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Measuring specific retention volumes in capillary gas chromatography with improved accuracy and precision[☆]

Jesús Eduardo Quintanilla-López, Rosa Lebrón-Aguilar, Ana María Tello,
José Antonio García-Domínguez*

Instituto de Química-Física "Rocasolano", CSIC, Serrano 119, E-28006 Madrid, Spain

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Abstract

The specific retention volume (V_g), which has traditionally been determined in gas chromatography using long, heavily loaded packed columns, should produce better, more reliable values if capillary columns are used. However, the smaller dimensions of some of the parameters involved introduces additional sources of error which have been overcome with a recently proposed equation. A careful consideration of the sources of error involved has been carried out using both the traditional and the new equations. The conclusion drawn is that the new equation will produce reliable V_g values with expected errors (1%) lower than those expected from packed columns (2%) using the traditional equation.

Keywords: Retention volume; specific

1. Introduction

The specific retention volume (V_g) of a solute on a particular stationary phase (SP) is the fundamental retention parameter of the substance in gas chromatography (GC). It is related to a number of other parameters, many of which are independent of the conditions of the experiment, with the exception of temperature. Parameters directly related to the solute–SP system, such as the Flory–Huggins interaction parameter and Gibbs free energy of mixing, may be obtained from carefully prepared chromatographic

runs. Other parameters related to one of the components of the system may also be deduced from V_g values, such as the Hildebrand solubility parameter and the enthalpy of vaporization of the solute, and also the solubility parameter of the SP if a few solutes are used.

Specific retention volumes, a concept introduced by Littlewood et al. [1], may be deduced with the following expression, if a soap-film flow meter is used to check the gas flow-rate:

$$V_g = \frac{F}{W_s} \cdot j t'_R \left(1 - \frac{p_w}{p_a} \right) \frac{273.15}{T_a} \quad (1)$$

where (with symbols according to IUPAC recommendations [2]) V_g is expressed in ml/g, F is the volumetric flow-rate of the carrier gas in the flow

* Corresponding author.

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meter saturated with water vapour (ml/min), W_s is the mass of SP in the column (g), j is James and Martin's correction factor [3], t'_R is the adjusted retention time of the solute (min), p_w is the vapour pressure of the water in the flow meter (bar), p_a is the ambient pressure (bar), and T_a is room temperature (K).

For many years after the appearance in 1952 of the paper on GC by James and Martin [3], packed columns were used extensively. Once capillary columns were introduced by Golay in 1957 [4,5], the new type of columns, with a higher resolving power, slowly found their way in everyday practice. However, it was not until the development of fused-silica capillary columns in 1979 [6,7] that easier and safer to handle wall-coated open-tubular (WCOT) columns gained universal acceptance.

In order to minimize experimental errors, long packed columns with high loadings of SP on the solid support have been used in the experimental determination of V_g values. Here, with a few exceptions, capillary columns have been ignored. However, some of the inherent qualities of the latter, such as the faster achievement of solute–SP equilibrium and improvements in the methods of suppression of the residual activity of the column walls, make them ideal for the purpose. Despite this, the scaling down of some parameters of Eq. 1 introduces additional sources of error, and this might be one of the reasons why capillary columns have not been used much to measure V_g values. Some workers have suggested indirect ways to calculate V_g values from capillary columns, either calculating the mass of SP in the column (W_s) from V_g values measured using packed columns [8] or using empirical parameters [9]. However, our impression is that, unless one uses data from packed columns obtained in a different laboratory, there is no point in measuring V_g values on a capillary column if the corresponding packed column is available.

Recently [10], a new equation has been proposed, which greatly simplifies both the experimental set-up and the number of experimental parameters which must be measured with precision in order to obtain reliable values of V_g with capillary columns. The equation, derived from Eq. 1, is

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

where $k [= (t_R - t_M)/t_M]$ is the capacity factor, C is the concentration of the SP used to prepare the column (g/ml), ρ is the density of the SP at the column temperature (g/ml), and T_c is the absolute temperature of the column.

