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Note

Simple and accurate determination of column dead time in gas chromatography

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The column dead time, t_m , plays an important role in solving theoretical and practical problems in gas chromatography and has special significance in the calculation of isothermal retention indices¹. Direct measurements of dead time are of limited value, as there are few substances that are not retained by the stationary phase but give a signal on flame-ionization detectors. The use of methane is questioned especially widely²⁻⁴.

Simple procedures for the mathematical prediction of dead time, such as those of Peterson and Hirsch⁵, Hansen and Andresen⁶ or Haferkamp⁷ (eqn. 1):

$$t_m = \frac{t_n^2 - t_{n+i} \cdot t_{n-i}}{2 t_n - t_{n+i} - t_{n-i}}; i = 1, 2, 3, \text{ etc.} \quad (1)$$

making use of measured retention times of three evenly spaced n -alkanes, are blamed⁸ for the centre point being weighted excessively. Thus, according to Wainwright and Haken's review⁸, small errors in the measurement of the retention time of the second alkane lead to gross errors in t_m . Further, different triplets of data points in this method give different dead times. Calculation of an arithmetic mean from dead times gained from different triplets can lead to a unique solution²; this, however, is tiresome and the result depends considerably on the choice of triplets for calculation of the average.

Kaiser⁹ proposed a computer program for calculation of dead time using the fitness of the equation

$$\frac{\log \left(\frac{t_2 - t_m}{t_1 - t_m} \right)}{\log \left(\frac{t_3 - t_m}{t_1 - t_m} \right)} - \frac{I_2 - I_1}{I_3 - I_1} = 0 \quad (2)$$

where t and I are the gross retention time and Kováts retention index, respectively.

Gröbler and Bálizs¹⁰ gave a computer program for the determination of the slope of the n -alkane line and of the dead time by use of two separate linear regression least-squares procedure involving logarithms.

Guardino *et al.*¹¹ developed an iterative method of calculation in which the squares of deviations of the theoretical retention indices of *n*-alkanes are minimized with respect to the retention calculated from the equation

$$\log t' = bI + a \quad (3)$$

where t' is the adjusted retention time and a and b are constants. The t_m referred to as the 'mathematical dead time' is obtained so that the adjustment of the experimental points to the straight line is optimized.

The last three methods, classified⁸ as iterative and statistical, are considered to be the most accurate, but they are pretentious in mathematical background and may be time consuming.

Below we propose a simple method for the calculation of dead time. It weights all of the available experimental data equally and leads to a unique solution for all *n*-alkane peaks in a chromatogram, provided the chromatographic conditions remain unchanged.

EXPERIMENTAL AND RESULTS

It is accepted in both classical methods⁵⁻⁷ and the iterative and statistical methods⁹⁻¹¹ that the slope of the logarithmic plot of the adjusted retention times of *n*-alkanes *versus* carbon number is constant over a wide range of carbon numbers, excluding the first few *n*-alkanes. In other words, relative retention for successive *n*-alkanes is constant over the linear part of the plot, as expressed by the equation

$$\frac{t'_{z+1}}{t'_z} = q \quad (4)$$

where z is the carbon number and q is the ratio of the adjusted retention times of successive members of the homologous series, or the relative retention. Substituting $t_{z+1} - t_m$ for t'_{z+1} and $t_z - t_m$ for t'_z , respectively, in eqn. 4, we obtain

$$\frac{t_{z+1} - t_m}{t_z - t_m} = q \quad (5)$$

Incidentally, it was found that eqn. 5 can be transformed so that t_{z+1} is expressed as a linear function of t_z (eqn. 6):

$$t_{z+1} = qt_z - t_m(q-1) \quad (6)$$

Data points of the t_{z+1} *versus* t_z plot should, therefore, fit a straight line. The slope of this straight line, q , is the relative retention, or the quotient of the geometric progression formed by *adjusted* retention times of successive *n*-alkanes. Once q is known, the intercept of eqn. 6 multiplied by -1 and divided by $q-1$ will result in the dead time, t_m .

