case values were 0.3, 0.7 and 1.3%.

For both the DB-1 and DB-624 data sets at any given isothermal condition there was a trend in the deviations from early-eluting to late-eluting compounds; however, the direction of the trend varied non-systematically with temperature.

When the DB-624 parameters were utilized to predict single-column temperature-programmed retention times via eqn. 7 for five different starting-temperature and temperature-program rate combinations the worst-case values were average 2.9%, maximum 4.6%, and range 6.9%. When analyzed in the same manner, the data reported by Dose [5] gave values of 0.5, 0.8 and 0.8%. Much of the larger error in the current work can be attributed to (1) the use of some retention times less than $3 t_M$ in the basis sets, which unfavorably emphasized the effects of holdup time, and (2) the reporting of retention times for each component in an unresolved peak in the test

TABLE I
THERMODYNAMIC PARAMETERS

Compound	Front column		Back column	
	ln <i>A</i>	ΔH	ln <i>A</i>	ΔH
Benzene	-13.151	9011	- 9.751	7581
1,4-Dioxane	-12.952	9109	-10.390	8280
Methylbenzene	-12.264	9070	-10.466	8604
Tetrachloroethene	-11.967	9135	-10.516	8804
Chlorobenzene	-11.947	9282	-10.730	9218
Ethylbenzene	-12.272	9601	-11.105	9517
1,3-Dimethylbenzene	-12.239	9623	-11.185	9614
1,4-Dimethylbenzene	-12.264	9689	-11.189	9617
Ethenylbenzene	-12.295	9758	-11.311	9838
1,2-Dimethylbenzene	-12.203	9724	-11.216	9767
Benzaldehyde	-12.300	10 048	-11.753	10 612
1-Chloro-4-methylbenzene	-12.298	10 106	-11.570	10 349
1-Chloro-3-methylbenzene	-12.275	10 071	-11.479	10 270
1-Chloro-2-methylbenzene	-12.225	10 030	-11.396	10 188
Benzonitrile	-12.438	10 229	-12.001	10 962
1,3,5-Trimethylbenzene	-12.669	10 443	-11.897	10 597
1,3-Dichlorobenzene	-12.385	10 398	-11.665	10 646
1,4-Dichlorobenzene	-12.451	10 466	-11.777	10 762
1,2-Dichlorobenzene	-12.397	10 535	-11.782	10 895
1-Fluoro-2-iodobenzene	-12.426	10 625	-11.831	11 035
1-Phenylethanone	-12.855	10 958	-12.546	11 702
Butylbenzene	-13.080	11 168	-12.424	11 394
Stationary phase	DB-1		DB-624	
Nominal dimensions	30 m × 0.32 mm I.D.		30 m × 0.32 mm I.D.	
Stationary phase	0.25 μm DB-1		0.25 μm DB-624	
Measured holdup volume	2.25 ml		2.25 ml	

mixture as the time of the combined peak. Higher-accuracy pressure gauges, precision controllers and careful editing of the basic sets can obviously improve agreement.

For serially coupled columns, the relative retentivity, ϕ , has been defined [18] as the ratio of the holdup time for a specified column to the holdup time for the system of combined serial columns. Thus, for the back column in a two-column system:

$$\phi_B = t_{MB}/(t_{MF} + t_{MB}) \quad (8)$$

The holdup time of a column is related to column geometry and carrier flow:

$$t_M = V_M^{\circ T}/F_T \quad (9)$$

Substitution in eqn. 8 for the holdup time affords the following:

$$\phi_B = F_{FT} V_{MB}^{\circ T}/(F_{FT} V_{MB}^{\circ T} + F_{BT} V_{MF}^{\circ T}) \quad (10)$$

Considering only pressure-regulated, single-oven systems, upon substituting the temperature-flow relation from eqn. 4 into the above equation for ϕ_B it becomes obvious that ϕ_B is essentially independent of temperature for isothermal multichromatography. Thus, as long as the pressures remain constant, ϕ_B determined at one isothermal temperature is valid at any other isothermal temperature, and may be used to specify the operating conditions of a temperature-programmed multichromatography system.

