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GAS CHROMATOGRAPHIC ANALYSIS OF COMPLEX HYDROCARBON MIXTURES

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SUMMARY

Kerosene fractions containing a wide variety of homologues and isomers of hydrocarbons of different types and complexities could be analyzed by gas chromatography on a squalane-coated open tubular column (50 m × 0.20 mm). The presence of unsaturated and saturated compounds up to a retention index (I) of 1150 was ascertained by using a mercury perchlorate post-subtraction column (1 ft. × $^1/_8$ in. O.D.) in series with an open tubular column, which could give only a tentative identification.

The temperature dependence of the retention indices (dI/dT) and the differences in retention indices on polar and non-polar phases (ΔI) have been considered as the basis of an extension of the Kováts retention index system, and this method of peak characterization of kerosene fractions has been investigated. SE-30 was used in a non-polar analytical column and I values were obtained at five isothermal column temperatures ranging from 130° to 170° in order to determine dI/dT values for all the peaks. For the determination of ΔI values, tetracyanoethylated pentaerythritol was used in a polar analytical column.

Positive and unambiguous characterization of the peaks has been made possible by using the above technique. The limitations of the present methods are discussed critically and schemes are suggested for improved analyses of complex hydrocarbon mixtures.

INTRODUCTION

In recent years, attempts have been made to standardize identification parameters for the precise identification and characterization of peaks in complex gas chromatograms[1-3]. In spite of the advances made in GC in combination with ancillary techniques, a number of problems in the unambiguous analysis of complex mixtures have yet to be solved. The potentialities of Kováts retention indices[4] for the characterization of peaks have been recognized by a number of workers[5-11]. Recently, a new approach has been demonstrated[12] for the improved separation and identification of petroleum naphtha by using an extension of the retention index system.

The object of the present investigation was to develop simple and reliable

methods for the unambiguous characterization of peaks in complex samples such as petroleum fractions without the need for pre-treatment or the addition of expensive pure reference compounds. Paraffins, naphthenes, bicyclic and polycyclic compounds, adamantanes and aromatics are the main constituents in kerosene[13-18] but their complete analyses have not so far been reported. The GC analysis of kerosene has mostly been restricted to normal paraffins[13,14,16] and hence it was used as sample in this study.

EXPERIMENTAL

The instrument used was a Varian Aerograph Model 600D gas chromatograph, equipped with a flame ionization detector and a Honeywell 2-mV recorder. A stainless-steel open tubular column (50 m × 0.20 mm I.D.) was coated with squalane by a technique developed in this laboratory. The injections were made with Hamilton micro-syringes. A glass subtraction column (1 ft. × $^1/_8$ in. O.D.) packed with mercury perchlorate coated on Chrom P was used in series with an open tubular column. The column temperature was maintained at 100°.

Two analytical columns (20 ft. × $^1/_8$ in. O.D.) were used. SE-30 on Gas-Chrom Q was used isothermally at several column temperatures ranging from 130 to 170° at 10° intervals for determining retention indices and their temperature coefficients for each separated peak on the chromatograms. Tetracyanoethylated pentaerythritol (TCEPE) was used as a polar column at 130°.

A sample of kerosene of boiling range 140–245° from the Barauni Oil Refinery was used, and methane and research-grade C_7–C_{14} n-paraffins were supplied by Phillips Petroleum Company, Oklahoma, U.S.A.

Hydrogen was used as the carrier gas and in the hydrogen flame. The oven temperature was controlled to within ± 0.5°. The injection point was marked by switching off the flame voltage. The gas hold-up time was determined by injecting pure methane.

The retention indices of the peaks and shoulders in the kerosene chromatograms for all three columns were measured with the help of peaks for normal paraffins present in the sample itself, which were previously located by injecting a synthetic mixture of n-paraffins under identical conditions. The retention indices on SE-30 were evaluated from the results published for squalane obtained graphically[19].

The linear plots of the adjusted retentions of normal paraffins *versus* carbon number were used as the basis of accurate instrumental and column performance.

PRINCIPLES OF THE EXTENSION OF THE RETENTION INDEX SYSTEM

Temperature dependence of retention index

The capability and limitations of using retention indices of solutes in a single liquid phase for characterizing GC peaks have been discussed elsewhere[12]. It has been shown by many workers[5,6,20-24] that the temperature variation of a retention index is a sensitive function of the chemical nature of a compound. Further studies on the relationship between *I* and *T* have been carried out on various solute and solvent combinations and showed the existence of a useful rectilinear relationship[1,21,23]. This result has been utilized in extrapolating retention data from one column temperature

to the other. The temperature coefficient of retention index (dI/dT) has been applied successfully as an identification parameter by many workers[6,7,24] for characterizing different types of hydrocarbons in light petroleum fractions. Depending on the nature of the stationary liquid, a classification of solutes into types[12] with strongly positive, medium positive, invariant and negative temperature coefficients is possible.

In Table I, dI/dT values of various types of hydrocarbons in polar and non-

TABLE I

VALUES OF $dI/10°$ OF HYDROCARBONS ON VARIOUS STATIONARY PHASES

Type of hydrocarbon	Squalane	SE-30	Apiezon L	CR-20W	TCEPE
Alkanes	0.2–2.5	0.2–2.6	—	(−)0.5–0.0	—
Mono-olefins	(−)0.1–(+)1.5	(−)0.5–1.5	—	(+)1.0–2.0	(−)0.5–0.0
Diolefins	0.25–0.8	(+)0.5–1.0	—	(+)3.0–5.0	(+)3.3–6.6
Cyclic olefins	1.0–2.5	2.5–3.0	—	2.0–0.0	—
Cyclic paraffins	2.0–3.0	2.0–3.0	—	—	—
Aromatics	2.0–3.0	2.8–3.5	—	—	—
Bicyclic paraffins	—	5.0–6.0	—	8.0–11.0	—
Tricyclic paraffins	6.0–7.5	7.0–9.0	7.0–11.0	11.0–16.0	16–30
Tetracyclic paraffins	—	—	12.0–0.0	—	33
Pentacyclic paraffins	—	—	14.5–16.0	—	—

polar phases are tabulated. By the application of dI/dT values, branched paraffins can be sub-classified into mono-, di-, tri- and tetra-substituted isomers[12], naphthenes into monocyclic, bicyclic, tricyclic and polycyclic, and aromatics into phenyl and biphenyl. Significant observations on dI/dT values and the structures of hydrocarbons have been discussed earlier[1]. Among naphthenes and aromatics, it has been shown that the number, nature and arrangement of rings exert a much stronger influence than alkyl substituents in the rings on dI/dT values. It has also been observed that dI/dT values are dependent on the nature and polarity of the liquid phase. There are considerable limitations to the use of dI/dT values for classifying hydrocarbons into types. For example, highly branched paraffins and cyclic olefins, cyclic paraffins and aromatics, and olefins and monoalkyl paraffins could not be distinguished by their dI/dT values.

