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Review

# Retention index in temperature-programmed gas chromatography

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## Abstract

A persistent feature in the development of temperature-programmed gas chromatography (TPGC) has been the search of a retention index  $I^T$ , defined as a relationship between the retention of the analyte and two members of an homologous series enclosing it. The motivation is to find for TPGC a parameter  $I^T$  resembling the properties of the isothermal Kováts index  $I$ . The latter is a relative thermodynamic parameter which provides basic information on solute–solvent interactions, independently from the chromatographic flow conditions, column’s dimensions and phase ratios. Several years ago, Rijks and coworkers pointed out that the isothermal Kováts index  $I$  and the TPGC index  $I^T$  are incommensurable. The implications from their remark have not received sufficient attention. As a consequence, in many recent publications  $I^T$  is still presented as a general useful parameter to be reported, specifically with reference to its correlation to solutes structural properties and their partition coefficients, analogous to the applicability of  $I$ . A renewed discussion on  $I^T$  is proposed, with the aim of divulging the unsolvable difficulties for obtaining relevant information from this that could be shared between laboratories. The influence of the column inlet pressure  $p_i$  and the ratio  $L/d_c$  on the reproducibility of  $I^T$  is utilized as an example to illustrate and discuss the basic concepts. Conditions were selected involving capillary gas chromatography of solutes presenting a retention reversal with the bracketing  $n$ -alkanes. Several important aspects of  $I^T$  were illustrated under these conditions. Since basic information of general applicability cannot be derived from  $I^T$ , it is concluded that only a compilation of thermodynamic parameters can reliably be shared by chromatographers. © 1999 Elsevier Science B.V. All rights reserved.

**Keywords:** Reviews; Retention indices; Temperature programming; Thermodynamic parameters; Alkanes

## Contents

1. Introduction .....	30
2. The retention index approach .....	30
2.1. The underlying concepts of the retention index .....	30
2.2. Advances in the retention index approach .....	31
3. The thermodynamic approach .....	32
3.1. The underlying concepts of the thermodynamic approach .....	32
3.1.1. The peak motion equation .....	32
3.1.2. The fluid dynamic functions .....	33
3.1.3. The thermodynamic functions .....	33
3.1.4. The solution of the peak motion equation .....	34

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3.1.5. The singular solution for $z=L$ .....	34
3.2. Advances in the thermodynamic approach .....	35
4. Factors that influence the reproducibility of $I^T$ and the elution order .....	36
4.1. A qualitative description .....	36
4.2. Precedents .....	37
4.3. A quantitative description .....	38
4.3.1. Experimental .....	38
4.3.2. The physical significance of $I^T$ .....	38
4.3.3. The isothermal separation functions .....	39
4.3.4. The effects of fluid dynamic factors on $I^T$ .....	39
5. Discussion .....	42
5.1. Thermodynamic considerations .....	42
5.2. Considerations on the $I^T$ accuracy .....	44
5.3. The $I^T$ standardization problem .....	46
5.4. Why a thermodynamic meaningful $I^T$ is not possible .....	47
6. Conclusions .....	47
References .....	48

## 1. Introduction

In the development of temperature-programmed gas chromatography (TPGC) two methods or lines of investigation can clearly be distinguished. One includes those works based on the definition of empirical or semi-empirical parameters, in order to report the information to be shared by chromatographers. The mainstream of this method was devoted to investigate the temperature programmed retention index  $I^T$ . For this reason, we shall identify this line of investigation as the “retention index approach”. The other method includes all those works oriented to the application of basic thermodynamic data for predicting the TPGC retention in different chromatographic conditions. The aim of these investigations is to develop calculation procedures necessary for the common use of relevant thermodynamic information. In this context the information to be reported and shared by different laboratories are thermodynamic parameters. The data concerning the specific conditions such as flow rates, column dimensions, phase ratios and temperature programs are applied only for individual use. This method will be identified as the “thermodynamic approach”.

The origins of both methods can be traced back through literature to the beginnings of the TPGC technique. Their developments may be viewed as parallel, and their concepts not necessarily as being opposed. But a major problem arises in the form the experimental data is reported in the retention index

approach. The problem originated due to two facts. First,  $I^T$  is not reproducible unless a strict standardization of the chromatographic conditions is performed. This standardization is not convenient from an analytical point of view, since the temperature interval of elution is the variable allowing the optimization of separations in each particular case. Second, contrary to what occurs in isothermal chromatography (GC) with the retention index  $I$ , the thermodynamic information cannot be determined from  $I^T$  in TPGC. The inverse, the calculation of retention indices from thermodynamic data, is possible either in GC or in TPGC. Therefore, experimental efforts reporting  $I^T$  cannot provide information of general applicability, and this is detrimental to the construction of a compilation of data that could be universally shared.

The purpose of this article is to review the underlying ideas involved in the above-mentioned methods, and their evolution. A critical viewpoint is adopted with respect to the retention index approach, promoting a discussion on the limitations of its perspective on the basis of results from the thermodynamic approach.

## 2. The retention index approach

### 2.1. The underlying concepts of the retention index

The historical inspiration for the development of

the programmed temperature index  $I^T$  is the isothermal Kováts index  $I$ . For this reason, prior to the introduction of notions concerning  $I^T$ , a review on the physical significance of  $I$  is presented.

The thermodynamic meaning of  $I$  immediately arises from its definition [1]:

$$\frac{I_x}{100} \equiv n + \frac{\log \frac{t'_{R_x}}{t'_{R_n}}}{\log \frac{t'_{R_{n+1}}}{t'_{R_n}}} = n + \frac{\Delta G_x - \Delta G_n}{\Delta G_{n+1} - \Delta G_n} \quad (1)$$

$\Delta G$  is the partial molar free energy of solution. The adjusted retention time is  $t'_R = t_R - t_M$ , where  $t_R$  is the retention time and  $t_M$  the gas hold-up time. The subscripts  $x$ ,  $n$  and  $n+1$  denote the analyte  $x$  and the number of carbon atoms of the reference  $n$ -alkanes which enclose the retention time of  $x$ . The dependence of retention with the fluid dynamics of the chromatographic system, represented by the gas hold up  $t_M$ , cancels out in the ratio of Eq. (1). This is possible due to the parametric nature of  $t_M$  in isothermal conditions. The consequence is that simultaneously are canceled the dependence with the viscosity of the carrier gas  $\eta$ , the column inlet pressure  $p_i$ , the outlet pressure  $p_o$  and the geometric parameters of the column. Overall fluid dynamic variable factors are present in the isothermal-capillary  $t_M$  function [2]:

$$t_M(T) = \frac{128 \eta(T)}{3p_o} \cdot \left(\frac{L}{d_c}\right)^2 \cdot \left(\frac{P^3(T) - 1}{[P^2(T) - 1]^2}\right) \quad (2)$$

$L$  is the length of the column and  $d_c$  the inner diameter, considering the stationary phase coating as part of the wall.  $P$  is the ratio  $p_i/p_o$ .

For the same reason it is eliminated in  $I$  the dependence of retention with the column phase ratio  $\beta$ , where  $\beta = V_G/V_L \approx d_c/4 d_f$ ,  $V_G$  and  $V_L$  are the volumes of the gas and liquid phases and  $d_f$  is the film thickness. This dependence arises from the relationship between  $\Delta G$  and the retention factor  $k = t'_R/t_M$ :

$$\ln k = -\ln \beta - \frac{\Delta G}{RT} \quad (3)$$

Consequently,  $I$  is purely thermodynamic. It only depends on the equilibrium interactions between the

solute and the stationary phase, as far as the bulk solution is the only significant contribution to retention. In a fixed stationary phase  $I$  is solely a function of the molecular structures of the solutes. In this way, basic thermodynamic information is provided in a relative form, using the solute–solvent interaction parameters of the  $n$ -alkanes as a framework of reference. One advantage of this reference scale is that  $\Delta G$  for all members of the series can be determined from a single expression  $\Delta G(n)$ , a function of  $n$ . For example, the empirical expression proposed by Martin [3]:  $\Delta G_n = \Delta G^+ + n \Delta G^m$ , ( $T = \text{constant}$ ).  $\Delta G^m$  is a contribution per methylene monomer to the free energy of solution, and  $\Delta G^+$  is a contribution independent of the chain length.

Of course,  $I$  will depend on geometric parameters of the column in those cases where interfacial phenomena significantly affect the retention, like in the case of  $n$ -alkanes solutes on polar stationary phases [4–8].

Contrary to the current suggestion that the reproducibility of  $I$  is linked to the linearity of the plot for the reference homologous series ( $\ln t'_R$  versus  $n$ ), one observation is that the reliable reproducibility of  $I$  in non-polar systems [9] is not due to this linearity. Actually, in non-polar stationary phases the greatest deviations from linearity of ( $\ln t'_R$  versus  $n$ ) for the  $n$ -alkanes [10,11] are observed. We must conclude that this reproducibility is the consequence of the precise physical meaning of  $I$ , its almost exclusive dependence on solute–solvent bulk interactions.

## 2.2. Advances in the retention index approach

With the aim of providing to the TPGC technique, a parameter that would resemble the utility of  $I$ , more than three decades ago Kratz and Van den Dool [12] defined their programmed temperature retention index:

$$\frac{I_x^T}{100} = n + \frac{T_{R_x} - T_{R_n}}{T_{R_{n+1}} - T_{R_n}} \quad (4)$$

$T_R$  denotes retention temperatures. The subscripts preserve the same meanings as Eq. (1). For single ramp linear temperature programs  $T_R$  can be replaced by the corresponding programmed temperature retention times  $t_R^T$ . In the same period as the

publication of [12], Guiochon [13] and Habgood and Harris [14,15] also suggested that the retention index concept could be applicable to TPGC. Thereafter, persistent efforts were made to study the relationship  $I-I^T$  and specially the general properties of the latter, generating numerous publications. Research groups headed by Guiochon [16], Garcia Dominguez [17] and Sun [18], sequentially reviewed the outstanding issues from this literature. The review by Sun et al. covers the first part of the present decade.

