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EVALUATION OF MATHEMETICAL PROCEDURES FOR THE CALCULATION OF DEAD-TIME

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SUMMARY

An extensive study has been made of three methods of determining dead-times mathematically from retention data of n-alkanes. It has been shown that the linearization procedure suggested by Grobler and Bálizs is sufficiently accurate for on-line data acquisition and that four alkanes are adequate to calculate accurately the dead-time provided that the retention times are not excessive.

INTRODUCTION

In a previous paper[1] the problem of the accurate calculation of mathematical dead-time was discussed and a comparison of several methods was made[2-4]. The effect of small changes in the retention times of n-alkanes on the calculated dead-time was examined and reasons for inaccurate dead-time estimates were suggested.

However, only four alkanes were used when calculating dead-time by each method and the number of determinations reported was limited, both features being constrained within limits which were considered compatible with routine laboratory mini-processors. With some comments advanced[5] concerning the depth of our earlier work, we report additional data from our studies together with a comparison of results obtained with retention times of air and methane, both of which are commonly used in the estimation of column dead-time.

In the present paper a total of 18 determinations using a single column with a thermal conductivity detector (TCD) and 14 determinations using dual columns and flame ionization detectors (FIDs) are presented. In each determination six n-alkanes, C_5-C_{10}, were used. Also the retention times for air and methane were measured using the thermal conductivity detector.

CALCULATIONS

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 set at 0.1 sec for those runs using the TCD and 0.5 sec for those runs involving the FIDs.

The retention times thus measured were then used to calculate the dead-times for three, four, five and six consecutive n-alkanes using each of three methods. The first was the method of Grobler and Bálizs[2] which was the method used for on-line analysis. Although the authors have claimed this method to be a non-linear regression technique, it in fact involves the calculation of the slopes and intercepts of two linear least squares lines. The values of b, c and t_m in the equation $\ln(t_r - t_m) = bZ + c$ are calculated by eqns. 1, 2 and 3. These equations are taken from our previous paper[1]:

$$b = \frac{(n-1)\sum\limits_{i=Z_1}^{Z_{n-1}} Z_i \log(t_{r(i+1)} - t_{r(i)}) - \sum\limits_{i=Z_1}^{Z_{n-1}} Z_i \sum\limits_{i=Z_1}^{Z_{n-1}} \log(t_{r(i+1)} - t_{r(i)})}{(n-1)\sum\limits_{i=Z_1}^{Z_{n-1}} Z_i^2 - \left(\sum\limits_{i=Z_1}^{Z_{n-1}} Z_i\right)^2} \quad (1)$$

$$t_m = \frac{\sum\limits_{i=Z_1}^{Z_n} q^{Z_i} \sum\limits_{i=Z_1}^{Z_n} t_{r(i)} \cdot q^{Z_i} - \sum\limits_{i=Z_1}^{Z_n} q^{2Z_i} \sum\limits_{i=Z_1}^{Z_n} t_{r(i)}}{\left(\sum\limits_{i=Z_1}^{Z_n} q^{Z_i}\right)^2 - n\sum\limits_{i=Z_1}^{Z_n} q^{2Z_i}} \quad (2)$$

$$c = \frac{\sum\limits_{i=Z_1}^{Z_n} \log t'_{r(i)} - b\sum\limits_{i=Z_1}^{Z_n} Z_i}{n} \quad (3)$$

where $t_{r(i)}$ is the uncorrected retention time of the ith n-alkane, $t'_{r(i)}$ is the corrected retention time of the ith n-alkane, Z_i is the ith n-alkane, q is antilog b and n is the number of n-alkanes used.

Thus the retention index for any compound can be calculated by

$$I = 100\,(\log t'_r - c)/b \quad (4)$$

The second method used was that of Guardino et al.[3] which uses an iterative technique to calculate t_m and a linear least squares method to evaluate b and c. The best estimates of t_m and b and c are obtained by minimising the sum of squares of the differences between the calculated and actual I values for the alkanes.

The third method was non-linear parameter estimation using flexible simplex for optimization. The method calculates t_m, b and c simultaneously. The minimization was effected by the use of the Flexible Simplex method of optimization described by Nelder and Mead[4].

All three methods were written in Fortran and run on a Cyber 72-26 digital computer to ensure maximum accuracy.

Seven series of calculation were conducted using the retention times of the following alkanes for each of the 46 sets of data: (a) C_5–C_7, (b) C_5–C_8, (c) C_6–C_9, (d) C_7–C_{10}, (e) C_5–C_9, (f) C_6–C_{10}, (g) C_5–C_{10}. Table I shows the retention times measured in each of the 46 runs.