Dependence of retention index on polarity

The difference in retention indices on polar and non-polar phases is denoted by ΔI. Some workers[25–27] plotted I values of various types of hydrocarbons in polar and non-polar phases and demonstrated "roofing tile" effects, representing the different types of hydrocarbons. The effect of the polarity of liquid phases on the retention of solute molecules has been used to give more positive information on peak characterisation. ΔI values for hydrocarbons of various types are collected in Table II. The alkyl paraffins, being non-polar and also not significantly polarizable, show very similar retention behaviours in both phases and therefore the contribution towards ΔI values is negligible. With polar liquids, the structure of the molecules influences the retention, while naphthenes, olefins, aromatics and hydrocarbons with condensed rings are polarizable, resulting in an interaction (Debye induction forces) which gives larger ΔI values, in order of their degree of polarisation. There are also many limita-

TABLE II

VALUES OF ΔI OF HYDROCARBONS ON DIFFERENT PHASES

Type of hydrocarbon	125°, $I_{TCEPE} - I_{Sq}$	125°, $I_{TCEPE} - I_{SE\text{-}30}$	150°, $I_{CW} - I_{SE\text{-}30}$
Alkanes	0.5	(−)5–(+)5	—
Mono-olefins	80–130	90–130	—
Diolefins	200–250	200–250	—
Cyclic olefins	150–200	150–200	—
Cyclic paraffins	60–100	60–100	60–70
Aromatics	400–425	400–430	325–350
Bicyclic paraffins	—	—	130–180
Tricyclic paraffins	200–300	200–250	200–250
Tetracyclic paraffins	300–350	300–350	—

tions to the use of the ΔI system for classifying hydrocarbons into types, which are discussed below.

When the efficacies of both extensions to the retention index system (dependence on temperature and polarity) are considered together, positive and unambiguous characterization of disputed peaks is possible. The two systems are therefore complementary and can be considered in terms of the following illustrations.

(1) Alkyl paraffins can easily be distinguished from other types of hydrocarbons by using the ΔI system but their further classification into sub-groups (mono-, di-, tri- and tetra-substituted alkanes) is possible only by dI/dT studies.

(2) Cyclic paraffins, cyclic olefins, aromatics and highly branched paraffins can be easily classified into their respective groups by using the ΔI system. The dI/dT method has great limitations here, as discussed above.

(3) Cyclic paraffins cannot be distinguished from mono-olefins, nor cyclic olefins from bicyclic compounds, by means of ΔI values, while dI/dT studies are highly useful in these classifications.

(4) Mono-olefins, diolefins and acetylenes can be characterized easily from the large differences in their ΔI values. The dI/dT system, although inapplicable in these instances, is very useful in distinguishing highly branched and non-branched olefins.

RESULTS AND DISCUSSION

Open tubular column

The kerosene sample was injected into the squalane open tubular column and the chromatogram obtained is shown in Fig. 1. The retention indices of all the peaks and shoulders were calculated nomographically[28]. Although the boiling range of kerosene is high and compounds up to C_{15} are present, gas chromatograms for compounds up to n-C_{13} were obtained. Hydrocarbons above n-C_{13} were not eluted from the open tubular column due to two reasons: (1) the hydrocarbon content of the capillary effluent in that range may not be sufficient and may also be too broadened for an instrumental response to be displayed; (2) the isothermal column temperature of 100° may not be suitable for eluting higher boiling hydrocarbons.

Programmed-temperature operation, although useful in complex analyses, could not be used owing to the difficulty in obtaining reproducible results. The selec-
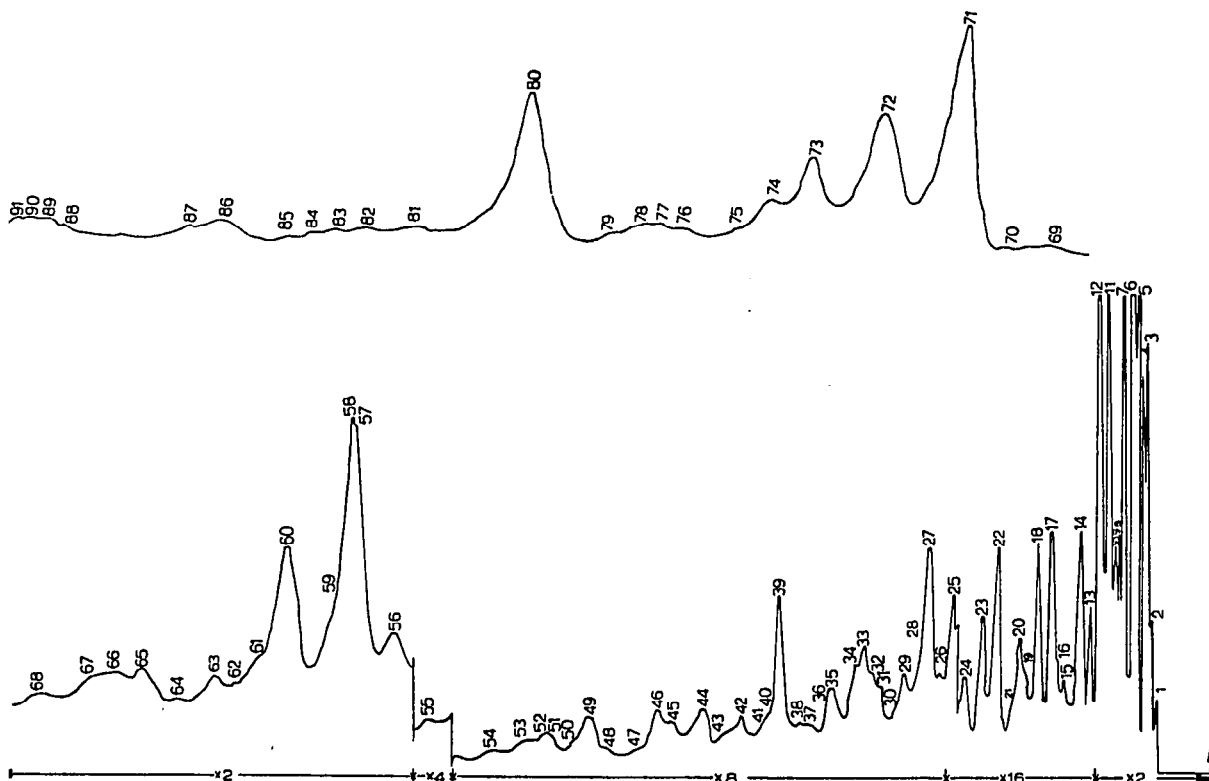
Fig. 1. Chromatogram of a kerosene sample on a squalane open tubular column at 100°.

tion of an isothermal column temperature higher than 100° is not advisable as squalane may be lost from the open tubular column.

