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RELATIVE RETENTION TIME LIBRARY FOR SELECTED
HYDROCARBONS VIA GLASS CAPILLARY GAS CHROMATOGRAPHY

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Mr. Paul Hayes, Jr.
Fuels Branch
Fuels and Lubrication Division

February 1982

Final Report June - August 1978

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NOTICE

This technical report has been reviewed and is approved for publication.

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This technical report describes an experimental study of the reliability of a glass capillary gas chromatographic system to assign tentative peak identity according to relative retention times under carefully controlled operating conditions. The first phase of the effort involved the set-up, calibration, and optimization of the capillary system. Optimization was realized with the maximum resolution between selected pairs of hydrocarbons in a minimum of sample analysis time. Peak resolution was investigated as a function of carrier capillary pressure and temperature programming rate. A reference hydrocarbon

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was chosen. The repeatability of relative retention times was determined for: normal alkanes, branched alkanes, olefins, alkyl benzenes, alkylated naphthalenes, saturated cyclic alkanes, and alkyl anilines that could be present in JP-4.

FOREWORD

This technical report describes an experimental study into the reliability of a glass capillary gas chromatographic system to assign tentative peak identity according to relative retention times under carefully controlled operating conditions. The work reported herein was performed under the In-House Work Unit 30480591, "Evaluation and Development of Aircraft Fuels", which was administered by the Fuels Branch (AFWAL/POSF), Fuels and Lubrication Division (AFWAL/POS), Air Force Aero Propulsion Laboratory (AFWAL/PO).

The effort detailed within is the result of systematic studies admirably performed by Mr Roy Parker, a summer aid from Carnegie-Mellon Institute, from June through August 1978. However, another student aid, Ms Elizabeth Tate, was responsible for calculating the relative retention times for the standards as well as the seven fuel samples analyzed. Ms Tate also organized and tabulated all of the results in this report. Particular gratitude is extended to Dr Ronald Butler of the Fuels Branch for his impetus and guidance throughout this project. This report was prepared by Mr Paul C. Hayes, Jr.

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ABBREVIATION	MEANING
$(GC)^2$	Glass Capillary Gas Chromatograph
n^1	effective theoretical plates
R	resolution of two components separated by a chromatographic process
ml	milliliters
min	minutes
t_R	component's absolute retention time
W_h	component's corresponding peak width time at half height
t'_R	adjusted retention time
RRT	relative retention time
JP-4	jet propulsion fuel, wide-distillate cut, conforming to MIL-T-5624L

SECTION I

INTRODUCTION

The experimental study detailed in this technical report is one step, albeit a necessary one, toward the prediction of the physical properties of hydrocarbon fuels from a detailed analysis of their components and application of the appropriate physical chemical equations. The first phase of this effort involved the set-up, calibration, and optimization of a Glass Capillary Gas Chromatographic $(GC)^2$ system. The system was optimized to obtain the maximum resolution between selected pairs of hydrocarbons in a minimum of sample analysis time. Peak resolution was investigated as a function of both carrier gas pressure and temperature programming rate. An optimized system could better repeat individual hydrocarbon's retention times and permit the amassing of a reliable hydrocarbon library.

The remarkable advantages of gas chromatography are speed of analysis, resolution of complex samples into individual components, sensitivity for trace analysis on very small sample volumes, and versatility to glean both qualitative and quantitative information from a wide variety of mixtures. In general, gas chromatography is the physical means of separating a sample into its individual components via distribution of the sample between two phases: a stationary phase (i.e., column's liquid coating) and a mobile phase (i.e., carrier gas) (Reference 1). The process requires that the sample be sufficiently volatile to be carried through the column. Due to the wide boiling character of conventional hydrocarbon fuels, temperature programming of the column was necessary. Temperature programming is the increase of column temperature with time. Components that elute or emerge early from the column can be well resolved and later peaks made to be sharp and uniformly distributed throughout the chromatogram. When the stationary phase is nonpolar, sample components are separated according to their relative volatility, akin to, but not strictly following, their atmospheric boiling point order.

Although the concept of capillary column chromatography was first described by M.J.E. Golay and co-workers over 20 years ago, capillary column technology has not advanced as rapidly as had been envisioned (Reference 2). There is a gap, consequently, of approximately 15 years between theory and actual practice of high resolution capillary chromatography (Reference 3). Fortunately, recent advances in capillary column preparation have enabled the transfer of $(GC)^2$ from research to routine analysis, particularly in the petrochemical field. Such complex mixtures as gasoline, naphtha, reformate, and similar products require a high resolution column to separate, tentatively identify, and quantitate individual components via retention time (Reference 4).

The absolute retention time of a particular component or peak is the time from the point of injection to the peak maximum as displayed on the recorder or logged by an integrator. The same peak on the same column under the same conditions will always have the same retention time. However, slight deviations of any of the operating conditions or for that matter, the quality or state of the column, can change this absolute retention time. For this reason, retention times relative to a reference hydrocarbon present in all samples of interest, called relative retention times, are far more reliable and repeatable from day to day, as will be demonstrated in this report. Whatever alters the retention time of the reference component will also affect the other components in a similar manner.

Resolution is the fundamental yardstick used in this report to evaluate system optimization for the eventual separation of as many fuel hydrocarbon components as possible. Simply, resolution is the quantitative measure of the separation between two peaks. The term resolution shall be defined here as the difference in the absolute retention times of any two peaks divided by the average of their peak widths (at half height), i.e.,

$$R = \frac{2 \, (t_{r1} - t_{r2})}{1.7 \, (w_{h1} + w_{h2})}$$

where:

    a)   R   = resolution between peak #1 and peak #2

    b) t_{r1} = absolute retention time of peak #1

           t_{r2} = absolute retention time of peak #2

    c) w_{h1} = peak width at half height for peak #1

           w_{h2} = peak width at half height for peak #2

    d)   all measurements in the same unit, i.e. time or millimeters.

For reference, an "R" value of 1.5 or greater means baseline separation between two peaks.

In the qualitative analysis of a complex mixture of individual components, the positive identification of the peaks emerging from a column is very difficult. There are two primary obstacles to identification: 1) the peaks represent only nano- or pico-grams of material, are 2) chromatographic retention times, be they absolute or relative, and not unique. It is possible for two compounds to have identical, if not very close, retention times; hence the need for the maximum resolution possible from a chromatographic system. To reiterate, retention time is not sufficient to positively identify particular peaks since the data is characteristic, but not definitive.

The use of high resolution glass capillary columns for the most probable assignment of hydrocarbons in a complex mixture, requires the components of a gas chromatographic system, i.e., the oven, inlet, detector, pneumatics, and integrator to be stable and re-setable. Given the unprecedented resolving power of capillary columns and the state of the art microprocessor controlled $(GC)^2$ systems, retention time reliability can be excellent and subsequent peak assignments given a high probability of accuracy.

SECTION II

EXPERIMENTAL APPROACH

1. INSTRUMENTATION

The basic analytical instrument utilized in this study was the
Varian Model 3700 Capillary Gas Chromatograph (GC) equipped with dual
flame ionization detectors. The chromatograph was factory-modified to
accept glass capillary columns, and also fitted with a Varian Model 8000
Automatic Liquid Sampler. A Varian Model CDS-111 Computing Integrator
controlled the automatic liquid sampler, the temperature programming, and
the data collection as well as the other GC functions.

The Varian chromatograph is equipped with an all glass injection
and detection system with dead volume eliminated or reduced to a practical
minimum by design and/or purging. The system provides a choice of sampling-
injection modes of which the normal split mode was used in this study.
The capillary pneumatics is a pressure regulated system, with all the
active components thermostated to better than +/- 1°C for maximum retention
time repeatability and detector baseline stability. The injector-splitter
features a true positive septum purge which effectively eliminates septum
bleed (Reference 5).

2. GAS CHROMATOGRAPHIC CONDITIONS

The glass capillary column used in this work was manufactured by
J&W Scientific, Inc. to the following specifications: column length of
60 meters, column internal diameter of 0.25 mm, and relatively nonpolar
stationary liquid phase of SE 30. The flow rate of the nitrogen carrier
gas (1.0 ml/min) was boosted to 35 ml/min at the detector via make-up
nitrogen, to sharpen the eluting peaks. The nitrogen was "high purity"
water-pumped. It was Air Force requisitioned (P.N. 6830-264-9087) from
Burdox Inc., Dayton, Ohio. The nitrogen was further purified via a train
of four Matheson Gas Products Gas Purifiers, Model 450, to remove any
gross contamination inadvertently introduced, i.e., oil, water, particulate
matter (> 5 microns). To further preserve the integrity of the glass
capillary column, a General Electric Model "Go-Getter" was installed after

the above four traps to remove any oxygen or water vapor present to less than 0.1 parts-per-million.

Other GC operating parameters were as follows:

a. Temperature program was from 40°C to 275°C at varying rates according to the particular experiment;

b. Flow rates of hydrogen and compressed air to the detector were 30 ml/min and 300 ml/min, respectively;

c. Injection port and detector were maintained at 300°C;

d. Electrometer was set at range, 10^{-11} and attenuation, 1;

e. Injection volume was fixed at one microliter;

f. Split ratio was adjusted to 100:1 for dilute, synthetic hydrocarbon calibration mixtures;

g. Column was conditioned prior to usage to remove volatile impurities at 280°C overnight with a carrier pressure of 5 psig (detector outlet unattached).

