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CHARACTERIZING PETROLEUM- AND SHALE-DERIVED JET FUEL DISTILLATES VIA TEMPERATURE-PROGRAMMED KOVÁTS INDICES

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SUMMARY

The Kováts retention indices of nearly 200 hydrocarbons expected to be found in jet fuel distillates of petroleum and shale oils were determined on two open tubular gas chromatographic columns of different polarity under conditions of linear temperature programming. The overall precision for the indices was indicated by the mean values of the 95% confidence levels, *i.e.* ± 0.06 for the OV-101 column and ± 0.09 for the OV-17 column. Several specification JP-4 jet fuels were characterized and tentative peak assignments made.

INTRODUCTION

Commercial hydrocarbon products such as gasoline, kerosene, and jet fuels are deceptively simple in appearance but are actually a blend of literally thousands of hydrocarbons. Knowledge of the chemistry of these products, however, can yield an immense wealth of practical information. Bulk properties and characteristics such as combustion behavior, storage stability, ignitability, and toxicological effects, as well as physical and generalized chemical properties, can all be predicted from a thorough chemical breakdown of a fuel's hydrocarbon composition.

Unfortunately, detailing the myriad of hydrocarbon components in these products is unassailable by any single, though sophisticated, state-of-the-art analytical technique. What is required is a judicious meshing of highly advanced chromatographic and spectroscopic techniques applied in a sequential mode of attack. This approach is not an original idea. A typical unified system for the detailed analysis of aircraft fuels, both conventional and experimental, without regard to their type of complexity, could consist of five distinct steps that include a fuel fractionation procedure followed by high-resolution gas chromatography-mass spectrometry (GC-MS) and proton and carbon-13 Fourier Transform nuclear magnetic resonance (NMR) analyses of the individual fractions¹.

Petroleum and shale-derived jet fuels are too complex to be unraveled by even the most efficient GC column. However, multi-dimensional gas-liquid partition chromatography (GLC) appears very promising. Heart-cut segments of the total hydro-

carbon profile are diverted automatically from one capillary column to another having greater selectivity. Unfortunately, few preparative-scale work-ups from multi-dimensional cuts for subsequent analyses by NMR, infrared spectroscopy, etc. have been published.

The primary purpose of this experimental study was to establish an optimization procedure and generate statistically reliable and chromatographically sound retention libraries of a large variety of pure reference hydrocarbons. Retention indices can be used to assign, with high probability, tentative identifications of the major components in JP-4 aircraft fuel. Furthermore, the indices can provide an authoritative judgement as to the integrity of separated fractions from any proposed preparative method of fractionating hydrocarbon fuels.

In their foundational article on GLC, James and Martin² proposed that both the retention volume and the retention time of a solute can be characteristic and an aid in its identification. The "retention index" system introduced by Kováts calculates the logarithmic retention of a solute interpolated between those of two standard compounds³. Any homologous series of organic compounds can be used as the standards. This system has proved especially well suited for the standardization of GC retention data. The Kováts system has proven so useful that the Discussion Group of the Institute of Petroleum recommended its use in the standardization of retention data⁴.

Van den Pool and Kratz⁵ have demonstrated that for a temperature-programmed GC run, the logarithmic relationship which exists under isothermal operation is replaced by the approximately linear relationship⁶:

$$I_{PT}^C = 100 \left[\frac{t_R(\text{unknown}) - t_R(C_z)}{t_R(C_{z+1}) - t_R(C_z)} \right] + 100z$$

where I_{PT}^C is the retention index of the unknown compound as determined on stationary phase C under conditions of linear temperature programming, $t_R(\text{unknown})$ is the absolute retention time of the unknown compound, $t_R(C_z)$ is the absolute retention time for the n -alkane that elutes prior to the unknown, $t_R(C_{z+1})$ is the absolute retention time for the n -alkane that elutes just after the unknown, and z is the number of carbon atoms in the n -alkane standard that elutes just prior to the substance of interest.

The Kováts Index unit is characteristically determined by the type and thickness of stationary phase liquid, the mobile phase, the molecular structure of the component of interest, and the temperature-programming rate.

