

# Contribution to the time balance in gas–liquid chromatography New definition equations of the retention times and retention volumes<sup>☆</sup>

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Received 21 June 2001; received in revised form 13 May 2002; accepted 17 May 2002

## Abstract

The numerous research groups and researchers, as well as IUPAC, that during the last half century have dealt with different theoretical and practical problems in gas–liquid chromatography (GLC), including its nomenclature, have failed in giving an exact definition equation of the net retention time. Using our earlier results and starting from a time balance of GLC we have solved this problem by introducing the so-called acceleration time,  $t_{ac}$ , in the absence of which, the theoretical plate number concept, including the stationary phase transfer, is misinterpreted. The measurements were carried out both on support coated and on wall-coated open tubular columns with apolar and polar stationary phases. Different relationships of  $t_{ac}$  with some solute properties and the column temperature for a series of  $n$ -alkanes on an apolar stationary phase under isothermal conditions were tested. The results obtained are presented in different tables and mathematical relationships. Published by Elsevier Science B.V.

**Keywords:** Gas chromatography; Retention times; Retention volumes; Alkanes

## 1. Introduction

The exact definition equation for the net retention time [1–4] has been hitherto missing [4]. The reason for this fact was a preceding formulation of the physico–chemical meaning of this term where the compressibility factor  $j$  according to James and Martin [5]:

$$j_2^3 = \frac{3}{2} \cdot \frac{(p_i/p_0)^2 - 1}{(p_i/p_0)^3 - 1} \quad (1)$$

appears multiplying the adjusted retention time [10]:

$$t_N = \frac{V_N}{F_c} = j t'_R \quad (2)$$

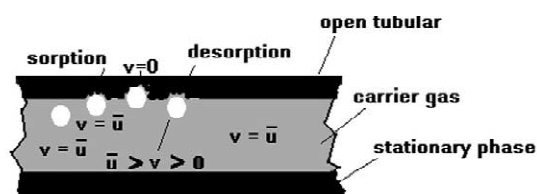
Davankov [6] rejected this assumption because  $j$  only corrects retention volumes, not retention times [7].

We have found that the molecules examined are accelerated after their desorption to the velocity of

<sup>☆</sup>Dedicated to the memory of Professor José A. García-Domínguez for his notable contribution to GLC nomenclature.

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the velocity values of one molecule examined under one phase transfer (on one "theoretical plate")

Fig. 1. The velocity values of one molecule examined under one phase transfer (on one "theoretical plate").

the carrier gas applied in the gas phase of the column used under each theoretical plate (Fig. 1). Researchers have neglected this time, the so-called acceleration time,  $t_{ac}$ , leading thereby to errors in the definition equation of the net retention time, in the net retention volume, and in specific retention values. Using our earlier results obtained in the field of programmed carrier gas flow [8,9], an acceleration time,  $t_{ac}$ , is defined, a new definition of the net retention time, based on a time balance of the gas–liquid chromatography (GLC) process is given, and a new concept of effective net retention time, and, subsequently, a new concept of retention volume are introduced. A series of empirical equations inspired in the refinements of Costa Neto et al. [10] on Van Deemter's equation, involving solute physico–chemical properties and carbon atom number for  $n$ -alkanes, were tested in order to evaluate  $t_{ac}$ .

## 2. Theory

The examination of gas chromatographic processes is unsuccessful if an analysis of the retention time is not carried out. For example, the substance examined stays initially in the stationary phase used with zero velocity, since the diffusion coefficient of the mentioned analyte through the stationary phase at the column temperature is generally very low, say  $1.0 \cdot 10^{-6} - 1.0 \cdot 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ , and therefore the longitudinal diffusion in the stationary phase is usually negligible. The  $i$ th segment of the residence time of the analyte in the stationary phase equals the  $i$ th segment of the net retention time, where  $i$  is a serial number. So the molecules examined after they are

desorbed from the stationary phase to the mobile gas are accelerated until reaching the speed of the carrier gas that flows through the applied column. During the last 50 years this time of acceleration of the analyte molecules, the so-called acceleration time,  $t_{ac}$ , has been neglected by the theoretical chromatographers, which has produced problems in the definition of the net retention time,  $t_N$  [1–4], which is not identical to the adjusted retention time, but is only related to the net retention volume according to Eq. (2). This problem has led to Davankov's criticism [6] and to the last IUPAC recommendations [11] that the net retention time concept be given up. However, in this work an effective net retention time is defined.