One measure of column efficiency is its number of effective theoretical plates, a concept derived from distillation theory. The greater the number of theoretical plates, the greater the probability of resolving closely boiling components. The effective plates were determined to be over 100,000, typical of most capillary columns of this length. The sample analyzed was a one microliter injection of a 1:20 hexane solution of normal hexadecane ($n-C_{16}$) run isothermally at 150°C with the same split ratio as above and at a carrier gas pressure of 10 psig. The equation used for measuring the column's effective theoretical plates (n') was:

$$n' = 5.545 \left[\frac{t_R'}{w_h}\right]^2$$

where:

a) t_R' = the adjusted retention time of $n-C_{16}$, i.e., its absolute retention time minus column dead volume time (for unretained methane);

b) w_h = the peak width at half the peak's height.

3.   OPTIMIZATION CRITERION

The optimum carrier pressure and programming rate should give the best compromise of high resolution between two closely boiling components and short analysis time. Of additional interest was the effect on the resolution of another pair of components that differed markedly in their boiling points. The boiling point gap in this latter pair was chosen to check resolution integrity over a substantial portion of the distillation range of a typical JP-4 hydrocarbon fuel. The closely boiling hydro-carbons selected were benzene and cyclohexane with literature boiling points (atmospheric) of 80.1 and 81.0°C, respectively. The widely boiling pair chosen was normal hexane and normal decane with literature boiling points (atmospheric) of 68.0 and 174.1°C, respectively.

4.   OPTIMIZATION EXPERIMENTS

a.   Programming Rate

Figures 1 and 2 display the data generated from the chromato-graphic runs (in triplicate) on the above component pairs, as 1:20 hexane solutions, at a carrier capillary pressure of 30 psig and using the aforementioned temperature programmed range. Both plots demonstrate the loss of resolution as a function of increasing column temperature pro-gramming rates. The relative drop in resolution from the 1°C/min rate to the 5°C/min rate is nearly identical for the two pairs of components studied, i.e., 6.35% for benzene versus cyclohexane, and 6.28% for hexane versus decane, based on their respective 1°C/min results. This implies that the temperature programming rate, in the range of 1-5°C/min can be altered significantly with minimal effect on peak resolution, but at a considerable saving of analysis time.

b.   Carrier Gas Capillary Pressure

Figures 3 and 4 show the data collected (in triplicate) at a temperature programming rate of 2°C/min over the same temperature span of 40-275°C. Both plots show the apparent loss of resolution between peaks as a function of increasing column flow rates as controlled by the capillary gas pressure. Each graph has a unique capillary pressure that permits maximum peak resolution. However, to best resolve both pairs of hydrocarbons, a capillary pressure between 15 and 20 psig should be chosen.
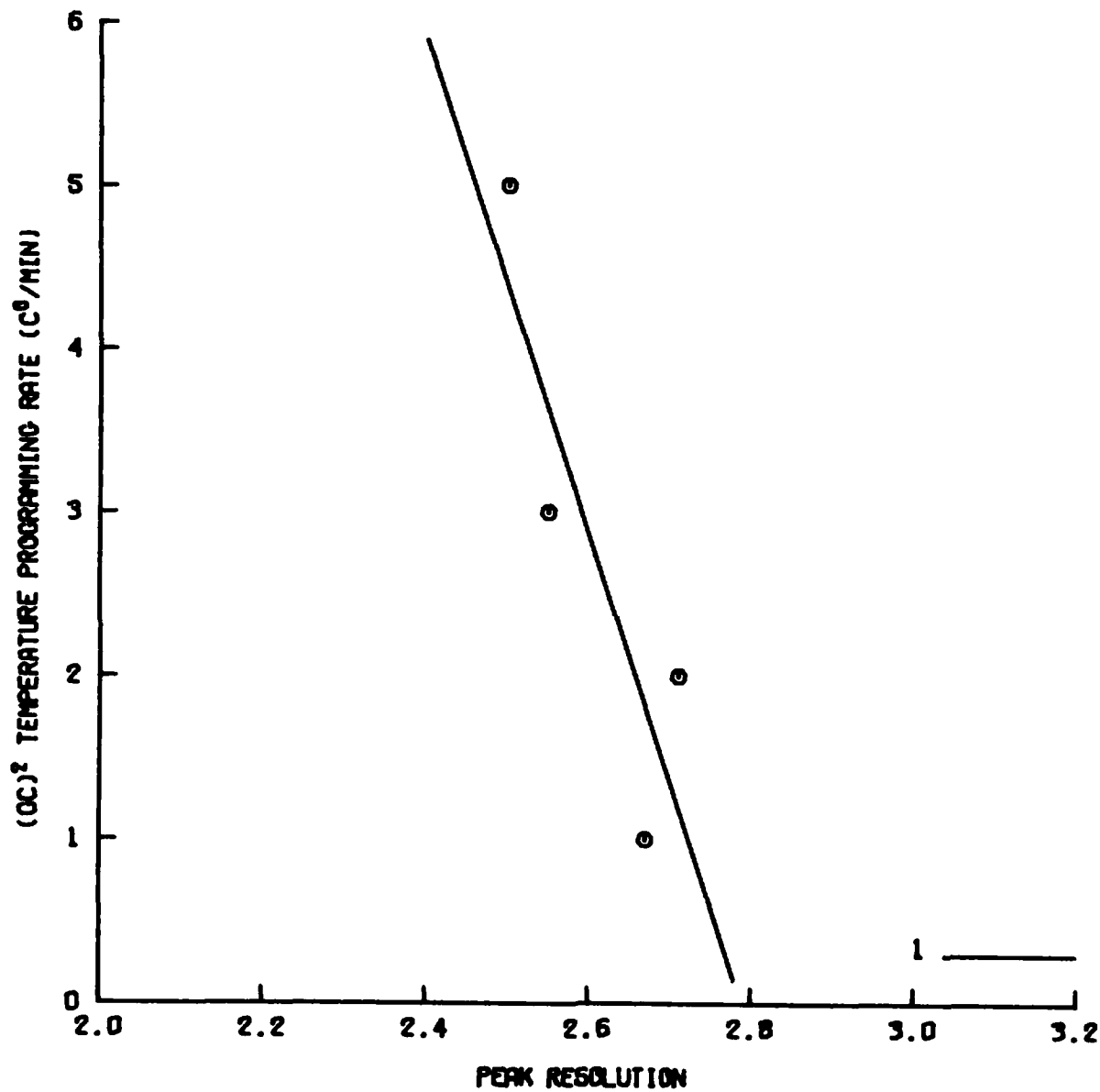
Figure 1.   Resolution vs Temperature Programming Rate: Benzene vs Cyclohexane
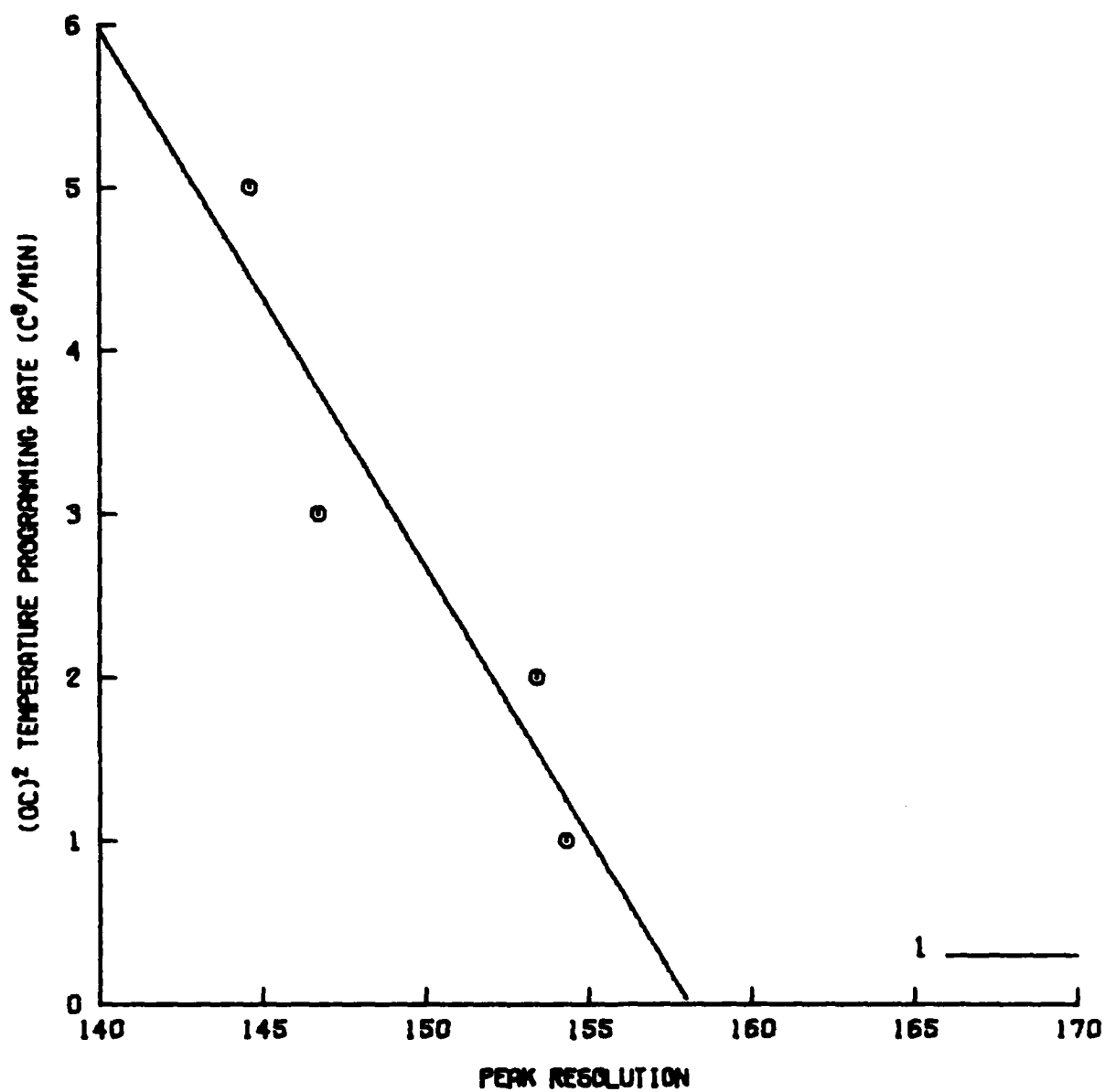
The caption is "Figure 2. Resolution vs Temperature Programming Rate: n-Hexane vs n-Decane". The y-axis is "(OC)² TEMPERATURE PROGRAMMING RATE (C°/MIN)". The x-axis is "PEAK RESOLUTION". Page number 8 at bottom. Header AFWAL-TR-81-2140.

