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CAPILLARY GAS CHROMATOGRAPHY OF AROMATIC COMPOUNDS FOUND IN COAL TAR FRACTIONS*

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SUMMARY

The Kováts retention indices of a large number of alkyl derivatives of benzene and naphthalene and related compounds expected to be found in coal tar fractions were determined by capillary gas chromatography on OV-101. The influence of the calculated retention time of *n*-alkanes and the interpolation interval on the precision of the determination of the Kováts retention index has been investigated. The possibility of using the retention indices for the identification and control of the production of coal tar fractions is demonstrated.

INTRODUCTION

The Kováts retention index[1] is the most reliable parameter for chromatographic identification of chemical compounds[2]. Computerized gas chromatographic–mass spectrometric (GC–MS) methods have subsequently been developed[3–5] on the basis of tables of such retention indices. However, few Kováts retention indices have been published for coal tar components on stationary phases such as Apiezon L[6–10], various polyesters[6,9–12], methylphenylsiloxane DC-550[6], SE-52[13,14], OV-17[15,16], cyanosiloxane OV-275[15], methylsiloxane SE-30[10,17], OV-101[16] and OV-1[18]. The last phases are particularly interesting because of their extensive use and lack of column bleeding (especially for preparative GC with UV detection). The Kováts retention indices of a number of aromatic compounds found in coal tar fractions have therefore been determined by capillary gas chromatography on OV-101.

EXPERIMENTAL

The inner surface of a capillary tube was cleaned by the method of Mon *et al.*[19] in order to remove contaminants and reduce adsorption. Various solvents (3 × 10 ml) were used in the following sequence: *n*-hexane, benzene, chloroform, acetone, methanol, distilled water, concentrated nitric acid, water, concentrated ammonia, water, methanol, acetone, chloroform, benzene and *n*-pentane. The capillary was

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flushed with the aid of nitrogen at a pressure of 1 bar, and between flushings the capillary was dried at the same nitrogen pressure for about 0.5 h. Estimation of the cleaning efficiency was made by means of controlled cleaning according to Ryba[20].

Dimethylsiloxane OV-101 with a relative polarity of 6% (with respect to benzene–cyclohexane) according to Rohrschneider[21] was used for the column coating. The column was prepared by the standard dynamic method using a 7.5% solution of OV-101 in *n*-pentane and a linear pump velocity of *ca.* 2.5 mm/sec. After coating, the column was heated slowly to 60°C under a nitrogen flow and held at this temperature for 2 h. The capacity ratio for 1,3,7-trimethylnaphthalene at 140°C was 3.5 and the efficiency corresponds to 73,000 theoretical plates.

The conditions for capillary gas chromatography are given in Table I.

TABLE I
CONDITIONS OF ANALYSIS

Parameter	*Model mixtures*	*Washing oils*	*Anthracene oils*
Apparatus		Tswett-102	
Detector		Flame-ionization	
Column material		Stainless steel	
Column length (m) and internal diameter (mm)		50 × 0.3	
Stationary phase		OV-101	
Carrier gas (nitrogen) pressure (bar)		0.4	
Splitting ratio		1:130	
Column temperature (°C)	100–180	140	180
Injection port temperature (°C)	250	300	400
Scale sensitivity (mV)	2	1	1
Sample size (μl)	0.02–0.08	1.0	1.0

To determine the Kováts retention indices of alkyl derivatives of benzene and naphthalene and related compounds, special mixtures of these pure substances with *n*-alkanes were prepared so that the components were completely separated at the operating temperatures. The samples were injected with a Gazokhrom-101 1-μl microsyringe in the form of a 10% solution of 12–15 components in benzene. Methane was injected simultaneously in order to determine the gas hold-up time. The retention times were measured by a stop-watch with an accuracy of ±0.05 sec. The Kováts retention indices were calculated from the retention times according to a special program compiled for the ES-1022 computer, and were taken as the average of four determinations for each compound.

