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Note

Identification of individual aromatic hydrocarbons in kerosene fraction (b.p. 150–250°)

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The method described is intended for the quantitative and qualitative analysis of aromatic hydrocarbons (mono- and bicyclic) in kerosene (b.p. 150–250°) by chromatographic methods. The problem could be simplified considerably if the aromatic part could be separated from paraffinic and cycloparaffinic hydrocarbons. Stuckey[1] described a rapid method using gas chromatography in two stages which gave an excellent separation between the saturated and aromatic hydrocarbons on 1,2,3-tris-(2-cyanoethoxypropane), and the separation of the aromatic hydrocarbons was achieved on Silicon DC-550.

The analysis of aromatic hydrocarbons using a prior separation of the paraffin–cycloparaffin content by adsorption chromatography and subsequent separation of the aromatic content by gas chromatography was prolonged and difficult, but was possible by a simple technique.

EXPERIMENTAL

The usual gas chromatographic techniques are not suitable for the analysis of kerosene (b.p. 150–250°) over such a wide temperature range, because this fraction contains many individual hydrocarbons with different structures. We carried out a vacuum rectification of kerosene on a rectification column with 20 theoretical plates and separated two narrower fractions (b.p. 150–200° and 200–250°). The aromatic hydrocarbons were separated from the saturated hydrocarbons by adsorption chromatography and fluorescent indicator adsorption (FIA).

The qualitative determination of the composition of the 150–200° fraction was carried out on a squalane capillary column at 110° and the 200–250° fraction at 130°, after prior separation of the paraffinic and cycloparaffinic from the aromatic hydrocarbons.

The apparatus and operating conditions were as follows: gas chromatograph, Chrom-3; detector, FID; column, stainless-steel capillary (100 m × 0.25 mm I.D.); stationary phase, squalane at 110° and 130°; injection port temperature, 220° and 260°; sample size, 0.6 μl; split ratio, 1:30; carrier gas, nitrogen at the flow-rate of 60 ml/min; hydrogen flow-rate, 30 ml/min; and oxygen flow-rate, 300 ml/min.

The identification of monosubstituted naphthalenes (1-ethyl- and 2-ethylnaphthalene) and disubstituted naphthalenes (1,3-dimethyl-, 1,4-dimethyl-, 1,5-dimethyl- and 2,3-dimethylnaphthalene) was carried out using pure substances. 1-Methyl-, 2-methyl-, 2,6-dimethyl- and 2,7-dimethylnaphthalene were isolated by preparative thin-layer chromatography.

TABLE I

KOVÁTS RETENTION INDICES OF AROMATIC HYDROCARBONS IN THE 150–250° FRACTION ON SQUALANE

Compound	*Kováts indices at 110°*	
	Literature	*Found*
Benzene	652.4	650.3
Toluene	759.6	759.3
Ethylbenzene	850.1	850.3
p-Xylene	863.8	865.4
m-Xylene	865.2	868.1
o-Xylene	886.8	888.4
Isopropylbenzene	909.6	909.7
n-Propylbenzene	938.9	939.0
1-Methyl-4-ethylbenzene	953.9	953.5
1-Methyl-2-ethylbenzene	967.5	969.3
Mesitylene	970.2	972.2
tert.-Butylbenzene	—	976.1
Pseudocumene	—	992.7
Isobutylbenzene	—	993.4
sec.-Butylbenzene	—	994.1
1-Methyl-3-isopropylbenzene	1005.5	1004.8
1-Methyl-4-isopropylbenzene	1013.9	1012.5
1,2,3-Trimethylbenzene	1015.7	1016.4
Indane	—	1019.4
1-Methyl-2-isopropylbenzene	1022.6	1023.6
1,3-Diethylbenzene	1031.5	1030.7
1-Methyl-3-*n*-propylbenzene	1036.0	1036.1
n-Butylbenzene	1038.8	1038.0
1,4- + 1,2-Diethylbenzene + 1-methyl-*n*-propylbenzene	1042.3	1042.0
1-Methyl-2-*n*-propylbenzene	1049.1	1049.3
1,3-Dimethyl-5-ethylbenzene	—	1051.0
1,4-Dimethyl-2-ethylbenzene	—	1062.4
1-Methylindane	—	1067.1
1,3-Dimethyl-4-ethylbenzene	1069.8	1069.4
trans-Decalin	—	1073.9
1,2-Dimethyl-3-ethylbenzene	—	1090.0
Durene	—	1110.7
cis-Decalin	—	1112.9
Isodurene	—	1116.3
1-Ethyl-2-*n*-propylbenzene	1120.9	1121.4
1,3-Diisopropylbenzene	—	1122.5
4-Methylindane	—	1129.9
n-Pentylbenzene + 1,2,3,4-tetramethylbenzene	1136.2	1138.8
Tetralin	—	1142.2
1-Methyl-2-*n*-butylbenzene	1146.5	1148.1
1,4-Diisopropylbenzene	—	1156.9
Naphthalene	—	1161.2

