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THE APPLICATION OF GAS CHROMATOGRAPHY,
TO THE ANALYSIS OF CERTAIN
HYDROCARBON FUELS

ROBERT CLEVE BEERS

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THE APPLICATION OF GAS CHROMATOGRAPHY
TO THE ANALYSIS
OF CERTAIN HYDROCARBON FUELS

by

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Lieutenant, Commander, United States Navy
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Submitted in partial fulfillment
for the degree of
MASTER OF SCIENCE IN CHEMISTRY
from the
UNITED STATES NAVAL POSTGRADUATE SCHOOL
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ABSTRACT

As part of an investigation of gas turbine regenerator fouling being conducted at the U. S. Naval Postgraduate School gas chromatography was used to compare and analyze certain hydrocarbon fuels. Because of the known relationship between fuel aromaticity and exhaust system fouling in gas turbine engines, particular emphasis was directed toward determination of the aromaticity of the fuels and of the particular aromatic compounds present. Fuels investigated included premium grade auto gasoline, aviation gasoline, several gas turbine fuels, and marine diesel fuel. Derivatives of cyclohexane and decahydronaphthalene were synthesized by hydrogenation of benzene and naphthalene derivatives with Raney nickel catalyst. Numerous branched-chain paraffins were synthesized by hydroisomerization of n-olefins under alkylation conditions. These synthetic products were used as standards in the identification of components of the fuels. The fuels investigated were found to contain from 35 to over 200 components. Component identification was from 30 to 60% complete.

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1. Introduction

The rapid advances made in the field of gas chromatography in recent years have dramatically expanded the researcher's ability to analyze very complex mixtures of chemical compounds.

The analysis and comparison of several representative hydrocarbon fuels (Table I) were undertaken, not only an overall comparison, but a partial component analysis as well. This analytical work was made possible only through the use of an extremely sophisticated gas chromatograph, the Beckman model GC-4. This gas chromatograph provides for carefully controlled linear temperature programming and is equipped with a highly sensitive hydrogen flame ionization detector. The GC-4 also uses a dual - or reference - column mode of operation which eliminates the typical base-line drift and noisy operation at the high temperatures required for the analysis.

Particular attention was given to the aromatic compounds and to the overall aromaticity of the fuels, since it has been shown [3, 4, 15] that the residue formation and sooting of these fuels can be directly attributed to their aromatic content.

Identification of the individual components was made exclusively by comparison of retention times, hydrogenation of aromatics, and/or the standard addition method. No attempt was made to isolate and identify individual components of these complex mixtures, containing from 35 to over 200 components (Table I).

TABLE I
Representative Hydrocarbon Fuels Investigated

Fuel	Component boiling range	Number of Components
Premium Gasoline	25° C - 230° C	83+
Aviation Gasoline	25° C - 195° C	35+
JP4 Gas Turbine fuel	25° C - 287.5° C	114+
JP5 Gas Turbine fuel	98.5° C - 303° C	175+
Canadian Gas Turbine fuel	98.5° C - 330° C	200+
Marine Diesel fuel	98.5° C - 350° C	200+

Reference standards for the analysis were procured from three sources: (1) Commercially available chemically pure compounds; (2) Hydrogenation over Raney nickel catalyst of aromatic compounds to yield substituted cyclohexanes, decahydronaphthalenes, and various other saturated analogs of aromatic compounds; (3) Hydroisomerization of normal olefins under alkylation conditions to yield numerous branched-chain alkanes.

2. Historical

As early as 1947 Jonash, Barnett, and Stricker [9] had investigated the problem of carbon deposition in gas turbine engines, experimenting with a full size jet propulsion engine and burning fuels available at that time. These fuels were complex hydrocarbon mixtures, and the effect of change in one fuel property at a time could not be determined. The work of Jonash and Wear [15] and later Busch [4] established the clear correlation of aromaticity to carbon deposition. Bert has shown in his work at California Research Corp. [3] that the most offensive aromatics were the naphthalenes and the highly alkylated benzenes. He also demonstrated the relative clean burning properties of the paraffins and naphthenes.

Kohler and Miller [10], supported by Bureau of Ships, Code 645, conducted an extensive investigation into the fouling effects in compact gas turbine regenerator matrices. This work is continuing at the U. S. Naval Postgraduate School. The research reported herein is in support of this fouling investigation.

Several recent advances in gas chromatography have indicated the possibility of analyzing the complex fuels used in gas turbine engines. Temperature programming [11, 12] of capillary columns [8] is now routine. The sensitive hydrogen flame ionization detector [5] and dual column operations [7] are also of significance. Albert [2] analyzed the gasoline portion of petroleum with a combination of gas chromatographic and molecular sieve techniques. Schwartz and Brasseux [14], among others, have used capillary columns to analyze

a relatively narrow petroleum cut. It was the purpose of this work to apply temperature programming, high temperature capability, hydrogen flame detection, and dual column operations to the analysis of a representative group of highly complex fuels (Table I).

3. Experimental

Gas Chromatography (GC)

A Beckman model GC-4 gas chromatograph was used in this work. This instrument combines the most advanced features in a high performance, modular package. Some of its characteristics are:

1. A well designed column compartment, featuring high velocity, uniform air flow, substantially reducing temperature gradients.
2. A temperature programming module, which makes possible a wide variety of precise linear and non-linear temperature programs, as well as isothermal operation. This module utilizes a Mylar programming sheet on which the temperature profile is traced with metallic tape. By optically tracking the tape with a photoelectric curve follower, the profile is converted into temperature.
3. A dual-hydrogen flame ionization detector of high sensitivity. Use of this type of detector allows sample size to be reduced by several orders of magnitude from that required by a thermal conductivity detector. This makes possible the use of a capillary column, which would be saturated by a sample size normally used with packed columns.
4. The use of dual columns. In gas-liquid chromatography, bleeding of the liquid phase is unavoidable. The column effluent always contains a certain amount of this bleed. Since the detector will respond to this substrate bleeding, a background signal is generated. If column temperature and flow rate are constant, (isothermal operation) the rate of bleeding is constant and the background signal can be electrically compensated. During temperature programmed operation, however, a linear column temperature rise leads to an exponential increase in the vapor pressure of the liquid substrate. This increases

the background signal in the same way, producing unwanted baseline drift. In the GC-4 two matched columns can be employed in conjunction with the dual hydrogen flame detectors. Since the column bleed is then essentially balanced, the detector system sees no differential between the two signals, and base-line stability results.

5. Ability to operate at high temperatures. Temperatures up to 500° C are possible in the column oven, inlet, and detector compartment. This capability is vital, since the higher molecular weight hydrocarbons investigated had boiling points as high as 400° C.

Both a conventionally packed column and capillary column were used:

<u>Substrate</u>	<u>Solid Support</u>	<u>Column</u>	<u>I.D.</u>	<u>o.o.</u>	<u>Length</u>	<u>Source</u>	<u>Max.Temp.</u>
SE 30 (20% wt)	Acid washed DMDS Chromo- sorb W	Stainless steel	.10"	.125"	12'	Beckman Instrument Co.	350° C
DC 550	capil- lary column	stainless steel	.01"	.0625"	200'	Perkin- Elmer Corp.	160° C

Instrument conditions were experimentally adjusted to optimize the resolution of compounds with boiling points ranging from 100° C to 300° C, at the same time affording reasonable resolution of the lower boiling components (below 100° C) (Table II).

TABLE II

Instrument Parameters for Chromatographic Experiments

<u>Parameter</u>	<u>Column I (SE 30)</u>	<u>Column 2 (DC 550)</u>
He flow rate (cc/min)	35	4
He make-up (cc/min)	85	85
Air (cc/min)	275	275
Hydrogen (cc/min)	55	55
Detector Temp (° C)	275	275
Column flash vaporizer (° C)	230	175
Recorder speed (in/hr)	40	40
Sample size (ul)	0.3-1.2	0.3-1.2
Split ratio	none	33:1
Temperature program gradient (see fig. 1)	5°/min	2.2°/min

Because of its low flow rate of carrier gas and the length of the capillary column, separate temperature profiles were necessary for each type of column. These profiles are shown in Figure 1. Curve 1 of Figure 1 represents the program used with the 12' SE 30 Columns, while curve 2 shows the temperature program for the DC 550 capillary column.

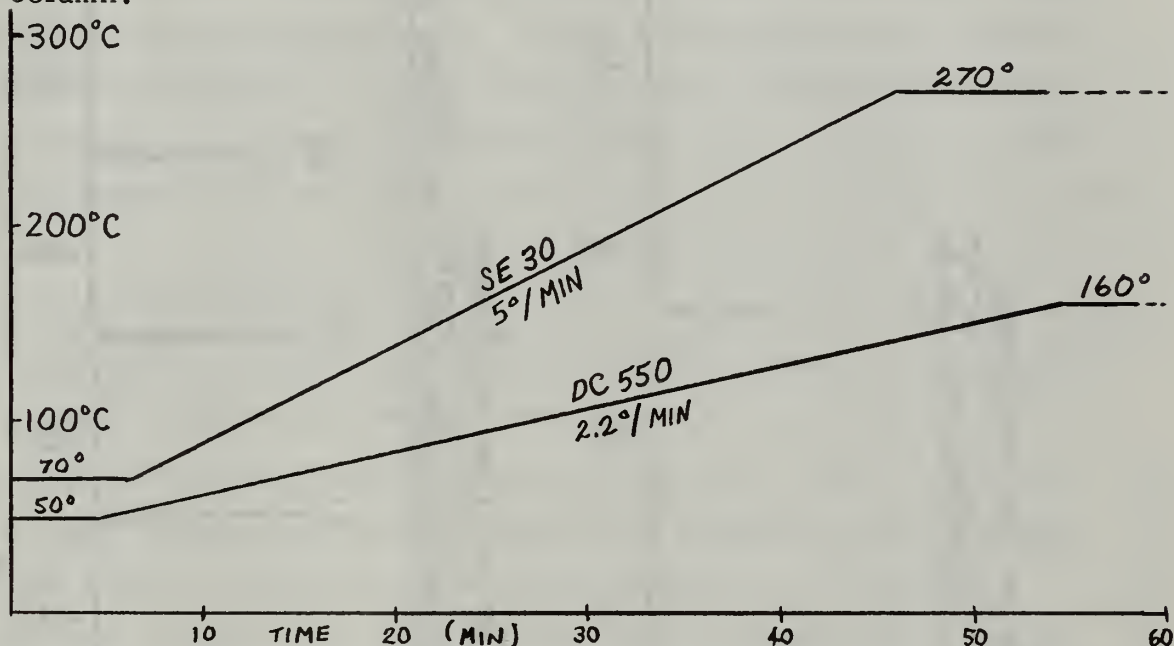


FIGURE 1 COLUMN TEMPERATURE PROGRAM PROFILES

The advantage of temperature programming is shown in Figure 2. Figure 2 is a comparison of the chromatograms of a mixture of n-alkanes, isothermal vs temperature programmed operation. The chromatograms were taken on the DC 550 capillary column. The first chromatogram demonstrates typical isothermal elution of a homologous series, with elution times increasing exponentially. The second chromatogram is of the same mixture, but programmed from 50° to 140° C at 6°/min. The members of the series elute in a linear manner after n-nonane.