About 90 peaks and shoulders of kerosene were obtained in the range n-C_7 to n-C_{13}, and the retention indices were determined with an accuracy of $\pm$ 1 unit. A large number of hydrocarbon components of different types may be involved in each peak if I values alone are considered. In order to characterize the peaks as saturated or unsaturated compounds, a subtraction column was fitted with the squalane capillary and the same kerosene sample was injected (3–4 μl).

Subtraction column

A column ($^1/_8$ in. O.D.) of mercury perchlorate developed in this laboratory[7] was used as a post-subtraction column after the capillary and successfully subtracted olefins and aromatics quantitatively. The sudden change in diameter of the columns from capillary to analytical considerably affected the sharpness of the peaks. The widening of peaks was increased with the longer retentions of the hydrocarbon components, resulting in non-elution of peaks with retention indices above 1130 in the dual column. By comparing the retention indices values and heights of the peaks with respect to normal paraffins for both columns (with and without subtraction), the type of hydrocarbons could be ascertained up to the peak index of 1130. The identification

TABLE III

CHARACTERISTICS OF PEAKS FROM THE KEROSENE FRACTION OBTAINED FROM
THE OPEN TUBULAR COLUMN IN SERIES WITH THE SUBTRACTION COLUMN

Peak No.	$^{100°}_{I_{Sq}}$	Type of hydrocarbon*	Tentative identifications*
1	700	Uns./sat.	n-Hp; Hp-2(t); 3-MH-2(c); 3-EP-2
2	714	Uns.	2,2-DMH-3(c)
3	725	Uns.	5,5-DMH-2(c); 2,4-DMH-3(c); 4,4-DMH-1; 4,M 3EP-1
4	736	Sat.	2,4-DMH; DCPr methane; 2,2,3,3-TMB; MCH; 1,1,3-TMCP
5	750	Uns.	3-M2-E P-1; 2,5-DMH-2; 3,5 DMH-2
6	763	Uns.	Tol; 3,4-DMH-2(t); 3,4,4-TMP-2(c)
7	792	Sat.	2,2,4-TMH; 1-c₂t₃TMCP
8	800	Sat.	n-O; 1-Mc₃ ECP; 1-Et₂ MCP; 1-Et₃MCP; 1-t₄ DMCH
9	830	Uns.	3-M1:7 O-diene; 2,4-DMH-1
10	835	Uns.	3-MO-1; 4-M, 1:7 O-diene
11	850	Uns.	E Bᵤ; 6-MO-1; 7-MO-1
12	868	Sat./uns.	m,p-Xyl; 2-MO-1; 1,3,5-TMCH(c); 2-MO; 4-MO
13	881	Uns.	o-Xyl; N-1
14	900	Sat.	n-N; 2,2,4-TMHₚ; 1,1,2-TMCH; 2,5-DM 2,3-DEH; 2,2,4,4-TMH
15	920	Sat.	4,4-DMO; 2,2,3-TMHₚ; 2,2-DMO; 1,2,3-TMCH(c)
16	928	Sat.	2,3,4,5-TMH; 2,4-DM 2,3-iso-Pr P; 5-M3-E Hp; 4-iso-Pr Hp
17	936	Sat.	iso-Pr CH; 2,4-DM 2,3-DEH; 4,5-DM 2,3-DEH; 1,2,4,5-TMCH
18	950	Uns.	m,p-E Tol
19	963	Sat.	4-MN; 2-MN; bicyclane
20	967	Uns.	1,3,5-TMBᵤ; o-E Tol
21	973	Sat.	E-CHp; 3-MN; 1-M4 iso-Pr CH(c)
22	988	Uns.	D-3; 1,2,4-TMBᵤ
23	1000	Sat.	n-D; 1,3-DECH
24	1010	Uns.	1,2,3-TMBᵤ; 1-M4 iso-Pr Bᵤ
25	1018	Uns.	Indane; 1-M2 iso-Pr Bᵤ
26	1027	Sat.	2,5-DMN
27	1032	Uns.	1-M 3n-Pr Bᵤ; n-BBᵤ; m,p,di-Eth Bᵤ
28	1038	Sat.	n-P Cp
29	1046	Uns.	1-M2n-Pr Bᵤ; o-DE Bᵤ
30	1052	Sat.	5-MD; 4-EN
31	1058	Sat.	4-MD
32	1062	Sat.	Bicyclane; 2-MD
33	1065	Uns.	1,3-DM 4E Bᵤ; 1-M indane
34	1070	Sat.	3-MD; decalin(t)
35	1079	Uns.	1,2-DM 4E Bᵤ
36	1080	Uns.	1,3-DM 4E Bᵤ
37	1087	Sat.	A
38	1093	Sat.	4,5-DEO; 1,2,3,4,5-PMCH
39	1100	Sat.	n-uD
40	1104	Sat.	Unidentified
41	1106	Sat.	Unidentified
42	1110	Sat.	1-MA
43	1114	Sat.	4-E 5-MN; decalin(c)
44	1121	Uns.	5-M indane; 1-E 2-n-Pr Bᵤ
45	1130	Sat.	1,3-DMA; 5,6-DMD; dicyclopentyl
46	1136	—	1,2,3,4-TMBᵤ; n-pentyl Bᵤ
47	1140	—	Tetrahydronaphthalene; 1,3,5-TE Bᵤ
48	1147	—	1-M, 2-n-BBᵤ; 1,3,5-TMA; 4-ED