However, in a linear temperature-programmed chromatogram, the retention data are not strictly linear for the n -paraffinic series. In the region of the lower paraffins, including hydrogen, the linearity is not very good⁷. Yet numerous investigators have utilized retention indices based on the n -paraffins^{5,8,9}, and other homologous series^{7,10,11} under temperature-programmed conditions. An alternate homologous series enables the use of detectors which are not sensitive to n -paraffins, e.g. n -alkyl trichloroacetates with an electron-capture detector or n -alkylbenzenes for an ultraviolet detector¹².

EXPERIMENTAL

The analyses were performed on a Varian Model 3700 capillary gas chromatographic system equipped with dual flame ionization detectors, a Varian 1070 all-glass injector in the split mode configuration, and fitted with a Varian 8000 automatic liquid sampler¹³. A Varian Model CDS-111 computer integrator controlled the automatic liquid sampler, the temperature programming and the data collection, and continuously monitored the system parameters. Chromatographic operating conditions, *e.g.* linear flow-rate, programming rate, initial column temperature, etc., were optimized for maximum resolution between the C_{11} and C_{12} *n*-alkanes in a reasonable analysis time since historically, this is the region of poorest separation in a JP-4 fuel chromatogram¹⁴. Those operating conditions are summarized in Table I.

TABLE I

CHROMATOGRAPHIC OPERATING CONDITIONS FOR THE OPEN TUBULAR GLC COLUMNS

Detector	Flame ionization detector
Detector temperature	300°C
Injector	Fritted glass insert (normal split mode)
Injector temperature	300°C
Liquid sample volume	1.0 μ l, split 1:50 (diluted 1:100 prior w/CS ₂)
Septum purge flow-rate	25 ml/min
Detector make-up flow-rate	30 ml/min
Detector hydrogen flow-rate	30 ml/min
Detector air flow-rate	300 ml/min
Columns	OV-101 and OV-17, both 0.25 mm I.D., both <i>ca.</i> 110 m long, both <i>ca.</i> 0.2 μ m film thickness
Carrier gas (helium) flow-rate (average linear velocity)	29.18 cm/sec (OV-101), 25.38 cm/sec (OV-17); $t_0(\text{CH}_4) = 6.23$ min (OV-101), 7.69 min (OV-17)
Column temperature profile	Initially 35°C, immediately programmed at 1°C/min to a final temperature of 200°C
Electrometer range	$4 \cdot 10^{-12}$ A/mV

Column efficiencies were measured and found to be in excess of 225,000 effective theoretical plates in each case. A 0.1% (w/w) solution of *n*-C₁₃ (capacity factor, $k' = 3.97$) in CS₂ was used to make the measurement. It has been pointed out that for identification using Kováts indices at high precision, open tubular columns of high resolution with effective theoretical plates of at least 50,000 should be used¹⁵. For this experimental study, the columns exhibited nearly five times this number of useable plates.

To avoid potential contamination problems, ultra-high-purity helium (99.999%) was used as the carrier gas. The helium was passed through a Hydrox Purifier, Model 8301 (Matheson Gas Products) to remove residual oxygen and/or water vapor present to less than 0.1 ppm each. The permeation of air and moisture and organic contamination, *i.e.* back-diffusion, was eliminated by the use of metallic diaphragm regulators¹⁶.

Column capacity also had to be considered. Progressive column overloading

causes typical "leading" peak shapes and shifting in retention index values. Symmetrical peaks can be obtained by lowering the sample load. Schomburg and Dielmann¹⁷ defined the "linear dynamic range of precise index determination" as the range limited by the smallest sample the detector can see (usually taken as twice the noise level) and the maximum sample load which does not give asymmetric peaks. GC-analyzed standards (nearly all purchased from Wiley Organics, Columbus, OH, U.S.A.) and jet fuels were diluted nearly 100:1 in a relatively non-interfering solvent (CS₂) to limit the amount of the most predominant hydrocarbon species entering the columns to less than 10 ng each.

RESULTS AND DISCUSSION

The method of applying the Kováts indices used in this report was to identify substances in fuel samples by matching their indices as determined on two capillary columns of different polarity against two corresponding libraries of over 200 standard hydrocarbons each. An identification window was established for each standard hydrocarbon on each polarity column and applied to suspect peaks in unknown fuel samples. Of course, all such qualitative judgements on compound identity were tentative and will later be checked by GC-MS. It was also feasible to predict the identity of major hydrocarbon fuel components that had not been included in the pure standards. Plots of retention indices *versus* carbon number of different homologous groups, *e.g.* 2-methylalkanes, *n*-alkylbenzenes, 1-olefins, *n*-alkylcyclohexanes, *etc.* all displayed a high degree of correlation¹⁴. These assignments can be considered entirely reasonable, but acquisition of the pure standard is always the final confirming route.

