STUDY OF GAS CHROMATOGRAPHIC DEAD-TIME MEASUREMENT

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SUMMARY

A rigorous investigation of the determination of gas chromatography column dead times has been carried out using air and methane retention data and also by the method of Peterson and Hirsch using *n*-alkanes.

It is shown that for polar and non-polar columns and a wide range of working temperature, methane is not retarded and gives identical times with an air peak allowing its use in conjunction with flame-ionization detectors.

It has also been demonstrated that the Peterson and Hirsch method of calculating t_m from *n*-alkane retention data is subject to very large errors over which the operator has no control and the use of this method in the evaluation of corrected retention times should be discontinued.

INTRODUCTION

Experimental determinations of dead time or column hold-up time are made by injection of air as a non-retarded substance and are identified as the time to the emergence of the air maximum. With the wide-spread use of flame-ionization detectors which are not sensitive to air, alternative methods have had to be devised. Presaturation of carrier gas by butane to give a negative air peak[1] is such a method. Methane has been suggested as a substitute for air when the flame-ionization detector is used, the objection to the use of methane being that at low temperatures, and employing oleophilic stationary phases, the solubility of the gas in the stationary phase could be appreciable[2]. The alternative approach to dead-time evaluation is a mathematical one, using consecutive *n*-alkanes, the Peterson and Hirsch method[3] being widely used. Gold[4] has derived an approach whereby any three homologues may be used in dead time calculation. Grobler and Bálizs[5] have used regression analysis of homologous alkane retention data, their method having been used by Haken *et al.*[6] to study the accuracy of dead-time measurement and compare the results obtained with those derived by iterative techniques of dead-time calculation such as that described by Guardino *et al.*[7].

The Peterson and Hirsch method for calculating the dead time, t_m, from the retention times of three *n*-alkanes $C_{(n)}$, $C_{(n+1)}$ and $C_{(n+2)}$ is

$$t_m = \frac{t_{C(n)} \cdot t_{C(n+2)} - t^2_{C(n+1)}}{t_{C(n)} + t_{C(n+2)} - 2t_{C(n+1)}} \qquad (1)$$

and is derived from the fact that the ratios of adjusted retention times in a homologous series are constant.

$$\frac{t'_{C(n+1)}}{t'_{C(n)}} = \frac{t'_{C(n+2)}}{t'_{C(n+1)}} \qquad (2)$$

where

$$t'_{C(n)} = t_{C(n)} - t_m, \text{ etc.} \qquad (3)$$

Whilst this calculation is mathematically viable, the authors have noted large variations obtained when the above expression is used to calculate t_m. The following hypothetical system will demonstrate the effects of small errors in n-alkane retention time measurement, errors of the magnitude obtained when the operator is timing the emergence of three n-alkane peaks with one stop-watch.

Suppose the gas chromatographic system is defined as one in which the adjusted retention time, $t'_{C(n)}$, of an n-alkane is 57.0 sec and of the next higher homologue, $t_{C(n+1)}$, is 97.5 sec. It is a simple matter now to calculate the adjusted retention time of a further homologue, $t'_{C(n+2)}$, as being 166.8 sec if the system is strictly linear. If a dead time, of 30.0 sec is now added to give retention times, t_R, of 87.0, 127.5 and 196.8 sec for $t_{C(n)}$, $t_{C(n+1)}$ and $t_{C(n+2)}$, respectively, use of eqn. 1 will, of course, give a t_m value of 30.0 sec. If small errors in measurement of retention times, of the order of 1 sec, are introduced as shown in Table I, surprisingly large variations in t_m are produced. These variations are much too large to be tolerated, all errors in Table I are less than 2 sec but they produce t_m values ranging from 16.3 to 40.7 sec.

TABLE I

A HYPOTHETICAL SYSTEM HAVING A 30.0-sec DEAD TIME SHOWING THE EFFECTS OF SMALL ERRORS IN A PEAK TIMING ON THE DEAD TIME AS CALCULATED BY THE METHOD OF PETERSON AND HIRSCH[3]

Alkane	t_R	Error	t_R	Error	t_R	Error	t_R	Error
C_n	87.0	0	87.0	0	87.0	0	86.0	−1
C_{n+1}	127.5	0	128.0	+0.5	126.2	−1.3	128.0	+0.5
C_{n+2}	196.8	0	196.8	0	198.6	+1.8	195.3	−1.5
t_m (calc.)	30.0		26.5		40.7		16.3	

The use of computing facilities and the sophisticated t_m calculations of regression analysis will not improve the accuracy of t_m determination. Indeed, Haken et al.[6], using a chromatograph interfaced to a digital computer and containing an automatically triggered, programmable real-time clock, have demonstrated (using a squalane column) that all the mathematical methods give a similar t_m spread of 59.8 to 69.7 sec. Obviously, the only factor of importance in dead-time calculations such

as these is the ability to obtain accurate retention times with an order of accuracy ($\pm$ 0.1 sec) which is impossible to achieve. The only accurate dead-time measurements will be those determined from the air peak time or, in the case of the flame-ionization detector, from methane retention times provided that the gas is not retarded.