### 2.1. New retention time definition. Time balance in a GLC process

Starting from the time balance of the gas–liquid chromatography process, we have introduced a new term ( $t_{ac}$ ) to describe the sum of the time segments of the accelerations that take place after the desorptions. This term also includes the time of the occasional diffusion in the gas phase (it should be noted that the diffusion coefficient of the substance examined in the carrier gas at constant column temperature depends on the carrier gas average pressure and on the nature of the substance studied, its value being usually  $0.01 - 1.00 \text{ cm}^2 \text{ s}^{-1}$ ). Furthermore, the theoretical plate number concept, comprising the phase transfers, is misinterpreted if  $t_{ac}$  is neglected. The equation for the total retention time of a component of the sample introduced in a chromatograph under isothermal conditions is:

$$t_R = t_{in} + t_v + t_a + t_d + t_G + t_N^{eff} + t_{ac} + t_{de} \quad (3)$$

where  $t_{in}$  is the actual time of sample introduction;  $t_v$ , the time of evaporation of the sample ( $t_v = 0$  if gas or vapor samples are introduced);  $t_a$ , the time it takes for the sample to be accelerated to the actual velocity of the carrier gas;  $t_d$ , the time it takes the solute vapor or gas component to travel through the volumes of the connecting lines and fittings (it can properly be called real "dead volume", and it does not play any role in the gas chromatographic process);  $t_G$ , the time during which the solute vapor or

gas probe is passing through the free gas volume of the column used with the actual velocity of the carrier gas:

$$t_G = \sum_{i=1}^N t_G(i) \tag{4}$$

where the time under the  $\Sigma$  is the  $i$ th segment of the transit time through the free gas volume of the column used.  $N$  is the theoretical plate number of the column, i.e., the number of the phase transfers in the gas–liquid chromatographic process. It should be noted that  $t_G(i) \neq t_G(i+1)$ , where  $i$  is a serial number, and that the sum of the  $t_G$  increments is not equivalent to  $Nt_G(i)$ .  $t_N^{\text{eff}}$  is the effective net retention time spent by the solute vapor or gas component in the stationary phase;  $t_{ac}(i)$  is the time segment necessary for the solute acceleration after the desorptions including the time of the occasional diffusion into the gas phase, and  $t_{de}$  is the time elapsed in the production of the detector response.

The effective net retention time  $t_N^{\text{eff}}$  can be expressed as:

$$t_N^{\text{eff}} = \sum_{i=1}^N t_N^{\text{eff}}(i) \tag{5}$$

where the time under the  $\Sigma$  is the  $i$ th segment of the real net retention time. It should be noted that  $t_N^{\text{eff}}(i) \neq t_N^{\text{eff}}(i+1)$  and that the sum of the  $t_N$  increments is not equivalent to  $Nt_N^{\text{eff}}$ . Similarly:

$$t_{ac} = \sum_{i=1}^N t_{ac}(i) \tag{6}$$

where the time under the  $\Sigma$  is the  $i$ th segment of the acceleration time after the  $i$ th desorption. Also it should be noted that  $t_{ac} \neq t_{ac}(i+1)$ , and that the sum of the  $t_{ac}$  increments is not equivalent to  $Nt_{ac}(i)$ .

The hold-up time,  $t_M$ , for an unretained substance is given by:

$$t_M = t_{in} + t_a + t_d + t_G + t_{de} \tag{7}$$

Subtracting Eq. (7) from Eq. (3) we obtain the adjusted retention time:

$$t'_R = t_R - t_M = t_v + t_N^{\text{eff}} + t_{ac} \tag{8}$$

Obviously, the central term (adjusted or classical

retention time) is larger than the effective net retention time, i.e.,  $t'_R > t_N^{\text{eff}}$ .

