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ADVANCES IN THE UTILIZATION OF THE RETENTION INDEX SYSTEM FOR CHARACTERIZING HYDROCARBONS IN COMPLEX MIXTURES BY GAS CHROMATOGRAPHY

G. D. MITRA, G. MOHAN and A. SINHA

Gas Chromatography Laboratory, Planning and Development Division, Fertilizer Corporation of India Ltd., Sindri, Bihar (India)

SUMMARY

The temperature coefficient of the retention index (dI/dT) and the difference between retention indices on polar and apolar phases (ΔI) have been considered as an extension of the retention index system. The retention index range of 700–1500 for kerosene, representing more than 80 peaks and shoulders on an apolar phase, has been shown to contain all of the C_7–C_{15} *n*-alkanes.

A total of six fractions were collected through a preparative SE-30 column on the basis of the retention index distribution of *n*-alkanes, such that fraction F_1 represented the hydrocarbon content up to 1000 index units and the remaining five fractions (F_2–F_6) were collected with a range of 100 retention index units each. Each of these fractions was further chromatographed on an analytical SE-30 column at different temperatures and on tetracyanoethylated pentaerythritol (TCEPE) for the determination of the dI/dT and ΔI values of the separated peaks. The dI/dT and ΔI values, the magnitudes of which depend on the structure of the molecules, have been shown to be useful in providing clues to the identification and characterization of hydrocarbon components in kerosene samples. The efficiency of the method was illustrated by obtaining the following information: (1) all of the fractions contain normal and branched alkanes and naphthenes but are devoid of alkenes; (2) alkyl-substituted benzenes are present in fractions F_1, F_2 and F_3 only up to a retention index of 1200 on SE-30; (3) fractions F_4, F_5 and F_6 consist mainly of polycyclic naphthenes; (4) polynuclear aromatic hydrocarbons were not found in kerosene; and (5) the percentage composition of each fraction has been determined.

INTRODUCTION

In recent years, attempts have been made to standardize parameters for precise identification and characterization of peaks in complex gas chromatograms[1–23]. Conventional qualitative gas chromatographic (GC) analysis involves comparison of the retention data of unknown compounds under specified conditions with the corresponding data for reference compounds. The growth of collections of retention index data and correlations with molecular structure have created more interest in its utilization

TABLE I

EXPERIMENTAL CONDITIONS FOR PREPARATIVE AND ANALYTICAL COLUMNS

Property	*Polar stationary liquid*		*Apolar stationary liquid*	
	Analytical	*Preparative*	*Analytical*	*Preparative*
Column dimensions	15 ft. × $\frac{1}{8}$ in.	33 ft. × $\frac{1}{4}$ in.	20 ft. × $\frac{1}{8}$ in.	20 ft. × $\frac{1}{4}$ in.
Liquid phase	TCEPE	TCEPE	SE-30	SE-30
Amount of liquid (wt.-%)	21.0	21.0	5.0	20.0
Solid support	Chrom P	Chrom P	Chrom W	Chrom W
Mesh size of support (B.S.S.)	60–80	60–80	60–80	60–80
Carrier gas	N_2	H_2	N_2	H_2
Column temperature (°C)	125/140	140	110–160	210/80–210
Thermal conditions	Isothermal	Isothermal	Isothermal	Isothermal/programmed
Volume of sample injected	0.2–0.7 μl	1 ml	0.2–0.7 μl	1 ml
Origin of liquid phase	Applied Science Labs.	Applied Science Labs.	BDH	Aerograph
Detector*	FID	TCD	FID	TCD
Detector temperature (°C)	—	225	—	225
Filament current (mA)	—	80	—	80
Collection tip temperature (°C)	—	100	—	100
Injector temperature (°C)	250	225	250	225
Collector tip	—	Ambient	—	Ambient
Instrument model	550 D	Auto-Prep 700	550 D	Auto-Prep 700

* FID = flame ionization detector; TCD = thermal conductivity detector.

in the characterization of substances by GC. In the identification of natural products by GC, difficulties arise as a result of the increasing number of possible isomers with increasing carbon number. Retention index data obtained on different stationary phases and at various column temperatures have proved useful in providing clues to the identification of the components present in complex samples.

The variation of retention indices with column temperature ($\mathrm{d}I/\mathrm{d}T$) has been suggested by many workers[6–13] as a means of identification. Saha and Mitra[7] showed that the $\mathrm{d}I/\mathrm{d}T$ values of hydrocarbons on apolar phases decreased in the order aromatics> cyclic paraffins> tetra-> tri-> di-> monoalkyl paraffins, and proposed the use of this property in the sub-classification of hydrocarbons into types. Widmer and co-workers[11,12] distinguished mono- and bicyclic alkanes by using $\mathrm{d}I/\mathrm{d}T$ values that are specific for hydrocarbon groups such as branched-chain alkanes, alkenes, dialkenes, cyclic alkenes and cyclic dialkenes.

A number of investigators[14–23] showed that the difference between retention indices on polar and apolar phases (ΔI) also has specific values for different types of hydrocarbons. Landa and co-workers[18–20] determined ΔI values for bicyclic and tricyclic hydrocarbons containing 5- and 6-membered rings on polar and apolar phases and demonstrated their characterization into types.

$\mathrm{d}I/\mathrm{d}T$ and ΔI values have been considered as an extension of the retention index concept, and some important progress has been made in this laboratory[14,15] in its application to the identification of the components of gasoline and kerosene fractions of petroleum.

