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ERROR IN THE DETERMINATION OF THE SPECIFIC RETENTION VOLUME

SPECIFIC RETENTION VOLUMES OF *n*-ALKANES ON APOLANE-87 STATIONARY PHASE AS FUNCTIONS OF COLUMN TEMPERATURE

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SUMMARY

The estimation of the maximum error in the determination of the specific retention volume, V_g , and the estimation of V_g values as functions of column temperatures are reported. The calculated values are compared with those measured on Apolane-87 stationary phase at different column temperatures.

INTRODUCTION

In the theoretical and practical fields of gas-liquid chromatography (GLC) an important parameter is the specific retention volume, V_g , introduced by Littlewood *et al.*¹. This parameter contains the most important basic parameters of GLC, namely the inlet and outlet pressures of the carrier gas, its volumetric flow-rate, the retention times of the components, the transit time of the inert material through the system, the column temperature, and the amount of the stationary phase. The accurate determination of V_g values is of great importance in the theory and practice of GLC.

Papers concerning the concept of specific retention volumes have been published by Ambrose and Purnell², Wicar *et al.*³ and Riedo *et al.*⁴, together with our earlier experience gained in a similar area of research⁵. We became deeply involved in the topic during a study of the efficiencies of the capillary columns and of the factors influencing those efficiencies. It was frequently required to know the approximate amount of the stationary phase, which can be determined only with difficulty even in the case of capillary columns.

Utilizing our results and experience gained in the study of the conditions of

fluid flow⁶, we assumed the specific retention volume of any component to be constant for inlet pressure values in the range

$$6 \cdot 10^5 \geq p_1 > 10^5 \quad (1)$$

and to be independent of the type of column used, if the quality of the applied stationary phase and carrier gas are always the same at otherwise constant column temperatures. In inequality 1, p_1 is the inlet pressure of the carrier gas expressed in pascals (Pa).

The amount of stationary phase in a packed column can be determined approximately by weighing after extraction. We used the results of several simultaneous weighings to determine the V_g values of n -alkanes used as models with the help of such packed columns, and hence to determine the amount of stationary phase in capillary columns while measuring the net retention volumes of single components on them, and to compute the amount of stationary phase on the basis of V_g values measured on packed columns. Such checking of results revealed good agreement in several cases, indicating the usefulness of our procedure. In many cases we wished to use the results obtained for the theoretical investigations at different column temperatures. Therefore we dealt, on one hand, with the estimation and computation of the maximum error made in the determination of the specific retention volume, on the other hand, with V_g values as functions of the column temperature.

THEORY

The maximum error (E_{\max}) of a determined value can be estimated by the appropriate partial derivatives of a function referring to a given process. In the case of the specific retention volume we start with eqn. 2

$$V_g = j(t_R - t_M)F_0(1 - p_w/p_0)273.16/m_1T_0 \quad (2)$$

where

- V_g = specific retention volume (ml carrier gas)/(gram stationary phase)
- j = compressibility factor according to James and Martin⁷
- t_R = retention time (min)
- t_M = transit time of the inert material through the system (min)
- F_0 = volumetric flow-rate of the carrier gas (ml/min) at pressure and temperature measured at the outlet of the column (p_0, T_0)
- T_0 = temperature measured at the outlet of the column ($^{\circ}\text{K}$)
- p_w = pressure of water vapour (Pa) at the temperature of the soap-film flow-meter connected to the outlet of the column
- p_0 = outlet pressure of the carrier gas (Pa) at the outlet of the column.
- m_1 = amount of stationary phase (g).

$$E_{\max} \leq |\partial V_g / \partial j| \Delta j + |\partial V_g / \partial F_0| \Delta F_0 + |\partial V_g / \partial t_R| \Delta t_R + |\partial V_g / \partial t_M| \Delta t_M \\ + |\partial V_g / \partial m_1| \Delta m_1 + |\partial V_g / \partial T_0| \Delta T_0 + |\partial V_g / \partial p_0| \Delta p_0 \\ + |\partial V_g / \partial p_w| \Delta p_w \quad (3)$$

where

$$E_{\max} = \text{maximum error in the determination of specific retention volume,} \\ (\text{ml carrier gas})/(\text{gram stationary phase}).$$

$$\bar{x} = 1/n \sum_{s=1}^n x_s \quad (4)$$

$$x = 1/n \sum_{s=1}^n |x_s - \bar{x}| \quad (5)$$

x = general symbol for the parameters (e.g. j , F_0)

n = number of parallel measurements

s = serial number of every single measurement.

