Theoretical calculation of gas hold-up time in capillary gas chromatography
Influence of column, instrument parameters and analysis conditions and comparison of different methods of dead time determination

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Abstract

The gas hold-up time or dead time, t_m, of some capillary columns with different bonded liquid or carbon layer stationary phases was calculated by using equations derived by the classical theory of gas behaviour in narrow tubing, e.g., Poiseuille's law. The parameters of the equations (pressure, temperature, gas viscosity, diameter and length of the column) were measured experimentally and the effect of the approximation of the measure on the final value of t_m was evaluated over a wide temperature range. The calculated t_m values were compared with those obtained by using the retention time of methane, the extrapolation of homologous series, the elution of the front of the solvent peak, flow-rate measurement with a bubble flow meter and the automatic systems of commercially available instruments.

1. Introduction

The measurement of the dead time or gas hold-up time, t_m, of a column is of great importance in gas chromatography. This parameter is a measure of the time spent in the column by the molecules of the carrier gas or of a substance that does not interact with the stationary phase and can be measured without problem when using detectors sensitive to organic and inorganic compounds, such as in thermal conductivity detection (TCD). In fact, the retention of some

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gases such as hydrogen, argon, neon and air corresponds well enough with that of the commonly use carrier gas helium, except on some specific adsorption phases such as molecular sieves or porous polymers at low temperature.

The use of specific detectors not sensitive to inorganic gases, such as the widely used flame ionization detection (FID), introduced some new problems in this field, mainly because the t_m on capillary columns is high with respect to the retention of fast-eluting compounds, and any uncertainty in its determination introduces a large error in the calculation of important parameters, such as the capacity factor, k', the

Kováts' retention index [1] and the Rohrschneider and McReynolds polarity systems [2,3]. Further, the exact knowledge of t_m at various temperatures is necessary in order to predict the retention times during temperature-programmed analyses by means of computer calculation by starting from the adjusted retention times measured in isothermal runs [4–8].

Two main directions were followed by many workers for the determination of t_m when using FID, one based on the use of the retention time of methane [9–12] and the order on a series of regression calculations used in order to deduce the elution time of a non-retained substance by extrapolating the behaviour of homologous series of compounds (n-alkanes, n-alkanols, ketones, esters, etc.) [9,13–28]. Both approaches have been subjected to some criticism and reviews on the advantages and drawbacks of the different methods have been published [12,23,27,29–31]. An empirical method employed for the determination of the adjusted or relative retention values of high-boiling compounds (pesticides, polychlorobyphenyls, polycyclic aromatic hydrocarbons, steroids, etc.) in high-temperature analyses takes as the zero time the front of the solvent peak. This is justified by the consideration that at high temperature the retention of a low-boiling compound is small and that the diffusion of the solvent molecules into the carrier gas stream can anticipate the output of the first-eluting portion of the solvent peak approaching the residence time of a non-retained substance.

The determination of the gas hold-up time based on measurements independent of the injection of a reference sample theoretically unretained by the stationary phase was carried out for packed columns by Kaiser [16], who measured the true gas volume of the system. When capillary columns are involved, the measurement of the true volume and of the actual flow-rate is often difficult, owing to their small values and to the use of various ionization detectors where auxiliary gas flows are added: hydrogen for FID, flame photometric (FPD) and thermionic detection (TSD), make-up carrier gas for FID, electron-capture detection (ECD) and

TSD, contributing to the total gas output from the detector. The actual carrier gas flow-rate can be measured, of course, by connecting a micro flow meter directly to the column exit, but this procedure cannot be applied during routine work and does not take into account the back-pressure due to the detector. On the other hand, the behaviour of the carrier gas in the capillary tubing can be deduced by using classical equations such as Poiseuille's law, if some parameters are known exactly: the length and diameter of the column, viscosity of the gas, temperature, etc. The essential value that permits the calculation of the flow-rate and of the velocity of the carrier gas is the pressure at the column inlet, which can be measured continuously before and during the analyses, without disconnecting the column. This approach has recently been followed by some producers of gas chromatographic equipment, by offering as an option to advanced instruments the possibility of measuring the inlet pressure and, sometimes, of calculating the flow-rate directly by using the built-in electronic system of the apparatus. Some useful measurements, however, can be made with simple laboratory manifolds and the results used to calculate the true flow-rate and the gas hold-up time.

