

The hold-up time in gas chromatography II. Validation of the estimation based on the concept of a zero carbon atoms alkane¹

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Abstract

The procedure of estimating the hold-up time in gas chromatography recently presented by Lebrón-Aguilar et al. [J. Chromatogr. A, 760 (1997) 219] as the retention of an alkane of zero carbon atoms has been exhaustively tested with packed and capillary columns of various stationary phase types, between 30 and 150°C. Several permanent gases injected have shown that there is not a general rule to decide which is the least retained gas under all circumstances. Results of hold-up times obtained with the new procedure have been compared with those of other well established methods. The conclusion arrived at is that the retention of an *n*-alkane of *n* carbon atoms is best described by the expression: $t_R(n) = A + \exp(B + Cn^D)$, and the best estimation of the hold-up time is obtained from that expression for $n=0$.

Keywords: Hold-up time; Retention times; Alkanes; Permanent gases

1. Introduction

The presentation of gas chromatography (GC) by James and Martin [1] in 1952 represents an important step forward in analytical separation methods. The technique has been used with tremendous success in analytical chemistry, but its enormous separation power has also been used to purify substances both at laboratory and industrial scales. GC has shown to be a valuable technique for studying physico-chemical properties of substances such as boiling points or solubility parameter of solutes, solvent-polymer interactions, glass transi-

tion points, polymer crystallinity, solubility parameter of polymers and polymer-polymer interactions, among other possibilities. For many of these applications, particularly those where chromatographic data must be related to structural or physico-chemical properties, great precision and accuracy are necessary in the retention data obtained under well defined experimental conditions. This implies, among other things, that the hold-up time (t_M) must be known without doubt. The hold-up time is the time that an infinitesimal amount of a non-adsorbed gas takes to pass through the chromatographic system under identical conditions as those of the sample being analysed.

Different gases have been suggested as indicators of the t_M value [1–3]. However, air and methane (the only one producing a signal in the most popular GC

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detection method, flame ionization detection, FID) have been reported to be retained in the chromatographic column even at high temperatures [3–5]. Neon has been shown to have the smallest gross retention volume in some chromatographic systems [3,6], but it is not detected by FID. Suitable changes in the experimental conditions of FID, have been proposed by some authors [7–9], so that a signal could be produced by gases that are not ionized in the detector. Of these methods, the most attractive seems to be one that implies the injection of a large amount (0.5 ml) of the carrier gas [8]. However, if a signal is obtained, it must be due to a change in the dynamic conditions in the detector, and it is not clear if the chromatographic parameters of the column have been altered during the run, making doubtful the validity of the results. These methods imply additional experimental difficulties and have not been widely accepted; besides, they do not eliminate the retention of inert gases in the column. Thus, whenever reliable studies to obtain correct adjusted retention parameters were carried out in the past, thermal conductivity detection (TCD) or mass spectrometry (MS) were used.

Several methods based on Kováts' concept of the retention index [10] were devised to estimate the t_M value when using FID. The value thus deduced is often referred to as mathematical dead time (t_{MM}). Smith et al. [11,12] carried out a review of some of the methods and compared results, to come to the conclusion that the most adequate methods were those based on a linear relationship between the logarithm of the adjusted retention time (t'_R) and the carbon number of a series of *n*-alkanes (semilog-plot) [5,13–17]. Nevertheless, all these methods give a value of t_M without real meaning, not related to the retention of true unretained substances, being useful only to obtain retention indices, which may be used for interlaboratory comparisons [3,11,18].

Adjusted retention times are considerably shorter in capillary columns than in packed columns of the same stationary phase run under equivalent chromatographic conditions. Therefore, errors in the estimation of the hold-up time in chromatograms obtained in capillary columns may induce considerable errors in the retention factor, retention index or specific retention volume of solutes [19]. Some authors proposed the use of methane in the cases of

this type of column, considering that its retention would be negligible at the normal working temperatures [20]. Estimation of the t_M value based on a knowledge of the temperature, flow-rate and inlet and outlet pressures of the capillary column has also been proposed [21]. Nevertheless, whenever reliable values of the adjusted retention times are needed, the direct determination of t_M by measuring the retention time of neon seems still advisable [12,22–25].

