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Prediction of programmed temperature retention indices on capillary columns of different polarities

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Abstract

Open tubular capillary columns filled with bonded liquid phases of different polarities were used for the separation of substituted aromatic compounds (chlorobenzenes and chlorophenols). The retention index values obtained during programmed temperature analyses were predicted by starting from retention data obtained under isothermal conditions. The calculation method previously used for the prediction of programmed temperature retention times was modified and simultaneously applied to the sample mixture and to the reference *n*-alkanes series. Experimental retention index values measured in different temperature programming conditions were found to agree with the calculated ones.

1. Introduction

The prediction of programmed temperature retention times (PTt_R) on capillary columns of different polarities by starting from isothermal data was previously carried out by several workers [1–17] and the precision of different methods was recently compared [18]. Some methods give a suitable approximation between calculated and experimental results and can be applied by simple BASIC programming on personal computers. The majority of them, however, deal with absolute retention times and are therefore suitable for routine application when a given column and instrument are used both for isothermal and programmed runs. The values obtained cannot be transferred to other systems with different experimental parameters as temperature, carrier gas flow-rate, film thickness, column length and diameter.

The use of retention index values [19] offers many advantages for the normalization of retention data: its application to isothermal and programmed temperature analysis was reviewed [20,21]. The prediction of isothermal retention index values at any temperature does not require complex calculations: in fact their dependence on temperature, previously investigated [22], can be considered as linear for practical purposes [21] and therefore the isothermal retention indices calculated by simple interpolation between values measured at two temperatures in the range of stability of the used liquid phase. However, the analysis of complex mixtures of

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compounds having a wide range of boiling points requires programmed temperature analyses to be carried out, in order to shorten the analysis time and yield peaks of comparable width. The prediction of programmed temperature retention indices, I_p, is therefore useful to assist in the separation and identification of many substances.

The application of prediction methods to the knowledge of retention indices should permit to obtain values rather independent of the experimental parameters listed above and only depending on the nature and polarity of the stationary phase. In theory, a suitable index prediction method should start from isothermal retention index values, I_t, obtained on a given stationary phase or found in the literature, and yield programmed temperature retention indices, I_p, for any programming rate on the same type of liquid phase, independent of column diameter, length and thickness of film in capillary columns. Another possible procedure is to employ isothermal retention times to predict the retention of a given compound and of the reference alkanes during any programmed run and apply to these values the standard equations for the calculation of I_p. [23]. We describe here the application of the latter procedure, using the methods previously tested for the prediction of programmed temperature retention times. Some aromatic compounds of low and high polarity (chlorobenzenes and chlorophenols) were analysed on non-polar and polar columns in isothermal conditions and the measured retention times were used to predict retention indices in linearly programmed temperature analysis.

2. Experimental

The analyses were carried out using a Varian (Palo Alto, CA, USA) Model 3400 gas chromatograph equipped with a flame ionisation detector and a split–splitless capillary injector. Two bonded-phase fused-silica capillary column (J and W Scientific, Folsom, CA, USA) 30 m long with an I.D. of 0.235 mm were used: a non-polar dimethylpolysiloxane (DB 1) with a film thickness of 0.25 μm and a polar polyethylene glycol (DB WAX) with a film thickness of 0.50 μm. Different film thicknesses were used in order to verify if the method permits the prediction of the behaviour of the columns in this instance too: previously published work on the prediction of absolute and relative retention times was carried out using columns of the same length and with equal amounts of polar and non-polar liquid phases.

Standard solutions in CS_2 at concentrations ranging between 0.1 and 0.5 g l^{-1} were injected (amount 1 μl) in the split mode. Dead times were determined by measuring the elution time of methane [24]. Nitrogen was used as the carrier gas and the make-up gas dispatched at the column end maintained a constant flow-rate of 30 ml min^{-1} through the detector. The injector and detector temperatures were 200 and 250°C, respectively. Five replicate isothermal runs were performed at various temperatures in order to obtain averaged values of isothermal retention times. Owing to the wide range of boiling points of the various compounds, different temperature ranges were selected, in order to obtain three values of the retention time for every compound and reference alkanes (see Table 1). Programmed temperature runs were carried out with an initial temperature of 50 and 100°C and with different programming rates. The temperature set by the programmer matched the actual column temperature within 1.3°C.