If a desirable relative retentivity is calculated for a given experiment then the instrument must be set to this state. There are several ways to determine either ϕ_B or the operating conditions for a desired ϕ_B . The direct route is either to measure flows and calculate holdup times using dead volumes, or to measure holdup times directly. This presents no problem for the back column if the detector effluent is accessible and there is no significant pressure gradient across the detector. However, for the front column a mid-point split to a second detector or flow measuring device would be required. This introduces the problem of determining the split ratio and non-column dead volume between junction point and the measuring device.

An indirect approach to setting an experimental ϕ_B , by calculating the various pressure settings from resistance to flow calibrations, has been proposed by Purnell *et al.* [19].

Another approach involves setting the column inlet, mid-point and outlet pressures. Depending on the detector, the latter can frequently be assumed equal to atmospheric pressure, leaving only two pressures to be set. Incorporating eqns. 9 and 1-3 into the definition of relative retentivity produces the pressure-dependent expression:

$$\phi_B = \frac{(P_m^3 - P_o^3)(P_i^2 - P_m^2)^2}{c^2(P_i^3 - P_m^3)(P_m^2 - P_o^2)^2 + (P_m^3 - P_o^3)(P_i^2 - P_m^2)^2} \quad (11a)$$

where $c = L_F r_B / (L_B r_F)$. Or, in an alternate form:

$$\phi_B = \left[1 + \frac{c^2(P_i^3 - P_m^3)(P_m^2 - P_o^2)^2}{(P_m^3 - P_o^3)(P_i^2 - P_m^2)^2} \right]^{-1} \quad (11b)$$

If the flows are approximated as simple functions of inlet and outlet pressures, *e.g.*, $F^T \propto r^4(P_i - P_o)/(\eta L)$, then the expression simplifies to:

$$\phi_B = \left[1 + \frac{c^2(P_m - P_o)}{(P_i - P_m)} \right]^{-1} \quad (12)$$

If the two columns have equal dimensions then:

$$\phi_B = (P_i - P_m)/(P_i - P_o) \quad (13)$$

Eqns. 11-13 differ from the equations obtained by Hinshaw and Etre [8] for the same purpose. In their derivation $(P_i - P_o)$ was apparently used for the pressure differential across the entire system. However, this is valid only when $P_m = (P_i + P_o)/2$ and does not produce a general solution.

Assuming the system outlet to be at atmospheric pressure, eqn. 13 could easily be used to solve for either ϕ_B , P_i or P_m , given the other two variables. However, at gauge pressures $P_i = 140$, $P_m = 70$, $P_o = 0$ kPa, eqn. 13 yields $\phi_B = 0.50$, in contrast to $\phi_B = 0.56$ from eqn. 11, a 12% error. Clearly, eqn. 11 must be used for accuracy.

Use of eqn. 11 to solve for ϕ_B from pressure settings can easily be done with a calculator. However, to obtain a desired ϕ_B , a more likely scenario, if predictive calculations have been made, requires setting P_i and P_m . One pressure may be set somewhat arbitrarily, depending on other factors such as analysis time, but the remaining value cannot be obtained directly from eqn. 11. Newton's method provides an approach by approximation:

$$P_m \approx P_{m,\text{approx}} - [(\phi_{B,\text{approx}} - \phi_{B,\text{known}})/(d\phi/dP_m)] \quad (14)$$

For columns of equal dimensions,

$$\begin{aligned} \frac{d\phi_B}{dP_m} = & \left\{ \frac{cP_m(P_m^2 - P_o^2)(P_i^2 - P_m^2)}{[(P_m^3 - P_o^3)(P_i^2 - P_m^2)^2 + c(P_i^3 - P_m^3)(P_m^2 - P_o^2)^2]} \right\} \\ & \{ (P_i^3 - P_m^3)(P_m^2 - P_o^2)[3P_m(P_i^2 - P_m^2) - 4(P_m^3 - P_o^3)] \} \\ & + \{ (P_m^3 - P_o^3)(P_i^2 - P_m^2)[3P_m(P_m^2 - P_o^2) - 4(P_i^3 - P_m^3)] \} \end{aligned} \quad (15)$$

The derivative equation has been left in a form with terms which are also used to calculate ϕ_B . Eqn. 12 can be used to obtain a starting value of $P_{m,\text{approx}}$ leading to starting values of $\phi_{B,\text{approx}}$ and $d\phi_B/dP_m$. Iterative use of eqn. 14 will produce an accurate estimate of P_m . Assuming the back column flow can be measured, all the parameters necessary for serial column operations are obtainable.

