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USE OF CAPILLARY GAS CHROMATOGRAPHY IN COLLECTING RETENTION AND CHEMICAL INFORMATION FOR THE ANALYSIS OF COMPLEX PETROCHEMICAL MIXTURES

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SUMMARY

A combined peak identification method is described for the analysis of aromatics in complex petrochemical mixtures. The method is based on both retention and chemical information on both authentic and generated hydrocarbons. The retention information is collected in the form of I , ΔI , and di/dT values, while the chemical information is obtained from pre-injection reactions. On the basis of this information the molar mass and the subtype of the hydrocarbons can be determined and, in more detail, a full component analysis can be achieved for all aromatics up to C_9 and for all alkylbenzenes up to C_{10} . The method offers a comprehensive identification of the aromatics in pyrolysis and fluid catalytically cracked naphthas.

INTRODUCTION

There are questions regarding the analysis of complex petrochemical mixtures that require very refined gas chromatographic (GC) methods and ancillary techniques. However, it is possible to use a combination of conventional or partly novel but simple techniques to obtain adequate answer to even very difficult questions in petroleum technology.

The aim of this paper is to contribute to these ancillary techniques by demonstrating that unsaturated hydrocarbons have versatile reaction capabilities that offer sources of chemical information that have apparently not previously been fully utilized. Of course, there are many tentative and refined retention-structure correlations for hydrocarbons in the literature, but their analytical power can probably be increased by combination with such chemical information. This is all the more reasonable as these kinds of ancillary techniques are available in practically any "chemically oriented" GC laboratory.

Pyrolysis naphtha (PN) and fluid catalytically cracked naphtha (FCCN) are complex hydrocarbon mixtures and are therefore good models. However, their analysis has not been reported frequently in the literature. A detailed component analysis of PN using GC-mass spectrometry has been described^{1,2}, but no reference is available to FCCN. The tentative hydrocarbon-type analysis described the two papers cited appears very useful, but the information on isomers is poor.

TABLE I

RETENTION INDICES OF HYDROCARBONS ON SE-30 AND PEG 20M AT 70°C, THEIR TEMPERATURE COEFFICIENTS AND CALCULATED M^* VALUES AND THEIR DIFFERENCES (Δ) FROM THE TRUE VALUES