Retention times were measured with a precision of 0.001 min using a Varian 4270 integrator. Calculations were performed with IBM personal computers using Lotus 123 and QPRO or BASIC programs. The retention index values were predicted starting from the isothermal retention times of the aromatic compounds, compared with those of linear alkanes measured with separate injections.

3. Theory

The retention index in a linearly programmed temperature run, I_p, is given by [23]

$$I_p = 100\,z + 100\,\frac{t_i - t_z}{t_{z+1} - t_z} \qquad (1)$$

Table 1
Range of isothermal runs for the measurement of ITt_R values used for the prediction of retention indices

Compound number	Temperature (°C)												
	50	70	75	90	100	110	125	130	135	150	175	200	220
Chlorobenzenes													
1–9	D	D		D		W		W		W			
10–12		D		D		D-W		W		W			
13				D		D-W		D-W		W			
14						D-W		D-W		D-W			
Phenols													
15–22	D		D		D					W	W	W	
23–24					D		D		D	W	W	W	
n-Alkanes													
C_8	D	D		D									
C_9	D	D	D	D	D								
C_{10}–C_{11}	D	D	D	D	D	D							
C_{12}		W	D	D-W	D	D-W	D	D					
C_{13}		W		D-W	D	D-W	D	D	D	D			
C_{14}					D	D-W	D	D-W	D	D-W			
C_{15}						D-W		D-W		D-W			
C_{16}–C_{17}						W		W		W			
C_{18}–C_{20}						W		W		W	W	W	
C_{21}–C_{25}										W	W	W	
C_{26}											W	W	W

D: DB-1 column, W: DB-WAX column. Identifying numbers in column 1 refer to compound names listed in Tables 2–5

where t_i is the retention time of the substance i, t_z and t_{z+1} are the retention times of the n-alkanes eluting before and after t_i. The use of this equation yields the best results when the programming rate elutes the reference probes, n-alkanes, with retention times linearly depending on the number of carbon atoms of alkanes, z.

The programmed temperature retention times, t_{pi}, can be predicted by starting from isothermal data and using different procedures. The method of Said [16,17] was used here. This and other methods were previously described and tested [18] and only the fundamental steps are summarized below.

The equation used to predict the t_p is

$$\int_0^{t_p} \frac{dt}{t_r} = \int_0^{L} \frac{dL}{L} = 1 \qquad (2)$$

where L is the length of the capillary column, dt is the differential time increment, corresponding to a increment of length dL, t_r is the isothermal retention time at the absolute temperature T.

The t_r change with temperature is expressed by the following approximate equation:

$$t_r = A + a\, e^{b/T} \qquad (3)$$

where a and b are taken at a first approximation as constants and A, which represents the gas hold-up time of the column, can be considered for practical purposes as a constant [16]. If the temperature programming is linear, then T depends linearly on the analysis time, t:

$$T = T_0 + rt \qquad (4)$$

where T_0 is the initial temperature (absolute) of the programmed run and r is the temperature increment in degrees per minute.

The following equation is obtained from Eqs. 2–4

$$1 = \frac{1}{r}\int_{\vartheta_0}^{\vartheta_t} \frac{\mathrm{d}\vartheta}{A + a\,\mathrm{e}^{b/(273+\vartheta)}} = \frac{1}{r}\int_{\vartheta_0}^{\vartheta_t} y\,(\vartheta)\mathrm{d}\vartheta \qquad (5)$$

where ϑ_0 and ϑ_t are the temperatures of the column corresponding to the inlet and to the elution of the solute and $y(\vartheta)$ is the reciprocal of the function of the retention time.

