Note

Evaluation of dead space in chromatographic systems

W. K. AL-THAMIR, J. H. PURNELL and C. A. WELLINGTON

Department of Chemistry, University College of Swansea, Swansea, Wales (Great Britain)

and

R. J. LAUB

Department of Chemistry, Ohio State University, Columbus, Ohio 43210 (U.S.A.)

(Received December 28th, 1978)

The determination of dead space, V_A, or dead time, t_A, in chromatographic systems is required both for the evaluation of specific retention volumes or of partition coefficients and of capacity factors (k'), these being of significance in that, amongst other things, they provide a basis for numerical definition of relative retention and, hence, of separation.

The most commonly employed method of assessing t_A is the elution of a non-sorbed solute. With most detectors in gas–liquid chromatography (GLC) this is, typically, air or inert gas, for which there is little danger of error as these gases are essentially insoluble in liquid stationary phases at the most useful working temperatures. In gas–solid (GSC) or liquid chromatography (LC), on the other hand, it is difficult to ensure that the chosen eluate is genuinely non-sorbed or completely insoluble; protracted procedures have, as a result, been developed over the years for these techniques and are still a matter of current concern, as is comprehensively described in the most recent publications[1–4]. Further, with flame-ionization detection, even GLC provides problems as the sample size of non-combustible gas required to yield a detector response may well cause much flow variation due to viscosity effects while methane cannot be guaranteed to have a sufficiently small capacity factor to offer a truly accurate result.

An alternative approach to the above is to take advantage of the well known fact that, in both GC and LC, the true retention volumes (V_R') or retention times (t_R') of members of homologous series are often connected via an equation of the form

$$\log t_R' = a'n + b' \tag{1}$$

where $t_R' = t_R - t_A$, a' and b' are series constants and n is a number representing the size of the homologous unit. As only the gross retention time, t_R, can be determined directly, the usual approach is to plot a graph of $\log t_R$ against n, extrapolate linearly the data for the highest values of n, use the intercept at $n = 0$ to correct values of t_R for all data points and re-plot the new data. The procedure must be reiterated to achieve linearity of the data according to eqn. 1, normally at least five times to achieve 5% accuracy of V_A. Complete accuracy, of course, demands an infinite num-

ber of iterations. If members very high in the homologous series are used, experiments become very time consuming but the number of iterations is reduced markedly.

We show here that all of the foregoing problems can be solved by a simple numerical variant of the second procedure.

Re-writing eqn. 1:

$$\ln(t_R - t_A) = an + b \tag{2}$$

we have

$$t_R = t_A + \exp(an + b) \tag{3}$$

Hence, for two successive homologues ($n = n$ and $n = n-1$),

$$^n t_R = t_A + \exp(an + b)$$

$$^{n-1} t_R = t_A + \exp[(n-1)a + b]$$

Thus

$$^n \Delta t_R = {}^n t_R - {}^{n-1} t_R = (1-e^{-a})\exp(an + b) \tag{4}$$

For the pair $n = n-1$ and $n = n-2$, correspondingly,

$$^{n-1} \Delta t_R = (1-e^{-a})\exp[a(n-1) + b] \tag{5}$$

Hence

$$^n \Delta t_R / {}^{n-1} \Delta t_R = e^a \tag{6}$$

Having evaluated a, it is a simple matter to evaluate b via eqn. 4 or 5. Hence t_A can be evaluated for all homologues employed and a consistent result will confirm its validity.

Table I illustrates application of the method to data for elution of C_1–C_4 alkanes from a GSLC column (alumina + squalane). The data here are reported simply in terms of chart millimetres. Application of our method yielded the values $a' = 0.617$ and $b' = -0.430$, as they apply in eqn. 1.

TABLE I

RETENTION DATA (CHART mm) FOR ELUTION OF C_1–C_4 ALKANES FROM A GSLC (Al_2O_3 + SQUALANE) COLUMN

Log $t_R' = 0.617n - 0.430$.

Alkane	t_R	t_R'	t_A
Methane	21.5	1.50	20.0
Ethane	26.5	6.40	20.1
Propane	46.5	26.40	20.1
n-Butane	129.5	109.10	20.4

We can see the excellent consistency of the data.

Table II shows a set of data, in terms of volumes, for elution of both n-alkanes and 1-alkenes from a 2% (w/w) column of dinonyl phthalate (DNP) on Chromosorb G. The relevant equations are quoted in the Table.

TABLE II

RETENTION DATA (ml) FOR n-ALKANE AND 1-ALKENE ELUTION FROM A COLUMN OF 2% DNP ON CHROMOSORB G AT 50°

Compressibility factor, $j = 0.375$.
Alkanes: $\log t_R' = 0.471n - 1.082$.
Alkenes: $\log t_R' = 0.405n - 0.777$.

