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Measurement and prediction of dead times and column diameter in capillary gas chromatography by using air, methane and some solvents

S. Vezzani, G. Castello*, D. Pierani

Università di Genova, Dipartimento di Chimica e Chimica Industriale, Via Dodecaneso 31, 16146 Genova, Italy

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Abstract

The experimental determination of the hold-up time of capillary columns when using flame ionisation detection is generally made by measuring the retention time of methane. In high-temperature analysis or when using specific detectors the front of the solvent peak is often taken empirically as the dead time marker. An evaluation of the accuracy of these procedures was carried out by taking into account the errors due to the selection of the peak front or apex. The behaviour of these values as a function of temperature was studied by using capillary columns coated with liquid phases of different polarity (polydimethylsiloxane and polyethylenglycol). The dead time values measured by injecting small amounts of inorganic gases, methane, methanol, dichloromethane and hexane, were compared with those calculated with Poiseuille's law using the column length and diameter and the carrier gas viscosity. The accuracy and precision of the dead time values differ when the retention times of various compounds and of the apex or front of their peaks is used. The effect of the uncertainty of the diameter of the column given by the manufacturer on the dead time calculation was investigated and a method for the determination of the diameter by using experimental measurement of retention times is suggested. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Hold-up times; Capillary columns; Column diameter

1. Introduction

The dead time or column hold-up time, t_M , corresponds to the time all analytes spend in the mobile phase or the column residence time of a substance that does not interact with the stationary phase [1,2]. On capillary columns its value is significant with respect to the retention of fast eluting compounds, and any error in its determination influences the calculation of parameters, such as the retention factor k , Kovàts' retention index [3],

Rohrschneider's and McReynolds' phase constants and ΔC polarity values [4–7], useful for the column characterisation, the prediction of retention and the evaluation of structure–retention correlations. The column hold-up time is easily measured when using detection methods sensitive to inorganic gases, such as thermal conductivity detection (TCD) or mass spectrometry (MS), because the retention of hydrogen, argon, neon or air corresponds well enough with that of the carrier gas. Flame ionisation detection (FID) is not sensitive to these dead time markers. The determination of t_M when using FID is often based on the use of the retention time of methane,

*Corresponding author.

t_{MCH_4} [8–11] or on regression calculation or iterative methods that obtain the elution time of an unretained substance by using the retention values of homologous series of compounds as the *n*-alkanes. Many equations and calculation procedures were proposed and tested, based on the hypothesis of a linear relationship between the logarithm of retention factors and carbon number or by taking into account the curvature of the *n*-alkane plot [12–18]. The effect of programmed temperature was also studied [19–24]. Compounds different from inert gases or methane are also used in order to measure t_{M} with specific detection methods: e.g., dichloromethane for electron-capture detection, acetonitrile for thermionic detection, sulphur hexafluoride for flame photometric detection. An empirical method often employed for the determination of the adjusted or relative retention values of high-boiling compounds in high-temperature analysis takes the front of the solvent peak as the t_{M} value. This simplified procedure is based on the hypothesis that at high temperature the diffusion of the solvent molecules into the carrier gas stream brings the retention time of the early eluting molecules of the solvent peak to approach the residence time of an unretained substance.

In a previously published paper [22], the determination of the column hold-up time based on measurements independent on the injection of a reference sample or an homologous series was described. The direct measurement of the carrier gas flow-rate at the column outlet must take into account the vapour pressure of water and the pressure and temperature gradient between the column and the flow meter, and a correction factor must be experimentally determined with a series of measurements carried out at different temperatures of the column and of the detector. As this procedure cannot be applied during routine work when the column outlet is connected to the detector, the use of external flow-meters is generally discontinued in capillary gas chromatography and t_{M} is calculated by using equations based on Poiseuille's law. The behaviour of the carrier gas in the capillary tubing can be correctly deduced if some parameters are exactly known: length and diameter of the column, viscosity of the gas, temperature, pressure at the column inlet and at the detector outlet. The inlet pressure can be continuously measured by using the equipment now avail-

able on many advanced chromatographic instruments which calculate the flow velocity by using the built-in electronic system of the apparatus. The knowledge of the true diameter of the column is an essential parameter for this calculation [22] and is also necessary in some methods used to predict the retention time of the compounds in different programmed temperature runs [23,25–27]. However, it was found that the nominal diameter given by the manufacturer is approximate and that unacceptable errors arise when its value is used in the calculation [22]. The measurement of the true diameter by optical or scanning electron microscopy (SEM) provides suitable results, but is inconvenient for routine work. Therefore, some procedure which allows its calculation by using the results of analytical separations may be useful, e.g., by measuring directly the t_{M} with a suitable probe and applying Poiseuille's law. It is necessary to check the error due to the choice of the dead time probe and its influence on the calculated column diameter. In this paper the results of a series of experiments carried out in order to compare the accuracy of the t_{M} values calculated with Poiseuille's law with those measured by using air, inert gases, methane and some solvents are reported, and a method which allows the calculation of the column diameter by starting from these data is described.