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Figure 2.   Resolution vs Temperature Programming Rate: n-Hexane vs
n-Decane

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(DC)² CARRIER CAPILLARY PRESSURE (PSIG)

25

20

15

10

5

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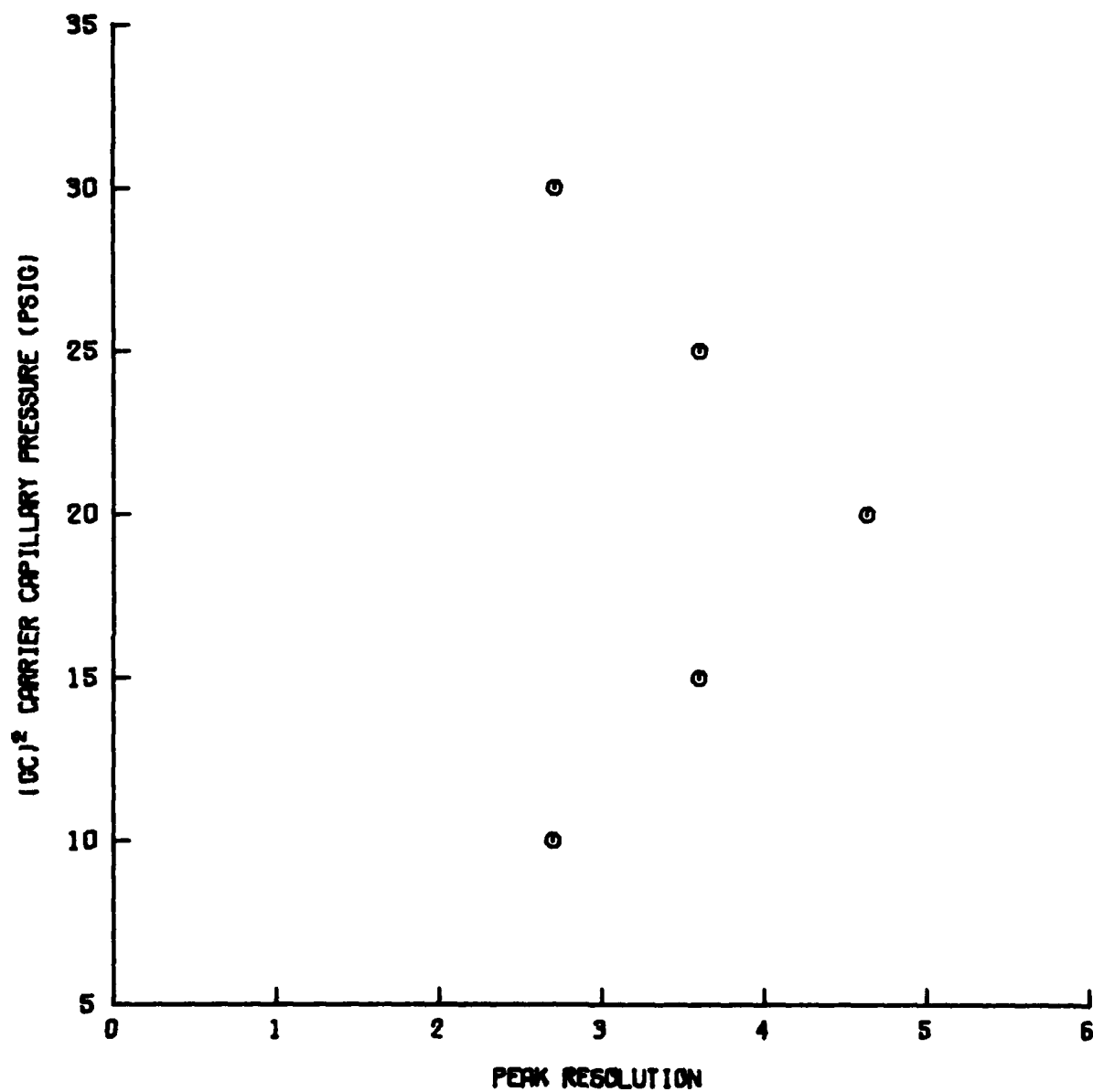
PEAK RESOLUTION

Figure 3.   Resolution vs Carrier Capillary Pressure: Benzene vs
Cyclohexane
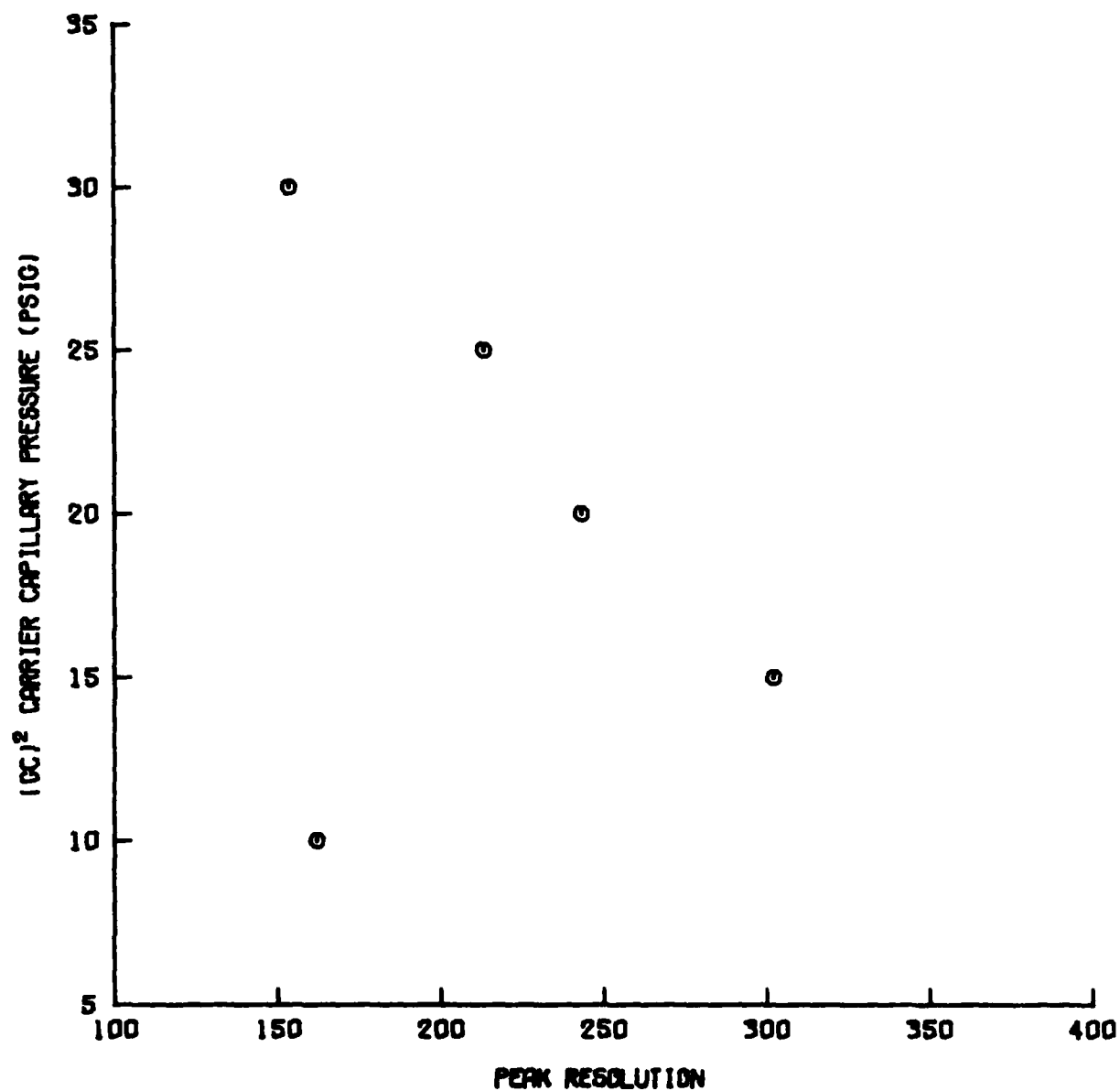
Figure 4.   Resolution vs Carrier Capillary Pressure: n-Hexane vs
            n-Decane

For the sake of a shorter analysis time and the maximum possible resolution between closely boiling components, such as benzene and cyclohexane (Figure 3), a capillary gas pressure of 20 psig, and a temperature programming rate equal to 2°C/min were selected for all subsequent data collection.

5. LIBRARY DATA COLLECTION

Approximately 5-10 microliters of pure hydrocarbon liquids (5-10 mg for solids) were dissolved in pentane with a dilution factor of 100:1 and chromatographed under the optimized conditions. This dilution step was an attempt to roughly approximate the actual volume percentages of these components found in typical JP-4 fuel. It was subsequently found that the retention time of any given hydrocarbon could be slightly shifted to later times when the volume percentage of that component in a sample was increased by an order of magnitude, i.e., from 0.1 to 1.0%.