The collections of Kováts retention indices for both the OV-101 and the OV-17 columns are listed in Table II. The compounds are listed numerically by their OV-101 Kováts indices from five glass capillary GC runs. These numbers are accompanied by their standard deviations and 95% confidence levels for five determinations. A Kováts index could not be computed for all compounds on both columns, due to peak coelution with other standard compounds, *n*-alkanes, or the solvent.

The overall precision for these computations is indicated by the mean values of the 95% confidence levels, *i.e.*, ± 0.06 for the OV-101 column and ± 0.09 for the OV-17 column. It should be noted that the 95% confidence levels of the low boiling compounds are much larger than those of the other compounds. This is a direct result of the shorter retention times of the low boiling compounds, where a slight difference in retention times for repeat runs has a larger effect on the 95% confidence level than the same absolute difference has for higher boiling components with much longer retention times.

Samples of both petroleum-derived and shale-derived jet propulsion fuels were prepared in solution with CS₂ at a dilution ratio of 1:100. These samples were then analyzed three times each on both the OV-101 and the OV-17 columns under the same conditions used for the standard solutions of the Kováts libraries. The Kováts index for each peak of the fuel samples was then calculated and statistically analyzed at the 95% confidence level for three determinations (see Tables III and IV).

During the preparation of the standard solutions it was noticed that the glass capillary GC system, under the conditions of this experiment, could not resolve two compounds, placed in the same solution, whose Kováts index differed by less than

TABLE II

KOVATS INDICES GENERATED ON TWO QUADREX CAPILLARY COLUMNS: COLUMN 510B, 108M OV-101; COLUMN 1029A, 117M OV-17

<i>Hydrocarbon name</i>	<i>K.I.-101</i>	σ	<i>95% C.L.*</i>	<i>K.I.-17</i>	σ	<i>95% C.L.*</i>
2-Methylbutane	464.94	0.35	0.43	462.44	0.49	0.60
2,2-Dimethylbutane	—	—	—	512.96	0.19	0.24
Cyclopentane	557.40	0.12	0.15	559.80	0.55	0.68
2,3-Dimethylbutane	557.92	0.25	0.31	532.93	0.33	0.41
2-Methylpentane	561.64	0.11	0.14	534.27	0.22	0.28