Published results seem to indicate that this new equation produces values of V_g which are more reliable than those obtained with the same capillary column using the traditional Eq. 1.

In this work, we carried out a statistical study of the errors expected with the use of either of the two equations, and established the contribution of each of the parameters of each equation to the total error expected. Values of specific retention volumes obtained with capillary columns under various experimental conditions (temperature, nature and flow-rate of the carrier gas, etc.) are compared, and conclusions drawn.

2. Experimental

2.1. Apparatus

An HP-5890A and an HP-5890 Series II gas chromatographs, both fitted with the standard back-pressure regulator to adjust the column head pressure, and a Varian 3300 apparatus, with the normal pressure regulator placed upstream of the injector port, all fitted with a split-type injection system and flame ionization detector, were used. All inlet pressures were checked with pressure transducers (Wika Tronic 891.13.500; Alexander Wiegand, Klingenberg, Germany) and numerical displays (Model PM-2900; Félix Mateo, Barcelona, Spain). The flow-rates were measured using a micro flow meter (1 ml full-scale) with a water-jacket surrounding the tube, connected to the jet of the detector with a copper tube.

2.2. Chromatographic columns

All results presented here were obtained on three borosilicate glass WCOT columns coated

with the same SP. The length was calculated from the diameter of the coils and the internal diameter was checked with a Nikon microcomparator. The tube walls were leached, washed, dehydrated and silanized following the method described by Grob [11]. The static method was followed to coat the inner walls of the tube. The amount of SP in the column (W_s) was calculated from the concentration data for the filling solution (C) and an estimation of the column volume. The filling solution (10 ml) was prepared in all cases by weighing 45–60 mg of SP. The characteristics of the columns are given in Table 1.

2.3. Chromatograms

Experiments were carried out isothermally at 100, 120 and 150°C. Nitrogen and argon were used as carrier gases at linear velocities from 6.5 to 27.0 cm/s, corresponding to inlet pressures from 1.24 to 1.89 bar. Linear gas velocities were deduced from the retention time of methane and the length of the column. Chromatograms were recorded with retention times expressed in tenths of a second. Solutes injected include C_6 – C_{12} *n*-alkanes and the ten probes used by McReynolds [12]. Adjusted retention times were

calculated using the hypothetical retention time of an unabsorbed gas, calculated mathematically from the retention times of at least four *n*-alkanes [13].

3. Results and discussion

3.1. Sources of error

It was first necessary to perform a statistical study in order to establish the most probable sources of error in the experimental determination of specific retention volumes.

The value of V_g of any solute depends on the temperature and the nature of the SP, but it is independent of the nature and flow-rate of the carrier gas, type and length of the column, film thickness, etc. Obviously, retention mechanisms other than those involved in the solubility of the solute in the SP (such as adsorption on the various interphases) may alter the value of V_g and must be eliminated or minimized, in both packed and capillary columns. Therefore, a statistical study of a few experimental results will allow us to detect the sources of variation associated with its determination. We used an analysis

Table 1
Characteristics of the chromatographic columns

Parameter	Column		
	1	2	3
Stationary phase (SP)	PS-255 ^a	PS-255	PS-255
Type	WCOT ^b	WCOT	WCOT
Length (m)	25.7	30.1	27.0
Internal diameter (mm)	0.233	0.225	0.244
Filling solution of SP (mg/ml) ^c	5.20	5.20	4.44
Mass of SP (mg)	5.70	6.22	5.61
Film thickness (μm)	0.30	0.29	0.25
Deactivation agent	HMDS ^d	HMDS	HMDS
TZ	40	46	39
N_{max} (plates/m)	4930	4810	4740
Capacity factor (<i>k</i>) used	5.2	5.1	4.5
Coating efficiency (CE) (%)	97	95	88

^a Polydimethylsiloxane containing 1–3% vinyl groups (Petrarch).

^b Wall-coated open-tubular column.