In view of current problems with the supply of petroleum, a thorough knowledge of distribution and content of hydrocarbon types in petroleum fractions is necessary in order to improve processing technology. A kerosene fraction containing components of all hydrocarbon types was selected as the sample for investigation as its systematic and specific component analysis has not been described in the literature[24–26].

EXPERIMENTAL

Various schemes for the analysis of kerosene (b.p. 140–240°) have been discussed in earlier work[15]. The operating conditions for preparative and analytical columns are given in Table I.

Preparative gas chromatography

A kerosene sample with a retention index range of 700 to 1500 obtained from the Barauni Oil Refinery (Indian Oil Corporation) was subjected to the preparative fractionation. The cut-points were determined from the increased peak heights of the kerosene sample dosed with all C_{10}–C_{14} *n*-alkanes after comparing the chromatograms of a blank sample under identical conditions. A total of six fractions were collected from a total of five injections of 1 ml each. The first fraction (F_1) was collected up to the retention index of *n*-decane, *i.e.*, 1000. The remaining five fractions (F_2–F_6) were collected with a range of 100 retention index units each, *i.e.* 1000–1100, 1100–1200, 1200–1300, 1300–1400 and 1400–1500 (see Fig. 1). Repeated collections of each fraction were made by observing simultaneously the preparative chromatograms, in order to ensure that reproducible cuts were obtained. All of these collections were made in specially designed weighed glass traps in an ice-bath.

Analytical gas chromatography

Two GLC analytical columns (polar and apolar) were used. All of the preparative fractions from an SE-30 column were re-chromatographed isothermally on SE-30 at different column temperatures in order to obtain I and $\mathrm{d}I/\mathrm{d}T$ values for the separated peaks. The isothermal chromatograms on a polar tetracyanoethylated pentaerythritol (TCEPE) column were also obtained for all of the fractions in order to determine ΔI values.

The retention indices of the peaks and shoulders in all of the chromatograms were measured nomographically[27] on the basis of *n*-alkane peaks present in the fractions which were located by injecting a synthetic mixture of reference compounds under identical conditions. The retention indices on SE-30 for peak identification were evaluated from published data[18-21] or otherwise determined graphically[23,28] using other apolar phases. The $\mathrm{d}I/\mathrm{d}T$ values on SE-30 and ΔI values on TCEPE/SE-30 for different types of hydrocarbons determined in this laboratory[14,15] were utilized for characterization of the substances.

The precision of the gas chromatographic conditions was tested as described earlier[15]. The gas hold-up time and injection points were determined as usual[14,15].

Three sets of liquid micro-syringes (Precision Sampling Corp., Baton Rouge, La., U.S.A.) were used in order to eliminate the stray peaks due to syringe contaminants. Fractions F_1, F_3, F_5 and F_2, F_4, F_6 were injected through two sets of syringes, while the third set was used only for injecting synthetic mixtures of *n*-alkanes.

RESULTS AND DISCUSSION

Preparative gas chromatography

In order to fractionate kerosene samples according to differences in structure, a polar TCEPE preparative column was tried but, owing to the poor separation and non-return of the recorder baseline, its use was discontinued. Preparative chromatograms of kerosene on SE-30 under temperature-programmed and isothermal conditions (Fig. 1) were also obtained and, on comparison, the latter is to be preferred because of the better resolution. We hope that improved preparative fractionation with minimal inter-fraction overlapping will be possible by establishing the optimal preparative conditions, which is the subject of a separate study.

Analytical gas chromatography

In order to establish the retention index distribution for each fraction from the SE-30 preparative column and to determine $\mathrm{d}I/\mathrm{d}T$ values for the separated peaks, all six fractions were re-chromatographed on an SE-30 analytical column at different temperatures.

A total of 24 isothermal chromatograms for fractions F_1, F_2 and F_3 at 110, 120, 130 and 140° and fractions F_4, F_5 and F_6 at 130, 140, 150 and 160° were obtained on the SE-30 column. As illustrations, chromatograms of each fraction at a single column temperature are shown in Figs. 2–7. In order to determine $\mathrm{d}I/\mathrm{d}T$ values for each peak from the chromatograms obtained at different temperatures, skill and experience are required. The retention indices of most of the hydrocarbon components in kerosene are highly dependent on temperature and a 10° interval in column temperature was

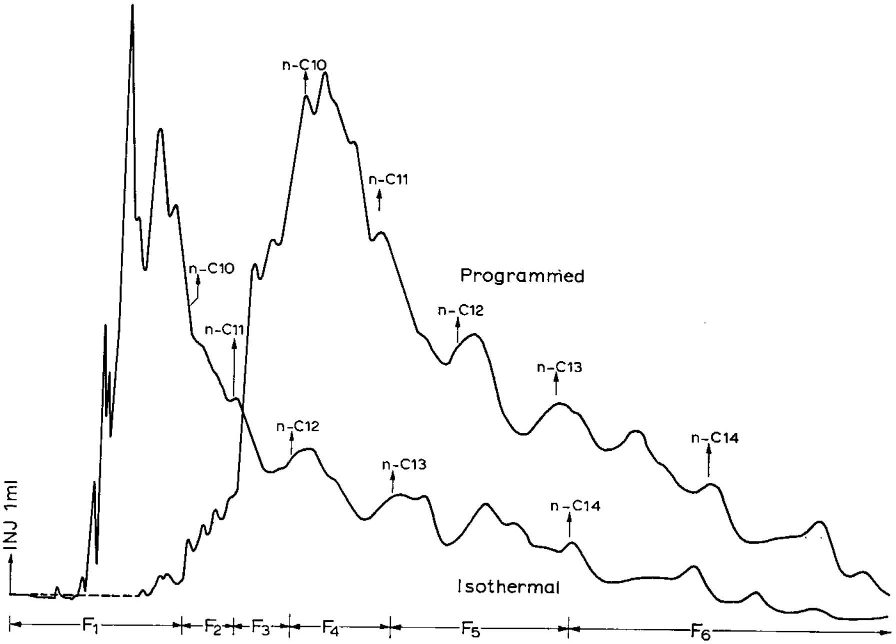

Fig. 1. Preparative chromatograms of kerosene on SE-30 under isothermal and temperature-programmed conditions.