No.	Comments*	Compound	SE-30		PEG 20M		M^*	Δ
			I	$\frac{dI}{dT}$	I	$\frac{dI}{dT}$		
1	P f	Benzene	657.1	0.20	954.5	0.29	77	-1
2	P F	Toluene	759.9	0.20	1049.5	0.35	92	0
3	P F	Ethylbenzene	851.4	0.21	1131.9	0.47	105	-1
4	P F	<i>m</i> -Xylene	859.6	0.20	1145.3	0.46	106	0
5	P F	<i>p</i> -Xylene	860.8	0.22	1138.9	0.49	107	+1
6	p	Ethynylbenzene	862.1	0.12	1357.2	0.17	95	-7
7	p	5-Vinyl-2-norbornene (<i>endo</i>)	877.9	0.30	1067.1	0.58	114	-6
8	P	Styrene	877.8	0.23	1255.1	0.47	104	0
9	P F	<i>o</i> -Xylene	882.2	0.26	1185.7	0.57	109	+3
10		5-Ethylidene-2-norbornene	908.2	0.22	1106.8	0.45	118	-2
11	g	2-Ethylnorbornane (<i>exo</i> ?)	915.9	0.33	1015.1	-	125	+1
12	g	2-Ethylnorbornane (<i>endo</i> ?)	919.9	0.39	1020.2	0.52	124	0
13	p f	Isopropylbenzene	911.3	0.24	1176.9	0.47	115	-5
14	p	Allylbenzene	932.6	0.31	1263.2	0.49	114	-4
15	p F	<i>n</i> -Propylbenzene	941.8	0.25	1210.1	0.52	119	-1
16	P F	1-Methyl-3-ethylbenzene	949.0	0.24	1224.9	0.55	119	-1
17	P F	1-Methyl-4-ethylbenzene	950.6	0.25	1223.4	0.53	120	0
18		<i>trans</i> -Hexahydrindan	949.8	0.45	1059.3	0.76	129	+5
19	P F	1,3,5-Trimethylbenzene	956.2	0.23	1242.2	0.57	120	0
20	p g	3-Methylethynylbenzene	960.5	0.21	1450.9	0.36	109	-7
21	P F	1-Methyl-2-ethylbenzene	964.6	0.29	1258.4	0.55	121	+1
22	P	α -Methylstyrene	966.4	0.30	1320.9	0.61	117	-1
23	p g	4-Methylethynylbenzene	965.9	0.23	1454.3	0.35	110	-6
24	P	<i>cis</i> - β -Methylstyrene	975.3	0.24	1324.3	0.51	119	+1
25	P	3-Methylstyrene	977.0	0.26	1348.1	0.62	118	0
26	P	2-Methylstyrene	977.5	0.26	1342.2	0.68	118	0
27	P F	1,2,4-Trimethylbenzene	977.5	0.28	1277.6	0.57	122	+2
28		<i>tert</i> -Butylbenzene	980.0	0.30	1237.5	0.51	125	-9
29		<i>cis</i> -Hexahydrindan	980.9	0.50	1107.3	0.85	132	+8
30	P	4-Methylstyrene	980.5	0.33	1348.6	0.63	119	+1
31		Isobutylbenzene	994.3	0.28	1241.3	0.52	127	-7
32		<i>sec</i> -Butylbenzene	997.0	0.30	1248.1	0.55	128	-6
33	p F	1,2,3-Trimethylbenzene	1006.0	0.39	1325.4	0.72	125	+5
34	g	1-Methyl-3-isopropylbenzene	1006.6	0.22	1266.5	0.46	128	-6
35	g	1-Methyl-4-isopropylbenzene	1009.5	0.25	1268.8	0.50	129	-5
36	P	<i>trans</i> - β -Methylstyrene	1009.9	0.29	1390.3	0.58	122	+4
37	P	Dicyclopentadiene (<i>endo</i>)	1011.9	0.48	1247.1	0.90	130	-2
38	p F	Indan	1015.7	0.46	1355.9	0.82	125	+7
39		Dipentene	1019.8	0.31	1200.0	0.54	135	-1
40	g	1-Methyl-2-isopropylbenzene	1020.6	0.26	1276.4	0.62	131	-3
41	P f	Indene	1023.3	0.46	1455.8	0.85	121	+5
42	f	1,3-Diethylbenzene	1034.8	0.31	1297.3	0.54	132	-2
43	f g	1-Methyl-3-propylbenzene	1034.8	0.28	1301.0	0.45	132	-2
44	f g	1-Methyl-4-propylbenzene	1038.1	0.30	1301.0	0.49	133	-1
45	f	<i>n</i> -Butylbenzene	1039.6	0.26	1309.1	0.50	132	-2

TABLE I (continued)