3-Methylpentane	578.11	0.22	0.27	549.70	0.48	0.60
1-Hexene	585.17	0.23	0.29	—	—	—
2,2-Dimethylpentane	617.92	0.06	0.08	559.72	0.41	0.51
Methylcyclopentane	620.07	0.04	0.05	623.49	0.28	0.35
2,4-Dimethylpentane	622.82	0.02	0.03	—	—	—
2,2,3-Trimethylbutane	627.82	0.07	0.09	606.81	0.43	0.53
Benzene	642.11	0.06	0.08	739.24	0.09	0.11
3,3-Dimethylpentane	646.27	0.06	0.08	628.32	0.23	0.29
Cyclohexane	650.27	0.10	0.12	687.73	0.20	0.25
2-Methylhexane	659.24	0.06	0.07	638.62	0.16	0.20
2,3-Dimethylpentane	661.36	0.04	0.05	649.08	0.39	0.48
Cyclohexene	667.29	0.10	0.12	722.96	0.08	0.10
3-Methylhexane	669.11	0.07	0.08	655.49	0.15	0.18
3-Ethylpentane	681.54	0.08	0.10	678.53	0.46	0.57
1-Heptene	684.69	0.15	0.18	705.53	0.15	0.18
2,2,4-Trimethylpentane	685.74	0.01	0.02	663.92	0.39	0.48
1-cis-2-Dimethylcyclopentane	714.85	0.03	0.05	737.03	0.08	0.10
Methylcyclohexane	715.63	0.05	0.06	739.15	0.10	0.13
2,2-Dimethylhexane	717.70	0.03	0.03	710.36	0.09	0.11
Ethylcyclopentane	725.43	0.05	0.06	749.43	0.10	0.12
2,5-Dimethylhexane	726.53	0.05	0.06	717.57	0.15	0.18
2,4-Dimethylhexane	728.30	0.04	0.04	720.98	0.08	0.11
3,3-Dimethylhexane	734.72	0.05	0.06	731.49	0.14	0.18
2,3,4-Trimethylpentane	743.05	0.06	0.08	743.58	0.10	0.12
2,3,3-Trimethylpentane	747.10	0.03	0.04	751.82	0.05	0.06
Methylbenzene	747.63	0.03	0.04	845.42	0.04	0.05
2,3-Dimethylhexane	754.03	0.05	0.06	751.82	0.13	0.17
3-Ethyl-2-Methylpentane	755.34	0.06	0.08	755.33	0.07	0.09
1-Methylcyclohexene	757.60	0.06	0.08	812.30	0.04	0.05
2-Methylheptane	760.60	0.07	0.09	753.77	0.05	0.06
4-Methylheptane	762.04	0.04	0.05	757.35	0.10	0.13
3-Ethyl-3-methylpentane	763.72	0.04	0.05	769.33	0.07	0.08
3,4-Dimethylhexane	763.74	0.07	0.08	765.11	0.03	0.04
2,2,4,4-Tetramethylpentane	765.88	0.07	0.08	759.30	0.17	0.21
3-Methylheptane	768.75	0.06	0.08	765.12	0.12	0.15
3-Ethylhexane	769.84	0.07	0.08	768.08	0.07	0.09
cis-1,3-Dimethylcyclohexane	769.96	0.05	0.06	794.50	0.12	0.14
trans-1,4-Dimethylcyclohexane	772.00	0.04	0.05	795.36	0.07	0.09
1,1-Dimethylcyclohexane	778.06	0.06	0.08	806.05	0.01	0.01
cis-1,4-Dimethylcyclohexane	—	—	—	822.91	0.06	0.08
2,2,5-Trimethylhexane	781.15	0.04	0.05	763.42	0.07	0.09
1-Octene	785.76	0.02	0.03	805.81	0.05	0.06
2,2,4-Trimethylhexane	788.87	0.04	0.05	777.93	0.08	0.09