The equation used for the calculation is the classical equation that permits the prediction of the permanent isothermal motion of a gas with constant mass flow [32]:

$$P_i^2 - P_o^2 = \frac{P_a Q_M^2}{\rho_a \pi^2 r^4} \left[\frac{\lambda L}{2r} + 2 \ln\left(\frac{P_i}{P_o}\right) \right] \tag{1}$$

where

P_i = column inlet pressure absolute (dyn cm^{-2});

P_o = column outlet pressure absolute (dyn cm^{-2});

P_a = atmospheric pressure, absolute (dyn cm^{-2});

Q_M = mass flow-rate (g s^{-1});

ρ_a = density of the carrier gas (g cm^{-3}) at P_a and at the column temperature, T_c;

r = column radius (cm);

L = column length (cm);

λ = resistance coefficient.

The resistance coefficient, λ, depends on the type of gas motion in the column. For laminar flow (Reynold's number $Re < 2300$) the following equations can be used:

$$\lambda = 64/Re \qquad (2)$$

$$Re = \rho u 2r/\mu \qquad (3)$$

where u is the gas velocity (cm s^{-1}), μ the dynamic viscosity (P) and ρ the density of the carrier gas (g cm^{-3}), both at the temperature of the column, T_c. By applying Eq. 3 with the conditions yielding the greatest value of Re for a capillary column of I.D. 0.32 mm, a Reynold's number <10 was always obtained, thus confirming the hypothesis of laminar flow, which is generally accepted (for example, the classical expression of the pressure gradient correction factor can be deduced by the differential form of the Poiseuille law by postulating laminar flow). As a consequence, the first term in brackets in Eq. 1 is of the order of magnitude of 10^5, and the second term can be neglected, being <2. With flow-rate $F = Q_M/\rho$, the ratio P/ρ being constant along the column and taking into account another expression of the Reynold's numbers:

$$Re = 2Q_M/\mu\pi r \qquad (4)$$

the equation that allows the determination of the calculated flow-rate, F_c (cm^3 min^{-1}), is

$$F_c = \frac{(P_i^2 - P_o^2)}{P_o} \frac{60\pi r^4}{16L\mu} \qquad (5)$$

and can be applied to the determination of the gas hold-up time if the parameters of the column, the nature of the carrier gas and the inlet and outlet pressure are known. The linear gas velocity at the column outlet (cm s^{-1}) is

$$u_o = F_c/60\pi r^2 \qquad (6)$$

The average linear carrier gas velocity, u, in the column must be calculated by taking into account the gas compressibility by means of the pressure gradient correction factor of James and Martin [33], j:

$$u = ju_o = \frac{3}{2} \cdot \frac{(P_i/P_o)^2 - 1}{(P_i/P_o)^3 - 1} \cdot u_0 \qquad (7)$$

The gas hold-up time, t_m (min), is therefore

$$t_m = \frac{L}{60u} = \frac{L\pi r^2}{jF_c} \qquad (8)$$

During routine work, only the knowledge of the P_i may be necessary, if all other terms are known and remain constant. Some characteristics of the equipment used or a change in the conditions of analysis can influence the final result; an investigation was therefore carried out in order to establish which corrections and additions should be made to Eq. 5 in order to obtain valid results.

2. Experimental

The measurements of the retention times were carried out by using two gas chromatographs, Models 3400 and 3600 (Varian, Palo Alto, CA, USA), each equipped with a split–splitless capillary injector and a flame ionization detector. Several capillary columns of different polarity were used: bonded-phase non-polar DB-1 (polydimethylsiloxane) (28 m × 0.32 mm I.D.) and polar DB-WAX (polyglycol) (30 m × 0.32 mm) (J & W Scientific, Folsom, CA, USA); bonded-phase non-polar SPB-1 and polar Supelcowax-10 (both 30 m × 0.32 mm I.D.); and carbon layer open-tubular (CLOT) (30 m × 0.32 mm I.D.), partially deactivated with a polyglycol-terephthalic acid liquid phase layer (Supelco, Bellefonte, PA, USA) [24–36]. Helium was used as the carrier gas. The results were integrated and the retention times measured with an accuracy of ±0.001 min by using a Varian DS 650 data system.

Temperatures were monitored by the built-in systems of the gas chromatograph (with a precision of ±1°C for the injector and detector and of ±0.2°C for the column oven) and independently by auxiliary external thermocouples or precision thermometers (precision ±0.1°C). Pressures were measured with mercury manometers or piezoelectric transducers, flow-rates at atmos-

pheric pressure and room temperature with a micro soap-bubble flow meter. Details of the procedures are discussed below.

