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New equation for specific retention volumes in capillary column gas chromatography

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Abstract

The evaluation of specific retention volumes in gas chromatography is subject to several sources of error. The use of wall-coated open-tubular columns should yield better values for specific retention volumes. However, on scaling down the flow-rate of the carrier gas, mass of stationary phase and column head pressure, new sources of error are introduced. A careful consideration of the possible sources of error is presented. It was found that, for the use of capillary columns, the classical equation describing the specific retention volume may be modified so that no flow-rates, column head and outlet pressures or mass of stationary phase in the column are necessary in order to obtain correct specific retention volumes.

1. Introduction

Although most often gas–liquid chromatography (GLC) is involved in analytical separations of substances, sometimes it is used for other purposes that involve the evaluation of the specific retention volume (V_g) of solutes, e.g., in thermodynamic studies by inverse gas chromatography (IGC). The parameter V_g is of the greatest importance in chromatography. It is related to the interactions of the solute with the stationary phase (SP). It may be used for identification purposes, although relative retention parameters, such as retention indices or relative retentions, are usually preferred because they are more reproducible and easier to determine. However, it is the key parameter in any work involving thermodynamic studies (such as in the characterization of stationary phases for GC or in the study of relationships between solvents and polymers or polymer–polymer interactions). The accurate determination of V_g values is of great importance in the theory and practice of GLC.

The value of V_g (expressed at 0°C) for a given solute in a particular SP at temperature T_c is given by the equation

$$V_g = \frac{F_c}{W_S} \cdot j(t_R - t_M) \cdot \frac{273.15}{T_c} \quad (1)$$

where

V_g = specific retention volume (ml/g);
F_c = volumetric flow-rate of the dry carrier gas at the column outlet, at the column temperature and ambient pressure (ml/min);
W_S = mass of SP in the column (g);
j = James and Martin's correction factor [1];

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t_R = experimental retention time of the solute (min);

t_M = retention time of a gas which is not retained by the SP (gas hold-up time) (min);

T_c = absolute temperature of the column (K); with symbols used throughout following the recommendations of IUPAC [2].

Retention times, temperatures and pressures are easily measured with the appropriate instruments. In order to have reliable values of V_g, two other magnitudes must be known if Eq. 1 is to be used: the flow-rate of the dry carrier gas at the column outlet (F_c) and the mass of SP in the column, W_S. Most often, a soap-bubble flow meter, capable of a precision of the order of 1% or better for flow-rates of about 5 ml/min or higher, is used to measure the flow of the carrier gas. There are commercial flow meters of various kinds claiming better precision even for lower flow-rates. The amount of SP in a packed column is easily determined using some extraction method [3]. However, when capillary columns are used, both F_c and W_S are very small and, therefore, the precision of the final value of V_g will normally be lower than that obtained on packed columns. With values of flow-rates which might be as low as 0.15 ml/min and amounts of stationary phase of the order of $5 \cdot 10^{-3}$ g, the errors involved may be considerable.

In the course of a study involving the determination of V_g values using capillary columns, we found important variations in the calculated specific retention volumes. Different values were obtained for the same solute in the same column at different flow-rates. Results obtained for the same solute and SP, at the same temperature on different columns, often differing only slightly in length, internal diameter or film thickness, were also different. A careful consideration of the various factors that may affect the precision of the values obtained for both the flow-rate and the mass of Sp in the column led us to establish an equation that is subject to lower experimental errors than the measure of the parameters involved in Eq. 1, when specific retention volumes are determined using capillary columns.

2. Experimental

2.1. Apparatus

Two Hewlett-Packard (HP) 5890A gas chromatographs and a Varian Model 3300 apparatus were used for the experiments with capillary columns. All three gas chromatographs were fitted with a split-type injection system and a flame ionization detector. The HP chromatographs had the standard back-pressure regulator to adjust the carrier gas flows, whereas the Varian apparatus was fitted with the normal pressure regulator placed upstream of the injection port. A few experiments with packed columns were run on an HP 5890 Series II apparatus fitted with a mass flow regulator. All inlet pressures were checked with pressure transducers (Wika Tronic 891.13.500; Alexander Wiegland, Klingenberg, Germany) and numeric displays (Model PM-2900; Félix Mateo, Barcelona, Spain). The pressure readings had a precision of ±67 Pa. Experiments were run isothermally at different temperatures and inlet pressures. Experiments involving mass spectrometry were carried out on a KNK 2000-C Series gas chromatograph (Konik, S. Cugat del Vallés, Spain) coupled to a modified AEI-MS-30 double-focusing mass spectrometer (ionization source, pumping system and detector from VG Analytical, Manchester, UK; electronic console and data system from Mass Spectrometric Services, Manchester, UK).