^c Concentration of the solution of SP used to prepare the capillary column.

^d Hexamethyldisilazane.

of variance (ANOVA), using the Statgraphics program (Statistical Graphics). The study was carried out with results obtained on column 1, at the three temperatures for all seventeen solutes. The nature and linear velocity of carrier gas were the parameters chosen, with V_g values calculated with both Eqs. 1 and 2. A significance level above 0.01 was taken as the criterion of homogeneity of the groups of values compared.

Effect of the linear gas velocity

Results obtained with Eq. 1 showed that the groups were generally homogeneous. However, there were a few cases of non-homogeneous groups. This indicates systematic errors, probably due to the measure of the flow-rate, which did not seem to follow any trend (see Fig. 1). When V_g values are calculated for the same set of experiments using Eq. 2, the significance levels obtained when mean values are compared are always higher than 0.01 (different compounds and experimental conditions).

In all cases, the variances show similar values. This means that, for any one column, there is not an optimum flow-rate, from the point of view of the determination of V_g values. The exception in our case is the temperature of 150°C. As shown in Fig. 2, the residuals increase with increase in carrier gas velocity, in other words, very short retention times are not recommended for V_g

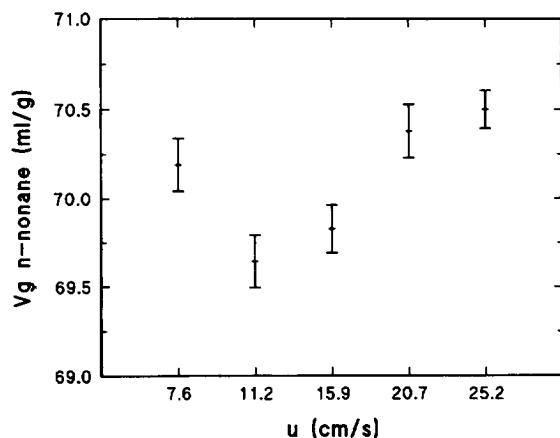


Fig. 1. Specific retention volumes of *n*-nonane on column 1 at 120°C, obtained at different linear gas velocities, showing the 99% confidence intervals. Eq. 1.

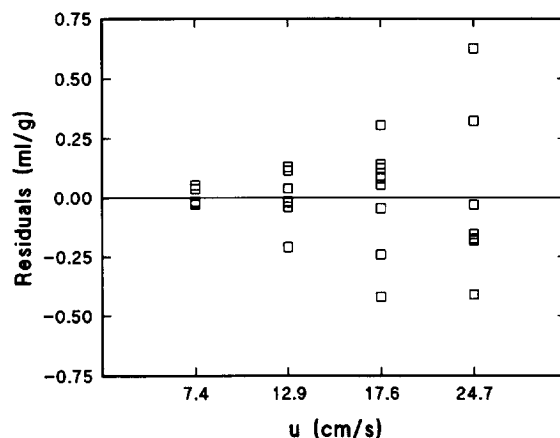


Fig. 2. Differences between experimental values and the mean value (residuals) of the specific retention volumes of *n*-nonane obtained at 150°C using Eq. 2 on column 1 at different linear gas velocities.

calculations. If the temperature is high, the gas velocity must be kept low (see the linear velocity of 7.4 cm/s in Fig. 2).

Effect of the nature of the carrier gas

Eq. 1 produces lower values of V_g when argon is used, but the differences with the values corresponding to nitrogen are always below 1% (Table 2). The differences observed are probably due to the fact that, for the same inlet pressure, lower flow-rates are obtained with argon, making it more difficult to estimate flow-rates with accuracy. Eq. 2 produces values of V_g which are independent of the gas used.

Effect of the equation used

Values of V_g obtained with Eq. 1 are lower than those calculated with Eq. 2 by ca. 2–3% in all cases. An example is presented in Table 2. This led us to the study of the maximum error expected from the application of either of the two equations to the same set of experimental results, so that the variables responsible for the small differences observed could be found.