3. Results and discussion

The influence of the various terms of Eq. 5 and of other parameters, such as the temperature and atmospheric pressure, was investigated experimentally and the variations of the calculated flow-rate and dead time as a function of the approximations of the measurement of the various parameters were evaluated.

3.1. Column diameter and length

These parameters are given by the producers of the capillary columns, and the accuracy of the values listed on the certification of the column is of paramount importance for the calculation. Column length can easily be checked by the number and diameter of coils, while the measure of the inner diameter requires the use of an optical microscope with a suitable reference scale to measure a section of the column, cut near the end to avoid influencing the total length. Of course, the manufacturing process should ensure constancy of the column diameter over the entire length. As the r value to the fourth power is involved in the equation, small errors in the knowledge of the diameter have a great effect on the calculation. On the other hand, if the flow-rate is measured directly and independently, e.g., with a bubble flow meter, differences between the calculated and measured values permit the r values to be corrected. As an example, a difference of -4.2% in the t_m of one of the columns tested was found when using for the calculation the certified diameter of 0.327 mm. The value of r calculated from the actual flow-rate measurement was 0.16 ± 0.0025 mm; by microscope observation the true diameter was found to be 0.320 mm. Fig. 1 shows the deviations from the best values of calculated t_m (first line) due to different approximations of the parameter of Eq. 5. The second and third lines show the maximum errors with an approximation
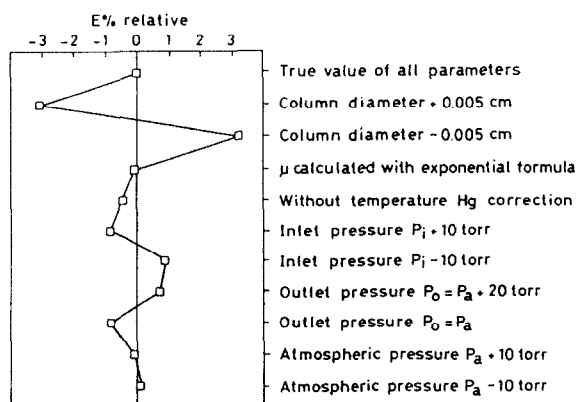

Fig. 1. Relative percentage error in the value of calculated gas hold-up time when the various terms of Eq. 5 are known with a positive or negative difference with respect of the true value. See also Table 1 for the effect of temperature.

of the column diameter of ± 0.005 cm. The uncertainty in the knowledge of this parameter is the main source of errors in the final results. The influence of the column temperature on this uncertainty is shown in Table 1.

3.2. Viscosity of carrier gas

The dynamic viscosity of the carrier gas, μ, changes with temperature [12,37–39]. Its value can be predicted by using two different expressions, a quadratic:

$$\mu = a + bT - cT^2 \tag{9}$$

or an exponential relationship [40]:

$$\mu = \alpha T^\beta \tag{10}$$

where T is the temperature in K and a, b, c, α and β are constant that depend on the gas used (see Table 2). Both expressions yield the μ values in micropoise (μP).

The difference in t_m values obtained by using the above two expressions is small: the average relative error for helium is smaller than -0.07%, as shown in the fourth line of Fig. 1 and the fourth column of Table 1, and therefore the use of the two expressions is almost indifferent with respect of the influence of other parameters. Owing to the different slopes of the two plots, the deviation assumes opposite signs at tempera-

Table 1

Relative percentage errors at different column temperature in the values of calculated gas hold-up time when the terms of Eq. 5 are known with a positive or negative deviation with respect to the true value (see also Fig. 1)

T (°C)	(1) t_{mo} (s)	Deviation from true value									
		(2) $d + 0.005$ (cm)	(3) $d - 0.005$ (cm)	(4) $\mu_{exp.}$ (P)	(5) Hg density correction	(6) $P_i + 10$ (Torr)	(7) $P_i - 10$ (Torr)	(8) $P_o = P_a + 20$ (Torr)	(9) $P_o = P_a$ (Torr)	(10) $P_a + 10$ (Torr)	(11) $P_a - 10$ (Torr)
23	40.2	-1.23	1.29	0.25	-0.17	-0.33	0.34	0.28	-0.33	-0.033	0.034
33	41.1	-1.26	1.32	0.23	-0.17	-0.34	0.35	0.28	-0.34	-0.034	0.035
45	42.2	-1.29	1.35	0.03	-0.18	-0.35	0.36	0.29	-0.35	-0.035	0.036
60	43.5	-1.33	1.39	-0.01	-0.20	-0.36	0.37	0.30	-0.36	-0.036	0.037
80	45.3	-1.38	1.45	-0.06	-0.20	-0.38	0.38	0.31	-0.37	-0.038	0.039
100	47.0	-1.43	1.50	-0.11	-0.21	-0.39	0.40	0.32	-0.38	-0.039	0.040
120	48.6	-1.48	1.56	-0.15	-0.22	-0.40	0.41	0.33	-0.40	-0.040	0.041
140	50.2	-1.53	1.61	-0.19	-0.23	-0.42	0.42	0.34	-0.41	-0.042	0.043
160	51.8	-1.58	1.66	-0.22	-0.23	-0.43	0.44	0.35	-0.42	-0.043	0.044
180	53.4	-1.63	1.71	-0.24	-0.24	-0.44	0.45	0.37	-0.44	-0.044	0.045
E(rel.) (%)		-3.05	3.20	-0.07	-0.44	-0.83	0.84	0.68	-0.82	-0.08	0.09