Compound	V_R	V_R'	V_A
Methane	19.05	0.25	18.80
Ethane	19.68	0.73	18.95
Propane	21.10	2.15	18.95
n-Butane	25.29	6.34	18.95
Ethene	19.68	1.08	18.60
Propene	21.35	2.75	18.60
Butene-1	25.59	6.97	18.60

Table II further confirms the validity of the method but establishes further its power in that it works admirably when $V_A \gg V_R'$, that is, we are able to achieve a highly accurate result even when retention is almost trivial. Two further points can be drawn out in addition. Firstly, the measurement of V_A attains greater credibility when, as here, the same value is derived from two different homologous series. Secondly, to evaluate V_A truly, retention volumes at the retention temperature must be used and the average then multiplied by the compressibility factor, j. Thus, the correct result from Table II is $V_A = 0.375 \times 18.78 = 7.04$ ml.

Finally, we show one of a number of successful examples we have drawn from the literature of high-performance liquid chromatography (HPLC)[5]. This relates to the analysis of a coal tar pitch cyclohexane extract run on a 25-cm Partisil 5 column. Consideration of the structures of the large number of compounds cited in this

TABLE III

RETENTION DATA[5] (ml OF n-HEXANE) FOR ELUTION FROM A PARTISIL 5 COLUMN

Compound	V_R	V_R'	V_A
Pyrene*	16.0	11.4	4.4
Benzo(a)pyrene	27.7	23.3	4.4
Dibenzo(ah)pyrene	51.2	46.8	4.4
Pyrene	16.0	12.2	3.8
Benzo(a)/benzo(e)pyrene**	28.5$_5$	24.7$_5$	3.8
Dibenzo(ae)pyrene	54.0	50.2	3.8
Anthracene*	16.8	13.1	3.7
Benzo(a)anthracene	27.3	23.6	3.7
Dibenzo(aj)anthracene	46.2	42.5	3.7
Phenanthrene	16.2	11.5	4.7
Benzo(a)anthracene	27.3	22.6	4.7
Dibenzo(ah)anthracene	49.1	44.4	4.7

* Detailed consideration of the data and chromatograms indicate that the listed retention volumes for these two compounds have been overestimated, probably due to the incomplete resolution attained. The values here are our best estimate of the correct calues.

** Data are taken as the average of those for elution of benzo(a)pyrene and benzo(e)pyrene.

admirable work reveals the possibility of four groups of three compounds each of which might fulfil the requirements of eqn. 1. These are as listed in Table III which contains also the data and calculated values of column dead volume.

The average value over the four groups is $V_A = 4.15$ ml. The authors[5] quote 4.2 ml. Despite this very satisfactory agreement we, on balance, prefer the lower value of 3.7–3.8 ml since 4.2 ml looks rather a large dead volume for a column of the quoted dimensions.

It is important to emphasise here that any three data points in which $\Delta_2 > \Delta_1$ will give a consistent value of V_A. If, therefore, only three points are available the quality of the data must be unquestioned. Even a quite small error in one will have profound effect on the value of V_A derived. On account of this, the use of several groups of related solutes is much to be recommended since, if all give a similar result, this can be accepted with confidence since coincidence of erroneous results is most unlikely.

Finally, it is worth emphasising that the method has one major advantage over most others, the exact value of n required in the calculations is unimportant, it is only necessary that the values used be in the correct ratio. In the first group of Table III, for example, the C numbers are 16, 20, 24 but the calculations can be carried out with $n = 4, 5, 6$, or any other multiples. We are thus relieved of the problems of (a) identifying the compound of $n = 0$ and (b) extrapolating over a long range of n, which characterise most other methods.

We believe the above to be a useful method and both more dependable and simpler than alternatives when direct determination of V_A by elution of totally non-sorbed materials is precluded or uncertain. It obviously has particular potential in HPLC, where the determination of k' is notoriously a problem.

REFERENCES

1 J. Ševčík and M. S. H. Löwentap, *J. Chromatogr.*, 147 (1978) 75.
2 R. J. Smith, J. K. Haken and M. S. Wainwright, *J. Chromatogr.*, 147 (1978) 65.
3 J. A. G. Cominguez, J. G. Munoz, E. F. Sanchez and M. J. Molera, *J. Chromatogr. Sci.*, 15 (1977) 520.
4 W. E. Sharples and F. Vernon, *J. Chromatogr.*, 161 (1978) 83.
5 D. W. Grant and R. B. Meiris, *J. Chromatogr.*, 142 (1977) 339.