(Continued on p. 184)

TABLE II (continued)

Hydrocarbon name	K.I.-101	σ	95% C.L.*	K.I.-17	σ	95% C.L.*
<i>trans</i> -1,2-Dimethylcyclohexane	791.91	0.05	0.07	815.18	0.03	0.03
<i>trans</i> -1,3-Dimethylcyclohexane	—	—	—	823.87	0.07	0.09
<i>n</i> -Propylcyclopentane	—	—	—	848.84	0.05	0.06
Ethylcyclohexane	—	—	—	854.06	0.06	0.07
2,2-Dimethylheptane	817.31	0.05	0.06	808.09	0.08	0.10
<i>cis</i> -1,2-Dimethylcyclohexane	820.39	0.04	0.05	851.27	0.04	0.05
2,2,3-Trimethylhexane	820.61	0.04	0.05	817.84	0.10	0.13
2,4-Dimethylheptane	821.03	0.06	0.07	812.35	0.08	0.10
4,4-Dimethylheptane	822.58	0.02	0.03	817.64	0.02	0.02
<i>cis,cis,cis</i> -1,3,5-Trimethylcyclohexane	825.38	0.04	0.05	838.47	0.04	0.05
2,6-Dimethylheptane	827.06	0.03	0.04	816.99	0.06	0.07
1,1,3-Trimethylcyclohexane	830.35	0.05	0.06	846.55	0.08	0.11
1,1,4-Trimethylcyclohexane	832.51	0.04	0.05	846.25	0.05	0.06
2,4-Dimethyl-3-ethylpentane	833.05	0.03	0.04	833.39	0.07	0.09
2,5-Dimethylheptane	833.18	0.04	0.05	825.03	0.02	0.03
2,3,3-Trimethylhexane	833.66	0.05	0.06	834.40	0.08	0.11
3,3-Dimethylheptane	834.68	0.03	0.04	830.23	0.08	0.10
Ethylbenzene	843.07	0.04	0.05	944.10	0.04	0.05
<i>cis,trans,trans</i> -1,2,4-Trimethylcyclohexane	844.82	0.03	0.04	861.39	0.08	0.09
<i>cis,cis,trans</i> -1,3,5-Trimethylcyclohexane	848.69	0.03	0.04	868.09	0.06	0.07
<i>m</i> -Xylene	851.82	0.02	0.03	950.03	0.06	0.08
<i>p</i> -Xylene	852.80	0.04	0.05	948.44	0.02	0.03
2,3-Dimethylheptane	853.26	0.06	0.07	849.82	0.06	0.07
4-Ethylheptane	858.32	0.06	0.07	853.31	0.08	0.10
4-Methyloctane	861.46	0.07	0.08	856.49	0.05	0.06
2-Methyloctane	862.66	0.06	0.07	856.17	0.06	0.07
<i>cis,trans,cis</i> -1,2,3-Trimethylcyclohexane	867.35	0.04	0.04	892.49	0.08	0.10
3-Ethylheptane	867.96	0.05	0.06	865.54	0.06	0.07
<i>cis,trans,cis</i> -1,2,4-Trimethylcyclohexane	869.09	0.03	0.03	894.23	0.07	0.09
3-Methyloctane	869.43	0.06	0.08	865.52	0.04	0.05
2,4,6-Trimethylheptane	874.13	0.03	0.03	856.84	0.06	0.07
<i>o</i> -Xylene	874.53	0.03	0.03	981.56	0.04	0.05
<i>cis</i> -1-Ethyl-3-methylcyclohexane	881.29	0.04	0.05	906.01	0.01	0.01
1-Nonene	887.15	0.04	0.05	906.46	0.00	0.00
<i>trans</i> -1-Ethyl-2-methylcyclohexane	901.06	0.04	0.05	927.63	0.05	0.07
1-Ethyl-1-Methylcyclohexane	903.14	0.05	0.06	933.95	0.04	0.05
<i>cis</i> -1-Ethyl-4-Methylcyclohexane	903.98	0.03	0.04	930.25	0.04	0.05
Cumene	908.92	0.04	0.05	1006.06	0.06	0.08
Isopropylcyclohexane	912.85	0.04	0.04	943.24	0.06	0.08
2,2-Dimethyloctane	917.78	0.03	0.04	908.18	0.08	0.10
4,4-Dimethyloctane	919.84	0.03	0.03	914.32	0.04	0.05
<i>cis</i> -1-Ethyl-2-Methylcyclohexane	920.98	0.04	0.05	954.58	0.04	0.05
<i>n</i> -Propylcyclohexane	923.29	0.01	0.01	950.92	0.06	0.08
(+)- γ -Pinene	926.55	0.04	0.05	964.40	0.02	0.03
2,7-Dimethyloctane	929.14	0.03	0.04	919.33	0.02	0.03
2,6-Dimethyloctane	933.62	0.04	0.05	925.44	0.04	0.05
3,3-Dimethyloctane	934.14	0.03	0.04	928.72	0.07	0.08
<i>n</i> -Propylbenzene	937.01	0.04	0.05	1035.65	0.05	0.06
3,4-Diethylhexane	937.44	0.05	0.06	936.07	0.03	0.04
3-Ethyl-3-methylheptane	940.32	0.04	0.05	946.53	0.04	0.05

TABLE II (continued)