Flexible Simplex and the method of Guardino et al. both use an iterative technique and thus require an objective function to be defined which is then minimised. In our previous paper we used the objective function suggested by Guardino et al. which is the sum of squares of the differences between the known and calculated Kováts indices as shown in eqn. 5:

$$\text{objective function} = (I - I_c)^2 \tag{5}$$

where I is the known Kováts index, and I_c is the calculated Kováts index.

However, since I is defined as 100 times the carbon number, Z, for n-alkanes, its value is known, and it is thus the independent variable. The objective function should, however, be based on the dependent variable which in our case is the retention time, t_R. This would suggest the use of the sum of squares of the differences between the experimental and calculated retention times as defined in eqn. 6:

$$\text{objective function} = (t_R - t_{R_c})^2 \tag{6}$$

where t_R is the experimental retention time and t_{R_c} is the calculated retention time. However, this function weights those alkanes with longer retention times and which are the least accurate as discussed in our previous paper. Therefore, to overcome this difficulty and to take account of the logarithmic nature of our model (eqn. 7), we chose an objective function based on the sum of squares of the difference between the logarithms of the experimental and calculated connected retention times as shown in eqn. 8:

$$\log t_R' = bZ + c \tag{7}$$

$$\text{objective function} = (\log t_R' - \log t_{R_c}')^2 = \left(\log \frac{t_R - t_m}{t_{R_c} - t_m}\right)^2 \tag{8}$$

where t_R = the experimental retention time, t_{R_c} = the calculated retention time, and t_m = the calculated dead-time.

The difference between the objective functions shown in eqns. 6 and 8 can be seen by reducing each to a simpler form, eqns. 9 and 10, respectively:

$$(t_R - t_{R_c})^2 = (t_R' - e^{bZ+c})^2 \tag{9}$$

$$\left(\log \frac{t_R - t_m}{t_{R_c} - t_m}\right)^2 = (\log t_R' - \log e^{bZ+c})^2 = (\log t_R' - bZ - c)^2 \tag{10}$$

Table II compares the three objective functions studied where it is apparent that the objective function used by Guardino et al. gives identical dead-times to five significant figures to the simplex method. When the objective function chosen in this

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TABLE 3

RETENTION TIMES (sec) OF n-ALKANES

The retention times that are not multiples of the sampling rate occur because the sampling programme averages retention times when the peak maxima occurs over more than one time sampling.

Run	Alkane					
	C_5	C_6	C_7	C_8	C_9	C_{10}
Single column using TCD						
1	65.35	74.95	92.8	124.85	183.45	293.3
2	66.8	76.6	94.5	127.15	187.15	297.65
3	66.0	75.45	93.4	125.65	185.0	293.9
4	66.85	76.1	94.65	127.65	187.65	298.25
5	65.95	75.45	93.05	125.6	184.85	295.05
6	66.25	76.05	93.85	126.3	185.45	292.0
7	66.65	75.55	93.35	125.7	185.15	294.9
8	65.65	75.5	93.2	125.65	185.75	295.05
9	65.8	75.45	93.25	125.95	186.05	295.15
10	65.85	75.55	93.25	125.85	185.50	295.1
11	65.55	75.05	92.75	125.25	184.15	291.7
12	65.35	75.1	92.75	124.85	184.0	292.5
13	65.4	75.0	92.6	125.05	184.2	292.3
14	65.2	75.05	92.65	125.05	183.6	292.55
15	65.5	75.1	92.85	125.1	184.7	292.8
16	65.3	74.95	92.55	124.65	183.3	289.4
17	65.4	74.95	92.45	124.85	183.2	290.45
18	65.55	75.2	92.95	125.2	184.35	292.45
Column A using FID						
19	76.0	87.5	108.0	145.5	214.0	338.0
20	76.0	87.5	108.0	145.5	213.5	338.0
21	75.5	86.5	107.0	144.0	211.5	335.0
22	74.75	86.0	106.0	142.5	209.5	330.5
23	74.5	85.5	106.0	142.5	209.0	330.0
24	74.5	85.5	105.5	142.0	208.5	329.0
25	75.0	86.0	106.0	143.0	210.0	331.5
26	75.0	86.0	106.0	143.0	209.5	331.0
27	74.5	85.5	106.0	142.5	209.0	330.5
28	74.5	85.5	105.5	141.75	208.0	328.0
29	74.0	85.0	105.0	141.5	207.5	328.0
30	74.0	85.0	104.5	141.0	206.5	326.5
31	73.5	84.5	104.5	140.5	205.5	324.75
32	73.0	84.0	103.5	139.25	204.0	322.0
Column B using FID						
33	91.0	102.0	122.0	158.25	224.0	343.5
34	90.5	102.0	122.0	158.25	224.25	343.25
35	90.0	101.0	121.0	156.75	222.0	340.25
36	89.0	100.0	119.5	155.5	220.0	336.25
37	89.0	100.0	119.5	155.0	219.5	335.75
38	89.0	99.5	119.25	154.75	218.75	334.5
39	89.25	100.0	119.5	155.5	220.0	336.25
40	89.0	100.0	119.5	155.0	219.5	335.5
41	89.0	99.75	119.75	155.0	219.25	335.25
42	88.5	99.5	118.75	154.0	217.75	332.75
43	88.5	99.0	118.5	154.0	217.5	332.5
44	88.5	99.0	118.0	153.5	216.5	329.0
45	88.0	98.5	117.5	152.75	215.75	329.5
46	87.0	97.5	116.5	151.25	213.5	325.75