In the preliminary stages of this work, when multichromatography was being investigated under isothermal conditions, it became apparent that the pressure regulators and gauges supplied with the instruments, combined with the method of coupling, did not provide the necessary level of control to set ϕ_B . In the absence of accurate controls a method for accurately determining the relative retentivity was required.

For a pair of columns whose dead volumes are known and for which compound retention parameters are known it is possible to obtain ϕ_B by using two compounds as standards under isothermal conditions. The retention time of the first compound would be:

$$t_1 = (V_{RF_1}^{\circ} + V_{MF}^{\circ})/F_F + (V_{RB_1}^{\circ} + V_{MB}^{\circ})/F_B \quad (16)$$

Combining eqns. 16 and 5 with the corresponding equations for the back column and for a second compound it is possible to show that:

$$F_{BT} = \frac{(V_{RB_2}^{\circ} + V_{MB}^{\circ})(V_{RA_1}^{\circ} + V_{MA}^{\circ}) - (V_{RB_1}^{\circ} + V_{MB}^{\circ})(V_{RA_2}^{\circ} + V_{MA}^{\circ})}{t_2(V_{RA_1}^{\circ} + V_{MA}^{\circ}) - t_1(V_{RA_2}^{\circ} + V_{MA}^{\circ})} \quad (17)$$

and that

$$t_{MB} = V_{MB}^{\circ} \frac{t_2(V_{RA_1}^{\circ} + V_{MA}^{\circ}) - t_1(V_{RA_2}^{\circ} + V_{MA}^{\circ})}{(V_{RB_1}^{\circ} + V_{MB}^{\circ})(V_{RF_1}^{\circ} - V_{RF_2}^{\circ})} \quad (18)$$

Eventually one arrives at:

$$\phi_B = \frac{t_2[(V_{RF_1}^{\circ}/V_{MF}^{\circ}) + 1] - t_1[(V_{RF_2}^{\circ}/V_{MF}^{\circ}) + 1]}{t_1(V_{RB_1}^{\circ}/V_{MB}^{\circ} - V_{RF_2}^{\circ}/V_{MF}^{\circ}) - t_2(V_{RF_1}^{\circ}/V_{MF}^{\circ} - V_{RB_1}^{\circ}/V_{MB}^{\circ})} \quad (19)$$

Eqns. 18 and 19 provide a check on an experimental setup using the retention times for two internal standards. The required retention volumes can be obtained for any compound in a basis data set via eqn. 5. It should be noted that relative retentivity is used only to determine the ratio of the corrected flows in the two columns. The above relationships, derived for isothermal multichromatography, cannot be used to determine elution times in temperature-programmed serial-column gas chromatography where each compound will experience a completely different range of temperatures in each column. The proper use of the equations is in verifying flow conditions in pressure-regulated, isothermal or temperature-programmed multichromatography.

The multichromatography system was tested by running the 23-compound mixture isothermally at three different values of ϕ_B . In Table II values of ϕ_B obtained via eqn. 11 from the pressure readouts are compared to those obtained experimentally using methylbenzene and fluoriodobenzene as internal standards. Much better agreement between calculated and experimental data was obtained using the internal standard ϕ_B values. Using internal standards the best agreement obtained ranged from -0.89 to 0.63% relative difference with an average absolute relative difference of 0.34% . Corresponding values for the worst set were -0.53 to 1.94% , and 0.42% , respectively.

TABLE II

COMPARISON OF RELATIVE RETENTIVITIES FROM PRESSURE SETTINGS AND INTERNAL STANDARDS

P_i (kPa)	P_m (kPa)	ϕ_B (calculated)	ϕ_B (internal standard)
140	110	0.27	0.23
140	70	0.56	0.49
140	40	0.75	0.71

For temperature-programmed, serially coupled columns in the same oven, solution of eqn. 7, using $F_{F,273}$ and the front-column thermodynamic parameters, affords T_c for the front column. This value becomes T_0 for the back column. A second solution of eqn. 7, using $F_{B,273}$ and the back-column thermodynamic parameters, affords T_c for the multichromatography system. Thus, two consecutive integrations provide the retention temperature for a compound under temperature-programmed

multichromatography conditions. It is then a simple matter, given the temperature program, to calculate the retention time.