Quite recently, a new procedure of estimating the hold-up time in chromatograms run on packed or capillary columns has been proposed [26,27] (hereafter the LQG method). The method produces reliable and reproducible values of t_M , which may be safely used to calculate either chromatographic or thermodynamic parameters. The value of t_M obtained is always shorter, but close to the retention time of neon in the same chromatogram. This seems reasonable considering that a real gas (neon) will be retained only very slightly. The procedure is based on the assumption that a mathematical relationship exists between the experimental retention times (t_R) of the *n*-alkanes and their carbon number, but in the new method, this relationship does not imply the linear relationship of the semilog-plot mentioned above. The new approach to the problem is that the hold-up time may be deduced from the retention of a hypothetical alkane of zero carbon atoms. The method has been applied to different types of columns (packed and capillary) but all with the same stationary phase (SP): polydimethylsiloxane.

In this paper, we carry out an exhaustive study covering a wider range of stationary phase polarities and temperatures, in order to test the method and generalize its utility. Results are also compared with those obtained with methods accepted by most chromatographers, based on linearization of the logarithms of the adjusted retention parameters.

2. Experimental

2.1. Apparatus

Experiments were carried out on a Fisons 8035 gas chromatograph coupled to a Fisons MD 800 quadrupole mass filter. Results presented here were obtained on six stainless-steel packed columns and

Table 1
Characteristics of the chromatographic columns

Parameter	Column ^a								
	1	2	3	4	5	6	7	8	9
Stationary phase (SP)	Squalane	PS-255	OV-3	OV-11	QF-1	SUPEROX	CPSIL-5CB	HP-5	HP-INNOWAX
Type	Packed	Packed	Packed	Packed	Packed	Packed	WCOT	WCOT	WCOT
Length (m)	4.0	4.0	2.0	2.0	2.0	4.0	50	60	60
Internal diameter (mm)	2.2	2.2	2.2	2.2	2.2	2.2	0.32	0.25	0.25
% SP in the packing	5.2	19.4	15.9	16.3	17.7	30.4			
Film thickness (µm)							0.43	0.25	0.25
Supplier	Laboratory-made	Laboratory-made	Laboratory-made	Laboratory-made	Laboratory-made	Laboratory-made	Chrompack	HP	HP

^a Squalane = 2,6,10,15,19,23-hexamethyltetracosane (Perkin-Elmer); PS-255 = polydimethylsiloxane containing 1–3% vinyl groups (Petrarch); OV-3 = poly(phenylmethylsiloxane) with 10% substitution of phenyl group (Ohio Valley Specialty Chemicals); OV-11 = poly(phenylmethylsiloxane) with 35% substitution of phenyl group (Ohio Valley Specialty Chemicals); QF-1 = poly(3,3,3-trifluoropropylmethylsiloxane) with 50% substitution of trifluoropropyl group (Dow Corning Chemicals); SUPEROX = SUPEROX 20M, poly(ethylene glycol) (Alltech); CPSIL-5CB = 100% polydimethylsiloxane; HP-5 = crosslinked poly(phenylmethylsiloxane) with 5% substitution of phenyl group; HP-INNOWAX = crosslinked poly(ethylene glycol); WCOT = wall-coated open-tubular; HP = Hewlett-Packard.

on three fused-silica capillary columns whose characteristics are summarized in Table 1. The gas leaving the chromatographic columns was fed to the mass spectrometer through a direct line of fused-silica tubing of 0.1 mm I.D. In this way, column outlet pressure was maintained at ambient pressure (i.e., normal chromatographic conditions).

2.2. Chromatograms

Isothermal chromatograms were obtained between 30 and 150°C. Helium was used as carrier gas. Solutes injected include *n*-alkanes from 1 to 17 carbon atoms and several permanent gases such as neon, nitrogen, oxygen and argon. Chromatograms were obtained by the selected ion recording mode (SIR), except for 30°C in column 7 where the full scan mode was used. The cycle time of the mass filter was 0.2 s in the case of packed columns and capillary columns 8 and 9. Whenever only gases were injected, the cycle time was 0.1 s. In the case of column 7, the cycle time was 0.04 s.