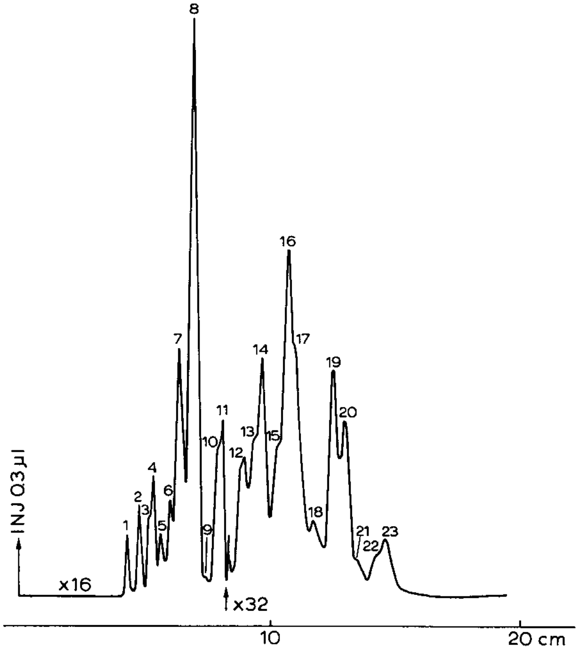

Fig. 2. Chromatogram of fraction F_1 on SE-30 at 110°.

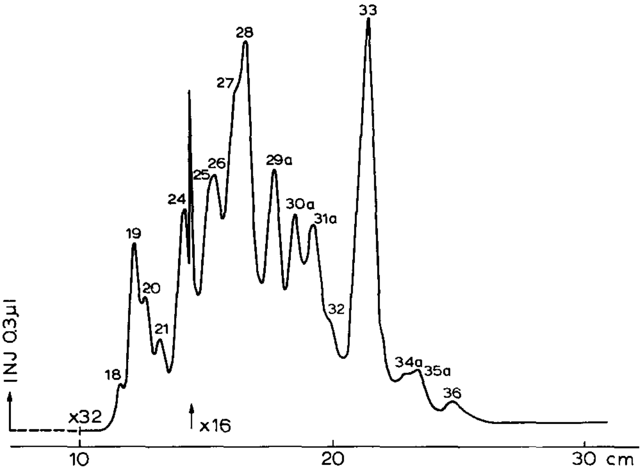

Fig. 3. Chromatogram of fraction F_2 on SE-30 at 110°.

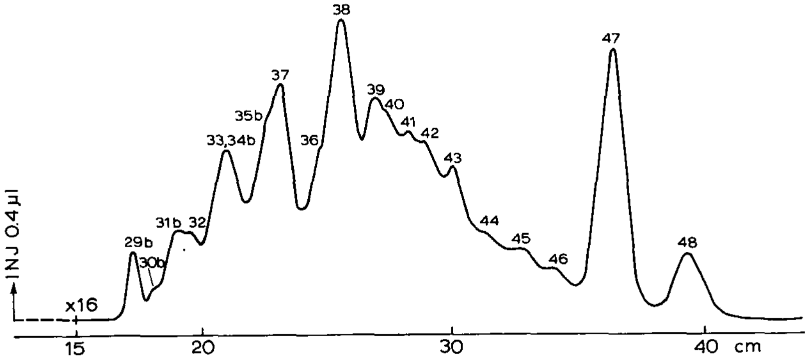

Fig. 4. Chromatogram of fraction F_3 on SE-30 at 110°.

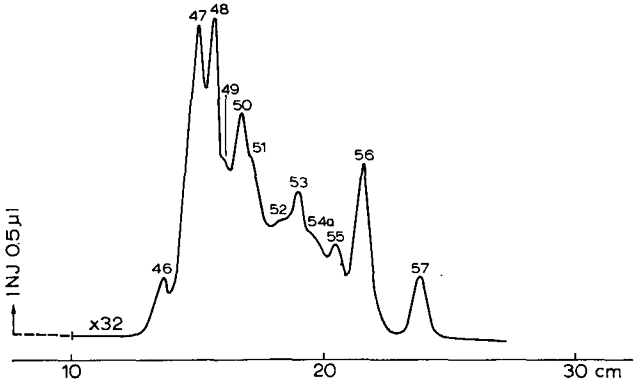

Fig. 5. Chromatogram of fraction F_4 on SE-30 at 140°.

