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## COMPARISON OF INTERPOLATION METHODS FOR THE INTERPRETATION OF RETENTION DATA IN GAS CHROMATOGRAPHY

L. SOJÁK

*Institute of Chemistry, Comenius University, Bratislava (Czechoslovakia)*

and

M. S. VIGDERGAUZ

*Institute of Organic and Physical Chemistry, Academy of Sciences of the U.S.S.R., Kazan (U.S.S.R.)*

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### SUMMARY

On the basis of high-precision measurements of the retention times of alkylbenzenes, the accuracies of the determinations of linear and logarithmic retention indices were compared, and the correlation between the structure and the retention of isomers of these two interpolation characteristics was investigated. The linear retention index can be measured more accurately than the logarithmic value. Fine correlations between structure and retention are different for the two types of retention indices; logarithmic retention indices are more suitable for these correlations.

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### INTRODUCTION

Retention quantities can be divided into absolute, relative and interpolation types<sup>1</sup>. Interpolation characteristics enable one to determine the elution moment of the maximum sorbate zone in the range of elution moments of the maximum zones of two standards. The most widespread is the logarithmic shape of the interpolation elution characteristics with standards created by two neighbouring *n*-alkanes, *z* and *z*+1, introduced by Kováts<sup>2</sup> as the retention index, *I*. Vigdergauz<sup>3</sup> suggested a linear shape for the interpolation characteristics, *i.e.*, the linear retention index, *J*. The analogous function (multiplied by 100) under the name of the arithmetical retention index was recommended by Harbourn<sup>4</sup>.

The linear retention index calculated on the basis of the measured retention times of the sorbate *x* ( $t_{R_x}$ ) and *n*-alkanes with *z* and *z*+1 carbon atoms in the molecules ( $t_{R_z}$ ,  $t_{R_{z+1}}$ ), or by measuring the respective distances between the ordinates of the maxima of peaks on the chromatogram [ $\Delta I_{(x,z)}$  and  $\Delta I_{(z+1,z)}$ ]:

$$J = \frac{t_{R_x} - t_{R_z}}{t_{R_{z+1}} - t_{R_z}} + z = \frac{\Delta I_{(x,z)}}{\Delta I_{(z+1,z)}} + z$$

The analytical relationship between the quantities  $J$  and  $I$  has the following form<sup>5</sup>:

$$J = \frac{\sigma^{\delta I/100} - 1}{\sigma - 1}$$

where

$$\sigma = \frac{t'_{R_{z+1}}}{t'_{R_z}} = \frac{t_{R_{z+1}} - t_{R_z}}{t_{R_z} - t_{R_{z-1}}}$$

and

$$\delta I = I - 100z$$

Hence the difference between the values  $100J$  and  $I$  depends on the value of the coefficient  $\sigma$ , *i.e.*, on the selectivity of the sorbent for a homologous series of  $n$ -alkanes with  $I \geq 100J$ . The value of  $\sigma$  varies between 1.4 and 3.4 for commonly used liquid phases, with the higher values corresponding to non-polar phases and room temperature<sup>1</sup>. The maximum of the difference  $I - 100J$  within this range, which corresponds to  $\delta I = 50-60$ , increases from 4.2 to 15.0 units. For squalane the maximum of the difference  $I - 100J$  increases from 8 to 16 units when the temperature is decreased from  $100^\circ$  to  $0^\circ$  and for polypropylene glycol from 7 to 14 units<sup>6</sup>.

A survey of the use of linear retention indices for describing separations in gas chromatography was published by Vigdergauz<sup>1</sup>. In comparison with logarithmic retention indices, for determining the values of linear retention indices there is no need for logarithmic calculations or the determination of the elution time of the non-sorbing gas ( $t_0$ ). Apart from the simple determination involved, the linear retention index also fulfils some of the other requirements of retention characteristics, for example the quantity  $J$  can be expressed with the help of the separation and activity coefficients of the sorbate and standards under consideration<sup>1</sup>.

The possibility of correlations with the structure of compounds being analysed is a significant feature of the logarithmic retention index. With linear retention indices these relationships have not yet been studied, even if the validity of such relationships is assumed. This paper is devoted to a comparison of the accuracies of the determinations of linear and logarithmic retention indices on the basis of high-precision measurements of the retention times of alkylbenzenes, and to a comparison of fine correlations between the structures and retentions of alkylbenzene isomers using these two interpolation characteristics.