TABLE III *(continued)*

Peak No.	$I_{sq}^{100°}$	Type of hydrocarbon*	Tentative identifications*
49	1152	—	Naphthalene; 6-MuD
50	1155	—	5-MuD; 5-ED
51	1161	—	4-MuD
52	1162	—	1,2,5,7 MA; 2-MuD
53	1168	—	2-MA; 2-MuD; 1,2,4-TEB$_z$
54	1173	—	3-MuD
55	1185	—	1,2,3,4,5,6-HMCH
56	1191	—	1,2,3-TECH
57	1198	—	1,2,3-TEB$_z$; 4,6-DMuD
58	1200	—	*n*dD;
59	1205	—	3,5-DMuD
60	1210	—	2,5-DMuD; 2,6-DMuD
61	1216	—	2,7-DMuD
62	1218	—	2,8-DMuD
63	1223	—	*n*-H B$_z$; 5,6-DMuD
64	1226	—	(Homo)A; 2,10-DMuD
65	1231	—	4,5-DMuD
66	1234	—	1-EA; 2,9-DMuD
67	1238	—	Unidentified
68	1245	—	1-E 3-MA; 3,4-DMuD
69	1251	—	6-MdD; 5-MdD; 2,3 DMuD
70	1258	—	2-EA; 4-MdD
71	1263	—	1-E 3,5DMA; 2-MdD
72	1271	—	1-E 3,5,7 TMA
73	1276	—	3MdD
74	1281	—	Unidentified
75	1283	—	*n*-OCP
76	1288	—	Unidentified
77	1289	—	Unidentified
78	1291	—	Unidentified
79	1294	—	Tetracyclo-dD
80	1300	—	*n*-tri-D
81	1309	—	Dicyclohexyl
82	1312	—	Unidentified
83	1313	—	Unidentified
84	1315	—	*n*-Hp B$_z$
85	1317	—	2-*iso*-Pr A
86	1322	—	1-Pr A
87	1324	—	Unidentified
88	1331	—	1-iso-Pr A
89	1332	—	Unidentified
90	1334	—	Unidentified
91	1336	—	2-Pr A

* Abbreviations: adamantane (A), butane/butyl/bi (B), benzene (B$_z$), *cis* (*c*), cyclo (c), di (D), ethyl/ethane (E), dodecane (dD), heptane/hepta/heptyl (Hp), hexane/hexa/hexyl (H), *meta* (*m*), methyl (M), normal (*n*), nonane (N), olefins/octane/octa/octyl (O), *ortho* (*o*), *para* (*p*), pentane/penta/pentyl (P), propyl/propane (Pr), saturates (sat.), toluene (tol), tri/tetra (T), *trans* (*t*), undecane (uD), unsaturates (Uns.), xylene (xyl).
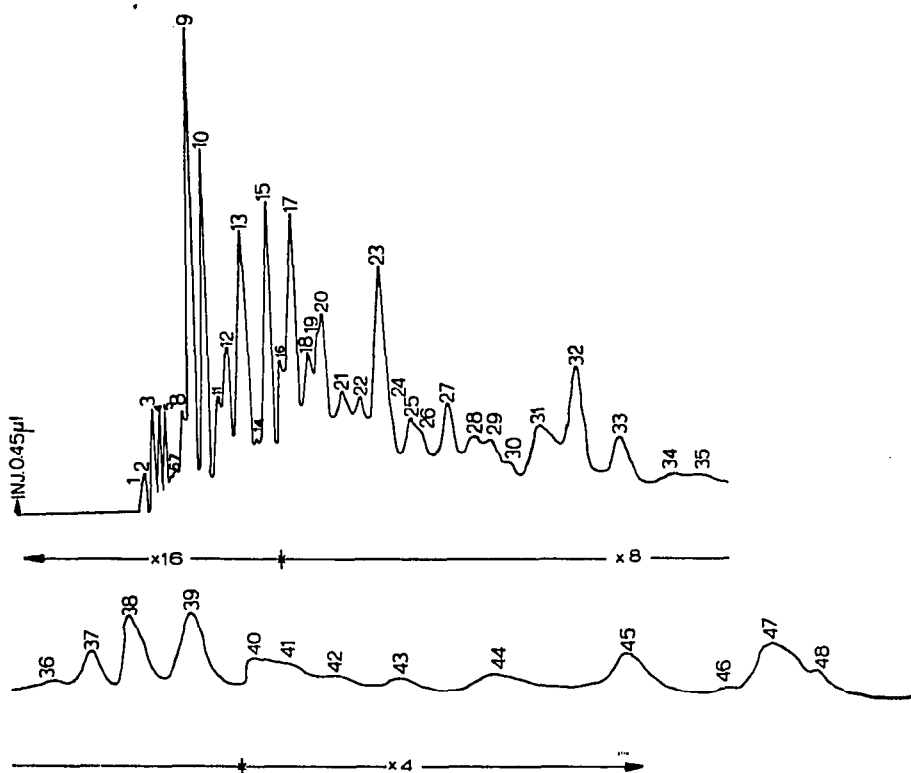
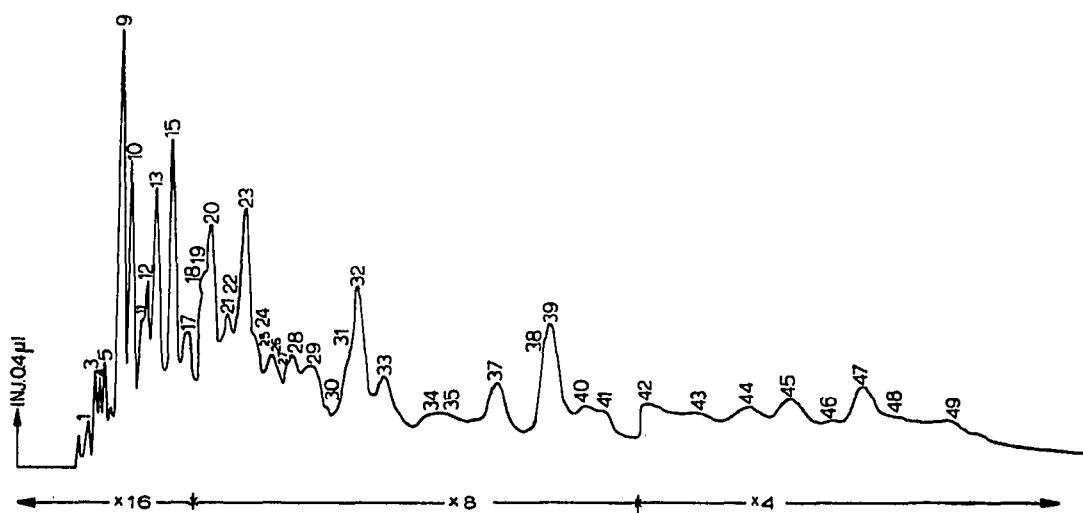Fig. 2. Chromatogram of a kerosene sample on SE-30 at 130°.