### 2.2. The acceleration time

We can calculate the term  $t_{ac}$  from the time of the “surge effects”,  $t_{se}$  [12–14], and the width of the peak on the baseline ( $w_b$ ), respectively. Bearing in mind the relationship between  $w_b$  and the width at half height,  $w_h$ :

$$w_b = \left( \frac{2}{\sqrt{2 \ln 2}} \right) \cdot w_h \tag{9}$$

we will have:

$$t_{ac} = w_b - t_{se} = \frac{2}{\sqrt{2 \ln 2}} \cdot w_h - t_{se} \tag{10}$$

where  $t_{se}$  is the so-called time of the “surge effects” [12–14]. The name obeys to the appearance of one component of the introduced sample on the end of the column used:

$$t_{se} = (v_s / jF_c) \tag{11}$$

where  $v_s$  is the volume of the component examined of the sample introduced, in  $\text{cm}^3$ , at the column temperature, actual carrier gas pressure, kPa, and at the actual carrier gas flow-rate,  $jF_c$ , at the end of the column used. All the times are measured in seconds.

Based in our earlier results [8,9] we can write the following equation for  $t_{ac}$  at constant temperature, using the relationship between  $w_h$  and the average linear velocity of the carrier gas given by Costa Neto et al. [10]:

$$t_{ac} = \frac{2}{\sqrt{2 \ln 2}} \cdot \left[ \frac{a}{(\bar{u})^2} + \frac{b}{\bar{u}} + c \right] - t_{se} \tag{12}$$

where  $a$ ,  $b$  and  $c$  are solute constants ( $a$  in  $\text{cm}^2 \text{s}^{-1}$ ,  $b$  in  $\text{cm}$  and  $c$  in  $\text{s}$ ), and  $\bar{u}$ , average linear velocity of the carrier gas ( $\text{cm s}^{-1}$ ).

Therefore, the new definition equation of the effective net retention time if the sample is in the liquid phase is:

$$t_N^{\text{eff}} = t'_R - t_{ac} - t_v \tag{13}$$

and if the sample is in the gas or vapor phase:

$$t_N^{\text{eff}} = t'_R - t_{ac} \tag{14}$$

and, subsequently, the new equations for the effective net retention volumes and specific retention volumes are, respectively:

$$V_N^{\text{eff}} = jF_c t_N^{\text{eff}} \quad (15)$$

Eqs. (13)–(15) are correct for the net retention times and volumes according to the effective gas chromatographic processes.

Furthermore, the effective specific retention volumes are given by:

$$V_g^{\text{eff}} = \frac{V_N^{\text{eff}}}{W_S} \quad (16)$$

### 3. Experimental

Table 1 summarizes the gas chromatographs, detectors, column characteristics, supports, and other work conditions under which experiments were carried out.

Supports were obtained from Johns Manville and Supelco. Packings and other gas chromatographic

accessories were supplied by Supelco and Hewlett-Packard. Argon, helium, nitrogen and hydrogen were supplied by Oxygen and Dissous Gas Factory, Budapest.

The experiments were carried out under isothermal conditions, with column temperature deviations of about  $\pm 0.1$  °C. Temperature values were checked by an original Hewlett-Packard and special thermistor-system by computer. Syringes from Hamilton (he Netherlands) and SGE (Australia) were applied for liquid sample introduction. A Vectra Hewlett-Packard computer was used for the calculations.

### 4. Results and discussion

#### 4.1. Calculations

We show only two examples. First, the calculation for *n*-octane on OV-1 in the wall-coated open tubular (WCOT) column under the following conditions:  $T=90$  °C,  $\beta=125$ ,  $jF_c=0.46$  cm<sup>3</sup> min<sup>-1</sup>,  $W_S=0.0084$  g,  $p_i=2.53$  Kp cm<sup>-2</sup>,  $t_v=0.2$  s,  $w_h=1.2$  s,