Further, the partial derivatives occurring in eqn. 3 are given in general forms, considering \bar{p}_w as a constant:

$$\partial V_g / \partial j = \bar{F}_0 (\bar{i}_R - \bar{i}_M) (1 - \bar{p}_w / \bar{p}_0) 273.16 / \bar{m}_1 \bar{T}_0 \quad (6)$$

$$\partial V_g / \partial \bar{F}_0 = j (\bar{i}_R - \bar{i}_M) (1 - \bar{p}_w / \bar{p}_0) 273.16 / \bar{m}_1 \bar{T}_0 \quad (7)$$

$$\partial V_g / \partial \bar{m}_1 = -j \bar{F}_0 (\bar{i}_R - \bar{i}_M) (1 - \bar{p}_w / \bar{p}_0) 273.16 / \bar{m}_1^2 \bar{T}_0 \quad (8)$$

$$\partial V_g / \partial \bar{i}_R = j \bar{F}_0 (1 - \bar{p}_w / \bar{p}_0) 273.16 / \bar{m}_1 \bar{T}_0 \quad (9)$$

$$\partial V_g / \partial \bar{i}_M = -j \bar{F}_0 (1 - \bar{p}_w / \bar{p}_0) 273.16 / \bar{m}_1 \bar{T}_0 \quad (10)$$

$$\partial V_g / \partial \bar{T}_0 = -j \bar{F}_0 (\bar{i}_R - \bar{i}_M) (1 - \bar{p}_w / \bar{p}_0) 273.16 / \bar{m}_1 \bar{T}_0^2 \quad (11)$$

$$\partial V_g / \partial \bar{p}_0 = j \bar{F}_0 (\bar{i}_R - \bar{i}_M) \bar{p}_w 273.16 / \bar{m}_1 \bar{T}_0 \bar{p}_0^2 \quad (12)$$

$$\partial V_g / \partial \bar{p}_w = -(\bar{i}_R - \bar{i}_M) 273.16 \bar{F}_0 j / \bar{p}_0 \bar{m}_1 \bar{T}_0 \quad (13)$$

Since eqns. 6–13 contain several identical expressions, the following abbreviations can be introduced:

$$j \bar{F}_0 = a \quad (14)$$

$$(\bar{i}_R - \bar{i}_M) = b \quad (15)$$

$$(1 - \bar{p}_w / \bar{p}_0) = c \quad (16)$$

$$273.16 / \bar{m}_1 \bar{T}_0 = d \quad (17)$$

Eqn. 3 can then be written in the following form:

$$E_{\max} \leq |\bar{F}_0 b c d| \Delta j + |j b c d| \Delta F_0 + |a c d| \Delta t_R + |-a c d| \Delta t_M + |-a b c d| 1 / \bar{m}_1 | \Delta m_1 + |-a b c d| 1 / \bar{T}_0 | \Delta T_0 + |a b d \bar{p}_w / \bar{p}_0^2| \Delta p_0 + |-a b d / \bar{p}_0| \quad (18)$$

If we eliminate the negative signs (because of absolute values) and factor out several common factors, eqn. 18 can be expressed in an even simpler form:

$$E_{\max} \leq b c d [\bar{F}_0 \Delta j + j \Delta F_0 + a (\Delta m_1 / \bar{m}_1 + \Delta T_0 / \bar{T}_0)] + a d [c (\Delta t_R + \Delta t_M) + b \bar{p}_w \Delta p_0 / \bar{p}_0^2 + b / \bar{p}_0] \quad (19)$$

In this form, eqn. 19 can be applied only in those cases where the volumetric flow-rate of carrier gas is measured with a soap-film flow-meter. If the flow-rate is checked by other means the partial derivatives in eqn. 3 should be rewritten accordingly. Eqn. 19 is suitable for studying the relationships between the experimental parameters and the error made in the determination of V_g values. However, this is a very complex process. If, for instance, the inlet pressure of the carrier gas is altered,

the outlet pressure, the volumetric flow-rate of the carrier gas, the compressibility factor, the retention time and transit time of the inert material will all change. Therefore these investigations should be made very carefully. It is advisable to perform the calculations using a computer that also allows simulative investigations.