## EXPERIMENTAL

Forty-seven aromatic hydrocarbons were studied by capillary gas chromatography: benzene and  $C_7-C_{15}$  alkylbenzenes on three stationary phases of different polarity [squalane (SQ), acetyltributyl citrate (ATC) and 1,2,3-tris(cyanoethoxy)propane (TCEP)] at two temperatures. A device securing a high accuracy of measurement was used for measuring retention times<sup>7</sup>. For the calculation of  $J$  values the same

TABLE I

LINEAR RETENTION INDICES OF ALKYL BENZENES ON SQUALANE, ACETYLTRI-BUTYL CITRATE AND 1,2,3-TRIS(CYANOETHOXY)PROPANE

Carrier gas: for SQ, 4.0 atm hydrogen; for ATC, 1.0 atm nitrogen; for TCEP, 1.0 atm nitrogen.

Compound	Squalane		Acetyltributyl citrate		1,2,3-Tris(cyanoethoxy)propane	
	$J_{80.8}$	$J_{95.4}$	$J_{81.5}$	$J_{95.2}$	$J_{84.7}$	$J_{94.2}$
Benzene	6.3459	6.3849	7.7450	7.7834	11.309	11.497
Toluene	7.4163	7.4581	8.7711	8.8098	12.230	12.411
Ethylbenzene	8.3213	8.3634	9.6622	9.7046	12.998	13.159
1,4-Xylene	8.4576	8.5025	9.7458	9.7842	13.091	13.266
1,3-Xylene	8.4788	8.5231	9.7893	9.8295	13.117	13.267
1,2-Xylene	8.6980	8.7548	10.0794	10.1093	13.624	13.894
Isopropylbenzene	9.0078	9.0344	10.2495	10.2803	13.235	13.425
<i>n</i> -Propylbenzene	9.2195	9.2595	10.5148	10.5564	13.531	13.771
1-Methyl-3-ethylbenzene	9.3353	9.3753	10.6282	10.6654	13.764	14.008
1-Methyl-4-ethylbenzene	9.3561	9.4001	10.6336	10.6720	13.781	14.029
1-Methyl-2-ethylbenzene	9.4842	9.5348	10.8961	10.9474	14.209	14.421
1,3,5-Trimethylbenzene	9.5314	9.5762	10.7954	10.8349	13.975	14.150
<i>tert</i> -Butylbenzene	9.5796	9.6345	10.9978	11.0223	13.782	14.024
1,2,4-Trimethylbenzene	9.7286	9.7865	11.0542	11.0817	14.393	14.625
Isobutylbenzene	9.7627	9.8233	11.0635	11.0906	13.676	13.936
<i>sec</i> -Butylbenzene	9.7724	9.8343	11.0882	11.1181	13.775	14.012
1-Methyl-3-isopropylbenzene	9.9650	10.0049	11.1855	11.2104	14.046	14.206
1,2,3-Trimethylbenzene	10.0306	10.0658	11.3234	11.3695	15.041	15.248
1-Methyl-4-isopropylbenzene	10.0311	10.0587	11.2257	11.2571	14.100	14.272
1-Methyl-2-isopropylbenzene	10.0723	10.1024	11.3649	11.4003	14.426	14.652
1,3-Diethylbenzene	10.1669	10.1996	11.4251	11.4589	14.317	14.523
1-Methyl-3-propylbenzene	10.2040	10.2395	11.4470	11.4834	14.289	14.498
<i>n</i> -Butylbenzene	10.2172	10.2577	11.5164	11.5593	14.349	14.554
1,2-Diethylbenzene	10.2468	10.2888	11.5931	11.6383	14.706	14.991
1-Methyl-4-propylbenzene	10.2477	10.2887	11.4825	11.5242	14.338	14.552
1,4-Diethylbenzene	10.2538	10.2954	11.5182	11.5604	14.424	14.656
1-Methyl-2-propylbenzene	10.3024	10.3491	11.6448	11.6927	14.737	15.005
1,3-Dimethyl-5-ethylbenzene	10.3388	10.3756	11.5867	11.6216	14.506	14.746
1,4-Dimethyl-2-ethylbenzene	10.4438	10.4900	11.7774	11.8211	14.980	15.164
1-Methyl-3- <i>tert</i> -butylbenzene	10.4735	10.5156	11.8143	11.8499	14.468	14.684
1,3-Dimethyl-4-ethylbenzene	10.5075	10.5584	11.8489	11.8985	15.036	15.226
2-Phenyl-2-methylbutane	10.5270	10.5934	11.9060	11.9687	14.407	14.635
1,2-Dimethyl-4-ethylbenzene	10.5566	10.6097	11.9222	11.9723	15.085	15.289
1,3-Dimethyl-2-ethylbenzene	10.5573	10.6142	12.0144	12.0436	15.324	15.577
1-Methyl-4- <i>tert</i> -butylbenzene	10.6029	10.6586	11.9404	11.9911	14.584	14.826
2-Phenylpentane	10.6320	10.6870	12.0052	12.0321	14.506	14.751
1,2-Dimethyl-3-ethylbenzene	10.7427	10.8083	12.1297	12.1661	15.487	15.729
1,2,4,5-Tetramethylbenzene	10.9969	11.0324	12.2222	12.2633	15.646	15.780
1,2,3,5-Tetramethylbenzene	11.0352	11.0714	12.2790	12.3227	15.724	15.964
1,3-Diisopropylbenzene	11.1034	11.1300	12.3296	12.3527	14.611	14.805
<i>n</i> -Pentylbenzene	11.1893	11.2288	12.4917	12.5325	15.133	15.332
1,2,3,4-Tetramethylbenzene	11.2111	11.2653	12.5823	12.6452	16.264	16.550
1,3-Dimethyl-5- <i>tert</i> -butylbenzene	11.3708	11.4010	12.6492	12.6733	15.176	15.385
1,4-Diisopropylbenzene	11.3876	11.4301	12.6697	12.7071	15.030	15.187
1,3,5-Triethylbenzene	11.8392	11.8750	13.1026	13.1183	15.498	16.016
Pentamethylbenzene	12.4143	12.4897	13.8709	13.9519	17.469	17.871
1,3,5-Triisopropylbenzene	12.7650	12.7737	14.0365	14.0359	15.550	15.698