Fig. 3. Chromatogram of a kerosene sample on SE-30 at 140°.
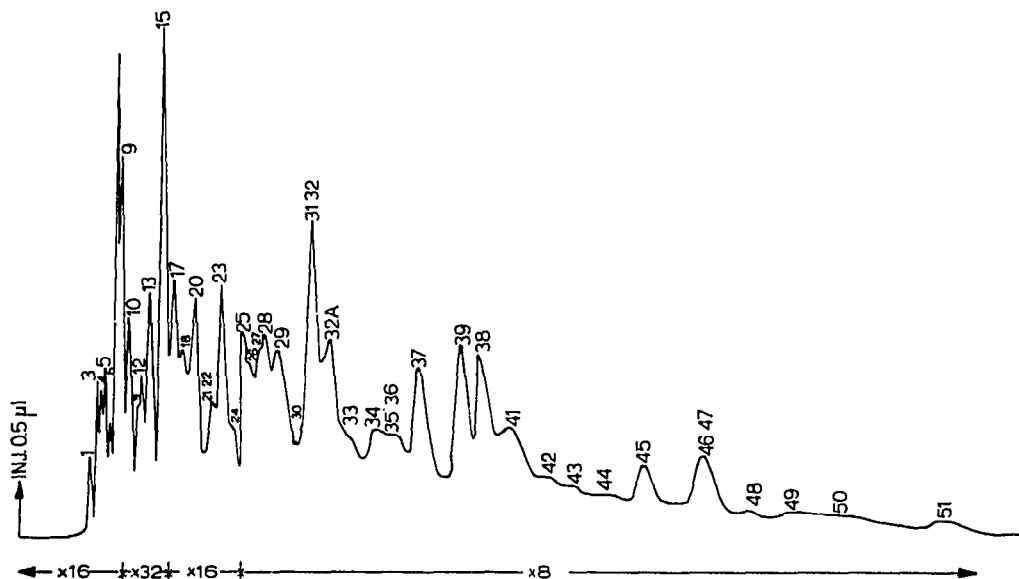
Fig. 4. Chromatogram of a kerosene sample on SE-30 at 150°.

of the type of hydrocarbons present in the retention index range from 1130 to 1336 thus posed a great problem.

Tentative identifications of the peaks from the kerosene fraction are given in Table III. The great limitation of the subtraction column is its inability to distinguish olefins from aromatics. When a peak has been assigned to represent saturated com-

Fig. 5. Chromatogram of a kerosene sample on SE-30 at 160°.

pounds after verification through subtraction, the difficulties of distinguishing paraffins from naphthenes still exist.
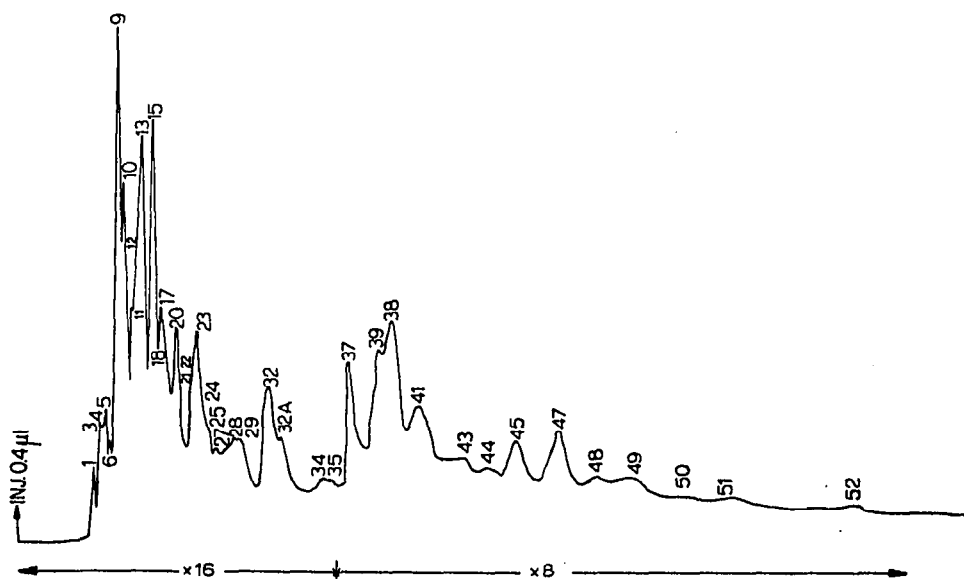
Analytical columns

The extensions of the retention index system (dI/dT and ΔI) were applied using both the non-polar and polar analytical columns for positive identifications.

Non-polar column. In GLC, squalane is the most widely used non-polar phase, as large numbers of retention indices for various types of hydrocarbons with boiling points up to 150° are available in the literature[21,29]. The practical working range of this phase is up to 140° and hence it has been used mostly in analyzing low-boiling petroleum fractions. It has been found in this laboratory[30] and elsewhere[31] that squalane is oxidised when it is stored or used for some time, which results in a change in retention indices restricted specifically to aromatics. The changes in I values for saturated compounds, olefins and naphthenes have been found to be negliglible. As kerosene is a complex mixture of C_7 to C_{15} hydrocarbons and considering the limitations of squalane, it was felt to be worthwhile to select another non-polar phase with a higher working temperature range, well defined and giving good reproducibility of results. Apiezon[32], although having a high working temperature range, was rejected as it is not well defined and pure, which in turn may give non-reproducible results. SE-30, being well defined and giving reproducible results, was chosen, especially as retention indices for lower and higher hydrocarbons are available in the literature[19,23,27,33].

Multiple column temperature. The importance of dI/dT values in the identification of GC peaks has already been discussed by a number of workers[6,7,20,21]. The chromatograms of the kerosene fraction at five isothermal column temperatures (130, 140, 150, 160 and 170°) were obtained on SE-30 (Figs. 2–6). The retention indices for
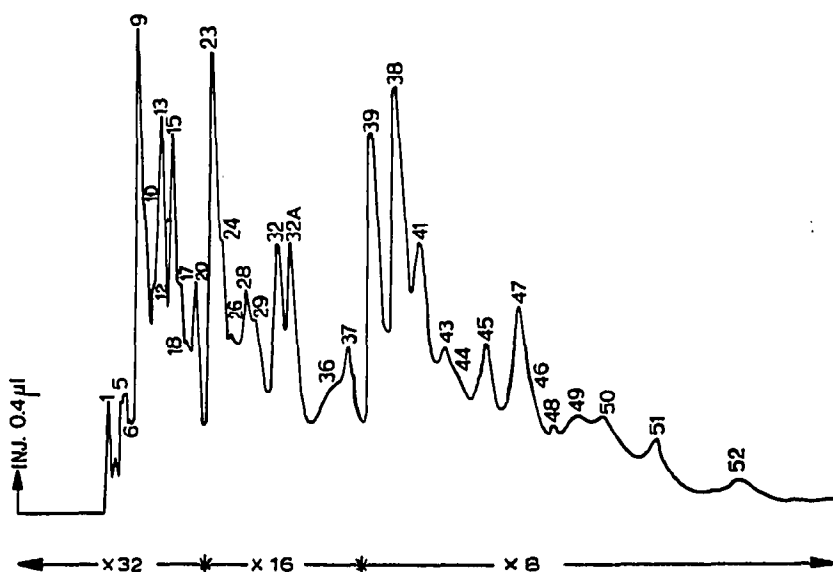