No.	Comments*	Compound	SE-30		PEG 20M		M*	A
			I	$\frac{dI}{dT}$	I	$\frac{dI}{dT}$		
46	f	1,4-Diethylbenzene	1040.0	0.30	1305.2	0.56	133	-1
47		<i>trans</i> -Decahydronaphthalene	1041.7	0.55	1160.9	0.95	141	+3
48	f g	1,3-Dimethyl-5-ethylbenzene	1042.6	0.25	1319.8	0.50	132	-2
49	f	1,2-Diethylbenzene	1043.5	0.32	1324.0	0.58	132	-2
50	f	1-Methyl-2-propylbenzene	1048.3	0.33	1327.7	0.49	133	-1
51	g	Dihydrodicyclopentadiene	1050.5	0.54	1252.7	0.99	138	+4
52	f g	1,4-Dimethyl-2-ethylbenzene	1059.0	0.32	1343.5	0.60	134	0
53	f g	1,3-Dimethyl-4-ethylbenzene	1061.7	0.32	1350.0	0.61	134	0
54	p	3-Ethylstyrene	1065.8	0.29	1423.7	0.52	131	-1
55	f g	1,2-Dimethyl-4-ethylbenzene	1066.1	0.31	1357.2	0.65	135	+1
56	f g	1,3-Dimethyl-2-ethylbenzene	1069.6	0.33	1372.1	0.67	135	+1
57	p	4-Ethylstyrene	1073.2	0.33	1431.3	0.60	132	0
58	p g	2,4-Dimethylstyrene	1075.4	0.20	1440.5	0.65	132	0
59	g	Tetrahydrodicyclopentadiene	1077.6	0.62	1243.4	1.00	144	+8
60	p g	2,5-Dimethylstyrene	1078.7	0.29	1432.2	0.59	133	+1
61		<i>cis</i> -Decahydronaphthalene	1081.5	0.61	1223.0	1.03	145	+7
62	f g	1,2-Dimethyl-3-ethylbenzene	1083.5	0.37	1394.8	0.69	136	+2
63	p	1,3-Divinylbenzene	1091.3	0.32	1541.0	0.55	130	0
64	p F	1,2,4,5-Tetramethylbenzene	1096.4	0.38	1406.8	0.72	138	+4
65	g	2-Methyl- <i>trans</i> - β -methylstyrene	1098.3	—	1464.0	0.72	135	+3
66	p F	1,2,3,5-Tetramethylbenzene	1099.5	0.40	1416.5	0.68	138	+4
67	p	1,4-Divinylbenzene	1100.0	0.33	1554.2	0.60	131	0
68	p g	2,3-Dimethylstyrene	1100.3	0.35	1485.1	0.71	134	+2
69	g	4-Methyl- <i>trans</i> - β -methylstyrene	1109.0	0.40	1428.7	0.66	136	+4
70	p F g	5-Methylindan	1112.2	0.43	1446.9	0.97	139	+7
71	p F g	4-Methylindan	1120.6	0.46	1467.9	1.04	139	+7
72	g	1,3-Dimethyl-5-propylbenzene	1126.0	0.21	1406.2	—	144	-4
73	p F	1,2,3,4-Tetramethylbenzene	1127.5	0.55	1461.6	0.72	141	+7
74	f	1,2,3,4-Tetrahydronaphthalene	1129.8	0.49	1490.4	0.89	140	+8
75	g	1,4-Dimethyl-2-propylbenzene	1140.0	0.26	1415.0	—	146	-2
76	f	<i>n</i> -Pentylbenzene	1140.5	0.36	1404.3	0.46	147	-1
77	g	1,3-Dimethyl-4-propylbenzene	1143.7	0.28	1429.0	—	146	-2
78	g	1,2-Dimethyl-4-propylbenzene	1149.5	—	1435.8	—	147	-1
79	P F	Naphthalene	1145.0	0.65	1620.0	1.15	136	+8
80	g	1,3-Dimethyl-2-propylbenzene	1152.2	0.27	1451.6	—	147	-1
81	g	1,2-Dimethyl-3-propylbenzene	1166.5	0.32	1458.6	—	149	+1

* p and P, minor and major component in PN, respectively; f and F, minor and major component in FCCN, respectively; g, generated compound.

In the utilization of PN for polymer-chemical purposes, the C₈-C₉ fraction requires a detailed component analysis, especially for aromatics with unsaturated side-chains. FCCN is produced for automotive purposes, and therefore the determination of C₆-C₁₀ aromatics with high octane numbers is important.

EXPERIMENTAL

Apparatus

A Packard-Becker 427 chromatograph equipped with a flame-ionization de-

tector and a capillary inlet system was used for the analytical separation, and a JGC-810 (JEOL, Japan) chromatograph with a thermal conductivity detector and a manual cryogenic sample trap was employed for collecting selective cuts. The retention times and peak areas were recorded with a Packard 603 computing integrator (at 0.1 sec resolution). To calculate the retention indices, the retention times were measured on an SE-30 capillary column at 60, 70 and 80°C and on a PEG 20M column at 70, 80 and 90°C. The measured retention indices at 70°C (I_{70}) and the calculated dI/dT values (where T = temperature) for both phases are given in Table I.

