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Note

A comparative study of mathematical dead-time and methane retention

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The widespread use of flame ionization detectors has led to a large number of methods of mathematically calculating dead-times[1-9]. These methods are based on the linearity of the relationship between the logarithm of the net retention time and the number of carbon atoms for the homologous n-alkanes. These methods differ only in the way in which the relationship given in eqn. 1 is treated. This relationship is

$$\log(t_r - t_m) = bZ + C \tag{1}$$

where t_m is the dead-time, t_r is the uncorrected retention time of the n-alkane with carbon number Z, and b and C are the slope and intercept, respectively.

In previous papers[10,11], the accuracy of many of these methods has been compared, and suggestions have been made for improving the accuracy of determining the dead-time mathematically. It was shown[10] that four alkanes are sufficient to provide an accurate estimate of dead-time if the uncorrected retention times are accurately measured.

The use of mathematical dead-times in the calculation of retention indices has resulted from the inability of the flame ionization detector to produce a signal with air and the doubt cast upon the accuracy of the methane retention as an estimate of dead time[3,9,12]. A recent paper by Sharples and Vernon[13] has re-opened the controversy surrounding the comparative merits of methane injection and mathematical dead-time estimates.

The present paper provides evidence to support the use of mathematical dead-time and highlights the inaccuracy of using methane retention times.

EXPERIMENTAL

The equipment used consisted of a Hewlett-Packard 5750 research chromatograph interfaced to a 16K P.D.P. 11/40 digital computer. Interfacing was achieved by the use of an LPS 11 Laboratory Peripheral System comprising a 12-bit analog-to-digital converter, a programmable real-time clock with two Schmitt triggers and a display controller with two 12-bit digital-to-analog converters. All on-line programming was written in CAPS II Basic with LPS options. The sampling rate was 0.5 sec.

Mixtures of methane and C_5 to C_9 n-alkanes were produced in a gas mixing

vessel and were diluted with high purity nitrogen. Samples were removed from the vessel using a gas-tight syringe and were injected into the chromatograph, which contained two columns connected by a splitter.

The retention times measured for the C_5 to C_9 alkanes were used to calculate the dead-times by the method of Grobler and Balizs[6]; this method has been proven to be simple and accurate[11]. The dead-time, t_m, the slope b, and intercept C were then used in eqn. 1 to estimate the uncorrected retention times, t_r, of the alkanes and methane. The experimental and calculated retention times are shown in Tables I and II for polar (OV-25) and non-polar (SE-30) columns; both columns were 10 ft. × 0.25 in. O.D. and contained 10% of the stationary phase supported on Chromosorb W (80–100 mesh).

RESULTS AND DISCUSSION

From Tables I and II it can be seen that, over a range of temperatures and flow-rates, the methane retention is always greater than the mathematical dead-time. Further, the measured and calculated retention times of the C_5 to C_9 alkanes are almost identical, indicating the excellent linearity of the logarithmic relationship for those compounds. More important is the excellent agreement between the measured and calculated retention times of methane.

The fact that the measured and calculated methane methane retention times are mutually consistent indicates that the logarithmic relationships is linear (at least for C_1 to C_9 alkanes) and is in agreement with the findings of Groenendijk and Van Kemenade[14] for higher alkanes. This relationship must hold for methane as well as for the higher alkanes in order that the Kovats index[15] method of correlating retention behaviour be valid.

Sharples and Vernon[13] have criticized the use of the Peterson and Hirsch[2] method of determining t_m. However, their criticism is wrongly directed. Instead of discrediting the use of the alkane line, they should have pointed to the weakness of the Peterson and Hirsch method of evaluating t_m from the line. The Peterson and Hirsch method, being the analysis of three equally spaced points, weights the centre point excessively, and small errors in the retention time of the middle alkane lead to gross errors in t_m. However, if the statistically sounder approach of Grobler and Balizs[6] is used for four or five alkanes, the mathematical dead-time will be an accurate estimate of t_m, as shown previously.