After determining the error in the calculation of the specific retention volume according to Ambrose and Purnell², we used the results of a study of the retention index as a function of column temperature⁸ to investigate V_g values as functions of the column temperature. We concluded that V_g as a function of column temperature is described by an Antoine-type equation:

$$\log V_g = A + B/(T + C) \quad (20)$$

where T is the column temperature and A , B and C are constants. Eqn. 20 shows a significant linear relationship in the restricted temperature interval used in GLC. This linear interval can be especially observed on non-polar stationary phases, so the following relationship can also be applied:

$$\ln V_g = a + b/T \quad (21)$$

where a and b are constants.

In the course of our work, in some cases, comparison has been made between the calculated and measured values at different column temperatures. The results of this comparison are presented in the Experimental part.

EXPERIMENTAL

Alkanes from n -C₅ to n -C₈ were used as model compounds to estimate the error in the determination of specific retention volume and to investigate its dependence on column temperature under the experimental conditions summarized in Table I.

TABLE I

GAS CHROMATOGRAPHIC PARAMETERS USED IN THE DETERMINATION OF SPECIFIC RETENTION VOLUMES OF n -ALKANES

Gas Chromatograph: Erba Science, Fractovap 2355
Integrator: minigrator
Detector: thermal conductivity
Bridge current: 140 mA
Sensitivity: 100%
Injection: 0.1-0.3 μ l of n -alkane mixtures
Column: stainless steel spiral (2 m \times 2 mm I.D.)
Column packing: Apolane-87, 3.6 wt. % on Chromosorb W, 60-80 mesh, AW, DMCS
Column temperature: 323 \pm 0.1 $^{\circ}$ K
Detector temperature: 448 $^{\circ}$ K
Injector temperature: 473 $^{\circ}$ K
Carrier gas: hydrogen
Inlet pressure of carrier gas: 0.17 MPa (1.75 kp/cm ²)
Volumetric flow-rate of carrier gas: 34.0 ml/min at 296.7 $^{\circ}$ K and at 0.1 MPa (759 torr)
Recorder: Speedomax W; 1.0 mV/ range; 1.0 s
Paper velocity: 12.7 mm/min

RESULTS AND DISCUSSION

Table II lists data used in a determination involving *n*-octane.

TABLE II

DATA USED TO ESTIMATE THE ERROR IN THE DETERMINATION OF THE SPECIFIC RETENTION VOLUME OF *n*-OCTANE ON APOLANE-87 STATIONARY PHASE

Parameter	Actual value	Δ parameter
\bar{j}	0.7103	0.0005
F_0	34.0 ml/min	0.07 ml/min
\bar{t}_R	1.820 min	0.005 min
\bar{t}_M	0.240 min	0.008 min
\bar{m}_1	0.0535 g	0.0006 g
T_0	296.7 °K	0.1 °K
\bar{p}_0	758.9 torr	0.2 torr
\bar{p}_w	22.77 torr	0.026 torr ¹¹

Applying eqn. (19) for *n*-octane:

$$E_{\max. \text{ n-octane}}^{\text{Apolane-87}}(50^\circ\text{C}) \leq 1.579 \times 0.97 \times 17.2086[34.0 \times 0.0005 + 24.1502(0.0006/0.0535 + 0.1/296.7) + 0.7103 \times 0.07] + 24.1502 \times 17.2086[0.97(0.005 + 0.008) + 1.579 \times 22.77 \times 0.2/758.9^2 + 1.579/758.9] = 15.19 \text{ ml } H_2/\text{g Apolane-87} \quad (22)$$

Since in this case the V_g value of *n*-octane was 785.0 ml H_2 /g Apolane-87, the maximum error in the determination is 1.93%.

Several remarks should be made concerning this relatively large error. (1) This is the maximum error (there was no possibility for error compensation because absolute values were used). (2) A relatively poorly wetted (3.6 wt. %) column was used where the absolute values of single parameters were small and difficult to determine. (3) No modification of the gas chromatograph was made to increase its accuracy.

Our experiences indicate that this error can be minimized by a thermostat and carrier gas system modified to give great accuracy.

The V_g values of several *n*-alkanes were determined at 50, 70 and 90°C to show the dependence on column temperature. The results are summarized in Table III.