Column 5 shows the error when the Hg density is not corrected for room temperature in the evaluation of pressure with an Hg manometer.

Table 2
Values of the constants used to calculate the viscosity, μ, of hydrogen, helium and nitrogen carrier gas as a function of temperature with a quadratic (Eq. 9) or exponential (Eq. 10) relationship

Carrier gas	a	$b \cdot 10^3$	$c \cdot 10^8$	α	β
He	48.36	5.77	2.15	5.024	0.648
H_2	18.69	2.56	0.79	1.624	0.701
N_2	10.00	6.39	2.81	2.791	0.727

tures lower and higher than the crossing point of the plots.

3.3. Pressure and flow-rate measurements

In order to apply the calculation method in its simplest version, given in Eq. 5, the values of P_o at the column outlet were taken as equal to the atmospheric pressure, P_a. The column end was therefore disconnected from the detector base, protruded from the column oven through a small hole in the insulating wall and connected to the soap-bubble flow meter by means of a short PTFE 1/8-in. tube. P_o was therefore equal to P_a, which was measured with a precision Fortin-type mercury barometer and corrected for the room temperature, T_m. If this correction, which takes into account the thermal expansion of the mercury, is not applied, the error in the final value of the calculated t_m is about $\pm 0.5\%$ (see the fifth column of Table 1 and Fig. 1). The pressure at the column inlet, P_i, was measured with a precision of ± 0.5 Torr (± 66.66 Pa), by connecting to the injector a U-type mercury manometer, and also corrected at T_m. Bourdon-type precision manometers or electronic piezoelectric pressure transducers can also be used during routine work. The accuracy of the final results depends strongly on the accuracy and precision of this equipment. Standard pressure transducers can measure the column head pressure in 0.25 p.s.i. (12.9 Torr) or 0.1 p.s.i. increments, with an uncertainty much greater than that offered by the simpler mercury manometer.

The values of the flow-rate calculated with Eq. 5, F_c, were compared with those measured at the column outlet by using a micro soap-bubble flow meter. The values measured with this manifold, F_s, were corrected by taking into account the vapour pressure of water and the gradient of pressure between the column outlet and the flow meter, with the equation

$$F_m = \frac{F_s(P_a - P_w)}{P_a} \cdot \frac{P_a}{P_o} \tag{11}$$

where P_o is the pressure at the column outlet, P_a is the atmospheric pressure at which the flow was measured and P_w is the vapour pressure of water at the temperature of the flow meter (room temperature, T_m, as checked by inserting two termocouples at the bottom and top of the calibrated glass tubing). F_m is therefore the gas flow-rate from the column (cm^3 min^{-1}) at T_m and P_a and corresponds exactly to F_c when the temperature of the column, T_c, is equal to that of the flow meter, T_m. If $T_c \neq T_m$, the values of F_m and F_c differ and a correction factor must be applied. Fig. 2 shows the change with temperature of the flow-rate and the increasing difference between F_m and F_c. The flow-rate determined by means of the bubble flow meter corresponds exactly to the true value at the column outlet when the two temperatures are equal. As the column temperature increases, the cooling of the carrier gas to room temperature at which the flow meter is operated causes a decrease in
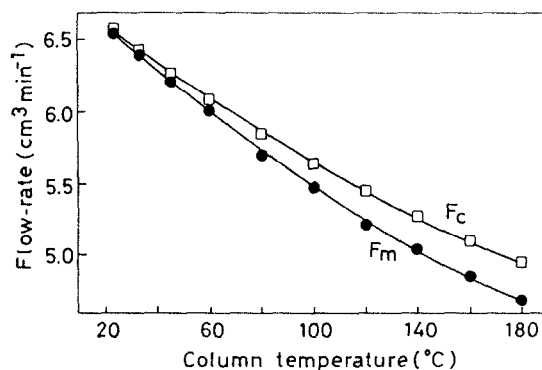