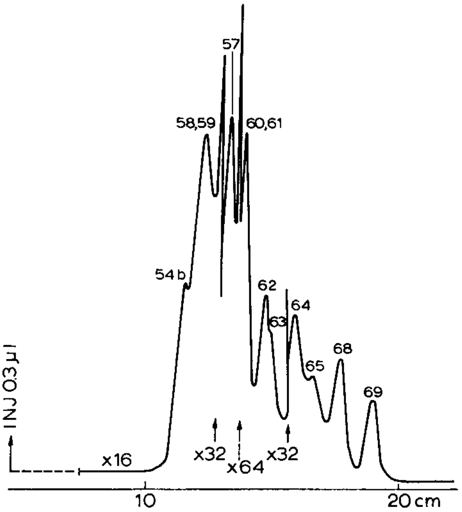

Fig. 6. Chromatogram of fraction F_5 on SE-30 at 160°.

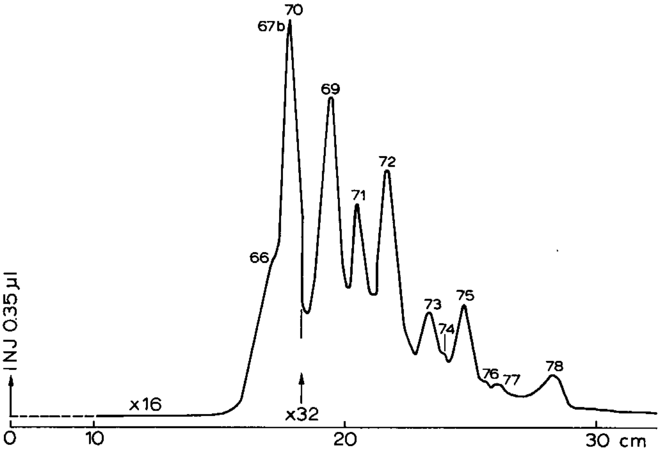

Fig. 7. Chromatogram of fraction F_6 on SE-30 at 160°.

chosen in order to locate easily the inversion, shifting and co-elution of peaks and hence to obtain dI/dT values.

For identifying structural types, TCEPE was used[15] in order to determine the change in retention index data caused by a change in polarity. Fractions F_1, F_2 and F_3 were chromatographed at 125 and 140° while fractions F_4, F_5 and F_6 were chromatographed only at 140° (see Figs. 8–13). By comparing the chromatograms of each fraction on two liquid phases, peak characterization was possible.

Basis of peak characterization

The magnitudes of the dI/dT values depend on the number and positions of substituents and also on the chemical nature of the molecule. By the application of

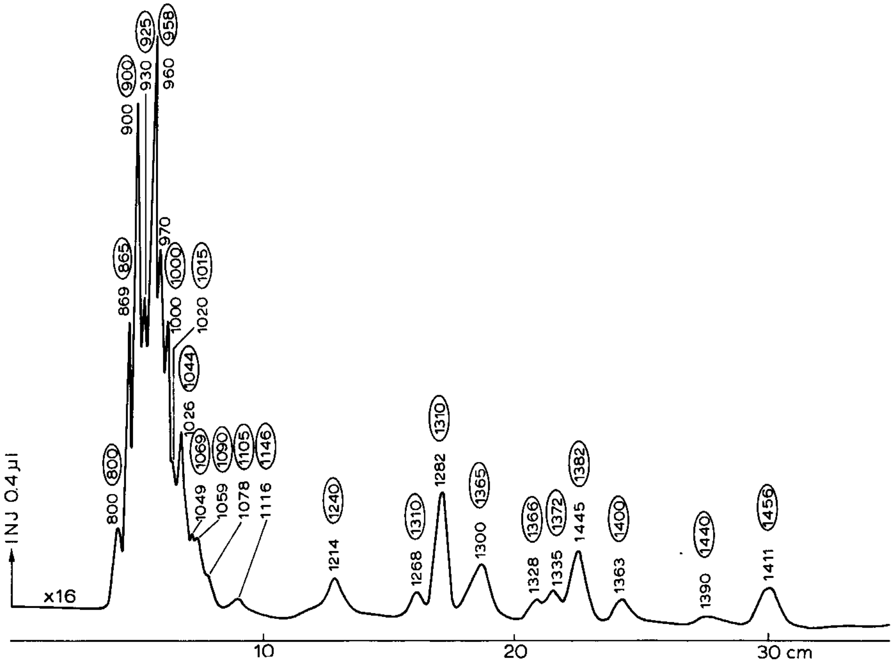

Fig. 8. Chromatogram of fraction F_1 on TCEPE at 125°. Retention indices are given on each peak, those in circles being values at 140°.

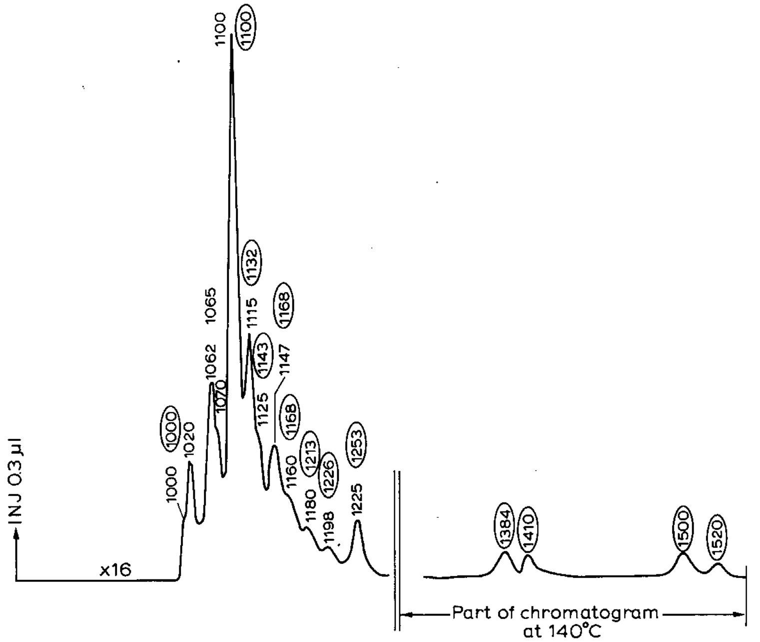

Fig. 9. Chromatogram of fraction F_2 on TCEPE at 125°. Retention indices are given on each peak, those in circles being values at 140°.