In this work the authors have explored the accuracy with which the Peterson and Hirsch method can be used with experimental retention data in order to illustrate the variations shown in Table I, and have obtained corresponding values for air and methane on two columns. It is necessary to study the effects over a wide range of column temperature and low temperature work on a paraffinic stationary phase should reveal the maximum discrepancies in air and methane retention due to the solubility of the latter. Whilst the n-alkanes used for the Peterson and Hirsch calculation will have high solubilities and therefore good resolution on a paraffin phase, a polar phase will tend to exclude the n-alkanes with resulting low retention times and poor resolution. As retention times decrease, the denominator in eqn. 1 tends towards zero with consequent increase in error in the calculation of t_m. The behaviour of both polar and non-polar stationary phases will therefore be investigated.

EXPERIMENTAL

Measurements were made using a Pye Series 104 dual column gas chromatograph with katharometer detectors. Retention times were obtained using a Pye-Unicam DP88 computing integrator measuring to 1 sec and manually by stop-watch to 0.1 sec. Two 5 ft. $\times$ $\frac{1}{4}$ in. O.D. columns containing 10% of stationary phase on a Chromosorb W AW DMCS (80–100 mesh) support were used, the stationary phases being the saturated hydrocarbon grease Apiezon MH[8] and diethylene glycol adipate.

Sample sizes injected were 10 μl of air or methane and 1 μl of liquid n-alkane mixtures. The n-alkanes were injected as mixtures of five consecutive homologues in order to calculate three mathematical dead times per injection. Carrier gas flow-rates were between 24 and 28 ml/min and 14 to 23 ml/min for Apiezon MH and diethylene glycol adipate columns, respectively. In order to make comparisons for different temperatures, all retention times have been multiplied by the flow-rate to give retention volume data.

RESULTS AND DISCUSSION

No variations between retention times of air and of methane were found for either column at any of the temperatures used. The assumption that methane will give inaccurate dead times due to its solubility in the stationary phase is baseless. In Table V, the air and methane results are given for the Apiezon MH column at 60°, conditions under which the solubility of methane should be maximized. However, it is seen that there is no significant variation neither between air and methane times nor between comparable times obtained by two operators carrying out manual timing. The large errors introduced into the mathematical calculation of dead time, as given in Table I are borne out by the experimental results in Tables II and III. Variations around 3 ml in dead volume, corresponding to 9-sec discrepancies in dead time at flow-rates of 20 ml/min are common place with such discrepancies reaching an incredible 13.8 ml or 41 sec in dead time for the Apiezon column at 60°. Furthermore,

TABLE II

DEAD-VOLUME MEASUREMENTS ON AN APIEZON MH COLUMN DETERMINED FROM AIR AND METHANE RETENTION TIMES AND BY THE PETERSON AND HIRSCH METHOD USING n-ALKANE RETENTION

Column temperature (°C)	Peterson and Hirsch method		V_m (air) (ml)	V_m (methane) (ml)
	n-Alkanes	V_m (calc.) (ml)		
60	5–7	14.6	15.9	15.9
	6–8	9.5		
	7–9	23.3		
100	5–7	13.5	14.1	14.1
	6–8	10.0		
	7–9	17.7		
140	5–7	14.0	13.2	13.2
	6–8	10.4		
	7–9	13.6		
180	8–10	13.4	13.6	13.5
	9–11	14.1		
	10–12	11.8		

TABLE III

DEAD-VOLUME MEASUREMENTS ON A DIETHYLENE GLYCOL ADIPATE COLUMN AS IN TABLE II.

Column temperature (°C)	Peterson and Hirsch method		V_m (air) (ml)	V_m (methane) (ml)
	n-Alkanes	V_m (calc.) (ml)		
60	7–9	19.2	19.0	19.0
	8–10	18.9		
	9–11	16.8		
100	9–11	17.2	16.8	16.8
	10–12	17.5		
	11–13	17.0		
140	10–12	19.3*	15.9	15.9
	11–13	16.8*		
	12–14	10.4*		
180	12–14	12.3	11.4	11.4
	13–15	11.2		
	14–16	15.9		

* Averages for three sets of data.

it must be stressed that these variations arise only from small errors in the timing of the five n-alkanes, the above-mentioned example of a dead volume of 9.5 or 23.3 ml depending only upon which three n-alkanes are used in the Peterson and Hirsch calculation.