Component identification in the fuels was accomplished in three ways:

1. Comparison of retention times of a library of known compounds with unknown peaks in the chromatogram of the fuel.
2. Hydrogenating the fuel over Raney nickel catalyst, then observing

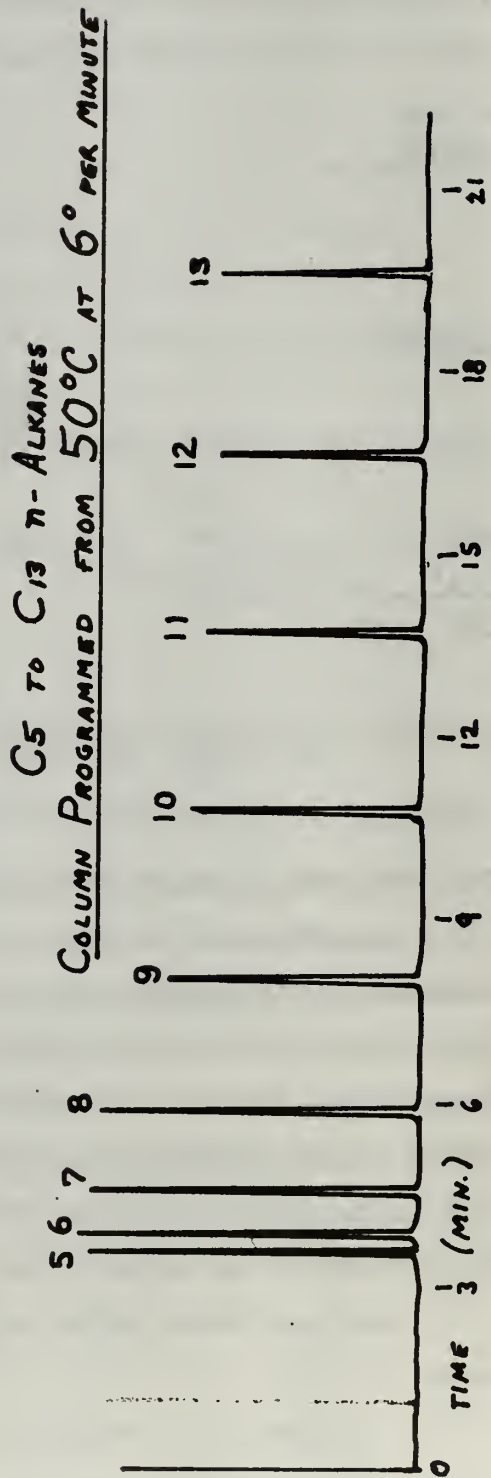
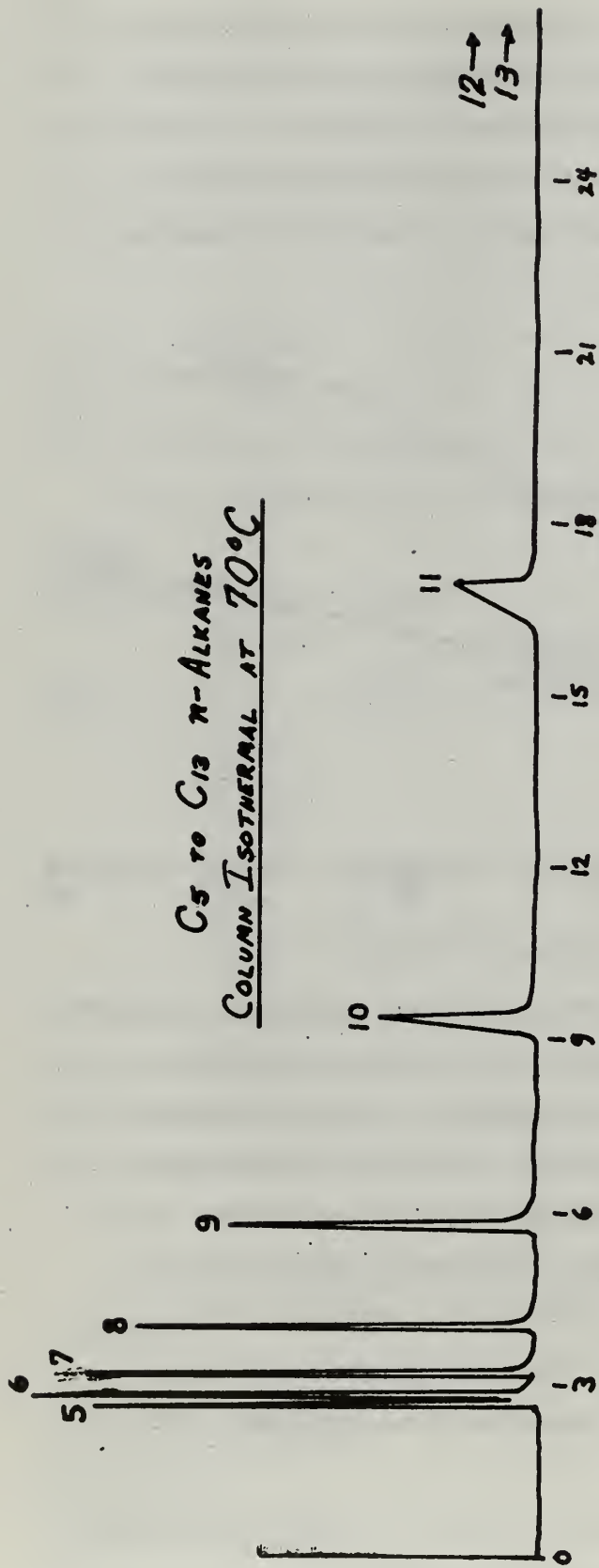


FIGURE 2

CHROMATOGRAMS OF ISOTHERMAL VS TEMPERATURE PROGRAMMED SEPARATION OF n-ALKANES.

the differences in the chromatogram after hydrogenation. All aromatic compounds are saturated by the reaction, and the saturated analogs elute at different times than the parent aromatic.

3. The standard addition method. A small amount of known compound which is believed to be contained in the fuel (from the methods above) is added to the fuel, and its chromatogram examined for a proportional peak-height increase. Figure 3 illustrates several examples of these techniques. In trace 1 several peaks of JP4 are tentatively identified by comparison of retention times. Trace 2 shows JP4 after hydrogenation. The suspected peaks corresponding to isopropyl benzene and 1, 2, 4-trimethyl benzene have been reduced in size, as would occur if they were aromatic. (The peak for n-decane remains unchanged.) Additionally, the peaks corresponding to the cataloged positions of isopropyl cyclohexane and the four isomers of 1, 2, 4-trimethyl cyclohexane have all increased in relative size. Trace 3 shows JP4 to which a small amount of the tentatively identified compounds has been added. The peaks for isopropyl benzene, 1, 2, 4-trimethyl benzene, and n-decane have all increased in relative size. Finally, trace 4 shows the hydrogenated JP4 to which a small amount of separately prepared isopropyl cyclohexane and 1, 2, 4-trimethyl cyclohexane has been added. The corresponding peaks are all increased in relative size. From this four-step procedure, the peaks for both aromatics are firmly identified. In addition, it can be concluded that the original JP4 contained the cyclohexane analogs.

Preparation of Raney Nickel Catalyst [1]

In a one liter filtering flask equipped with a thermometer and a mechanical teflon stirrer, are placed 160 grams of sodium hydroxide in a 600 cc of distilled water. The resulting solution is cooled to 50° C in an ice bath. Then 125 grams of powdered Raney nickel-aluminum alloy is added with constant stirring in small portions over a period of 30-40 minutes, while maintaining the temperature below 55° C. The suspension is then digested at 50° C for one hour with constant stirring. The ice-