In their paper, Sharples and Vernon[13] also criticized the work of Guberska[12] and Hansen and Andresen[3], each of whom found that methane had retention times greater than those calculated from the alkane lines. The criticisms were directed at the methods of measuring the uncorrected retention times of the alkanes and the methods of calculation. Such arguments cannot be used to invalidate the results of this study, in which a computer was used to measure the retention times and in which a proven method of statistical estimation of t_m has been employed. The consistently higher value of the methane retention relative to the calculated value of t_m cannot be questioned in this study.

The results of this study are consistent with those of Garcia Dominguez et al.[9], who found that methane was retained on various chromatographic columns of different polarityes for the temperature range 100–180°. The results are also consistent

TABLE I

RETENTION TIMES OF n-ALKANES ON SE-30 AT THREE TEMPERATURES AND THREE FLOW-RATES

Temp. (°C)	Flow-rate (ml/min)	Retention times (sec)*						Column characteristics		
		Methane	Pentane	Hexane	Heptane	Octane	Nonane	Dead-time (sec)	Slope	Intercept
140	45	80.5 (80.7)	95.0 (95.0)	106.0 (106.2)	125.0 (124.8)	156.5 (156.1)	208.5 (208.5)	78.6	0.51656	0.21824
		80.5 (81.3)	95.5 (95.5)	106.5 (106.5)	125.0 (125.1)	156.5 (156.2)	208.5 (208.6)	79.3	0.519228	0.18868
		81.0 (81.2)	95.5 (95.5)	106.5 (106.7)	125.5 (125.3)	157.0 (156.6)	209.0 (209.0)	79.1	0.51656	0.22331
	40	103.0 (103.0)	121.5 (121.5)	135.5 (135.5)	158.7 (158.8)	197.5 (197.3)	261.0 (261.0)	100.1	0.504677	0.53877
		103.0 (102.5)	121.0 (121.0)	135.0 (135.1)	158.5 (158.4)	197.0 (197.2)	260.5 (261.5)	99.7	0.506606	0.554932
		103.0 (103.5)	121.5 (121.5)	135.2 (135.4)	158.5 (158.5)	197.5 (197.1)	261.5 (261.6)	100.9	0.51308	0.461739
	30	112.0 (112.3)	132.5 (132.5)	148.0 (148.1)	174.2 (174.1)	217.5 (217.5)	290.0 (290.0)	109.3	0.512756	0.58203
		112.0 (112.3)	132.5 (132.5)	148.0 (148.1)	174.0 (174.0)	217.7 (217.5)	290.0 (290.1)	109.4	0.513826	0.572308
		112.0 (112.4)	132.5 (132.5)	148.0 (148.0)	174.0 (174.0)	217.5 (217.5)	290.2 (290.3)	109.5	0.515321	0.559279
130	45	80.5 (80.7)	98.0 (98.0)	112.0 (112.0)	136.0 (136.0)	177.0 (177.1)	247.7 (247.7)	78.4	0.53951	0.27538
		82.5 (82.4)	99.5 (99.5)	113.5 (113.4)	137.0 (137.4)	179.0 (178.6)	249.5 (249.6)	80.2	0.543034	0.24579
		83.0 (83.2)	100.5 (100.5)	114.5 (114.5)	138.5 (138.6)	180.0 (179.8)	250.5 (250.5)	80.9	0.539731	0.27594
	40	94.5 (94.7)	114.0 (114.1)	129.5 (129.7)	157.0 (156.6)	203.0 (203.8)	282.0 (282.0)	92.2	0.540028	0.38564
		99.5 (95.4)	114.5 (114.5)	130.0 (130.2)	157.5 (157.2)	204.0 (203.7)	284.0 (283.9)	92.9	0.544882	0.34845
		94.5 (95.3)	114.5 (114.6)	130.0 (130.2)	157.5 (157.2)	204.0 (203.7)	283.7 (283.7)	92.9	0.543944	0.35593
	30	112.0 (112.5)	136.0 (136.1)	155.0 (155.2)	188.5 (188.2)	245.5 (245.1)	343.0 (343.0)	109.5	0.543774	0.55906
		111.0 (110.7)	135.0 (135.0)	154.5 (154.5)	187.7 (187.8)	245.0 (244.8)	342.0 (342.0)	107.5	0.535626	0.63712
		111.5 (112.0)	135.5 (135.6)	154.5 (154.7)	188.0 (187.7)	245.0 (244.6)	342.5 (342.5)	109.0	0.543774	0.55906
120	45	83.5 (82.9)	103.5 (103.5)	121.0 (121.0)	152.0 (151.9)	206.5 (206.4)	302.5 (302.5)	80.9	0.567067	0.29885
		83.5 (83.1)	103.5 (103.5)	121.0 (121.9)	151.5 (151.8)	206.5 (206.3)	302.5 (302.6)	80.8	0.569606	0.27541
	40	98.5 (99.1)	122.5 (122.6)	142.5 (142.5)	179.5 (178.8)	243.0 (242.7)	356.0 (356.3)	96.5	0.574834	0.38641
		98.5 (97.8)	122.0 (122.0)	142.5 (142.6)	174.0 (178.8)	242.7 (242.6)	355.0 (354.9)	95.0	0.565855	0.46790
	30	116.0 (116.2)	144.5 (144.6)	168.5 (168.8)	212.0 (211.7)	288.0 (287.5)	421.5 (421.5)	113.0	0.569597	0.59560
		116.0 (116.6)	144.5 (144.6)	168.5 (168.7)	211.7 (211.5)	288.0 (287.6)	422.7 (422.7)	113.5	0.57431	0.56535