Examples of study on the relationship  $I-I^T$  are found in the early attempts by Giddings [19], Guiochon [13] and Lee and Taylor [20] seeking an equivalent temperature  $T_{\text{eq}}$ , such that  $I^T = I(T_{\text{eq}})$ . Krupcik et al. [16], Johansen et al. [21] and Habgood and Harris [15], later admitted that the agreement between  $I$  and  $I^T$  is not satisfactory for identification purposes. Previously, Golovnya and Uraletz [22] had showed that  $I^T$  is dependent on the velocity  $u$  of the carrier gas. Hence, it is dependent on the flow control system of the chromatograph and the geometric parameters of the column. Even so, they continued seeking for a relation between  $I$  and  $I^T$ , proposing the equivalence:  $I^T = I(T_0/r_T)$ , where  $T_0$  is the initial temperature of the program, and  $r_T$  is the heating rate. Afterwards, other relationships were introduced by Erdey et al. [23] making  $I^T$  equal to the mean  $I(T)$  in the temperature elution-interval  $[T_0, T_R]$ . Krupcick et al. [24] attempted to correlate, in a direct way, the TPGC retention to  $I$  and its temperature increment.

Up to the mid-1980s there was a continuous search for improving the reproducibility of  $I^T$  by substituting linear Eq. (4) by non-linear interpolations. The investigation of a generalized non-linear TPGC retention index generated several proposals [18,25–32], and the aim presently persists.

In the same period, Curvers et al. [2] stated that the direct conversion from isothermal to programmed temperature indices is not feasible ( $I \leftrightarrow I^T$ ). This is due to the dependence of the TPGC retention with the varying gas hold-up time  $t_M(T)$ , fluid dynamic function present in the peak motion equation. This was also obvious in the earlier work of Ref. [22], and it appears likely that subsequent efforts to reconcile  $I^T$  with  $I$  should have been abandoned, considering the precise thermodynamic significance of  $I$ .

Despite the work reported in [2] and the well-known fact that  $I^T$  depends on fluid dynamic param-

eters and the phase ratio of the columns, the idea that it can be useful for reporting and sharing the chromatographic information is still being treated as an advisable proposal. This information can be expressed in the classical form of Eq. (4), or by non-linear interpolations [18,30–37]. The persistence of this idea has generated some confusion.  $I^T$  has been correlated to molecular structural properties of the solutes [38–40] or their distribution coefficients [41]; that is to say, univocally assuming a thermodynamic relevance.

Simultaneously to  $I^T$ , several parameters concerning chromatographic conditions must be reported in order to make this information conditionally useful for other laboratories. The number of required additional or complementary parameters to  $I^T$  have not yet been clearly established [18,35,36]. Beside the initial temperature of the program  $T_0$ , one proposed parameter is the ratio  $(r_T t_M/\beta)$  [34]. This has a sound theoretical basis, as will be described in Section 4, but it is not strictly applicable to all cases.

### 3. The thermodynamic approach

#### 3.1. The underlying concepts of the thermodynamic approach

Ref. [2] is the first work to explicitly state that  $I$  and  $I^T$  are incommensurable. The importance of this statement, with its implications, was partially assumed. As a consequence, a new trend was stimulated retaking the pioneer investigations, initiated by Dal Nogare [42] and continued by others [15,43–48], for a rigorous prediction of the TPGC retention from thermodynamic data [2,49–64]. These procedures concern the theoretical treatment for the particular fluid dynamic behaviors of the chromatographic systems during temperature programs, and the determination of basic thermodynamic parameters. In this context the relevant information shared by chromatographers are thermodynamic parameters, playing the same role as  $I^T$  plays in the other method.

##### 3.1.1. The peak motion equation

The fundamentals of this approach are the most basic hypothesis, those inherent to the starting point

of the chromatographic theory, the differential equation of peak motion [42,43]:

$$\frac{dz}{dt} = \frac{u(z, t)}{[1 + k(t)]} \quad (5)$$

The left-hand side of Eq. (5) is the local migration velocity of the solute peak in the column, at the position  $z$  where the local velocity of the carrier gas is  $u(z, t)$ . In temperature programmed conditions  $u$ , in a given position  $z$ , is a function of time. The equation describes the chromatographic process as a combination of two factors. First, a fluid dynamic effect represented by  $u$ , the transportation of the solute by the gas stream. The other factor is the thermodynamic represented by the retardation factor  $R=1/(1+k)$ . This is the probability for finding the solute molecule in the gas stream, and concerns the solute–solvent interactions. The variables of the differential equation ( $z, t$ ) are, respectively, the position of the peak in the column, and the time elapsed from injection when this position is reached. The absolute temperature  $T$  and the time  $t$  are interchangeable variables, since the exact mathematical relationship between them is known through the selected temperature program,  $T=f(t)$ . Therefore, in a non-isothermal interval, it is indistinct to express the equation in terms of  $t$  or  $T$ .

In order to solve the differential equation, the explicit form of the fluid dynamic function  $u(z, t)$  and the thermodynamic  $k(T)$  must be known<sup>1</sup>.

### 3.1.2. The fluid dynamic functions

The isothermal steady-state motion of the carrier gas is described in capillary GC by the differential form of Hagen–Poiseuille's equation:

$$u = -\frac{d_c^2}{32\eta} \cdot \frac{dp}{dz} \quad (6)$$

The local pressure gradient  $dp/dz$  is that at the position  $z$  where  $u$  is determined. Although Hagen–Poiseuille's equation is valid only for incompressible newtonian fluids [65], the application to a differential

element assures can be assumed the incompressibility of the gas due to the extremely low pressure drop in such an element.

By using Eq. (6), and introducing the equation of state of the gas through the continuity equation [65],  $u(z, t)$  can be expressed in terms of measurable parameters and other known functions. For the ideal gas equation of state:

$$u(z, t) = \frac{d_c^2}{64\eta L} \cdot \frac{p_o(P^2 - 1)}{[P^2 - (z/L)(P^2 - 1)]^{1/2}} \quad (7)$$

$P$  contains the pressure program  $p_i(t)$ . This latter function of time is defined by the configuration of the flow control system in the chromatograph [66]. Similarly, the isothermal gas hold-up function given by Eq. (2) is directly derived from Eq. (6). Then,  $u(z, t)$  can also be expressed in terms of other well-known fluid dynamic functions:  $u(z, t) = L/[Q(z, t) t_M(t)]$ , where  $Q = p(z, t)/\bar{p}(t) = j[P^2 - (z/L)(P^2 - 1)]^{1/2}$ . The local pressure at  $z$  position and time  $t$  is  $p(z, t)$ , and the space-averaged pressure in the column at that time is  $\bar{p}(t)$ . The compressibility correction factor is  $j(t)$ .

All the parameters and functions from Eq. (7) are selected, or can be measured by the chromatographer, so the functional form of the fluid dynamic factor can be established a priori for any particular case. Different laboratories do not share the conditions concerning this factor unless an adequate standardization is performed.

### 3.1.3. The thermodynamic functions

In the expression of  $k(T)$ , given by Eq. (3),  $\Delta G(T)$  is the common term for different columns using the same stationary phase. Therefore, this latter function is the only relevant for sharing information between laboratories. Since the variation of  $\Delta G(T)$  along the elution interval  $[T_o, T_R]$  must be known in order to solve Eq. (5), this implies that the temperature derivatives of this function should be determined. These concern the following thermodynamic functions<sup>2</sup>: the partial molar enthalpy of solution,  $\Delta H(T)$ ; the partial molar entropy of solution,  $\Delta S(T)$ , and the partial molar isobaric heat capacity differ-

<sup>1</sup>The thermodynamic variables are ( $p, T$ ), but in the literature cited here, concerning capillary chromatography with  $p_i < 3$  bar (abs.), the pressure dependence of  $k$  is neglected.

<sup>2</sup>These derivatives are:  $\Delta S = -(\partial \Delta G / \partial T)_{p,n}$ ,  $\Delta C_p = -T(\partial^2 \Delta G / \partial T^2)_{p,n}$ .

ence  $\Delta C_p(T)$ . Functions involving higher-order derivatives were shown to be unobtainable from the chromatographic retention data [67]. Hence, the temperature dependence of  $\Delta G$  in the chromatographic range can be established by the following set of basic thermodynamic relationships:

$$\Delta G(T) = \Delta H(T) - T \Delta S(T) \quad (8)$$

$$\Delta H(T) = \Delta H(T^0) + \Delta C_p (T - T^0) \quad (9)$$

$$\Delta S(T) = \Delta S(T^0) + \Delta C_p \ln(T/T^0) \quad (10)$$

$T^0$  is any reference temperature and  $\Delta C_p$  has been assumed to be constant. Therefore, function  $k(T)$  [Eq. (3)] is defined if  $\Delta H$ ,  $\Delta S$ , and  $\Delta C_p$  are reported at any reference temperature. Gas chromatographic determination of these three parameters can be performed using capillary columns [62].

### 3.1.4. The solution of the peak motion equation

Once the particular flow conditions and the temperature program are selected, and provided that the thermodynamic information is available through knowledge of a set of values [ $\Delta H(T^0)$ ,  $\Delta S(T^0)$ ,  $\Delta C_p$ ], Eq. (5) can be solved. For doing this, an additional hypothesis is needed. The global TPGC process has to be assumed as a succession of isothermal-steady state differential processes.

Eq. (5) is an ordinary differential equation. Only when  $p_i(t)$  is constant the separation of variables becomes feasible [2,47,61], allowing to advance one further step. In the most general situation  $p_i(t)$  is not constant. In this latter case, standard numeric procedures for the solution of ordinary differential equations are well established in numerical mathematics [68]. These involve algorithms of finite differences. Specifically for the solution of Eq. (5), descriptions of algorithms are available in the literature [42,58,61]. The solution of Eq. (5) through an algorithm of finite differences provides a relationship between the position of the peak and the elapsed time:  $z=F(t)$ ; this is the integral solution. The interest is mainly centered on the particular value ( $z=L$ ,  $t=t_R^T$ ).