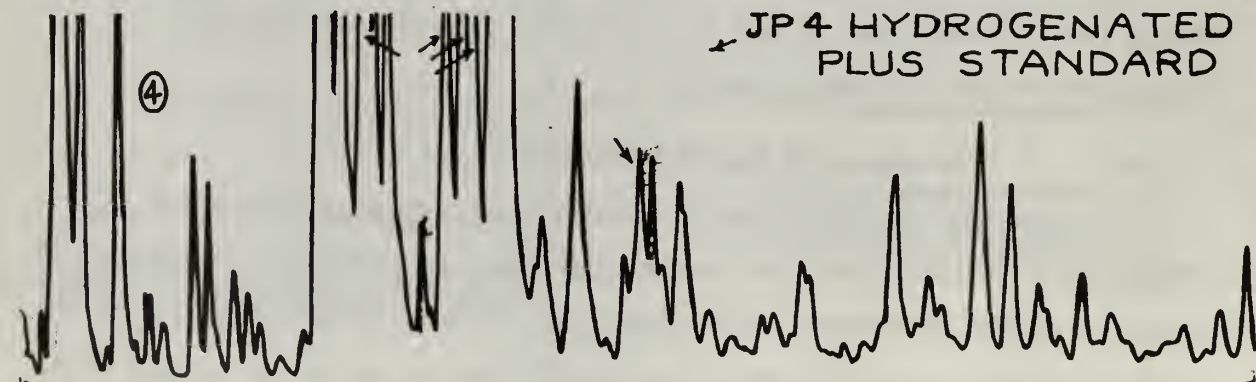
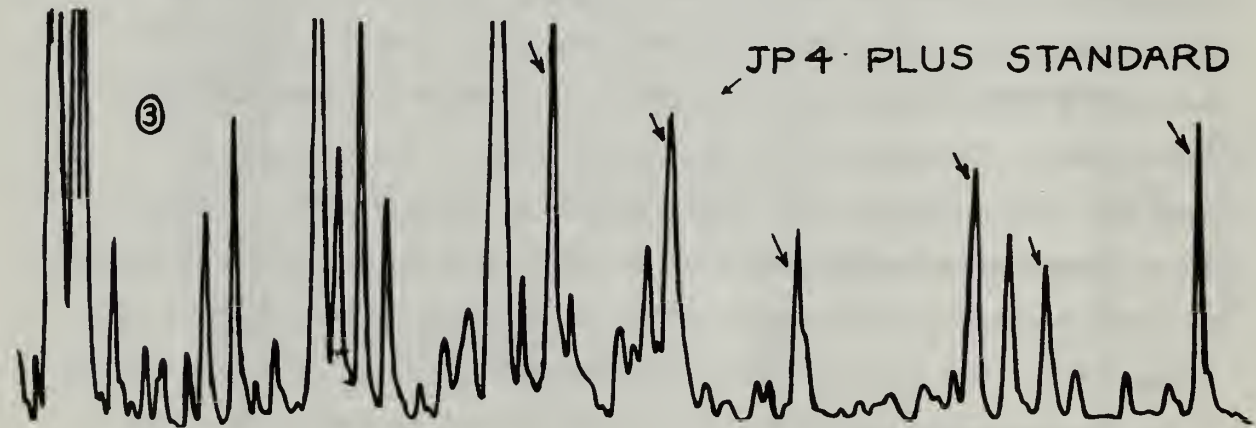
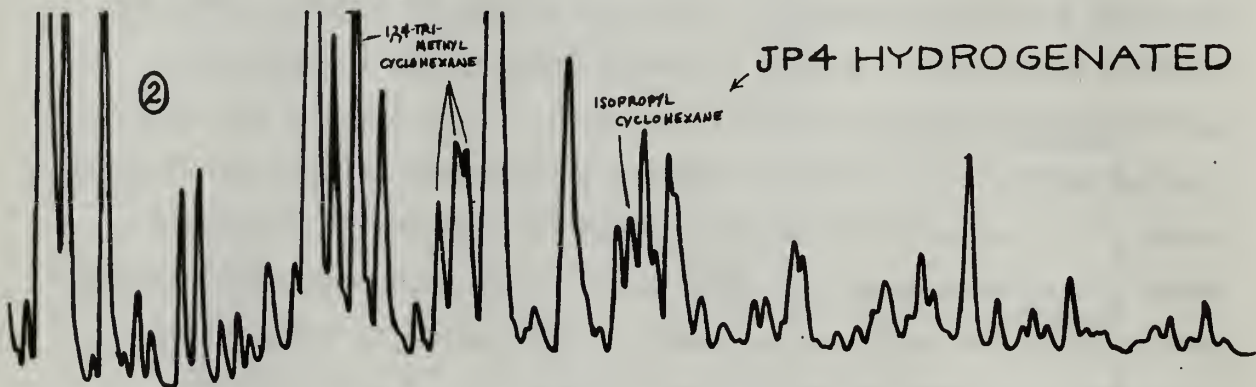
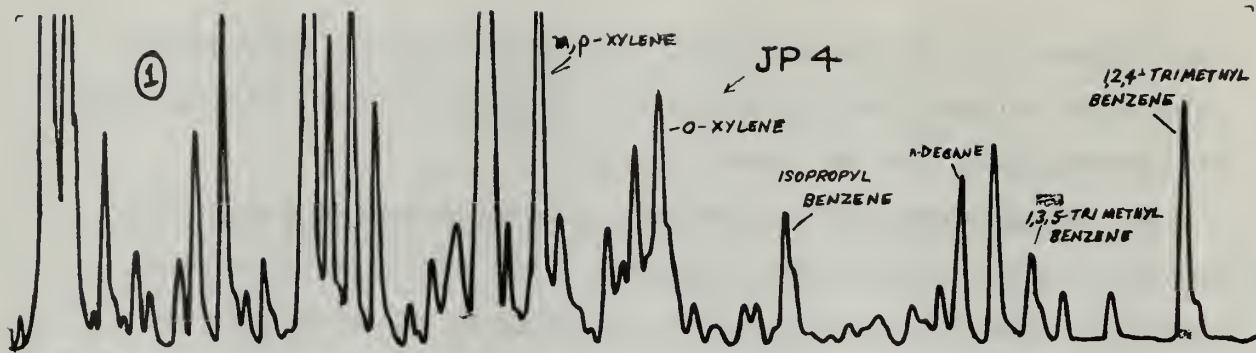


FIGURE 3
CHROMATOGRAPHS ILLUSTRATING IDENTIFICATION PROCEDURES

bath is removed during this period and replaced with a warm-water bath to maintain the temperature.

After digestion is complete, the catalyst is washed three times by decantation. The catalyst is then washed with a continuous flow of tap-water until the washings are neutral to indicator paper. Washing is then continued for another 30 minutes. The total wash time is about $1\frac{1}{2}$ hours. The apparatus for washing is illustrated in Figure 4. The stirrer is operated at a speed which suspends the catalyst to a height of about 3 inches. Wash water flows through the system at about 50 cc/min.

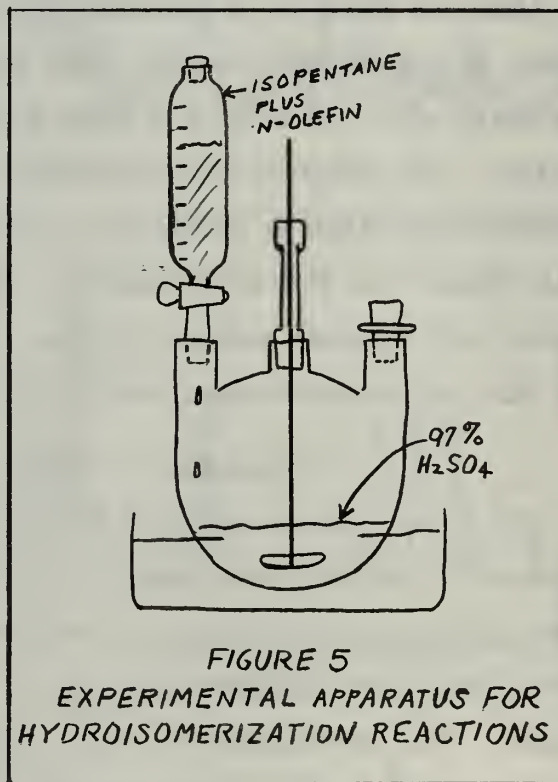
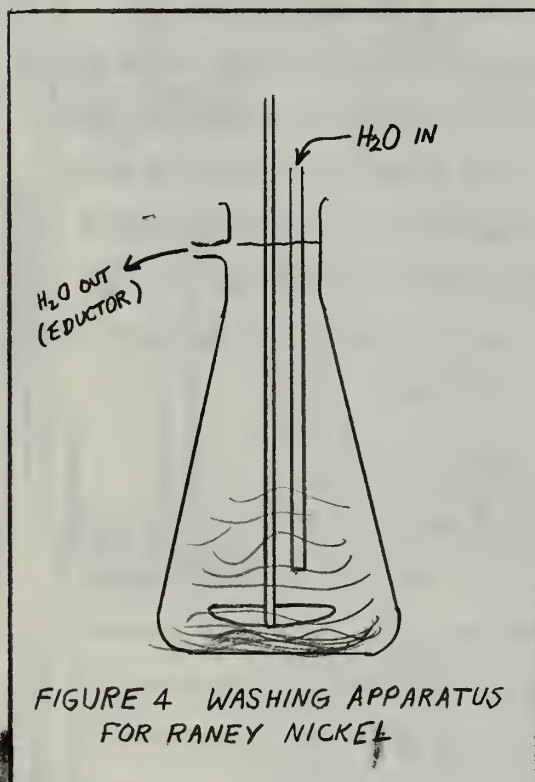
After the washing is complete, the water is decanted from the settled sludge of Raney nickel. The catalyst is then washed three times by stirring with 150 ml at 95% ethyl alcohol, decanting after each addition. The catalyst is then washed three times with absolute ethyl alcohol. The catalyst is stored in a refrigerator in a cork-stoppered bottle filled with 95% ethyl alcohol. The catalyst maintains its activity for extended periods of time. A batch prepared 10 January, 1966 was still quite active when used on 20 April 1966.

Hydrogenation of Organic Compounds

The Raney nickel produced was used to catalyze the reduction of a series of aromatic compounds, producing a new series of reference standards for use in component identification. JP4, JP5, and Marine Diesel Fuel were also hydrogenated in order to determine aromatic content. The hydrogenations were carried out in a Parr pressure reaction apparatus (Parr Instrument Co., Inc., Moline, Illinois). The substance to be hydrogenated was placed inside a pyrex liner along with 2-3 grams of catalyst, and the liner was then sealed inside the stainless steel pressure vessel. The vessel was purged of air with hydrogen, then was pressurized to 2000 psi hydrogen. The hydrogenations were carried out at various temperatures and for varying lengths of time. The absorption of hydrogen was in every experiment within $\pm 10\%$ of that required for the formation of the saturated analogs.

Attempts were made to partially hydrogenate various aromatic compounds. In each case, only the unreacted aromatic and the completely saturated analog were found.

The resulting products from the hydrogenation reaction were then gas chromatographed to determine purity, and the extent of reaction, where reaction was not allowed to go to completion. Cis and trans isomers were identified as such on the basis of boiling points, when known. Before including any of the reaction products in the library of reference standards, their infrared spectra were examined to confirm their complete saturation.



Hydroisomerization of n-olefins

The hydroisomerization of n-olefins to isoparaffins and the coupling of the isoparaffins used as hydrogen donors have been studied by Peterson, Phillips, and Kelly. [13] This method of alkylation of isopentane and isobutane with n-olefins has long been a commercial process for producing high octane gasoline.

The overall reaction results in a mixture of isomers of the paraffin resulting from the olefin, coupling products of the isopentane with itself or with the heavier isoparaffins present, disproportionation products, and products of cracking. Hence the resulting product mixture is quite complex. If the isopentane is in large excess, polymerization is suppressed and the olefin reacts completely.