TABLE III

SPECIFIC RETENTION VOLUMES OF SEVERAL *n*-ALKANES ON APOLANE-87 STATIONARY PHASE AT DIFFERENT COLUMN TEMPERATURES

Compound	Specific retention volume (ml H_2 /g Apolane-87)		
	50°C	70°C	90°C
<i>n</i> -Hexane	116.0	66.0	40.2
<i>n</i> -Heptane	322.2	161.1	88.1
<i>n</i> -Octane	785.0	364.0	185.1

Using the data in Table III, we obtained the following equations:

$$\ln V_g(n\text{-C}_6, \text{Apolane-87}, T) = 3252.33/T - 5.26546 \quad (23)$$

$$\ln V_g(n\text{-C}_7, \text{Apolane-87}, T) = 3730.75/T - 5.79658 \quad (24)$$

$$\ln V_g(n\text{-C}_8, \text{Apolane-87}, T) = 4211.21/T - 6.31791 \quad (25)$$

Applying an Antoine-type approximation we obtained the following relationship for *n*-octane:

$$\ln V_g(n\text{-C}_8, \text{Apolane-87}, T) = -6.57390 + 4388.72/(T + 7.13) \quad (26)$$

A comparison of the results of the linear eqn. 25 and those of eqn. 26 with measured values is presented in Table IV. It is apparent that in given circumstances both approximations yield good results on Apolane-87 stationary phase.

TABLE IV

COMPARISON OF MEASURED VALUES WITH THOSE CALCULATED BY EQNS. 25 AND 26 FOR *n*-OCTANE ON APOLANE-87 STATIONARY PHASE AT SEVERAL COLUMN TEMPERATURES

Column temperature (°C)	V_g (<i>n</i> -octane), (ml H ₂ /g Apolane-87)					
	Measured (M)	By eqn. 25	By eqn. 26	Deviation		
				M - Eqn. 25	M - Eqn. 26	Eqn. 25 - eqn. 26
60	558.0	556.8	557.2	+1.2	+0.8	-0.4
80	273.2	272.2	272.3	+1.0	+0.9	-0.1
100	143.4	143.6	143.5	-0.2	-0.1	+0.1
110	107.4	107.0	106.8	+0.4	+0.6	+0.2
120	81.4	80.9	80.6	+0.5	+0.8	+0.3

The importance and practical applicability of the specific retention volume in physicochemical calculations is obvious^{9,10}, and we present here a possible new application: the determination of the exact amount of stationary phase in a capillary column, utilizing the basic law of GLC (*i.e.* at the inlet pressure interval of the carrier gas indicated in eqn. 1 and at steady-state gas-chromatographic conditions, the specific retention volume of any component is a constant and depends neither on the type and geometrical characteristics of the applied column nor on the inert carrier).

The point of our computational method is to determine the net retention volumes of three or more *n*-alkanes using a packed column containing the stationary phase. The amount of stationary phase on the carrier can also be determined by the method of extraction and repeated weighing. From these data one can compute the specific retention volumes of the examined components, and the error in the determination of the specific retention volume can be estimated by eqn. 19. If the maximum error is less than, or equal to 5%, the results might be used to compute the amount of a stationary phase of the same chemical composition and quality in a capillary column. By measuring the net retention volumes of the examined components at the

same gas-chromatographic conditions one can compute the amount of the stationary phase:

$$m_1 = \frac{\bar{j}(t_R - t_M) F_0(1 - p_w/p_0) 273.16}{V_g T_0} \quad (27)$$

where the symbols have the same meanings as in eqn. 2, because with three or more n -alkanes in one series of experiments the results are very reliable. As an example we set out here the calculation of the amount of squalane in a squalane-wetted, classic, capillary column (50 m \times 0.25 mm I.D.) at a volumetric flow-rate of nitrogen carrier gas of 0.68 ml/min, at 23.0°C and 762 torr. Under these conditions the vapour pressure is 21.1 torr (a correction should be made for dry condition because of the soap-film flow-meter). A compressibility factor of 0.4009 belongs to the 3.52 kp/cm² inlet pressure of the carrier gas. At these conditions and at a column temperature of 50°C the peak maximum of the inert material is 3.567 min, and that of n -hexane is 11.120 min. Earlier the specific retention volume of n -hexane was 151.30 ml N₂/g squalane at the same gas-chromatographic conditions on a filled column. Thus eqn. 27 is as follows:

$$m_1 = \frac{0.4009 \times 0.68 \times (11.120 - 3.567) \times 273.16 \times 0.97}{151.64 \times 296.16} = 0.012 \text{ g squalane} \quad (28)$$

This value is comparable with the values (from 0.009 to 0.015) computed from the amounts of squalane prepared from aliquot portions of capillary columns of the same geometry and liquid content.

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