An example of the peak timings will reveal the extent of the errors. In Table III the data for the DEGA column at 100° is given for the C_9 to C_{13} n-alkanes. In the

first run, for which the dead volumes, V_m, are those given in Table III, the retention times were 80, 99, 132, 190 and 291 sec for C_9 to C_{13}. A second run gave 81, 99, 133, 190 and 290 sec for the retention times, two values being identical with those of the first run and the other three varying by only 1 sec. From these values, the dead volumes calculated were: C_{9-11}, 17.2 and 19.2 ml; C_{10-12}, 17.5 and 15.4 ml; C_{11-13}, 17.0 and 18.2 ml; whilst air and methane retention volumes were constant 16.8 ml. Large variations in retention index values quoted by different laboratories are therefore unavoidable if the Peterson and Hirsch method is used for t_m evaluation, these variations arising from (i) very small errors in n-alkane retention time measurement and (ii) the choice of the three alkanes for the calculation. Iterative techniques, averaging a large number of n-alkane retention times, will not solve this basic problem, the results in Table III for the DEGA column at 140° are in fact averages of three runs but still show large variation. The only way in which consistently accurate retention index values may be obtained is by the use of the air or methane peak retention times for t_m. Methane has been discredited in the literature but for the wrong reasons. Guberska[9] has compared t_m(calc.) with t_m(methane) values for column temperatures of 140 and 184° and obtains values which appear to be significantly high for methane. It would seem, in the light of the present work, that Guberska's methane results were accurate and the calculated dead times in error. The accuracy with which measurements were made justifies this conclusion as the author gives a t_m(calc.) of 12.25 ± 2.44 (a 20% error) against a t_m (methane) of 13.30 ± 0.20 (a 1.5% error). Hansen and Andresen[10] have also published data comparing calculated dead times with the methane retention and apparently show that the methane retention is 5% on squalane at 50° and 3–4% on Carbowax 20M at 130°. These authors, however, used chart distances (cm) in order to carry out the calculations. In addition to assuming a constant and regular chart speed, these authors measured distances in the 0.5- to 6.0-cm range ignoring the fact that estimates to the nearest 0.02 cm are virtually impossible to achieve. The errors introduced are therefore considerably greater than those inherent in an actual peak timing method and consequently their results are invalidated.

The data given in Tables IV and V on the accuracy of manual timing of air and methane peaks took approximately 1½ h to obtain as each operator had to determine ten air and ten methane retention times alternately. During this period, no significant variation in either column temperature or carrier gas flow-rate was found which could contribute to errors in measurement. The only significant factor causing variation in retention times was found to be the sample size. When the usual sample size of 10 μl was increased to 50 μl, increases of 1 sec on a 60-sec retention time were

TABLE IV

DEAD VOLUMES FROM AIR PEAKS AND BY THE PETERSON AND HIRSCH METHOD BY DIFFERENT OPERATORS USING STOP-WATCH TIMING

Operator	Column temperature (°C)	V_m (calc.) (ml) using C_6–C_8	V_m (air) (ml)
1	140	12.5	13.1
2		13.0	13.6

TABLE V

OPERATOR ACCURACY AND STANDARD DEVIATIONS CALCULATED FOR TEN
REPLICATE TIMINGS OF AIR AND OF METHANE ON THE APIEZON MH COLUMN

Operator		Average t_m (sec)		Standard deviation	
		Air	Methane	Air	Methane
1	60	60.15	60.13	0.16	0.15
2		60.16	60.27	0.07	0.09

observed. In this case the recorder pen deflection increased from 10 to 50% of full
scale. Further increases using sample sizes of up to 1 ml were made, the detector
output being attenuated to maintain a peak height corresponding to 50% of the
recorder scale. In these instances retention times of 61 sec independent of sample size
were observed thus proving that the 1-sec error arose from a slow recorder response.
This being found to be the main source of error in manual dead-time determination,
it is recommended that sample size/attenuation should be adjusted to give a 10%
recorder deflection when determining retention data.

The retention data for the DEGA column at 180° introduced a further possible
source of error in that on this polar column, which rejects alkanes, consecutive hydro-
carbons could not be separated at 180°, values for Table III were obtained at this
temperature by chromatographing two mixtures, (i) C_{12}, C_{14}, C_{16} and (ii) C_{13}, C_{15}, in
quick succession. The results in Table III are reasonably consistent and are, in fact,
better than the results obtained at 140° where a sample of the five homologues was
chromatographed. Although not good practice, this was the only way in which data
for the Peterson and Hirsch calculation of t_m could be obtained and highlights the
problems of n-alkane retention and measurement on polar phases.

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