2.2. Chromatographic columns

Three glass WCOT columns were used in the collection of most of the results reported in this paper. One stainless-steel packed column was used in some experiments. The capillary columns were prepared in our laboratories from borosilicate glass tubes, drawn on a Shimadzu GDM-1B glass drawing machine. The length of the columns was calculated from the diameter of the coils, and the internal diameter was checked with a Nikon microcomparator. The tube walls were leached, washed and dehydrated following the

Table 1
Characteristics of the chromatographic columns

Parameter	Column[a]			
	1	2	3	4
Stationary phase (SP)	PS-255	TFPS35	TFPS35	OV-25
Type	WCOT	WCOT	WCOT	Packed
Length (m)	30.0	23.6	23.6	2.0
I.D. (mm)	0.238	0.225	0.226	2.2
Mass of SP (mg)	6.53	4.92	5.34	2600
Percentage of SP in the packing				15.66
Filling solution of SP (mg/ml)[b]	4.89	5.24	5.64	
Film thickness (μm)	0.29	0.30	0.32	
Deactivation agent	HDMS	TFPMCS	TFPMCS	None
Immobilization agent	DCUP	None	None	None

[a] PS-255 = Polydimethylsiloxane containing 1–3% vinyl groups (Petrarch); TFPS35 = poly(3,3,3-trifluoropropylmethylsiloxane) with 35% substitution of trifluoropropyl group (synthesized in our laboratories [7]); WCOT = wall-coated open-tubular; HDMS = hexamethyldisilazane; TFPMCS = 3,3,3-trifluoropropylmethylcyclosiloxane; OV-25 = polymethylsiloxane with 75% substitution of phenyl groups (Ohio Valley Specialty Chemicals); DCUP = dicumyl peroxide.
[b] Concentration of the solution of SP used to prepare the capillary column.

method described by Grob [4]. The tube was then silanized (see Table 1) according to Blomberg's or Grob's procedures [4–6]. The static method was followed to coat the inner walls of the tube. The amount of SP in the column was calculated from the concentration data of the filling solution and an estimation of the column volume. The packing of the packed column was prepared by evaporation of the mixture of solid support with a solution of the SP in an appropriate solvent, and the percentage of coating was deduced by extraction [3]. The characteristics of the columns are given in Table 1.

2.3. Flow meters

The flow meters used belong to the soap-film type. They were constructed using commercial precision tubes from pipettes. The full scale volumes were 1, 2 and 10 ml. All were made with a water–jacket surrounding the tube. A glass bubble containing part of the soap solution was also fitted inside the water jacket, so that the temperatures of the flow-meter scale and the solution were the same. The volumes of gas monitored in the flow meter were dependent on the actual flow-rate, but they were adjusted so that the time reading was kept at ca. 1 min, in order to minimize errors due to the monitoring of too short times or a different time for each value of the flow-rate. Flow-rates were measured by connecting a rubber tube of the polysiloxane type (I.D. ca. 2 mm) to the flame ionization detector jet (see later for other materials).

2.4. Chromatograms

Chromatograms obtained on capillary columns were measured isothermally at different temperatures from 80 to 160°C, with nitrogen or argon as the carrier gas and with inlet pressures ranging from about 107 to 193 kPa (column outlet pressures ca. 93 kPa). Ambient pressure was checked several times during the day with a mercury barometer (precision 13 Pa). Electronic integrators were used to compute retention times. A mathematical gas hold-up time method [8], based on the retentions of at least four *n*-alkanes, was used to calculate adjusted retention times (t'_R). Once the conditions of the experiment had been established (temperature, column head pressure, etc.), sufficient time was

allowed to elapse to reach equilibrium (see Results for details).

3. Results

3.1. Preliminary results

Specific retention volumes are independent of the chromatographic conditions, with the exception of temperature and the nature of the solute and stationary phase. Therefore, in our preliminary experiments we paid little attention to column length, flow-rate (its effect on column efficiency), film thickness, etc. Our preliminary results for values of V_g obtained with capillary columns for the same solute–SP pair, at the same temperature but at different carrier gas (nitrogen) head pressures for the same column, or values obtained on different columns, were disappointing, with variations (which seemed systematic) as large as 15% (Fig. 1).