values of  $t_R$  were used as were used for the  $I$  values that were used for comparison<sup>8</sup>. The calculated values of the linear retention indices of alkylbenzenes on SQ at 80.8° and 95.4°, on ATC at 81.5° and 95.2° and on TCEP at 84.7° and 94.2° are shown in Table I.

## RESULTS AND DISCUSSION

### *Accuracy of measurement of linear and logarithmic retention indices*

The standard deviations for linear and logarithmic retention indices of alkylbenzenes on SQ, ATC, TCEP are compared in Table II.

TABLE II

COMPARISON OF MEAN STANDARD DEVIATIONS OF LINEAR AND LOGARITHMIC RETENTION INDICES ON SQUALANE, ACETYLTRIBUTYL CITRATE AND 1,2,3-TRIS(CYANOETHOXY)PROPANE

<i>Squalane</i>		<i>Acetyltributyl citrate</i>				<i>1,2,3-Tris(cyanoethoxy)propane</i>					
80.8°		95.4°		81.5°		95.2°		84.7°		94.2 °C	
<i>I</i>	100 <i>J</i>	<i>I</i>	100 <i>J</i>	<i>I</i>	100 <i>J</i>	<i>I</i>	100 <i>J</i>	<i>I</i>	100 <i>J</i>	<i>I</i>	100 <i>J</i>
0.03	0.03	0.03	0.03	0.09	0.06	0.05	0.04	0.22	0.13	0.21	0.12

The standard deviations of the values of 100  $J$  and  $I$  were identical (*ca.* 0.03) for the most accurate measurements on squalane. On ATC and especially on TCEP the standard deviations of  $J$  were significantly smaller. The differences in the accuracies of the values of  $J$  and  $I$  are due to the fact that errors caused by the inaccuracy of the determination of  $t_0$  do not affect  $J$ . Further, when determining  $J$ , errors arising from errors in the determination of the differences  $t_{R_x} - t_{R_z}$  and  $t_{R_{x+1}} - t_{R_z}$  are less dependent on the fluctuations in the operating conditions in the range from injection to  $t_{R_z}$  than when determining  $I$ . In this connection, a significant influence of column ageing on the accuracy of  $I$  was found on ATC and especially on TCEP, *e.g.*, the retention indices of alkylbenzenes on TCEP decreased by 0.3 unit in 1 day<sup>8</sup>.