The reaction is carried out in a one liter, three necked pyrex flask fitted with a mechanical stirrer, a thermometer, and a measuring flask or funnel for introducing the olefin. The reaction vessel (Figure 5) is charged with 100 cc of 97% weight sulfuric acid and 100 cc of isopentane. The mixture is maintained at $22^{\circ}\text{C} \pm 2^{\circ}\text{C}$. Addition of a mixture of 100 cc isopentane and 0.5 moles n-olefin was begun through the measuring flask. The addition rate is maintained so as to add the entire mixture over a period of 30 minutes. Stirring is continued for five minutes after completion of the addition. The organic phase is then separated. Any acid remaining is removed from the organic phase by swirling with sodium hydroxide. The organic phase is then washed sufficiently with water to remove any soaps which may have formed. Washing is continued until the organic layer gives a neutral reaction to indicator paper. The product mixture is then examined gas chromatographically. Completeness of reaction is confirmed if both the chromatogram and the infrared spectra indicate absence of the n-olefin.

4. Presentation and Discussion of Data

The hydrogen of JP4, JP5, and Marine Diesel Fuels provides an overall comparison of their aromaticity. Table III summarizes the results of these hydrogenations:

Table III

Results of Fuel Hydrogenations. (3000 psi, 250° C)

<u>Run</u>	<u>Fuel</u>	<u>Sample</u> <u>(gms)</u>	<u>Catalyst</u> <u>(gms)</u>	<u>Time</u> <u>(hrs)</u>	<u>Moles H₂ consumed</u> <u>per gram of fuel</u>
3	JP4	20	2	24	.0102
2	JP4	20	2	36	.0105
5	JP4	20	4	36	.0105

Table III (Cont'd)

<u>Run</u>	<u>Fuel</u>	<u>Sample (gms)</u>	<u>Catalyst (gms)</u>	<u>Time (hrs)</u>	<u>Moles H₂ consumed per gram of fuel</u>
9	JP5	20	2	24	.0105
11	JP5	20	2	36	.0105
10	JP5	20	4	36	.0110
1	MD	20	2	36	.0095
6	MD	20	4	36	.0100
8	MD	20	4	48	.0095

After hydrogenation, the products were gas chromatographed and examined in the infrared to determine completeness of the reaction. From Table III it is concluded that the three fuels are roughly equal in aromatic content, their relative aromaticity varying no more than 15%

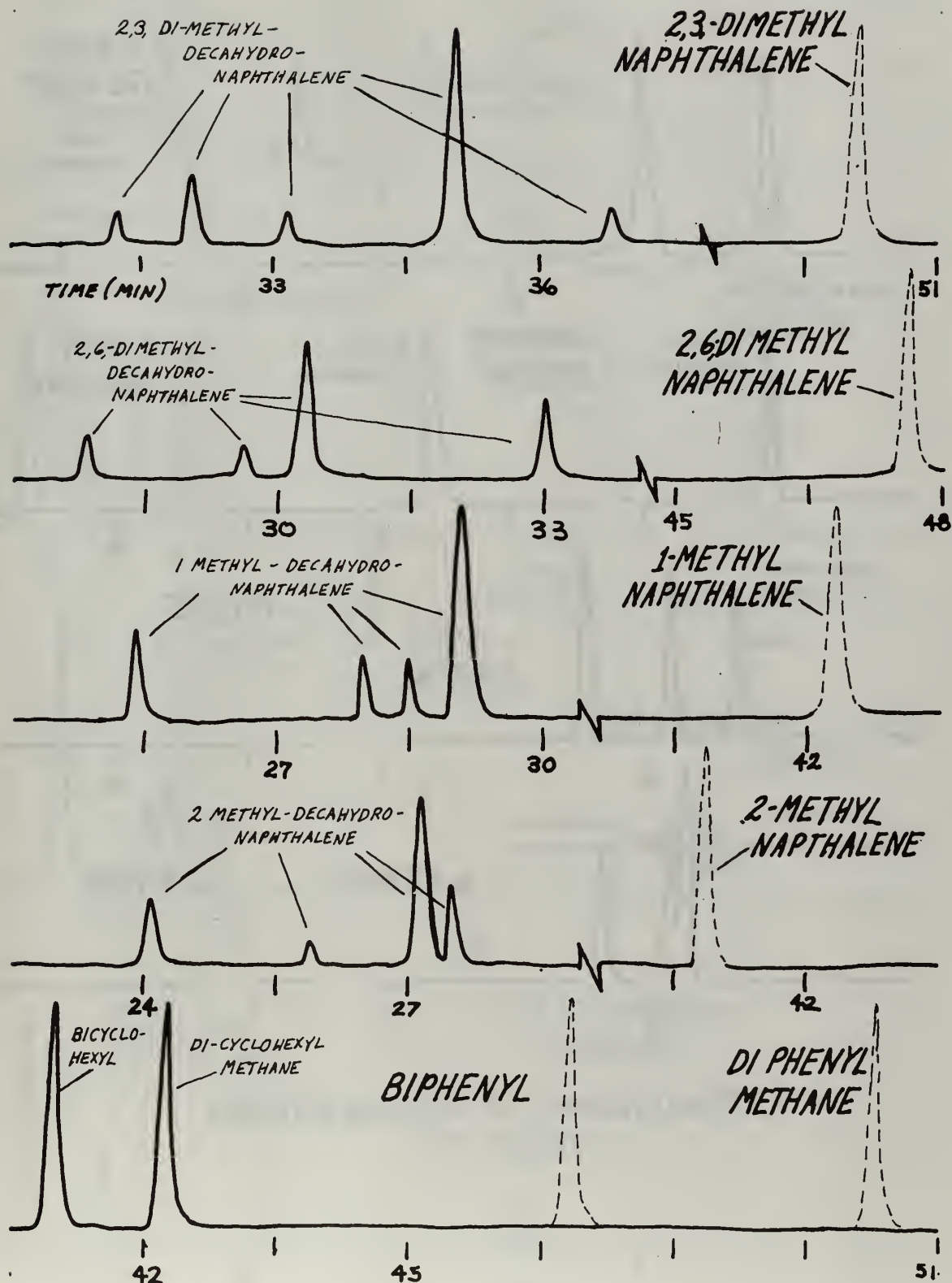
The olefinic unsaturation present was determined to be small (Table IV). Truesdail Laboratories, Inc., Los Angeles, Cal., confirmed this data for Marine diesel fuel, reporting .0003 grams of hydrogen consumed per gram of fuel. The data presented in Table IV is necessarily unreliable since the pressure drop of approximately 5 psi cannot be determined to within less than ± 5 psi.

Table IV

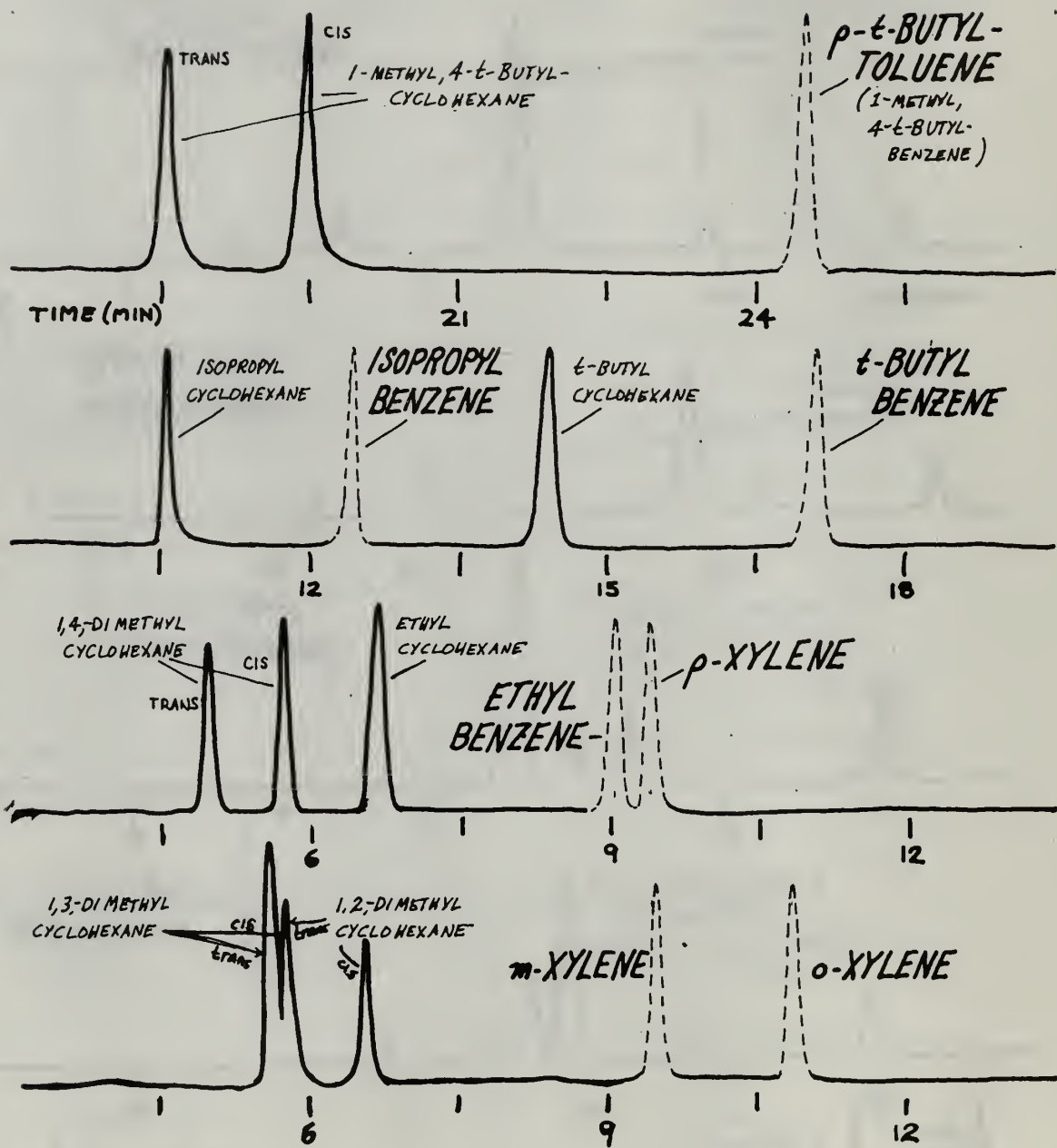
Results of Mild Fuel Hydrogenations (50 psi, 22° C)