Fig. 2. (●) Carrier gas flow-rate, F_m, measured by bubble flow meter at room temperature $T_m = 23°C$ and (□) effective flow-rate at the temperature of the column outlet, F_c, as a function of column temperature.

volume and therefore the value of F_m is under-estimated with respect of the true flow-rate at the column outlet. A correction factor depending on temperature, γ, should therefore be applied to the results of flow meter measurements in order to obtain the true flow-rate at the column outlet, F_c:

$$F_c = F_m \left(\frac{T_c}{T_m}\right)^\gamma \qquad (12)$$

This expression agrees with the application of Poisson's equation for an adiabatic transformation [41] because the carrier gas temperature quickly decreases from T_c to T_m in an insulating tube. The heat exchange between the cooling carrier gas and the external ambient is negligible and the temperature change is related only to the internal energy of the gas and the adiabatic transformation can be applied. In order to calculate γ for a given experimental apparatus, a least-squares regression starting from F_c and F_m measured over a wide temperature range is applied, yielding the final expression for γ:

$$\gamma = \frac{\Sigma \ln(T_c/T_m) \ln F_c - \Sigma \ln(T_c/T_m) \ln F_m}{\Sigma [\ln(T_c/T_m)]^2} \qquad (13)$$

In the present instance, $\gamma = 1.134$ and its application to the measured F_m exactly compensates for the effect of the temperature difference between the column and the flow meter. Fig. 3 shows the correspondence between the F_c and the flow meter values corrected by using the γ term, F_m. The two values of the dead time agree with a relative error of -0.03%, mainly due to the stop-watch operation in the measurement of the transit time of the bubble in the flow meter and therefore fully stochastic, as shown by the lower graph in Fig. 3. The error due to the difference between T_m and T_c is much greater than that made by neglecting the correction for the vapour pressure of water, P_w (Eq. 10) and therefore any determination of the flow-rate by means of an external flow meter should be corrected by using the γ value calculated for that equipment.

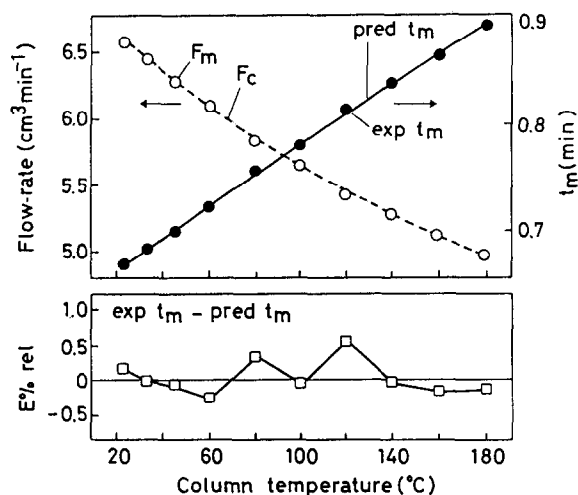The flow-rate measured directly at the column outlet does not correspond exactly to that exist-

Fig. 3. Effect of the column temperature on the difference between the calculated flow-rate and that measured by the flow meter at room temperature and corrected with the adiabatic term γ. In the upper graph the open circles and the dashed line (both referred to the left-hand scale) show the experimental values corrected with $\gamma(F_m)$ and the flow-rate trend calculated by Eq. 5 (F_c), respectively. The t_m values obtained from the experimental flow meter values (upper graph, closed circles) are compared with the behaviour predicted with Eq. 5 (full line, right-hand scale). The relative percentage error between the experimental and predicted t_m (i.e., the distance between the closed circles and the full line) is shown in the lower graph.