It follows from the comparison of the accuracies of the linear and logarithmic retention indices that the former can be measured more accurately than (or at least as accurately as) the latter.

### *Correlations between structure and retention indices*

A number of dependences between the structures of alkylbenzenes and their retentions expressed as logarithmic retention index have been demonstrated previously<sup>9-11</sup>. Our aim was to establish correlations between values of  $\Delta J$  and  $dJ/dT$  and the structures of alkylbenzenes using linear retention indices.

*Difference in retention indices on two stationary phases.* Semencenko *et al.*<sup>12</sup>, by correlating the differences in the linear indices of oxygen-containing compounds on polyethylene glycol 6000 (PEG) and Apiezon L (APL) ( $\Delta J = J^{\text{PEG}} - J^{\text{APL}}$ ), and  $J^{\text{APL}}$  achieved the group identification of esters, acids, peroxides and primary, secondary and tertiary alcohols, in a similar manner to results with logarithmic retention indices. The identification of isomers on the basis of such dependences is usually difficult. However, through correlations between accurate values of  $\Delta I$  and the structures of alkylbenzene

isomers, characteristic dependences have been found<sup>11</sup>. These dependences have not been confirmed by comparing the corresponding correlations of  $\Delta J$  values on SQ, ATC, TCEP for mono-, di-, tri-, tetra- and pentaalkylbenzenes, not only for the corresponding differences in the separate values of  $\delta(\Delta J)$  or  $\delta(\Delta I)$ , but sometimes also for the characteristic sequence of their quantities for the respective positional and configurational isomers. For example, it can be seen from Table III that the values of  $\Delta I$  for trialkylbenzenes increase in the order 1,3,5- < 1,2,4- < 1,2,3-trialkylbenzenes; the values of  $\Delta J_1 = J^{\text{ATC}} - J^{\text{SQ}}$ , however, increase in the order 1,3,5- < 1,2,3- < 1,2,4-trimethylbenzene. Similar differences can be seen from Table III for other alkylbenzenes.

TABLE III

COMPARISON OF DIFFERENCES IN RETENTION INDICES,  $\Delta J$  AND  $\Delta I$  VALUES, AND STRUCTURES OF ALKYL BENZENES AT 80°

$$\Delta J_1 = J^{\text{ATC}} - J^{\text{SQ}}; \Delta I_1 = I^{\text{ATC}} - I^{\text{SQ}}; \Delta J_2 = J^{\text{TCEP}} - J^{\text{SQ}}; \Delta I_2 = I^{\text{TCEP}} - I^{\text{SQ}}$$

Alkylbenzene	100 $\Delta J_1$	$\Delta I_1$	100 $\Delta J_2$	$\Delta I_2$
1,3,5-Trimethylbenzene	126.2	121.8	436.0	425.2
1,2,4-Trimethylbenzene	132.6	127.7	455.3	455.8
1,2,3-Trimethylbenzene	129.0	136.3	490.9	488.8
1,3-Dimethyl-5-ethylbenzene	124.6	123.4	405.1	404.3
1,3-Dimethyl-4-ethylbenzene	133.9	128.1	443.8	432.3
1,4-Dimethyl-2-ethylbenzene	133.2	128.7	444.8	432.6
1,2-Dimethyl-4-ethylbenzene	136.3	129.1	443.0	434.4
1,2-Dimethyl-3-ethylbenzene	138.7	136.7	462.8	462.7
1,3-Dimethyl-2-ethylbenzene	145.7	136.8	464.5	462.0
1,3,5-Trimethylbenzene	126.2	121.8	436.0	425.2
1,3,5-Triisopropylbenzene	127.2	123.4	271.3	273.2
1,3,5-Triethylbenzene	126.4	126.0	340.4	358.7
1,3,5-Trimethylbenzene	126.2	121.8	436.0	425.2
1,3-Dimethylbenzene	130.9	126.2	456.7	446.3
Methylbenzene	135.3	130.9	472.6	476.4
1,3,5-Triethylbenzene	126.4	126.0	340.4	358.7
1,3-Diethylbenzene	125.6	128.2	404.9	405.2
Ethylbenzene	133.9	132.0	460.0	448.2
1,3,5-Triisopropylbenzene	127.2	123.4	271.3	273.2
1,3-Diisopropylbenzene	122.5	126.3	341.3	343.7
Isopropylbenzene	124.0	131.4	413.5	418.5