Hydrocarbon name	<i>K.I.</i> -101	σ	95% <i>C.L.</i> *	<i>K.I.</i> -17	σ	95% <i>C.L.</i> *
1-Ethyl-3-methylbenzene	944.83	0.02	0.02	1046.12	0.03	0.03
4-Propylheptane	944.91	0.05	0.06	937.76	0.06	0.07
3-Ethyl-2-methylheptane	946.34	0.04	0.05	—	—	—
1,3,5-Trimethylbenzene	952.83	0.02	0.02	1051.36	0.04	0.05
2,3-Dimethyloctane	953.33	0.02	0.03	949.98	0.06	0.07
4-Methylnonane	954.97	0.05	0.06	950.20	0.06	0.07
5-Methylnonane	959.55	0.05	0.06	954.84	0.03	0.04
4-Ethylactane	961.30	0.03	0.04	956.33	0.05	0.06
1-Ethyl-2-methylbenzene	961.45	0.03	0.04	1070.46	0.05	0.07
2-Methylnonane	963.97	0.05	0.06	957.96	0.04	0.05
(-)- β -Pinene	965.11	0.03	0.04	1025.80	0.01	0.01
3-Ethylactane	966.99	0.01	0.01	964.56	0.06	0.07
<i>trans</i> -1-Methyl-4-isopropylcyclohexane	969.71	0.03	0.04	992.19	0.08	0.10
3-Methylnonane	970.32	0.04	0.06	966.96	0.04	0.05
3,3,4,4-Tetramethylhexane	970.78	0.02	0.03	993.77	0.03	0.04
<i>tert.</i> -Butylbenzene	975.93	0.02	0.03	1073.60	0.04	0.05
1,2,4-Trimethylbenzene	976.91	0.03	0.03	1080.84	0.03	0.03
<i>cis</i> -1-Methyl-4-isopropylcyclohexane	983.78	0.03	0.03	1012.55	0.05	0.07
1-Decene	987.87	0.02	0.03	1006.67	0.03	0.04
Isobutylbenzene	992.48	0.03	0.04	1082.90	0.03	0.04
3-Ethylnonane	992.53	0.00	0.00	1064.57	0.04	0.04
<i>sec.</i> -Butylbenzene	995.09	0.03	0.04	1090.33	0.07	0.09
1,2,3-trimethylbenzene	1003.68	0.03	0.04	1120.33	0.05	0.06
1-Methyl-3-isopropylbenzene	1006.59	0.03	0.04	1103.84	0.04	0.04
<i>p</i> -Cymene	1009.38	0.03	0.04	1104.61	0.05	0.07
Indan	1013.44	0.03	0.03	1147.39	0.02	0.02
D-Limonene	1018.23	0.01	0.01	1083.41	0.05	0.07
<i>n</i> -Butylcyclohexane	1025.65	0.04	0.05	1054.03	0.04	0.05
1,3-Diethylbenzene	1032.94	0.03	0.04	—	—	—
1-Methyl-3-propylbenzene	1035.51	0.04	0.05	1134.57	0.03	0.04
1,4-Diethylbenzene	1038.88	0.02	0.02	1142.00	0.03	0.03
1-Methyl-4-propylbenzene	1039.05	0.03	0.04	—	—	—
<i>n</i> -Butylbenzene	1039.90	0.02	0.03	1139.89	0.04	0.05
1,3-Dimethyl-5-ethylbenzene	1042.81	0.04	0.05	1144.78	0.05	0.06
<i>trans</i> -Decalin	1042.88	0.02	0.02	1102.06	0.03	0.04
Neopentylbenzene	1048.25	0.03	0.03	1135.95	0.03	0.03
1-Methyl-2-propylbenzene	1049.75	0.04	0.05	1154.98	0.00	0.00
1,4-Dimethyl-2-ethylbenzene	1060.58	0.01	0.02	1166.50	0.04	0.04
4-Methyldecane	1061.06	0.01	0.02	1056.61	0.00	0.00
1,3-Dimethyl-4-ethylbenzene	1062.14	0.02	0.02	1168.99	0.03	0.04
2-Methyldecane	1064.77	0.01	0.02	1059.14	0.06	0.07
2,2,4,6,6-Pentamethylheptane	1066.61	0.04	0.05	971.86	0.06	0.07
1,2-Dimethyl-4-ethylbenzene	1068.04	0.02	0.03	1176.59	0.03	0.03
1,2-Dimethylpropylbenzene	1068.81	0.03	0.04	1161.92	0.02	0.03
1-Ethylpropylbenzene	1071.03	0.02	0.02	—	—	—
1- <i>tert.</i> -Butyl-3-methylbenzene	1071.55	0.02	0.03	1167.39	0.01	0.02
1,3-Dimethyl-2-ethylbenzene	1073.15	0.04	0.04	1187.93	0.03	0.04
<i>tert.</i> -Pentylbenzene	1076.00	0.02	0.03	1176.49	0.03	0.04
<i>p-tert.</i> -Butyltoluene	1076.12	0.05	0.06	1170.49	0.01	0.02
<i>cis</i> -Decalin	1084.51	0.05	0.06	1158.23	0.04	0.05

(Continued on p. 186)

TABLE II (continued)