For each mixture of 8-10 hydrocarbons in pentane, there was a qualitatively identical sample prepared but with varying amounts of several of the components. This duplication step aided in establishing elution order and helped establish retention time repeatability for small (within a factor or two) changes in component concentration.

Characteristic plots of absolute retention time for each member of a hydrocarbon series, versus atmospheric boiling points (°C) are shown in Figures 5 and 6 for several aromatic hydrocarbons and normal alkanes, respectively. Note the near linear relationships, as expected, when the capillary column is linearly temperature programmed. The lines curve slightly at lower boiling components because the capillary column was not sufficiently cooled to condense the more volatile hydrocarbons. A liquid nitrogen accessory has subsequently been incorporated into the capillary system which should make the chromatography of low boiling hydrocarbons (liquid at room temperature) closer to ideality.

As mentioned earlier, relative retention times, relative to a hydrocarbon naturally occurring in JP-4 samples, is a more reproducible quantity, at least on a day-to-day basis. Such an internal reference peak, present in all the JP-4 samples analyzed in this laboratory was
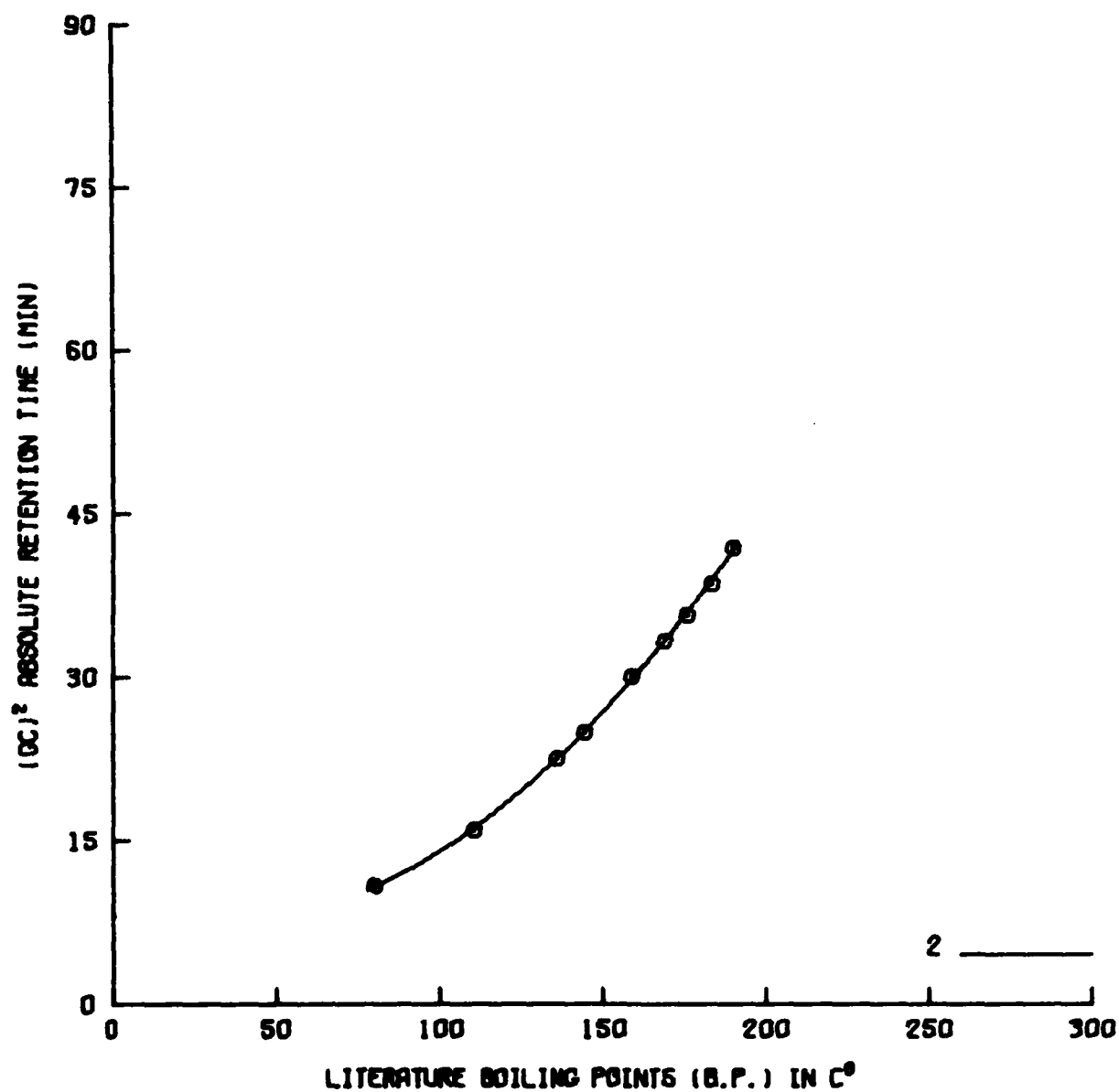
Figure 5. B.P. of Selected Aromatics vs $(GC)^2$ Absolute Retention Time
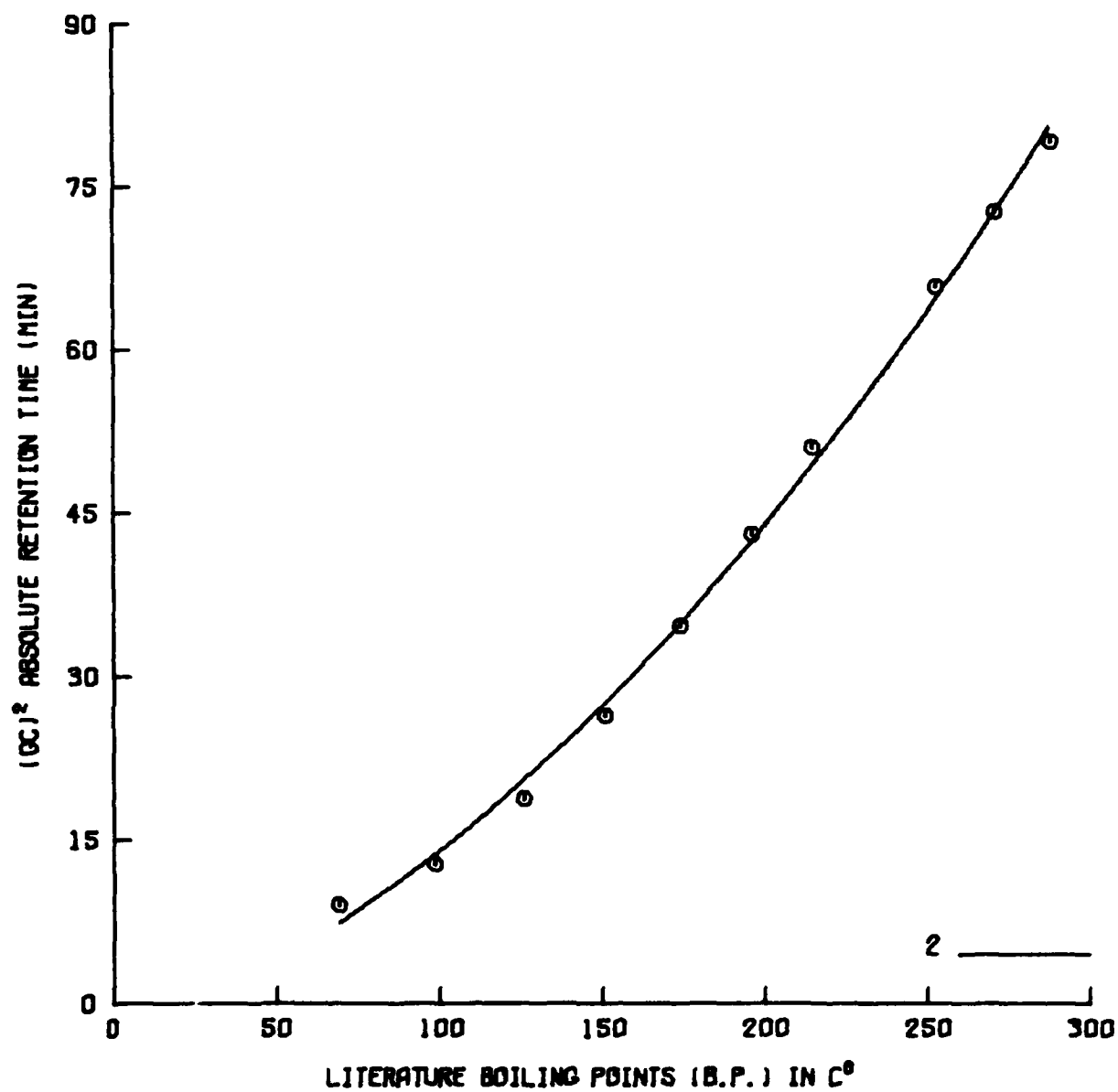
Figure 6.   B.P. of Selected Alkanes vs $(GC)^2$ Absolute Retention Time

normal heptane (b.p. = 98.4°C). Table 1 is a compendium of relative retention times derived from the qualitative hydrocarbon mixtures described previously but spiked also with heptane. The adjusted retention time of each component was divided by that of the heptane spike, and reported as that component's "relative retention time". All sample preparations were chromatographed in triplicate and the relative standard deviation of the calculated relative retention times displayed in Table 1. Note that the vast majority of those relative retention times had relative standard deviations of about 0.10%.