Nowadays, facilities for the numerical calculation provided by the widespread use of computers makes this task accessible for all laboratories. As a conse-

quence, we must assume that the TPGC retention can be determined on a rigorous basis under any specific chromatographic condition, by any laboratory, if the thermodynamic information is available. No standardization of pressure programs  $p_i(t)$ , column dimensions, phase ratios  $\beta$  and temperature programs ( $T_0$ ,  $r_T$ ) are necessary for the comparison of experimental results between laboratories and for sharing the relevant information. This has been the motivation of the thermodynamic approach. It should be noticed that the concept of  $I$  relies on the same principle.

### 3.1.5. The singular solution for $z=L$

If the mobile phase is an incompressible fluid like in liquid chromatography,  $u$  is constant along the column being only a function of time in programmed temperature conditions. Therefore, variable separation in Eq. (5) becomes feasible, leading to the solution:

$$z_i = \int_0^{t_i} \frac{u(t)}{[1 + k(t)]} dt,$$

where  $z_i$  is any given position. The differential form of Hagen–Poiseuille equation is applied in gas chromatography. Then, it is physically expected that the summation of the differential contributions along the whole process should yield back a singular solution for Eq. (5) in  $z=L$  preserving the form of the incompressible fluid solution, but replacing  $u$  by an average. In the case of TPGC with constant pressure control ( $p_i(t)=\text{constant}$ ) this solution is also obtainable by direct variable separation [2,47,61]:

$$1 = \int_0^{t_R^T} \frac{dt}{t_M(t)[1 + k(t)]} = \int_{T_0}^{T_R} \frac{dT}{r_T(T) t_M(T) [1 + k(T)]} \quad (11)$$

It should be noted that here the isothermal temporal average  $\bar{u}=L/t_M$  plays the role of the local  $u$  in the incompressible fluid solution. In the total summation along the elution interval, local values can be replaced by average values corresponding to hypothetical isothermal columns of length  $L$ . For constant

$p_i(t)$  and  $z < L$ , it is obtained a completely different mathematical form, compared to the incompressible fluid solution or Eq. (11). In this case the factor  $[1/(P^3 - 1)]\{P^3 - [P^2 - (z_i/L)(P^2 - 1)]^{3/2}\}$  replaces the factor 1 in Eq. (11). For flow control systems of variable  $p_i(t)$ , it was exposed the mathematical reason for the existence of a singular solution for Eq. (5) in  $z=L$  with the form of Eq. (11) [61].

Eq. (11) is not defined for isothermal conditions ( $dT/dt = r_T = 0$ ). Being a singular solution for  $z=L$ , it is not applicable for  $z < L$ . Although it yields the correct final retention time  $t_R^T$ , it is unable to provide the correct peak position and local flow conditions at intermediate times of the process. When using Eq. (11) in multi-step TPGC, apart an initial isothermal interval, intermediate or final isothermal tracts cannot be calculated separately on a rigorous basis. Despite this limited applicability, the advantage of the equation is that allows giving an insight to the phenomenology of TPGC. When any variable factor is modified, the evolution of  $t_R^T$  or  $T_R$  can be analyzed through simple reasoning by the application of Eq. (11) in conjunction with Eq. (2) (see Section 4.1).

### 3.2. Advances in the thermodynamic approach

The foundational stone of the theory of this approach is the work by Dal Nogare and Langlois [42]. Although it was specifically dedicated to systems with constant mass flow control of the carrier gas, its generality is implicit [61]. All the basic notions leading to a rigorous solution of the peak motion equation were developed in this historical contribution. Giddings published a contemporary work [43] with the same objective, but his efforts were oriented to obtain an approximate solution of Eq. (5). This endeavor characterized the development of the discipline in the posterior two decades, a period in which computational facilities were not yet popularized. Paradigmatic examples of proposed approximations or simplifications are found in the text by Habgood and Harris [15], and later in the work of Hollis and Grant [47]. The advent of personal computers created the conditions for a rigorous calculation of  $t_R^T$ , but the practice of making approximations was not abandoned. These can be mathematical, concerning the solution of Eq. (5);

fluid dynamical, concerning  $u(z, t)$  and  $t_M(T)$ ; or thermodynamic, concerning  $\Delta G(T)$ . Examples approximating the form of  $t_M(T)$ , whose rigorous expression is Eq. (2), are found in early works [2,49,52,53,56]. One usual thermodynamic simplification in the literature was to assume constant  $\Delta H(T)$  and  $\Delta S(T)$  in the temperature elution-interval  $[T_0, T_R]$  [2,47–52,58–60,64]. Empirical expressions of  $k(T)$ , equivalent to the consideration of the temperature dependence of  $\Delta H$  and  $\Delta S$  through  $\Delta C_p$  (see Eqs. (8)–(10)), have been applied [57,63]; as well as the explicit calculation of all three parameters [62]. In the past decade, Dose [49] proposed that the retention indices viable for TPGC should be nothing else than thermodynamic parameters obtained from isothermal measurements. He proposed the values of  $\Delta H$  and  $\Delta S$ , assuming them constant in the elution interval. With this approximation, in most cited works,  $t_R^T$  was calculated with an average error of about 1% using intra-laboratory obtained thermodynamic data; even when additional approximations are introduced. For example, in [60] the TPGC retention under different flow control systems was calculated applying Eq. (11), including intermediate isothermal intervals. Although this is not methodologically rigorous, the average errors are in the same order of those strictly calculated through an algorithm of finite differences, determining local conditions [58].

Guan [51] and Snijders et al. [58] calculated the programmed temperature retention applying the thermodynamic information obtainable from  $I$ . In this important contribution, the authors applied the thermodynamic parameters derived from the reported  $I$  in the Sadtler library [69] at two temperatures. In this way, an inter-laboratory source of thermodynamic data was used. By this procedure  $\Delta H$  and  $\Delta S$  can be determined at one reference temperature  $T^0$ , but not the partial molar heat capacity difference  $\Delta C_p$ . Even with such a limitation, it was shown that the average error of the predicted  $t_R^T$  is less than 4%. They simulated multi-linear temperature programs with a constant pressure flow control ( $p_i = \text{constant}$ ), including intermediate isothermal intervals. The equation of peak motion was rigorously solved through an algorithm of finite differences, thus calculating the correct local values of  $u$ .

Another important contribution to this field is by

Vezzani et al. [63]. It was shown in this work that the standard error in the prediction of  $t_R^T$  is reduced to the same order of the standard error of measurement if a precise temperature monitoring of the oven is carried out during the elution process. Thus, it was shown that the main source of errors, when predicting  $t_R^T$ , is not the theoretical approach. The most important source of errors is instrumental, the discrepancy between the assumed preset temperature program and the real temperature program taking place in the oven.

With the fast computers presently available, it is not necessary to make any approximation in the simulation of the TPGC process. Nevertheless, as shown by Vezzani et al. [63], the only obstacle for a precise theoretical prediction and a reliable reproducibility of the conditions are the temperature controls of the chromatographs.

The thermodynamic approach has been applied for optimization of temperature programs with the objective to obtain the best separation in a given mixture [70,71]. The cited optimization procedures are applications of the Simplex method. The response function defined by Dose [70] was also utilized by Snijders et al. [71]. This imposes two constraints, one is the retention time of the last eluting solute, and the other is the resolution of a critical pair, although the easily resolved pairs are not ignored. The physical effect of any optimization is to modify the position and extension of the elution interval  $[T_0, T_R]$  of the analytes, considering that the thermodynamics of the separation is the decisive factor, and  $T$  is the thermodynamic variable. This can be done by changing the temperature program  $(T_0, r_T)$ , or other factors capable of modifying the extension of the interval  $[T_0, T_R]$ , such as the pressure program  $p_i(T)$ . The convergence is assured because every pair  $(x, y)$  has a temperature interval where the thermodynamic factor of the separation, i.e. the difference of probabilities  $R_x - R_y$  for finding the molecules of  $x$  and  $y$  in the gas phase, is maximum (see Section 4).

The methods for predicting  $t_R^T$  from thermodynamic data also have been applied for the calculation of  $I^T$  [51,59,72,73–75], with an excellent agreement to the experimental indices. It should be noted that in this case the retention information is already provided by the thermodynamic parameters employed in

the calculation. In some way  $I^T$  results a redundant report.

#### 4. Factors that influence the reproducibility of $I^T$ and the elution order

##### 4.1. A qualitative description

The objective of this section is to provide a previous overview on the factors in TPGC that affect the reproducibility of the relative retention or  $I^T$ , and in some extreme cases the elution order. The description of this issue is synthesized in the problem of how can different factors modify the temperature elution-interval  $[T_0, T_R]$  of the solutes. For the sake of simplicity, in what follows we shall refer to a simple linear temperature program. Then,  $T_R$  in Eq. (4) can be replaced by retention times  $t_R^T$ . We shall also make use of the following equivalency of constraints from (a) to (d). (a) When the chromatographic conditions are changed<sup>3</sup> from condition c1 to c2, we impose the constraint that the relative retention ( $RR$ ) for each solute pair  $(x, y)$  in the injected mixture must be reproducible. (b) The ratio of retention times  $t_R^T$  in condition c1 and c2, for each solute individually, must be constant for all solutes in the mixture. (c) The relative separation ( $RS$ ) between a pair of solutes  $(x, y)$ , in condition c1 and c2 must be constant for all solute pairs in the mixture. (d) The retention index for each solute must be reproducible from c1 to c2. Summarizing:

$$(a) \quad RR(x, y) = \left( \frac{t_{R_x}^T}{t_{R_y}^T} \right)_{c1} = \left( \frac{t_{R_x}^T}{t_{R_y}^T} \right)_{c2}, \forall (x, y)$$

$$(b) \quad \frac{t_{R_x}^T}{t_{R_x}^T} = \text{const.} = \forall x$$

$$(c) \quad RS(x, y) = \frac{(t_{R_x}^T - t_{R_y}^T)_{c1}}{(t_{R_x}^T - t_{R_y}^T)_{c2}} = \text{const.} = \forall (x, y)$$

<sup>3</sup>The meaning for 'change in the chromatographic conditions' is that any variable factor can be modified; e.g. the flow control system of the chromatograph  $(p_i(t))$ , the column dimensions  $(L/d_c)$ , the phase ratio  $(\beta)$ , the carrier gas  $(\eta)$  or the temperature program  $(T_0, r_T)$ .



$$(d) \quad I_x^T]_{c1} = I_x^T]_{c2}, \forall x \quad (12)$$

These equivalent relationships are equal to say that if  $RR$  or  $I_x^T$  are reproducible from  $c1$  to  $c2$ , the chromatogram should be uniformly compressed or expanded in the  $T$  scale by effect of this change in the chromatographic conditions [see Eq. (4)]. Obviously, if no expansion or compression of the chromatogram in the  $T$  scale takes place when changing from  $c1$  to  $c2$ ,  $RR$  and  $I_x^T$  will be reproducible.