2. Experimental

The experiments were carried out using a Varian 3600 gas chromatograph (Varian Associates, Palo Alto, CA, USA) equipped with a split-splitless capillary injector and a FID system. Some measurements were made by connecting the column directly to the analysis side cell of a micro-TCD system built by using two 3.6 Ω filaments and a Wheatstone bridge circuit. The cell volume of the TCD system and of the column-to-cell connection was less than 40 μl . Bonded-phase capillary columns having a length of 30 m were used: a non-polar polydimethylsiloxane SPB-1 and a polar polyglycol Supelcowax-10 (Supelco, Bellefonte, PA, USA) with a nominal I.D. given by the manufacturer of 0.32 ± 0.02 mm and a film thickness of 0.25 μm ; a

slightly polar poly(95% dimethyl, 5% phenyl)siloxane DB-5 (J&W Scientific, Folsom, CA, USA) having a nominal I.D. of 0.32 mm; a carbon layer open tubular (CLOT) column partially deactivated with polyglycol-terephthalic acid liquid phase (Supelco) [28,29], with a total thickness of the carbon layer plus deactivating agent of 1.3 μm . The true internal diameter of the columns was checked by SEM (Stereoscan 440, Leica Cambridge, Cambridge, UK) and found to be 299.0 (SPB-1), 299.3 (Supelcowax-10), 291.7 (DB-5) and 311.0 μm (CLOT). The true thickness of the layer in the CLOT column was 1.46 μm . The retention times were measured at the peak apex, by injecting very small amounts of sample in order to obtain peaks as narrow and symmetrical as possible. The chromatograms were integrated and the retention times measured with an accuracy of ± 0.001 min using a Varian DS 650 data system. The interactive graphic of this instrument was used in order to display the chromatograms with enlarged scale and measure the exact time at the peaks start and at the apex, the symmetry and the tailing factor. In the experiments carried out with the FID system, methane, dichloromethane, *n*-hexane and methanol were used as dead time markers and helium or nitrogen as the carrier gas. The split setting of the chromatograph had no appreciable effect on the dead time values, notwithstanding the change of the shape and width of the peaks when relatively large amount of sample entered into the column at splitless or low split ratio. For example, the start of the methane peak, measured on the SPB-1 column at 62.2°C, inlet pressure 21.7 p.s.i.g., was 0.805 ± 0.001 min within the range from zero up to 50/1 split ratios. It is possible that in different injector types the split setting may have some effect; therefore it is advisable to measure the dead time by using conditions as similar as possible to those used for analysis of the samples. With the micro-TCD system, air, hydrogen, neon and methane were used when the carrier gas was helium; hydrogen, helium and methane when the carrier gas was nitrogen. Some measurements were also made by using a ion trap MS system (Saturn, Varian) with helium as the carrier gas and comparing the retention of the peaks of air and methane.

The t_{M} values obtained measuring the times of the unretained peaks on all columns and with the three

detectors were compared with those calculated by using Poiseuille's law:

$$t_{\text{MC}} = \frac{16L^2 \mu(T)}{60jr^2} \cdot \frac{P_o}{P_i^2 - P_o^2} \quad (1)$$

where t_{MC} is the calculated dead time (min), L the column length (cm), r the column radius (cm), P_o the column outlet pressure absolute (dyne cm^{-2}), P_i the column inlet pressure absolute (dyne cm^{-2}), j the pressure gradient correction factor of James and Martin [30] and $\mu(T)$ the dynamic viscosity of the used carrier gas (Poise).

The number 60 in the denominator is necessary to obtain the values in minutes, $\mu(T)$ depends on temperature and can be obtained from tabulated data or calculated with exponential (Eqs. (2) and (3)) or quadratic (Eq. (4)) formulas [22,31]:

$$\mu(T) = \alpha T^\beta \quad (2)$$

$$\mu(T) = m(T/273.15)^n \quad (3)$$

$$\mu(T) = a + bT - cT^2 \quad (4)$$

3. Results and discussion

3.1. Air and methane as dead time markers

The analyses carried out with micro-TCD connected to the capillary columns have shown that the retention time of methane, t_{MCH_4} , can be used as a dead time marker with a negligible error with respect of that of air, t_{MA} , or other inorganic gases in gas-liquid chromatography. By injecting small amounts of helium, hydrogen and methane when the carrier gas was nitrogen and of hydrogen, air, neon and methane when the carrier gas was helium, a small difference between the retention of these gases was observed: a maximum delay of the methane peak of about 0.2% was observed on non-polar phases with respect to the air peak; at room temperature unresolved twin peaks were observed for the pairs air-methane, hydrogen-methane, helium-methane. The methane is slightly retained owing to its small solubility mainly in non-polar stationary phases [32], but this effect decreases with increasing column temperature. This agrees with previously