The integral of Eq. 5 does not have an analytical solution and must therefore be solved by using approximate or iterative methods [12–18]. The Said method used here employs a curve fitting approximation in order to replace the function $y(\vartheta)$ with another function that can be integrated. The values of the "constants" A, a and b can be obtained by measuring experimentally the isothermal retention times, of n-alkanes, $t^{IA}_{R\,exp}$, and of other compounds, $t^{IX}_{R\,exp}$, at three temperatures, and with these values the programmed temperature retention times, $t^{IA}_{R\,calc}$ and $t^{PX}_{R\,calc}$ are predicted.

Fig. 1 shows the schematic diagram of the procedure used for calculations, through the following steps:

(1) Measurement of $t^{IX}_{R\,exp}$ values of chlorobenzenes and chlorophenols at three temperatures on polar and non-polar columns;

(2) Measurement of $t^{IA}_{R\,exp}$ of linear alkanes in the same experimental conditions as above;

(3) Calculation of the $t^{PA}_{R\,calc}$ and $t^{PX}_{R\,calc}$ of chlorobenzenes, chlorophenols and n-alkanes. All the calculation methods tested previously [18] can be used. In this instance the simplest methods, suggested by Said [16,17] was applied in order to predict the PTt_R values for many different programming rates and initial temperatures.

(4) The programmed temperature retention values of the samples, $t^{PX}_{R\,calc}$, and of the reference compounds n-alkanes, obtained as above, were combined in order to calculate the programmed temperature retention indices, I_p, with Eq. 1 [25].

(5) The predicted indices, I_p, were compared with those measured experimentally, I_e, in various programmed temperature runs.

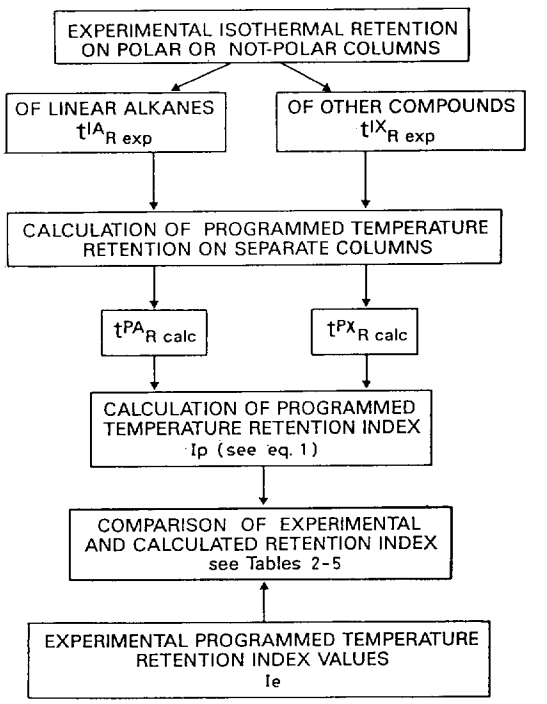

Fig. 1. Schematic diagram of the procedure used for the prediction of programmed temperature retention indices I_p and comparison with experimental values I_e.

4. Results and discussion

The accuracy of the calculated retention indices depend on the possibility to predict correctly the PTt_R values of the sample and of the linear alkanes. Figs. 2 and 3 show the values of t^{PA}_R measured experimentally in different programmed runs for many linear alkanes in the range C_8–C_{15} (used as references for chlorobenzenes on the DB-1 column), C_{12}–C_{21} (chlorobenzenes on DB-WAX), C_9–C_{14} (chlorophenols on DB-1) and C_{18}–C_{26} (chlorophenols on DB-WAX) compared with calculated trends of t^{PA}_{Rcalc} (lines). The values correspond well also when, in programmed runs starting from 100°C, the retention times of n-alkanes are not linear as a function of the number of carbon atoms, showing that the selected program is not an "ideal" one, i.e. capable of converting the exponential elution order of homologous compounds in the