Hydrocarbon name	<i>K.I.-101</i>	σ	95% C.L.*	<i>K.I.-17</i>	σ	95% C.L.*
1-Methylbutylbenzenc	1086.41	0.04	0.05	1182.26	0.02	0.03
1,2,4,5-Tetramethylbenzene				1208.65	0.04	0.05
1,2-Dimethyl-3-ethylbenzene	1086.88	0.03	0.04	1206.44	0.03	0.04
1-Undecene	1088.37	0.04	0.05	1106.70	0.03	0.04
1-Ethyl-3-isopropylbenzene	1088.54	0.03	0.04	1186.05	0.03	0.04
2-Methylbutylbenzene	1101.75	0.06	0.07	1197.03	0.00	0.00
1,2,3,5-Tetramethylbenzene	1102.85	0.04	0.04	1216.82	0.02	0.03
3-Methylbutylbenzene	1106.52	0.06	0.07	1201.01	0.03	0.04
1- <i>tert.</i> -Butyl-2-methylbenzene	1114.57	0.07	0.08	1228.54	0.03	0.04
2,6-Dimethyldecane	1119.35	0.04	0.06	1109.50	0.03	0.04
1,2,3,4-Tetramethylbenzene	1132.90	0.02	0.02	1257.40	0.04	0.05
Tetralin	1136.43	0.02	0.02	1288.39	0.05	0.06
1,3-Di-isopropylbenzene	1138.86	0.06	0.07	1231.47	0.02	0.02
<i>n</i> -Pentylbenzene	1141.13	0.03	0.04	1242.74	0.02	0.03
Naphthalene	1156.25	0.06	0.07	1344.95	0.05	0.06
1,4-Diisopropylbenzene	1157.71	0.01	0.02	1257.77	0.05	0.06
1- <i>tert.</i> -Butyl-3,5-dimethylbenzene	1163.06	0.03	0.04	1258.21	0.02	0.02
2-Methylundecane	1164.88	0.05	0.06	1159.30	0.05	0.06
1- <i>tert.</i> -Butyl-4-ethylbenzene	1165.62	0.02	0.03	1266.63	0.04	0.05
1-Dodecene	1188.62	0.03	0.04	1206.80	0.04	0.05
2-Methylpentylbenzene	1190.88	0.03	0.04	1285.14	0.03	0.04
1,3,5-Triethylbenzene	1206.13	0.04	0.05	1312.11	0.04	0.05
2,6-Dimethylundecane	1215.87	0.07	0.09	1205.25	0.05	0.07
1,2,4-Triethylbenzene	1223.09	0.04	0.05	1334.53	0.04	0.05
<i>n</i> -Hexylbenzene	1243.89	0.04	0.05	1345.67	0.04	0.04
Pentamethylbenzene	1261.35	0.05	0.06	1392.52	0.00	0.01
2-Methylnaphthalene	1267.22	0.08	0.09	1458.02	0.03	0.03
1,1-Diethylpropylbenzene	1274.63	0.05	0.07	1382.32	0.07	0.08
1-Methylnaphthalene	1281.76	0.13	0.16	1484.30	0.01	0.01
1-Tridecene	1288.83	0.03	0.03	1306.95	0.05	0.07
Phenylcyclohexane	1296.28	0.05	0.06	1442.07	0.03	0.04
1- <i>tert.</i> -Butyl-3,4,5-trimethylbenzene	1306.82	0.06	0.07	1421.50	0.04	0.05
<i>n</i> -Heptylbenzene	1347.56	0.02	0.03	1450.47	0.04	0.05
Biphenyl	1349.53	0.09	0.11	1563.26	0.02	0.02
2-Ethyl-naphthalene	1366.22	0.09	0.11	1559.59	0.02	0.02
1-Ethyl-naphthalene	1367.46	0.05	0.06	1572.55	0.03	0.04
2,6-Dimethylnaphthalene	1377.27	0.03	0.03	1570.18	0.03	0.04
1-Tetradecene	1389.14	0.07	0.08	1407.42	0.04	0.04
1,3-Dimethylnaphthalene	1391.04	0.07	0.09	1594.52	0.07	0.08
1,4-Dimethylnaphthalene	1408.81	0.10	0.12	1621.95	0.03	0.04
2,3-Dimethylnaphthalene	1410.50	0.06	0.08	1616.16	0.06	0.08
Hexamethylbenzene	1430.72	0.04	0.05	1583.98	0.04	0.05
<i>n</i> -Octylbenzene	1451.16	0.02	0.02	1555.23	0.04	0.05
<i>n</i> -Nonylbenzene	1555.41	0.06	0.08	1660.62	0.04	0.05
<i>n</i> -Decylbenzene	1659.28	0.05	0.06	1765.55	0.08	0.10
Hexaethylbenzene	1682.39	0.06	0.08	—	—	—

$$* 95\% \text{ Confidence limit for five determinations} = \frac{2.776 \sigma}{2.236}$$