Table 1  
Chromatographic columns and operating variables used in this work

	Gas chromatograph				
	PE F6/4F	HP-5890	HP-5880/2	HP-5880/2	PE-900
Detection	FID	FID	FID	FID	FID
Attenuation	$1 \cdot 10^{-9}$	$1 \cdot 10^{-9}$	$1 \cdot 10^{-9}$	$1 \cdot 10^{-9}$	$1 \cdot 10^{-9}$
Detector temperature (°C)	250±1	250±1	250±0.5	250±0.5	250±0.5
Vaporizator temperature (°C)	250±1	250±1	250±0.5	250±0.5	250±0.5
Sample amount	1.0 µl	1.0 µl	1.0 µl	1.0 µl	1.0 µl
Column material	Steel	Fused silica	Fused silica	Fused silica	Glass
Column type	Packed	WCOT	WCOT	WCOT	WCOT
Column parameters					
<i>L</i> (m)	2.0	50	25	25	25
I.D. (mm)	3.0	0.20	0.20	0.32	0.25
<i>d<sub>r</sub></i> (µm)	–	0.50	0.50	0.52	0.55
Support: Chromosorb R AW DMCS,	60–80 mesh				
Stationary phase	DC-200 10%	Petrocol DH	OV-1	HP-Ultra #1	Apiezon L (treated)
Column temperature	100–170 °C	90–130 °C	90–130 °C	120±0.05 °C	70–130 °C
Carrier gas	Argon	Helium	Helium	Helium	Helium
Inlet pressure (kp cm <sup>-2</sup> )	$2.00 < p_i < 2.75$	$1.85 < p_i < 2.52$	$1.85 < p_i < 2.82$	$1.85 < p_i < 2.97$	$1.75 < p_i < 2.62$
Flow-rate (cm <sup>3</sup> min <sup>-1</sup> )	20.0–55.0	0.3–1.2	0.1–52	0.52	0.3–15.2
Auxiliary gases	Hydrogen	Hydrogen	Hydrogen	Hydrogen	Hydrogen
Flow-rate (cm <sup>3</sup> min <sup>-1</sup> )	25.0	21.4	23.7	24.0	25.1
Air (cm <sup>3</sup> min <sup>-1</sup> )	322.0	367.0	372.0	372.0	347.0

FID=Flame ionization detection.

$w_b = 2w_h / \sqrt{2 \ln 2} = 2.038$  s,  $t_R = 256.7$  s, and  $t_M = 103.2$  s. So  $t'_R = 153.5$  s = 2.558 min.  $V_N = 0.46 \cdot 2.558 = 1.18$  cm<sup>3</sup>, and  $V_g = 1.18 / 0.0084 = 140.48$  cm<sup>3</sup> g<sup>-1</sup>.

The effective net retention time is calculated as:  $t_N^{\text{eff}} = 153.5 - 1.8 - 0.2 = 151.5$  s.  $V_N^{\text{eff}} = 0.46 \cdot 151.5 / 60 = 1.16$  cm<sup>3</sup> and  $V_g^{\text{eff}} = 1.16 / 0.0084 = 138.09$  cm<sup>3</sup> g<sup>-1</sup>.

In the second place, calculations of retention times and volumes of *n*-heptane on a WCOT Supelco Petrocol DH apolar column (see Table 1) at  $T = 60.0$  °C are carried out. The chromatographic variables are:  $p^0 = 210.24$  Torr (1 Torr = 133.322 Pa),  $W_s = 0.0153$  g,  $\beta = 125$ ,  $jF_c = 0.46$  cm<sup>3</sup> min<sup>-1</sup> of helium;  $p_i = 2.52$  Kp cm<sup>-2</sup>, and  $j = 0.53581$ .

The chosen model solute *n*-heptane was first injected from a *n*-alkane mixture, for which the sum of the times of evaporation under conditions of dynamical equilibrium was 3.90 s (0.065 min). The measured retention times for *n*-heptane were:  $t_R = 8.885$  min,  $t_M = 3.447$  min, and therefore  $t'_R = 5.438$  min.  $w_h = 2.43$  s =  $4.05 \cdot 10^{-2}$  min. The calculations of the classical retention times and volumes:  $V_N = jF_c t'_R = 0.46 \cdot 5.438 = 2.50$  cm<sup>3</sup>, and  $V_g = 2.50 / 0.0153 = 163.4$  cm<sup>3</sup> g<sup>-1</sup>.  $t_N^{\text{eff}} = t'_R - t_{\text{ac}} - t_V = 5.438 - 0.0405 - 0.065 = 5.332$  min, and  $V_N^{\text{eff}} = 0.46 \cdot 5.332 = 2.45$  cm<sup>3</sup>, therefore,  $V_g^{\text{eff}} = V_N^{\text{eff}} / W = 2.45 / 0.0153 = 160.1$  cm<sup>3</sup> g<sup>-1</sup>.