3.2. Effect of the various parameters on V_g

An examination of the various factors in Eq. 1 led to the conclusion that, for any one column, errors should not lie on either $T_c(\pm 0.2$ K), $p_i(\pm 67$ Pa), $t_R(\pm 0.1$ s) or W_S (which could be erroneous, but would have the same value for different chromatograms). The factors to be examined more closely are p_o (affecting the values of both j and F_c), t_M (which might give erroneous adjusted retention times) and F_c, for a single column, and also W_S if two or more columns are to be compared. A few checks on the different parameters were carried out with the following results.

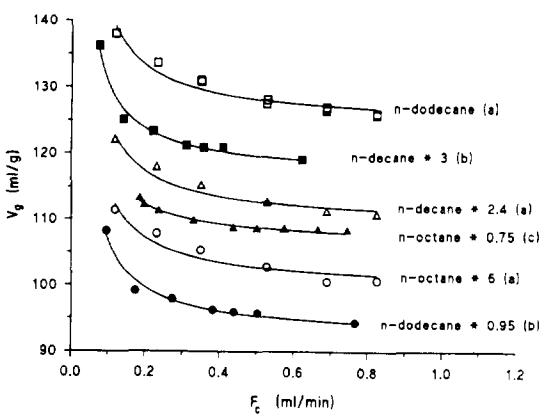

Fig. 1. Specific retention volumes of a few solutes at different flow-rates. Preliminary results. (a) Column 3 (Table 1), 120°C; (b) column 1, 160°C; (c) column 1, 80°C. Carrier gas, nitrogen. *n*-Decane * 3, for example, means that the value of V_g of *n*-decane shown in the plot is three times the correct value.

Gas hold-up time (t_M)

If our method to calculate t_M was erroneous, the values of t'_R would carry larger errors in the early-eluting peaks than for the higher *n*-alkanes. Table 2 gives results for three different columns for various flow-rates. Errors, expressed as a percentage of the lowest value, are roughly independent of the retention time of the solute, indicating that there is no significant error in the gas hold-up time method used to calculate t_M.

Column head and outlet carrier gas pressures (p_i, p_o)

An error of 67 Pa in the value of p_i will produce an error in j below 0.1%. The ambient pressure was measured with a precision of 13 Pa. However, the narrow jet tip of the flame ionization detector, bearing in mind the addition of about 35 ml/min of H_2, 30 ml/min of make-up gas (N_2) and the high temperature of the detector (viscosity of gases increases with temperature), might produce an appreciable pressure drop, with an effect on p_0 (and hence j) and also on the real value of the flow-rate, governed by Poiseuille's law, which for capillary columns is given [9] by the expression

$$F_c = \frac{\pi r_c^4}{16\eta L} \cdot \frac{p_i^2 - p_o^2}{p_o} \qquad (2)$$

were r_c is the column radius, η is the viscosity of the gas, L is the column length and p_i and p_o are the inlet and outlet carrier gas pressures respectively. Considering the effect of p_o on both F_c and j, an unobserved increase of 1.3 kPa in p_o would produce an experimental value of V_g 1.1% higher than the real value, for a head pressure of