For evaluation of the temperature-programmed multichromatography calculations the chromatograph was set to a series of inlet and mid-point pressures. After each change in instrument settings the test mixture was run isothermally to obtain two internal-standard retention times needed to calculate the experimental flows and ϕ_B . The test mixture was then analyzed under various temperature-programmed conditions. A comparison of the calculated and observed retention times from these temperature-programmed multichromatography experiments with the 23-compound mixture is presented in Table III. The agreement of these results varied from a best-case average absolute relative difference of 1.63% over a range from -0.13 to -2.61% (Trial 1) to the worst-case average of 2.64% over a range from -0.30 to -5.39% (Trial 2). Although both of these trials show only negative differences, this was not the case with the other three trials.

Probably the greatest contribution to differences between the calculated and observed retention times is the fact that in many cases the elution temperatures of the compounds significantly exceeded the upper range of the basis sets. Any inadequacies in holdup volumes, which were not measured outside of the basis set temperature range, would become more important at higher temperatures where retardation by the stationary phase diminishes rapidly. Many other retention times with notable differences were close to the dead time for the system and would also be greatly influenced by otherwise minor errors in the dead volumes. The early-eluting compounds would also have the least-reliable basis data.

Errors in multichromatography retention time predictions are inherently greater than those for single columns due to compounding of predecessor column errors. Therefore, more stringent conditions on functional forms and parameter evaluations should be necessary to achieve equal accuracies. These considerations have implications for (1) the temperature ranges over which data are collected, (2) the acceptance of data for parameter evaluation and (3) the form of the thermodynamic equation. However, the evaluation of conventional instruments and typical functional forms was the object of this investigation.

These results indicate that prediction of retention times in temperature-programmed multichromatography is adequate to guide optimal analytical separations. The necessary calculations may readily be performed on a personal computer. On an IBM PS2/60, using a coprocessor, calculation of a temperature-programmed multichromatography experiment with an integration interval equivalent to 0.01 min typically required 2.3 min for the 23-compound test set. The same calculation was much slower with software floating point arithmetic, requiring 34.2 min. Although the current version of the computer program used for this study is limited to single linear-ramp temperature programs, there is no major impediment to the use of multiple ramps in the calculations.

Theoretically, if the thermodynamic parameters are calculated relative to the amount of stationary phase in the column, they may be transferred between different-dimension columns with the same stationary phase. This remains to be verified, especially in cases where phase thicknesses are drastically different. Differences between column manufacturers may well be significant in this matter. Nonetheless, the ability to change the scale of a temperature-programmed GC method

without major recalibration is a potential, major advantage of the thermodynamic approach.

SYMBOLS

IUPAC symbols, when available, with supplementary subscripts and superscripts following the convention of Harris and Habgood [1], are used in the text. They are as follows:

A	constant in the expression for net retention volume at standard temperature
F	volumetric flow of carrier, measured at outlet if subscript o, otherwise corrected for pressure gradient
ΔH	constant in the expression for net retention volume at standard temperature
j	pressure-gradient correction factor
L	length of a column
P	absolute pressure
r	internal radius of a column
s	rate of a temperature program
t	time; may be numerically subscripted to indicate different times
T	temperature, K; may be numerically subscripted to indicate different temperatures
	T_0 – temperature at the start of a temperature program
	T_c – compound elution temperature in temperature programmed GC
V_M°	pressure-gradient corrected holdup volume
V_R°	pressure-gradient corrected retention volume
η	viscosity of the carrier gas
ϕ	relative retentivity

Superscript over volume or flow indicates temperature to which the parameter was corrected; no superscript indicates correction to 273 K. Subscripts: number or T variable indicates temperature in the column; o, i, m means outlet, inlet, mid-point or column junction; M means holdup time or volume; F, B indicates front, back column.

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