Fig. 1 shows the dependence of the difference in the values of  $I_{80.8}^{\text{SQ}} - 100J_{80.8}^{\text{SQ}}$  on  $I_{80}^{\text{SQ}}$  for alkylbenzenes. It can be seen that this difference increases from zero for an alkylbenzene eluted with an *n*-alkane *z* up to a maximum value of 10.2 units corresponding to an alkylbenzene with a retention index  $I = 100z + 50$ , then it decreases to zero for an alkylbenzene eluted with an *n*-alkane *z*+1. Hence the smallest values of *J* compared with *I* are shown by alkylbenzenes eluted in the middle between neighbouring *n*-alkanes. Similar dependences were determined on SQ even at a temperature of 95.4° as well as on ATC and TCEP at both temperatures. Fig. 2 shows the dependence of the value of the difference  $I - 100J$  on the values of *I* on SQ, ATC and TCEP at two temperatures. It can be seen that  $I - 100J$  increases with decreasing

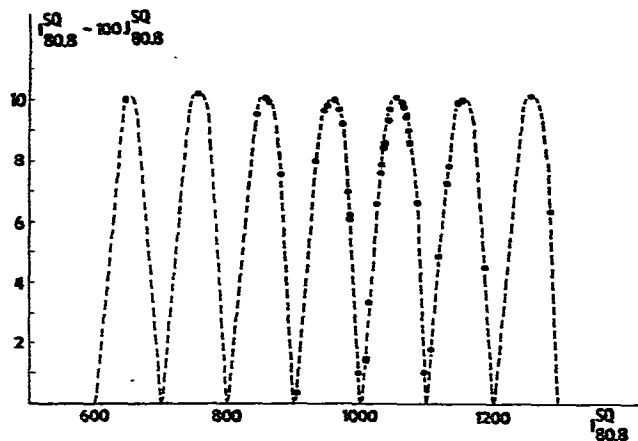


Fig. 1. Dependence of the difference  $I_{80.8}^{SQ} - 100 J_{80.8}^{SQ}$  on  $I_{80.8}^{SQ}$  for alkylbenzenes.

polarity of the stationary phase in the series TCEP > ATC > SQ and with decreasing column temperature.

It follows from the above results that the deviations in correlations of the values of  $\Delta J$  and  $\Delta I$  are the greater the nearer to the middle of the  $n$ -alkanes  $z$  and  $z+1$  the given sorbate is eluted, the less polar is the stationary phase and the lower is the temperature.

*Temperature increments of retention indices.* The dependences between the linear and logarithmic retention indices and the column temperature were studied by Saha and Mitra<sup>6</sup>. It follows from their results<sup>1</sup> that the dependence between  $J$  and column temperature can be approximated by a straight line, in a similar manner to the temperature dependence of  $I$ , and that the slope  $d(100J)/dT$  is usually greater than  $dI/dJ$ . It is assumed that the values of  $dJ/dT$  are specific for materials of a certain structure in the same way as the values of  $dI/dT$ , which means that they can be used for purposes of identification with the same results.