published results [17,18]: at 30°C on non-polar CP-SIL-5CB capillary columns, a difference of $0.16 \pm 0.2\%$ was observed between the retention times of methane and those of neon, nitrogen or oxygen; at 120°C the difference was 0.11 and 0.17%, respectively. No difference between the retention of methane and that of inorganic gases was observed on polyglycol capillary columns. The methane peak can therefore be used with enough confidence for the evaluation of dead times in bonded-phase capillary columns. By using packed non-polar columns [17] the difference between methane and inorganic probes was much greater: about 5% at 30°C and near 4% at 120°C. This might be due to adsorption effects of the solid support of the packing. In fact, also in capillary columns whose separation power is due to adsorption or size-exclusion mechanisms (molecular sieves and the porous polymer beads), the use of methane may give incorrect results mainly at low temperature, as it is considerably retained. In this instance, hydrogen can be used with TCD, whereas for detection methods not sensitive to this gas, theoretical calculation of the dead time offers the most accurate results. The results obtained previously [33] by measuring the dead times with FID operated at reduced air and flow-rates which gave a negative signal for the inert gases are therefore confirmed: no significant difference is observed in t_M values obtained with air or

inert gases, whereas the methane time is slightly greater but, for capillary columns at moderate temperature, is closer to the real dead time than the values calculated from the log plot of the *n*-alkanes [34].

3.2. Prediction of the dead time with Poiseuille's law

Theoretical prediction of the hold-up time is possible when all the parameters of Eqs. (2)–(4) are exactly known. The choice of a suitable correlation between gas viscosity and temperature is important. Table 1 shows the values of $\mu(T)$ at different temperatures calculated with the three equations shown above and the coefficients α , β , a , b , c , m and n taken from different sources or calculated with linear or quadratic regression by starting from tabulated values [35]. The t_{MC} values calculated with all equations follow the small curvature of the gas viscosity. However, as can be seen in Fig. 1, straight-line relationships approximate reasonably well the dependence of the dead time on the column temperature.

The equation which gives the viscosity values yielding the best approximation of the calculated t_{MC} with t_{MA} and t_{MCH_4} is the quadratic one (Eq. (4)) with the a , b and c parameters listed in the column G

Table 1
Values of the viscosity $\mu(T)$ calculated with Eqs. (2)–(4) (see Section 2) and different parameters, as a function of temperature

Source: range °C: equation: coefficients:	Ref. [22]	Ref. [35]	Ref. [35]	^a	Ref. [31]	^b	Ref. [35]
		0/250°C	–257.4/817°C		–258.1/300°C		0/250°C
	2	2	2	2	3	4	4
	$\alpha = 5.024$ $\beta = 0.648$	$\alpha = 4.5342$ $\beta = 0.6617$	$\alpha = 4.5419$ $\beta = 0.663$	$\alpha = 4.12$ $\beta = 0.68014$	$m = 188.7$ $n = 0.647$	$a = 48.36$ $b = 0.577$ $c = 0.000215$	$a = 53.193$ $b = 0.530354$ $c = 0.000165446$
T (°C)	A	B	C	D	E	F	G
40	208.1	203.2	205.1	205.3	206.1	208.0	203.0
60	216.6	211.7	213.7	214.1	214.6	216.7	211.5
80	225.0	220.0	222.1	222.8	222.8	225.3	219.9
100	233.1	228.2	230.4	231.3	230.9	233.7	228.1
120	241.2	236.2	238.5	239.6	238.8	242.0	236.1
140	249.1	244.1	246.4	247.9	246.6	250.0	244.1
160	256.8	251.9	254.3	256.0	254.3	257.9	251.9
180	264.4	259.5	262.0	263.9	261.8	265.7	259.5
200	271.9	267.0	269.6	271.8	269.2	273.2	267.1

^a Values obtained from Internet: http://rott.esa.lanl.gov/Manual/section2_7_3.html#SECTION007310000000000000.

^b Values used in 3600 GC model of Varian, private communication.

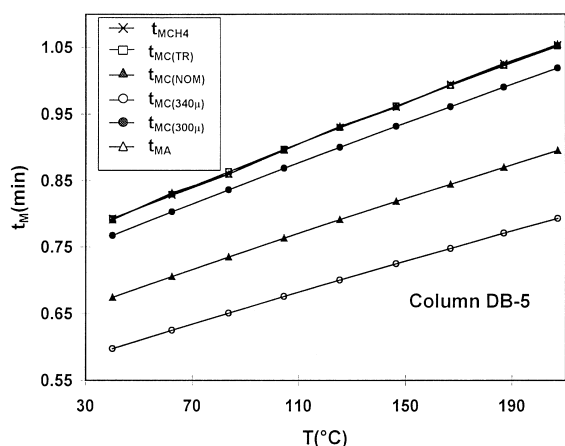


Fig. 1. Column hold-up time increases with temperature due to the increased viscosity of the carrier gas. The values calculated by applying Poiseuille's law with the true column diameter, $t_{MC(TR)}$ and those measured with air, t_{MA} , or methane, t_{MCH_4} , on the DB-5 column fairly correspond. The values calculated with the nominal diameter of the used column, $t_{MC(NOM)}$ and with the upper and lower diameter range given by the manufacturer ($320 \pm 20 \mu\text{m}$) are also shown. The $t_{MC(300\mu)}$ approximates the true t_M .