3.2. Maximum error in calculations of V_g

The maximum error (E_{\max}) of any magnitude may be estimated from the partial derivatives of

Table 2
Mean values of specific retention volumes of *n*-alkanes obtained at different linear gas velocities (column 1, 120°C)

Alkane	Eq. 1		Eq. 2	
	Nitrogen ^a	Argon ^b	Nitrogen	Argon
<i>n</i> -Hexane	12.72	12.61	13.07	13.06
<i>n</i> -Heptane	22.43	22.22	23.06	23.02
<i>n</i> -Octane	39.63	39.31	40.73	40.74
<i>n</i> -Nonane	70.11	69.45	72.07	71.99
<i>n</i> -Decane	123.9	122.6	127.3	127.1
<i>n</i> -Undecane	218.5	216.1	224.6	224.0
<i>n</i> -Dodecane	384.7	380.3	395.3	394.2

^a Each value is the average of 31 runs.

^b Each value is the average of 18 runs.

the expression used to calculate it, with respect to each of the variables used in the expression. From Eq. 1, we may derive

$$E_{\max} \leq \left| \frac{\partial V_g}{\partial F} \right| \Delta F + \left| \frac{\partial V_g}{\partial W_s} \right| \Delta W_s + \left| \frac{\partial V_g}{\partial j} \right| \Delta j + \left| \frac{\partial V_g}{\partial t'_R} \right| \Delta t'_R + \left| \frac{\partial V_g}{\partial p_w} \right| \Delta p_w + \left| \frac{\partial V_g}{\partial p_a} \right| \Delta p_a + \left| \frac{\partial V_g}{\partial T_a} \right| \Delta T_a \quad (3)$$

where Δx is an estimator of the maximum error expected for the parameter x . In our study, we took for Δx the minimum precision of the instrument used to measure x in those cases where x is measured directly (temperature, pressure, etc.). In cases where the value of the variable x is obtained through an experimental process of measure (mass and density of SP, flow-rate, etc.), the standard deviation was taken for Δx . As an example, Table 3 shows the values of the variables and the corresponding estimators for *n*-nonane on column 1 at 120°C and a linear gas velocity of nitrogen of 11.2 cm/s.

The partial derivatives for Eq. 1 are as follows:

$$\frac{\partial V_g}{\partial F} = \frac{j}{W_s} \cdot t'_R \left(1 - \frac{p_w}{p_a} \right) \frac{273.15}{T_a} \quad (4)$$

$$\frac{\partial V_g}{\partial j} = \frac{F}{W_s} \cdot t'_R \left(1 - \frac{p_w}{p_a} \right) \frac{273.15}{T_a} \quad (5)$$

$$\frac{\partial V_g}{\partial W_s} = -\frac{Fj}{W_s^2} \cdot t'_R \left(1 - \frac{p_w}{p_a} \right) \frac{273.15}{T_a} \quad (6)$$

$$\frac{\partial V_g}{\partial t'_R} = \frac{Fj}{W_s} \left(1 - \frac{p_w}{p_a} \right) \frac{273.15}{T_a} \quad (7)$$

$$\frac{\partial V_g}{\partial p_w} = -\frac{Fj}{W_s} \cdot t'_R \cdot \frac{273.15}{T_a p_a} \quad (8)$$

$$\frac{\partial V_g}{\partial p_a} = \frac{Fj}{W_s} \cdot t'_R \left(\frac{p_w}{p_a^2} \right) \frac{273.15}{T_a} \quad (9)$$

$$\frac{\partial V_g}{\partial T_a} = -\frac{Fj}{W_s} \cdot t'_R \left(1 - \frac{p_w}{p_a} \right) \frac{273.15}{T_a^2} \quad (10)$$

Table 3

Example of data used to estimate the error in the determination of the specific retention volume of *n*-nonane at a linear gas velocity of nitrogen of 11.2 cm/s (column 1)