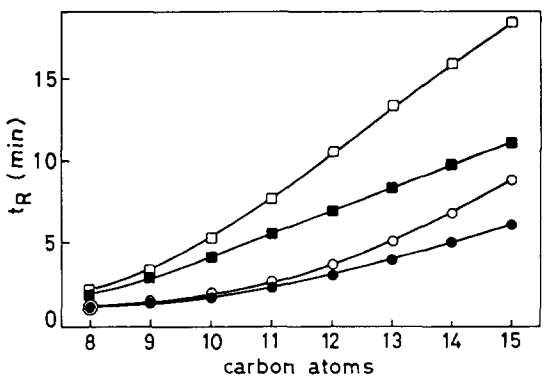

Fig. 2. Retention times of *n*-alkanes on DB-1 column in different temperature programmed runs. Initial temperature: (□,■) 50°C; (○,●) 100°C. Programming rate: 5°C/min: open symbols; 10°C/min: filled symbols.

isothermal runs to a straight line as a function of z.

The results of the application of the method are shown in Tables 2–5, where the experiments retention indices, I_e, and the differences between the experimental and predicted values, $I_e - I_p$, of chlorobenzenes and chlorophenols are listed for four different programmed runs on polar and non-polar capillary columns. The average percentual deviation between experimental and calculated index values is shown in Table 6 for different columns and programmed temperature

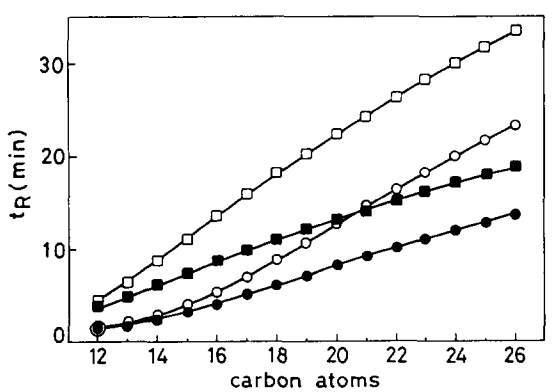

Fig. 3. Retention times of *n*-alkanes on DB-WAX column in different temperature programmed runs. Symbols as in Fig. 2.

runs. Its value is small ($< 0.16\%$) and does not depend appreciably on the polarity of the column, on the initial temperature and on the programming rate. In Tables 2–5 the compounds are listed by following the elution order from the different columns, while the identifying numbers refer to the elution order of chlorobenzenes and phenols on the non-polar DB-1 with initial temperature 50°C and programming rate 5°C/min. This permits easy identification of the compounds that show an inversion of the elution order depending on temperature program (see compounds 4 and 5 in Table 2) or on the polarity of the column and emphasizes the fact that the prediction of the retention indices is accurate notwithstanding these inversions.

The values of I_e and of the difference $I_e - I_p$ are shown with two decimal figures, in order to permit the comparison of the results with the same approximation. The calculated I_p values can therefore be obtained by adding to I_e the listed differences. In experimental measurements a reproducibility of about one index unit might be expected with a non-polar phase and 2–3 units with a highly polar phase [25]. The differences show therefore that the predicted I_p are approximate enough for practical purposes, differing from I_e values of a magnitude comparable with the fluctuation of experimental data between different runs. The accuracy of the I_p values depends on that of the ITt_R used as the starting data: automatic determination of t_R by electronic integrators is theoretically correct within 0.001 min, but small fluctuations of the carrier gas velocity and delays between the injection and the start of time counting make more acceptable retention values rounded up to 0.01 min. The accuracy of the retention index values, predicted and measured experimentally, depends therefore on the difference between the ITt_R of the reference alkanes, mainly for fast eluting compounds. As an example, the ITt_R values at initial temperature 100°C, program rate 10°C/min on DB-1 are 1.41 and 1.79 min. respectively for *n*-nonane and *n*-decane. The variation of ± 0.01 min. in these values results in an uncertainty of 3 retention index units for a compound bracketed by these alkanes. The

Table 2
Experimental retention indices on DB-1 measured in different programmed runs, I_e, and differences between experimental and predicted values, $I_e - I_p$