6. FUELS CHARACTERIZATIONS

Samples of both petroleum derived and shale derived jet propulsion fuels were analyzed in triplicate on the SE 30 column under the same conditions used for the standard solutions, but without dilution with pentane. The relative retention time, i.e. RRT, of each resolved peak was calculated, averaged, and compared with the library of standards' relative retention times. An assurance limit of +/- 0.01 RRT units (equal to three standard deviations) was used for matching an unknown peak in the fuel with a known standard in the library.

The following tables list the seven jet propulsion fuels selected for analysis for this report. Table 2 presents the individual hydrocarbons in the library with their respective RRT's along with the RRT's of those peaks in each of the unknown fuels that matched, in accordance with the above assurance window. Of the 133 compounds in the library, the most peaks tentatively identified in a fuel were 83 for the shale JP-4, the least identified were 57 for the imported kerosene-type fuel. Table 3 displays the corresponding weight percent of each matched peak, assuming that area percent (without calibration factors) is roughly the same as weight percent. For hydrocarbons this is approximately correct. Note that the maximum amount of any fuel tentatively identified was only about 56% (Petroleum JP-4) and that for the imported kerosene fuel it was only about 30%!

TABLE 1
RELATIVE RETENTION TIME DATA FOR HYDROCARBON LIBRARY

Individual Hydrocarbons	Boiling Point (°C)	Relative Retention Time	Relative Standard Deviation %
NORMAL ALKANES			
N-Pentane	36.04	.1849	0.46
N-Hexane	68.74	.4583	0.11
N-Heptane	98.43	1.0000	----
N-Octane	125.67	1.8193	0.07
N-Nonane	150.82	2.9118	0.06
N-Decane	174.15	4.0770	0.26
N-Undecane	195.89	5.2591	0.07
N-Dodecane	216.3	6.3866	0.05
N-Tetradecane	253.7	8.4748	0.04
N-Pentadecane	270.63	9.4342	0.04
N-Hexadecane	287.0	10.3445	0.06
N-Octadecane	316.1	12.0087	0.08
N-Nonadecane	329.7	12.4482	0.09
N-Eicosane	343.8	12.7941	0.10
BRANCHED ALKANES			
2,2-Dimethyl Butane	49.74	.2605	0.30
2,3-Dimethyl Butane	57.99	.3403	0.41
2-Methyl Pentane	60.27	.3529	0.06
3-Methyl Pentane	63.28	.4020	0.05
2,4-Dimethyl Pentane	80.50	.5868	0.07
2,2,3-Trimethyl Butane	80.87	.5610	0.05
2,3-Dimethyl Pentane	89.78	.6204	0.06
3-Methyl Hexane	91.85	.8459	0.06
2,2,4-Trimethyl Pentane	99.24	.9272	0.08
2,2-Dimethyl Hexane	106.84	1.2255	0.10
2,5-Dimethyl Hexane	109.10	1.2451	0.07
2,3,4-Trimethyl Pentane	118.47	1.3866	0.09
2-Methyl Heptane	117.65	1.5210	0.09
3-Methyl Heptane	118.92	1.5994	0.08
2,2,5-Trimethyl Hexane	124.08	1.7073	0.11
2-Methyl Octane	143.26	2.5476	0.07
3-Methyl Octane	144.21	2.6218	0.04
2-Methyl Decane	189.19	4.8683	0.06
OLEFINS			
Cyclopentene	44.24	.2913	0.35
4-Methyl-1-Pentene	53.87	.3081	0.07
C-4-Methyl-2-Pentene	56.39	.3417	0.06
2-Methyl-1-Pentene	62.12	.4104	0.08
1-Hexene	63.48	.4146	0.08
2-Ethyl-1-Butene	64.68	.4552	0.17

TABLE 1 (Cont'd)

Individual Hydrocarbons	Boiling Point (°C)	Relative Retention Time	Relative Standard Deviation
C-2-Hexane	68.89	.5126	0.10
Cyclohexene	82.98	.8235	0.10
1-Heptene	93.64	.9230	0.03
C-2-Heptene	97.95	1.0728	0.06
2,4,4-Trimethyl-1-Pentene	101.46	1.0728	0.05
2,2,4-Trimethyl-1-Penetne	112.3	1.0742	0.06
2,4,4-Trimethyl-2-Pentene	104.91	1.1975	0.10
3,5,5-Trimethyl-1-Hexene	---	1.5406	0.08
2-Ethyl-1-Hexene	120	1.7129	0.05
1-Octene	121.27	1.7423	0.06
Bicyclo (2,2,1)Hept(2,5) Diene	89.5	2.0154	0.04
4-Ethenyl cyclohexene	128.9	2.1317	0.06
1-Nonene	147	2.7675	0.05
C-7-Nonene	N/A	2.8249	0.07
t-7-Nonene	N/A	2.8417	0.06
Pinene	156.2	3.2703	0.05
Camphene	158.5/159.5	3.4202	0.10
1-Decene	170.56	3.9160	0.08
d-Limonene	178	4.2143	0.07
Dipentene	170(685mmHg)	4.3501	0.06
1-Undecene	192.7	5.0354	0.05
1-Dodecene	213.4	6.2059	0.05
1-Tridecene	232.8	7.2675	0.06
1-Tetradecene	232-234	8.2759	0.06
1-Hexadecene	284.4	10.1303	0.05
1-Octadecene	179	11.8067	0.08
1-Eicosene	341	12.8067	0.04
1-Docesene	---	14.8277	0.08
ALKYL BENZENES			
Benzene	80.10	.7199	0.05
Methyl	110.63	1.4370	0.53
Ethyl	136.18	2.3683	0.05
1,4-Dimethyl	138.35	2.4902	0.05
1,3-Dimethyl	139.10	2.4902	0.07
1,2-Dimethyl	144.41	2.6709	0.93
i-Propyl	152.39	3.0504	0.06
n-Propyl	159.22	3.3908	0.06
1-Methyl-3-Ethyl	161.30	3.5154	0.06
1-Methyl-4-Ethyl	161.99	3.5350	0.04
1,3,5-Trimethyl	164.72	3.6036	0.07
1-Methyl-2-Ethyl	165.15	3.6975	0.06
1,2,4-Trimethyl	169.35	3.8543	0.05

TABLE 1 (Cont'd)

Individual Hydrocarbons	Boiling Point (°C)	Relative Retention Time	Relative Standard Deviation %
t-Butyl	169.15	3.8978	0.05
i-Butyl	172.76	4.0658	0.03
Sec-Butyl	173.33	4.0938	0.11
1,2,3-Trimethyl	176.08	4.2213	0.06
1-Methyl-3-i-Propyl	175.18	4.2379	0.07
1-Methyl-4-i-Propyl	177.13	4.2801	0.05
1-Methyl-2-i-Propyl	178.18	4.4146	0.05
1-Methyl-3-n-Propyl	182.00	4.5644	0.05
1,3-Diethyl	181.14	4.5784	0.04
1-Methyl-4-n-Propyl	183.34	4.6246	0.05
n-Butyl	183.31	4.6337	0.09
1,4-Diethyl	183.79	4.6807	0.08
1,2-Diethyl	183.46	4.7255	0.04
1-Methyl-2-n-Propyl	184.83	4.7885	0.07
t-Amyl	192.38	4.9356	0.06
1-Methyl-3-sec-Butyl	194.00	5.0490	0.09
1-Methyl-4-sec-Butyl	197.22	5.0518	0.11
n-Pentyl	202.1	5.7357	0.06
Tetralin	207.65	5.8361	0.06
n-Hexyl	227.4	6.9188	0.05
Pentamethyl	231.8	7.1457	0.06
Cyclohexyl	237.5	7.5700	0.06
n-Heptyl	235.00	7.9972	0.04
Hexamethyl	265.00	8.9026	0.07
n-Octyl	265.00	9.0126	0.05
1,1-Diphenyl-Ethylene	286.0	9.5294	0.25
n-Nonyl	275.0	9.9748	0.07
n-Decanyl	297.0	10.8894	0.05
Hexaethyl	298.0	11.1036	0.09
n-Undecanyl	313.2	11.7521	0.05
n-Dodecanyl	179	12.5756	0.05
n-Tridecanyl	189	13.3557	0.05
n-Tetradecanyl	196	14.1176	0.06
n-Pentadecanyl	366	15.4972	0.07
ALKYL NAPHTHALENES			
Naphthalene	217.94	6.0896	0.08
2-Methyl	241.10	7.2339	0.09
1-Methyl	244.68	7.4848	0.10
2,6-Dimethyl	262	8.4244	0.04
1,3-Dimethyl	263	8.5994	0.03
1,4-Dimethyl	268	8.8529	0.05
ANILINES			
Aniline	184.13	3.7927	0.06
N,N-Dimethyl	194.15	5.2997	0.03
2,6-Dimethyl	215	5.8375	0.04
2,3-Dimethyl	224	6.1975	0.03

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TABLE 1 (Cont'd)

Individual Hydrocarbons	Boiling Point (°C)	Relative Retention Time	Relative Standard Deviation
CYCLOALKANES			
1-C-2-Dimethyl-Cyclopentane	99.53	.3417	0.29
Methyl-Cyclopentane	71.81	.5840	0.15
Cyclohexane	80.74	.7633	0.08
Methyl-Cyclohexane	100.93	1.1667	0.05
1,1-Dimethyl-Cyclohexane	119.55	1.7171	0.11
1-t-2-Dimethyl-Cyclohexane	123.43	1.8277	0.10
1-C-2-Dimethyl-Cyclohexane	129.74	2.1232	0.07
n-Butyl-Cyclohexane	180.95	4.4930	0.08
t-Decalin	187.25	4.7255	0.08
C-Decalin	195.65	5.2521	0.12