2.3. Mathematical treatment

The experimental retention times of a series of *n*-alkanes were used to estimate the value of t_M of the chromatogram, by application of a computer program, as follows.

2.3.1. The LQG method

Data were fitted by a regression procedure that obtains least squares estimates of the parameters in a non-linear regression model by minimizing the residual sum of squares. The algorithm used was developed by Marquardt [28]. Calculations in columns 2 and 7 were carried out using the Statgraphics program (Statistical Graphics) in an Epson computer equipped with a 486-DX processor at 33 MHz. For the rest of the calculations a program was written in FORTRAN and the equality of the results confirmed. The hold-up time was calculated as the retention time of a hypothetical *n*-alkane of zero carbon atoms.

2.3.2. Other methods

Two programs were used: the method of García-Domínguez et al. [5] was applied with a program written in FORTRAN by the authors; the program

used with the methods of Parcher et al. [6] and Guardino et al. [15] was written in BASIC by Furr [29].

3. Results and discussion

3.1. The retention of gases

Some permanent gases mixed with a few light hydrocarbons were injected in all columns at several temperatures. Mean retention times of five runs are shown in Table 2. Retention times of the permanent gases (Ne, N₂, O₂ and Ar) in the capillary columns used did not show significant differences, values falling always within the limits of the experimental error (cycle time of the MS system). Accordingly, any of these gases may be used as a marker of the t_M value for this type of column. Retention of gases in the packed columns showed a clear dependence on the SP. Surprisingly, contrary to what is generally accepted, neon is not the least retained gas in all cases, as shown in Table 2. In some of these columns neon is eluted even after methane. Except in the case of column 2, nitrogen shows the shortest retention time, being eluted either alone or together with some of the other gases. Methane is clearly retained even at high temperatures in all column types, so it is not advisable to use it as a t_M marker, even if it is the only choice when FID is being used. Besides, although differences between the retention times of the permanent gases and methane are small in capillary columns, they could lead to important errors, particularly in the case of early eluting substances.

From the above discussion, it becomes obvious that there is not a general rule to decide which is the right choice of the gas to be used as a marker of the hold-up time, particularly in the case of packed columns. Besides, the generalized use of FID limits the choice to methane, a gas which is retained by all type of chromatographic columns under any condition and SP type. Therefore, a method which truly estimates the hold-up time of any chromatogram run on any type of column and with any type of detector is still a necessity if true retention factors, retention indices or specific retention volumes are to be obtained.

Table 2

Retention times (s) of several gases under different experimental conditions (each figure is the average of five values)

Temperature (°C)	Substance	Column								
		1	2	3	4	5	6	7	8	9
30	Ne	211.7	129.4	118.2	114.2	119.3	178.3	181.9	303.3	299.5
	N ₂	211.3	130.7	118.2	114.0	119.1	177.8	181.9	303.3	299.5
	O ₂	211.3	132.0	118.6	114.3	119.4	177.8	182.0	303.3	299.4
	Ar	211.2	132.3	118.7	114.4	119.6	177.8	182.0	303.3	299.4
	Methane	212.2	136.1	120.8	115.8	120.6	178.0	182.3	303.8	299.6
	Ethane	215.5	171.6	135.8	125.0	126.7	177.9	184.8	306.2	299.8
	Propane		258.0	174.9	150.2	142.1		191.0	312.6	
	<i>n</i> -Butane		521.6	297.5	229.2	177.7		209.6	331.6	
60	Ne	223.8	136.8	127.0	120.2	128.7	189.7	194.8	323.2	319.4
	N ₂	223.1	137.9	127.0	120.0	128.4	189.2		323.3	319.4
	O ₂	223.1	139.5	127.5	120.3	128.6	189.2		323.3	319.3
	Ar	223.1	139.6	127.7	120.4	128.7	189.2		323.3	319.4
	Methane	224.5	142.8	129.5	121.2	130.0	189.3	195.3	323.4	319.5
	Ethane	226.0	167.9	139.7	127.4	134.2	189.3	197.0	325.4	319.8
	Propane		217.3	162.3				200.5	328.5	
	<i>n</i> -Butane		345.0	221.4				209.7	338.0	
90	Ne		145.2	141.4	135.3	144.0	203.2	210.9	343.6	340.8
	N ₂		146.3	141.5	135.0	143.6	202.7		343.8	340.8
	O ₂		147.8	142.0	135.5	143.8	202.7		343.8	340.6
	Ar		148.2	142.1	135.6	143.8	202.8		343.8	340.7
	Methane		151.1	144.2	137.2	145.6	202.9	211.4	344.2	340.9
	Ethane		170.3	151.8	141.6	148.5	202.7	212.7	345.4	341.2
	Propane		202.4					215.0		
	<i>n</i> -Butane		274.4					220.3		
120	Ne		152.7	150.5	144.9			244.2	361.3	358.3
	N ₂		153.9	150.4	144.4				361.3	358.2
	O ₂		155.5	150.9	144.8				361.3	358.2
	Ar		156.2	151.1	144.9				361.4	358.2
	Methane		158.6	153.5	147.3			224.6	361.7	358.4
	Ethane		173.9	159.6	151.2			225.6	362.7	358.5
	Propane		196.1					227.4		
	<i>n</i> -Butane		240.9					230.3		
150	Ne		161.3					235.7	376.8	
	N ₂		162.5						376.6	
	O ₂		164.4						376.7	
	Ar		164.8						376.8	
	Methane		166.6					236.0	377.1	
	Ethane		180.1					236.9	377.8	
	Propane		196.4							
	<i>n</i> -Butane		224.9							