TABLE II

COMPARISON OF DEAD-TIMES CALCULATED BY THE ITERATIVE METHODS USING DIFFERENT OBJECTIVE FUNCTIONS

Run	$(I - I_c)^2$			$(t_{R_c} - t_R)^2$		$ln\left(\dfrac{t_R - t_m}{t_{R_c} - t_m}\right)$	
	Grobler and Bálizs	Flexible Simplex	Guardino et al.	Flexible Simplex	Guardino et al.	Flexible Simplex	Guardino et al.
1	53.735	53.772	53.772	54.351	53.936	53.769	53.735
2	55.001	55.067	55.067	55.277	55.117	55.067	55.001
3	54.664	54.480	55.480	54.386	54.494	54.478	54.664
4	54.982	55.008	55.008	55.136	55.037	55.007	54.982
5	54.677	54.626	54.626	54.692	54.650	54.625	54.677
6	54.282	54.255	54.255	54.036	54.200	54.255	54.282
7	53.626	53.814	53.814	54.295	53.916	53.812	53.626
8	53.784	53.924	53.924	53.994	53.918	53.923	53.784
9	54.259	54.181	54.180	53.880	54.110	54.180	54.259
10	54.228	54.250	54.250	54.259	54.247	54.250	54.228
11	54.147	53.969	53.969	53.663	53.916	53.968	54.147
12	53.547	53.670	53.670	53.934	53.723	53.670	53.547
13	53.836	53.837	53.837	54.201	53.936	53.835	53.836
14	53.234	53.404	53.404	53.916	53.512	53.402	53.234
15	53.958	53.904	53.904	53.716	53.864	53.903	53.958
16	53.546	53.573	53.573	53.376	53.504	53.546	53.546
17	53.911	53.834	53.834	53.725	53.813	53.833	53.911
18	53.889	53.871	53.871	53.885	53.881	53.871	53.889

work is substituted in both methods, it is evident that the method of Guardino *et al.* gives identical dead-time estimations to those of Grobler and Bálizs[2].

RESULTS AND DISCUSSION

The dead-times for six *n*-alkanes (C_5–C_{10}) calculated by each of the three methods are shown in Table III. The differences between Flexible Simplex and the method of Grobler and Bálizs is also shown.

Table III shows that results by the method of Guardino *et al.* are identical to those of the method of Grobler and Bálizs using the new objective function to five significant figures. The table also shows that the average difference for a sampling rate of 0.1 sec is 0.081 sec with the maximum 0.186 sec. The average difference for a sampling rate of 0.5 sec is 0.118 sec with a maximum deviation of 0.300 sec. Therefore there is no significant difference between the three methods and the faster sampling rate gives a smaller deviation between the methods. The first point is emphasized by the very small difference in the means for the three sets of data. Therefore as was pointed out in our previous paper[1], the method of Grobler and Bálizs is most appropriate for on-line analysis because it does not involve a search and thus can be executed faster than either of the other two methods.

The effect of using three, four, five or six consecutive *n*-alkanes was then investigated using the method of Grobler and Bálizs and the results are shown in Table IV. Only one set of results are shown for three consecutive *n*-alkanes, C_5–C_7,

TABLE III

DEAD-TIMES CALCULATED BY THREE METHODS USING DIFFERENT SAMPLING RATES

The dead-times calculated by the method of ref. 3 were identical with those obtained by the method of Grobler and Bálizs to five significant figures and have not been entered in this table. The dead-times have been calculated from the retention data of the C_5–C_{10} series of alkanes.