The analytical columns were SE-30 on fused silica (15 m \times 0.25 mm I.D.) (JEW, U.S.A.) and PEG 20M Pyrex glass (30 m \times 0.30 mm I.D.), laboratory-made by the barium carbonate procedure³, with nitrogen as the carrier gas at a flow-rate of 11 cm/sec, splitting ratio 1:75, sample amount $2 \cdot 10^{-6}$ – 10^{-8} g in 1 μ l of carbon disulphide solution or in a solvent required by the reactions and attenuation $32 \cdot 10^{-12}$ A f.s. Preparative columns were stainless steel (2.5 m \times 10 mm I.D.), 30% SE-30 on 40–60-mesh Celite 545 and 30% TCEP on 40–60-mesh Chromosorb P both at 120°C with nitrogen as the carrier gas at a flow-rate of 6 cm/sec.

Standard generation

The following well known reactions were utilized for the generation of hydrocarbons (g in Table I): *alkylbenzenes*, Friedel–Crafts alkylation with aluminium chloride catalyst and dimethyl sulphate or ethyl bromide; *styrenes*, Friedel–Crafts acylation followed by lithium aluminium hydride reduction and dehydration with dimethyl sulphoxide; *ethynylbenzenes*, from styrene dibromides by alkaline dehydrohalogenation; *β -methylstyrenes*, from benzaldehydes by Grignard reaction with ethyl bromide and dehydration of the arylalkylcarbinols with acetic anhydride and phosphorus oxychloride.

Pre-injection reactions

The reactions used were as follows. For *hydrogenation*, 0.1–1 ml of diethyl ether containing 1–5 mg of palladium–charcoal catalyst was placed into a vial of appropriate volume (1–20 ml depending on the hydrogen consumption) cooled by dry-ice, then 1–20 μ l of sample were added, flushed with hydrogen and closed by a screw-cap lined with a PTFE septum. The vial was allowed to warm up and was shaken for 10–60 min. After sedimentation, the supernatant was ready for GC analysis. *Ozonolysis* was performed at dry-ice–acetone temperature in carbon disulphide solution using a Micro-Ozonizer (Supelco, U.S.A.) according to the manufacturer's procedure. *Epoxidation* was performed by shaking the sample in, e.g., chloroform solution, with peracetic acid for 5–60 min. *Adduct formation* was tested by refluxing or shaking the sample with maleic anhydride or tetracyanoethylene at a temperature between ambient and 150°C with or without solvent. The unreacted hydrocarbons from these pre-injection reactions were used for GC after appropriate purification.

RESULTS AND DISCUSSION

Retention information

High-precision I , ΔI , and dI/dT values are needed in order to have adequate

retention data for both structure correlations and for identification of the individual peaks. In particular, the advanced fine-structural correlations published for alkylbenzenes⁴ require ΔI values for two stationary phases of different polarity. In collecting the retention parameters, however, even the measurement of these valuable ΔI data is difficult for multi-component systems owing to problems with matching corresponding peaks.

There are some laboratories where the problem could be solved by advanced multi-column switching (in-line) techniques. Otherwise, one must laboriously match narrow preparative fractions of the whole sample to the corresponding peaks. This (off-line) technique was employed in this work by the use of the SE-30 and the TCEP preparative columns for the analysis of PN and FCCN.

Simultaneously, an idea based on a simple, long "tandem capillary column" was tested. The basic feature is to make at least three precise retention time measurements: the first on a capillary column with a pure stationary phase (e.g. a polar one); the second one on the polar + non-polar tandem column (with a suitable short non-polar section permitting the clear observation of shifts in the peaks and the third on the same tandem but in the reverse direction (i.e., non-polar + polar combination). ΔI values can be calculated theoretically on the basis of the additivity of the relevant products of the dead times and of the capacity factors. The partial dead times for the individual tandem sections can be determined (calibrated) by using compounds of known capacity factors for both pure stationary phases.

This technique has not yet been investigated adequately to give a comprehensive quantitative interpretation. The qualitative pictures, however, are very convincing. When a short SE-30 glass capillary was coupled to a longer PEG-20M capillary column (in the ratio 100:5) and the chromatogram obtained was compared with that obtained with the pure PEG 20M column, the following main features could be recognized.