Initial temperature (°C)		50		50		100		100	
Programming rate (°C/min)		5		10		5		10	
		I_e	$I_e - I_p$	I_e	$I_e - I_p$	I_e	$I_e - I_p$	I_e	$I_e - I_p$
1	Chlorobenzene	830.08	1.05	832.61	0.74				
2	Bromobenzene	914.51	0.37	917.89	0.67	927.27	3.46	927.03	2.70
3	1,3-Dichlorobenzene	984.97	1.20	990.24	0.90	1002.27	−4.87	1013.51	2.70
4	1,4-Dichlorobenzene	991.19	1.14	995.93	0.85	1009.09	−0.43	1013.51	2.70
5	2-Bromotoluene	1011.52	0.73	1020.00	0.58	1029.41	−2.47	1033.33	0.00
6	1,2-Dichlorobenzene	1015.64	1.12	1016.43	0.60	1025.00	−2.54	1029.63	0.00
7	1-Bromo-2-chlorobenzene	1093.83	0.88	1100.00	0.72	1111.43	−0.95	1120.37	−1.85
8	1,3,5-Trichlorobenzene	1109.40	0.75	1115.28	0.11	1122.86	−1.90	1127.63	−1.32
9	1,2,4-Trichlorobenzene	1150.00	1.13	1156.94	0.39	1161.90	−2.86	1168.42	−1.32
10	1,2,3-Trichlorobenzene	1182.71	0.75	1190.28	0.62	1199.05	−1.90	1203.95	−1.32
11	1,2,3,5-Tetrachlorobenzene	1294.85	2.71	1305.63	2.19	1308.94	−1.23	1316.82	−0.93
12	1,2,4,5-Tetrachlorobenzene	1298.53	4.24	1306.34	0.13	1311.17	−0.69	1317.76	−1.87
13	1,2,3,4-Tetrachlorobenzene	1341.70	3.47	1352.94	2.21	1351.96	−0.02	1361.68	0.00
14	Pentachlorobenzene	1483.27	0.20	1496.15	0.00	1491.50	−0.54	1503.51	−0.88

Table 3
Experimental retention indices of chlorobenzenes on DB-WAX measured in different programmed runs, I_e, and differencies between experimental and predicted values, $I_e - I_p$

Initial temperature°C		50		50		100		100	
Programming rate°C/min		5		10		5		10	
		I_e	$I_e - I_p$	I_e	$I_e - I_p$	I_e	$I_e - I_p$	I_e	$I_e - I_p$
1	Chlorobenzene	1220.51	−0.80	1226.05	0.39	1240.38	−3.25	1243.90	0.72
2	Bromobenzene	1348.92	−3.56	1358.59	−2.31	1373.68	−2.32	1381.03	0.00
3	1,3-Dichlorobenzene	1417.70	1.30	1375.21	0.22	1438.32	−1.87	1445.33	0.00
5	2-Bromotoluene	1437.45	3.43	1449.23	1.54	1431.71	0.84	1432.76	0.00
4	1,4-Dichlorobenzene	1446.09	0.60	1407.84	−1.68	1403.26	−0.04	1401.61	−1.56
6	1,2-Dichlorobenzene	1488.07	0.77	1431.67	−0.20	1511.85	0.74	1519.77	0.23
8	1,3,5-Trichlorobenzene	1517.60	1.36	1529.51	−0.33	1517.48	0.32	1517.29	−0.62
7	1-Bromo-2-chlorobenzene	1633.76	−1.28	1650.41	−0.81	1653.05	0.61	1665.31	0.66
9	1,2,4-Trichlorobenzene	1643.59	−1.28	1658.54	−0.81	1659.76	−0.61	1671.43	0.72
10	1,2,3-Trichlorobenzene	1726.64	−1.87	1744.44	1.39	1742.31	0.23	1757.28	2.04
11	1,2,3,5-Tetrachlorobenzene	1782.97	−2.12	1802.65	−0.73	1734.12	0.12	1813.33	1.41
12	1,2,4,5-Tetrachlorobenzene	1792.86	1.62	1808.23	0.44	1808.90	0.65	1806.94	−0.20
13	1,2,3,4-Tetrachlorobenzene	1920.95	−1.98	1944.44	−0.09	1931.77	0.09	1951.96	1.08
14	Pentachlorobenzene	2028.86	−3.27	2056.73	−14.70	2037.50	−3.16	2061.39	−17.02
			(−0.82)		(0.01)		(0.87)		(0.25)

Numbers in the first colum identify the compounds and refer to the elution order observed on non-polar DB-1 column (Table 2) to show the inversion due to polarity of the column. Values in parentheses show the differencies obtained for I_p of pentachlorobenzene by using ITt_R values of n-C_{19} and n-C_{20} (see text).