Fig. 6. Chromatogram of a kerosene sample on SE-30 at 170°.

all the peaks and shoulders were calculated by Hupe's method[28]. The matching of peaks for all the chromatograms and ascertaining their dI/dT values require skill and experience. The choice of a 10° interval in the column temperature to determine $dI/10°$ values for all the peaks has great significance in peak matching. The interval of 15–25° in the column temperature for studying dI/dT values of peaks in naphtha or gasoline did not give rise to any difficulties due to the fact that the $dI/10°$ values in non-polar liquids for aromatics and naphthenes are found to be in the range 2–3. On the other hand, kerosene is a complex mixture of polyaromatic and polynaphthenic compounds which have $dI/10°$ values in the range 7–16 in non-polar phases. The high temperature coefficients of the components in kerosene are mainly responsible for the inconvenience in peak matching of SE-30 chromatograms.

Polar column. It has been found that stationary liquids that contain strongly polar groups, such as nitriles, selectively retard the retention of naphthenes, olefins and aromatics. Of nitrile phases, although 1,2,3-tris-(2-cyanoethoxy)propane (TCEP) has been found to be more suitable, tetracyanoethylated pentaerythritol (TCEPE) was used because of the non-availability of TCEP in this laboratory. An isothermal temperature of 130° was maintained in the TCEPE column in order to obtain the chromatogram of the kerosene fraction (Fig. 7). The retention indices of the separated peaks
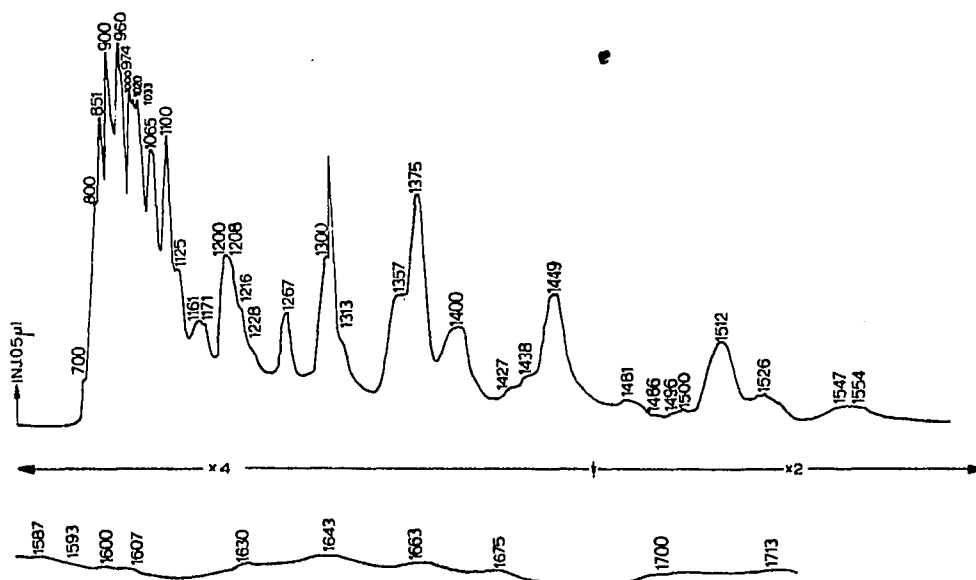
Fig. 7. Chromatogram of a kerosene sample on TCEPE at 130°.

are displayed on the chromatogram. On comparing the chromatograms on SE-30 and TCEPE at 130°, much valuable information regarding peak identification was obtained. Compounds eluting in the range 1500–1730 from the retention index range of 700–1730 on TCEPE represent hydrocarbons other than saturated paraffins. Peak retention indices of 974, 1033 and 1065 on TCEPE and their absence on SE-30 at

130° shows conclusively the presence of substances other than saturated compounds, but these peaks cannot represent aromatics, as otherwise peak indices less than 700 on SE-30 would have been obtained. Hence these compounds can only be naphthenes. Aromatics and polycyclic compounds or adamantanes cannot be present in the retention index range 1350–1500 on SE-30, otherwise peaks with retention indices greater than 1713 would have appeared on TCEPE. The polar TCEPE column therefore gives complementary information for the identification of peaks obtained on SE-30.

Basis of peak identification

A large number of probable hydrocarbon components of different types may be present in a peak when its retention index is simply compared with the reported literature value. The use of the extension of the retention index system, based on classification by compound types, is more useful:

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

(b) after following condition (a), the study of dI/dT values on a non-polar phase reflects the distribution between non-branched and highly branched paraffins;

(c) when the I values of peaks on a non-polar phase are absent in a polar phase, the peaks represent compounds other than saturated paraffins, such as olefins, naphthenes and aromatics;

(d) after following condition (c), the dI/dT value on a non-polar phase is easily applicable in distinguishing olefins, naphthenes and aromatics.

Identification of peaks

The separation and identification of the components in the kerosene sample were carried out mainly on the non-polar SE-30 phase and the results of the qualitative analysis listed in Table IV are given strictly on the basis of the extended retention index system.

Peaks 1, 5, 10, 15, 23, 32, 39, 47 and 52 on SE-30 are identified as normal paraffins on the basis of conditions (a) and (b). These peak identifications were further confirmed by injecting a synthetic mixture of n-paraffins. The plot of corrected retention distance against carbon number was used for determining the retentions of higher n-paraffins.

Peaks 2 and 3 on SE-30 were found to represent olefins on the basis of conditions (c) and (d).

Peaks 4, 6, 7, 9, 11, 12, 14, 16, 18, 19, 20, 21, 22, 24, 25, 27, 31, 34, 35, 37, 38, 41, 42, 43, 46, 48 and 49 on SE-30 may represent aromatics and/or naphthenes (mono-, bi-, tri- or poly-cyclic compounds or adamantanes) on the basis of conditions (c) and (d).