* Calculated values are shown in brackets following the experimental ones.

TABLE II

RETENTION TIMES OF *n*-ALKANES ON OV-25 AT 120° AND 130° WITH A FLOW-RATE OF 45 ml/min

Temperature (°C)	Retention times (sec)*						Column characteristics		
	Methane	Propane	Hexane	Heptane	Octane	Nonane	Dead-time (sec)	Slope	Intercept
130	191.5 (189.7)	207.7 (207.8)	222.0 (222.4)	247.5 (247.1)	290.0 (289.0)	361.0 (361.0)	187.2	0.532860	0.362304
	191.0 (189.7)	208.0 (208.1)	222.2 (222.7)	248.0 (247.5)	290.5 (289.4)	360.5 (360.6)	187.1	0.527629	0.407383
	190.7 (187.7)	206.7 (206.8)	221.5 (221.7)	247.5 (246.9)	289.0 (289.3)	361.0 (360.8)	185.0	0.522386	0.467924
120	197.2 (194.0)	217.2 (217.3)	236.0 (236.2)	269.5 (268.7)	324.0 (324.7)	421.2 (421.0)	191.0	0.542493	0.448489
	197.5 (195.7)	217.5 (217.5)	235.7 (235.7)	267.5 (267.6)	323.5 (323.3)	420.5 (420.5)	193.0	0.55791	0.405791
	197.0 (195.0)	217.3 (217.1)	236.0 (235.5)	266.5 (267.5)	323.0 (323.1)	419.5 (419.7)	192.3	0.553156	0.448489

* Calculated values are shown in brackets following the experimental ones.

with those of an earlier study[14] in which it was observed that the use of the methane retention times as an estimate of column dead-time produced curvature in the logarithmic plot for the *n*-alkanes. The solubility of methane in liquid phases has been shown elsewhere[16].

As an indication of the error introduced by using the methane retention as a method of estimating dead-time, we can see the curvature produced in Fig. 1, where the straight lines represent the retention times of the alkanes corrected using the mathematical dead-time and the curved lines are the retention times corrected by assuming no hold-up of methane in the columns.
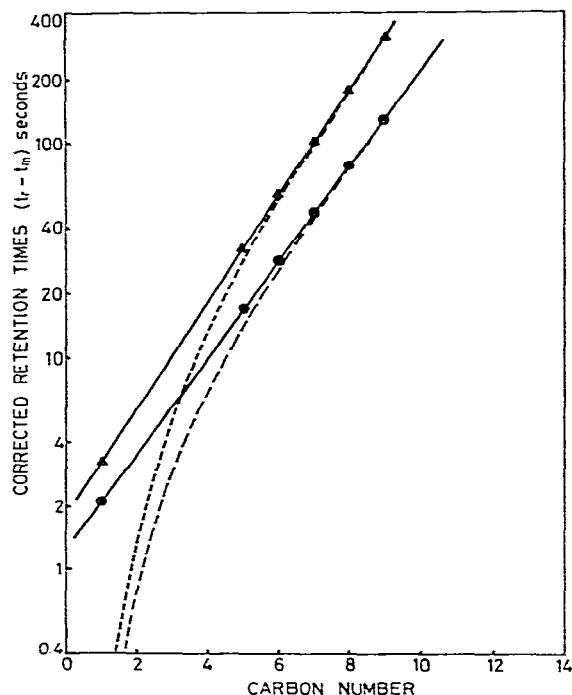