ing in the column when it is connected to the detector, because of the back-pressure due to the restriction of the flame jet (in FID and TSD) or of the outlet tubings in ECD. This effect might be neglected if the flow of gas through the detector was only that coming from the capillary column (a few cm^3 min^{-1}), but in practice the correct detector operation requires the addition of hydrogen and/or make-up gas, depending on type and model. This means that the flow-rate through the flame jet may be as high as 60 cm^3 min^{-1} (hydrogen plus carrier plus make-up gas) and through a pulsed-type ^{63}Ni electron-capture detector of about 30 cm^3 min^{-1} (carrier plus N_2 or $Ar–CH_4$ ionizable counting gas). The difference between P_o and P_a, P_d, is therefore not negligible. Its value for FID with a flame jet having an inner diameter of 0.020 in. (0.13 mm), suitable for capillary operation, was measured by connecting the manometer to the tubing normal-

ly used for the hydrogen inlet, the flow meter to the flame tip, and increasing the flow-rate through the make-up line. The difference in pressure, P_d, between the column outlet (P_o) and the top of the flame jet (P_a) ranged from 2 Torr (about 8 cm^3 min^{-1} of carrier gas only) to 11 Torr (no make-up, carrier plus 20 cm^3 min^{-1} of hydrogen) to 20 Torr (60 cm^3 min^{-1} of carrier plus hydrogen plus make-up gas). Table 1 (8th and 9th columns) and Fig. 1 show the positive and negative variations for the extreme hypotheses of $P_d = 0$ and $P_d = 20$ Torr.

The uncertainty or the approximation of the P_a, P_o and P_i values influences the values of the flow-rate and t_m. The approximations may have synergistic effect or be partially compensated for, depending on their values and signs. Table 1 (columns 6–11) and Fig. 1 show the percentage errors due to a difference of ±10 Torr in the determination of the true values of the pressure. The application of all the necessary correction factors leads to the final expression for F_c:

$$F_c = \frac{P_i^2 - (P_a + P_d)^2}{P_a + P_d} \cdot \frac{60\pi r^4}{16L\mu} \quad (14)$$

where the various terms have the same meanings as in Eqs. 1 and 5 and P_d is a constant measured as described for a given detector. When all the constant values are known, the calculation of F_c requires only the exact measure of the inlet pressure, P_i, and of the atmospheric pressure, P_a, and the correction of the μ value for its dependence on column temperature by means of Eq. 9 and 10.

3.4. Comparison of different methods for t_m calculation

The results obtained by applying the method described above and by corrected flow meter measurements were compared with those given by various methods in the literature, using all the capillary columns listed under Experimental.

Retention time of methane

The t_m (CH$_4$) values obtained by injecting very small amounts of CH$_4$ over a wide tempera-
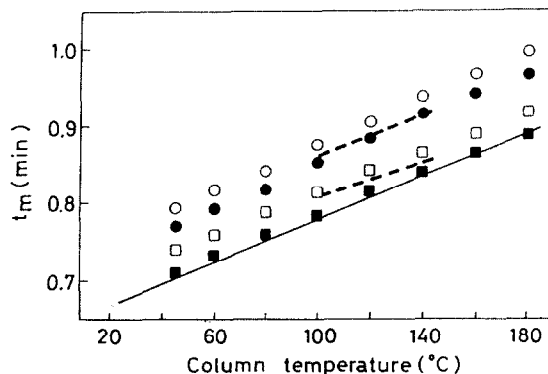

Fig. 4. Comparison between the calculated gas hold-up times, t_m, and the values measured experimentally with various methods. The full line shows the trend calculated with Eq. 14 at various temperatures on GC and CLOT columns; the symbols show the values measured at the apex of the methane peak on (○) GC and (□) CLOT columns, measured at the front of the methane peak on (●) GC and (■) CLOT columns and calculated with extrapolation from n-alkanes on GC (upper dashed line) and CLOT columns (lower dashed line).

ture range are shown in Fig. 4 and compared with t_m calculated with Eq. 14 (lowest straight line in the graph). The temperature dependence, due to the change in the gas viscosity, is the same for all the plots, but t_m (CH$_4$) values obtained on all the bonded-phase columns (polar, non-polar, Supelco, J & W Scientific) by measuring the time at the methane peak apex (open circles) are coincident and much greater than the t_m values obtained by calculation or measurement of the flow-rate. This is due to the non-negligible solubility of methane in the liquid phase [42]. When the CLOT column is used, the highly graphitized non-porous carbon layer, further deactivated by the addition of the polar modifier, reduces to a minimum the interaction with the methane molecules and a t_m (CH$_4$) closer to t_m is obtained (open squares). If the time of the methane peak front edge is measured (by elaboration of the chromatogram by means of the Varian DS 650 data system) and taken as the residence time in the column of that fraction of methane molecules less absorbed in the liquid phase, values corresponding to t_m are obtained for CLOT columns (closed squares) and smaller than that measured at the peak apex for GLC

columns (closed circles) but still greater than t_m. The hold-up time measured by using the methane peak is therefore correct only if a negligible interaction with the stationary phase can be postulated, as with CLOT columns.