3.2. Comparison of several methods to obtain t_M values

The dependence of the retention time of a *n*-alkane on its carbon number *n*, may be expressed as:

$$t_R(n) = f(A, B, C, \dots, n) \quad (1)$$

where *A*, *B*, *C*,... are adjustable parameters that depend on the experimental conditions (column, stationary phase, flow-rate, temperature, etc.)

Two expressions have been selected (out of a total of 25 [26,27]) as those that best describe the behaviour of the *n*-alkanes in a chromatographic column:

$$t_R(n) = A + \exp(B + Cn + Dn^2) \quad (2)$$

$$t_R(n) = A + \exp(B + Cn^D) \quad (3)$$

either of which offers a better fit of the experimental retention times than the universally accepted expression:

$$t_R(n) = A + \exp(B + Cn) \quad (4)$$

which is the base of all procedures of estimating t_M based on linearization. In these procedures, Eq. (4) is used in the form $\ln(t_R - A) = B + Cn$, and the value of A is taken as the mathematical dead time (t_{MM}). In the LQG procedure [26,27] Eq. (2) or Eq. (3) are used to estimate the value of (t_M) as the retention time of a *n*-alkane of $n=0$ ($t_M = A + \exp B$).

In order to test the applicability of the LQG method in other cases, a number of injections of *n*-alkanes, mixed with permanent gases were carried out at different temperatures. Eq. (2) and Eq. (3) were used to estimate the t_M value. The same set of experimental data were used in each case to determine the t_M or t_{MM} values according to the procedures of Refs. [5,6,15]. Results are shown in Tables 3–6. The retention time of the least retained gas in each case is also included in the tables for comparison.

A few facts may be observed. The values of t_M obtained by the LQG method (Eqs. (2,3)), and by Parcher and Johnson's method are close to, and slightly shorter than, the retention time of the least adsorbed gas, showing a good agreement with one another. The latter method however, failed to produce a result in two of the cases tried. This has also been observed by Wainwright and Haken [30], who mentioned that perhaps the assignment of a carbon number of 0.5 to methane does not always work. In general, the other two procedures [5,15]

Table 3
Retention times (s) and t_M values obtained by the methods tested, at 60°C (each figure is the average of five values)