It can be seen through Eq. (11) that when the analyte has a different temperature dependence of  $k(T)$ , with respect to the reference  $n$ -alkanes, and if the elution interval  $[T_0, T_R]$  is modified by changing conditions from  $c1$  to  $c2$ ,  $I_x^T$  will not be reproducible. The reason is that when the solutes have different temperature dependencies of  $k(T)$ , the resultant modification of the interval  $[T_0, T_R]$  will not be proportionally the same for all. In the most general situation the chromatogram cannot be uniformly compressed or expanded in the  $T$  scale due to the different temperature dependencies of  $\Delta G(T)$  for the solutes present in the injected mixture. In the extreme case when the analyte has an inversion of the elution order with the reference alkane, due to their different temperature dependencies of  $\Delta G$  (i.e. when the sign of  $(R_n - R_x)$ ,  $[k_x(T) - k_n(T)]$  or  $[\Delta G_x(T) - \Delta G_n(T)]$  changes in the  $T$  interval), this lack of reproducibility in  $I_x^T$  will become more evident. In this case is obvious that the modification of the interval  $[T_0, T_R]$  can lead to the inversion of the TPGC elution order of  $x$  and  $n$ .

The temperature dependence of  $\Delta G$  is determined by the structural characteristics of the solute molecule, in a great extent through the value of  $\Delta C_p$  [see Eqs. (8)–(10)]. In turn, the contributions to  $\Delta C_p$  arise mainly from the vibrational degrees of freedom of the molecule. Therefore, those solutes showing a great difference in their structural properties (as, e.g., linear-flexible molecules versus rigid rings) will present a more marked difference in their temperature dependence of  $k(T)$ . Pairs of these substances will likely present isothermal elution reversals along the  $T$  scale.

The simultaneous inspection of Eqs. (11) and (2) allows to examine a priori how the elution interval  $[T_0, T_R]$  is affected by changing any of the variable factors. In what follows it is assumed a fixed  $T_0$ .

Considering that the value of the integral in Eq. (11) is normalized, if we e.g., decrease the contribution of each differential element of the integrand, implies that  $T_R$  will be increased. This reduction in the values of the integrand can be done through an increase of  $t_M(T)$ . Any variable factor present in Eq. (2) can produce this effect. For example, by diminishing  $p_i$  the extension of  $[T_0, T_R]$  will be incremented. The factors affecting this extension, and in consequence the scanned  $T$  interval of the thermodynamic functions  $\Delta G(T)$ , are:  $r_T$ ,  $p_i(t)$ ,  $p_o$ ,  $(L/d_c)$ ,  $\eta$  and  $\beta$ . The factor  $(L/d_c)$  will have a pronounced effect, since the square of this affects  $t_M(T)$  [see Eq. (2)]. When the same flow controls are used [same function  $t_M(T)$ ] and  $\beta$ , it can be inferred from Eq. (11) that if the product  $[r_T t_M]$  remains constant in the change from  $c1$  to  $c2$ , the interval  $[T_0, T_R]$  will not be modified. For strongly retained solutes, i.e. when  $k = (K/\beta) \gg 1$ ,  $\beta$  can be factored out from  $[1+k]$  in the denominator of Eq. (11). In this case the constancy of Sun's standardization parameter for  $I^T$  [34, 76], the ratio  $(r_T t_M/\beta)$ , assures an invariant  $[T_0, T_R]$  between laboratories; provided that the same flow control system is used.

#### 4.2. Precedents

From their experimental observation, Knoppel et al. remarked that the reproducibility of  $I^T$ , in different chromatographic conditions, is invariably linked to the chemical structure of the analyte [77]. Recently, from retention indices measured in poly(dimethylsiloxane) capillary columns, compiled from reports of different laboratories, it was concluded that the aromatic solutes are those presenting the lowest reproducibility of  $I^T$  [36]. These observations are in agreement with the report of White and coworkers [75], who established, in gasoline fractions, that the order of decreasing reproducibility depends on the molecular structure of the analyte according to: branched aliphatic > aliphatic cycles > aromatic. The latter shows the less reproducible  $I^T$  among the components of the gasoline fractions and also present many cases of inversion of the retention order. Pell and Gearhart [78] had previously reported the inversion of the elution order in capillary columns, without modifying the temperature program. These authors showed that, although the same tem-

perature program is used, the elution of certain [aliphatic/aromatic] critical pairs is inverted by only modifying the pressure drop in the column. When the reference homologous series has the same structural properties of the analytes, a good reproducibility of  $I^T$  should be observed, as in the case of polychlorinatedbiphenyls [79–81]. Recently, it was found that the relative separation  $RS$ , between a constant  $p_1$  (CP) and a linear pressure program (PP), renders different values for the (aromatic/alkanes) couples when compared to the value of  $RS$  corresponding to (alkane/alkane) [60].

The relationship between the change in the elution order [analyte/ $n$ -alkane] and the extension of the elution temperature interval [ $T_0$ ,  $T_R$ ] was shown in a quantitative approach through the application of Eq. (11) [62]. This study was applied to non-polar and polar systems. Those solutes presenting the greatest difference in the temperature dependence of  $\Delta G$ , with respect to the  $n$ -alkanes, were selected in the study. Here we shall use the same examples for illustrating the effect of the modification of the elution temperature interval [ $T_0$ ,  $T_R$ ] specifically on the reproducibility of  $I^T$ .

### 4.3. A quantitative description

#### 4.3.1. Experimental

The equipment employed in the experiments were Hewlett-Packard 5880A and 5890 II Plus chromatographs. The flow control systems were constant pressure with the former, constant pressure and constant mass flow with the latter. The column inlet pressure was measured in a mercury column of 150 cm connected to the 5880A. Flame ionization detection was applied. Three non-polar poly(dimethylsiloxane) columns were used. The specifications are: AT-1, 30 m $\times$ 0.25 mm, 0.25  $\mu$ m (AllTech, USA); HP1, 50 m $\times$ 0.20 mm, 0.33  $\mu$ m; HP1 12 m $\times$ 0.20, 0.33  $\mu$ m. The solutes were sampled from head space vapors and injected with gas tight syringes, using the lowest amount which allowed reliable detection in a very low attenuation. Selected split ratios were in the order of 1:100. The gas hold up was determined, approximately, from the retention of methane.

#### 4.3.2. The physical significance of $I^T$

The physical meaning of  $I^T$  completely differs from that of  $I$ . Only two features are common to these indices. First, both are dimensionless. Second, by definition both coincide in their arbitrary scale of values for the  $n$ -alkanes. As will be shown,  $\beta$  and the fluid dynamic factor  $t_M(T)$  do not exactly cancel out in the retention ratio of Eq. (4), as occurs to  $I$  in Eq. (1). The development that follows takes the linear interpolation of Eq. (4) as the example for illustrating the basic concepts. Nevertheless, the effects described here will similarly affect the reproducibility of a non-linearly interpolated  $I^T$ .

The following expression for the TPGC separation of a solute pair ( $x$ ,  $n$ ) can be derived from the application of Eq. (11) to both solutes, by taking the difference and using the Theorem of the Media:

$$T_{R_x} - T_{R_n} = \frac{1}{t_{R_x}^{-1}} \int_{T_0}^{T_{R_n}} I_{x,n}(T) dT \quad (13)$$

The separation may also be expressed in terms of retention times, considering that in a single linear temperature program is:  $T_{R_x} - T_{R_n} = r_T(t_{R_x}^T - t_{R_n}^T)$ . In Eq. (13) the separation has been factored into two contributions, one which does not depend on the retention difference between both solutes, and another concerning this difference. In the first factor,  $t_{R_x}^{-1}$  denotes the average reciprocal isothermal retention time of  $x$  in the temperature interval [ $T_{R_n}$ ,  $T_{R_x}$ ]. In this temperature interval the peak of  $n$  has already eluted and  $x$  is migrating alone. This factor of the separation only depends on the retention of  $x$ . No local separation of the solute pair takes place in this temperature interval. In the second factor,  $I_{x,n}(T)$  is the isothermal separation function of the pair ( $x$ ,  $n$ ), whose physical meaning is the difference of probabilities for finding the solute molecules  $n$  and  $x$  in the gas stream ( $R_n - R_x$ ), per unit time spent in the gas (per unit  $t_M$ ), at a given temperature  $T$ :

$$I_{x,n}(T) \equiv \frac{1}{t_M(T)} \cdot \left[ \frac{1}{[1 + k_n(T)]} - \frac{1}{[1 + k_x(T)]} \right] \\ = \frac{t_{R_x}(T) - t_{R_n}(T)}{t_{R_x}(T)t_{R_n}(T)} \quad (14)$$

$t_R(T)$  are isothermal retention times measured under the same pressure program  $p_i(T)$  taking place during the temperature program. The factor  $t_{R_x}^{-1}$  in Eq. (13) is always positive. Therefore, the elution order, i.e. the sign of the separation ( $t_{R_x}^T - t_{R_n}^T$ ), is defined by the sign of the integral. If  $\int_{T_0}^{T_{R_n}} I_{x,n}(T) dT > 0$ , implies that  $x$  elutes after  $n$ , and conversely if it is  $< 0$ .