The samples of oils and some *n*-alkanes with methane were injected with a MS-10 10μl microsyringe. *n*-Octane, *n*-decane, *n*-hexadecane, *n*-heptadecane and *n*-octadecane were added to washing oil as probes, and *n*-nonane, *n*-hexadecane, *n*-heptadecane, *n*-eicosane and *n*-docosane to anthracene oils. The samples of anthracene oils were dissolved in 1,4-dioxane. The retention times and peak areas of the oil components were measured with the aid of a I-02 digitizer-computer (Experimental Design Bureau of Automatics, Moscow, U.S.S.R.).

The oil components were identified by means of the Kováts retention indices of the pure compounds and by published data[10,17,18] and confirmed by the addition of standards.

RESULTS AND DISCUSSION

The Kováts retention indices measured for the compounds investigated are shown in Tables II and III. The reproducibility was ±0.3 i.u. In Table IV, the

TABLE II

RETENTION INDICES OF ALKYLBENZENES ON OV-101 AND THEIR TEMPERATURE COEFFICIENTS

Compound	$I_{100^\circ C}$	$I_{120^\circ C}$	$I_{140^\circ C}$	$10\ (\partial I/\partial T)$
Benzene	663.6	670.7	677.8	3.55
Toluene	766.4	771.5	781.5	3.78
Ethylbenzene	858.9	864.2	870.1	2.80
m-Xylene	866.6	871.1	876.6	2.49
p-Xylene	867.7	872.5	878.3	2.65
o-Xylene	890.3	896.4	903.2	3.24
Isopropylbenzene	920.4	925.6	931.8	2.84
n-Propylbenzene	949.3	954.6	960.7	2.93
1-Methyl-3-ethylbenzene	955.9	961.3	967.0	2.78
1-Methyl-4-ethylbenzene	958.2	963.2	970.1	2.98
1-Methyl-2-ethylbenzene	974.2	978.0	986.7	3.13
1,3,5-Trimethylbenzene	963.3	967.9	973.5	2.55
1,2,4-Trimethylbenzene	988.4	994.1	1001.3	3.23
1,2,3-Trimethylbenzene	1015.9	1022.8	1031.2	3.83
tert.-Butylbenzene	987.6	993.5	1000.9	3.33
sec.-Butylbenzene	1005.7	1011.9	1019.2	3.38
n-Butylbenzene	1048.1	1053.6	1060.0	2.97
1-Methyl-3-isopropylbenzene	1011.9	1018.5	1024.3	3.10
1-Methyl-4-isopropylbenzene	1017.8	1022.9	1028.5	2.68
1-Methyl-2-isopropylbenzene	1032.3	1038.4	1044.9	3.15
1-Methyl-3-*n*-propylbenzene	1043.4	1048.2	1054.4	2.90
1-Methyl-4-*n*-propylbenzene	1047.5	1052.6	1057.7	2.54
1-Methyl-2-*n*-propylbenzene	1059.0	1065.4	1072.9	3.48
1,3-Diethylbenzene	1040.4	1045.3	1050.7	2.58
1,4-Diethylbenzene	1047.9	1053.4	1059.3	2.85
1,2-Diethylbenzene	1052.7	1058.9	1065.9	2.85
1,2,4,5-Tetramethylbenzene	1107.2	1114.4	1121.2	3.49
1,2,3,5-Tetramethylbenzene	1110.5	1117.5	1125.0	3.63
tert.-Pentylbenzene	1085.5	1093.3	1102.4	4.48
Isopentylbenzene	1112.6	1118.6	1125.3	3.18
n-Pentylbenzene	1145.3	1150.9	1157.4	3.03
1-Methyl-4-*tert.*-butylbenzene	1084.6	1091.3	1097.3	3.17
1-Methyl-3-*n*-butylbenzene	1140.7	1145.7	1151.5	2.70
1-Methyl-4-*n*-butylbenzene	1146.1	1151.6	1158.1	3.00
1-Methyl-2-*n*-butylbenzene	1154.8	1161.2	1168.7	3.47
1-Ethyl-3-isopropylbenzene	1093.9	1098.4	1105.0	2.78
1-Ethyl-2-isopropylbenzene	1099.7	1105.7	1114.3	3.00
1-Ethyl-4-isopropylbenzene	1104.9	1110.1	1114.3	2.60
1-Ethyl-3-*n*-propylbenzene	1125.8	1130.8	1136.4	2.65
1-Ethyl-2-*n*-propylbenzene	1134.8	1140.4	1146.7	2.98
1-Ethyl-4-*n*-propylbenzene	1141.9	1146.0	1150.0	2.03