Table 4
Experimental retention indices of substituted phenols on DB-1 measured in different programmed runs, I_e, and differencies between experimental and predicted values, $I_e - I_p$

Initial temperature (°C)		50		50	
Programming rate (°C/min)		5		10	
		I_e	$I_e - I_p$	I_e	$I_e - I_p$
15	2-Chlorophenol	973.02	−0.25	975.21	−1.26
16	Phenol	978.31	−0.30	975.21	−2.10
17	*o*-Chresol	1043.75	−0.83	1042.03	−1.86
18	*p*-Chresol	1066.25	−0.42	1064.49	−0.26
19	*m*-Chresol	1067.50	−0.83	1065.22	−0.97
20	2-Nitrophenol	1093.75	−0.42	1098.55	−0.73
21	2,4-Dimethylphenol	1134.60	−0.12	1132.87	−1.16
22	2,4-Dichlorophenol	1147.91	0.74	1151.05	−0.34
23	4-Chloro-3-methylphenol	1280.37	2.43	1277.46	1.41
24	2,4,6-Trichlorophenol	1325.77	2.99	1329.63	0.22

difference between the retention times of compounds eluting closely depends therefore on temperature: the accuracy of the final results increases for compounds showing long retention times and with decreasing temperature.

The most accurate values of I_p are obtained when the ITt_R of the *n*-alkanes bracketing a given compound are measured at the same temperatures as that of the compound itself. This is shown clearly by the values of pentachlorobenzene on DB-WAX (Table 5). The differences between the I_e and the I_p calculated using eicosane (*n*-C20) and heneicosane (*n*-C21) as the reference alkanes are much greater with respect of those obtained for other compounds, mainly when the programmed runs start at 100°C. This is probably due to the fact that the calculation of PTt_R of n-C_{21} was carried out using ITt_R values measured at 150, 175 and 200°C, whereas pentachlorobenzene and n-C_{20} were analysed at 110, 130, 150°C. Using *n*-nonadecane and *n*-eicosane as the reference compounds for the calculation of I_p, more accurate results of I_p are obtained (values in parentheses in Table 5). It is therefore more convenient to use the Eq. 1 for extrapolation, i.e. using as the references *n*-alkanes not exactly bracketing the compound, but those whose ITt_R where measured at the same temperature of that of the compound itself, rather than alkanes whose ITt_R was measured in different temperature ranges.

Some experiments carried out with columns of different lengths filled with the same liquid phases showed that the change of the retention indices is negligible and therefore the results can be applied to predict the behaviour of columns of various lengths. The effect of the film thickness was also investigated using two DB-1 (nonpolar) columns having a film thickness of 0.25 and 3 μm respectively. The retention indices were measured at 10°C intervals in the range 90–150° C. The results show that the average difference between the *I* values measured on the column with a film thickness of 3 μm and those measured on the column with 0.25 μm of liquid phase at the same temperature is 3.02 index units, while the averaged difference on the same column operated with a temperature shift of 10°C is 6.45 index units for 0.25 μm DB-1 and 5.23 for 3 μm DB-1. The effect of a 12-fold increase of the thickness of the liquid phase is therefore much smaller than a change of 10°C in temperature and index values predicted with a given film thickness can be applied with good confidence to other capillary columns filled with different amounts of the same liquid phase.