Sampling rate = 0.1 sec

Run	Flexible Simplex	Grobler and Bálizs	Difference	Run	Flexible Simplex	Grobler and Bálizs	Difference
1	53.769	53.735	0.034	19	62.070	61.932	0.138
2	55.067	55.001	0.066	20	62.070	61.912	0.158
3	54.478	54.664	-0.186	21	62.033	62.162	-0.129
4	55.007	54.982	0.025	22	61.151	60.980	0.171
5	54.625	54.677	-0.052	23	60.833	60.970	-0.137
6	54.255	54.282	-0.027	24	61.089	61.104	-0.015
7	53.812	53.626	0.186	25	61.642	61.712	-0.070
8	53.923	53.784	0.139	26	61.606	61.674	-0.068
9	54.180	54.259	-0.079	27	60.870	60.986	-0.116
10	54.250	54.228	0.022	28	61.063	61.050	0.013
11	53.968	54.147	-0.179	29	60.553	60.567	-0.014
12	53.670	53.547	0.123	30	60.768	60.669	0.099
13	53.835	53.836	-0.001	31	59.943	59.913	0.030
14	53.402	53.234	0.168	32	59.651	59.491	0.160
15	53.903	53.958	-0.055				
16	53.546	53.573	-0.027				
17	53.833	53.911	-0.078				
18	53.871	53.889	-0.018				
Mean*	54.077	54.074	0.081	Mean*	61.096	61.080	0.094

Sampling rate = 0.5 sec

Run	Flexible Simplex	Grobler and Bálizs	Difference
33	77.489	77.496	-0.007
34	76.440	76.141	0.299
35	76.415	76.379	0.036
36	75.474	75.428	0.046
37	75.530	75.393	0.137
38	75.828	76.128	-0.300
39	75.986	76.110	-0.124
40	75.511	75.384	0.127
41	75.486	75.623	-0.137
42	75.053	74.855	0.198
43	75.384	75.639	-0.255
44	74.421	74.302	0.119
45	75.077	75.193	-0.116
46	73.965	74.047	-0.082
Mean*	75.576	75.580	0.142

* For differences mean is the average of the absolute differences.

TABLE IV

MATHEMATICAL DEAD-TIMES CALCULATED BY THE METHOD OF REF. 2 FOR DIFFERENT NUMBERS OF ALKANES

Run	Series of alkanes						
	C_5-C_7	C_5-C_8	C_6-C_9	C_7-C_{10}	C_5-C_9	C_6-C_{10}	C_5-C_{10}
1	54.179	53.691	53.017	55.270	53.660	53.576	53.735
2	54.943	54.923	55.076	55.626	54.979	55.180	55.001
3	55.494	54.769	53.585	54.882	54.684	53.774	54.664
4	54.872	55.001	54.997	54.995	54.954	55.103	54.982
5	54.808	54.785	54.324	54.485	54.651	54.496	54.677
6	54.245	54.300	54.419	53.826	54.319	54.231	54.282
7	53.244	53.410	54.071	54.947	53.568	54.246	53.626
8	53.290	53.597	54.523	54.260	53.791	54.347	53.784
9	54.374	54.317	54.198	53.625	54.300	54.014	54.259
10	54.089	54.223	54.376	54.132	54.224	54.353	54.228
11	54.544	54.348	53.538	53.113	54.171	53.528	54.147
12	53.317	53.386	53.887	54.445	53.524	53.942	53.547
13	53.880	53.960	53.394	53.900	53.753	53.824	53.836
14	52.681	53.142	53.637	53.935	53.143	53.905	53.234
15	54.192	53.947	53.823	53.939	53.997	53.670	53.958
16	53.587	53.587	53.634	53.259	53.602	53.498	53.573
17	53.928	54.072	53.687	53.014	53.899	53.735	53.911
18	54.053	53.878	53.724	54.115	53.893	53.760	53.889
19	61.306	61.778	62.736	62.125	61.930	62.558	61.932
20	61.306	61.778	62.510	62.442	61.855	62.585	61.912
21	62.763	62.256	61.369	62.276	62.168	61.544	62.162
22	60.286	60.759	61.930	61.432	60.984	61.710	60.980
23	61.763	61.030	59.989	61.520	60.977	60.234	60.970
24	61.056	61.118	61.207	60.790	61.124	61.092	61.104
25	61.556	61.840	61.845	60.449	61.741	61.637	61.712
26	61.556	61.840	61.620	60.540	61.669	61.592	61.674
27	61.763	61.030	59.989	61.747	60.977	60.310	60.986
28	61.056	61.003	61.137	61.210	61.0675	61.071	61.050
29	60.556	60.618	60.478	60.380	60.551	60.547	60.567
30	59.765	60.706	61.455	59.738	60.628	61.371	60.669
31	60.056	59.886	59.597	60.691	59.854	59.922	59.913
32	58.765	59.359	60.246	59.766	59.449	60.222	59.491
33	77.556	77.503	77.407	77.568	77.491	77.451	77.496
34	74.941	75.755	77.523	77.290	76.090	77.398	76.141
35	76.556	76.266	76.263	77.293	76.370	76.371	76.379
36	74.765	75.477	76.087	74.367	75.432	75.862	75.428
37	74.765	75.231	76.176	75.604	75.388	76.013	75.393
38	77.081	76.408	74.827	75.208	76.176	74.920	76.128
39	76.043	76.327	76.087	74.367	76.149	75.862	76.110
40	74.765	75.239	76.176	75.485	75.388	75.975	75.384
41	76.507	75.645	74.624	76.393	75.644	74.840	75.623
42	73.833	74.664	75.980	75.012	74.828	75.802	74.855
43	76.250	75.949	74.705	74.191	75.674	74.730	75.639
44	72.875	74.334	75.697	72.537	74.313	75.245	74.302
45	75.029	75.424	75.241	73.298	75.225	75.016	75.193
46	74.029	74.201	73.980	72.953	74.068	73.868	74.047