Table 2
Calculated specific retention volumes

p_i (kPa)	F_c (ml/min)	Specific retention volume (ml/g)						
		n-Hexane	*n*-Heptane	*n*-Octane	*N*-Nonane	*n*-Decane	*n*-Undecane	*n*-Dodecane
Column 1, 80°C								
117	0.186	35.88	73.33	150.9	310.4	639.4	1307	2650
120	0.198	35.53	72.89	149.5	307.5	632.8	1295	2649
135	0.331	34.38	70.26	146.3	303.7	625.7	1280	2618
147	0.438	34.47	70.53	144.9	297.8	611.6	1250	2552
153	0.502	34.47	70.53	144.7	297.3	610.5	1248	2547
160	0.577	34.47	70.53	144.6	297.1	609.8	1246	2543
175	0.745	34.38	70.35	144.4	296.1	607.8	1242	2533
$\Delta V_g(\%)$[a]		4.4	4.1	4.5	4.8	5.2	5.3	4.6
Column 1, 160°C								
107	0.090	7.10	11.23	17.98	28.60	45.44	71.93	113.9
120	0.174	6.58	10.44	16.58	26.31	41.67	65.96	104.4
133	0.273	6.58	10.35	16.40	25.96	41.14	65.18	103.1
147	0.382	6.40	10.18	16.14	25.53	40.44	64.04	101.3
153	0.439	6.40	10.09	15.96	25.44	40.26	63.77	101.0
160	0.503	6.40	10.09	16.05	25.44	40.26	63.68	100.8
186	0.766	6.31	10.00	15.79	25.00	39.74	62.81	99.32
$\Delta V_g(\%)$[a]		12.7	12.0	13.9	14.4	14.4	14.5	14.7
Column 3, 120°C								
107	0.119	6.77	11.14	18.57	30.74	50.78	83.78	138.0
119	0.232	–	–	17.97	29.67	49.10	80.94	133.6
131	0.350	6.40	10.60	17.55	29.03	47.97	79.32	130.9
147	0.368	6.26	10.20	17.14	28.34	46.86	77.44	127.9
160	0.479	6.05	10.04	16.77	27.90	46.28	76.61	126.8
171	0.573	6.10	10.12	16.81	27.85	46.11	76.22	126.0
$\Delta V_g(\%)$[a]		12.3	11.2	11.1	10.6	10.2	10.0	9.6

[a] ΔV_g is the percentage error calculated as $100(V_{gl} - V_{gh})/V_{gh}$, where V_{gl} and V_{gh} are the V_g calculated at low (l) and high (h) flow-rates, respectively.

200 kPa, and an increase of 3.4% when the head pressure is 133 kPa. Experiments carried out with jet tips of large I.D., with and without make up gas, produced values of V_g that differed by only about 0.3% from those obtained with the normal narrow jet tip.

Flow-rate

The last factor to be considered for measurements corresponding to a single column is the flow-rate, which, according to the previous discussion, should be the source of the observed errors. The flow-rate measured is the volumetric flow-rate of the carrier gas in the flow meter, F, saturated with water vapour in the case of the soap-film type. Its relationship to the flow-rate at the column outlet is

$$F_c = F\left(1 - \frac{p_w}{p_a}\right)\frac{T_c}{T_a} \quad (3)$$

where p_w is the calculated vapour pressure of the water at the temperature of the flow meter, p_a is the ambient pressure and T_a is the absolute temperature of the flow meter.

An important point that is sometimes overlooked is the time needed to reach stable conditions after a change of column, head carrier gas pressure or column temperature. Our experience is as follows: whenever a column is installed in the gas chromatograph, a minimum

of 12 or even 24 h are needed to reach stable conditions. Retention times measured after 6 h are larger than those obtained on the following and subsequent days. This long period of time does not depend on the temperature of the column, which can be left cold overnight. Once retention times are reproducible after this long period, a change of inlet pressure produces reproducible retention times in little more than 1 h, and they remain constant for hours or days. Finally, our experience with a change of temperature is that reproducibility is reached in only a few minutes.

The various factors involved in Eq. 3 will not affect the value of F_c in the same way. T_a, p_a and T_c can be measured very accurately, and the errors would never justify the observed variations in V_g for one solute and column. The value of p_w is known, but it might happen that the gas in the flow meter was not saturated with water vapour. If this was the case, the experimental V_g values would be higher for the high flow-rates. The tendency observed in Fig. 1 is the opposite, so this could not be the cause of the errors in V_g.

Other possibilities were considered: diffusion of gas through the soap film, evaporation of water from the soap solution and diffusion of the gas through the walls of the tube connecting the gas chromatograph to the flow-meter.

If an appreciable diffusion of nitrogen through the soap film takes place, it is reasonable to consider that the effect should be less evident with a heavier gas [10]. In order to check this further, argon was used as the carrier gas. Again, errors that seem to be associated to the flow rate were found, but in this case the variations observed have the opposite sign to that with nitrogen: V_g values corresponding to low flow-rates are low. Fig. 2 shows the two curves obtained with N_2 and Ar for the same substance. The curves seem to converge on a value at high flow-rates, suggesting that errors are smaller for the higher flow-rates.