of Table 1. This is confirmed by the correspondence between the coefficients of the straight lines representing the t_{MCH_4} and the $t_{MC(TR)}$ calculated with the true column diameter as a function of column temperature. For example, on the DB-5 column the slope of the lines are identical (0.0015) for both t_{MC} (G) and t_{MCH_4} , whereas the intercept values at 0°C are, respectively, 0.7065 and 0.7055 with correlation coefficients 0.9998 and 0.9997. As a consequence of this, the lines representing the behaviour of calculated t_{MC} , t_{MA} and t_{MCH_4} in Fig. 1 fairly correspond. The exponential equation (Eq. (2)) with the α and β

parameters of column B of Table 1 also yields acceptable results if a straight line relationship is used to correlate the calculated dead time and the column temperature (slope 0.0015, intercept 0.7075, correlation coefficient 0.9996). If the regression coefficients are calculated for curves instead of straight lines following the curvature of $\mu(T)$, values of the correlation coefficient equal to unity are obtained, but for practical purposes the straight line approximation is good enough, as it allows dead time predictions at any temperature using only two or three experimental results.

Table 2 shows the dead times measured at different temperatures on the DB-5 column by using methane, t_{MCH_4} and air, t_{MA} , calculated with the nominal diameter of $320 \mu\text{m}$ given by the manufacturer, $t_{MC(NOM)}$, and with the true diameter of $291.7 \mu\text{m}$ measured by SEM, $t_{MC(TR)}$. The $\mu(T)$ values of Table 1, column G, were used. The temperatures listed were measured with the approximation of 0.1°C by means of a calibrated thermocouple applied to the column, because it was found previously [22,27] that the uncertainty in the temperature of the column is one of the main sources of error in the prediction of the column hold-up and of the retention times. The differences between the various t_M values are also reported, and show that a negligible error is made when the values obtained experimentally by injecting methane or air, or calculated with the true diameter are compared. This is shown in Fig. 1 by the correspondence of the plots for t_{MCH_4} , t_{MA} and $t_{MC(TR)}$ calculated with the true diameter of $291.7 \mu\text{m}$ measured by SEM. The lines obtained by using the nominal diameter value given by the manufac-

Table 2

Dead times measured on the DB-5 column with the retention of methane, t_{MCH_4} , air, t_{MA} , calculated with Poiseuille's law using the true (TR) and the nominal (NOM) column diameter

T ($^\circ\text{C}$)	t_{MCH_4}	t_{MA}	$t_{MC(TR)}$	$t_{MC(NOM)}$	Δ		
					$\text{CH}_4\text{-A}$	$\text{CH}_4\text{-C(TR)}$	$\text{CH}_4\text{-C(NOM)}$
62.3	0.834	0.832	0.831	0.690	0.002	0.003	0.144
83.3	0.868	0.865	0.865	0.719	0.003	0.003	0.149
104.3	0.900	0.899	0.898	0.746	0.001	0.002	0.154
125.2	0.934	0.932	0.931	0.774	0.003	0.003	0.160
146.1	0.964	0.962	0.963	0.800	0.002	0.001	0.164
166.4	0.995	0.994	0.994	0.826	0.001	0.001	0.169
186.5	1.025	1.023	1.023	0.850	0.002	0.002	0.175

True diameter measured by SEM was $291.7 \mu\text{m}$. Inlet pressure 21.7 p.s.i.g. ($1.496 \cdot 10^{-5} \text{ Pa}$).

turer, $t_{MC(NOM)}$ and the upper and lowest limit of the range ($320 \pm 20 \mu\text{m}$) are also shown and differ substantially from the true value, confirming that the exact knowledge of the true diameter is of great importance for the correct calculation. This also confirms that the manifolds installed in some gas chromatographic equipment to automatically perform the calculation of flow-rate and of the dead time [36] can give suitable results if the measurement of the pressure at the column inlet is accurate and if the factors depending on the structure and back pressure of the instrument pneumatic circuit are correctly evaluated and taken into account in the calculation software.

3.3. Organic solvents as dead time markers

The retention of some solvents (*n*-hexane, dichloromethane and methanol) is often used as the dead time value for the calculation of adjusted retention times when high-boiling compounds of high molecular mass (pesticides, polychlorinated biphenyls and furanes, dioxins, polyaromatic hydrocarbons, steroids, etc.) are analysed at high temperature on a routine basis. In this instance, the results are influenced by the fact that the retention of the low-boiling solvent may sometimes be much greater than the true t_M , depending on its interaction with the stationary phase. In Table 3 the dead times calcu-

Table 3

Dead times calculated with true diameter of the columns, $t_{MC(TR)}$, and retention values (min) of methane, *n*-hexane, dichloromethane and methanol on different columns at various temperatures