The classical and effective retention times and retention volumes, and their deviations and relative errors are gathered in Table 2.

We can determine the  $t_v$  value of the analytes introducing the same substance, under identical gas chromatographic parameters, in liquid phase and in vapor phase, respectively. For example, the  $t_v$  value of *n*-nonane was about 0.1 s, practically equal to the intrinsic error of the introduction.

#### 4.2. Results

We present our new results in some relationships and in tables where some calculated values are compared with measured data.

Table 3 shows the compared values of classical and effective net retention volumes of *n*-alkanes on the packed column described in Table 1 at 100–160 °C. Reasonable agreement between the two values is found in all cases. Except for 100 °C,  $V_N > V_N^{\text{eff}}$ . Relative errors,  $\epsilon\%$ , range between 0.3 and 3.0 (100 °C), 2.1 and 2.6 (120 °C), 5.4 and 6.6 (140 °C), and 3.5 and 5.4 (160 °C).

At constant  $jF_c$  the  $t_{\text{ac}}$  value temperature dependence has been calculated by computer with the expression:

$$t_{\text{ac}} = \frac{a_1 + a_2 T}{1 + a_3 T} \quad (17)$$

where  $a_1$  (s),  $a_2$  (s K<sup>-1</sup>) and  $a_3$  (K<sup>-1</sup>) are constants for each substance. Table 4 summarizes the results of applying Eq. (17) for some *n*-alkanes on OV-1.

Table 2  
Classical and effective retention data values for two *n*-alkanes on Petrocol DH

Retention magnitude	Classical value	Effective value	Absolute error, $\delta^a$	Relative error, $\epsilon\%^b$
<i>n</i> -Octane				
$T = 90$ °C				
$t_N$ (s)	153.5	151.5	2.0	1.3
$V_N$ (cm <sup>3</sup> )	1.18	1.16	0.02	1.7
$V_g$ (cm <sup>3</sup> g <sup>-1</sup> )	140.5	138.1	2.4	1.7
<i>n</i> -Heptane				
$T = 60$ °C				
$t_N$ (s)	326.3	319.9	6.4	1.9
$V_N$ (cm <sup>3</sup> )	2.50	2.45	0.05	2.0
$V_g$ (cm <sup>3</sup> g <sup>-1</sup> )	163.4	160.1	3.3	2.0

<sup>a</sup>  $\delta$  = Classical value minus effective value.

<sup>b</sup>  $\epsilon\% = (1/100)[\delta/\text{classical value}]$ .

Table 3

Classical ( $V_N$ ) and effective ( $V_N^{\text{eff}}$ ) net retention volumes of *n*-alkanes on DC-200 (see Table 1) at several temperatures

Compound	Temperature (°C)											
	100			120			140			160		
	$V_N$	$V_N^{\text{eff}}$	$\delta$	$V_N$	$V_N^{\text{eff}}$	$\delta$	$V_N$	$V_N^{\text{eff}}$	$\delta$	$V_N$	$V_N^{\text{eff}}$	$\delta$
<i>n</i> -Heptane	37.6	37.4	0.2	35.0	34.1	0.9	28.9	27.0	1.9	–	–	–
<i>n</i> -Octane	68.7	68.2	0.5	61.4	59.8	1.6	47.5	44.7	2.8	–	–	–
<i>n</i> -Nonane	126.7	126.3	0.4	107.8	105.1	2.7	77.9	73.7	4.2	29.5	27.9	1.6
<i>n</i> -Decane	235.3	237.2	–1.9	189.2	184.8	4.4	128.4	121.2	7.2	53.3	51.1	2.2
<i>n</i> -Undecane	440.2	447.4	–7.2	332.2	324.8	7.4	211.8	200.1	11.7	91.9	88.2	3.7
<i>n</i> -Dodecane	829.3	854.4	–25.1	583.6	571.4	12.1	349.9	330.3	19.6	155.1	149.7	5.4

$$\delta = V_N - V_N^{\text{eff}}$$

Table 4

Temperature dependence of the acceleration time (s) of *n*-alkanes on OV-1 at constant flow-rate of 0.46 cm<sup>3</sup> min<sup>–1</sup>