Substance	Column								
	1	2	3	4	5	6	7	8	9
Methane	224.5	142.8		124.7	130.0	189.1	195.3	322.8	319.3
<i>n</i> -Pentane	287.4	637.3		284.3	209.2		230.9	359.5	
<i>n</i> -Hexane	377.7	1310.7		510.0	296.6		379.5	410.3	330.1
<i>n</i> -Heptane	588.2	2849.4		1033.2	471.7		390.5	527.5	342.0
<i>n</i> -Octane	1079.5			2247.3	822.2	221.5	642.5	796.3	366.8
<i>n</i> -Nonane	2229.5				1522.4	258.6	1212.7	1410.1	418.1
<i>n</i> -Decane						338.4	2498.3		524.3
<i>n</i> -Undecane						511.4			744.1
<i>n</i> -Dodecane						888.1			1199.0
<i>n</i> -Tridecane						1708.9			2141.4
<i>n</i> -Tetradecane									
<i>n</i> -Pentadecane									
<i>n</i> -Hexadecane									
<i>n</i> -Heptadecane									
t_R (gas) ^a	223.1	136.8		122.5	128.0	188.9	194.8	322.3	319.1
t_M (LQG, Eq. (2))	223.0	133.2		121.6	127.5	189.1	194.4	322.0	319.1
t_M (LQG, Eq. (3))	223.0	133.3		121.7	127.5	189.1	194.5	322.1	319.1
t_M [6]	223.1	131.2		121.2	126.5	189.0	194.4	321.9	319.1
t_{MM} [5]	219.8	113.3		113.3	121.8	190.0	192.4	320.3	318.9
t_{MM} [15]	219.9	113.2		113.4	121.8	190.1	192.3	320.1	318.9

^a t_R (gas) = retention time (s) of the least retained gas in each chromatographic column.

Table 4
Retention times (s) and t_M values obtained by the methods tested, at 90°C (for more details see Table 3)

Substance	Column								
	1	2	3	4	5	6	7	8	9
Methane		151.1	146.1	138.6	145.5	202.1	211.4	344.0	340.8
<i>n</i> -Pentane		417.7	278.7	230.9			230.9	363.7	
<i>n</i> -Hexane		707.0	428.6	335.9	237.9		252.1	385.8	
<i>n</i> -Heptane		1287.4	733.8	550.3	316.5		294.6	430.2	352.7
<i>n</i> -Octane		2447.3	1352.7	986.5	456.2		379.3	519.3	363.3
<i>n</i> -Nonane			2605.3	1870.9	704.2		547.4	698.0	382.6
<i>n</i> -Decane					1143.1	245.9	880.1	1054.6	417.9
<i>n</i> -Undecane					1920.1	284.3	1536.5	1764.1	482.8
<i>n</i> -Dodecane						356.7	2828.1		601.8
<i>n</i> -Tridecane						494.0			820.0
<i>n</i> -Tetradecane						755.5			1219.2
<i>n</i> -Pentadecane						1255.8			1949.3
<i>n</i> -Hexadecane									
<i>n</i> -Heptadecane									
t_R (gas) ^a		145.2	142.4	136.1	143.4	201.8	210.9	343.6	340.7
t_M (LQG, Eq. (2))		142.7	142.0	135.8	143.1	202.0	210.6	343.3	340.6
t_M (LQG, Eq. (3))		142.7	142.1	135.9	143.1	202.0	210.7	343.4	340.6
t_M [6]		139.4	140.6	134.9	141.6	—	210.5	343.1	340.5
t_{MM} [5]		129.1	133.0	129.3	136.1	203.2	209.2	341.7	340.1
t_{MM} [15]		128.8	132.8	129.1	135.9	203.5	209.1	341.6	340.1

Table 5
Retention times (s) and t_M values obtained by the methods tested, at 120°C (for more details see Table 3)

Substance	Column								
	1	2	3	4	5	6	7	8	9
Methane		158.6	154.3	149.1			224.6	361.8	358.3
<i>n</i> -Pentane		321.0	234.9				236.7		
<i>n</i> -Hexane		465.3	310.5	262.1			247.4	384.9	
<i>n</i> -Heptane		725.0	448.6	363.7			266.7	404.9	
<i>n</i> -Octane		1191.9	699.1	548.2			301.2	440.9	370.8
<i>n</i> -Nonane		2025.7	1156.4	884.7			362.9	505.7	379.4
<i>n</i> -Decane			1985.2	1493.2			472.7	622.0	394.0
<i>n</i> -Undecane				2594.6			667.7	830.2	418.2
<i>n</i> -Dodecane							1013.4	1202.2	458.8
<i>n</i> -Tridecane							1623.7	1864.5	526.3
<i>n</i> -Tetradecane								638.6	
<i>n</i> -Pentadecane								825.4	
<i>n</i> -Hexadecane								1134.9	
<i>n</i> -Heptadecane								1647.9	
t_R (gas)		152.7	150.5	146.4			224.2	361.5	358.3
t_M (LQG, Eq. (2))		151.2	150.7	146.3			224.1	361.2	358.2
t_M (LQG, Eq. (3))		151.1	150.7	146.4			224.1	361.3	358.2
t_M [6]		146.4	148.7	144.8			223.6	360.8	—
t_{MM} [5]		138.9	142.6	137.3			222.9	359.6	357.7
t_{MM} [15]		138.1	142.4	137.1			222.8	359.5	357.6