Set temperature (°C):	60	80	100	120	140	160	180
Actual temperature (°C):	62.2	83.5	104.4	125.3	145.3	166.8	186.9
$t_{MC(TR)}$							
SPB-1	0.808	0.842	0.874	0.906	0.937	0.967	0.996
DB-5	0.831	0.865	0.898	0.931	0.963	0.994	1.023
Supelcowax-10	0.806	0.840	0.872	0.904	0.935	0.965	0.994
CLOT	0.748	0.779	0.809	0.838	0.867	0.895	0.922
Methane							
SPB-1	0.812	0.845	0.875	0.908	0.938	0.966	0.995
DB-5	0.834	0.868	0.900	0.934	0.964	0.995	1.025
Supelcowax-10	0.807	0.840	0.875	0.904	0.937	0.966	0.995
CLOT	0.758	0.787	0.812	0.841	0.862	0.887	0.916
<i>n</i> -Hexane							
SPB-1	0.975	0.950	0.946	0.962	0.983	1.004	1.021
DB-5	0.957	0.931	0.924	0.936	0.953	0.983	1.008
Supelcowax-10	0.835	0.868	0.899	0.923	0.952	0.977	1.010
CLOT	0.818	0.818	0.825	0.843	0.867	0.891	0.820
Dichloromethane							
SPB-1	0.889	0.898	0.914	0.937	0.955	0.981	1.004
DB-5	0.893	0.886	0.906	0.926	0.948	0.978	1.008
Supelcowax-10	1.137	1.012	0.979	0.966	0.975	0.990	1.016
CLOT	1.510	1.183	1.050	0.991	0.970	0.958	0.966
Methanol							
SPB-1	0.829	0.859	0.883	0.912	0.941	0.969	0.997
DB-5	0.824	0.849	0.878	0.906	0.939	0.967	0.996
Supelcowax-10	1.068	0.983	0.950	0.956	0.970	0.987	1.014
CLOT	1.300	1.062	0.975	0.933	0.925	0.925	0.929

Inlet pressure 21.7 p.s.i.g. ($1.496 \cdot 10^{-5}$ Pa).

lated with Eq. (1) and the true column diameters, $t_{MC(TR)}$, are compared with the retention of methane and that of the solvents, measured at the peak apex, as a function of the column temperature (the temperature programmer settings and the actual column temperatures are shown) [22,27]. In Figs. 2–4 the retention times of the different solvents on the bonded-phase capillary columns are compared with those of methane, which is very close to the calculated $t_{MC(TR)}$.

The substances most retained on the polyglycol column are the polar compounds dichloromethane and methanol, with dipole moment values of 1.60 and 1.69 Debye, respectively and the possibility of forming hydrogen bonds, whereas the non-polar *n*-hexane, being insoluble in the polyglycol liquid phase, exhibits a retention time similar to that of methane. On the non-polar polydimethylsiloxane (SPB-1 column) the greatest retention time is shown by *n*-hexane, soluble in the liquid phase, whereas the retention time of methanol fairly approximates the true dead time, mainly at high temperature. On the slightly polar DB-5 column, the behaviour of *n*-

hexane and dichloromethane is similar to that on the SPB-1, whereas the methanol retention time is greater than that of methane even at high temperature. With increasing temperature, on all the capillary columns tested also the retention of the solvents interacting with the liquid phase quickly decreases and at high temperature (about 100–120°C above the boiling point of the used solvent) their retention approximates the t_{MCH_4} and may be used as a dead time marker with the same confidence as the retention time of methane discussed above. Fig. 5 shows the results obtained with the CLOT column. In this instance the calculated $t_{MC(TR)}$ and the t_{MCH_4} are very close but not completely coincident at low temperature, and the retention time of *n*-hexane approximates reasonably well the column hold-up time above 120°C. Methanol and dichloromethane are very well retained on this column and the apex of their peaks cannot be used as dead time markers below 180–200°C.

In high-temperature analysis used for the determination of traces of high-boiling compounds, the large amount of the low-boiling solvent injected results in

