

Notes

CHROM. 404I

Relationship between net retention volume and column temperature in gas chromatography

One of the most important characteristic data of classical gas chromatography is net retention volume. It is generally known that at a constant temperature, under unchanged gas chromatographic conditions, it is constant for any one substance. However, as we have shown in an earlier study, this constancy does not exclude the well-defined and correlated changes of p_i, j, F and t_M (ref. 1). We became interested in these changes while calculating the optimum value of column temperature; we had sought in vain for data on the relationship between net retention volume and column temperature in the literature.

Theory

Let us begin with the generally known relationship, according to which the logarithm of the specific retention volume is a linear function of the reciprocal of column temperature:

$$\log V_g = m \cdot \frac{1}{T} + b \quad (1)$$

where

- V_g = specific retention volume (ml carrier gas/g stationary phase);
- m = slope of the straight line (log ml carrier gas/g stationary phase \cdot $^{\circ}$ K);
- b = axial section Y of the straight line (log ml carrier gas/g stationary phase);
- T = column temperature ($^{\circ}$ K).

Substituting into eqn. (1) the value of the known specific retention volume

$$V_g = \frac{V_N \cdot 273}{m_s \cdot T} \quad (2)$$

where

- V_N = net retention volume (ml carrier gas);
- m_s = mass of stationary phase (g)

we obtain

$$\log \frac{V_N \cdot 273}{m_s \cdot T} = m \cdot \frac{1}{T} + b \quad (3)$$

Transferring the constant factor from the left-hand side to the right-hand side

$$\log \left(\frac{V_N}{T} \right) = m \cdot \frac{1}{T} + \left(b - \log \frac{273}{m_s} \right) \quad (4)$$

and introducing the following symbol

$$\left(b - \log \frac{273}{m_s}\right) = M \tag{5}$$

we can multiply both sides of eqn. (4) by T

$$T \cdot \log \left(\frac{V_N}{T}\right) = M \cdot T + m \tag{6}$$

Eqn. (6) offers, in implicit form, a readily applicable relationship. The explicit relationship is obtained using the following form of eqns. 4 and 5:

$$\log \left(\frac{V_N}{T}\right) = m \cdot \frac{1}{T} + M \tag{7}$$

Thence

$$V_N = T \cdot 10^{m \cdot \frac{1}{T} + M} \tag{8}$$

A similar equation may also be obtained from suitable data, assuming that the natural logarithm is used in the calculations:

$$V_N = T \cdot e^{m' \cdot \frac{1}{T} + M'} \tag{9}$$

where

m' = slope of the straight line (ln ml carrier gas/g stationary phase · °K);

M' = $(b' - \ln 273/m_s)$;

b' = axial section Y of the straight line (ln ml carrier gas/g stationary phase).

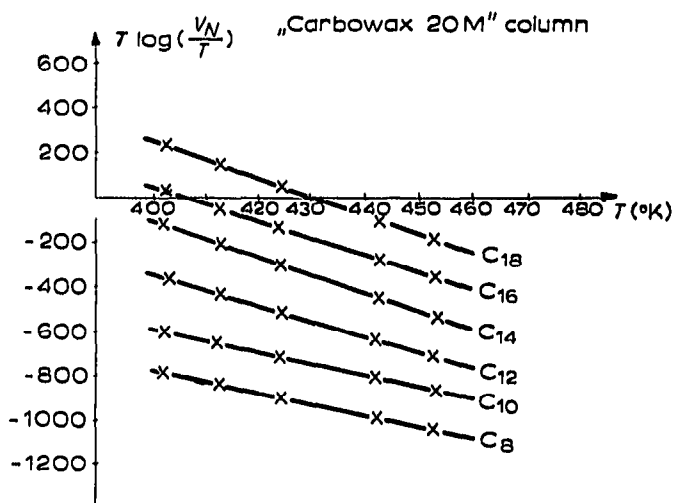
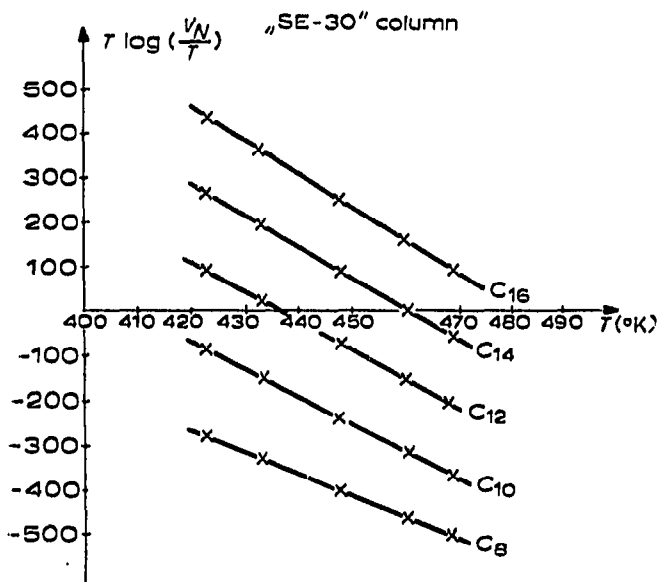


Fig. 1. $T \log (V_N/T)$ vs. T on SE-30 column. The components in the figure are normal hydrocarbons.

Fig. 2. $T \log (V_N/T)$ vs. T on Carbowax 20M column. The components in the figures are normal hydrocarbons.

Experimental

The theoretical relationships have been verified experimentally using data taken from the literature² as well as data from our own measurements. For practical work, eqn. (6) is easier to apply. The results obtained are presented in Figs. 1 and 2 (data taken from the literature²) and Figs. 3 and 4 and Table I (our data).