The TPGC retention index written in terms of isothermal separation functions is, by using Eq. (13):

$$\frac{I_x^T}{100} = n + \frac{\overline{t_{R_{n+1}}^{-1}}}{t_{R_x}^{-1}} \cdot \frac{\int_{T_0}^{T_{R_n}} I_{x,n} dT}{\int_{T_0}^{T_{R_n}} I_{n+1,n} dT} \quad (15)$$

where  $\overline{t_{R_{n+1}}^{-1}}$  is the average reciprocal retention time of the  $n$ -alkane ( $n+1$ ) in the interval  $[T_{R_n}, T_{R_{n+1}}]$ . We should note that  $t_M(T)$  and  $\beta$  cannot be eliminated from this relation if we intend, as in Eq. (1), to factor out a term only depending on  $\Delta G$ . In the unique situation in which  $I^T$  becomes independent of  $t_M(T)$  and  $\beta$  is when  $T_{R_n} \rightarrow T_0$ , or  $r_T \rightarrow 0$ ; namely, when the process tends to isothermal conditions:

$$\lim_{r_T \rightarrow 0} \frac{I^T}{100} = n + \frac{e^{-\Delta G_x/RT} - e^{-\Delta G_n/RT}}{e^{-\Delta G_{n+1}/RT} - e^{-\Delta G_n/RT}}$$

Only at very low heating rates  $I^T$  will resemble the properties of  $I$  (see Eq. (1)).

For a constant pressure control  $t_M(T)$  is a monotonously increasing function [62,82]. For a linear pressure programs  $p_i(t)$  or a constant mass flow control, the isothermal gas hold-up is a decreasing function [66]. On the other hand, the thermodynamic factor of  $I_{x,n}$ , (the difference  $R_n - R_x$ ) is a combination of exponential terms; function whose form depends on the difference in the temperature dependence of  $\Delta G_x(T)$  and  $\Delta G_n(T)$ . Thus, the decisive features of the separation function  $I_{x,n}$  are given by the thermodynamic factor, while the fluid dynamic factor  $1/t_M$  only shifts the scale and slightly deforms the curve.

#### 4.3.3. The isothermal separation functions

The members of homologous series are non-cross-

ing solutes, only tending to coelution when  $\Delta G/RT$  tends to zero. Fig. 1 shows a typical plot  $\ln k$  versus  $1/T$  of  $n$ -alkanes. This is equivalent to the plot  $-\Delta G/RT$  versus  $1/T$ , shifted a constant factor  $-\ln \beta$  in the ordinate [see Eq. (3)]. It is also represented the curve of *sec*-butylbenzene. With respect to the  $n$ -alkanes, this solute has a different temperature dependence crossing  $n$ -decane in the chromatographic range. Experimental values are represented by symbols. The filled lines are regression curves to a theoretical expression corresponding to Eqs. (8)–(10) (see Ref. [62]). When greater is  $\Delta C_p$ , greater is the curvature of the plot.

Fig. 2 shows the experimental thermodynamic factor of  $I_{n+1,n}$  for several consecutive couples of  $n$ -alkanes, represented by geometric symbols. These were obtained from experimental isothermal retention times  $t_R(T)$  and gas hold up  $t_M(T)$  [see Eq. (14)]. The filled lines are theoretical curves calculated from the set of thermodynamic parameters  $[\Delta H(T^0), \Delta S(T^0), \Delta C_p]$ . It can be seen that this function is a slightly skewed distribution. Fig. 2 represents the distribution of the difference in probabilities for finding the molecules of alkanes  $n$  and  $n+1$  in the gas phase ( $R_n - R_{n+1}$ ).

Fig. 3 shows the complete experimental function  $I_{n+1,n}$ , obtained from  $t_R(T)$  using Eq. (14). No qualitative changes are introduced with respect to the thermodynamic factor represented in Fig. 2. Only a scale shift arises from the local product with  $1/t_M(T)$ . The temperature of the maximum  $T_m(n+1,n)$  corresponds to the maximum separation in the shortest analysis time. This increases linearly with  $n$ :  $T_m = a + bn$ .

Fig. 4 represents the separation function  $I_{x,n}$  of the crossing-pair *sec*-butylbenzene ( $x$ )/decane ( $n$ ). This function presents a maximum, a minimum and a null value at the coelution temperature  $T_{ce}$  ( $T = T_{ce}$ ,  $I_{x,n} = 0$ ). When  $T = T_{ce}$  is  $\Delta G_x - \Delta G_n = 0$  due to the complete mutual compensation of the enthalpy and entropy differences:  $\Delta H_x - \Delta H_n = T_{ce}(\Delta S_x - \Delta S_n)$ . The filled line of Fig. 4 represents  $I_{x,n}$  calculated theoretically from the thermodynamic parameters  $[\Delta H(T^0), \Delta S(T^0), \Delta C_p]$  and function  $t_M(T)$ .

#### 4.3.4. The effects of fluid dynamic factors on $I^T$

In the determination of  $I_x^T$ , one current procedure for the standardization of conditions sets constant the

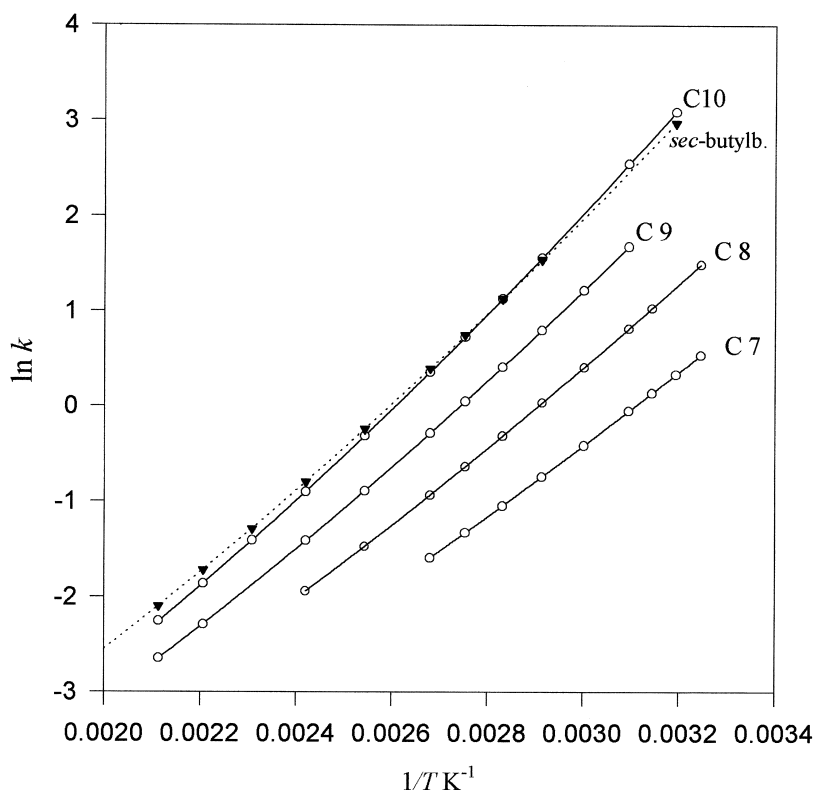


Fig. 1.  $\ln k$  as function of the reciprocal absolute temperature  $1/T$  for  $n$ -alkanes. The circles are the experimental values obtained from  $t_R$  measured in the column AT1, using the chromatograph HP 5890 II. The filled lines are regression curves. The experimental values of the crossing solute *sec*-butylbenzene are represented as triangles and the regression curve as a dotted line.

initial temperature of the program  $T_0$  and the heating rate  $r_T$  [36]. Under such constraints, the upper integration limit  $T_{R_n}$  in Eq. (15) or Eq. (11) will vary by changing  $p_i(T)$ ,  $p_o$ ,  $(L/d_c)$ ,  $\eta$  or  $\beta$ .

Fig. 5 shows the experimental variation of the retention temperature  $T_{R_n}$  with  $p_i$ , in successive chromatographic runs taken with the constant pressure mode of flow control.  $T_0$ ,  $r_T$  and the remaining variable parameters were preserved unaltered. Therefore, the extension of the temperature interval of integration in Eq. (13) [ $T_0$ ,  $T_{R_n}$ ] is progressively reduced as  $p_i$  is incremented between runs. From the viewpoint of Fig. 4, this corresponds to a reduction in the extension of the covered area in the graph from  $T_0$  to  $T_{R_n}$ . According to Eq. (15), the area decrease under the curves  $I_{x,n}(T)$  and  $I_{n+1,n}(T)$  should be proportionally the same if  $I_x^T$  is invariant with the changing conditions. The greater the profile differences between  $I_{x,n}$  and  $I_{n+1,n}$ , greater the lack of

constancy of the ratio  $\int I_{x,n} dT / \int I_{n+1,n} dT$ , when the upper integration limit  $T_{R_n}$  is modified by the chromatographic conditions.

The first factor of Eq. (15), the ratio  $t_{R_{n+1}}^{-1} / t_{R_x}^{-1}$ , introduces some variation in  $I_x^T$  by changing the extension of the temperature interval in the TPGC elution process, but compared with the ratio of the average separation functions it is insignificant.

In comparison with the other accompanying factors in Eq. (15),  $I_{x,n}$  of the crossing analyte presents the most outstanding changes taking place within the elution interval [ $T_0$ ,  $T_{R_n}$ ]. Now, let us visualize in Fig. 4 an initial condition of very low  $p_i$ , such that the covered positive area is greater than the negative. In this condition  $x$  elutes after  $n$ . If in successive runs we increase the pressure, the reduction in the scanned  $T$  interval will lead to a point in which the covered negative area is equal to the positive. This situation, characterized by  $\int_{T_0}^{T_{R_n}} I_{x,n} dT = 0$ , is the