Water could evaporate from the walls of the flow meter if the gas was not saturated with water vapour. Passing several bubbles through the tube before the actual reading is taken should minimize this effect [11]. Even so, the

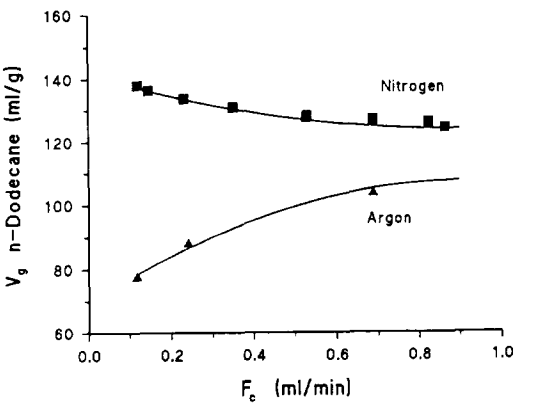

Fig. 2. Experimental specific retention volumes of *n*-dodecane on column 3 (TFPS35) at 120°C, with nitrogen and argon as carrier gases.

effect, if present, could be more evident if a larger volume is used to monitor flow-rates. Table 3 shows that above, say, 0.3 ml (a reading of about 60 s) the error of the flow reading does not depend on the actual volume monitored.

The last possibility to be considered is that gas passes through the walls of the tube that connects the gas chromatograph to the flow meter in a sufficient amount to affect the low flow-rates used in connection with capillary columns. To this end, different tube lengths were used to monitor a given flow-rate, confirming that the ratio of the V_g values obtained with low and high flow-rates were roughly proportional to the tube length used, for both nitrogen and argon (Fig. 3). This might explain why the experimental points in Fig. 1 are slightly scattered round each curve: we did not always use the same length of rubber tubing in our preliminary experiments. Considering that all checks had been carried out using the normal polysiloxane tubing often found in laboratories, other tube materials were used: copper, stainless steel, PTFE and nylon. Table 4 shows that the flow-rate measured does not seem to depend on the material of the connecting tube, with the exception of polysiloxane, which gives high values with nitrogen and low values with argon. Experiments carried out at higher flow-rates (packed column) showed that the errors involved with the use of the polysiloxane material are insignificant for flow-rates above

Table 3
Effect of the volume used in the flow meter to monitor flow-rates

Parameter	Volume in the flow meter meter (ml)					
	0.1	0.2	0.3	0.4	0.6	0.8
F (ml/min)	0.309	0.310	0.312	0.314	0.314	0.313
R.S.D.[a] (%)	0.6	0.5	0.4	0.2	0.3	0.4

Each point is the average of five measurements. p_i = 153 kPa; column 1, 160°C.
[a] Relative standard deviation.

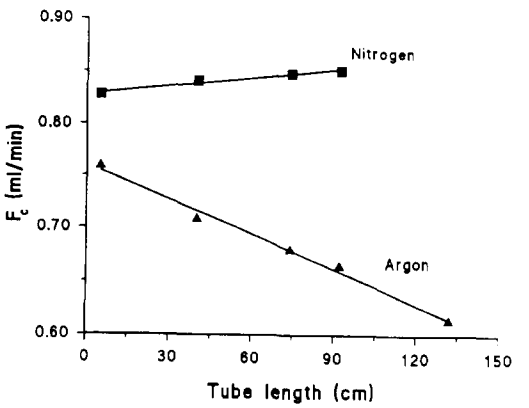

Fig. 3. Effect of the length of the polysiloxane connecting tube (chromatographic column–flow meter) on the experimentally measured flow-rate. Column 3, 120°C; inlet pressure for N_2, 173 kPa; inlet pressure for Ar, 186 kPa.

about 3 ml/min (ambient pressure). Table 5 shows that the specific retention volumes do not depend on the nature of the carrier gas or the flow-rate if the latter is measured using a copper connecting tube. The small difference between low and high flow-rates is probably due to the fact that the copper tube was connected to the gas chromatograph and to the flow meter using a very short length of polysiloxane tubing.

The last experiments described seem to indicate that air (or oxygen) could diffuse through the walls of the polysiloxane tube (when nitrogen is the carrier gas) in sufficient amount to increase the flow-rate reading. In other words, the flow through the column is lower than the flow through the flow meter, and the difference is constant but more evident at low flow-rates. When argon is used as the carrier gas, the argon, with a higher atomic mass, diffuses through and out of the walls at a higher rate than the air diffuses through into the tube, so the reading at the flow meter is lower than the value at the end of the column, and this is more evident at low flow-rates.