<u>Fuel</u>	<u>Sample (gms)</u>	<u>Catalyst (gms)</u>	<u>Time (hrs)</u>	<u>Moles H₂ consumed per gram of fuel</u>
JP4	20	4	24	.00054
JP5	20	4	24	.00027
JP5	30	4	24	.00029
MD	20	4	24	.00027

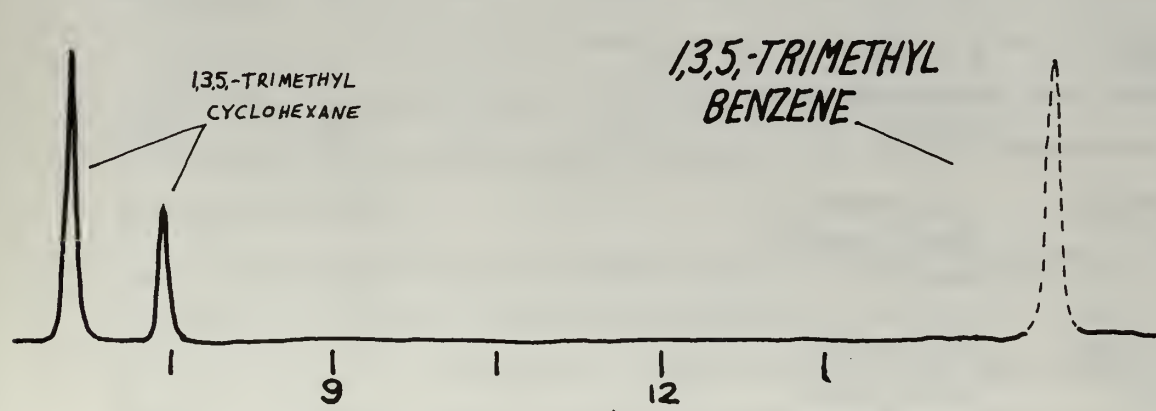
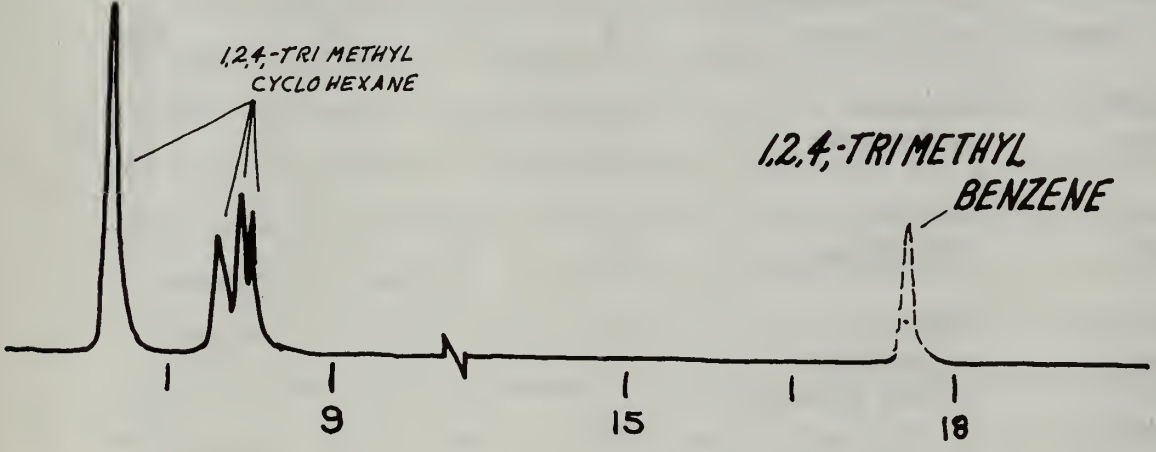
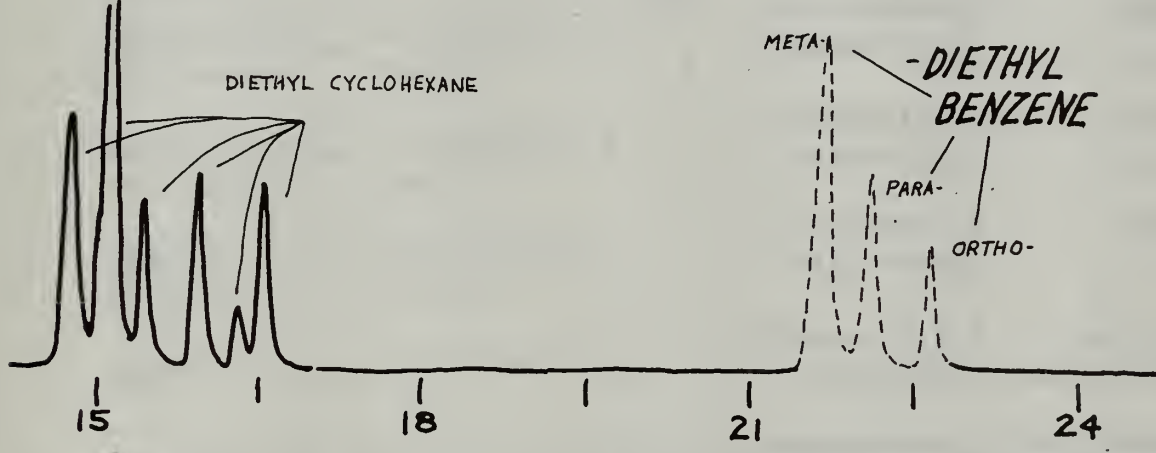
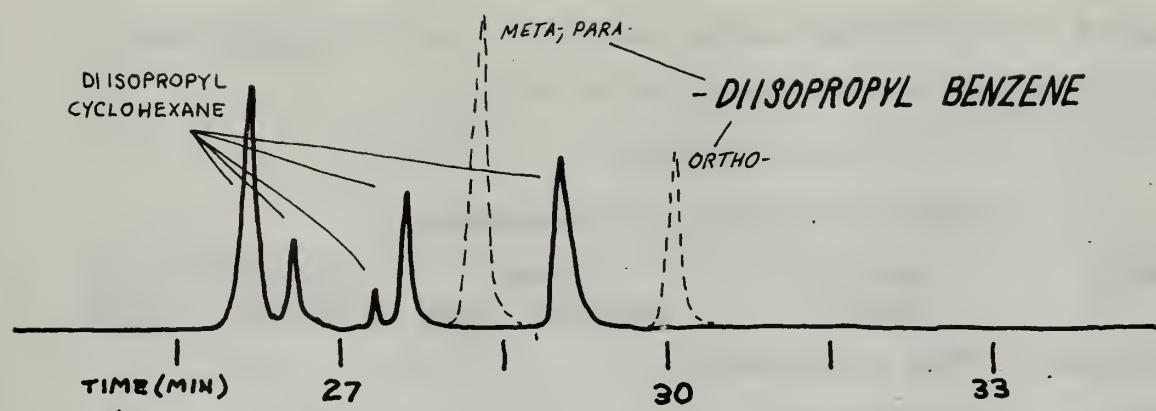
The hydrogenation of individual aromatic species was also carried out. In general, it was found that the highly alkylated benzenes and naphthalenes were more easily saturated, although none resisted saturation at temperatures above 200° C. Figures 6, 7, and 8 show some of the shifts in retention time and the several geometric isomers produced by this hydrogenation process. Cis and trans designations



CHROMATOGRAMS OF HYDROGENATIONS
FIGURE 6



CHROMATOGRAMS OF HYDROGENATIONS
 FIGURE 7



CHROMATOGRAMS OF HYDOGENATIONS
FIGURE 8

are applied to isomers when boiling point data is available. The results of these hydrogenations are summarized in Table V.

Table V
Results of Individual Hydrogenations

<u>Compound</u>	<u>Saturated Analog</u>	<u>Isomers</u>		<u>Isomers Resolved</u>	
		<u>Expected</u>	<u>Found</u>	<u>SE30/Column</u>	<u>DC550</u>
Ethyl benzene	Ethyl cyclohexane	1	1	-	-
p-Xylene	1,4-Dimethyl cyclohexane	2	2	yes	yes
m-Xylene	1,3-Dimethyl cyclohexane	2	2	yes	yes
o-Xylene	1,2-Dimethyl cyclohexane	2	2	yes	yes
1,3,5-Tri-methyl benzene	1,3,5-Trimethyl cyclohexane	2	2	yes	yes
1,2,4-Tri-methyl benzene	1,2,4-Trimethyl cyclohexane	4	4	no	yes
Isopropyl benzene	Isopropyl cyclohexane	1	1	-	-
t-Butyl benzene	t-Butyl cyclohexane	1	1	-	-
Diethyl benzene (mixed isomers)	Diethyl cyclohexane (mixed isomers)	6	6	no	yes
p-t-Butyl toluene	1-t-Butyl, 4-Methyl cyclohexane	2	2	yes	yes
p-Isopropyl toluene	1-Isopropyl, 4-Methyl cyclohexane	2	1	no	no
Diisopropyl benzene	Diisopropyl cyclohexane (mixed isomers)	6	5	no	yes