Peaks 8, 13, 17, 26, 28, 29, 30, 32A, 33, 36, 40, 44, 45 50 and 51 could represent highly branched paraffins on the basis of conditions (a) and (b).

Limitations and suggested scheme

The full potentialities of the extended retention index system could not be achieved for the following reasons:

(a) because of the use of analytical columns of low efficiency; this may be overcome by using open tubular columns with both polar and non-polar phases.

TABLE IV

CHARACTERIZATION OF PEAKS FROM FIVE ISOTHERMAL CHROMATOGRAMS OF KEROSENE ON SE-30 ANALYTICAL COLUMN

Peak No.	$I_{130°}$	$I_{140°}$	$I_{150°}$	$I_{160°}$	$I_{170°}$	Refined identifications*
1	700	700	700	700	700	n-Hp
2	717	—	—	—	—	3MH-2(c)
3	752	752	751	752	—	3,4,4 TMP-2
4	772	776	778	781	785	Tol
5	800	800	800	800	800	n-O
6	822	—	829	833	836	1-C_2C_3 TMCP; 1-T_3 DMCH; 1-C_4 DMCH
7	835	837	—	—	—	iso-Pr CP
8	851	—	—	—	—	Saturated paraffins
9	868	872	875	877	880	EB_z; 1,3,5-TMCH(c)
10	900	900	900	900	900	n-N
11	929	932	935	937	940	iso-Pr B_z
12	943	946	948	950	952	n-Pr CH
13	964	966	965	967	968	2-MN; 3-EO
14	986	—	—	—	—	1,3,5-TM B_z
15	1000	1000	1000	1000	1000	n-D
16	1015	—	—	—	—	sec.-B B_z
17	1026	1025	1025	1024	1026	2,2 D-MN; 2,4 DMN
18	1035	—	1040	1043	1045	1,2,4,5-TMCH(t)
19	1050	1054	—	—	—	1,2,4,5-TMCH(c)
20	1057	1060	1062	1063	1066	n-B B_z; 1-M_3 n-Pr B_z
21	1073	1080	1085	1089	—	1,2,3,4,5-PMCH; 1,3DM 5 EB_z; 1-M 2-n-Pr B_z; Bicyclanes
22	1081	1080	1085	1089	—	2-M indane; 1,4-DM 2-E B_z
23	1100	1100	1100	1100	1100	n-uD
24	1108	1110	1113	1115	1119	1,2-DM 3-EB_z
25	1120	1128	1131	1130	—	Adamantane; bicyclanes
26	1128	1134	1138	—	1137	Highly branched sat. para
27	1139	1144	1149	1150	—	1,2,3,5-TM B_z
28	1158	1158	1156	1157	1158	5-MuD
29	1163	1164	1166	1166	1167	2MuD; 4MuD
30	1172	1176	1181	—	—	Methyl undecanes
31	1187	1192	1200	—	—	2-MA
32	1200	1200	1200	1200	1200	n-doD
32A	—	—	1210	1215	1217	Highly branched sat. para
33	1218	1222	1227	—	—	Highly branched sat. para
34	1236	1243	1247	1255	—	1,2-DEA
35	1244	1251	1258	1265	—	Spiro (A; 2,1-cyclo-Pr)
36	1265	—	1265	—	1265	M doD
37	1276	1278	1278	1280	1280	Aromatics
38	1286	1295	1306	1312	1320	Bicyclanes; 2-EA; (peak inversion)
39	1300	1300	1300	1300	1300	n-C_{13}
40	1313	1313	—	—	—	Sat. para
41	1320	1322	1326	1328	1339	Tricyclane
42	1330	1336	1341	—	—	para-Hydroanthracene; tricyclane
43	1338	1344	1349	1353	1358	Bicyclanes
44	1362	1365	1367	1367	1368	Highly branched sat. para
45	1378	1380	1382	1380	1385	Highly branched sat. para
46	1388	1394	1400	—	1410	Bicyclane (peak inversion)
47	1400	1400	1400	1400	1400	n-C_{14}

TABLE IV *(continued)*

Peak No.	$I_{130°}$	$I_{140°}$	$I_{150°}$	$I_{160°}$	$I_{170°}$	Refined identifications*
48	1408	1412	1415	1418	1420	Bicyclanes
49	—	1422	1428	1432	1436	Bicyclanes
50	—	—	1435	1441	1445	Highly branched sat. *para*
51	—	—	1465	1466	1465	Some monoalkyl *para*
52	—	—	—	1500	1500	n-C_{15}

* Abbreviations as in Table III.

(b) I and dI/dT values of hydrocarbons are not available to a great extent in the literature for polar phases such as ODP[12], TCEP and TCEPE.

(c) the non-availability of I values on non-polar phases of higher hydrocarbons boiling above 150°; relative retention data for higher hydrocarbons, although available, are not reliable.

As discussed earlier[12], the preparative fractionation of such complex samples is

Kerosene (700–1500 retention index range)

Preparative GC on SE-30
Fractions collected according to
retention index ranges of 100
units

700–800 800–900 900–1000 1000–1100 1100–1200 1200–1300 1300–1400 1400–1500

A B

Open tubular SE-30
at multiple column
temperatures

Types of hydrocarbons
by comparing dI/dT
values

Open tubular TCEP at a
single column temperature

700–800	800–900	900–1000	1000–1100	1100–1200
Saturates	Olefins or naphthenes	Cyclic olefins, diolefins or bicyclic olefins	Polycyclics, or adamantanes	Aromatics

