

Notes

CHROM. 3362

Calculation of the retention time of the "air peak" in gas chromatograms

On gas chromatograms determined by an ionization detector the "air peak" does not normally show up due to the fact that oxygen and nitrogen are not ionized under the conditions used. Knowledge of the retention time corresponding to the "air peak" is necessary when chromatograms are to be compared, when the adjusted retention time is to be calculated, or when certain parameters, such as the partition ratio, are to be calculated.

It is possible to inject a low molecular weight hydrocarbon, preferably methane, and then take the retention time for methane as the retention time for the "air peak". However, methane is more or less soluble in almost all stationary phases, and the method is therefore only applicable if the retention times to be corrected are large in comparison with the retention time of the "air peak".

PETERSON AND HIRSCH¹ have published a method for the calculation of the retention time or distance of the "air peak" utilizing the fact that a straight line relationship exists between the logarithm of the adjusted retention time and the number of carbon atoms in the members of a homologous series, which have to be equally spaced with respect to carbon numbers. The method does not give the retention time of the "air peak" directly, but the difference between this and an ancillary line put arbitrarily in the chromatogram. GOLD² has published a method without the above-mentioned restriction with respect to carbon numbers, but his equations for the determination of the "air peak" can only be solved by successive approximation.

Without knowledge of the above-mentioned methods, we have developed a method for the calculation based on the fact that a straight line relationship exists between the logarithm of the adjusted retention time and the Kovats index of the members of a homologous series. The method is similar to that of PETERSON AND HIRSCH¹, but it gives the position of the "air peak" directly and utilizes the retention times of the hydrocarbons otherwise used for the calibration with regard to Kovats index, we therefore believe our method to be of interest.

Theory

The Kovats index for a normal alkane is defined as the number of carbon atoms in the alkane multiplied by 100, and the linear relationship between the logarithm of the adjusted retention time or distance and the Kovats indices for three normal alkanes with equally spaced numbers of carbon atoms might therefore be represented by the following equations:

$$\log(t_1 - t_a) = m \cdot z \cdot 100 + q \quad (1)$$

$$\log(t_2 - t_a) = m \cdot (z + b) \cdot 100 + q \quad (2)$$

$$\log(t_3 - t_a) = m \cdot (z + 2b) \cdot 100 + q \quad (3)$$

where:

t_1 = the unadjusted retention time or distance for the n -alkane with z carbon atoms;

t_2 = the unadjusted retention time or distance for the n -alkane with $z + b$ carbon atoms;

t_3 = the unadjusted retention time or distance for the n -alkane with $z + 2b$ carbon atoms;

t_a = the retention time or distance for the "air peak".

m = constant;

q = constant;

b = a whole positive number.

If we subtract eqn. (1), from eqn. (2), we obtain:

$$\log(t_2 - t_a) - \log(t_1 - t_a) = m \cdot (z + b) \cdot 100 - m \cdot z \cdot 100 + q - q$$

or:

$$\log \frac{t_2 - t_a}{t_1 - t_a} = m \cdot b \cdot 100 \quad (4)$$

If we subtract eqn. (2) from eqn. (3), we obtain:

$$\log(t_3 - t_a) - \log(t_2 - t_a) = m \cdot (z + 2b) \cdot 100 - m \cdot (z + b) \cdot 100 + q - q$$

or:

$$\log \frac{t_3 - t_a}{t_2 - t_a} = m \cdot b \cdot 100 \quad (5)$$

Eliminating $m \cdot b \cdot 100$ from eqn. (4) and eqn. (5), we obtain:

$$\log \frac{t_2 - t_a}{t_1 - t_a} = \log \frac{t_3 - t_a}{t_2 - t_a}$$

or:

$$\frac{t_2 - t_a}{t_1 - t_a} = \frac{t_3 - t_a}{t_2 - t_a} \quad (6)$$

From eqn. (6) we obtain:

$$t_a = \frac{t_2^2 - t_1 t_3}{2t_2 - t_1 - t_3} \quad (7)$$

Examples

Four determinations on a 2 m 1/8 in. diameter stainless steel column with 10 % squalane on Gas Chrom Z, mesh 80-100, mounted in a Perkin Elmer F-11 with a pyrolysis attachment at an oven temperature of 50°, have given the results shown in Table I.

Two determinations on a 3 m 1/8 in. diameter stainless steel column with 10 % Carbowax 20 M terephthalic acid on Gas Chrom Z, 80-100 mesh, mounted in an Aerograph 204 at an oven temperature of 130°, have given the results shown in Table II.

TABLE I

DETERMINATIONS ON THE SQUALANE COLUMN

Run No.	Retention distance (cm)				
	<i>n</i> -propane t_1	<i>n</i> -butane t_2	<i>n</i> -pentane t_3	"air peak" t_a	methane
1	0.61	0.80	1.29	0.49	0.52
2	0.65	0.82	1.29	0.55	0.58
3	0.64	0.80	1.32	0.57	0.60
4	0.63	0.81	1.32	0.53	0.56

TABLE II

DETERMINATIONS ON THE CARBOWAX COLUMN

Run No.	Retention distances (cm)				
	<i>n</i> -decane t_1	<i>n</i> -dodecane t_2	<i>n</i> -tetradecane t_3	"air peak" t_a	methane
1	1.78	2.91	5.88	1.09	1.14
2	1.77	2.94	5.96	1.03	1.08

Conclusions

It is believed that the method presented here for the determination of the retention time or distance of the "air peak" might prove to be an easy and accurate way of obtaining this information, if the results are to be expressed in Kovats indices. Furthermore, determinations of this kind might prove to be of value in comparing different gas chromatographs with regard to "dead volumes".

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