to show that these give the largest deviations from the dead-times calculated using six alkanes. The results using any three higher alkanes give even larger deviations. This shows that at least four alkanes must be used.

Comparison of the other dead-times for the 0.1-sec sampling rate with the TCD (runs 1–18) shows that the results of the lower four and lower five alkanes are very similar to those for six alkanes with an average difference of less than 0.1 sec. The dead-times for the upper four and five alkanes show larger deviations.

Comparison of the dead-times for the 0.5-sec sampling rate (runs 19–46) shows that the lower five alkanes give very similar results to those using six alkanes. The lower four alkanes give slightly larger deviations with the average deviation being approximately half the sampling rate. The higher alkanes again give larger deviations.

These results show that four alkanes can be used to give accurate estimates of the dead-time as long as a high sampling rate and the lower alkanes are used.

The dead-times calculated from six alkanes by the method of Grobler and Bálizs are compared with the retention times of air and methane in Table V. In all cases the dead-time calculated by the method of Grobler and Bálizs is less than the retention time of either air or methane. This is to be expected because air and methane must be retarded to some extent because they will be absorbed by the stationary phase used. An estimation of the errors in retention values due to sorption have been made by Ezrets and Vigdergauz[6]. Table V also shows that the retention times for methane is almost always greater than for air. The standard deviations show that the value using six alkanes is more reproducible than using either methane or air. Therefore, for high accuracy dead-times should be calculated by some mathematical method rather than using methane, air or some other substance which is only slightly retarded.

TABLE V

COMPARISON OF RETENTION TIMES OF METHANE AND AIR WITH MATHEMATICAL DEAD-TIME USING THE METHOD OF REF. 2

Run	Dead-time (sec)		
	Grobler and Bálizs	Air	Methane
1	53.74	54.00	54.8
3	54.66	54.95	55.0
4	54.98	55.7	56.85
5	54.68	55.8	55.85
6	54.28	55.2	55.0
7	53.63	54.95	55.45
8	53.78	54.90	55.0
9	54.26	54.85	55.05
11	54.15	54.3	55.35
12	53.55	54.6	55.55
13	53.84	54.6	54.8
14	53.23	54.9	54.95
15	53.96	54.6	56.85
16	53.57	55.7	55.8
17	53.91	56.65	56.55
18	53.89	55.35	55.5
Mean	54.01	55.07	55.52
Standard deviation	0.4695	0.6559	0.6935

CONCLUSIONS

It has been shown that the method of Grobler and Bálizs for calculating dead-time is as accurate as more complex iterative methods and is more appropriate for on-line analysis.

Using a judicious selection of alkanes, it has been shown that four alkanes are as accurate as using a larger number although more than four alkanes should be used when either higher alkanes are used or the sampling rate is insufficiently accurate.

Finally it has been shown that the use of the retention times of methane or air introduces inaccuracies and should be avoided if accurate dead-times are required.

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