Compound	Temperature (°C)				
	90	100	110	120	130
<i>n</i> -Nonane	4.08	3.30	2.80	2.32	2.11
<i>n</i> -Decane	7.14	5.60	6.79	5.26	2.94
<i>n</i> -Undecane	11.80	9.70	7.80	6.26	4.01
<i>n</i> -Dodecane	21.47	16.80	11.38	8.60	6.26
<i>n</i> -Tridecane			19.11	13.49	10.22

Using the Hewlett equation:

$$t_{\text{ac}}(n\text{-decane}) =$$

$$\frac{2}{\sqrt{2 \ln 2}} \cdot \left[ \frac{27.07}{(\bar{u})^2} + \left( \frac{79.05}{\bar{u}} + 0.11 \right) \right] - 0.20 \quad (18)$$

we have examined the relationship between the linear velocity of the carrier gas and the acceleration time ( $t_{\text{ac}}$ ) of *n*-decane on OV-1 stationary phase at 120.0 °C, comparing measured and calculated data in Table 5.

Table 5

Comparison of the measured and calculated acceleration time of *n*-decane at 120 °C for several velocities of the carrier gas

$\bar{u}$ (cm s <sup>–1</sup> )	Measured $t_{\text{ac}}$ (s)	Calculated $t_{\text{ac}}$ (s)	Absolute error, $\delta$ (s)	Relative error, ε%
9.7	14.75	14.32	0.43	2.9
15.3	9.50	8.20	0.54	5.7
25.7	5.20	5.28	–0.08	–1.5

Stationary phase: OV-1.

#### 4.2.1. Acceleration time empirical relationships

Table 6 lists the relationships between  $t_{\text{ac}}$ , the baseline peak width, solute vapor pressure, molecular volume and its multiplication product for *n*-alkanes on Apiezon L at 120 °C.

The calculated acceleration times have been fitted with Eqs. (19)–(22):

$$t_{\text{ac}}(\text{calc.}) = -4.593 - \frac{70.656}{Z - 15.308} \quad (19)$$

$$t_{\text{ac}}(\text{calc.}) = -4.802 - \frac{1181.076}{V^{\text{M}} - 282.145} \quad (20)$$

$$t_{\text{ac}}(\text{calc.}) = 2.431 - \frac{1862.848}{p^0 + 88.906} \quad (21)$$

$$t_{\text{ac}}(\text{calc.}) = 2.258 + \frac{315\,383.5}{(V^{\text{M}} p^0) + 12\,443.5} \quad (22)$$

$Z$ ,  $p^0$  and  $V^{\text{M}}$  are given in Table 6 (see also Nomenclature).

Table 7 lists the measured and calculated  $t_{\text{ac}}$  values for *n*-alkanes on Apiezon L at 120 °C, with Eqs. (19)–(22). The squared deviations divided by the *n*-alkane number are an index of the goodness of the equations. The largest values, i.e., the worse

Table 6  
Acceleration time, baseline peak width and solute physico-chemical properties for *n*-alkanes on Apiezon L at 120 °C

Compound	$p^0$ (Torr)	$V^M$ (cm <sup>3</sup> mol <sup>-1</sup> )	$(p^0V^M)$ (Torr cm <sup>3</sup> mol <sup>-1</sup> )	$w_b$ (s)	$t_{ac}$ (s)
<i>n</i> -Octane	647.60	162.49	105 228.52	6.60	5.10
<i>n</i> -Nonane	310.87	178.64	55 533.82	7.90	6.60
<i>n</i> -Decane	151.31	194.92	29 493.35	9.60	8.70
<i>n</i> -Undecane	74.34	211.23	15 702.84	12.40	11.80
<i>n</i> -Dodecane	36.89	227.12	8378.46	17.30	16.80
<i>n</i> -Tridecane	18.25	243.88	4450.81	27.80	26.00

$p^0$ , Solute vapor pressure;  $V^M$ , solute molecular volume;  $w_b$ , baseline peak width;  $t_{ac}$ , acceleration time.

results, 7.50 and 5.0, are obtained for Eqs. (21) and (22), respectively.