In order to check the validity of this argument, two series of experiments involving a mass spec-

Table 4
Experimental flow-rates measured using different connecting tubes between the chromatograph and the flow-meter

Material	Column 3 (capillary)			Column 4 (packed)		
	Nitrogen		Argon	Nitrogen		
Polysiloxane	0.153	0.714	0.687	1.07	2.49	9.20
Copper	0.142	0.689	0.787	1.04	2.46	9.18
Nylon	0.141	0.689	0.786	1.05	2.46	9.18
Stainless steel	0.142	0.689	0.789	–	–	–
PTFE	0.142	0.691	0.787	1.05	2.46	9.18
p_i(kPa)	98	162	186	101	110	146

Column temperature, 120°C.

Table 5
Experimental specific retention volumes of *n*-alkanes using copper tubing to connect the gas chromatograph to the flow-meter

Alkane	V_g(ml/g)			
	Nitrogen		Argon	
n-Hexane	6.16	6.08	6.16	5.94
n-Heptane	10.17	10.03	10.35	9.79
n-Octane	16.77	16.50	16.75	16.27
n-Nonane	27.78	27.30	27.64	27.01
n-Decane	45.87	45.01	45.61	44.59
n-Undecane	75.81	74.20	75.25	73.66
n-Dodecane	124.91	122.09	123.79	121.28
p_i(kPa)	112	163	130	187
F_c(ml/min)	0.141	0.689	0.249	0.787

Column 3, 120°C.

trometer were performed. In the first series, the gas leaving the chromatographic column (helium) was fed directly into the ionization source of a mass spectrometer through a direct line of fused-silica tubing of 0.06 mm I.D. The column–direct line connection was done using various tubes of different materials. The mass peaks of air (*m/z* 28 and 32) in the carrier gas increased for the different materials in the order copper <nylon <PVC <PTFE <polysiloxane. Taking the nitrogen level in the carrier gas when a copper tube is used as the background value of the mass spectrometer, the effect of the air intake on V_g would be that an inlet pressure of about 113 kPa would give approximate errors as follows: nylon, +0.03%; PVC, +0.1%; PTFE, +1%; and polysiloxane, +10%. In the second series of experiments, the polysiloxane tube (4 mm O.D.) that connects the GC column to the fused-silica tubing, was surrounded with a nylon tube (6 mm I.D.). Helium was passed through both tubes, and the gas leaving the outer tube was fed to the mass spectrometer to check the presence of a peak at a nominal mass of 40. Later, the gas in the inner tube was changed to argon, and a few minutes later the presence of a mass peak at a nominal value of 40 could be detected in the gas leaving the outer tube, at a concentration that was independent of the flow-rate in the inner tube. These two experiments confirm that the permeability of the polysiloxane tube is sufficient to invalidate any reading of low flow-rates such as those used in capillary column gas chromatography.

3.3. New equation for V_g

The above discussion makes it clear that measuring specific retention volumes of solutes in capillary columns is subject to serious sources of error. The precise determination of low flow-rates is such a case, even if attention is paid to the tube material used to connect the chromatographic column to the flow-meter. To know the exact amount of SP in the column, which involves a precise knowledge of both its length and its internal diameter, and the values of both head and ambient pressures with sufficient precision are other sources of error that should be eliminated if a reliable value of V_g is to be expected. In order to eliminate some of the sources of error, Eq. 1 must be modified. Some of the magnitudes in Eq. 1 can be expressed as follows:

$$F_c = V_M/t_M = V_M^0/t_M j \quad (4)$$

$$V_M^0 = (L\pi/4)(d_c - 2d_f)^2 \quad (5)$$

$$W_S = CL\pi d_c^2/4 \quad (6)$$

where

F_c = flow-rate of carrier gas expressed at am-

bient pressure and column temperature, T_c(ml/min);
V_M = hold-up volume (cm^3);
V_M^0 = corrected gas hold-up volume (cm^3);
d_c = I.D. of the column tube (cm);
d_f = SP film thickness (cm);
L = length of the column (cm);
C = concentration of the SP in the solution used to fill the capillary tube in the preparation of the chromatographic column (g/ml).