Parameter	Actual value	Δx
F (ml/min)	0.344	0.005
<i>j</i>	0.7433	0.0003
W_s (g)	0.0057	0.0003
p_w (mbar)	32.626	0.035
p_a (mbar)	943.4	0.1
T_a (K)	298.7	0.1
t'_R (s)	105.5	0.5
T_c (K)	393.2	0.1
<i>k</i>	0.542	0.004
<i>C</i> (g/ml)	0.00520	0.00003
$\rho_{120^\circ\text{C}}$ (g/ml)	0.885	0.004

Table 4
Specific retention volumes and maximum errors of *n*-alkanes

Alkane	Eq. 1		Eq. 2	
	V_g (ml/g)	E_{\max} (% E_{\max})	V_g , ml/g	E_{\max} (% E_{\max})
<i>n</i> -Hexane	12.62	±0.87 (6.9)	13.06	±0.15 (1.1)
<i>n</i> -Heptane	22.26	±1.55 (7.0)	23.03	±0.26 (1.1)
<i>n</i> -Octane	39.36	±2.64 (6.7)	40.72	±0.37 (0.9)
<i>n</i> -Nonane	69.61	±4.60 (6.6)	72.02	±0.56 (0.8)
<i>n</i> -Decane	123.0	±8.10 (6.6)	127.3	±0.96 (0.8)
<i>n</i> -Undecane	217.2	±14.5 (6.7)	224.7	±1.85 (0.8)
<i>n</i> -Dodecane	382.4	±25.6 (6.7)	395.7	±3.34 (0.8)

For experimental conditions, see Table 3. Each value is the average of five runs.

In the case of Eq. 2, E_{\max} is given by the expression

$$E_{\max} \leq \left| \frac{\partial V_g}{\partial k} \right| \Delta k + \left| \frac{\partial V_g}{\partial C} \right| \Delta C + \left| \frac{\partial V_g}{\partial \rho} \right| \Delta \rho + \left| \frac{\partial V_g}{\partial T_c} \right| \Delta T_c \quad (11)$$

with the following partial derivatives:

$$\frac{\partial V_g}{\partial k} = \frac{1}{C} \left(1 - \frac{C}{2\rho} \right)^2 \frac{273.15}{T_c} \quad (12)$$

$$\frac{\partial V_g}{\partial C} = k \left(\frac{1}{4\rho^2} - \frac{1}{C^2} \right) \frac{273.15}{T_c} \quad (13)$$

$$\frac{\partial V_g}{\partial \rho} = k \left(\frac{1}{\rho^2} - \frac{C}{2\rho^3} \right) \frac{273.15}{T_c} \quad (14)$$

$$\frac{\partial V_g}{\partial T_c} = -\frac{k}{C} \left(1 - \frac{C}{2\rho} \right)^2 \frac{273.15}{T_c^2} \quad (15)$$

Application of Eqs. 3 and 11 to all experimental results gave values which are very similar in all instances for each equation. In other words, E_{\max} did not depend much on the experimental conditions, but the two equations produced very different values. As an example, Table 4 shows the values for *n*-alkanes on column 1 obtained under the experimental conditions given in Table 3. The estimated maximum error expected, if the

Table 5
Contribution of each parameter to the maximum error (E_{\max})

Equation (1)		Equation (2)	
Parameter	E_{\max} (% E_{\max})	Parameter	E_{\max} (% E_{\max})
W_s	3.6572 (79.6)	C	0.4179 (74.9)
F	0.7792 (17.0)	k	0.1195 (21.4)
t'_R	0.1071 (2.33)	T_c	0.0183 (3.28)
j	0.0256 (0.56)	ρ	0.0019 (0.32)
T_a	0.0233 (0.51)		
p_w	0.0027 (0.06)		
p_a	0.0004 (0.01)		
V_g	4.5955 (100)	V_g	0.5577 (100)
V_g of <i>n</i> -nonane (ml/g)	69.61		72.02

Specific retention volumes of *n*-nonane at 120°C, column 1, 11.2 cm/s.

traditional Eq. (1) is used, is of the order of 6.7%. The new Eq. 2 will produce results with a maximum expected error below 1%. As mentioned above, these figures were obtained in all cases examined.