Table 5
Experimental retention indices of substituted phenols on DB-WAX measured in different programmed runs, I_e, and differencies between experimental and predicted values, $I_e - I_p$

Initial temperature (°C)		50		50		100		100	
Programming rate (°C/min)		5		10		5		10	
		I_e	$I_e - I_p$	I_e	$I_e - I_p$	I_e	$I_e - I_p$	I_e	$I_e - I_p$
20	2-Nitrophenol	1813.76	2.13	1835.40	3.26	1825.65	0.26	1840.95	−0.80
15	2-Chlorophenol	1861.01	−3.64	1868.14	−1.50	1863.35	−2.79	1866.67	−4.21
17	*o*-Chresol	2014.43	−3.85	2020.19	−2.14	2017.19	−2.39	2019.80	−3.20
16	Phenol	2015.92	−4.38	2024.04	−2.18	2018.23	−3.46	2023.76	−3.24
21	2,4-Dimethylphenol	2098.97	3.09	2098.02	−1.98	2094.74	−2.09	2098.99	−1.01
18	*p*-Chresol	2092.27	−6.19	2100.99	−1.95	2094.21	−5.26	2100.00	−3.96
19	*m*-Chresol	2100.00	4.64	2109.90	0.10	2102.63	−3.19	2109.09	−2.79
22	2,4-Dichlorophenol	2182.99	−2.06	2192.08	−1.06	2184.21	−2.03	2192.93	−1.13
24	2,4,6-Trichlorophenol	2343.02	0.48	2355.43	1.27	2344.63	1.06	2359.34	5.17
23	4-Chloro-3-methylphenol	2508.93	−0.60	2517.86	−0.22	2509.04	−1.08	2522.35	4.28

Numbers in the first column identify the compounds and refer to the elution order observed on an non-polar DB-1 column (Table 4) to show the inversion due to polarity of the column.

Table 6
Absolute percent error $|E\%| = |(I_e - I_p)100/(I_e)|$ between experimental, I_e and predicted, I_p, retention indices

Column	T_i (°C)	Programming rate (°C/min)	$\|E\%\|$ a	$\|E\%\|$ b
DB-1	50	5	0.12	0.08
		10	0.06	0.10
	100	5	0.14	
		10	0.11	
DB-WAX	50	5	0.11	0.16
		10	0.06	0.09
	100	5	0.07	0.12
		10	0.05	0.15

a = chlorobenzenes; b = phenols.

5. Conclusions

The procedure tested permits the prediction of linearly programmed temperature retention indices with an accuracy good enough to identify the elution order of many polar and non-polar compounds, even when the elution order of the peaks changes in different programmed runs. The differences between the calculated and measured values are acceptable, if one takes into account that, for sake of simplicity, some approximations have been made in the choice of the calculation method. To consider the terms A, a and b in Eqs. 3 and 5 as constant is in fact incorrect theoretically, because the gas hold-up time represented by A changes with temperature and the values of a and b, correlated with the entropy and enthalpy of the solute–solvent interaction, also depend on temperature [26].

A more rigorous treatment should be obtained using other calculation methods described previously: the constant A could be replaced by the true value of the gas hold-up time, calculated with Poiseuille's law by using the structural parameters of the column (length, diameter, input and output pressure, viscosity of the carrier gas) [24]; iterative methods for the prediction of PTt_R values can be used [18,26] instead of the approximate Said procedure.

The increased complexity of the computer program necessary to perform these calculations, however, may not be justified for practical applications, because the main sources of error are the experimental determination of the ITt_R values, the difference of temperature between the isothermal analyses of the compounds and the reference n-alkanes, and the uncertainty of the temperature increment of programmed temperature runs. When the reproducibility of these parameters has the order of magnitude acceptable for routine work, the use of the approximate Said's method does not introduce in the final results errors greater than those depending on the experimental parameters.

Further, the use of retention indices instead of absolute retention times partially compensates for the possible errors in the determination of the different oven temperature in the isothermal runs used to measure the ITt_R (see Table 1). If the ITt_R values of each compound and of the reference alkanes used for the calculation of its retention index are measured at the same temperature, the "relative" nature of the index makes negligible the difference between analyses carried out at temperatures differing by 2–3 degrees, on columns filled with different film thicknesses of the same liquid phase and on columns of different lengths.

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