Extrapolation methods

Many methods for the calculation of t_m not depending on the retention time of methane have been suggested (see Introduction and references) and have been reviewed by Haken and co-workers in several papers [27,29–31]. By using the retention times of linear alkanes, we applied to our columns at 100, 120 and 140°C the methods of Hafferkamp [14], Grobler and Balisz [17] and Al-Thamir et al. [22]. The final results of the three methods are coincident, which is not surprising as they used equations that follow the same mathematical approach. Fig. 4 shows the values obtained on all the polar and non-polar (upper dashed line) and on CLOT (lower dashed line) columns. The values obtained lie between those measured at the top and at the beginning of the methane peak.

Retention time of solvents

In order to check if the use of the front of the solvent peak as a measure of the gas-hold-up time is acceptable, small amounts of some widely used solvents (*n*-hexane, dichloromethane, methanol) were injected at various temperatures on to the tested columns. Fig. 5 shows that at low temperature the retention of the solvents used (measured at the apex of the peak) is greater than the true t_m and than the retention time of methane, depending on the interaction of the injected substance with the stationary phase used (e.g., the most retained substance on CLOT and on polyglycol GL columns is dichloromethane, whereas on non-polar polydimethylsiloxane the greatest retention time is shown by hexane). With increase in temperature, the retention of the solvents quickly decreases and at high temperature the difference from the retention of methane becomes negligible. The front of the solvent peak, often used as the reference time for the calculation of adjusted or relative retention in the analysis of high-boiling
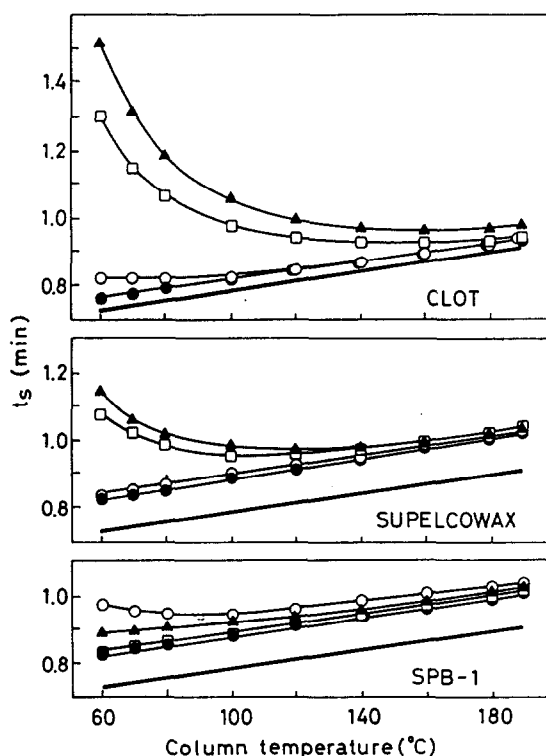

Fig. 5. Retention time of the apex of the peak of some common solvents as a function of temperature on three columns (CLOT, Supelcowax, and SPB-1, 30 m × 0.32 mm I.D.). ○ = Hexane; □ = methanol; ▲ = dichloromethane. The retention time of methane (●) and the calculated t_m (lowest straight line) are also shown

compounds, is generally eluted, with the column length used, 0.02–0.03 min before the peak apex (nearly independently of temperature) with the exception of methanol (peak front about 0.1 min before the peak apex) and *n*-hexane (peak front 0.01 min before the peak apex), both on the CLOT column. The use of the solvent peak is therefore acceptable at high temperature suitably approximating the true t_m and being equivalent to the values obtained by using the methane retention or the extrapolation of homologous series.

3.5. Automatic calculation of t_m

Some modern gas chromatographs are equipped with automatic pressure-sensing units

(e.g., Model 8700, Perkin-Elmer, Norwalk, CT, USA), and some of them can calculate directly the carrier gas flow-rate or linear velocity by means of a built-in microcomputer (e.g., Model 5890, Hewlett-Packard, Boise, ID, USA [43]; Model CP-9001, Chrompack, Middelburg, Netherlands; Model 3600, Varian).