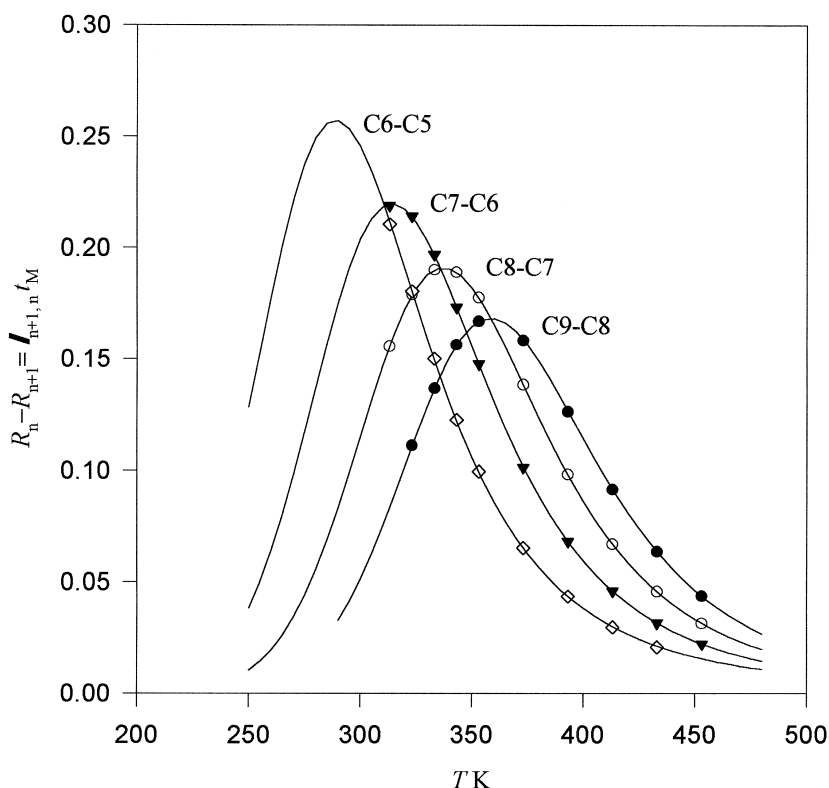


Fig. 2. Experimental distribution of the thermodynamic factor ( $R_n - R_{n+1}$ ) for different  $n$ -alkane couples (symbols). These were obtained from  $t_R$  and  $t_M$  measured in the column HP1, 50 m, with the chromatograph HP 5880A. The filled lines are theoretical curves calculated from the thermodynamic parameters [ $\Delta H(T^0)$ ,  $\Delta S(T^0)$ ,  $\Delta C_p$ ].

coelution condition in TPGC [62]. According to Eq. (13), in this condition the separation between *sec*-butylbenzene and decane has been reduced to zero, or according to Eq. (15)  $I_x^T$  has been progressively reduced, from a certain initial value, to 1000. If we continue incrementing  $p_i$ , the covered negative area of the separation function is greater than the positive, so *sec*-butylbenzene elutes before decane and  $I_x^T$  is reduced below 1000. Fig. 6 shows the correspondent experimental variations of  $I_x^T$  (circles) and the theoretical [continuous line, Eqs. (11) and (15)].

The variation of the retention index will be similar in a non-linearly interpolated  $I^T$ , as consequence that the inversion [analyte/ $n$ -alkane] is a physical fact independent of the arbitrary scale of  $I^T$ . The inversion in TPGC is possible by only modifying the fluid dynamic factor  $t_M(T)$  or  $\beta$ , even when all the variable parameters are fixed with the exception of one of them. This could be in turn  $T_0$ ,  $r_T$ ,  $p_i$ ,  $p_o$ ,

$L/d_c$ ,  $\eta$  and  $\beta$ . Here we only present examples on the effect of  $r_T$ ,  $p_i$  and  $L/d_c$  because these are closely accessible in the practice. When between two conditions only is varied  $p_i$ , while all the other factors remain constant, the order of variation of  $I^T$  for *sec*-butylbenzene is  $\delta I^T \approx 10$  units.

Fig. 7 shows the variation of  $I^T$  for *sec*-butylbenzene when  $L/d_c$  is changed, preserving the other parameters. There we illustrate the experimental results from two HP1 columns (symbols). Their specifications only differ in the length  $L$ . Once more, the continuous line represents  $I^T$  calculated from thermodynamic parameters and the theoretical  $t_M(T)$  [Eqs. (11), (15), (2)]. The resultant  $\delta I^T$  from the change in  $L/d_c$  is about twice the difference generated by changing five times the pressure drop in the column. The effect is similar to the modification of  $r_T$  in a great proportion, as can be seen from the comparison of Figs. 6 and 7. This effect of  $L/d_c$  on

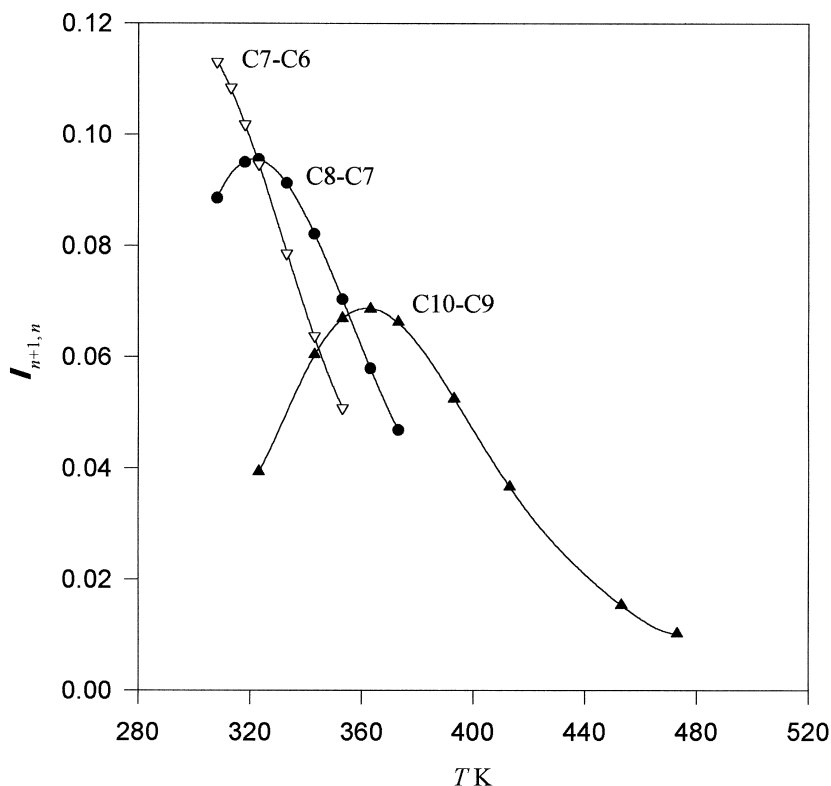


Fig. 3. Experimental isothermal separation function  $I_{n+1,n}$  of  $n$ -alkanes (symbols). Retention times were measured with the AT1 column and HP 5890 II chromatograph. The same pattern of the thermodynamic factor (Fig. 2) is observed.

$I^T$  should be expected a priori, considering that the square of this ratio affects  $t_M(T)$  [see Eq. (2)].

The variation of  $p_i$  indicated in Figs. 6 and 7 is the maximum allowed by the chromatograph employed in the experiments (maximum indicated  $p_i = 30$  p.s.i.g. = 2311 Torr abs.; 1 Torr = 133.322 Pa). Some difficulties in the manual injection at the higher pressures were encountered, due to transient depressions caused by “blows” during septum puncture. These transient pressure fluctuations were only detected in the mercury column manometer.

## 5. Discussion

### 5.1. Thermodynamic considerations

From the exposed issues in the preceding sections, we must conclude that a decrease is expected in the

reproducibility of  $I_x^T$  when the discrepancy is greater in the profiles of the separation functions  $I_{x,n}$  and  $I_{n+1,n}$ . This discrepancy is the direct consequence of the different temperature dependence of  $\Delta G(T)$  for the analyte  $x$ , with respect to the  $n$ -alkanes. When lower is the variation of  $[\ln k$  versus  $1/T]$  (or  $-\Delta G/RT$  versus  $1/T$ ) of the analyte with respect to the  $n$ -alkanes, greater will be the profile differences between  $I_{x,n}$  and  $I_{n+1,n}$ . If  $x$  and  $n$  have different temperature dependencies of  $\Delta G$  and a low separation, the crossing-over occurs. In this case the coelution temperature  $T_{ce}$  may lie in the temperature elution-interval  $[T_0, T_{R_n}]$ . A close value of  $\Delta G$ , in conjunction with different temperature dependencies, implies that the structural properties of  $x$  and  $n$  should be quite different.

Due to the fact that the translational and the internal partition functions of a molecule are rigorously separable in classical statistical thermody-

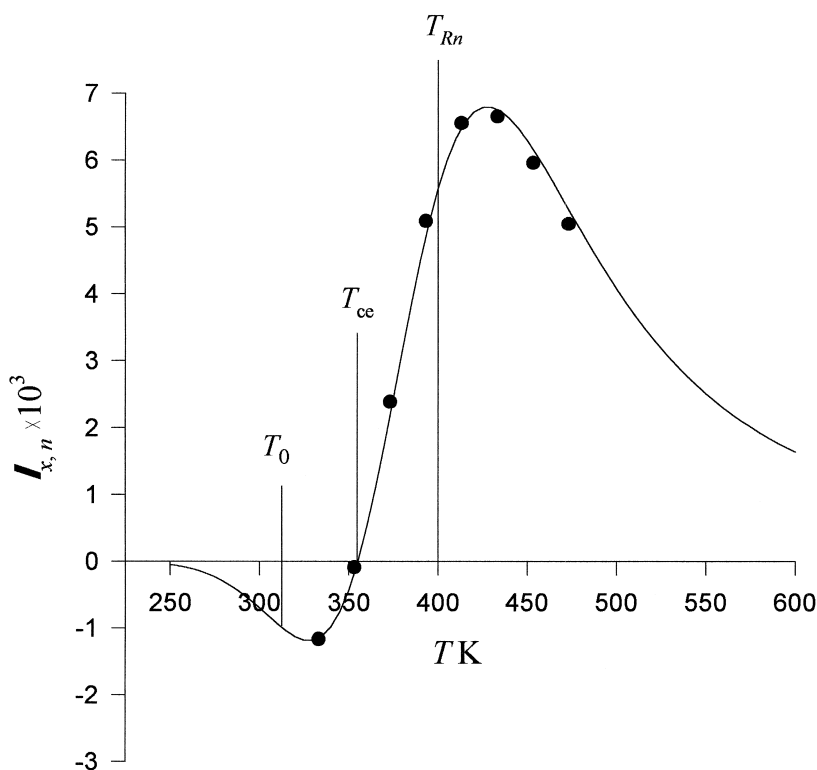


Fig. 4. Isothermal separation function  $I_{x,n}$  for the crossing pair *sec.*-butylbenzene/*n*-decane. Filled circles are the experimental values obtained from  $t_R$  measured with the column HP1, 50 m, and the chromatograph HP 5880 A. The continuous line is the theoretical curve calculated as in Ref. [62].  $T_0=313$  K indicates the initial temperature for all programs in the measurement of data for Figs. 5–7. The retention temperature  $T_{Rn}$  of *n*-decane corresponds to a very low  $p_i$ , so the scanned positive area under the curve is greater than the negative.

namics,  $\Delta G$  may be viewed as being basically the sum of two contributions [83–86]:

$$-\frac{\Delta G}{RT} \approx -\frac{E_i}{2kT} + \ln \frac{{}^L q_{r,v}}{{}^G q_{r,v}} \quad (16)$$

The first term on the right-hand side is the energy of interaction with the stationary phase assuming the solute molecule as a rigid interacting particle. This term concerns only the three translational degrees of freedom of the molecule assimilated to a spherical particle. The second term contains the ratio of the molecular internal partition functions in the liquid  ${}^L q_{r,v}$  and in the gas phase,  ${}^G q_{r,v}$ . This term involves the internal degrees of freedom of the molecule, rotational and vibrational; introducing an additional dependence with  $1/T$  to the one correspondent to the

rigid particle. These two contributions have different temperature dependencies and relative importance according to the nature of the solvent. In the case of *n*-alkanes both are linear functions of the carbon number  $n$  [87].

