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Note

A simple relationship between retention parameters in isothermal and programmed-temperature gas chromatography

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A number of methods[1–6] have been published which correlate isothermal with programmed-temperature gas chromatography (PTGC) retention parameters. Some of these methods involve integrals whose solutions are only readily obtained by the use of a computer, others involve the calculation of approximate Kováts' indices and there are practical objections[7–9] to this method. Schmit and Wynne[8] have shown that for PTGC a simple parameter, the relative elution temperature (T_{RE}, the ratio of the elution temperatures of any compound and a standard) was very reproducible, and independent of flow-rate, temperature programme rate and initial temperature. During our work on the GC of terpeneols and derivatives[10], it was noted that both the logarithm of the retention volume, log V_r, and T_{RE} varied with boiling point in an identical manner. This implied that there was a direct relationship between log V_r and T_{RE}. We have therefore studied this relationship for a number of fatty acid methyl esters, terpeneols and their trimethylsilyl (TMS) ethers and acetates, short-chain triglycerides, normal alcohols, normal paraffins and squalene.

MATERIALS AND METHODS

Fatty acid methyl esters ($C_{16:1}$–$C_{22:1}$), normal alcohols ($C_{14:0}$–$C_{18:0}$, $C_{18:1}$), tributyrin (all 99% pure), and phytol (>95% pure) were obtained from Sigma Chemical Co., London, Great Britain; geraniol, nerolidol, farnesol, and squalene (all >90% pure) were bought from Koch-Light Labs., Colnbrook, Great Britain. Tripropionin was supplied by Mann Research Labs., New York, U.S.A. Tri-$C_{5:0}$, tri-$C_{6:0}$, and tri-$C_{7:0}$ were synthesised by the method of Bourne *et al.*[11].

GC analyses were carried out using a 168 cm × 6.5 mm O.D. glass column packed with 3% SE-30 (methyl polysiloxy gum) on 100–120 mesh Gas-Chrom Q (Applied Science Labs., State College, Pa., U.S.A.). The column had been in use for about six months and was giving normal satisfactory resolution. Temperatures of isothermal analysis were either 195° or 202° with flow-rates of oxygen-free nitrogen (British Oxygen Ltd., Birmingham, Great Britain) of 40 ml/min or 55 ml/min.

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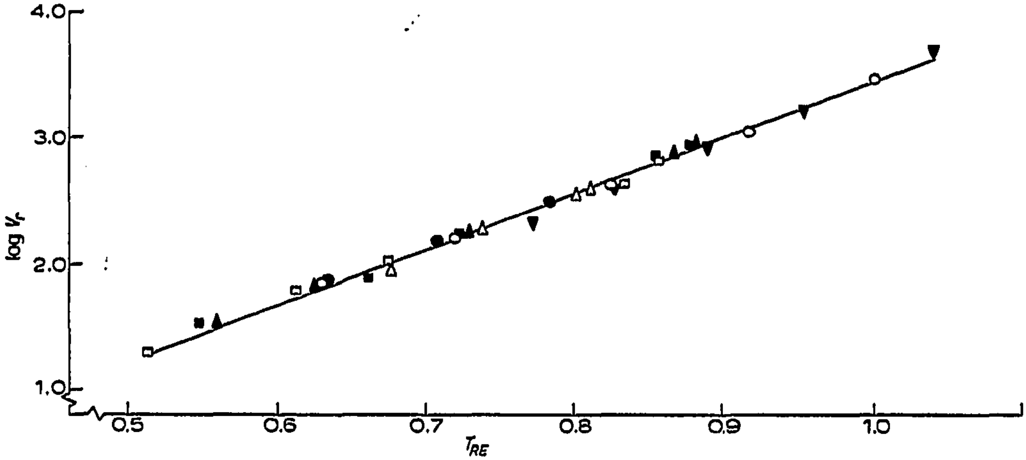

Fig. 1. The relationship between log V_r and T_{RE} for terpeneols (□), triglycerides (○), normal alcohols (△), methyl esters (▽), and hydrocarbons (●), run isothermally at 202 °with a nitrogen flow-rate of 55 ml /min, and for terpeneol TMS ethers (■), terpeneol acetates (▲), and squalene (▼), run isothermally at 195 ° with a nitrogen flow-rate of 40 ml/min. The column was 3% SE-30 and temperature programming was 120°–280° at 3.71 °/min. Glycerol triheptanoate was assigned a T_{RE} = 1.0.

A temperature programme of 120°–280° at 3.71 °/min was employed, and tri-$C_{7:0}$, which had an elution temperature of 254 ±1 °, was assigned a value for $T_{RE} = 1.0$.

RESULTS AND DISCUSSION

Fig. 1 shows the relationship for a variety of compounds between log V_r and T_{RE} when analyses were carried out either at 202° or 195° with nitrogen flow-rates of 55 or 40 ml/min, or temperature programmed at 3.71°/min. It is clear that there is a direct relationship which is well obeyed by each class of compound analysed and which is almost independent of the class. The most deviant classes were the normal hydrocarbons and the methyl esters. We may therefore write:

$$\log V_r = cT_{RE} - d \tag{1}$$

where c and d are constants.

An expression for deriving the value of T_{RE} of any compound z from isothermal data and a value for d may be obtained thus:

$$\log V_{r_z} = cT_{RE_z} - d$$

and for standard s:

$$\log V_{r_s} = c - d$$

Substitution in eqn. 1 for c gives

$$\log V_{r_z} = (\log V_{r_s} + d)T_{RE_z} - d$$

Hence

$$T_{RE_z} = \frac{\log V_{r_z} + d}{\log V_{r_s} + d} \tag{2}$$

Since T_{RE} is independent[8,9] of the rate of temperature programming, carrier gas flow-rate, per cent stationary phase, and initial programme temperature (T_0) (as long as $T_0 - T_e \geqslant 20$), the constant d need to be determined only once using one set of operational parameters. Eqn. 2 is valuable in that it does not rely on the homologous series relationship.

It is also of interest that for a homologous series and a given set of isothermal and programmed temperature conditions, eqn. 1 may be written

$$\log V_{r_z} = hT_{e_z} - d \tag{3}$$

where T_{e_z} is the elution temperature of compound z and $h = c/T_{e_s}$ is a constant, T_{e_s} is being the elution temperature of the standard.

This linear relationship, as described for the normal alkanes[1] was the basis for the earlier propositions of a PTGC Kováts' index[2,3], defined simply by substituting T_e values for log V_r values. However, the variation of the constants h and d for different classes of compounds was not accounted for, and in any case could not be determined for a single compound. Thus, if we substitute for log V_r in the isothermal Kováts' index equation[12], according to eqn. 3 we obtain:

$$I_{pr} = 100(y-x)\frac{h'T_{e_z} - h''T_{e_x} - d' + d''}{h''(T_{e_y} - T_{e_x})} + 100x \tag{4}$$

Though this is a more precise expression than that proposed originally[2,3], it still relies on the homologous series relationship where h and d can be calculated. Also eqn. 4 does not entirely account for the variation of the elution temperatures with operational parameters, even though these would tend to be internally cancelling[2,13]. Therefore we prefer eqn. 2 to eqn. 4.

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