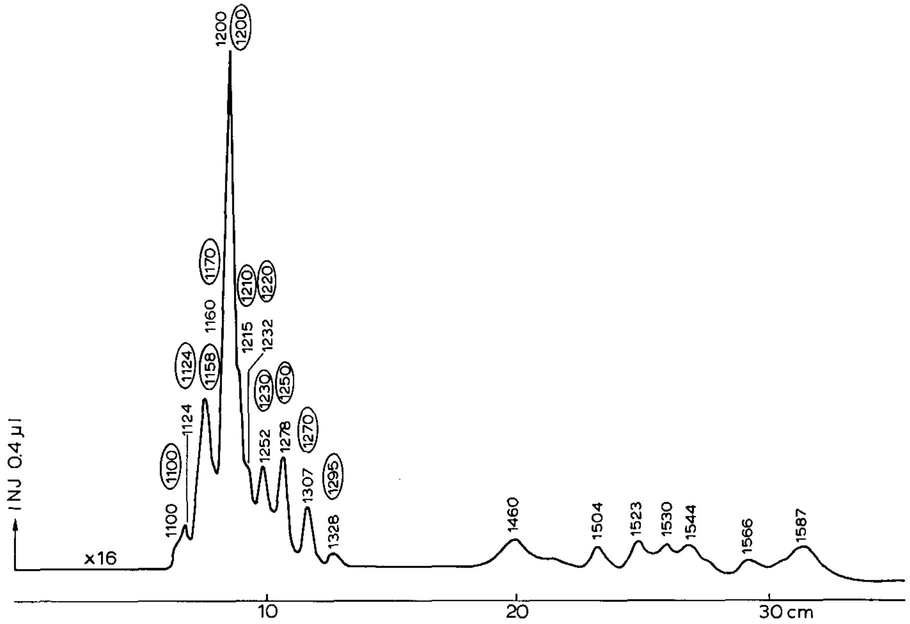

Fig. 10. Chromatogram of fraction F_3 on TCEPE at 140°. Retention indices are given on each peak, those in circles being values at 125°.

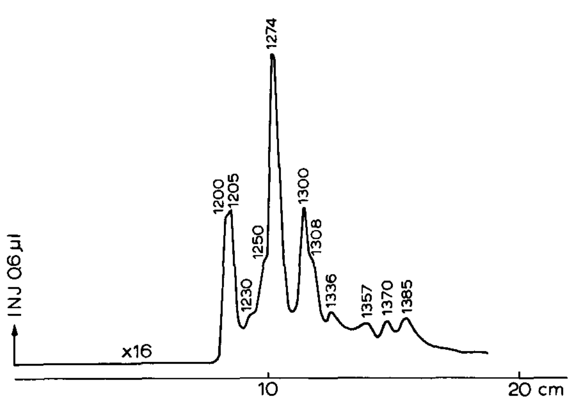

Fig. 11. Chromatogram of fraction F_4 on TCEPE at 140°. Retention indices are given on each peak.

dI/dT values, branched alkanes can be sub-classified into mono-, di-, tri- and tetra-substituted compounds, naphthenes into monocyclic and bicyclic compounds and aromatics into phenyl and biphenyl compounds. Some limitations of the dI/dT method exist in distinguishing highly branched alkanes from cyclic alkenes, cyclic alkanes from aromatics and alkenes from mono-substituted alkanes, but this problem can easily be overcome by the application of the ΔI system.

The difference between retention indices on polar and apolar phases (ΔI) reflects the presence of particular types and positions of functional group and also

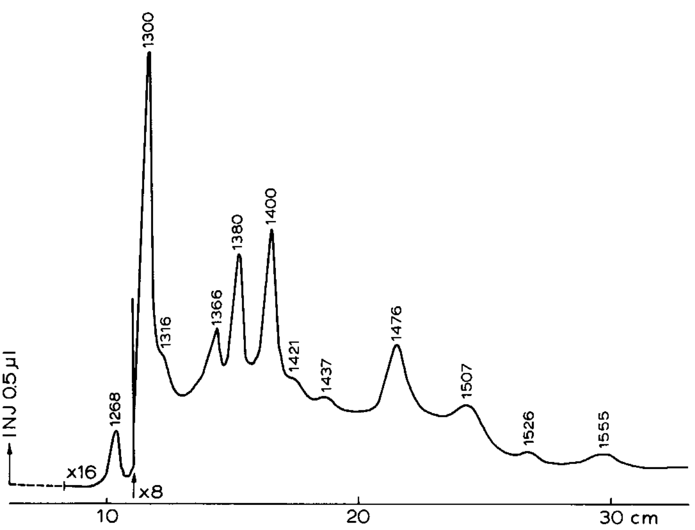

Fig. 12. Chromatogram of fraction F_5 on TCEPE at 140°. Retention indices are given on each peak.