Very characteristic shifts can be detected in the chromatograms of complex multi-component hydrocarbon mixtures. Alkylbenzenes were taken as reference peaks as they shifted consistently (preserving their relative positions). The other types of components, having higher or lower ΔI values, shifted characteristically with respect to the reference peaks. Thus, grouping of the other compounds could be performed if the shorter column was used with a "suitable" length. The change in the chromatograms as a whole resembles the picture obtained when dI/dT data are collected with a multi-component mixture on a high-performance column with different temperature steps, but in this instance, instead of dI/dT values, the different ΔI values produce the effects.

Obviously, a stepwise lengthening of the shorter column may supply more and more information permitting further subgrouping of the components along with the determination of refined ΔI values.

After the retention indices on the polar and the non-polar column had been verified, the retention information collected for hydrocarbon-type correlations was processed to give ΔI vs. dI/dT plots, which seems to be the most promising method of interpretation, as demonstrated for hydrocarbons of low⁵ and moderate polarity⁴.

In Fig. 1 the ΔI values are plotted against $dI^{PEG\ 20M}/dT$ values, based on the data in Table I. A clear tendency for the points to form clusters for different types of hydrocarbons can be seen. Although boundary lines among the cluster types are

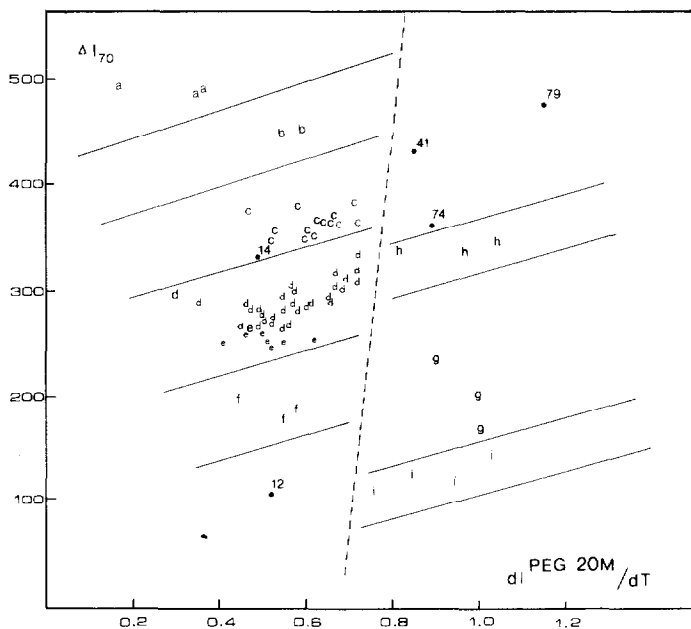


Fig. 1. Plot of ΔI values against dI/dT . a = Ethynylbenzenes; b = divinylbenzenes; c = vinylbenzenes; d = *n*-alkylbenzenes; e = isoalkylbenzenes; f, g = cyclo adducts; h = indans; i = perhydroindans and naphthalenes. Numbering as in Table I.

tentative in some instances because the number of points is small, it can be stated that the clusters are arranged according to the hydrogen content along the ordinate and according to the asymmetry of the substitution and, especially, to the ring number of the solute along the abscissa.

Calculation of molar mass from retention data

In an earlier paper⁶ it was shown that in an $I^{\text{PEG 20M}}$ vs. $I^{\text{SE-30}}$ plot, parallel equidistant straight lines, slanting from the points for *n*-alkanes with a slope *S*, can be recognized for compounds of identical molecular mass, which were designated "iso-molecular-mass lines". One of the consequences of this correlation is that the molar mass (M^*) of a given solute can be calculated from the measured retention index by the following equation:

$$M^* = \frac{I^{\text{PEG 20M}} - S I^{\text{SE-30}}}{100(1-S)} \cdot 14 + 2 \quad (1)$$

In this work, nearly 100 hydrocarbons were studied. The values of the slope (*S*) were optimized only for the data for 35 *n*-alkylbenzenes to give the minimum standard deviation (S.D.). It was assumed that the extreme deviations might be more characteristic of the types of hydrocarbons by this method. An *S* value of 3.5 was obtained with S.D. 1.9 g/mol. The calculated M^* values for all compounds derived from this slope are given in Table I. As expected, it shows that the larger deviations are really characteristic. In these instances the type of the hydrocarbon in question differs sig-