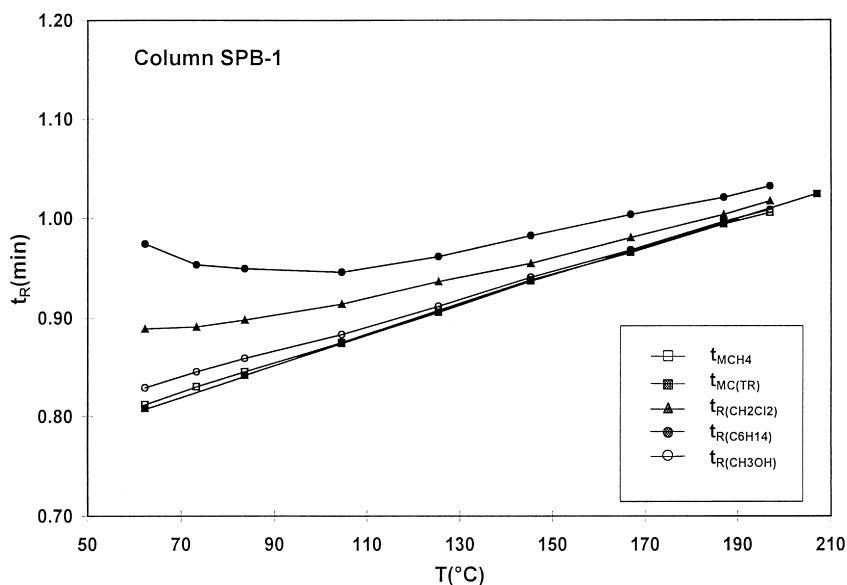


Fig. 2. Retention time of methane and of some solvents on the non-polar SPB-1 column as a function of temperature. At the used scale the dead time calculated with the true column diameter, $t_{MC(TR)}$, is close to the retention of methane, t_{MCH_4} . At high temperature the retention of polar methanol approximates that of methane.

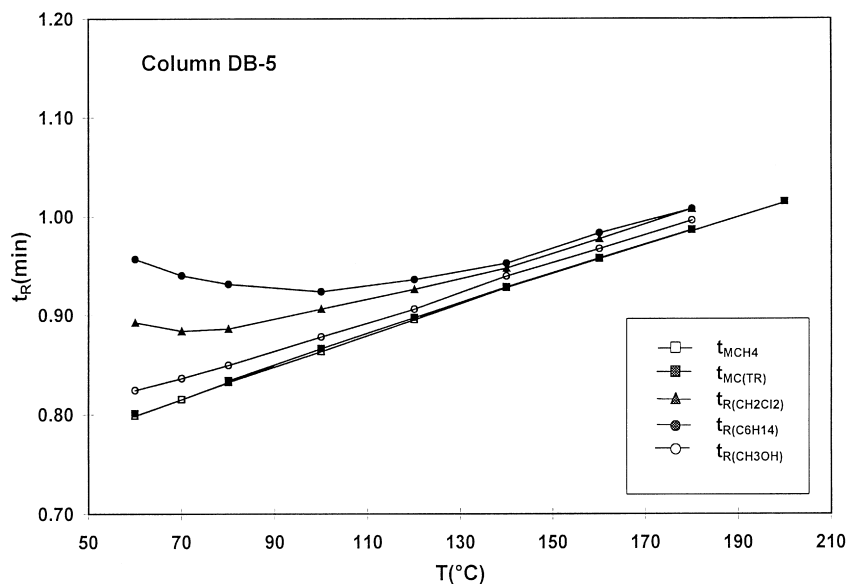


Fig. 3. Retention time of methane and of some solvents on the slightly-polar DB-5 column as a function of temperature. At the used scale the dead time calculated with the true column diameter, $t_{MC(TR)}$, is very close to the retention of methane, t_{MCH_4} . The retention of methanol is ever greater than that of methane.

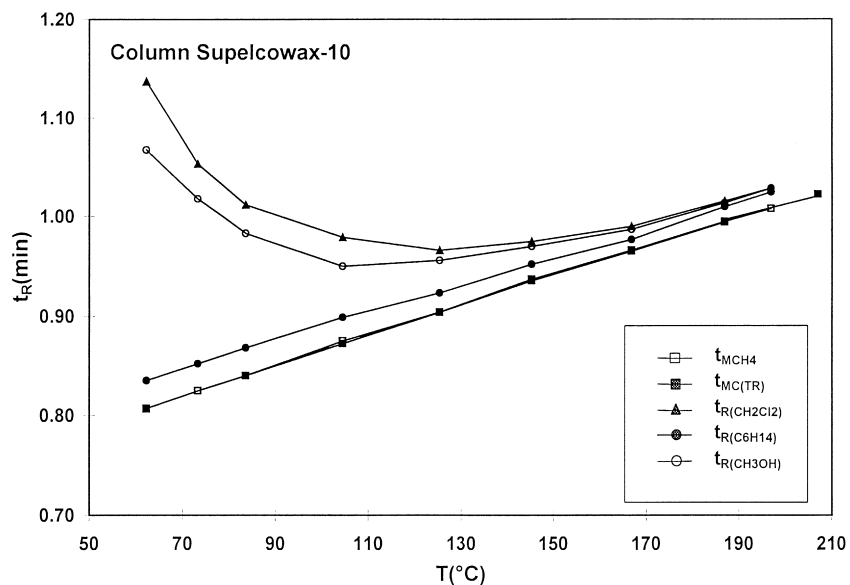


Fig. 4. Retention time of methane and of some solvents on the polar Supelcowax 10 column as a function of temperature. The dead time calculated with the true column diameter, $t_{MC(TR)}$, corresponds to that of methane, t_{MCH_4} . The retention of non-polar *n*-hexane is slightly greater than that of methane at all temperatures.