Table 6

Retention times (s) and t_M values obtained by the methods tested, at 150°C (for more details see Table 3)

Substance	Column								
	1	2	3	4	5	6	7	8	9
Methane		166.6					236.0		377.4
<i>n</i> -Pentane		276.8					244.1		
<i>n</i> -Hexane		358.5					250.2		391.5
<i>n</i> -Heptane		493.0					260.2		401.7
<i>n</i> -Octane		714.3					276.6		418.6
<i>n</i> -Nonane		1076.9					303.3		446.4
<i>n</i> -Decane		1668.4					347.1		492.3
<i>n</i> -Undecane		2631.6					418.3		567.5
<i>n</i> -Dodecane							534.2		690.6
<i>n</i> -Tridecane							722.1		891.9
<i>n</i> -Tetradecane							1026.0		1220.1
<i>n</i> -Pentadecane							1517.2		1754.0
<i>n</i> -Hexadecane									
<i>n</i> -Heptadecane									
t_R (gas)		161.3					235.7		377.1
t_M (LQG, Eq. (2))		160.2					235.5		376.8
t_M (LQG, Eq. (3))		160.1					235.6		376.9
t_M [6]		153.5					235.0		376.4
t_{MM} [5]		148.5					234.4		375.4
t_{MM} [15]		147.8					234.3		375.3

produce t_{MM} values for the same chromatogram in poor agreement both with t_R (gas) and with the t_M values deduced by the former methods, although they agree with each other fairly well.

The value of t_M deduced with the LQG method, does not depend on the number of *n*-alkanes used [27] as long as a minimum of four (plus methane) are injected in the chromatograph. Table 7 shows the behaviour of all the methods tested when the number of *n*-alkanes or their size is changed. Results corre-

sponding to the capillary column 7 (CPSIL-5CB) at 90°C have been arbitrarily selected as an example. Similar results are produced in all other cases of capillary and packed columns. It may be observed that the methods of Refs. [5,15] are more sensitive than the others to the carbon number of the lightest hydrocarbon used for the fitting. All methods seem rather insensitive to the elimination of the heavier *n*-alkanes, as long as a minimum of four are maintained. The effect of the successive elimination of

Table 7

Effect of the number of *n*-alkanes on the t_M value (column 7, 90°C)

Substance	t_M (s)				
	LQG (Eq. (2))	LQG (Eq. (3))	[6]	[5]	[15]
CH ₄ + C ₅ –C ₁₂	210.58	210.69	210.45	209.20	209.06
CH ₄ + C ₆ –C ₁₂	210.59	210.71	210.43	208.64	208.47
CH ₄ + C ₇ –C ₁₂	210.66	210.73	210.40	207.97	207.72
CH ₄ + C ₈ –C ₁₂	210.70	210.74	210.39	206.63	206.38
CH ₄ + C ₉ –C ₁₂	210.72	210.75	210.37	204.80	204.66
CH ₄ + C ₅ –C ₁₂	210.58	210.69	210.45	209.20	209.06
CH ₄ + C ₅ –C ₁₁	210.69	210.84	210.47	209.31	209.20
CH ₄ + C ₅ –C ₁₀	210.72	210.76	210.48	209.42	209.34
CH ₄ + C ₅ –C ₉	210.75	210.75	210.50	209.51	209.46
CH ₄ + C ₅ –C ₈	210.78	210.77	210.52	209.61	209.57