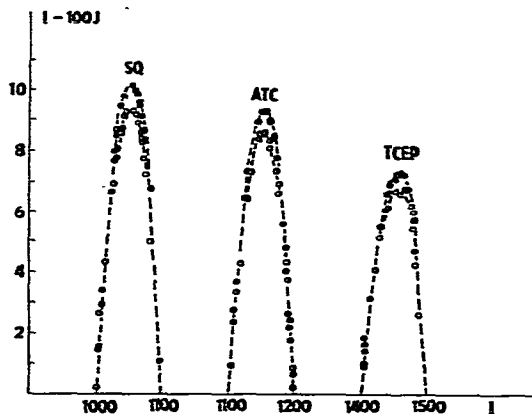


Fig. 2. Dependence of the difference  $I - 100J$  on  $I$  for squalane (SQ), acetyltributyl citrate (ATC) and 1,2,3-tris(cyanoethoxy)propane (TCEP) at two temperatures. SQ: ●, 80.8°; ○, 95.4°. ATC: ●, 81.5°; ○, 95.2°. TCEP: ●, 84.7°; ○, 94.2°.

The temperature increments of the retention indices ( $dI/dT$ ) of the alkylbenzenes reflect the fine structural differences of isomers<sup>10</sup>. These correlations were not confirmed for values of  $dJ/dT$ . Table IV compares the values of  $100 dJ/dT$  and  $dI/dT$  with the structures of trialkylbenzenes. It can be seen that the orders of the  $dI/dT$  values for the positional isomers of trialkylbenzenes on all three stationary phases are identical: 1,3,5- < 1,2,4- < 1,2,3-trialkylbenzenes. For the values of  $dJ/dT$  on SQ, however, there is the following sequence: 1,2,3- < 1,3,5- < 1,2,4-trimethylbenzene, on ATC 1,2,4- < 1,3,5- < 1,2,3- and on TCEP 1,3,5- < 1,2,3- < 1,2,4-trimethylbenzene. Similar differences in the values of  $100 dJ/dT$  and  $dI/dT$  can also be seen in Table IV for some other alkylbenzenes.

TABLE IV

COMPARISON OF TEMPERATURE INCREMENTS,  $100 dJ/dT$  AND  $dI/dT$  VALUES, AND STRUCTURES OF ALKYL BENZENES ON SQUALANE, ACETYLTRIBUTYL CITRATE AND 1,2,3-TRIS(CYANOETHOXY)PROPANE

Alkylbenzene	SQ		ATC		TCEP	
	$100 dJ/dT$	$dI/dT$	$100 dJ/dT$	$dI/dT$	$100 dJ/dT$	$dI/dT$
1,3,5-Trimethylbenzene	0.310	0.239	0.290	0.206	1.83	2.20
1,2,4-Trimethylbenzene	0.400	0.288	0.200	0.264	2.44	2.38
1,2,3-Trimethylbenzene	0.240	0.337	0.340	0.312	2.20	2.65
1,3-Dimethyl-5-ethylbenzene	0.250	0.218	0.250	0.182	2.53	2.18
1,4-Dimethyl-2-ethylbenzene	0.320	0.260	0.320	0.229	1.94	2.32
1,3-Dimethyl-4-ethylbenzene	0.350	0.281	0.360	0.249	2.00	2.46
1,2-Dimethyl-4-ethylbenzene	0.360	0.286	0.370	0.253	2.15	2.49
1,3-Dimethyl-2-ethylbenzene	0.400	0.309	0.210	0.287	2.66	2.63
1,2-Dimethyl-3-ethylbenzene	0.450	0.329	0.270	0.303	2.55	2.73
1,3,5-Triisopropylbenzene	0.060	0.015	0.040	-0.074	1.55	1.28
1,3,5-Triethylbenzene	0.250	0.167	0.110	0.117		2.20
1,3,5-Trimethylbenzene	0.310	0.239	0.290	0.206	1.83	2.20
1,3,5-Trimethylbenzene	0.310	0.239	0.290	0.206	1.83	2.20
1,3-Dimethylbenzene	0.300	0.245	0.290	0.213	1.58	2.07
Methylbenzene	0.290	0.245	0.280	0.213	1.91	2.03
1,3,5-Triethylbenzene	0.250	0.167	0.110	0.117		2.20
1,3-Diethylbenzene	0.220	0.244	0.250	0.201	2.20	2.19
Ethylbenzene	0.290	0.265	0.310	0.225	1.69	2.14
1,3,5-Triisopropylbenzene	0.060	0.015	0.040	-0.074	1.55	1.28
1,3-Diisopropylbenzene	0.180	0.195	0.170	0.137	2.04	1.94
Isopropylbenzene	0.180	0.264	0.220	0.214	2.00	2.11