As we used a Varian Model 3600 instrument, equipped with pressure- and temperature-sensing units and with a computing unit that automatically calculates the splitting ratio, the carrier gas velocity and the column flow-rate, the results obtained with this system were compared with those given by the application of Eq. 14 when all its parameters are exactly known. The equation used by the automatic system to give the automatic flow-rate F_a (adjusted to the volume as measured by the flow meter at room temperature) is as follows using the same symbols as used in Eqs. 1, 5 and 14:

$$F_a = \frac{60\pi r^4}{16L\mu} \cdot \frac{P_i^2 - P_o^2}{P_a} \cdot \frac{T_{ref}}{T_c} \qquad (15)$$

P_i is measured by the pressure transducer connected near to the back-pressure regulator of the splitter (in 0.25 p.s.i. increments; 1 p.s.i. = 6894.76 Pa), the column outlet pressure, P_o, is taken as equal to atmospheric pressure, P_a, and P_a is defined to be constant at 760 Torr (1 Torr = 133.322 Pa), T_c is monitored by the temperature-sensing probe of the column oven (±0.1 K) and T_{ref} is taken as constant (293 K). The operator enters the column length and diameter and the type of carrier gas; the value of μ for the selected gas (H_2, He or N_2) is calculated by using the actual T_c value and the quadratic Eq. 9. As seen above, this value differs from the actual flow-rate at the column outlet, F_c, because $P_o \neq P_a$, owing to the detector back-pressure, P_d, and to the effect of the correction factor, γ, in Eqs. 12 and 13.

The accuracy of the system depends on the exact inputs of column length and diameter, on the pressure transducer sensing increments, on the difference between the actual room temperature and the fixed 293 K value and on the deviation of atmospheric pressure from the set

value of 1 atm. The difference between P_o and P_a due to the detector restriction cannot be corrected for and, by using a split–splitless injector, the pressure transducer connected near to the back-pressure regulator will read a lower pressure than that actually at the column top when a significant gas flow is diverted through the split line. By placing the transducer connection as close to the injector as feasible, this difference can be reduced. On the other hand, the difference between the P_i value measured by the transducer connected in its standard position and that measured at the injector by using the mercury manometer was small (6 Torr) and therefore both this sources of error in the P_i value and the difference between P_o and P_a due to the detector are of the same order of magnitude as the precision of the sensing element (0.25 p.s.i. $\approx$ 13 Torr). Also, the atmospheric pressure changes due to altitude (about 13 Torr for a 500 m rise above sea level) and to weather are comparable to the transducer error. By operating the instrument at constant atmospheric pressure (757 Torr) and room temperature (23.5°C), fairly corresponding values of gas hold-up times were therefore found (Table 3). It should be taken into account, however, that all the deviations due to the splitter effect, to the detector back-pressure, to the altitude and to meteorological events may have the same sign

Table 3
Relative percentage errors at different column temperatures between values of gas hold-up time calculated with Eq. 14 (t_c) and those displayed by the automatic system of the gas chromatograph (t_a)

T (°C)	t_a (s)	t_c (s)	E(rel.) (%)
23	40.7	40.2	1.00
33	41.6	41.1	0.98
45	42.5	42.2	0.66
60	43.7	43.5	0.28
80	45.5	45.3	0.56
100	47.2	47.0	0.60
120	48.9	48.6	0.66
140	50.4	50.2	0.36
160	52.0	51.8	0.32
180	53.7	53.4	0.54

and, summed together, yield automatic velocity carrier gas values which, at the level concerned, may differ from those calculated with the actual values of all the parameters.

Other instruments that use the same equation applied to the P_i values measured at the pressure-flow control unit of the gas chromatographs and that take as constant room temperature and atmospheric pressure may give the same approximation as the tested model. Therefore, the ideal automatic system should have, in addition to the pressure sensor connected as near as possible to the injector septum, a transducer of the atmospheric pressure and a probe for the room temperature and employ for calculation the extended Eq. 14, with the possibility of inputting the value of the detector back-pressure.

4. Conclusions

The method of calculation of t_m by using the actual values of temperature and pressure at the inlet and outlet of the column was found to give values corresponding to those obtained by effective measurement of the volumetric flow-rate, mainly if the flow meter reading is corrected by taking into account the difference between the temperature of the column and that at which the flow was measured.

The t_m values based on the retention time of methane, on extrapolation of homologous series or on solvent retention are greater than the actual values, depending on the interaction of the probe used with the stationary phase of the column. When the interaction is strongly reduced by using deactivated graphitized carbon layer columns, the calculated and experimental values correspond reasonably well.

By using the inlet and the atmospheric pressure and the column and room temperature measured with simple instruments and applying the corrections for the gas viscosity as a function of temperature, the calculation of t_m is easily achieved. The values obtained by using automatic systems may differ from the actual values more or less, depending on the difference between the true values of the various parameters

and the standard conditions taken as constant in the simplified equations.

Acknowledgements

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