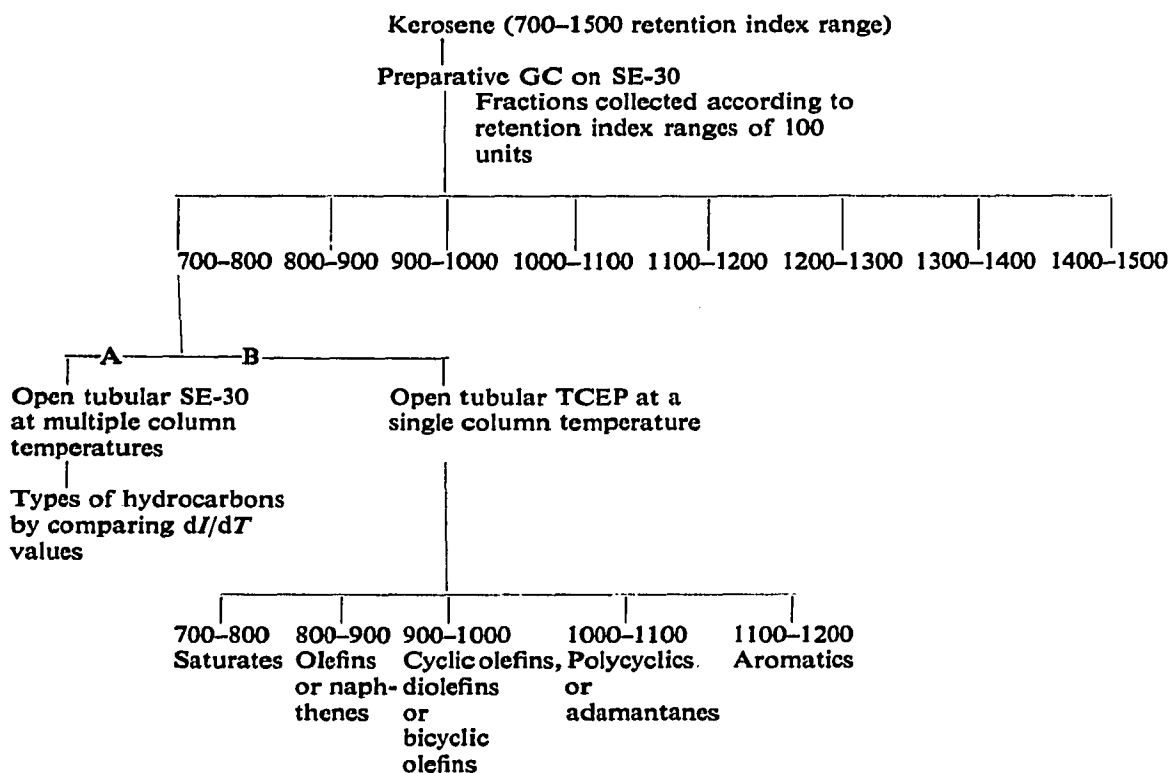Fig. 8. Procedure for the separation of kerosene fraction. Scheme I: single preparative. Notes: (1) The other preparative fractions are treated in the same manner as the preparative fraction 700–800. (2) Procedure (A) is not essential if I and dI/dT values of a large number of hydrocarbons on TCEP are available. (3) Further sub-classification is possible by the use of dI/dT values on TCEP.

essential but base-line separation is difficult to achieve on polar phases. The obvious use of polar phases in preparative columns remains as long as more retention data on polar phases are not available. This limitation may be overcome by double prepara- tive GC fractionation, which is not practicable for quantitative analysis. Considering the above limitations, two schemes (see Figs. 8 and 9) have been suggested which may

```
                    Kerosene
                    |   700-1500
                    |   retention index range
                    Preparative GC
                    |   Fractionation on
                    |   SE-30
          ----------------------------------------
          |                                      |
      700-1000                              1000-1500
          |                                      |
   Preparative GC                        Preparative GC
   on TCEPE                              on TCEPE
                                              |
   ----------------------------------------------------------------------------------
   |         |          |          |          |          |          |          |
1000-1100 1100-1200 1200-1300 1300-1400 1400-1500 1500-1600 1600-1700 1700-1800
                                              |
                                   Open tubular SE-30
                                   at multiple column temperatures
                                              |
   --------------------------------------------------------------------------
   |         |              |              |                          |
1000-1100 1100-1200     1200-1300      1300-1400                  1400-1500
Aromatics Polycyclics    Cyclic olefins  Olefins                   Saturates
          or             or             or
          Adamantanes    diolefins      naphthenes
                         or
                         Bicyclic olefins
```
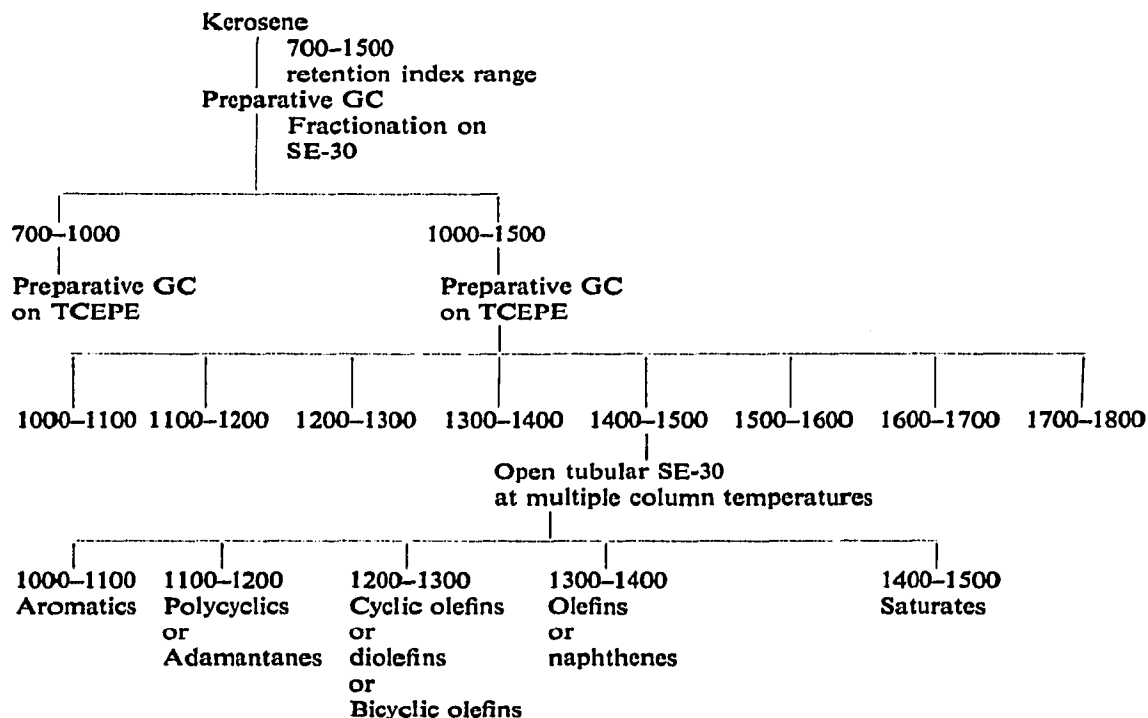
Fig. 9. Procedure for the separation of kerosene fraction. Scheme II: double preparative. Notes: (1) The other preparative fractions are treated in the same manner as fraction 1400–1500. (2) Further sub-classification is possible by the use of dI/dT values obtained on the SE-30 column. (3) Scheme II is preferable as retention index data on SE-30 are available.

give improved separations and refined identifications. In this laboratory work along these lines is in progress.

The future availability of I and dI/dT values on polar phases will definitely enhance our knowledge of the utilization of the extended retention index system in gas chromatography.

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