The contribution of each experimental parameter to the maximum error expected may be deduced from Table 5, where again the *n*-nonane corresponding to the same experimental conditions as in Tables 3 and 4 has been chosen as an example. In both cases the highest contribution to the maximum expected error lies in the mass of SP (W_s in Eq. 1 and C in Eq. 2) with a contribution of the order of 75%. The flow-rate

is an important contributor to E_{\max} in Eq. 1, near 20%, which is absent in Eq. 2. These two parameters represent, in the case of Eq. 1, an expected error of the order of 6.4% of the final value of V_g , while they may introduce a maximum error below 0.7% of V_g if Eq. 2 is used.

One parameter which is present in Eq. 2 and is absent in Eq. 1 is the density of the SP at the column temperature. We may accept that its value may be difficult to measure accurately. However, its contribution to E_{\max} is only of the order of 0.32% of E_{\max} , representing an error of about 0.003% in the final value of V_g . In any case, even if the density of SP is not measured, but assumed, the error on V_g will not be larger than 0.2% [10].

Considering that the largest contribution to E_{\max} lies in W_s , F and C , it is worth considering these factors more closely. Bearing in mind that $W_s = \pi r^2 LC$, the factor to be considered should be the flow-rate of carrier gas and the parameters which decide the volume of the column: L and r , as the concentration of the SP solution (C) is now common to both equations. For this purpose, results obtained on the three columns are compared with one another in Table 6. Only *n*-alkanes are considered. In the table, the value corresponding to one column and a solute is the average of several values of V_g obtained at the same temperature but with chromatograms run at different linear gas velocities. The dispersion of the mean values of the three columns for each solute is more than ten times larger in the case of values obtained with the traditional Eq. 1 (about 9%) than in the case of Eq. 2 (below 1%).

On the other hand, when values obtained with Eq. 1 are compared with the corresponding value from Eq. 2, it may be observed that the value is lower for column 1, almost equal for column 2 and considerably larger for column 3. The cause of these differences cannot lie in the flow-rate, as the values in the tables are in all cases the average of several measurements at different flow-rates. The observed differences are necessarily due to differences in the estimated volume of the column (and, hence, in W_s), perhaps because the column radius is not constant along its length.

Table 6

Mean values of specific retention volumes of *n*-alkanes at 120°C and at different linear gas velocities

Alkane	Column	V_g (ml/g) ^a	
		Eq. 1	Eq. 2
<i>n</i> -Hexane	1	12.71	13.07
	2	12.98	13.06
	3	13.89	13.07
<i>n</i> -Heptane	1	22.42	23.02
	2	22.87	22.98
	3	24.57	23.01
<i>n</i> -Octane	1	39.63	40.72
	2	40.45	40.68
	3	43.40	40.75
<i>n</i> -Nonane	1	70.11	71.95
	2	71.50	71.92
	3	76.78	72.15
<i>n</i> -Decane	1	123.9	127.2
	2	126.3	127.1
	3	135.9	127.7
<i>n</i> -Undecane	1	218.5	224.2
	2	222.7	224.1
	3	239.7	225.6
<i>n</i> -Dodecane	1	384.7	394.6
	2	392.0	394.4
	3	422.8	397.8

^a The number of experimental values used to calculate the figures presented in the table were 176 for column 1, 85 for column 2 and 80 for column 3.