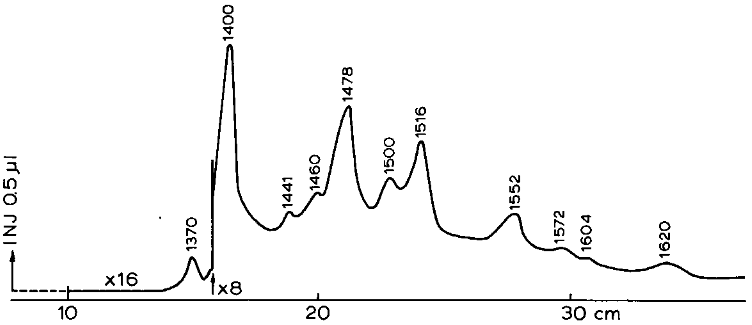

Fig. 13. Chromatogram of fraction F_6 on TCEPE at 140°. Retention indices are given on each peak.

the structure and configuration of molecules. From the definition of retention index system, it follows that the ΔI values of all *n*-alkanes are zero, while for branched alkanes the ΔI values are -5 to $+5$. Monocyclic alkanes and alkenes appear to be slightly more polar than branched alkanes and have positive ΔI values in the range 80–100. With an increase in the number of rings, the corresponding ΔI values increase. For example[15], the ΔI values of bicyclic, tricyclic and tetracyclic alkanes range from 150 to 200, 200 to 275 and 250 to 350, respectively. The ΔI values for aromatic hydrocarbons[14,15] are higher, in the range 400–425, while polynuclear aromatic hydrocarbons have the highest ΔI values (the expected ΔI value for naphthalene is about 550).

The extensions to the retention index system (dependence on temperature and polarity) are therefore complementary and their combination to give unambiguous substance characterization are considered in terms of the illustration discussed in detail earlier[14,15].

Qualitative analysis

The basic problem in using GC for the analysis of samples such as petroleum fractions lies in their complexity combined with the difficulty of assigning peak identities even when a reasonable separation has been accomplished. The use of the extension of retention index system on which the peak identification and characterization was based is summarized as follows:

(a) when the *I* values of peaks on phases of opposite polarity are the same, they represent alkanes;

(b) after satisfying condition (a), a study of d*I*/d*T* values on an apolar phase indicates the distribution between non-branched and highly branched alkanes;

(c) when the *I* values of peaks on an apolar phase are absent in a polar phase, the peaks represent compounds other than saturated alkanes, such as alkenes, naphthenes and aromatics;

(d) after satisfying condition (c), d*I*/d*T* values on an apolar phase are easily applicable in distinguishing between alkenes, naphthenes and aromatics;

(e) when the *I* values of peaks on both phases are the same and have different areas or heights with respect to some standard, they represent all types of hydrocarbons (alkanes, alkenes, naphthenes and aromatics).

TABLE II

ANALYSIS OF FRACTION F_1

Peak No.	*Retention indices on SE-30*				*Identification**
	110°	*120°*	*130°*	*140°*	
1	745	743	742	741	Monosubstituted alkenes
2	770	773	776	778	Toluene
3	793	800	800	800	2,2,4-TMH
4	800	800	800	800	*n*-O
5	818	820	823	827	1-C_2-C_3-TMCP, 1-T_3-DMCH, 1-C_4-DMCH
6	830	833	835	838	*iso*-Pr CP
7	848	851	853	857	1-C_2-DMCH, *n*-Pr CP
8	864	866	870	873	E B_z, 3,3,4-TMH, 1,2,4-TMCH(*t*), 1,3,5-TMCH(*c*)
9	882	886	—	—	*m*, *p*-xylene
10	896	900	—	—	*o*-xylene
11	900	900	900	900	*n*-N
12	922	927	930	932	*iso*-Pr B_z, *iso*-Pr CH, 2,2,3-TMHp
13	934	938	942	945	*n*-Pr CH
14	940	944	946	949	*n*-BCP
15	952	—	—	968	*n*-Pr B_z
16	959	—	—	968	Dimethyloctanes
17	965	964	966	968	2-MN, 4-MN, 3-EO
18	977	980	984	988	1-M-2-E B_z, bicyclane
19	988	—	—	1000	1,3,5-TMB_z
20	1000	1000	1000	1000	*n*-D
21	1009	1012	1015	1020	Highly branched alkanes
22	1018	1023	—	—	Highly branched alkanes
23	1021	1023	1025	1025	2,2-DMN, 2,4-DMN

* Abbreviations: adamantane (A), butane/butyl/bi (B), benzene (B_z), *cis* (*c*), cyclo (C), di/decane (D), dodecane (dD), ethyl/ethane (E), heptane/hepta/heptyl (Hp), hexane/hexa/hexyl (H), *meta* (*m*), methyl (M), normal (*n*), nonane (N), octane/octa/octyl (O), *ortho* (*o*), *para* (*p*), pentane/penta/pentyl (P), propane/propyl (Pr), tri/tetra (T), *trans* (*t*), undecane (uD).