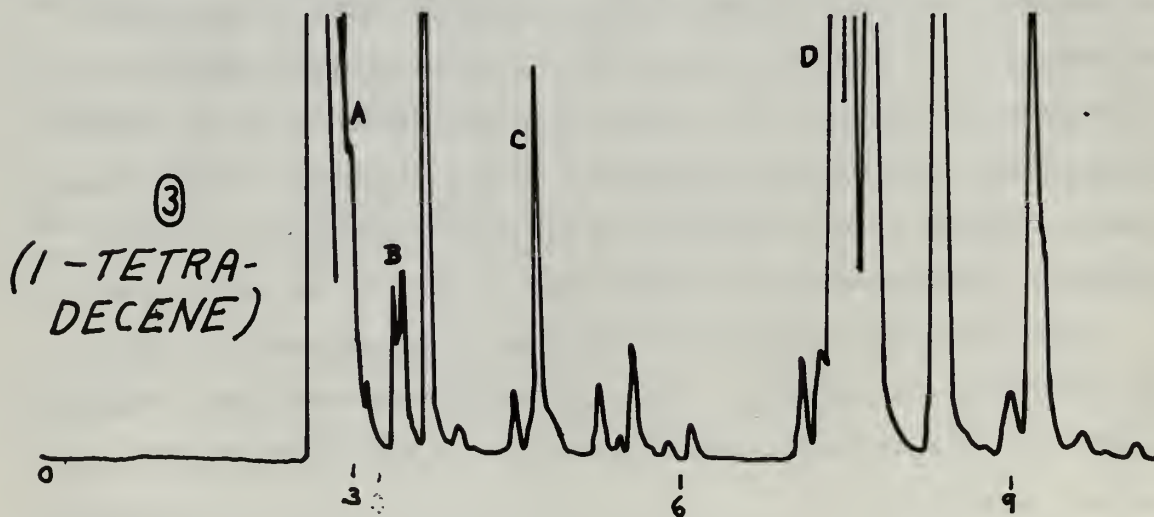
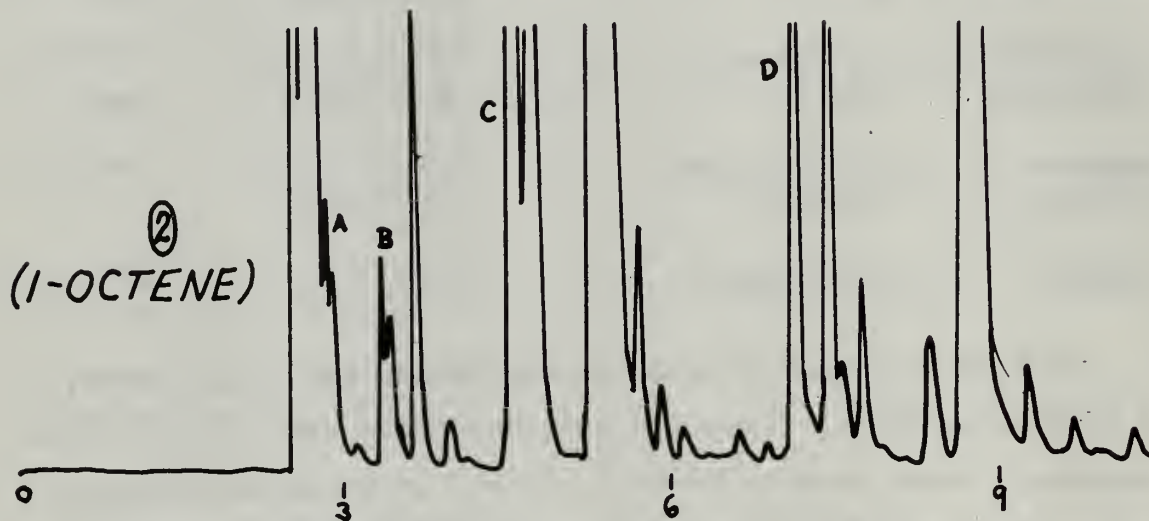
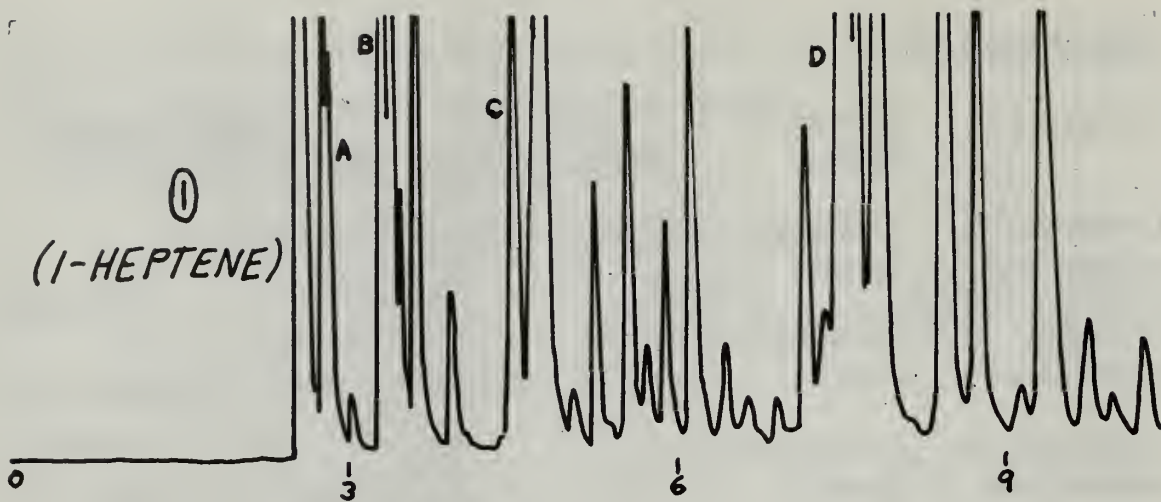
Table V (Cont'd)

<u>Compound</u>	<u>Saturated Analog</u>	<u>Isomers</u>		<u>Isomers Resolved</u>	
		<u>Expected</u>	<u>Found</u>	<u>SE30/Column/DC550</u>	<u>DC550</u>
1-Methyl naphthalene	1-Methyl decalin	4	4	no	yes
2-Methyl naphthalene	2-Methyl decalin	4	4	yes	yes
2,3-Dimethyl naphthalene	2,3-Dimethyl decalin	6	5	yes	yes
2,6-Dimethyl naphthalene	2,6-Dimethyl decalin	6	4	yes	yes
Diphenyl Methane	Dicyclohexyl methane	1	1	-	-
Biphenyl	Bicyclohexyl	1	1	-	-

The hydroisomerization reactions each resulted in a large variety of isomeric paraffins. Figure 9 is a representative portion of the chromatograms of these reaction products. Curve 1 is the chromatogram of the reaction involving isopentane and 1-Heptene; curve 2 represents isopentane and 1-Octene; while curve 3 illustrates the isopentane-1-Tetradecene reaction. The groups of peaks labeled A, B, C, and D, respectively, correspond to isomers of hexane, heptane, octane, and nonane. Similar groups appear at longer retention times for isomers of decane, pentadecane, and in the case of curve 3, for tetradecane.

These reaction products were examined in the infrared to confirm the absence of unsaturation. These chromatograms were then used to tentatively identify many unknown peaks in the fuel chromatograms as isomeric paraffins.

Using the techniques of identification outlined in section 3... and Figure 3, peaks on the chromatograms were identified. Table VII is the Key used to identify the numbered peaks of the fuel chromatograms. The chromatograms for the fuels listed in Table I are shown in Figures



CHROMATOGRAMS OF HYDROISOMERIZATION PRODUCTS
FIGURE 9

10-12. Figure 12 reproduces the chromatograms on the DC 550 column, while figures 10 and 11 are reproductions of the chromatograms on the SE 30 column. In addition to the numbered peaks, certain peaks have been identified as aromatic, but otherwise unidentified. The aromatic nature of such peaks is based on their reduction when the hydrogenated fuel gas chromatogram is compared with that of the unreacted fuel. These peaks are marked with a (+) on figures 10 - 12. Similarly, other peaks have been tentatively identified as isomeric paraffins by comparison of the fuel GC with the GC of the hydroisomerization reaction products. These peaks are marked with a (°) on figures 10 - 12. The completeness of identification achieved with each fuel of the two columns is summarized in Table VI.

Table VI
Summary of Component Identification

<u>Fuel</u>	<u>Peaks</u>		<u>Identified</u>		<u>Partially Identified</u> ^{**}	
	<u>SE 30</u>	<u>DC550</u>	<u>SE 30</u>	<u>DC550</u>	<u>SE 30</u>	<u>DC 550</u>
Premium Gasoline	55	83	32	37	4	28
Aviation Gasoline	17	35	14	21	1	12
JP4	61	124	37	45	16	32
JP5	65	175	31	44	9	49
Canadian	88	200*	36	-	10	-
Marine Diesel	90	200*	35	-	16	-

(* Estimated) (**Either (+) or (°))

In each case the DC 550 capillary column resolved the fuels into many more components than were found on the SE 30 column. The Canadian gas turbine fuel and marine diesel fuel were not analyzed on the DC 550 column, since DC 550 does not have a sufficient temperature

range when used as liquid phase in a capillary column.

Table VII
Key for the Component Identification of the Peaks
on Fuel Chromatograms

<u>Peak</u> <u>Number</u>	<u>Chemical</u> <u>Compound</u>	<u>Uncorrected Retention Time</u> <u>(min)</u>	
		<u>SE 30 column</u>	<u>DC550 column</u>
1	Propane	1.23	2.58
2	n-Butane	1.35	2.64
3	2-Methylbutane	1.56	2.70
4	n-Pentane	1.77	2.76
5	2,2-Dimethylbutane	2.13	2.85
6	2,3-Dimethylbutane	2.50	2.94
	and 2-Methylpentane	-	-
7	3-Methylpentane	2.71	3.00
8	n-Hexane	2.97	3.06
8A	Methylcyclopentane	-	3.33
9	Heptane isomer	3.48	3.38
10	Benzene	2.70	3.90
11	Heptane isomer	2.85	3.45
12	Cyclohexane	2.95	2.60
13	Heptane isomer	3.15	2.68
14	1-Heptene	3.70	2.48
15	n-Heptane	3.94	3.75
16	Methylcyclohexane	5.05	4.22
17	Toluene	7.93	5.69
18	trans-1, 4-Dimethyl cyclohexane	9.00	4.80
18A	trans-1, 3-Dimethyl- cyclohexane	8.92	5.13
19	2,2,4-Trimethylhexane	9.03	4.74
20	n-Octane	9.63	5.33

Table VII (Cont'd)