The facts presented so far seem to indicate that Eq. 2 overcomes the difficulties of estimating the mass of SP in the column and of measuring small flow-rates, allowing the use of capillary columns to estimate specific retention volumes with confidence. The results also show that the expected errors are smaller than those predicted for packed columns, calculated by Egri et al. [8] to be about 2%. A further consideration of Eq. 2 may be deduced from an examination of the standard deviations of all values obtained on the three columns for each solute, gathered in Table 7. The experimental errors obtained are in most cases lower than the maximum expected error calculated earlier. The values are slightly different from those in Table 4, because now all linear gas velocities have been considered. It may be deduced that the three columns are equivalent (from the point of view of obtaining V_g values) and that errors are only due to the parameters included in the equation. No other source of

error has been detected. In the case of some of the McReynolds' probes, the few injections and the asymmetry presented by some of the chromatographic peaks may explain the larger values of the standard deviation.

4. Conclusions

It has been proved that the traditional equation used to evaluate specific retention volumes in gas chromatography from experiments carried out with packed columns is not appropriate for capillary columns, as it produces values of V_g with expected errors which are at least three times as large as those expected from packed columns. For capillary columns, the equation of Lebrón-Aguilar et al. [10] should be used. This equation will give values of V_g with maximum expected errors well below 1%, a considerable improvement over the expected error if the

Table 7

Mean values of specific retention volumes on PS-255 obtained at different linear gas velocities using Eq. 2 (columns 1, 2 and 3)

Compound	100°C			120°C			150°C		
	V_g	S.D. ^a	E_{max}	V_g	S.D.	E_{max}	V_g	S.D.	E_{max}
<i>n</i> -Hexane	20.48	0.04	0.22	13.07	0.01	0.15	7.37	0.05	0.12
<i>n</i> -Heptane	38.53	0.07	0.42	23.00	0.02	0.29	11.95	0.07	0.20
<i>n</i> -Octane	72.98	0.20	0.68	40.72	0.04	0.39	19.38	0.07	0.22
<i>n</i> -Nonane	137.9	0.17	1.17	72.01	0.13	0.62	31.49	0.04	0.34
<i>n</i> -Decane	260.9	0.86	2.15	127.3	0.35	1.05	51.12	0.03	0.47
<i>n</i> -Undecane	492.1	1.93	4.09	224.6	0.86	1.79	82.87	0.15	0.72
<i>n</i> -Dodecane	925.7	3.82	7.86	395.6	1.93	3.14	134.1	0.48	1.12
Benzene	30.42	0.22	0.32	19.18	0.10	0.21	–	–	–
<i>n</i> -Butanol	26.71	0.23	1.14	16.52	0.32	0.23	–	–	–
2-Pentanone	31.49	0.41	0.33	19.32	0.25	0.21	–	–	–
1-Nitropropane	41.08	0.46	0.32	24.69	0.17	0.27	–	–	–
Pyridine	47.94	1.17	0.79	28.85	0.89	0.29	–	–	–
2-Methyl-2-pentanol	43.15	0.29	0.47	25.52	0.07	0.27	–	–	–
1-Iodobutane	79.32	0.40	0.72	45.52	0.26	0.42	–	–	–
2-Octyne	110.2	0.98	0.81	58.28	0.19	0.50	–	–	–
1,4-Dioxane	37.11	0.43	0.32	22.66	0.22	0.20	–	–	–
<i>cis</i> -Hydrindane	251.6	0.82	2.05	130.5	0.41	1.06	–	–	–
<i>Number of injections for columns 1, 2 and 3:</i>									
<i>n</i> -alkanes	47, 51, 44			176, 85, 80			24, 28, 29		
McReynolds' probes	6, 6, 10			15, 6, 16			–		

^a Standard deviation of V_g for the three columns used.

traditional packed columns are used. The equation may be applied without much attention to the experimental conditions which affect column performance, with the only precaution of avoiding too short retention times: lower flow-rates will improve the accuracy in experiments at high temperatures, even if they represent linear gas velocities below the optimum.

The greater simplicity of the experimental set-up needed for the application of the new equation, the general advantages of capillary columns over packed columns and the smaller amount of stationary phase used offer a good perspective for the thermodynamic characterization of new stationary phases and other polymeric materials, and will certainly facilitate interlaboratory comparison of data.

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