As can be seen, the procedure for the calculation of t_m according to eqn. 6 is very simple and does not even involve logarithms. The method weights all of mea-

TABLE I
COMPARISON OF DEAD TIMES FOR C₁-C₇ n-ALKANES OBTAINED BY DIFFERENT METHODS

t = Gross retention time in seconds measured by Wainwright and Haken¹³; t_m = dead time in seconds calculated¹³ by the Gröbler and Bálizs¹⁰ method; t_M = dead time in seconds calculated according to eqn. 6 (this work); $\Delta\%$ = $100(1 - t_m/t_M)$; r = correlation coefficient as obtained for eqn. 6.

Stationary phase*	t							t_m^{***}	t_M^{***}	$\Delta\%$	r^2
	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆	C ₇				
SE-30	200.6	212.6	233.6	281.5	379.9	582.9	1003.0	189.2	189.0	-0.10	0.999958
OV-25**	-	214.5	226.6	263.9	359.6	620.8	1312.5	208.3	204.5	-1.86	0.999969
Porasil C	158.5	182.5	229	335.3	568	1079	2206	141.4	141.4	0.00	0.999998
Squalane + Porasil C	136	164.5	222.5	373	730	1576.5	3556.5	109.7	108.2	-1.39	0.999998
Porapak S	58.5	72.3	94.3	139.5	225.8	389.8	703.3	44.3	44.6	0.67	0.999998
Porapak PS	61.5	72.5	94	147	263.8	519.5	1080.3	49.0	49.4	0.81	0.999999
Porapak Q	71.5	90.5	117.5	168.3	258	419	707.9	55.4	54.1	-2.40	0.999994
Porapak R	44.5	55.3	71.0	102.5	162.5	278.5	491.0	35.4	35.8	1.12	0.999998

* For the chromatographic conditions, see the original papers^{13,14}.

** Data in this row taken from ref. 14.

*** Based on C₄-C₇ n-alkanes.

sured gross retention times involved in the least-squares procedure equally and provides a unique solution common for all peaks in a chromatogram of n -alkanes.

It is of interest that b , the slope of the n -alkane line (eqn. 7):

$$\log t' = bz + c \quad (7)$$

emerges as an intermediate result in the calculation of dead time, because

$$\log q = b \quad (8)$$

as can be seen by inspection of eqns. 4 (or 5) and 7. Hence a run of a *single* linear curve-fitting program in a programmable minicalculator results in t_m and b simultaneously. This feature of the proposed method may offer an advantage in the calculation of Kováts retention indices¹², which represents one of the most frequent uses of the dead time regardless of the way it has been obtained.

The examples below are intended to show that our method produces dead times with high precision, as follows from the closeness of our dead times to those calculated by more sophisticated methods.

Example I

Wainwright and co-workers^{13,14} reported a large set of experimental retention times for C_1 - C_7 n -alkanes obtained by conventional gas-liquid chromatography on SE-30 and OV-25 and by gas-solid chromatography on columns of Porapaks, Porasil and squalane on Porasil C. The investigation was aimed at the examination of the linearity of the n -alkane plot with respect to the first members of the homologous series and at determination of effective carbon numbers. Adjusted retention times were obtained by subtracting the dead time, t_m , calculated by the Gröbler and Bálizs¹⁰ method, from measured gross retention times.

Table I gives the reported gross retention times and compares the dead time calculated by Wainwright and co-workers^{13,14} using the Gröbler and Bálizs¹⁰ method with those we calculated in this work using eqn. 6. The gas chromatographic conditions are given in the original papers^{13,14}.

It is apparent from Table I that our dead times are very close to those obtained^{13,14} by the other method¹⁰, and the differences between them do not seem to depend on either the nature and polarity of the stationary phase or the size of the dead times themselves.