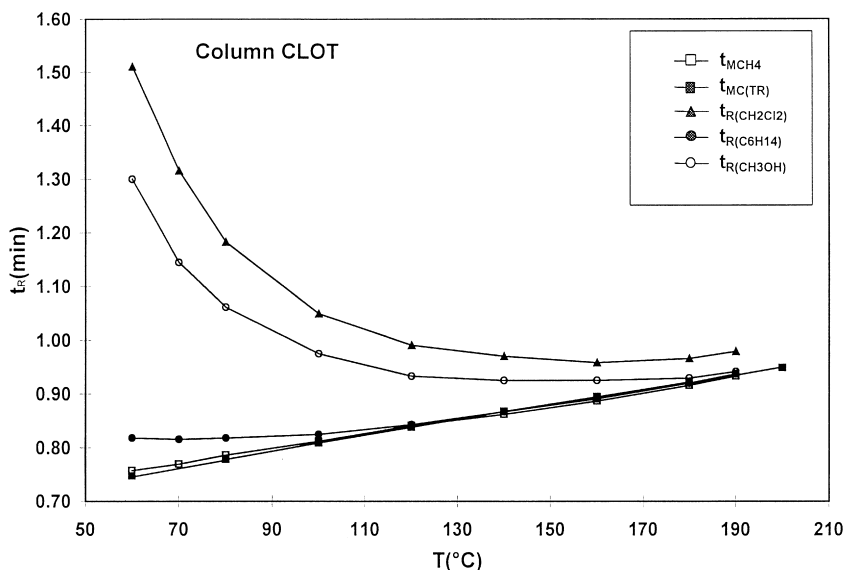


Fig. 5. Retention time of methane and of some solvents on the graphitized carbon layer CLOT column, compared with t_{MCH_4} and $t_{MC(TR)}$, as a function of temperature. *n*-Hexane can be used as a dead time marker above 120°C as its retention is very close to t_{MCH_4} and $t_{MC(TR)}$.

a large and tailing peak, often off-scale of the integration device, whose retention time at the peak apex cannot be measured exactly and cannot therefore be used as a dead time marker. In this instance, the retention time of the front of the solvent peak is often subtracted from the gross retention times of the analysed compounds to give the adjusted retention times. Some integration softwares use this method for the routine determination of corrected and relative retention values and for the calculation of retention indices. In order to verify if the index values obtained with this simplified procedure are correct enough to be used for the identification of compounds, the retention values of the peak front obtained with the three solvents tested were compared with the true dead time values. Fig. 6 shows the values at the lowest and highest temperature tested (60 and 190°C) for the various solvents and columns, calculated as $(t_x - t_M)/t_M$, i.e., with the formula of the retention factor k , where t_x is the time of the peak front or of the peak apex and t_M is the dead time, corresponding to the retention time of methane. On gas-liquid bonded phase capillary columns at low temperature the use of the solvent peak as the dead time marker is suitable for compounds unretained by the stationary phase due to

different polarity, as the methanol on SPB-1 and DB-5 and *n*-hexane on Supelcowax-10; the difference between the results obtained with the peak front or apex is small. At high temperature, the retention of all the three solvents approximates the column hold-up time. The front of the asymmetric methanol peak elutes before the true carrier column hold-up time on the non-polar SPB-1 column, owing to longitudinal diffusion (hyperbolic term in the Van Deemter–Jones equation) of molecules very slightly retained by the stationary phase. On the CLOT column, only the peak of *n*-hexane can be used at high temperature as the dead time marker. The CH_2Cl_2 is retained too much and the peak of methanol is very broad.

4. Calculation of the column internal diameter from the t_M value

As shown above, the dead times measured by using the retention of inert gases, air or methane on capillary columns are close enough to the true column hold-up time to be used for practical purposes for the calculation of the retention factors, the retention indices etc. By using a modified version of

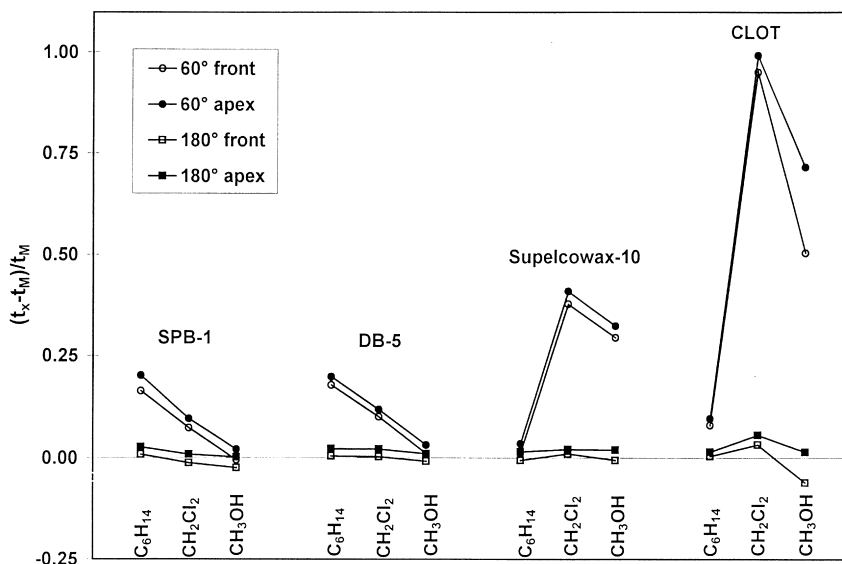


Fig. 6. The difference between the retention time of the peak front and apex of some solvents, t_x , and the column hold-up time, t_M , is divided by the t_M values. The values at 60 and 180°C are shown for the three bonded-phase capillaries of different polarity and for the CLOT column. When the ratio $(t_x - t_M)/t_M$ is close to zero, the solvent can be used as a dead time marker.