The remarkable characteristic of the *n*-alkanes linear flexible molecule is the great incidence of its  $(3n-5)$  internal degrees of freedom contributing to  $\ln({}^L q_{r,v}/{}^G q_{r,v})$  [57]. For the same carbon number  $n$ , it is expected that as the number of degrees of freedom of the molecule is reduced from the linear alkanes (by branching, cycle formation or double bonding), the contribution of  $\ln({}^L q_{r,v}/{}^G q_{r,v})$  will be reduced. As a consequence, the dependence of  $-\Delta G/RT$  with  $1/T$  will be lowered with respect to that of the linear alkanes. The extreme case of internal degrees of freedom reduction is found in the

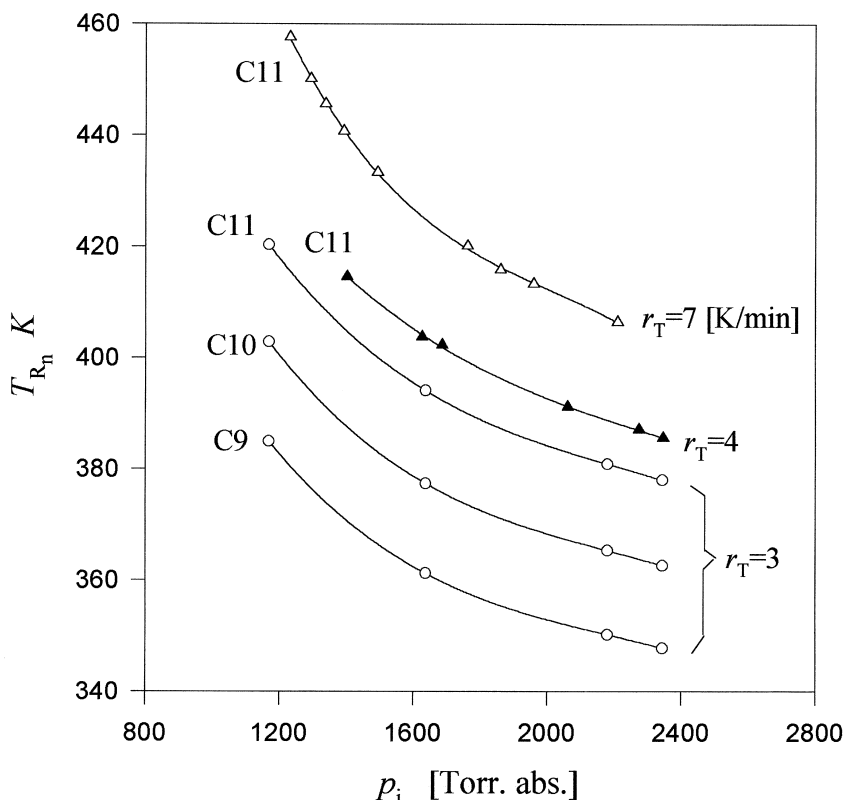


Fig. 5. The effect on  $T_{R_n}$  of increasing  $p_i$ . All the other variable parameters are constant. It is also shown the effect of the heating rate.

example of polynuclear aromatic substances. They constitute semi-rigid molecules. The GC manifestation of these molecular structural differences is that aromatic compounds are crossing solutes of the  $n$ -alkanes, although  $T_{ce}$  might not lie in the elution interval. The curvature of  $\ln k$  versus  $1/T$  is lower for aromatic substances, presenting smaller values of  $\Delta C_p$  [62], as they have fewer vibrational degrees of freedom. These are the basic reasons why the aromatic solutes yield the worst  $I^T$  reproducibility in non-polar capillary columns [36,75].

The early notable work by Ettre and Billeb [88] is adequate for illustrating the effect of reduction in the number of internal degrees of freedom in a sequence of solute molecules. The more gentle the slope in a plot  $\ln k$  versus  $1/T$ , with respect to the  $n$ -alkanes, the steeper is the  $I$  versus  $T$  curve. From Figs. 2, 3 and 4 in Ref. [88] it can clearly be seen how, for a given carbon number, the slope of  $I(T)$  increases according to:

$n$ -alkanes < increasing degree of branching  
< aliphatic cycles < aromatic

This is the theoretically expected sequence of decreasing  $I^T$  reproducibility when only  $(T_0, r_T)$  are standardized, sequence that has been partially observed by White et al. [75].

In the only case in which the isothermal separation functions will preserve the same pattern for  $(x, n)$  and  $(n+1, n)$  is when the analyte and the reference possess the same structural properties. This situation will provide the most advantageous condition for the reproducibility of  $I^T$  [79–81], although this will never be as precise as  $I$ .

## 5.2. Considerations on the $I^T$ accuracy

The information contained in the retention indices relies enclosed in the ratios of  $\log t'_R$ , in Eq. (1), and in the ratio of  $T_R$  values in Eq. (4). The numbers



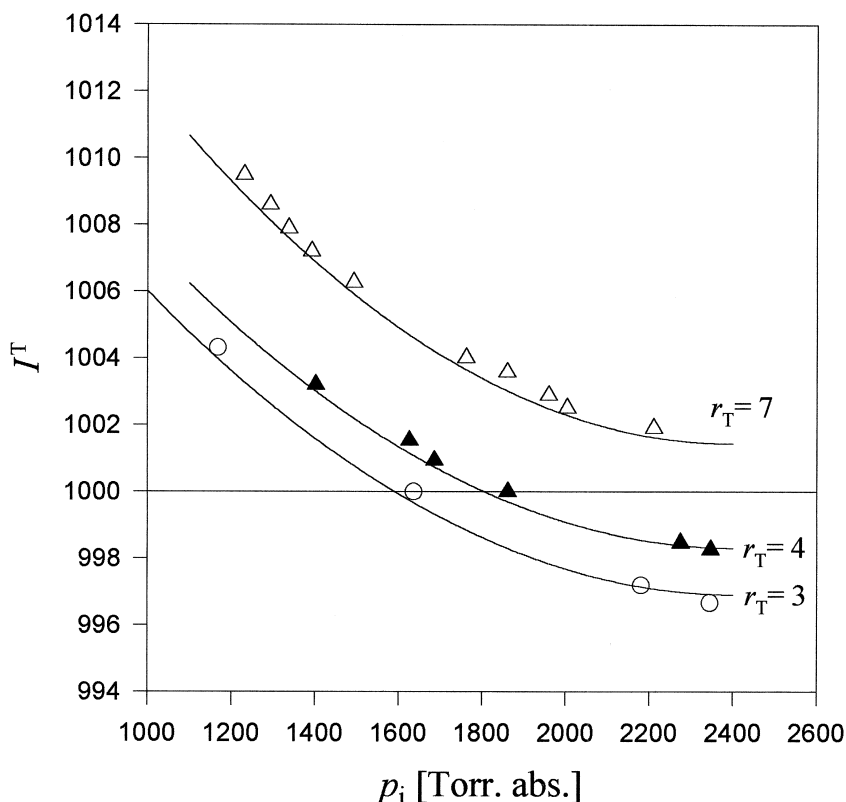


Fig. 6. The effect of increasing  $p_i$  on  $I^T$ . This was measured with the column HP1, 50 m, and the HP 5880A chromatograph. All other variable parameters are constant. Also the effect of increasing the heating rate is shown. Filled lines are theoretical curves [Eqs. (11), (2), (15)].

(100,  $n$ ) do not provide any retention information, beside  $n$  denoting the identity of the reference alkane. Current capillary GC at least renders four significant digits for the retention times. For example, if  $I^T = 1023 \pm 4.87$  is reported for limonene in inter-laboratory determinations on poly(dimethylsiloxane) columns [36], this means that it is actually informed  $1023.00 \pm 4.87$ . In this example the reported standard deviation concerning  $I^T$  is 0.48%. But in terms of retention information, that contained in the second term of Eq. (4), this corresponds to a standard deviation of 21.2%, which clearly contrasts with the former form of report. In the case of naphthalene<sup>4</sup> the inter-laboratory standard deviation

<sup>4</sup>Naphtalene has a retention reversal with  $n$ -dodecane in poly(dimethylsiloxane) stationary phases. The coelution temperature is  $T_{ce} = 448.5$  K. This usually falls out of the TPGC elution interval [62].

is 19.1% in terms of retention ratios [36]. Of course,  $\delta I^T$  in two chromatographic conditions is mainly systematic if only  $(T_0, r_T)$  are standardized, and should not be treated statistically reporting values of inter-laboratory standard deviations. For example, for naphthalene in two columns from the same manufacturer (DB-1), same  $d_c$  and  $\beta$ , is reported the difference  $\delta I^T = 23$  units [36]. The reason for this discrepancy immediately arises from the comparison of the column length difference:  $L = 30$  and 60 m. The fact that the square of  $L/d_c$  affects  $t_M(T)$  (Eq. (2)), and this in turn affects the extension of the temperature elution-interval  $[T_0, T_{R_n}]$  (Eq. (15)), is the basis for this variation of  $I^T$ , not random events.