<u>Peak Number</u>	<u>Chemical Compound</u>	<u>Uncorrected Retention Time</u> <u>(min)</u>	
		<u>SE 30 column</u>	<u>DC 550 column</u>
21	trans-1, 2-Dimethyl- cyclohexane	9.75	5.13
22	cis-1, 4-Dimethyl- cyclohexane	10.06	5.33
22A	cis-1, 3-Dimethyl- cyclohexane	10.08	5.84
23	cis-1, 2-Dimethyl- cyclohexane	11.00	6.60
24	1, 2, 4-Trimethylcyclo- hexane isomer	12.15	7.24
25	trans-1, 3, 5-Trimethyl- cyclohexane	11.25	6.50
26	Ethylcyclohexane	11.43	6.75
27	Ethylbenzene	12.06	9.15
28	1, 2, 4-Trimethylcyclo- hexane isomer	13.26	8.22
29	1, 2, 4-Trimethylcyclo- hexane isomer	13.35	8.40
30	cis-1, 3, 5-Trimethyl- cyclohexane	12.30	7.35
31	para-Xylene	12.45	9.49
31A	meta-Xylene	12.45	9.49
32	1, 2, 4-Trimethylcyclo- hexane isomer	13.45	8.55
33	ortho-Xylene	13.45	10.96
34	n-nonane	14.04	8.78
35	Isopropylbenzene (Cumene)	14.77	12.50
36	Cyclooctane	15.03	11.10
37	Isopropylcyclohexane	15.10	10.50
38	1, 3, 5-Trimethylbenzene (Mesitylene)	16.57	15.50
39	t-Butylbenzene	17.58	17.00

Table VII (Cont'd)

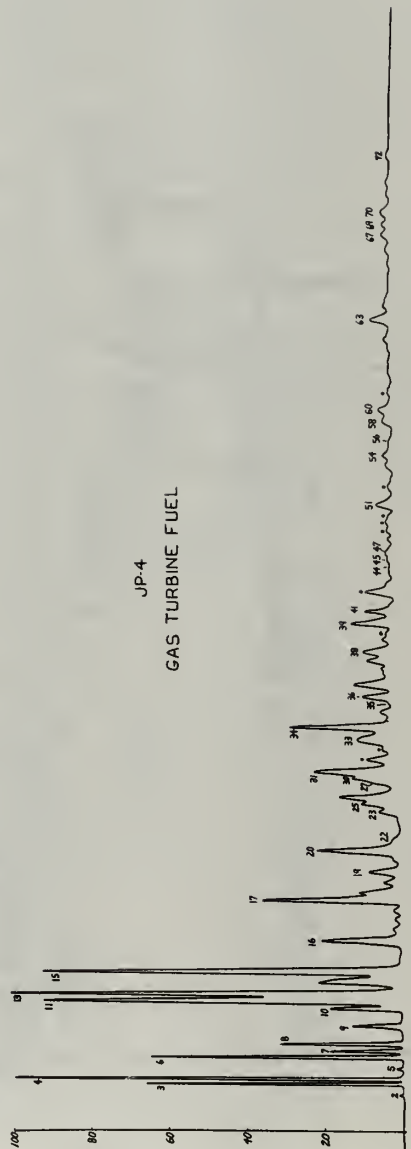
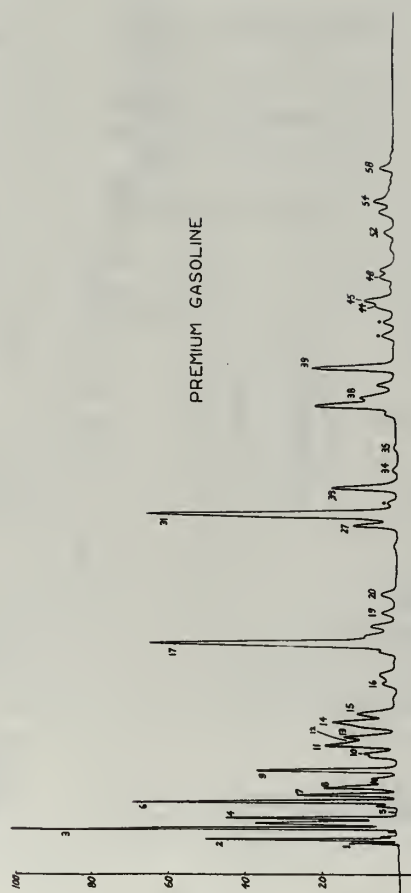
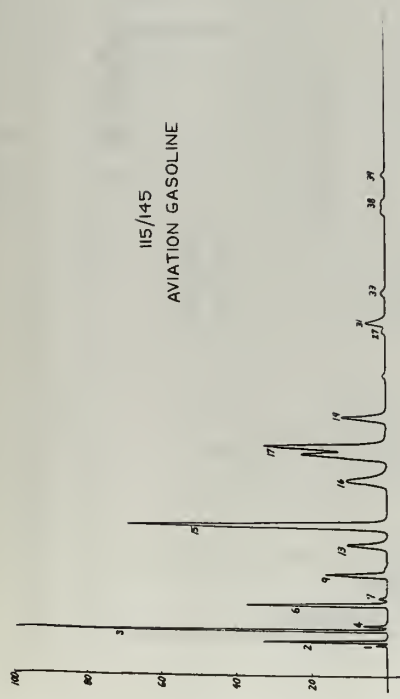
<u>Peak Number</u>	<u>Chemical Compound</u>	<u>Uncorrected Retention Time</u> (min)	
		<u>SE 30 column</u>	<u>DC 550 column</u>
40	t-Butylcyclohexane	17.85	14.48
40A	1-Isopropyl, 4-Methyl- cyclohexane	-	13.64
41	n-Decane	18.03	14.56
42	Diethylcyclohexane isomer	18.18	14.86
42A	" "	18.45	15.15
42B	" "	18.67	15.42
42C	" "	18.97	15.88
42D	" "	19.27	16.30
42E	" "	19.42	16.48
43	sec-Butylcyclohexane	19.27	17.20
43A	1, 2, 4-Trimethylbenzene	19.35	17.37
44	meta-Diethylbenzene	19.65	21.35
45	para-Diethylbenzene	19.92	21.75
46	trans-1-t-Butyl, 4-Methyl- cyclohexane	19.95	18.00
47	ortho-Diethylbenzene	20.17	22.35
48	trans-Decahydronaphthalene	20.55	20.00
48A	1-Isopropyl, 4-Methylbenzene (p-cymene)	-	19.29
49	cis-1-t-Butyl, 4-Methylcyclo- hexane	20.65	19.30
50	para-t-Butyltoluene	21.33	24.15
51	n-Undecane	21.75	21.90
52	cis-Decahydronaphthalene	22.15	23.60
53	2-Methyl decahydronaph- thalene isomer	22.62	23.97
53A	" "	23.47	25.65
53B	" "	24.00	26.98
53C	" "	24.15	27.30
54	meta-and para-Diisopropyl- benzene	23.40	28.45

Table VII (Cont'd)

<u>Peak Number</u>	<u>Chemical Compound</u>	<u>Uncorrected Retention Time</u>	
		<u>SE 30 column</u>	<u>DC 550 column</u>
55	Tetrahydronaphthalene isomers	23.82	30.66
56	ortho-Diisopropylbenzene	24.03	30.25
57	1-Methyldecahydronaphthalene isomer	23.46	25.11
57A	" "	24.37	27.70
57B	" "	24.60	28.20
57C	" "	24.99	28.84
58	Naphthalene	24.59	33.45
58A	Triethylbenzene isomer	-	33.67
59	Diisopropylcyclohexane isomer	23.94	26.40
59A	" "	24.15	26.74
59B	" "	24.67	27.48
59C	" "	25.20	27.82
59C	" "	25.74	29.25
60	n-Dodecane	25.15	29.11
61	2, 6-Dimethyldecahydro- naphthalene isomer	24.57	27.75
61A	" "	25.50	29.41
61B	" "	25.86	30.30
61C	" "	26.67	32.85
62	2, 3-Dimethyldecahydro- naphthalene isomer	26.10	30.37
62A	" "	26.43	30.90
62B	" "	27.69	31.80
62C	" "	28.35	32.70
62D	" "	29.11	34.74
63	n-Tridecane	28.32	36.00
63A	2-Methylnaphthalene	28.32	40.69
64	1-Methylnaphthalene	28.68	42.07

Table VII (Cont'd)

<u>Peak Number</u>	<u>Chemical Compound</u>	<u>Uncorrected Retention Time</u> <u>(min)</u>	
		<u>SE 30 column</u>	<u>DC 550 column</u>
65	Bicyclohexyl	29.10	40.92
66	Biphenyl	30.48	46.59
67	n-Tetradecane	31.20	42.30
68	Dicyclohexylmethane	31.20	42.15
69	2, 6-Dimethylnaphthalene	31.50	47.52
70	Diphenylmethane	31.92	42.30
71	2, 3-Dimethylnaphthalene	32.55	49.90
72	n-Pentadecane	33.93	48.09
73	n-Hexadecane	36.45	54.22
74	n-Heptadecane	38.76	60.00
75	2, 6, 10, 14-Tetramethyl- pentadecane	39.18	60.30
76	n-Octadecane	41.13	
77	n-Nonadecane	43.29	
78	n-Eicosane	45.33	
79	n-Unocosane	47.37	
80	n-Docosane	49.83	
81	n-Tricosane	52.53	
82	n-Tetracosane	55.50	