Our measurements were performed on a Perkin-Elmer Fractometer Model F/6.

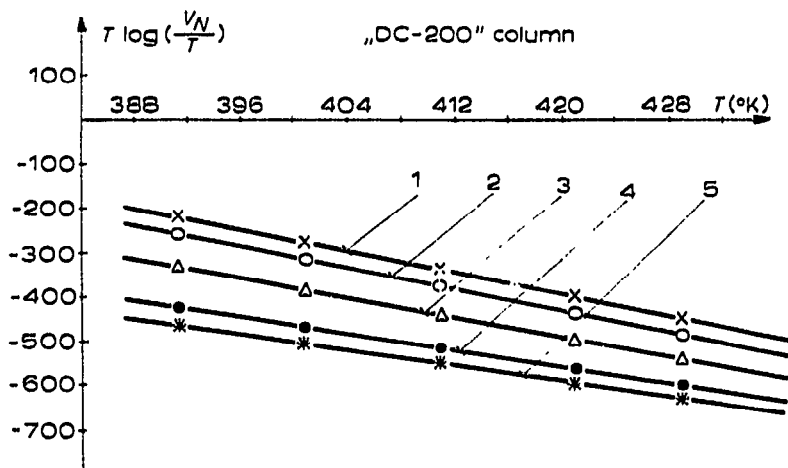


Fig. 3. $T \log(V_N/T)$ vs. T on DC-200 column. The components in the figures are as follows: 1, *n*-nonane; 2, ethylbenzene; 3, *n*-octane; 4, *n*-heptane; 5, benzene.

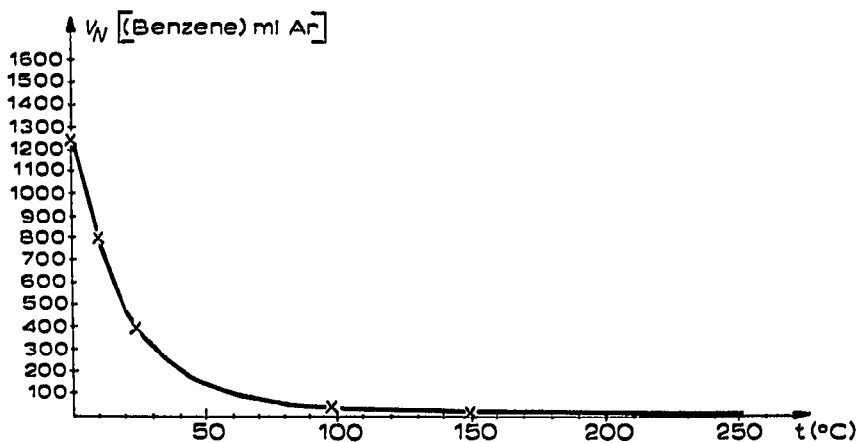


Fig. 4. V_N of benzene vs. column temperature on DC-200 stationary phase. Perkin-Elmer F₆/4, F.I.D. Column: 2.0 m × 4.65 mm (I.D.). Packing: 10.0% DC-200 silicone oil on 60-80 mesh Chromosorb R. Temperature of evaporator: 250.0 ± 1.0° C. Sample introduction: 1.0 μl by a Hamilton syringe. Carrier gas: 99.99% argon. Flow rate of carrier gas: 42.0 (ml/min) at 21.3° C and 759.0 mm Hg. Inlet pressure of carrier gas: 1.25 (kp/cm²). Recorder: Honeywell, 2.5 mV/10 in.; 1.0 sec. Paper speed: 10.0 (mm/min).

Discussion

The equation describing the relationship of temperature to net retention volume is of general value, since no restrictions were used in the calculations. The results are useful for precalculation of the optimal column temperature as well as for determination of the relationship between retention index and column temperature. In the latter case, because the effective quantity of the stationary phase cannot be reliably calculated, the use of specific retention volume makes the experimental results unclear.

TABLE I

COMPARISON OF MEASURED AND CALCULATED DATA

Measurements were performed at $118.0 \pm 0.1^\circ\text{C}$ column temperature; stationary phase, DC-200; carrier gas, argon. Using eqn. (8) for benzene on stationary phase DC-200, we obtain:

$$V_N(\text{benzene}) = T \cdot 10 \frac{-5.17 \cdot T + 1591.41}{T} \text{ ml argon} \quad (10)$$

Compound	Net retention volume (ml carrier gas)		Difference between measured and calculated values	
	Measured	Calculated	ml carrier gas	%
Benzene	27.07	27.00	+0.07	+0.26
<i>n</i> -Heptane	33.51	33.40	+0.11	+0.33
<i>n</i> -Octane	58.39	58.40	-0.01	-0.02
Ethylbenzene	83.28	83.00	+0.28	+0.33
<i>n</i> -Nonane	103.74	103.90	-0.16	-0.15

Symbols

- p_i = inlet pressure of carrier gas (in kp/cm², or another pressure unit);
 j = gas compressibility correction factor according to JAMES-MARTIN;
 F = flow rate of the carrier gas (ml/min);
 t_M = the observed retention time of an unabsorbed gas (min);
 V_g = specific retention volume (ml carrier gas/g stationary phase);
 m_s = mass of stationary phase (g);
 V_N = net retention volume (ml carrier gas);
 T = column temperature ($^\circ\text{K}$);
 m = slope of the straight line (log ml carrier gas/g stationary phase);
 m' = slope of the straight line (ln ml carrier gas/g stationary phase);
 b = axial section Y of the straight line (log ml carrier gas/g stationary phase);
 b' = axial section Y of the straight line (ln ml carrier gas/g stationary phase).

Acknowledgement

The authors wish to thank Professor L. ERDEY for his continued interest and help.

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Received January 28th, 1969