Other regressions inferred from Table 6 are:

$$t_{ac}(\text{calc.}) = 99.1 - 1.121V^M + 0.0034(V^M)^2 \quad (23)$$

$$t_{ac}(\text{calc.}) = 75.03 - 51.38 \log p^0 + 9.49 (\log p^0)^2 \quad (24)$$

$$t_{ac}(\text{calc.}) = 295.7 - 117.5 \log(p^0V^M) + 11.9 \log(p^0V^M)^2 \quad (25)$$

$$t_{ac}(\text{calc.}) = 67.06 - 14.84Z + 0.895Z^2 \quad (26)$$

The correspondent correlation coefficients of these curves are:  $r^2=0.993$ ,  $0.991$ ,  $0.992$  and  $0.990$ , respectively.  $t_{ac}$  increases with increasing  $Z$  in a parabolic dependence: although  $\log(t_{ac})$  vs.  $Z$  gives a

good straight line ( $r^2=0.990$ ), the parabola yields a better fit ( $r^2=0.9995$ ).

Some of these equations are used in calculations, and a final Table 8 comparing deviations of  $t_{ac}$  evaluating the sum of squares deviations to *n*-alkanes number ratio when using Eqs. (19)–(22), and when using the corresponding parabolic ones, i.e., Eqs. (23), (25), (24) and (26), respectively, is given. Eqs. (24) and (25) yield a better performance than Eqs. (21) and (22), while Eqs. (19) and (20) yield a better performance than Eqs. (26) and (23), respectively.

## 5. Conclusions

Some corrections must be done in the definition of the net retention time, as well as, net retention volume and specific retention volume, in light of

Table 7  
Comparison of measured and calculated acceleration time(s) for *n*-alkanes on Apiezon L at 120 °C

Compound	$t_{ac}(\text{meas.})$	$t_{ac}(\text{calc.})^a$	$\delta$	$t_{ac}(\text{calc.})^b$	$\delta$	$t_{ac}(\text{calc.})^c$	$\delta$	$t_{ac}(\text{calc.})^d$	$\delta$
<i>n</i> -Octane	5.10	5.08	0.02	5.07	0.01	4.96	0.14	4.94	0.16
<i>n</i> -Nonane	6.60	6.61	-0.01	6.61	-0.01	7.09	-0.49	6.90	-0.30
<i>n</i> -Decane	8.70	8.72	-0.02	8.74	-0.04	10.19	-1.49	9.78	-1.08
<i>n</i> -Undecane	11.80	11.81	-0.01	11.85	-0.05	13.84	-2.04	13.46	-1.66
<i>n</i> -Dodecane	16.80	16.76	0.04	16.66	0.14	17.24	-0.44	17.41	-0.61
<i>n</i> -Tridecane	26.00	26.02	-0.02	26.06	-0.06	19.82	6.18	20.93	5.07
$\Sigma\delta_i^2/6$			0.0005		0.005		7.50		5.0

$\Sigma(\delta_i)^2/6$  = Arithmetic mean of the squares deviations.

<sup>a</sup> Values obtained with Eq. (19).

<sup>b</sup> Values obtained with Eq. (20).

<sup>c</sup> Values obtained with Eq. (21).

<sup>d</sup> Values obtained with Eq. (22).