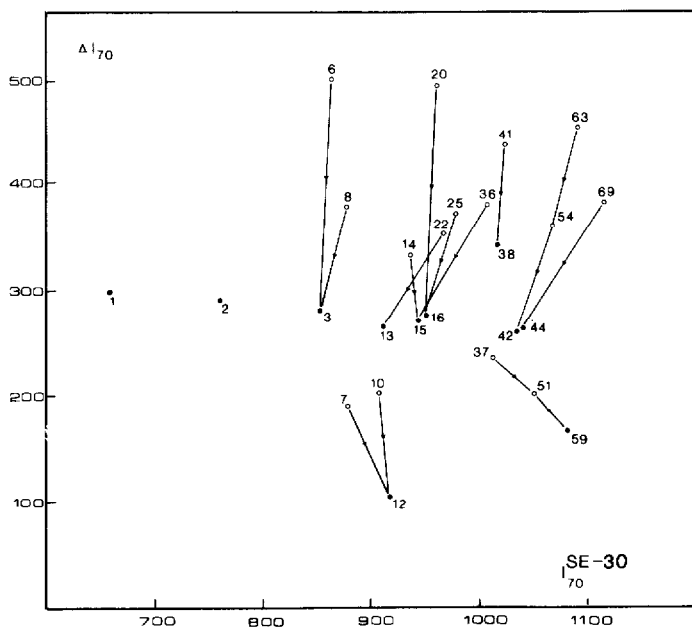


Fig. 2. Hydrogenation vectors in the ΔI vs. I plot.

nificantly in structure from the *n*-alkylbenzenes, as reflected by the cluster position in the plot of ΔI vs. dI/dT (Fig. 1). Thus, even when the deviations are higher, the carbon number can be determined by using a type-dependent correction value.

These correction values can be calculated as the average Δ values, $\bar{\Delta}$, of a given type that can be recognized by its position in the ΔI vs. dI/dT plot. These values are as follows: $\bar{\Delta} = -5.9$, S.D. = 1.86 for the seven isoalkyl compounds, $\bar{\Delta} = +6.5$, S.D. = 1.65 for the ten bicyclic compounds and $\bar{\Delta} = -6.7$, S.D. = 0.58 for the three enthylnbenzenes.

Chemical information

The pre-injection reactions used were surveyed briefly in the Experimental section. The classical hydrogenation method allows highly selective and quantitative reactions with the unsaturated hydrocarbons. As the number of the possible isomers is reduced by the hydrogenation, it is reasonable approach to the recognition of the carbon skeleton. This advantage can be increased by the combination of this chemical information with the relevant retentions.

In the retention index plot in Fig. 2, the peak shifts caused by hydrogenation are shown by arrows from the index points of the unsaturated compounds to the saturated compounds, which are called "hydrogenation vectors". It can be seen in the plot (in which only some of the measured vectors are shown) that these vectors are significantly different for the different structures. It can be stated as a general trend that multiple saturation and abolition of conjugations cause longer vectors, whereas the directions of the vectors belonging to the bridged multi-ring-type cyclic adducts differ from those for vinyl aromatics.