Eq. (4), these values allow one to calculate the internal diameter of the capillary column, which is an essential parameter in the built-in programs of many modern gas chromatographs. In fact, the calculation of the carrier gas velocity is automatically done by the computer of the instrument when the length and diameter of the column are inputted by the operator, the inlet pressure is measured by an electronic transducer and the outlet pressure is taken as equal to 1 bar or to the actual atmospheric pressure. Moreover, the knowledge of the column radius is necessary for the correct application of some procedures that predict the retention time of the compounds in programmed temperature analysis [22,23,25–27]. Eq. (1) can therefore be modified as follows, if the methane retention is taken as the column hold-up time with FID analysis, and the internal radius of the columns calculated:

$$r^2 = \frac{16L^2 \mu(T)}{60j t_{\text{MCH}_4}} \cdot \frac{P_o}{P_i^2 - P_o^2} \quad (5)$$

with the symbols having the same meaning as in Eq. (1). Table 4 shows the values of the diameter calculated at different temperatures for some bonded phase columns. The results show that the tempera-

ture of the column has a negligible effect on this calculation and that the diameters obtained with this procedure are much closer to the true values checked by microscopy than the nominal ones given by the manufacturers. It is therefore possible to obtain a value very close to the true diameter of a new column used for the first time on a gas chromatograph equipped with FID by measuring the retention of methane at a given inlet pressure and applying Eq. (5). The nominal value of the internal diameter inputted during the initial set-up of the instrument can then be replaced with the calculated one in order to obtain, using the instrument software, a more accurate value of the carrier linear velocity.

5. Conclusions

The experiments described have shown that the retention time of methane can be used as a dead time marker with a negligible error with respect to the values based on the retention time of inert gases or air in gas-liquid chromatography on bonded-phase capillary columns. Methane may be slightly retained owing to its small solubility in non-polar stationary phases, but this effect becomes negligible as soon as

Table 4

Value of internal diameters of capillary columns calculated with Eq. (5) (CALC), compared with those measured by electron microscope (TRUE)

Columns	Diameter (TRUE) (μm)	T ($^{\circ}\text{C}$)	t_{MCH_4} (min)	Diameter (CALC) (μm)	CALC – TRUE (μm)
DB-5	291.70	62.3	0.834	291.14	–0.56
		104.3	0.900	291.42	–0.28
		146.1	0.964	291.54	–0.16
		186.5	1.025	291.44	–0.26
SPB-1	299.04	62.2	0.812	298.48	–0.56
		104.4	0.875	299.03	–0.01
		146.4	0.938	299.01	–0.03
		186.9	0.995	299.43	0.39
Supelcowax-10	299.33	62.2	0.807	299.38	0.05
		104.4	0.875	299.03	–0.30
		146.4	0.937	299.23	–0.10
		186.9	0.995	299.36	0.03

Diameter given by the manufacturer $320 \pm 20 \mu\text{m}$. Inlet pressure 21.7 p.s.i.g. ($1.496 \cdot 10^{-5}$ Pa).

the temperature of the column increases. On columns whose separation power is due to absorption or size-exclusion mechanisms, as the molecular sieves and the porous polymer beads, both in packed and in porous layer open tubular capillary columns, the use of the retention of methane may give incorrect results mainly at low temperature, as this compound is considerably retained. In this instance, hydrogen can be used with thermal conductivity detectors, whereas for detectors not sensitive to this gas, the mathematical calculation of the dead time offers more accurate results.

Mathematical calculation of the dead time, t_{MC} , by using the actual values of temperature and pressure measured at the inlet and at the outlet of the column and applying Poiseuille's law was found to give values corresponding with those obtained experimentally with air or methane and is therefore suitable for routine work, mainly when the pressure is continuously monitored by proper transducers installed in the instrument. The correct calculation of t_{MC} requires the knowledge of the exact length and internal diameter of the column.

The experimental measurement of the dead time by using the retention of inert gases, air or methane allows the true internal diameter of the capillary column to be obtained if the inlet and outlet pressures are known. An exact knowledge of the true internal diameter of the column is necessary for the

application of the algorithms used in many commercially available instruments to calculate the carrier gas velocity on the basis of pressure measurements. The application of formulas based on Poiseuille's law yields values of the internal diameter more accurate than the nominal values provided by the column manufacturers and can replace the direct measurement of the diameter by optical or SEM.

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