TABLE III

ANALYSIS OF FRACTION F_2

Peak No.	*Retention indices on SE-30*				*Identification**
	110°	*120°*	*130°*	*140°*	
18	978	982	—	988	1-M-2-E B_z, bicyclane
19	990	—	1000	1000	1,3,5-TMB_z
20	1000	1000	1000	1000	*n*-D
21	1008	1012	1016	1019	Highly branched alkanes
24	1020	1025	1028	1032	Monocyclanes
25	1033	—	—	—	1-M-2-*iso*-Pr B_z, 1,2,3-TMB_z, indane
26	1036	1040	1044	1048	1,2,4,5-TMCH(*t*)
27	1047	1053	1055	1056	1,2,4,5-TMCH(*c*), 1,3-DE B_z
28	1051	1056	1059	—	*n*-BB_z, 1-M-3-*n*-Pr B_z, monocyclane Highly branched alkanes
29a	1064	1065	1068	1069	2-MD
30a	1074	1073	—	—	3-MD
31a	1080	1078	1079	1080	Mono-substituted alkanes
32	1084	1086	1090	1096	2-M indane
33	1100	1100	1100	1100	*n*-uD
34a	1108	—	1108	1110	Branched alkanes
35a	1114	1117	1119	1123	Highly branched alkanes
36	1126	1130	—	1136	Highly branched alkanes

* Abbreviations as in Table II.

TABLE IV

ANALYSIS OF FRACTION F_3

Peak No.	*Retention indices on SE-30*				*Identification**
	110°	*120°*	*130°*	*140°*	
29b	1063	1069	1074	1079	1,2,3,4,5-PMCH, 1,3-DM-5-E B_z, 1-M-2-*n*-Pr B_z, bicyclanes
30b	1074	—	—	—	1,4-DM-2-E B_z, Naphthenes
31b	1080	1085	1089	1093	1,3-DM-4-E B_z
32	1085	—	—	1098	2-M indane
33	1100	1100	1100	1100	*n*-uD
34b	—	1104	1106	1109	1,2-DM-3-E B_z
35b	1113	1117	1120	1125	Adamantane, bicyclanes, highly branched alkanes
37	1118	1124	1128	1134	1,2,4,5-TM B_z, 1-MA
36	1130	1133	—	—	Highly branched alkanes
38	1135	1137	1140	1145	1,2,3,5-TM B_z
39	1143	1148	1152	1157	1,3,5-TMA
40	1150	1152	1152	—	5-MuD
41	1155	1160	1165	1168	1,2,3,4-TM B_z
42	1160	1165	1168	1173	Tetrahydronaphthalene, 3-MuD
43	1166	1175	1182	—	2-MA
44	1172	1183	1189	—	1,4-DMA
45	1180	1183	—	—	Branched alkanes
46	1188	1188	—	—	Branched alkanes
47	1200	1200	1200	1200	*n*-dD
48	1215	1214	1211	1216	Highly branched alkanes

* Abbreviations as in Table II.

Peak identification

More than 80 peaks and shoulders of kerosene were obtained, representing compounds in the C_7–C_{15} range. The identification and peak characterization were carried out by applying the above conditions and the results are given in Tables II–VII.

Peaks 4, 11, 20, 33, 47, 57, 69 and 73 are identified as *n*-alkanes on the basis of conditions (a) and (b), which was confirmed further by injecting a synthetic mixture for comparison.

The first and only peak with a retention index value of 745 at 110° on SE-30 was found to be alkenes on the basis of conditions (c) and (d).

Peaks 3, 16, 17, 21, 22, 23, 29a, 30a, 31a, 34a, 35a, 36, 40, 45, 46, 48, 52, 53,

TABLE V

ANALYSIS OF FRACTION F_4

Peak No.	*Retention indices on SE-30*				*Identification**
	130°	*140°*	*150°*	*160°*	
46	1186	1185	1185	–	Branched alkanes
47	1200	1200	1200	1200	*n*-dD
49	1209	1212	1215	1218	Monocyclanes
48	–	1216	–	–	Branched alkanes
50	1224	1227	1229	1232	Highly branched alkanes, monocyclanes
51	1230	1233	1235	–	Highly branched alkanes, monocyclanes
52	1239	1241	1243	1243	Branched alkanes
53	1251	1253	1252	1253	Branched alkanes
54a	1258	1260	1263	1269	Tricyclane
55	1267	1268	1269	1269	Methyldodecanes
56	1275	1275	1276	1278	Highly branched alkanes
57	1300	1300	1300	1300	*n*-TD

* Abbreviations as in Table II.

TABLE VI

ANALYSIS OF FRACTION F_5

Peak No.	*Retention indices on SE-30*				*Identification**
	130°	*140°*	*150°*	*160°*	
54b	1259	1260	1264	1268	Highly branched alkanes
58	1269	1270	1272	1280	Bicyclanes
59	1280	1280	1281	1286	Naphthenes
57	1300	1300	1300	1300	*n*-TD
60	1310	1312	1316	–	Naphthenes
61	1313	1313	–	1314	Branched alkanes
62	1322	1321	1324	1330	Tricyclanes
63	1333	1333	1340	–	Naphthenes
64	1339	1345	1349	1351	Bicyclanes
65	1350	1365	1362	1364	Highly branched alkanes
66	1356	–	–	–	Highly branched alkanes
67a	1367	–	–	–	Highly branched alkanes
68	1380	1379	1378	1379	Branched alkanes
69	1400	1400	1400	1400	*n*-TD

* Abbreviations as in Table II.