RETENTION TIME [MINUTES] FIGURE 10 FUEL CHROMATOGRAMS ON SE-30 PACKED COLUMN

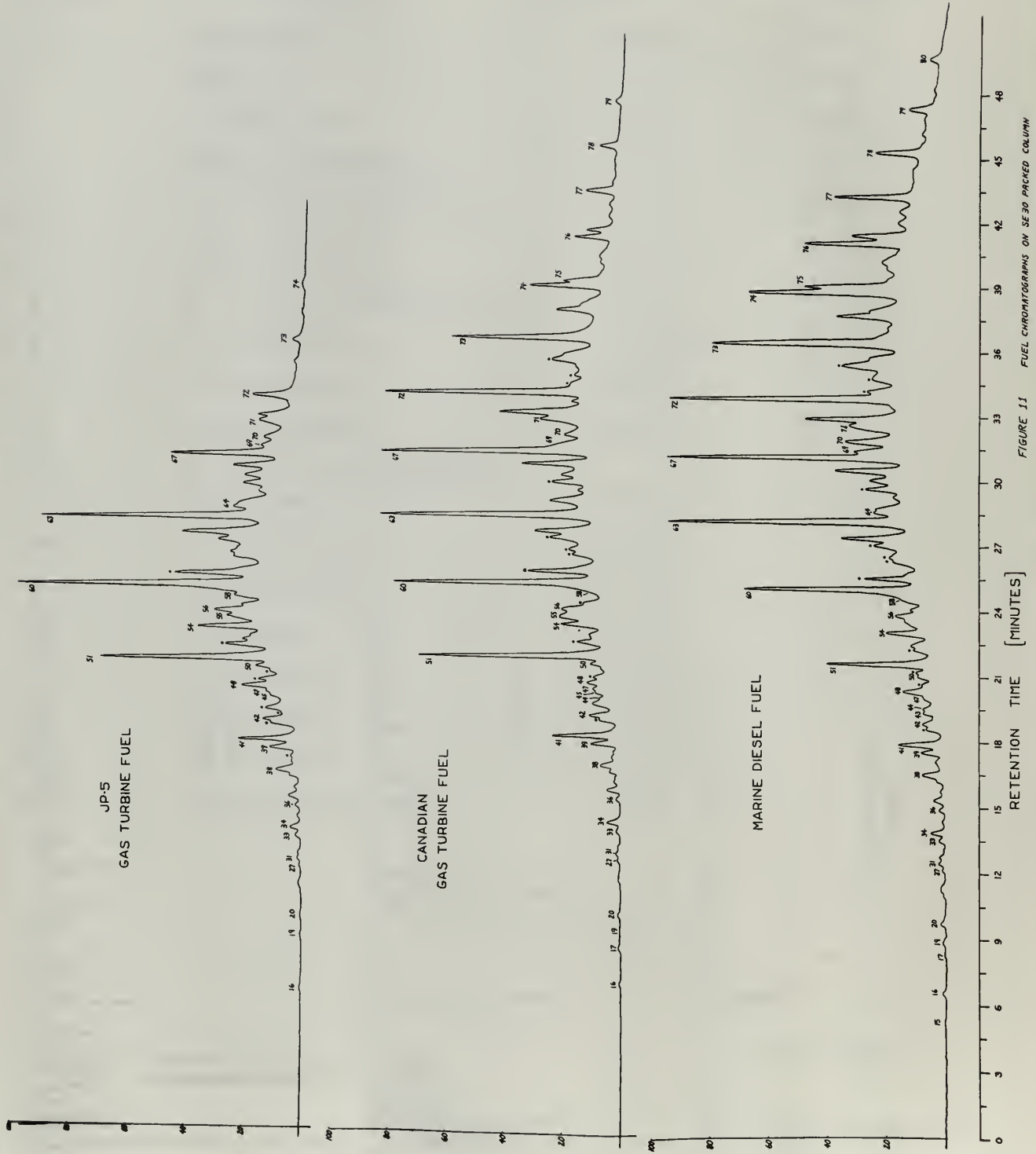


FIGURE 11 FUEL CHROMATOGRAMS ON SE 30 PACKED COLUMN

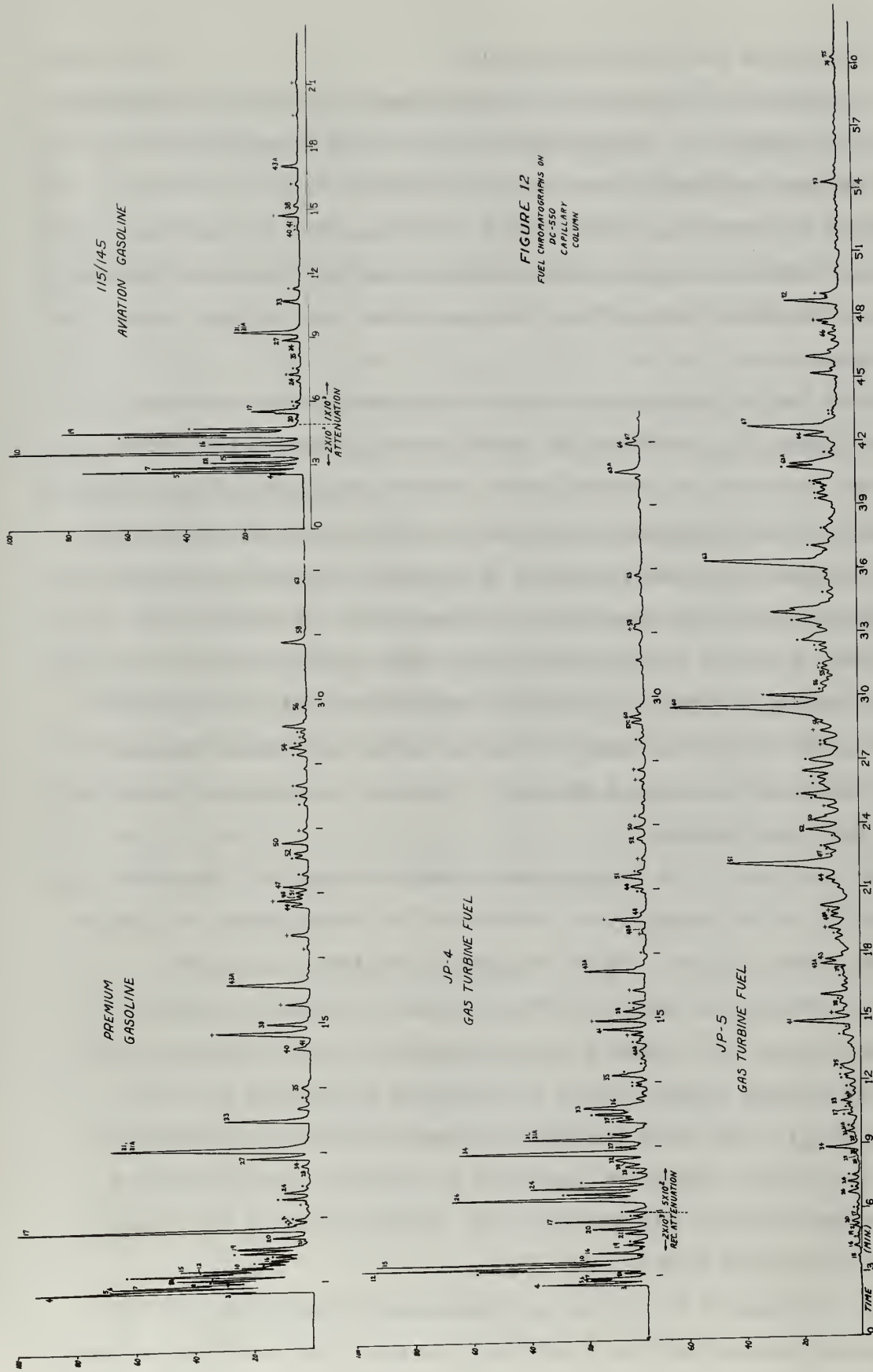


FIGURE 12
FUEL CHROMATOGRAMS ON
DC-550
CAPILLARY
COLUMN

5. Conclusions and Acknowledgements

The overall gas chromatograms show clearly the relative complexity of the fuels analyzed. Marine diesel fuel and the Canadian gas turbine fuel are considerably more complex than the others. The chromatograms of these two, along with that of JP5, show the typical gaussian distribution of a straight boiling point cut from a distillation column. The other fuels, JP4 and the gasolines, are blended, synthetic mixtures.

All of the gas turbine fuels investigated are high in aromatic content (Table III). Additionally, each contains many of the highly alkylated benzenes and naphthalenes, which contribute heavily to the formation of carbonaceous residue due to their incomplete combustion.

No simple, economical method is presently available to reduce the aromaticity of large quantities of these fuels. However, it is considered practical to blend these fuels with paraffinic stock from another source, in order to reduce the relative amounts of aromatics present. Since the aromaticity of various crude oils varies considerably, judicious choosing of the parent crude oil in preparing these fuels would also be of benefit.

The analysis of the fuels is necessarily incomplete. The non-availability of iso-paraffins as references for identification is a major problem. This problem is most serious in the higher molecular weights: decane and heavier. The multitude of isomers possible in these molecules will render a complete analysis most difficult, since the fuels studied contain traces of molecules as complex as tetra-cosane (C_{24}), with major quantities between decane and octadecane.

The following items are suggested as possible ways to improve the analysis of these gas turbine fuels, as well as being applicable to other analytical work of this type:

(a) Combine SE 30 and its high temperature capability with the high resolution available in a capillary column. Such a SE 30 capillary column would provide an excellent tool for the analysis of marine

diesel fuel.

(b) Investigate the applicability of the methylene insertion reaction for generating isomeric paraffin standards. Dvoretzky, Richardson, and Durrett [6] have shown that the statistical methylene insertion reaction can be used for the small scale synthesis and elution-time calibration of many hitherto unavailable compounds. With each hydrocarbon type reacted, the insertion of methylene into the carbon-hydrogen bonds of the parent molecule allows the predictable synthesis of isomeric next-higher homologs. Their work with n-heptane, various isomeric hexanes, octanes, and nonanes should be capable of extension to the heavier paraffins.

(c) Expand the work which has begun in hydrogenation of aromatics and hydroisomerization at n-olefins. Of particular interest here might be the isolation and identification of many geometric isomers of poly-alkylated cyclohexanes and decahydronaphthalenes.

The writer wishes to express his appreciation for the assistance and encouragement given him by Professor Glenn H. Spencer of the U. S. Naval Postgraduate School. Appreciated also was the assistance of Professor Charles F. Rowell who aided in the hydrogenation and hydroisomerization portion of the investigation.

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13. ABSTRACT

As part of an investigation of gas turbine regenerator fouling being conducted at the U. S. Naval Postgraduate School gas chromatography was used to compare and analyze certain hydrocarbon fuels. Because of the known relationship between fuel aromaticity and exhaust system fouling in gas turbine engines, particular emphasis was directed toward determination of the aromaticity of the fuels and of the particular aromatic compounds present. Fuels investigated included premium grade auto gasoline, aviation gasoline, several gas turbine fuels, and marine diesel fuel. Derivatives of cyclohexane and decahydronaphthalene were synthesized by hydrogenation of benzene and naphthalene derivatives with Raney nickel catalyst. Numerous branched-chain paraffins were synthesized by hydroisomerization of n-olefins under alkylation conditions. These synthetic products were used as standards in the identification of components of the fuels. The fuels investigated were found to contain from 35 to over 200 components. Component identification was from 30 to 60% complete.

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Gas Chromatography Gas Turbine Fuels Hydrocarbon Fuels Jet Fuel Hydrogenation Hydroisomerization Aromatic Fuels Fuel Aromaticity						

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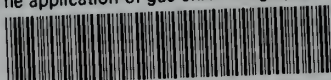
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