Example II

In this example we compare dead times obtained from eqn. 6 with those reported by Guardino *et al.*¹¹. They evaluated the influence of the method of calculation of the dead time on the accuracy of the retention index by using different values of the dead time and then comparing the values of the resulting retention indices with theoretical values. They calculated the retention indices from

$$I = \frac{\log(t - t_m) - a}{b} \cdot 100 \quad (9)$$

where a and b are the intercept and the slope, respectively, of the straight line obtained when the least-squares procedure was applied to $\log(t - t_m)$ values versus carbon number, t being the measured gross retention time and t_m the dead time as calculated by different methods. Table II gives three different sets of retention indices as obtained by Guardino *et al.*¹¹ using three different methods of calculation of the dead time. The methods are (i) the use of eqn. 1 involving the last three hydrocarbons (I_1); (ii) the use of eqn. 1 taking the largest possible even spacing (C_{20} , C_{28} , C_{36}) (I_2); and (iii) the iterative method of Guardino *et al.*¹¹ involving the 'mathematical dead time' using all hydrocarbons (I_3).

The column in Table II headed I_4 contains retention indices we obtained by using eqn. 9 with insertion of our value of the dead time calculated from eqn. 6 involving the nine gross retention times in the second column.

The dead time calculated by eqn. 6 using all of the retention data in Table II, 227.31 sec, is in good agreement with that of Guardino *et al.* (229.16 sec). The good agreement becomes excellent when the calculation according to eqn. 6 is carried out neglecting the gross retention time of the highest n -alkane (1990.0 sec), the resulting dead time being 229.44 sec. As a consequence, retention indices (column headed I_5 in Table II) recalculated with this dead time according to eqn. 9 fall as close to the theoretical values as Guardino *et al.*'s values (column I_3).

As follows from the nature of the dead time calculations involving mathematical processing of experimental (gross) retention times, the accuracy of any dead time calculated by these procedures depends on the reliability of the raw experimental data. The values in the columns headed I_4 and I_5 in Table II exemplify this dependence in the particular case discussed.

The proposed method for the calculation of the dead time (and the slope of the n -alkane line) is simple and rapid. The relationship shown by eqn. 6 is linear, and

TABLE II

INFLUENCE OF THE METHOD OF CALCULATION OF THE DEAD TIME ON THE ACCURACY OF THE RETENTION INDEX

Theoretical retention index*	Retention time ^{*,**} (sec)	Calculated retention index				
		I_1^*	I_2^*	I_3^*	I_4	I_5
700	254.0	721.37	693.18	700.67	704.81	700.05
800	271.0	799.93	798.49	798.45	798.57	798.45
900	301.0	891.02	903.15	899.82	899.02	900.11
1000	352.5	989.03	1005.28	1001.17	998.84	1001.53
1100	440.0	1090.75	1105.19	1101.70	1099.67	1102.00
1200	580.0	1190.00	1199.35	1197.17	1195.89	1197.37
1300	839.0	1299.54	1301.0	1300.83	1300.64	1300.86
1400	1267.0	1405.95	1398.68	1400.51	1401.56	1400.36
1500	1990.0	1512.35	1495.54	1499.63	1501.99	1499.28
t_m (sec)		218.03	232.17	229.16	227.31	229.44
r^{2***}		0.998284	0.999772	0.999973	0.999910	0.999972

* Data taken from ref. 11.

** Stainless-steel capillary column (30 m \times 0.3 m I.D.); stationary phase, Apiezon L; temperature, 120°C.

*** r = Regression coefficient.

does not require the use of logarithms. It can include any number of measured data, which will be weighted equally and result in a unique value valid for all peaks involved, provided the chromatographic conditions remain unchanged.

The uncertainties that may be a consequence of shifts in marking the instant of the sample injection (as pointed out by Ševčík¹⁵ can be overcome by using an arbitrary reference origin, as is done in the Peterson and Hirsch⁵ method.

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