Fig. 3 shows the dependence of the difference  $dI^{SQ}/dT - 100 dJ^{SQ}/dT$  on  $I_{80.8}^{SQ}$  for alkylbenzenes. It can be seen that this difference gradually changes with increasing retention of alkylbenzenes between the alkanes  $z$  and  $z+1$  from positive to negative values. Alkylbenzenes eluted immediately after  $n$ -alkane  $z$  have the greatest positive values of difference (the values of  $100 dJ/dT$  are significantly lower than  $dI/dT$ ). Alkylbenzenes eluted immediately before  $n$ -alkane  $z+1$  have the greatest negative values of the difference (the values of  $100 dJ/dT$  are significantly higher than  $dI/dT$ ). Alkylbenzenes with a retention index  $I_{80.8}^{SQ} \approx 100z + 40$  have  $d(100 dJ)/dT \approx dI/dT$ . A similar course of the dependence of the difference  $dI/dT - 100 dJ/dT$  on

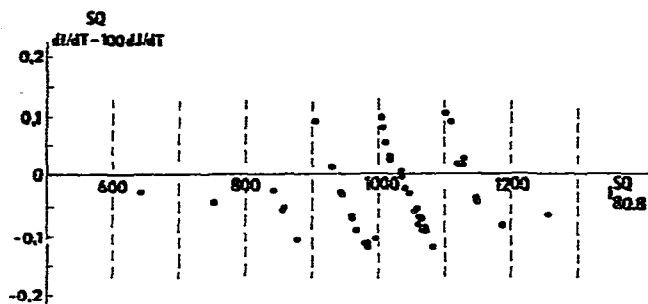


Fig. 3. Dependence of the difference  $dI^{SQ}/dT - 100 dJ^{SQ}/dT$  on  $I^{SQ}_{80.8}$  for alkylbenzenes.

$I$  was determined on SQ also for a temperature of  $95.2^\circ$  and was also confirmed on ATC and TCEP at both temperatures. On TCEP, on which the temperature increments of the retention indices are an order of magnitude higher than on ATC and SQ, at  $94.2^\circ$ ,  $100 dJ/dT \approx dI/dT$  for alkylbenzenes with  $I^{TCEP}_{94.2} \approx 100z + 60$ .

The dependences of the difference  $dI/dT - 100 dJ/dT$  on  $I$  show that the correlations found between structure and  $dI/dT$  are not valid for values of  $100 dJ/dT$ , because the dependence of the positions of the peak maxima between neighbouring  $n$ -alkanes also has to be considered. Deviations between the correlations of structure and temperature increments for linear and logarithmic retention indices are the greater the closer the analysed compounds are eluted to the  $n$ -alkane  $z$  or  $z+1$ .

The correlation found between structure and the pressure variation coefficients of retention indices  $(dI/dP)^{10}$  for alkylbenzenes on TCEP, could not be confirmed for values of  $dJ/dP$  owing to the dependence of  $J$  on the positions of the peak maxima between the  $n$ -alkanes  $z$  and  $z+1$ . For examples, the values of  $dI/dP$  are less for 1,4- than for 1,2-alkylbenzenes, but  $dJ/dP$  for 1-methyl-4-ethylbenzene is greater than that for 1-methyl-2-ethylbenzene.

## CONCLUSION

The relationship between linear retention indices and the structures of alkylbenzenes was studied on three stationary phases at two temperatures under the conditions of high-efficiency and high-precision capillary gas chromatography. The results were compared with those published previously for logarithmic retention indices. It was found that under identical experimental conditions, the linear retention index can be measured more accurately than the logarithmic value. Fine correlations between the structures of alkylbenzenes and values of the temperature increments of the retention indices, and also the differences in the retention indices on two stationary phases, show that the differences in these dependences are different for the linear and logarithmic retention indices. These differences are due to the fact that for structural correlations of linear retention indices the dependence of the positions of the peak maxima of the sorbate between two neighbouring  $n$ -alkanes must also be considered. As the relationships between structure and linear retention indices are more complicated than those of logarithmic retention indices, the latter interpolation characteristics are more suitable when using the correlation between structure and retention behaviour as a means of identification.



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