TABLE 2

CHARACTERIZATION OF SELECTED FUELS VIA COMPONENTS' RELATIVE RETENTION TIMES

Individual Hydrocarbons	Boiling Point(°C)	COMPONENT RELATIVE RETENTION TIME (RRT)							
		RRT Library	Petrol JP-4	Shale JP-4	Syncrude JP-4	Petrol JET A	Syncrude JET A	Petrol JP-7	Imported Fuel
NORMAL ALKANES									
N-Petane	36.04	.1849	.1849	.1861	.1854				
N-Hexane	68.74	.4583	.4607	.4569	.4574				
N-Heptane	98.43		1.000	1.000	1.000	1.000	1.000	1.000	1.000
N-Octane	125.67	1.8193	1.8095	1.7972	1.8019	1.7952	1.8117		
N-Nonane	150.82	2.9118	2.9173			2.8941		2.9349	
N-Decane	174.15	4.0770	4.0868			4.0571	4.0529	4.1244	4.0571
N-Undecane	195.89	5.2591	5.2591		5.2552	5.2451		5.3224	5.2284
N-Dodecane	216.3	6.3866	6.3865	6.3375	6.3598				6.3384
N-Tetradecane	253.7	8.4748	8.4607		8.4100	8.4331		8.5700	8.4136
N-Pentadecane	270.63	9.4342				9.3955			9.3746
N-Hexadecane	287.0	10.3445					10.3082		10.2994
N-Octadecane	316.1	12.0087							
N-Nonadecane	329.7	12.4482							
N-Eicosane	343.8	12.7941							
BRANCHED ALKANES									
2,2-Dimethyl Butane	49.74	.2605	.2633						
2,3-Dimethyl Butane	57.99	.3403	.3431	.3416	.3417				
2-Methyl Pentane	60.27	.3529	.3529	.3500	.3500				
3-Methyl Pentane	63.28	.4020	.4005	.3972			.4058		
2,4-Dimethyl Pentane	80.50	.5868	.5812	.5777	.5774		.5871	.5871	
2,2,3-Trimethyl Butane	80.87	.5910	.5812	.5777	.5774	.5877	.5871		
2,3-Dimethyl Pentane	89.78	.6204	.6218			.6169			
3-Methyl Hexane	91.85	.8459	.8417	.8347	.8354	.8412	.8423		
2,2,4-Trimethyl Pentane	99.24	.9272	.9229	.9166	.9191	.9275	.9274		
2,2-Dimethyl Hexane	106.84	1.2255	1.2324	1.2319	1.2357	1.2144			
2,5-Dimethyl Hexane	109.10	1.2451	1.2507	1.2319	1.2357		1.2440		
2,3,4-Trimethyl Pentane	113.47	1.3866	1.3851	1.3763					
2-Methyl Heptane	117.65	1.5210	1.5280	1.5152	1.5843	1.5320	1.5230		
3-Methyl Heptane	118.92	1.5994	1.6008	1.5805	1.5843		1.5913	1.5997	
2,2,5-Trimethyl Hexane	124.08	1.7073	1.7002	1.6861	1.6903		1.7001		
2-Methyl Octane	143.26	2.5476				2.5278			2.5348
3-Methyl Octane	144.21	2.6218	2.6302	2.6083	2.6164	2.6058	2.5969		
2-Methyl Decane	189.91	4.8683		4.8430	4.8591	4.8412	4.8396		4.8440
OLEFINS									
Cyclopentene	44.24	.2913				.2924			
4-Methyl-1-Pentene	53.87	.3081				.3203			
C-4-Methyl-2-Pentene	56.39	.3417	.3431	.3416	.3417				
2-Methyl-1-Pentene	62.12	.4104	.4005	.3972	.3974		.4058		
1-Hexene	63.48	.4146	.4005	.3972	.3974		.4058		
2-Ethyl-1-Butene	64.68	.4552	.4607	.4569	.4574				
C-2-Hexene	68.89	.5126							

TABLE 2 (Cont'd)

COMPONENT RELATIVE RETENTION TIME (RRT)

Individual Hydrocarbons	Boiling Point(°C)	RRT Library	Petrol JP-4	Shale JP-4	Syncrude JP-4	Petrol JET A	Syncrude JET A	Petrol JP-7	Imported Fuel
Cyclohexene	82.98	.8235	.8249	.8194	.8214				
1-Heptene	93.64	.9230	.9229	.9166	.9191	.9164	.9274		
C-2-Heptene	97.95	1.0728							
2,4,4-Trimethyl-1-Pentene	101.46	1.0728							
2,2,4-Trimethyl-1-Pentene	112.3	1.0742							
2,4,4-Trimethyl-2-Pentene	104.91	1.1975				1.1727			
3,5,5-Trimethyl-1-Hexene	N/A	1.5406	1.5406	1.5152	1.5202	1.5320	1.5355		
2-Ethyl-1-Hexene	120	1.7129		1.7883	1.7126		1.7001		
1-Octene	121.27	1.7423	1.7408	1.7416	1.7461		1.7419		
Bicyclo (2,21) Hept (2,5) Diene	89.5	2.0154	2.0042	1.9875	1.9944	2.0013			
4-Ethenyl cyclohexene	128.9	2.1317	2.1428	2.0958	2.1394		2.1129		
1-Nonene	147	2.7675	2.7619	2.7402	2.7475	2.7381	2.7615	2.7615	
C-7-Nonene	N/A	2.8249	2.8291	2.8069	2.8172	2.8091	2.8131		
t-7-Nonene	N/A	2.8417	2.8291	2.8069	2.8172	2.8286	2.8284		
Pinene	156.2	3.2703	3.2773	3.2677		3.2412	3.3097		
Camphene	158.5-159.5	3.4202	3.4033	3.3805	3.3919	3.2399	3.4030		
1-Decene	170.56	3.9160	3.9145	3.8861	4.0362	3.8802	3.9121	3.9519	
d-Limonene	178.	4.2143	4.2044	4.1759	4.1938	4.1824	4.2078	4.2545	4.1818
Dipentene	170(685mmHg)	4.3501	4.3641	4.3097	4.3235	4.3328	4.3375		4.3370
1-Undecene	192.7	5.0854	5.0700	5.0402	5.0571	5.0278	5.0460	5.1258	
1-Dodecene	213.4	6.2059			6.1966	6.1545	6.1799	6.2687	6.1532
1-Tridecene	232.8	7.2675	7.2619	7.2180	7.2412	7.2186	7.2538	7.3451	7.2172
1-Tetradecene	232-234	8.2759	8.2815			8.2311	8.2468	8.3592	8.2311
1-Hexadecene	284.4	10.1302							10.0807
1-Octadecene	179(15mmGh)	11.8067							
1-Eicosene	341	12.8067							
1-Docosene	N/A	14.8277							
ALKYL BENZENES									
Benzene	80.10	.7199	.7226	.7166					
Methyl	110.63	1.4370	1.4369	1.4291	1.4309	1.4178	1.4315		
Ethyl	136.18	2.3683	2.3781	2.3375	2.3682	2.3523	2.3556		
1,4-Dimethyl	138.35	2.4902	2.4732	2.4625	2.4700	2.4818	2.4853		
1,3-Dimethyl	139.10	2.4902	2.4732	2.4625	2.4700	2.4818	2.4797		
1,2-Dimethyl	144.41	2.6709				2.6448	2.6736		
i-Propyl	152.39	3.0504	3.0350			3.0403		2.6973	
n-Propyl	159.22	3.3908	3.3767	3.3527	3.3640		3.3723	3.4342	
1-Methyl-3-Ethyl	161.30	3.5154	3.5154	3.4930	3.5062	3.4916	3.4023	3.5473	3.4874
1-Methyl-4-Ethyl	161.99	3.5350		3.4930		3.5278	3.5160		3.5153
1,3,5-Trimethyl	164.72	3.6036	3.6120	3.5861	3.5983	3.5809	3.5815	3.6463	3.5849
1-Methyl-2-Ethyl	165.15	3.6975	3.7002	3.6736	3.6850	3.6908	3.6652	3.7425	3.6824
1,2,4-Trimethyl	169.35	3.8543					3.8284	3.7425	3.8259
t-Butyl	169.15	3.8978	3.9145	3.8569		3.8802	3.8800	3.9369	3.8788
i-Butyl	172.76	4.0658	4.0532	4.0208	3.7573	4.0571	4.0529		4.0571
Sec-Butyl	173.33	4.0938	4.0868			4.0571		4.1244	4.0877

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TABLE 2 (Cont'd)