TABLE II

KOVÁTS RETENTION INDICES OF AROMATIC HYDROCARBONS IN THE 200–250° FRACTION ON SQUALANE

Compound	*Kováts indices at 130°*	
	Literature	*Found*
Isobutylbenzene + *sec.*-butylbenzene	—	998.5
1-Methyl-3-isopropylbenzene	1009.3	1010.2
1-Methyl-4-isopropylbenzene	1018.3	1018.0
1-Methyl-2-isopropylbenzene	1031.0	1028.7
1,3-Diethylbenzene	1036.8	1035.8
1-Methyl-3-*n*-propylbenzene	1040.6	1041.1
n-Butylbenzene	1043.6	1044.6
1,2- + 1,4-Diethylbenzene + 1-methyl-4-*n*-propylbenzene	1047.5	1047.9
1-Methyl-2-*n*-propylbenzene	1054.8	1055.4
1,4-Dimethyl-2-ethylbenzene	—	1063.4
1,3-Dimethyl-4-ethylbenzene	1073.2	1075.3
trans-Decalin	—	1083.9
2-Methyl-2-phenylbenzene + 1-methyl-4-*tert.*-butylbenzene	—	1088.1
1,2-Dimethyl-3-methylbenzene	—	1099.3
1,3-Dimethyl-5-isopropylbenzene	—	1104.9
Durene	—	1116.9
Isodurene	—	1122.5
cis-Decalin	—	1122.9
1,2- + 1,3-Diisopropylbenzene + 1-ethyl-2-*n*-propylbenzene	1126.9	1126.6
n-Pentylbenzene + 1,2,3,4-tetramethylbenzene + 1-ethyl-3-*tert.*-butylbenzene	1142.3	1142.1
1-Methyl-2-*n*-butylbenzene	1152.8	1153.3
Tetralin	—	1155.2
1,3-Dimethyl-*tert.*-butylbenzene	—	1159.7
1,4-Diisopropylbenzene	—	1161.8
Naphthalene	—	1172.8
1,3,5-Trimethyl-2-ethylbenzene + 1-ethyl-4-*tert.*-butylbenzene + 1,2,7-trimethyl-5-ethylbenzene	—	1180.7
1-Methyl-4-(1,1-dimethylpropyl)benzene	—	1191.8
2,4-Dimethyl-4-*tert.*-butylbenzene	—	1194.8
1,3,5-Triethylbenzene	—	1197.7
1,2,4-Trimethyl-3-ethylbenzene + 1-ethyl-1-phenylbenzene	—	1201.1
1-Methyl-3,5-diisopropylbenzene	—	1206.3
2,4-Dimethyl-3-phenylpentane	—	1212.3
1-Methyl-4-*n*-propylbenzene + 1-phenylhexane	—	1219.8
2,4-Dimethyl-1-phenylpentane	—	1246.6
2-Methylnaphthalene	—	1279.5
2-Phenylheptane	—	1281.4
Pentamethylbenzene	—	1282.7
1-Methylnaphthalene	—	1294.4
2-Ethylnaphthalene	—	1336.3
1-Ethylnaphthalene	—	1337.3
1,2,6- + 2,7-Dimethylnaphthalene	—	1371.6
1,3-Dimethylnaphthalene	—	1385.0
1,6-Dimethylnaphthalene	—	1386.9
1,4-Dimethylnaphthalene	—	1397.4
1,5- + 2,3-Dimethylnaphthalene	—	1399.5

RESULTS AND DISCUSSION

The identification was achieved by the standard method and by reference data for Kováts retention indices[2–5], I, using correlations between I and the boiling points, T_b, of the compounds, and the reference data[6].

The Kováts retention indices taken from the literature extrapolated to the temperatures used in this work and the experimental retention indices obtained for aromatic hydrocarbons (150–250°) are given in Tables I and II. The experimental retention indices were obtained with four replicate tests and they showed good repeatability (difference 0.1–2.9 index units).

Table III gives the boiling points of aromatic hydrocarbons in kerosene calculated from log I/T_b.

Identification of the mono- and disubstituted bicyclic hydrocarbons was achieved by determining the boiling points. The boiling points obtained agreed closely with the literature data.

TABLE III

BOILING POINTS OF SOME AROMATIC HYDROCARBONS IN KEROSENE DETERMINED FROM LOG I/T_b

Compound	*Boiling point*		
	Literature	*Found*	ΔT
1-Methyl-3-ethylbenzene	161.3	160.0	1.3
1-Methyl-4-ethylbenzene	161.99	162.2	0.2
1-Methyl-2-ethylbenzene	165.15	166.0	0.85
1-Methyl-3-isopropylbenzene	175.14	174.3	0.84
1-Methyl-4-isopropylbenzene	177.1	178.0	0.9
1-Methyl-2-isopropylbenzene	178.15	180.0	1.85
1-Methyl-3-*n*-propylbenzene	181.8	183.0	1.2
1-Methyl-2-*n*-propylbenzene	184.8	183.5	1.3
2-Methylindane	186.0	185.8	0.2
1,4-Dimethyl-2-ethylbenzene	186.9	185.8	1.1
1,3-Dimethyl-4-ethylbenzene	189.75	187.8	2.25
1,2-Dimethyl-3-ethylbenzene	193.9	192.0	1.9
4-Methylindane	202.0	200.0	2.0
1,2,3,4-Tetramethylbenzene	205.0	202.5	2.5

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