(Continued on p. 12)

TABLE II (*continued*)

Compound	$I_{100^\circ\mathrm{C}}$	$I_{120^\circ\mathrm{C}}$	$I_{140^\circ\mathrm{C}}$	$10\ (\partial I/\partial T)$
Pentamethylbenzene	1260.3	1270.4	1280.5	5.04
n-Hexylbenzene	1243.6	1249.7	1256.2	3.15
1,3-Diisopropylbenzene	1142.7	1146.8	1150.7	2.00
1,2-Diisopropylbenzene	1152.4	1157.2	1162.2	2.45
1,4-Diisopropylbenzene	1161.6	1166.7	1171.3	2.43
1,3,5-Triethylbenzene	1207.1	1211.0	1215.1	1.99
Hexamethylbenzene	1415.6	1428.2	1441.6	6.50
1,3,5-Triisopropylbenzene	1324.9	1325.7	1326.7	0.48
Styrene	885.0	890.5	897.3	3.08
α-Methylstyrene	972.5	977.4	983.1	2.65
o-Methylstyrene	987.5	993.2	1000.4	3.23
m-Methylstyrene	985.9	991.4	997.8	2.98
Allylbenzene	938.9	943.6	950.5	2.90
2,3-Dihydroindene	1027.4	1036.1	1046.0	4.65
Indene	1034.1	1043.3	1053.8	4.93

TABLE III

RETENTION INDICES OF SOME BI- AND TRICYCLIC AROMATIC AND RELATED COMPOUNDS ON OV-101 AND THEIR TEMPERATURE COEFFICIENTS

Compound	$I_{140^\circ\mathrm{C}}$	$I_{160^\circ\mathrm{C}}$	$I_{180^\circ\mathrm{C}}$	$10\ (\partial I/\partial T)$
trans-Decaline	1082.5	–	1106.4	5.98
cis-Decaline	1124.8	1137.7	1152.2	6.86
1,2,3,4-Tetrahydronaphthalene	1168.7	1179.8	1194.0	6.33
1,2-Dihydronaphthalene	1171.4	1183.2	1197.8	6.60
Naphthalene	1191.0	1203.8	1217.3	6.58
2-Methylnaphthalene	1293.9	1307.1	1323.5	7.40
1-Methylnaphthalene	1309.0	1322.9	1340.2	7.80
2-Ethylnaphthalene	1384.9	1398.1	1413.8	7.23
2,6-Dimethylnaphthalene	1395.6	1408.8	1424.3	7.18
1,7-Dimethylnaphthalene	1409.0	1422.4	1438.7	7.42
1,4-Dimethylnaphthalene	1425.9	1441.1	1459.1	8.30
2,3-Dimethylnaphthalene	1427.3	1441.7	1459.1	7.95
1,2-Dimethylnaphthalene	1439.7	1455.1	1473.7	8.52
1,8-Dimethylnaphthalene	1456.8	1472.4	1491.5	8.68
2,3,6-Trimethylnaphthalene	1529.4	1544.1	1561.6	8.05
Biphenyl	1366.3	1377.9	1392.0	6.44
3-Methylbiphenyl	1464.4	1475.6	1489.2	6.21
4-Methylbiphenyl	1472.7	1484.5	1500.1	6.86
Diphenylmethane	1412.4	1429.4	1436.8	6.10
1,2-Diphenylethane	1496.7	1509.3	1524.9	7.05
Acenaphthene	1463.9	–	1501.1	9.30
Fluorene	1552.1	–	1591.3	9.80
Phenanthrene	1719.6	–	1767.1	11.90
Anthracene	1729.0	–	1776.5	11.90
Dicyclopentadiene	1047.3	–	–	–
Benzo[*b*]furan	1005.8	–	–	–
Benzo[*b*]thiophene	1196.0	–	1223.3	6.80
Quinoline	1247.7	–	–	–
Isoquinoline	1272.9	–	–	–
Indole	1281.1	–	1298.3	4.30
Dibenzofuran	1494.9	–	1531.1	9.00
Dibenzothiophene	1694.3	–	1739.8	11.20
Carbazole	1761.1	–	1803.6	10.62

TABLE IV

COMPARISON OF PUBLISHED RETENTION INDICES WITH THOSE OBTAINED IN THIS WORK FOR AROMATICS

Our data were corrected to the published temperatures by means of $\partial I/\partial T$ values.