Individual Hydrocarbons	Boiling Point(°C)	COMPONENT RELATIVE RETENTION TIME (RRT)							
		RRT Library	Petrol JP-4	Shale JP-4	Syncrude JP-4	Petrol JET A	Syncrude JET A	Petrol JP-7	Imported Fuel
1,2,3-Trimethyl	176.08	4.2213	4.2044	4.1805		4.1824	4.2078	4.2545	4.1880
1-Methyl-3-i-Propyl	175.18	4.2479	4.2563	4.2236	4.2370	4.2226		4.2998	4.2311
1-Methyl-4-i-Propyl	177.13	4.2801	4.2843	4.2527	4.2677	4.2465	4.2510		4.2613
1-Methyl-2-i-Propyl	178.18	4.4146	4.4229		4.4100	4.4610	4.3960	4.4631	4.4038
1-Methyl-3-n-Propyl	182.00	4.5644	4.5546	4.5208	4.5355	4.5445	4.5536	4.5983	4.5389
1,3-Diethyl	181.14	4.5784				4.5445	4.5536		
1-Methyl-4-n-Propyl	183.34	4.6246	4.6358	4.6013	4.5955	4.5377	4.6108	4.6704	4.5891
n-Butyl	183.31	4.6387	4.6358	4.6691	4.6164		4.6108	4.6874	4.6100
1,4-Diethyl	183.79	4.6807	4.6652	4.6750			4.6596	4.7171	4.6378
1,2-Diethyl	183.46	4.7255	4.7114	4.7675	4.7168	4.6991	4.7085	4.7835	4.7103
1-Methyl-2-n-Propyl	184.83	4.7885	4.7983	4.7625	4.7782		4.7601	4.8472	4.7715
t-Amyl	192.38	4.9356	4.9495		4.9260	4.9122	4.9107	4.9900	4.9192
1-Methyl-3-sec-Butyl	194.00	5.0490		4.0097	5.0543		5.0153	5.0862	5.0194
1-Methyl-4-sec-Butyl	197.22	5.0516		5.0097	5.0543		5.0460	5.0862	5.0194
n-Pentyl	202.1	5.7857	5.7913	5.7361	5.7559	5.7562		5.8316	5.7979
Tetralin	207.65	5.8361	5.8749	5.7805	5.7991	5.8077	5.8228	5.8896	5.7910
n-Hexyl	227.4	6.9188	6.9103	6.8527	6.8722	6.8732		6.9900	6.8670
Pentamethyl	231.8	7.1457	7.1456	7.0847	7.1073	7.1016	7.1157	7.2319	7.0974
Cyclohexyl	237.5	7.5700	7.5784			7.5181	7.5383	7.6463	
n-Heptyl	235.00	7.9972	8.0014			7.9526	7.9567	8.0650	7.9470
Hexamethyl	265.00	8.9020				8.8649	8.8688		8.8690
n-Octyl	265.0	9.0126	9.0236						9.0440
1,1-Diphenyl-Ethylene	286.0	9.5294					9.5006		
n-Nonyl	275.0	9.9748					9.9177		
n-Decanyl	297.9	10.8894							
Hexaethyl	298.	11.1036							
n-Undecanyl	313.2	11.7521							
n-Dodecanyl	179(13mmHg)	12.5756							
n-Tridecanyl	189(10mmHg)	13.3557							
n-Tetradecanyl	196(9mmGh)	14.1176							
n-Pentadecanyl	366	15.4972							
ALKYL NAPHTHALENES									
Naphthalene	217.94	6.0896				6.0543	6.0627	6.0543	
2-Methyl	241.10	7.2339		7.1708	7.1952	7.1852	7.1952	7.1852	7.1852
1-Methyl	244.68	7.4818		7.4041	7.4672		7.4672	7.5601	7.4568
2,6-Dimethyl	262.	8.4244	8.5756	8.3375		8.3830	8.3947	8.4950	
1,3-Dimethyl	263	8.5994	8.5756			8.7096	8.5620		8.5668
1,4-Dimethyl	268	8.8529					8.8270	8.9321	8.8175
ANILINES									
Aniline	184.13	3.7927	3.7983	3.7736	3.7852	3.7674	3.7656	3.8359	3.7799
N,N-Dimethyl	194.15	5.2997	5.2983			5.2799	5.2510	5.3493	
2,6-Dimethyl	215	5.8375	5.8249	5.7805	5.7991	5.8077	5.8228	5.8896	5.7910
2,3-Dimethyl	224	6.1975	6.1820	6.1319		6.1545	6.1799	6.2545	
CYCLOALKANES									
1-C-2-Dimethyl-Cyclopentane	99.53	.3417	.3435	.3416	.3417		.3486		.3412
Methyl-Cyclopentane	71.81	.5840	.5812	.5777	.5763		.5871		.5779
Cyclohexane	80.74	.7633		.7475	.7475		.7559		.7465
Methyl-Cyclohexane	100.93	1.1667	1.1736	1.1527	1.1534	1.1559	1.1617	1.1471	1.1518
1,1-Dimethyl-Cyclohexane	119.55	1.7171	1.7198	1.7083	1.7126	1.7172	1.7001		1.7103

TABLE 2 (Cont'd)

Individual Hydrocarbons	Boiling Point(°C)	COMPONENT RELATIVE RETENTION TIME (RRT)							
		RRT Library	Petrol JP-4	Shale JP-4	Syncrude JP-4	Petrol JET A	Syncrude JET A	Petrol JP-7	Imported Fuel
1-t-2-Dimethyl-Cyclohexane	123.43	1.8277	1.8095	1.7972	1.8019		1.8117	1.8486	
1-C-2-Dimethyl-Cyclohexane	129.74	2.1232	2.1092	2.0958	2.1018		2.1129		2.0988
n-Butyl-Cyclohexane	180.95	4.4930	4.5014	4.4583	4.4728	4.4610	4.4867	4.5360	4.4665
t-Decalin	187.25	4.7255	4.7366	4.6750	4.7122	4.7091	4.7085	4.7835	4.7103
C-Decalin	195.65	5.2521	5.2591						

TABLE 3
APPROXIMATE CONCENTRATION OF TENTATIVELY IDENTIFIED COMPONENTS IN SELECTED FUELS

Individual Hydrocarbons	Boiling Point(°C)	COMPONENT APPROXIMATE WEIGHT PERCENTAGE (wt.)						
		Petrol JP-4	Shale JP-4	Syncrude JP-4	Petrol JET A	Syncrude JET A	Petrol JP-7	Imported Fuel
NORMAL ALKANES								
N-Pentane	36.04	.93	.76	.70		t	t	
N-Hexane	68.74	1.94	.73	.70		t	t	
N-Heptane	98.43	4.00	7.60	7.46	.09	1.54	.02	12.88
N-Octane	125.57	.29	.23	.22	.26	.05	t	
N-Nonane	150.82	2.15			.12		.35	t
N-Decane	174.15	1.80			1.05	.05	1.25	.08
N-Undecane	195.89	2.20			.92		3.15	.74
N-Dodecane	216.3	2.50	2.46	2.51				.68
N-Tetradecane	253.7	1.02			1.26		3.49	1.00
N-Pentadecane	270.63			t			.66	.13
N-Hexadecane	287.0					1.78	.26	
N-Octadecane	316.1					.06	t	t
N-Nonadecane	329.7						t	t
N-Eicosane	343.8							
BRANCHED ALKANES								
2,2-Dimethyl Butane	49.74	.10	t	t	t			
2,3-Dimethyl Butane	57.99	.26	.10	.09	t	t	t	
2-Methyl Pentane	60.27	.14	.66	.64	t	t	t	
3-Methyl Pentane	63.28	.80	.40	.38	t	.07	t	
2,4-Dimethyl Pentane	80.50	.97	.43	.41		.09	t	
2,2,3-Trimethyl Butane	80.87	.97	.43	.41		.09	t	
2,3-Dimethyl Pentane	89.78	.04			.11			
3-Methyl Hexane	91.85	2.40	1.59	1.55	.05	.32	t	t
2,2,4-Trimethyl Pentane	99.24	.41	.81	.80	.08	.17		
2,2-Dimethyl Hexane	106.84	.51	.97	.96	.03		t	
2,5-Dimethyl Hexane	109.10	.83	.97	.96		.20	t	
2,3,4-Trimethyl Pentane	113.47	.08	.02	t		t		
2-Methyl Heptane	117.65	3.03	3.24	3.20	.16	.54	t	
3-Methyl Heptane	118.92	4.03	1.08	1.06	t	.24	.02	
2,2,5-Trimethyl Hexane	124.08	.10	.13	.13		.36		
2-Methyl Octane	143.26		t	t	.36			.02
3-Methyl Octane	144.21	.05	.09	.10	.45	.37	t	t
2-Methyl Decane	189.91	.27	.36					.24
OLEFINS								
Cyclopentene	44.24				.02			
4-Methyl-1-Pentene	53.87	t			.02			
C-4-Methyl-2-Pentene	56.39	.26	.10	.09	t	t	t	
2-Methyl-1-Pentene	62.12	.80	.40	.38	t	.07	t	
1-Hexene	63.48	.80	.40	.38	t	.07	t	
2-Ethyl-1-Butene	64.68	1.94	.73	.70		t	t	

t = trace

TABLE 3 (Cont'd)

Individual Hydrocarbons	Boiling Point(°C)	COMPONENT APPROXIMATE WEIGHT PERCENTAGE (wt)						
		Petrol JP-4	Shale JP-4	Syncrude JP-4	Petrol JET A	Syncrude JET A	Petrol JP-7	Imported Fuel
C-2-Hexene	68.89	t						
Cyclohexene	82.98	.11	.09	.08	t	t	t	t
1-Heptene	93.64	.41	.81	.80	.08	.09		
C-2-Heptene	97.95	t	t	t	t			
2,4,4-Trimethyl-1-Pentene	101.46	t	t	t	t			
2,2,4-Trimethyl-1-Pentene	112.3	t	t	t	t			
2,4,4-Trimethyl-2-Pentene	104.91				.25			
3,5,5-Trimethyl-1-Hexene	N/A	1.10	3.24	3.20	.03	.13	t	
2-Ethyl-1-Hexene	120.	t	.32	.31		.63		
1-Octene	121.27	.08	.81	.81		.05		
Bicyclo (2,2,1) Hept (2,5) Diene	89.5	.11	.04	.04	.20	t	t	
4-Ethenyl cyclohexene	128.9	.54	.19			.04	t	
1-Nonene	147.	.27	.23	.22	.24	.12	.09	t
C-7-Nonene	N/A	.05	.11	.10	.16	.05	t	t
t-7-Nonene	N/A	.05	.11	.10	.29	.05	t	
Pinene	156.2	.12	.37	.37		.26	.07	
Camphene	158.5-159.5	.38	.61	.62	.20	.36	.22	
1-Decene	170.56	.18	.09	.10	.07	.12	.22	t
d-Limonene	178.	.50	1.00	1.00	.62	.67	.12	.04
Dipentene	170.(685mmhg)	.48	.45	.44	.51	.34	.69	.05
1-Undecene	192.7	.23	.17	.18	.79	.13	.47	
1-Dodecene	213.4	.46		.32	1.36	.43	.72	.53
1-Tridecene	232.8	.58	.03	.04	.71	.76	.56	.99
1-Detradecene	232-234	.22	t	t	.14	1.17	2.39	.75
1-Hexadecene	284.4						t	.37
1-Octadecene	179.(15mmhg)							t
1-Eicosene	341.							
1-Docosene	N/A							
ALKYL BENZENES								
Benzene	80.10	.17	.02	.02		t		
Methyl	110.63	1.01	1.55	1.52	.03	.33	t	
Ethyl	136.18	.21	.78	.12	.08	.18	t	
1,4-Dimethyl	138.35	.19	.08	.07	.14	.03	t	
1,3-Dimethyl	139.10	.19	.08	.07	.14	.03	t	
1,2-Dimethyl	144.41		t	t	.09	.03	t	t
i-Propyl	152.39	.14	t	t	.82	t	.03	t
n-Propyl	159.22	.38	.13	.13		.08	.22	t
1-Methyl-3-Ethyl	161.30	.23	.47	.48	.49	.46	.06	.04
1-Methyl-4-Ethyl	161.99		.47	.48		.29		.03
1,3,5-Trimethyl	164.72	.17	.15	.15	.76	.22	.13	.02
1-Methyl-2-Ethyl	165.15	.30	.47	.47	.35	.27	.10	.04