Fig. 1. Graphs showing corrected retention times of *n*-alkanes using calculated dead-times and methane retention: ▲, Calculated dead-time (solid line) and methane retention (dotted line) each at 120°; ●, calculated dead-time (solid line) and methane retention (dotted line) each at 140°.

The experimental procedure of this investigation is far superior to that of any method reported for comparison of mathematical dead-time and methane retention. This has been achieved by injecting a gaseous mixture of methane and the condensable alkanes made up in nitrogen; injection of the higher alkanes as a gaseous mixture overcomes the criticism that retention data for the alkanes are subject to errors introduced by vaporization in the needle and associated problems. The method could find general use for obtaining the alkane line by using mixtures of alkanes in nitrogen that may be stored in cylinders. This would enable consistency of mathematical dead-time calculation in inter-laboratory studies.

APPENDIX A

Comment by Dr. F. Vernon

We have not criticized the concept of mathematical dead-time, nor the excellent method of Grobler and Balizs for its derivation. Our paper was not intended for the "select few" with interfaced computing facilities, but to draw to the attention of the many "stop-watch workers", in gas chromatography the fact that the Peterson and Hirsch method introduces large errors and that the retention time of air for the dead-time may be derived from the retention of methane.

In our comparison of air and methane retention, we have shown the times to be *identical* for polar and non-polar phases over a wide temperature range. Since the definition of t_m is the retention or transit time of air (or other non-retained gas) methane must, by definition, give t_m. If the definition of t_m is at fault, we can hardly be blamed for that.

If the air–methane results in our paper are accepted by Wainwright, Haken and Srisukh, together with their own methane-retention data, perhaps they would care to explain the logical conclusion. How does air become retained by the liquid phase to the same extent as methanes Our air–methane comparisons are not referred to in the above paper, and this is an unfortunate omission, which I would hope that the authors will correct.

The most significant difference in experimental technique between the work of the authors and our own has not been mentioned in their paper. This is that we, like most other workers, used a *liquid* sample of alkanes for injection, whereas they used *vapour* samples. The importance of this is that the total retention time for an alkane as determined by us also includes a sample-volatilization time, which, being a function of carbon number, will produce a different value for the slope, b. Finally, the 10-ft. columns and dead-times of around 100 sec are not the norm in gas chromatography. Wainwright, Haken and Srisukh have demonstrated an apparent methane hold-up of 2 to 3 sec in a dead-time of 100 sec, which would correspond to a 1-sec error on a dead-time around the 40-sec region. This, we claim, is a vast improvement on dead-times that may be calculated by using the Peterson and Hirsch method.

APPENDIX B

Comments by the referees of the paper by Drs. Sharples and Vernon

We would like to draw the authors' attention to the paper by Soják *et al.* [*Chromatographia*, 7 (1974) 26], who found that plots of log t'_R *versus* carbon number for homologous *n*-alkanes are not strictly linear. This slight non-linearity can cause serious errors in the mathematically extrapolated dead-retention time. On the other hand, we agree that there are systems (column packings) in which the retention time of methane is longer than that of air. The authors' results are convincing, but equally convincing have been the results presented by Sharples and Vernon[13], who compared directly measured retention times of methane and air under identical conditions. In our opinion, the problem is still open, and any good arguments against or for using the mathematical dead-time is welcome.

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