Compound	I^{OV-101}	$I^{OV-1}_{130^{\circ}C}$ *(ref. 18)*	$I^{SE-30}_{65^{\circ}C}$ *(ref. 17)*	$I^{SE-30}_{100^{\circ}C}$ *(ref. 22)*
o-Xylene	878.9		878.9	
Isopropylbenzene	910.5		910.1	
1-Methyl-4-ethylbenzene	947.8		948.2	
1-Methyl-4-isopropylbenzene	1017.8			1017.1
2,3-Dihydroindene	1012.2		1011.8	
Indene	1018.0		1017.5	
1,2,4,5-Tetramethylbenzene	1095.0		1094.9	
n-Pentylbenzene	1135.5		1135.2	
Naphthalene	1184.4	1183.7		
2-Methylnaphthalene	1286.5	1286.3		
1-Methylnaphthalene	1301.2	1301.7		
2-Ethylnaphthalene	1377.6	1377.4		
2,6-Dimethylnaphthalene	1388.4	1388.2		

retention indices of some aromatic compounds determined in our laboratory are compared with published values for the capillary column and stationary phases of the same chemical structure (OV-101, OV-1, SE-30). Our data have been corrected to the published temperature by means of $\partial I/\partial T$ values. The good agreement of these data allows the published retention indices to be used for identification. On the other hand, the retention indices of such hydrocarbons measured on the same stationary phase (OV-101) for both capillary and packed columns may differ as illustrated in Table V.

In order to investigate the composition of the oils by means of the Kováts retention index, *n*-alkanes which are eluted before and after the main components and are separated completely were added to the oil samples. Two methods of determination of the Kováts retention index were employed. In the first, the log t'_R values of

TABLE V

COMPARISON OF RETENTION INDICES OBTAINED ON CAPILLARY AND PACKED COLUMNS

Capillary column: this work. Packed columns[16]: I = stainless-steel (1 m × 3 mm), 15% OV-101 on Chromaton N AW GMDS (60–80 mesh); II = glass (10 m × 1.5–2 mm), 5% OV-101 on Gas-Chrom Q (100–120 mesh).

Compound	$I_{230^{\circ}C}$		
	Capillary	*Packed I*	*Packed II*
2-Methylnaphthalene	1358.6	—	1354
1-Methylnaphthalene	1381.9		1380
Acenaphthene	1549.7		1550
Dibenzofuran	1577.9		1580
Fluorene	1640	1646	1645
Phenanthrene	1824	1837	1836
Fluoranthene	2071	2095	2091

n-alkanes obtained according to Castello and Parodi[23] are used for the calculation of Kováts retention indices of the oil components from the simplified equation[2]:

$$I = 100\,[n + (\log t'_{Rx} - \log t'_{Rn})/a]$$

However, extrapolation of the "theoretical" values of the n-alkanes to homologues without side chains results in discrepancies. The size of the discrepancy, ΔI, *i.e.*, the difference between the retention indices based on experimental and calculated log t'_R values for n-alkanes, increases with the extent of extrapolation even for the straight line dependence of log $t'_R = a \cdot n_c + b$ (correlation coefficient $r > 0.9999$), as illustrated in Fig. 1. An appreciable index discrepancy is also observed when the extrapolation distance is smaller than $3k$ as it is for the last standard n-alkane. Moreover, index discrepancies greater than 1 i.u. are observed in the region of the absent n-alkane even when the "theoretical" values are calculated using experimental data for all the other n-alkanes. Neu *et al.*[2] described a similar phenomenon. Obviously, the limiting condition[25] of "the largest extrapolation distance that can be used" should be altered.