TABLE VII

ANALYSIS OF FRACTION F_6

Peak No.	*Retention indices on SE-30*				*Identification**
	130°	*140°*	*150°*	*160°*	
66	1359	1363	1366	1370	Highly branched alkanes
67b	—	1378	—	—	Naphthenes
70	1378	1380	1384	1387	Naphthenes
71	1393	1400	1408	1415	Tricyclanes
69	1400	1400	1400	1400	*n*-TD
72	1408	1415	1423	1432	2-*iso*-BA, tricyclanes
73	1424	1431	1443	1451	Highly branched alkanes, tricyclanes, 1-BA
74	1438	1444	1450	1457	Highly branched alkanes
75	1455	1461	1465	1468	Highly branched alkanes, tricyclanes, 2-BA
76	—	1467	1472	1476	Highly branched alkanes
77	—	1482	1483	1481	Monoalkyltetradecanes
78	1500	1500	1500	1500	*n*-PD

* Abbreviations as in Table II.

54b, 55, 56, 61, 65, 66, 67a, 68, 74, 76 and 77 represent highly branched alkanes, according to conditions (a) and (b).

Peaks 2, 5, 6, 7, 9, 10, 13, 14, 15, 18, 19, 24, 25, 26, 27, 29b, 30b, 31b, 32, 34b, 37, 38, 39, 41, 43, 44, 49, 54a, 58, 59, 60, 62, 63, 64, 67b, 70, 71 and 72 were characterized as alkyl aromatics and/or mono-, di- and tri-cyclic compounds on the basis of conditions (c) and (d).

Peaks 8, 12, 28, 35b, 42, 50, 51, 73 and 75 were shown to contain all types of hydrocarbons, according to condition (e).

Supporting information

The chromatograms of fractions F_1, F_2 and F_3 at 125° and 140° and of fractions F_4, F_5 and F_6 at 140° obtained on the TCEPE column, when compared with the chromatograms obtained on SE-30, showed considerable differences in the positions of peaks. The location of peaks for a particular compound on the two phases remains difficult if adequate retention index data are unavailable. Studies of such retention behaviour on the two phases have been carried out in order to give more detailed information.

Compounds that are eluted on TCEPE in the retention index ranges 800–1000 for fraction F_1 (Fig. 8), 1000–1100 for F_2 (Fig. 9), 1100–1200 for F_3 (Fig. 10), 1200–1300 for F_4 (Fig. 11), 1268–1400 for F_5 (Fig. 12) and 1370–1500 for F_6 (Fig. 13) are obviously branched alkanes. The $dI/15°$ values of all of the peaks from fractions F_1, F_2 and F_3 in these ranges are found to be very small, which further indicates the presence of these compounds.

The peaks that are eluted in the retention index range 1026–1411 at 125° for fraction F_1 clearly indicate the presence of 14 cyclic alkanes and alkylbenzenes. On the same basis, one can establish the presence of 11 and 12 compounds of such types in the retention index ranges 1132–1520 for fraction F_2 and 1232–1587 for F_3, respectively. The very high $dI/15°$ values further support these peak assignments.

The chromatograms of fractions F_4, F_5 and F_6 on TCEPE indicate the absence of aromatics, as otherwise retention indices above 1600, 1700 and 1800, respectively, from each of these three fractions would have been recorded. In fraction F_4, the retention indices on TCEPE from 1308–1385 for five peaks represent mono- and bicyclic alkanes. Tricyclic and polycyclic alkanes are considered to be absent, as retention indices above 1385 were not found. In fraction F_5 six peaks and in fraction F_6 five peaks in the retention index ranges 1421–1555 and 1516–1620, respectively, are considered to contain cyclic alkanes with one, two and three condensed rings.

Naphthalene, the first member of the polynuclear aromatics, expected to have a retention index of about 1200 on SE-30 at 130°, should be eluted in fraction F_2 or F_3, is considered to be absent as no peak retention index of 1700 or above on TCEPE was recorded for any of the six fractions (the expected ΔI value for naphthalene would be about 530). The numbers of peaks for all of the fractions on both phases are about the same, which implies the absence of multicomponent peaks. However, this statement is not strictly accurate as separation on an apolar phase cannot resolve multiplets that contain hydrocarbons of different structural types, whereas on a polar phase, adequate resolution of compounds of such types is achieved at the cost of poor separation of the corresponding saturated compounds.

Refinement of the method

The full potentialities of the extended retention index system could be achieved by collecting sharp preparative cuts on polar or apolar phases with no interfraction overlapping and obtaining GLC separations on open tubular columns of both phases.

An application of the extension of the "James–Martin Rule", as proposed by Ladon and Sandler[29], may be applied to determine the carbon numbers of all of the separated peaks, which will simplify peak characterization.

Quantitative analysis

Kerosene is a high-boiling mixture and there is no risk of collection losses occurring by evaporation during preparative chromatography. However, a loss of 10% is still incurred during total fraction collection, which is attributed to the use of syringes with which complete preparative injections could not be made because of a small degree of sample back-flushing.

The percentage composition of individual peaks could not be determined because of the difficulties in obtaining well resolved chromatograms on the analytical columns. The percentages of carbon number ranges or hydrocarbon component distributions from the preparative fractions F_1, F_2, F_3, F_4, F_5 and F_6 are 30.1, 18.4, 9.2, 7.68, 27.0 and 7.66, respectively. It is interesting to note that the kerosene sample contained 30% of the gasoline or naphtha fraction of petroleum.

CONCLUSION

When the retention index data for a large number of hydrocarbons of different types on polar and apolar phases are available, the analysis of complex samples by the proposed method will be more effective. In the future, GC may be considered as the most efficient method, especially in terms of its simplicity and low cost.

It is hoped that the present investigation will initiate the development of programmes to establish a systematic method for the identification of components of synthetic and natural complex mixtures.

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