Bearing in mind that the retention factor (also called capacity factor) k is equal to $(t_R - t_M)/t_M$, Eq. 1 may be rewritten as

$$V_g = \frac{k}{C} \cdot \frac{(d_c - 2d_f)^2}{d_c^2} \cdot \frac{273.15}{T_c} \quad (7)$$

The magnitudes k, C and T_c are easily measured, but both the I.D. of the column and the film thickness are more difficult to estimate. If a microcomparator or other magnifying device is available, the I.D. of the column may be measured, but with the uncertainty about the homogeneity or consistency of the column diameter along its length. We have no experience about the precision with which the commercial fused-silica tubes are sold.

The uncertainty in the estimation of V_g through Eq. (7) stems from the term $(d_c - 2d_f)^2/d_c^2$, which can be expressed in a different form. The film thickness, d_f, is a function of both the mass, W_S, and the density, ρ of the SP, and the internal surface of the column ($L\pi d_c$):

$$d_f = \frac{1}{\rho} \cdot C \cdot \frac{L\pi d_c^2}{4} \cdot \frac{1}{L\pi d_c} = \frac{Cd_c}{4\rho} \quad (8)$$

hence

$$\frac{(d_c - 2d_f)^2}{d_c^2} = \left(1 - \frac{C}{2\rho}\right)^2 \quad (9)$$

and therefore

$$V_g = \frac{k}{C}\left(1 - \frac{C}{2\rho}\right)^2 \frac{273.15}{T_c} \quad (10)$$

With this equation, neither d_c nor d_f is needed. The main uncertainty that remains in Eq. 10 lies in the value of the density of the SP, ρ, at the column temperature. The densities of the polymers or other substances normally used as SPs in GC or substances used in IGC experiments may vary [12] from 0.8 to 1.25 at 50°C and from 0.7 to 1.1 at 250°C. Table 6 summarizes the percentage error involved in the estimation of V_g, if a fixed value of 0.9 or 1.0 g/ml is selected for the density of the SP. Considering the small effect that the value of ρ has on the final value of V_g calculated according to Eq. 10, and bearing in mind that its determination involves a careful experimental set-up, it seems reasonable to use the following simplified expression:

$$V_g = \frac{k}{C}\left(1 - \frac{C}{2}\right)^2 \frac{273.15}{T_c} \quad (11)$$

This equation should be reasonably safe for temperatures up to about 100 or 150°C, whereas for higher temperatures (150–250°C) a density of 0.9 for the SP might be selected for a safer estimation of V_g.

The use of Eq. 10 or 11 has several important advantages over Eq. 1. Determination of specific retention volumes with capillary columns is reduced to the careful preparation of the solution of the SP in an appropriate solvent, the making of the column by the static method and the measure of retention times in a chromatograph in which the temperature of the column oven should be homogeneous, and known with a certain precision. No flow-rates, head and ambient pressures (allowing for detector pressure drop) or mass of stationary phase in the column are needed in order to obtain reliable specific retention volumes with errors not larger than those involved in the evaluation of the concentration of SP in the filling solution if Eq. 10 is used, or an additional 0.20% or less if Eq. 11 is preferred.

Table 7 shows values of V_g calculated with Eq. 11 using the same set of chromatograms that served to plot some of the points shown in Fig. 1 (*n*-octane, *n*-decane and *n*-dodecane at 120°C). It may be observed that the specific retention volumes obtained for the same solute do not depend on the inlet pressure or the nature of the

Table 6
Percentage errors in the specific retention volumes calculated with Eq. 10 for stationary phases of different densities if a density of 0.9 or 1.0 is assumed

Real density of SP	Concentration of the filling solution, C (g/ml)					
	0.004		0.005		0.006	
	Value taken for ρ		Value taken for ρ		Value taken for ρ	
	0.9	1.0	0.9	1.0	0.9	1.0
0.7	0.13[a]	0.17	0.16	0.21	0.19	0.25
0.8	0.06	0.10	0.07	0.13	0.08	0.15
0.9	0.00	0.05	0.00	0.06	0.00	0.07
1.0	−0.04	0.00	−0.06	0.00	−0.07	0.00
1.1	−0.08	−0.04	−0.10	−0.05	−0.12	−0.05
1.2	−0.11	−0.07	−0.14	−0.08	−0.17	−0.10
1.3	−0.14	−0.09	−0.17	−0.12	−0.21	−0.14
d_f (μm)[b]	0.25		0.31		0.38	

