REPRODUCIBILITY OF INTERPOLATED VALUES FOR CHROMATOGRAPHIC RETENTION

V. A. Dubrovina and M. S. Vigdergauz

UDC 543.544

In quantitative chromatographic analysis, the basic quantities are the interpolated retention values, among which we may class the logarithmic Kovats index I [1] and the linear index I [2].* The latter parameter has a number of advantages, in terms of simplicity of determination, its relationships to distribution coefficients and activity of sorbates in a stationary liquid solution, etc. [3]. In this connection, it is of interest to compare the reproducibility of the indicated interpolation functions. Such work was reported in [4] in application to data obtained in precision equipment.

In our studies of the applicability of the logarithmic and linear retention indices for C_6-C_{15} aromatic hydrocarbons, we used a regular-production Tsvet analytical chromatograph (Model 122) with a flame ionization detector. The temperature was held within ±0.15°C, and the flow rate of carrier gas (nitrogen) within ±0.02 cm^3/min. In this work we used packed columns with a length of 3 m and an inside diameter of 3 mm, and capillary columns with a length of 45 m and an inside diameter of 0.25 mm. A total of 43 aromatic hydrocarbons were analyzed. The stationary phases were squalane (SQU), acetyl tributyl citrate (ATC), dinonyl phthalate (DNP), Apiezon L (ApL), polyethylene glycol 3000 (PEG-3000), and a eutectic mixture of liquid crystals, i.e., azoxyanisole and azoxyphenetole (LC). The liquid phases (10%) were deposited on Chromosorb P.

Values were calculated for the linear and logarithmic retention indices on squalane at 120 and 130°C; on ATC at 95, 120, and 130°C; on Apiezon L at 140, 150, and 180°C, on the liquid crystals at 120 and 140°C, on DNP at 120 and 140°C, and on PEG-3000 at 120 and 130°C. In Table 1 we have listed the standard deviations of results obtained in the determination of linear and logarithmic retention indices. From a comparison of these values it can be seen that the error in determining the linear retention index is no greater, or possibly even smaller, than that in determining the logarithmic retention index. These slightly smaller errors are observed even with the use of the standard analytical instrument. The chromatographic identification of components in mixtures being analyzed is often based on graphical or analytical relationships between the retention values and such characteristics as the boiling point, number of carbon atoms in the molecule, vapor pressure, etc. For this purpose we may use the linear retention index. The logarithm of the vapor pressure of isomeric hydrocarbons at the column temperature is essentially a linear function of either the logarithmic or

* As in Russian original – Translator.

TABLE 1. Data on Standard Deviations for Values of 100J and I

Compound	Squalane at 120°C		ATC at 95°C		LC 130°C at 130°C		DNP 120°C at 120°C	
	100J	I	100J	I	100J	I	100J	I
Ethylbenzene	0,49	0,50	0,55	0,61	0,59	0,61	0,59	0,60
Isopropylbenzene	0,38	0,36	0,56	0,59	0,53	0,56	0,46	0,52
1,3-Diisopropylbenzene	0,31	0,32	0,46	0,46	0,75	0,77	0,19	0,21
1,4-Diisopropylbenzene	0,30	0,29	0,63	0,66	0,49	0,52	0,56	0,58
1,3,5-Triethylbenzene	0,43	0,44	0,75	0,77	0,56	0,59	0,59	0,60
1,3,5-Triisopropylbenzene	0,42	0,43	—	—	0,73	0,74	0,45	0,46
1,1-Diphenylethane	0,45	0,46	—	—	0,60	0,61	0,59	0,62

Kuibyshev Polytechnic Institute. Translated from Khimiya i Tekhnologiya Topliv i Masel, No. 11, pp. 56-58, November, 1979.

0009-3092/79/1112-0851 $07.50

TABLE 2. Data on $\Delta J_1 = (J^{DNP} - J^{SQU})$ and AI_1, and on $\Delta J_2 = (J^{ATC} - J^{SQU})$ and ΔI_2

Compound	$100\Delta J_1$	ΔI_1	$100\Delta J_2$	ΔI_2
Toluene	87,72	90,14	128,31	129,97
Ethylbenzene	88,20	87,61	135,13	128,42
Isopropylbenzene	87,20	88,60	125,39	127,93
1,3-Dimethylbenzene	86,30	87,30	126,23	127,77
1,3-Diethylbenzene	80,01	87,52	117,87	117,54
1,3,5-Trimethylbenzene	85,10	86,10	124,74	122,20
1,2,4-Trimethylbenzene	88,90	91,22	126,36	126,98
1,3-Diisopropylbenzene	73,51	67,36	117,32	111,46
1,3,5-Triethylbenzene	73,08	83,06	119,10	121,45
1,3,5-Triisopropylbenzene	87,67	89,51	127,10	122,76