t = trace

TABLE 3 (Cont'd)

Individual Hydrocarbons	Boiling Point(°C)	COMPONENT APPROXIMATE WEIGHT PERCENTAGE (wt%)						
		Petrol JP-4	Shale JP-4	Syncrude JP-4	Petrol JET A	Syncrude JET A	Petrol JP-7	Imported Fuel
1,2,4-Trimethyl	169.35					.03		.03
t-Butyl	169.15	.25	1.52	1.51	.07	1.12	.10	.02
i-Butyl	172.76	.05	.04	.04	1.05	.05	1.25	.08
Sec-Butyl	173.33	1.80		7.25	1.05		1.25	.08
1,2,3-Trimethyl	176.08	.50	1.00	1.00	.62	.67	.12	.05
1-Methyl-3-i-Propyl	175.18	.00	.32	.32	.31	.27	.16	.04
1-Methyl-4-i-Propyl	177.13	.02	.05	.06	.22	.27	.06	.09
1-Methyl-2-i-Propyl	178.18	.14	t	.18	5.03	.03	.18	.19
1-Methyl-3-n-Propyl	182.00	.50	.60	.61	.35	.65	.52	.04
1,3-Diethyl	181.14				.35	.48		.14
1-Methyl-4-n-Propyl	183.34	.35	.42	.43	.72	.48	.18	
n-Butyl	183.31	.35	.30	.30		.27	.13	.38
1,4-Diethyl	183.79	.10	.10	.11	1.01		.09	
1,2-Diethyl	183.46	.17	.08	.18	.87	.11	.04	.25
1-Methyl-2-n-Propyl	184.83	.22	.23	.23	1.04	.28	.32	.07
t-Amyl	192.38			.59	.61	.31	.08	.21
1-Methyl-3-sec-Butyl	194.00		.11	.11		.12	.18	.12
1-Methyl-4-sec-Butyl	197.22		.11	.11		.13	.18	.12
n-Pentyl	202.1		.33	.35	.22		.53	.24
Tetralin	207.65	.29	.14	.14	.31	.24	.74	.49
n-Hexyl	227.4	.17	.06	.06	.48		.53	
Pentamethyl	231.8	.38	.06	.07	.69	.19	1.28	1.24
Cyclohexyl	237.5	.29			3.07	.37	.43	.48
n-Heptyl	235.00	.19	t	t	.08	.22	.75	
Hexamethyl	·265.0			t	.15	.23		1.40
n-Octyl	265.0	.08	t	t		.16		.63
1,1-Diphenyl-Ethylene	286.0				t	.20		.23
n-Nonyl	275.0					.23		.35
n-Decanyl	297.9					.04		.31
Hexaethyl	298.0					.03		.32
n-Undecanyl	313.2							.02
n-Dodecanyl	179(13mmHg)							t
n-Tridecanyl	189(10mmHg)							
n-Tetradecanyl	196(9mmHg)					t		
n-Pentadecanyl	366.							
ALKYL NAPHTHALENES								
Naphthalene	217.94				.56	.77	.22	
2-Methyl	241.		.02		.12	1.22	2.74	.37
1-Methyl	244.68		.02		.27	5.97	5.96	.42
2,6-Dimethyl	262.				.16	.63	.89	.44
1,3-Dimethyl	263.				t	.20	.64	·	.78
1,4-Dimethyl	268.				t	.16		.38	.27
ANILINES								
Aniline	184.13	.08		.18	.33	.11	.10	
N,N-Dimethyl	194.15	.11			.35	7.26	.11	.20

t = trace

25

TABLE 3 (Cont'd)

Individual Hydrocarbons	Boiling Point(°C)	COMPONENT APPROXIMATE WEIGHT PERCENTAGE (wt)						
		Petrol JP-4	Shale JP-4	Syncrude JP-4	Petrol JET A	Syncrude JET A	Petrol JP-7	Imported Fuel
2,6-Dimethyl	215.	.29		.14	.31	.24	.74	.49
2,3-Dimethyl	224.	.46			1.36	.43	.72	.53
CYCLOALKANES								
1-C-2-Dimethyl-Cyclopentane	99.53	.26	.10	.09	t	.02	t	
Methyl-Cyclopentane	71.81	.97	.43	.41		.09	t	
Cyclohexane	80.74		.14	.13		.09	t	
Methyl-Cyclohexane	100.93	.15	1.95	1.91	.06	.38	.02	
1,1-Dimethyl-Cyclohexane	119.55	.10	.32	.31	.31	.03		
1-t-2-Dimethyl-Cyclohexane	123.43		.23			.05	.02	
1-C-2-Dimethyl-Cyclohexane	129.74	.12	.19	.19		.04	t	
n-Butyl-Cyclohexane	180.95	.26	.45	.46	.79	.38	.40	
t-Decalin	187.25	.17	.08	.18	.87	.14	.04	.25
C-Decalin	195.65	2.20			.92			.74
TOTAL APPROXIMATE WT%	PREDICTED =	55.69	47.03	53.72	38.44	39.22	36.73	30.74

t = trace

SECTION III

CONCLUSIONS AND RECOMMENDATIONS

The excellent repeatability of the calculated relative retention times is exemplified by the low relative standard deviations exhibited in Table 1. This repeatability translates into a high confidence level assured when hydrocarbon peak assignments are made on unknown hydrocarbon fuel samples analyzed by a fully automated glass capillary gas chromatographic system. The optimization criteria, i.e. resolution of selected hydrocarbons, determined the operating conditions best suited for characterizing wide-boiling fuels like JP-4 on one specific open tubular capillary column. However, this optimization procedure would have to be reinstituted on each new capillary column of different dimensions, e.g. internal diameter, film thickness, column length, etc.

Significant improvements on the reliability of the tentative hydro-carbon assignments can be realized by using longer, higher efficiency capillary columns with a carrier gas like helium and, for better resolution of the light ends of JP-4, cryogenic cooling of the oven. It is a generally accepted practice that excellent retention time data correlation between an unknown and a selected reference compound on two columns of different polarity is sufficient for positive identification of the unknown. In this vein, a similar relative retention time library should be generated on a polar stationary phase, such as OV-17. Hopefully, ambiguities on the nonpolar column can be eliminated by cross-referencing all deter-minations with the polar, OV-17 column.

In addition, extending the sheer number of pure hydrocarbon reference standards, judiciously selected, for the library to several hundred com-pounds would greatly increase the number of components and amount of total fuel characterized by capillary gas chromatography.

Furthermore, it was subsequently calculated that nearly 500 nanograms was injected for the major hydrocarbon components in some of the fuel samples. This could very well be 10 times the amount of a given component that would be optimum to ensure no peak overloading on the column. Over-loaded peaks traditionally show poor retention time repeatability.

SECTION IV

FUTURE WORK

The retention index system introduced by Kovats is one of the most widely accepted methods of reporting data (Reference 6) in gas chromatography, besides relative retention times. Retention is determined relative to a series of homologous n-paraffins, thus each unknown peak is referenced to two standards instead of just one as in the relative retention time method. A recent paper (Reference 7) states that a standard deviation of only +/- 0.05 index units could easily be attained when using programmed temperature gas chromatography on aromatic hydrocarbons. Thus for peaks that eluted between n-C_{11} and n-C_{12}, a relative standard deviation of +/- 0.0043% was possible. However, according to the results of RRT's presented in this technical report, for the same hydrocarbon region, a typical repeatability of +/- 0.10% was attainable. Such a significant improvement in repeatability with the Kovats system would substantially bolster the credibility of tentative hydrocarbon peak assignments. Furthermore, jet propulsion fuels are distinguished by their characteristic n-paraffin profile which means the Kovats reference standards are already present in the samples of interest!

In summary, a better qualitative identification system could be that of Kovats employed on two, 60 meter open tubular columns cryogenically cooled with helium gas as carrier and referencing several hundred standard hydrocarbons. However, relative retention times would still be useful for use with detectors that ignore the normal paraffins, i.e., ultra-violet detector for aromatic compounds, thermionic specific detector for nitrogen compounds, etc. In these instances, one or more appropriate internal standards could be introduced into the sample for subsequent relative retention time calculations.

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