[a] 0.13, for example, means that the value obtained is 0.13% higher than the correct value.
[b] Thickness of the stationary phase film for a hypothetical column of 0.25 mm I.D. and a value of ρ of 1 g/ml.

carrier gas. For any one column, the small variations, which decrease as the number of carbon atoms of the alkane increases, suggest that they are due to small errors in the measurement of the corresponding retention times. The systematic difference observed between columns (below 2%) is due to errors in the preparation of the solution of the SP. Fig. 4 shows the result of applying Eq. 11 to the experimental results which served to create Fig. 2. The broken horizontal line represents the average value of the specific retention volume of *n*-dodecane obtained with Eq. 11. It may be observed that the new experimental V_g values are independent of the nature of the carrier gas or flow-rate (pressure drop).

4. Conclusions

Many of the errors involved in the determination of specific retention volumes in GC using

Table 7
Values of specific retention volume obtained with Eq. 11 (mean values ± standard deviation of between five and fourteen experiments)

Column	p_i (kPa)	Gas	V_g(ml/g)						
			n-Hexane	*n*-Heptane	*n*-Octane	*n*-Nonane	*n*-Decane	*n*-Undecane	*n*-Dodecane
2	115	N_2	5.97 ± 0.03	9.84 ± 0.04	16.23 ± 0.06	26.87 ± 0.04	44.34 ± 0.04	73.13 ± 0.07	120.34 ± 0.17
	130	Ar	5.98 ± 0.05	9.85 ± 0.09	16.27 ± 0.09	26.88 ± 0.08	44.39 ± 0.12	73.18 ± 0.15	120.39 ± 0.24
	161	N_2	5.97 ± 0.06	9.83 ± 0.11	16.26 ± 0.06	26.89 ± 0.09	44.44 ± 0.10	73.26 ± 0.10	120.54 ± 0.13
	186	Ar	6.09 ± 0.10	10.02 ± 0.17	16.45 ± 0.17	27.08 ± 0.16	44.53 ± 0.20	73.22 ± 0.23	120.38 ± 0.27
3	112	N_2	5.90 ± 0.05	9.74 ± 0.08	16.08 ± 0.09	26.60 ± 0.09	43.94 ± 0.10	72.60 ± 0.19	119.62 ± 0.37
	130	Ar	5.93 ± 0.05	9.79 ± 0.09	16.15 ± 0.05	26.65 ± 0.07	43.99 ± 0.02	72.57 ± 0.08	119.41 ± 0.21
	163	N_2	5.91 ± 0.11	9.76 ± 0.18	16.07 ± 0.19	26.56 ± 0.20	43.83 ± 0.19	72.29 ± 0.32	118.98 ± 0.47
	187	Ar	5.80 ± 0.01	9.56 ± 0.01	15.90 ± 0.01	26.39 ± 0.08	43.57 ± 0.06	71.98 ± 0.16	118.50 ± 0.19

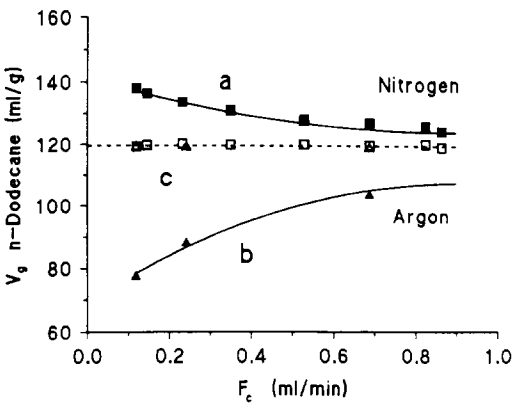

Fig. 4. Experimental specific retention volumes of *n*-dodecane on column 3 (TFPS35) at 120°C, with nitrogen and argon as carrier gases, obtained by applying Eq. 1 (curves a and b), and values obtained by applying Eq. 11 to the same set of experimental results using (△) argon and (□) nitrogen. Line c represents the average value of the specific retention volumes obtained with Eq. 11.

capillary columns are eliminated by the use of the new equation proposed here (Eq. 10 or its simplified version, Eq. 11). Reliable values of V_g will be obtained from data from the chromatogram and the concentration of the solution that served to prepare the chromatographic column. The experimental set-up is also simplified by the elimination of the need for measuring carrier gas pressures or flow-rates. Good pressure regulation and temperature control of the column oven is all that is required of the gas chromatograph.

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