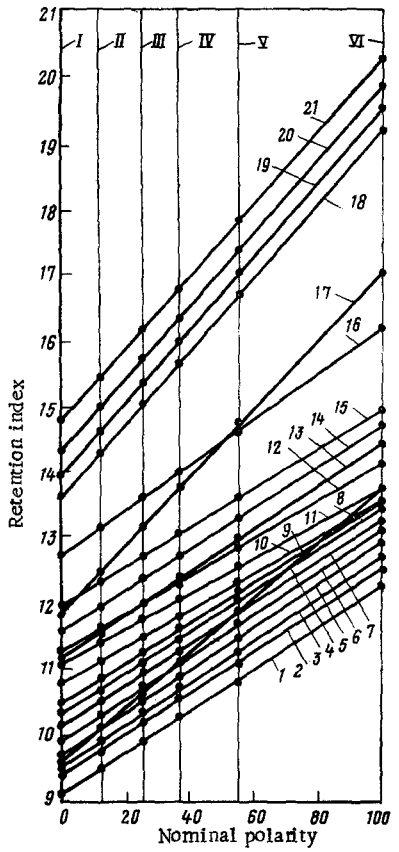

Fig. 1. Generalized relationship between linear retention index I of hydrocarbons and nominal polarity P of stationary phase: I) squalane, 130°C; II) Apiezon L, 140°C; III) dinonyl phthalate, 130°C; IV) Citroflex A-4, 130°C; V) eutectic mixture of liquid crystals of azoxyphenetole and azoxyanisole, 120°C; VI) PEG-3000, 130°C; 1) isopropylbenzene; 2) n-propylbenzene; 3) m-ethyltoluene; 4) styrene; 5) 1,3,5-trimethylbenzene; 6) 1,2,4-trimethylbenzene; 7) 1,4-methylisopropylbenzene; 8) 1,3-diethylbenzene; 9) 1,4-diethylbenzene; 10) 1,3-ethylisopropylbenzene; 11) 1,4-ethylisopropylbenzene; 12) 1,3-diisopropylbenzene; 13) 1,2,4,5-tetramethylbenzene; 14) 1,4-diisopropylbenzene; 15) 1,3,5-triethylbenzene; 16) n-hexylbenzene; 17) naphthalene; 18) biphenyl; 19) diphenylmethane; 20) 1,1-diphenylethane; 21) 1,2-diphenylethane.

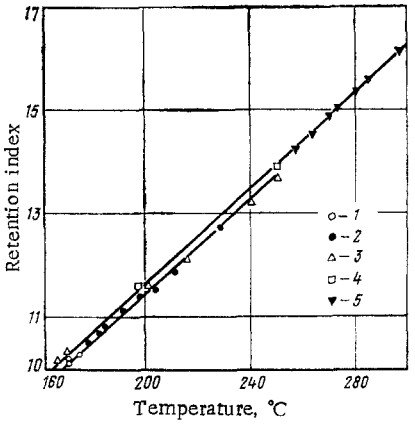

Fig. 2

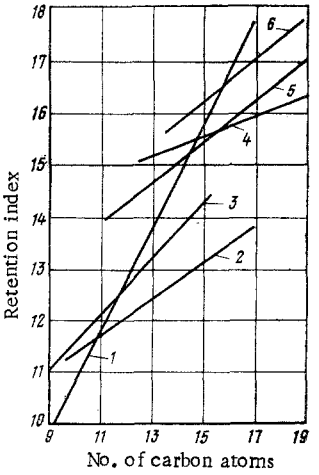

Fig. 3

Fig. 2. Linear retention index as a function of boiling point of aromatic hydrocarbons (Apiezon L, 140°C): 1) n-alkylbenzenes; 2) dialkylbenzenes; 3) trialkylbenzenes; 4) tetraalkylbenzenes; 5) diphenylalkanes and diphenylalkylalkanes.

Fig. 3. Linear retention index of aromatic hydrocarbons as a function of number of carbon atoms in molecule (Apiezon L, 140°C): 1) n-alkylbenzenes; 2) 1,3,5-trialkylbenzenes; 3) 1,2,4,5-tetraalkylbenzenes; 4) 1,2-diphenylethane and other 1,2-diphenylalkanes; 5) 1,1-diphenylalkanes; 6) 1,3-diphenyl-2-alkylalkanes.

the linear retention index [5]. A correlation of the values of ΔI and the structure of isomeric alkylbenzenes has revealed many regular relationships [6, 7]. By a comparison of the corresponding correlations for values of ΔJ on SQU, ATC, and DNP, these relationships were fully supported in the case of the mono-, di-, and trialkylbenzenes (Table 2).

The relationship between the linear retention index and the nominal chromatographic polarity of the stationary phases (Fig. 1) was constructed by a method analogous to that described in [8] for saturated hydrocarbons. We took squalane at 130°C as the stationary phase with a zero nominal polarity, and PEG-3000 at 130°C as the stationary phase with a 100% nominal polarity.

Upon comparing the graphs used for identification of aromatic hydrocarbons, it is evident that the values of P for the stationary phases as determined on the basis of linear or logarithmic indices show very little difference. Plots of the relationship between the retention index of the hydrocarbons and the boiling point or number of carbon atoms in the molecule, which we used in identifying the hydrocarbons in a polyalkylbenzene tar, are shown in Figs. 2 and 3. Similar relationships were obtained for the logarithmic retention indices of the aromatic hydrocarbons.

Thus, we see that linear retention indices represent a simple and convenient form for the interpretation of data on chromatographic retention; these indices may be used widely, both in quantitative chromatographic analysis and in physicochemical measurements.

LITERATURE CITED

1. E. Kovats, Helv. Chim. Acta, No. 41, 1915 (1958).
2. M. S. Vigdergauz (Wigdergauz), Proceedings of Sixth Symposium on Gas Chromatography (Berlin), Akad. Verlag, Berlin (1968), p. 625.
3. M. S. Vigdergauz, Zh. Anal. Khim., 31, 2222-2235 (1978).
4. L. Sojak and M. S. Vigdergauz (Wigdergauz), J. Chromatogr., No. 148, 159 (1978).
5. N. C. Saha and C. D. Mitra, Technology (India), 8, 3 (1971).
6. L. Sojak, J. Janak, and L. A. Rijks, J. Chromatogr., 135, 71 (1977).
7. C. E. Döring, D. Estel, and R. Fischer, J. Prakt. Chem., 316, No. 1, 1-12 (1974).
8. M. S. Vigdergauz, Gas Chromatography as a Method for Investigation of Petroleum [in Russian], Nauka, Moscow (1973), p. 28.