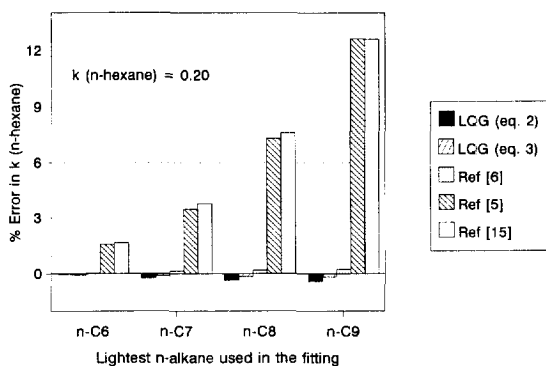


Fig. 1. Percentage error in the retention factor of *n*-hexane deduced by the different procedures when the lightest *n*-alkanes are eliminated from the data, compared with the value deduced by the same procedure when all *n*-alkanes from 5 to 12 carbon atoms are included.

the lightest *n*-alkane used for the fitting (except methane in the cases where its inclusion is mandatory) on the value of the retention factor of *n*-hexane ($k \approx 0.2$) and *n*-nonane ($k \approx 1.6$) has been presented in Figs. 1 and 2 (data of the same column, taken from Tables 4 and 7). The diagrams represent percentage error of the retention factor, as compared with the value of k corresponding to the value of t_M (or t_{MM}) deduced with the same method using all *n*-alkanes from 5 to 12 carbon atoms. The different behaviour of the methods is evident. The elimination of only one *n*-alkane from the fitting (*n*-pentane)

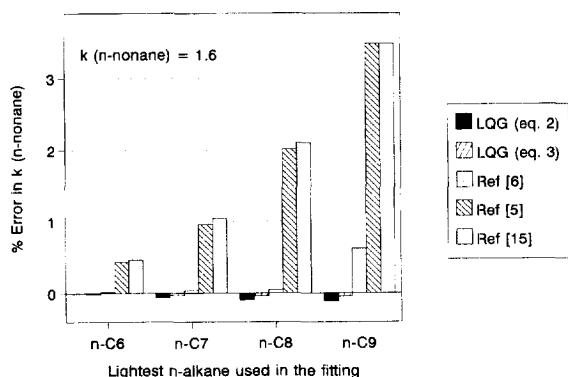


Fig. 2. Percentage error in the retention factor of *n*-nonane deduced by the different procedures when the lightest *n*-alkanes are eliminated from the data, compared with the value deduced by the same procedure when all *n*-alkanes from 5 to 12 carbon atoms are included.

introduces an error above 2% for *n*-hexane, and about 0.5% for *n*-nonane with any of the last two methods (and higher errors if more alkanes are not considered), while the effect is negligible in the other cases. Even if *n*-nonane is the lightest alkane included, the value of k for *n*-nonane have errors of 4.7 and 4.8% respectively, when compared with the value deduced for k with the LQG method.

4. Conclusions

Results presented in this paper show that there is not a gas which may be taken under any circumstances as the hold-up time indicator in GC. For capillary columns, nitrogen, air, neon or argon may be used without fear for solutes with a retention factor of 0.1 or higher. For packed columns, neon or nitrogen may represent a good choice, but a check should always be carried out. Methane must never be used. The existence of a reliable method of estimating the hold-up time of chromatograms which may be used with any detector is, nevertheless, very convenient. This implies the use of a mathematical procedure.

The methods of García-Domínguez et al. [5] and Guardino et al. [15] have been reported to be acceptable methods for calculating retention indices [11], especially if the lightest *n*-alkane used is close enough to the first eluting solute of interest. They are not, however, recommended to calculate true hold-up times. The method of Parcher and Johnson produces t_M values that may be considered as hold-up times of the chromatograms, but it suffers from the drawback that it sometimes does not give the desired result. The LQG method here discussed [26,27] has proved to produce the best results under any circumstances. The two equations selected produce equivalent values, but a closer look to the results of all the chromatograms tried, shows that Eq. (3) is better, with lower values of the root mean squares of the fittings and better self-consistency when the light *n*-alkanes are not considered. Therefore we propose the use of Eq. (3) as the best way so far to estimate the hold-up time of chromatograms, regardless of column type, stationary phase polarity or type of solid support in the packed column.

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