In a complex mixture, the elution of more than one solute may be comprised in an interval of about 10 units of  $I^T$ . The question to immediately raise is what is the utility of  $I^T$  in these conditions if the

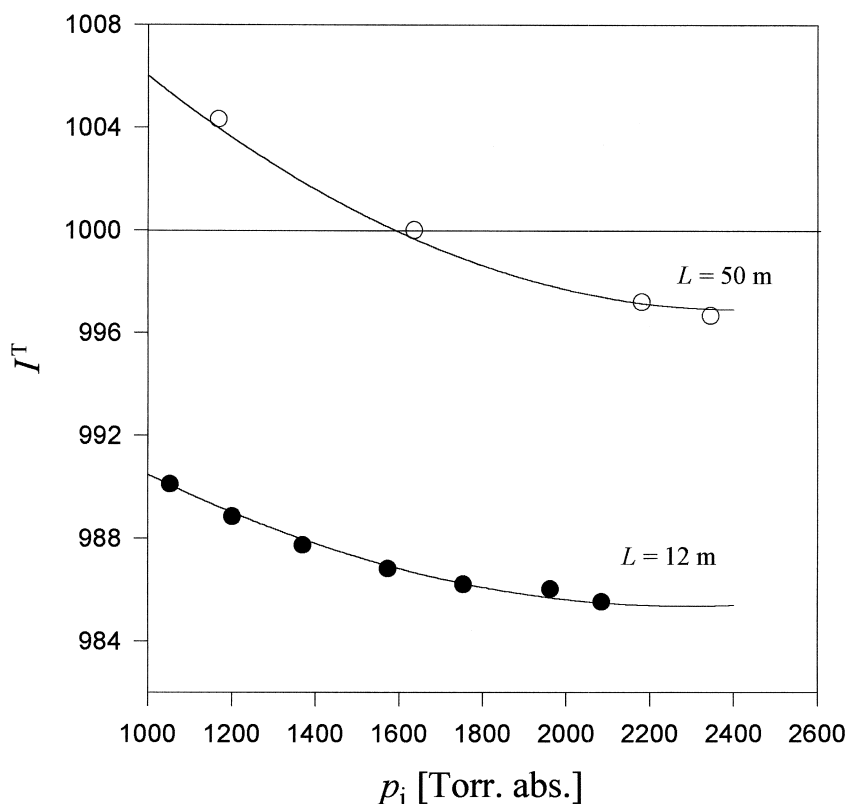


Fig. 7. Effect on  $I^T$  by the modification of the parameter  $L/d_c$ . Symbols are experimental results obtained in two HP1 columns bearing the same specifications, with the exception of  $L$ . The initial temperature and heating rate are respectively:  $T_0=313$  K and  $r_T=3$  K/min. Continuous lines are the theoretical calculations.

reproducibility is of this order? In a simple mixture this may not be a major problem, but it would be of little help for oil fractions containing a myriad of aliphatic and aromatic compounds.

### 5.3. The $I^T$ standardization problem

Presently, the simplest standardization parameter presenting a theoretical basis is the one proposed by Sun [34],  $S=r_T t_M/\beta$ . In addition, this requires the standardization of the initial temperature of the program  $T_0$  and the flow control system, namely the standardization of the  $t_M(T)$  function. The dependence of  $S$  with  $\beta$  is not the one exactly yielding a constant temperature elution-interval  $[T_0, T_R]$  for different columns [see Eq. (11)]. Also it is expected to be inadequate for low retained solutes. However,  $S$  undertakes the factors that should be standardized,

providing an approximate relationship. Although it was proposed at the beginning of this decade, it was not adopted in some recent compilations of  $I^T$  [36]. In the following example this parameter is utilized to show how certain standardization conditions may be inadequate for other columns. Suppose that  $I^T$  for a fraction of hydrocarbons in the range of  $C_{14}-C_{18}$  is reported in the following conditions: column of PDMS  $100\text{ m}\times 0.25\text{ mm}$ ,  $0.5\text{ }\mu\text{m}$ , initial  $t_M=6$  min,  $r_T=2$  K/min, i.e.  $S\sim 0.1$  K. Another laboratory intends to apply the report to a column with specifications  $25\text{ m}\times 0.25\text{ mm}$ ,  $0.2\text{ }\mu\text{m}$ , which in normal conditions presents an initial  $t_M$  in the order of 1.4 min. One possibility is to select the heating rate required to match the standard condition:  $r_T=22.3$  K/min. But this implies a condition in which thermal gradients along the oven are steeply increased, so a departure from thermal equilibrium is likely occur-

ring [89,90]. Another possibility is to reduce  $r_T$  to 10 K/min by increasing the initial  $t_M$  to 3 min, so increasing the peak dispersion. Therefore, the laboratory is compelled to use conditions that are not adequate for its column. Moreover, columns with higher  $\beta$  are excluded from the application of the  $I^T$  report.

The main problem of a standardization of the temperature elution interval  $[T_0, T_R]$  is that excludes the possibility of making optimizations of the temperature program with the aim to improve the specific separation of critical pairs in a given mixture. As can be observed in Fig. 3 and Fig. 4 the separation functions of close eluting pairs present maximums. The area under the separation function  $I_{x,y}$ , comprising the interval  $[T_0, T_{Ry}]$ , is proportional to the final separation of  $x$  and  $y$  [see Eq. (13)]. Thus, the optimization of the separation of a critical pair ( $x, y$ ) implies selecting the maximum area under  $I_{x,y}$  in the shortest interval of  $T$  possible (shortest analysis time). Namely,  $[T_0, T_{Ry}]$  has to be located right under the maximum of the  $I_{x,y}$  function. This is not possible if the location of  $[T_0, T_{Ry}]$  is already fixed by standardization.

#### 5.4. Why a thermodynamic meaningful $I^T$ is not possible

In isothermal chromatography the integration of the differential equation of peak motion, Eq. (5), yields an explicit expression for the retention:  $t_R = t_M(1+k)$ , depending parametrically on the fluid dynamic factor. Therefore, by means of an appropriate relationship of retention values, like  $I$ , the influence of the fluid dynamic parameter  $t_M(L/d_c, p_i, p_o, \eta)$  can be eliminated, as well as the parameter  $\beta$  from  $k$ . Instead, in TPGC the integration of the equation of peak motion renders an implicit function, Eq. (11). For linear TPGC this can be written in the general implicit form:  $[r_T/(T_{R_x} - T_0)] - t_{R_x}^{-1} = 0$ . The average reciprocal isothermal retention time  $t_{R_x}^{-1}$  in the interval  $[T_0, T_{R_x}]$  is a summation of the product of two functions, the fluid dynamic factor  $1/t_M(T)$  and the thermodynamic  $1/[1+k_x(T)]$ . It is also a function of the initial values of the program ( $T_0, p_i^0$ ) and the retention  $T_{R_x}$  itself. In correspondence to the nature of the process, there are no mathematical

means allowing an explicit expression of the retention as function of both factors. In other words, there is no way to express the TPGC retention ( $T_{R_x}$  or  $t_{R_x}^T$ ) as an explicit function, for example of  $I$  or  $\Delta G$ . Consequently, the fluid dynamic factor and  $\beta$  cannot be eliminated through a relationship of retention values. We must conclude that any  $I^T$  defined as a relationship of programmed temperature retention will invariably depend on  $r_T, L/d_c, p_i(T), p_o, \eta(T), \beta$  and the initial values  $T_0$  and  $p_i^0$ . Thus, any empirical correlation of  $I^T$  as function of thermodynamic parameters, or structural factors, is only valid in the specific condition in which it is determined.

## 6. Conclusions

In gas chromatography the decisive factor allowing the separation of mixtures into its components is the chemical composition of the stationary phase. This defines the solute–solvent thermodynamic interactions. One basic issue is how the information concerning these interactions is reported for general use between laboratories, taking advantage of the experimental efforts in the most efficient form possible. The potential utility of a compilation of gas chromatographic data depends on the nature of the reported information. Relative to this question, the conclusions of this article derive from the comparison of two conceptions here reviewed, the retention index approach and the thermodynamic approach.

Presently, it is not possible to define a purely thermodynamic  $I^T$  in terms of TPGC retention relationships. Therefore,  $I^T$  depends also on the fluid dynamic history of the TPGC elution process and the phase ratio of the employed columns. For this reason, when  $I^T$  is reported, also a series of complementary data concerning the applied conditions and standardization parameters ought to be informed. One example could be the initial temperature of the program  $T_0$ , the flow control system of the carrier gas and Sun's standardization parameter  $r_T t_M / \beta$ . In this context, the report of  $I^T$  will provide information on the elution pattern of the analytes only in the specific standard condition. No reliable correlation of

$I^T$  to the molecular structure is possible. This information does not allow the possibility of making specific optimizations of the temperature program for the particular critical pairs contained in the injected mixture. The application of the information to multi-step programs is excluded.

On the other side, the relevant information shared in the context of the thermodynamic approach is thermodynamic. Presently, for non-polar systems, this should be done through the report of a set of three parameters [ $\Delta H(T^0)$ ,  $\Delta S(T^0)$ ,  $\Delta C_p$ ]. These provide direct information on the elution pattern, as well as the possible alteration of this pattern by retention reversals. The feasibility of such events can be established by the direct comparison of  $\Delta C_p$  values. By using this information and applying the procedures of the thermodynamic approach the retention times can be predicted for any chromatographic condition, allowing the performance of specific optimizations and the utilization of multi-step programs.

The preceding comparison clearly suggests where the experimental efforts for the construction of gas chromatographic data compilations should be focused.

The important incidence of interfacial phenomena on the retention of non-polar solutes in polar stationary phases, and vice-versa, generates a problem for the determination of real bulk solution thermodynamic parameters [ $\Delta H(T^0)$ ,  $\Delta S(T^0)$ ,  $\Delta C_p$ ]. In the same way, these phenomena affect the reproducibility of  $I$  and  $I^T$ . The simple geometry of capillary columns provides the adequate means for studying interfacial effects.

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