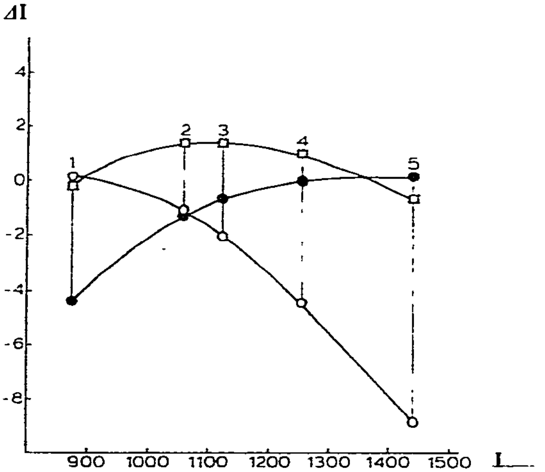

Fig. 1. Dependence of the retention index discrepancy (in i.u.) of alkylbenzenes on the n-alkanes chosen for the "theoretical" calculation based on experimental log t'_R data. ○—○, n-C_8H_{18}–n-$C_{10}H_{22}$; ●—●, n-$C_{12}H_{26}$–n-$C_{15}H_{32}$; □—□, n-C_8H_{18}–n-$C_{15}H_{32}$ except n-$C_{11}H_{24}$. Compounds: 1 = m-xylene; 2 = n-butylbenzene; 3 = 1,2,4,5-tetramethylbenzene; 4 = n-hexylbenzene; 5 = hexamethylbenzene.

In the second method, experimental log t'_R values for n-alkanes are used to calculate the retention indices according to Kováts formula[1] with an interpolation interval of $m > 1$. In this case the retention index discrepancy, ΔI, *i.e.*, the difference between retention indices based on successive and non-successive log t'_R values for n-alkanes, increases with the size of the interpolation interval, as illustrated in Fig. 2. However, it is smaller for aromatic compounds which are retained with high capacity ratios, k, and approaches the within-laboratory reproducibility for retention indices if $k \geqslant 2.0$. Fig. 2 shows the discrepancy size for a set of retention indices as a function of the capacity ratio. Thus, in order to obtain a reliable determination of Kováts reten-

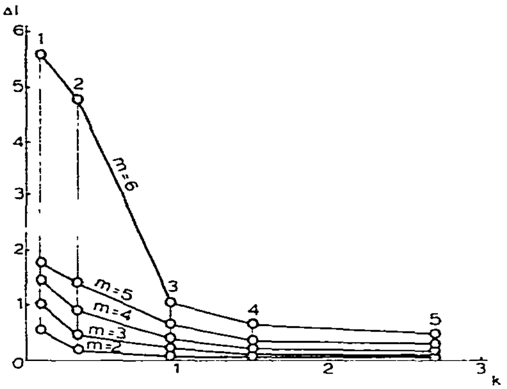

Fig. 2. Dependence of the retention index discrepancy (in i.u.) of alkylbenzenes on the interpolation interval, *m*, and the capacity ratio, *k*. Stationary phase: OV-101. Column temperature: 140°C. Compounds: 1 = *m*-xylene; 2 = 1,4-diethylbenzene; 3 = *n*-hexylbenzene; 4 = 1,3,5-triisopropylbenzene; 5 = hexamethylbenzene.

tion indices of oil components, the chromatographic conditions should be chosen so as to provide a capacity ratio of $k \geqslant 2.0$ and the calculations should employ an interpolation interval of $m \leqslant 6$.

The retention indices obtained under these experimental conditions were used for the identification of the oil components. Some naphthalene, fluorene, phenanthrene and anthracene homologues were identified by means of retention indices based on the methylene group increments.

CONCLUSION

The Kováts retention indices of more than 80 aromatic and related compounds have been determined on the dimethylsiloxane OV-101. The relationship between the capacity ratio and the error in the retention index has been found and used in order to obtain precise retention indices for many compounds expected to be present in washing and anthracene oils.

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