Table 8

Comparison of deviations  $\delta = t_{ac}(\text{meas.}) - t_{ac}(\text{calc.})$  obtained with  $t_{ac}(\text{calc.})$  from Eqs. (19)–(22) and from a parabolic fit

Compound	Eq. (21)	Eq. (24)	Eq. (22)	Eq. (25)	Eq. (19)	Eq. (26)	Eq. (20)	Eq. (23)
<i>n</i> -Octane	0.14	−0.49	0.16	−0.47	0.03	0.05	0.02	−0.05
<i>n</i> -Nonane	−0.49	0.68	−0.30	0.66	−0.01	0.28	−0.01	0.10
<i>n</i> -Decane	−1.49	0.58	−1.08	0.58	−0.04	0.29	−0.02	0.09
<i>n</i> -Undecane	−2.04	−0.32	−1.66	−0.27	−0.05	0.08	−0.01	−0.01
<i>n</i> -Dodecane	−0.44	−0.98	−0.61	−0.99	0.14	0.06	0.04	0.04
<i>n</i> -tridecane	6.18	0.68	5.07	0.67	−0.06	0.98	−0.02	−0.02
$\Sigma \delta_i^2/6$	7.50	0.43	5.02	0.42	0.005	0.19	0.0005	0.004

criticisms of Davankov [6,16–20] and of prolonged controversy [15–26]. We have found that the molecules examined are accelerated after their desorption until reaching the velocity of the carrier gas applied in the gas phase of the column used in each theoretical plate (Fig. 1). Neglect of this so-called acceleration time leads to problems in the definition equation of the net retention time, in the theoretical plate concept and in the phase transfers.

Therefore, new concepts of effective net retention time and net retention volume are given in this work. The first is deduced from a time balance of the GLC process, resulting finally as the difference between the adjusted retention time and the acceleration time, if the sample is introduced as vapor in the chromatograph. Effective net retention time and classical (adjusted) retention time, on the one hand, and classical net retention volume and effective net retention volume, on the other hand, show deviations lower than 2%.

The acceleration time is postulated as a function of the averaged linear carrier gas velocity, and an equation for *n*-alkanes on OV-1 at 120 °C is tested.

A clear dependence of  $t_{ac}$  on temperature is observed for *n*-alkanes on OV-1 and DC-200.  $t_{ac}$  is also affected by the solute vapor pressure ( $p^0$ ), the solute molecular volume ( $V^M$ ) and the carbon atom number ( $Z$ ) for *n*-alkanes. Some equations involving these parameters are compared, in general resulting in an acceptable agreement between measured and calculated  $t_{ac}$ .

Finally, there is an interesting case: measuring the hold-up time with methane a smaller deviation has been found than that when using an inert gas as carrier gas, because the methane suffers some partition between the carrier gas and the stationary phase

used. Thus, there is an error smaller than 1% according to the values of retention volumes, if the dead time was measured with methane, as in old research work.

## 6. Nomenclature

$j$ or $j_2^3$	Factor of James and Martin
$t_N$	Net retention time
$V_N$	Net retention volume
$V_N^{\text{eff}}$	Effective net retention time
$V_g$	Specific retention volume
$V_N^{\text{eff}}$	Effective net retention volume
$V_g^{\text{eff}}$	Effective specific retention volume
$F_c$	Actual flow-rate of the carrier gas at the end of the column
$p_i$	Carrier gas inlet pressure
$p_0$	Carrier gas outlet pressure
$t_M$	Hold-up time
$t_R$	Retention time
$t'_R$	Adjusted retention time
$t_{in}$	Actual time of the sample introduction
$t_v$	Time of evaporation of the sample
$t_a$	Time of acceleration of the sample after its injection
$t_G$	Time of passing of gas probe through the free gas volume of column
$t_{ac}$	Acceleration time
$t_N^{\text{eff}}$	Effective net retention time
$t_{de}$	Time elapsed up to the detector response
$t_d$	Time of the sample in the dead volume connecting lines and fittings



$t_{se}$	Time of the “surge effects”
$N$	Theoretical plate number of a column
$w_b$	Baseline peak width
$w_h$	Half height width peak
$v_s$	Volume of the component of the sample introduced
$\bar{u}$	Average linear velocity of the carrier gas
$a, b, c$	Constants for a substance in Eq. (12)
$a_1, a_2, a_3$	Constants for a substance in Eq. (17)
$W_s$	Grams of stationary phase in the column
$\beta$	Phase ratio
$Z$	Carbon atom number for $n$ -alkanes
$p^0$	Solute partial vapor pressure for $n$ -alkanes
$V^M$	Solute molecular volume for $n$ -alkanes
$i$ th segment	A theoretical plate
$i$	Serial number

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