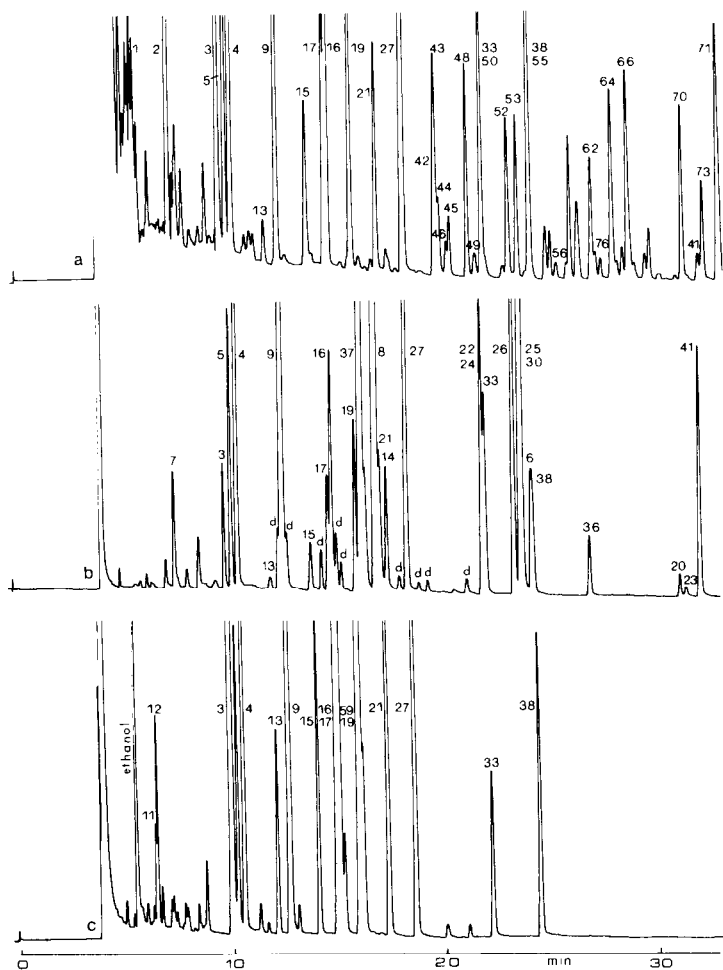


Fig. 3. Chromatograms of (a) whole FCCN and a distillation fraction of PN (b) before and (c) after hydrogenation. Column: 30 m \times 0.30 mm I.D., glass; stationary phase, PEG 20M; temperature, 60°C for 10 min then increased at 2°C/min to 120°C; carrier gas, nitrogen at inlet pressure 0.38 kPa. Peak Nos. as in Table I; d = cyclo adduct in (b).

Ozonolysis, a widely used technique for double-bond location, was also applied simply for “screening” peaks of unsaturated hydrocarbon origin. After ozonolysis all those peaks (except ethynylbenzenes) that are active in hydrogenation disappear from the chromatogram.

The other two reactions proved to be less selective for screening any subtypes of unsaturated hydrocarbons in PN. It can be stated, however, that not only the complete disappearance of a peak but also the relative rates of decrease of peak area are informative and can be utilized for identification, if the reactions are carried out stepwise.

Analysis of FCCN and PN fractions

A chromatogram of the whole FCCN on the PEG 20M capillary column is shown in Fig. 3a. The identified peaks are marked with the Compound numbers (see Table I). It was easily established by both hydrogenation and selective preparative cuts that neither vinyl aromatics nor cyclo adducts are characteristic compounds of this naphtha. The detailed analysis of alkylbenzenes was carried out by means of selective preparative cuts and by the stated retention information and retention correlations.

The analysis of aromatics in PN is more complicated, because of the high concentration and the large number of different aromatics, and particularly owing to the cyclo adduct background. In this paper only the results of the most comprehensive analysis of the important C₈-C₉ fraction are mentioned. Chromatograms of this fraction before and after hydrogenation are shown in Fig. 3b and c [No. 8 (styrene) and No. 7 (5-vinyl-2-norbornene) comprised 40% and 0.5% respectively].

The peak identification of this PN fraction was tested by all the mentioned techniques, but for routine analysis of this kind of fraction, hydrogenation and ozonolysis give enough information. By calculation of the component balance before and after these reactions all the individual C₆-C₉ aromatics (26 compounds) could be determined. As far as we know, 5-vinyl-2-norbornene, the ethynylbenzenes and the individual *cis/trans*- β -methylstyrenes have not previously been detected in PN.

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REFERENCES

- 1 E. J. Gallegos, I. M. Whittemore and R. F. Klaver, *Anal. Chem.*, 46 (1974) 157-161.
- 2 M. Herrera, E. Murgia, M. de Hazos and J. Lubkowitz, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 6 (1981) 297-299.
- 3 K. Grob and G. Grob, *J. Chromatogr.*, 125 (1976) 471-485.
- 4 L. Soják, J. Janák and J. A. Rijks, *J. Chromatogr.*, 142 (1977) 177-189.
- 5 J. A. Rijks, *Thesis*, University of Technology, Eindhoven, 1973.
- 6 T. Tóth, *Magy. Kém. Foly.*, 80 (1974) 328-331.