TABLE III
PETROLEUM-DERIVED JP-4 FUEL IB-792009

Hydrocarbon name	OV-101						OV-17					
	K.I.-101	K.I.-SAMP.	σ	95% C.L.*	A%	K.I.-17	K.I.-SAMP.	σ	95% C.L.*	A%		
2-Methylbutane	464.94	465.10	0.68	1.69	0.98	462.44	461.97	0.46	1.14	0.98		
2-Methylpentane	561.64	562.08	0.10	0.26	2.41	534.27	534.06	0.20	0.49	2.79		
3-Methylpentane	578.11	578.24	0.22	0.54	2.01	549.70	549.92	0.29	0.72	1.87		
Methylcyclopentane	620.07	620.06	0.13	0.32	0.84	623.49	623.62	0.00	0.00	0.83		
2,2,3-Trimethylbutane	627.82	627.74	0.00	0.00	0.07	606.81	607.04	0.00	0.00	0.12		
Benzene	642.11	641.83	0.00	0.00	0.48	739.24	739.10	0.16	0.41	(739.15)*		
Cyclohexane	650.27	650.11	0.00	0.00	0.98	687.73	687.44	0.00	0.00	0.96		
2-Methylhexane	659.24	659.06	0.00	0.00	5.14	638.62	638.86	0.58	1.44	5.01		
2,3-Dimethylpentane	661.36	661.30	0.00	0.00	1.88	649.08	649.58	0.29	0.72	1.78		
3-Methylhexane	669.11	669.13	0.00	0.00	6.63	655.49	655.78	0.00	0.00	6.67		
3-Ethylpentane	681.54	681.36	0.13	0.32	0.93	678.53	678.39	0.00	0.00	0.78		
2,2,4-Trimethylpentane	685.74	685.53	0.13	0.32	0.11	663.92	663.65	0.29	0.72	0.11		
Methylcyclohexane	715.63	715.56	0.05	0.14	1.00	739.15*	739.10	0.16	0.41	1.44		
2,2-Dimethylhexane	717.70	717.57	0.05	0.13	0.47	710.36	710.26	0.19	0.48	0.40		
Ethylcyclopentane	725.43	725.35	0.05	0.11	0.15	749.43	749.12	0.09	0.22	0.31		
2,5-Dimethylhexane	726.53	726.44	0.05	0.11	0.68	717.57	717.53	0.08	0.21	0.90		
2,4-Dimethylhexane	728.30	728.17	0.09	0.22	1.16	720.98	720.98	0.09	0.23	1.10		
3,3-Dimethylhexane	734.72	734.54	0.04	0.10	0.36	731.49	731.36	0.17	0.43	0.36		
2,3,4-Trimethylpentane	743.05	742.89	0.04	0.09	0.17	743.58	743.43	0.04	0.11	0.12		
Methylbenzene	747.63	747.48	0.04	0.09	1.57	845.42	845.41	0.09	0.23	1.49		
2,3-Dimethylhexane	754.03	753.89	0.04	0.09	0.84	751.82	751.76	0.15	0.37	0.76		
2-Methylheptane	760.60	760.42	0.04	0.09	2.83	753.77	753.75	0.18	0.45	2.90		
4-Methylheptane	762.04	762.03	0.05	0.11	1.35	757.35	757.39	0.14	0.36	1.37		
3-Methylheptane	768.75	768.56	0.04	0.09	3.31	765.12	765.12	0.14	0.34	3.59		
3-Ethylhexane	769.84*	769.77	0.04	0.09	1.01	768.08	767.94	0.13	0.33	0.90		
cis-1,3-Dimethylcyclohexane	769.96	769.77	0.04	0.09	(769.84)*	794.50	794.55	0.18	0.44	0.40		
1,1-Dimethylcyclohexane	778.06	778.07	0.05	0.12	0.05	806.05	806.47	0.06	0.14	0.15		
trans-1,2-Dimethylcyclohexane	791.91	791.98	0.06	0.15	0.16	815.18	815.11	0.01	0.02	0.13		

(Continued on p. 188)

TABLE III (continued)

Hydrocarbon name	OV-101					OV-17				
	K.I.-101	K.I.-SAMP.	σ	95% C.L.*	A%	K.I.-17	K.I.-SAMP.	σ	95% C.L.*	A%
2,2-Dimethylheptane	817.31	817.19	0.04	0.09	0.10	808.09	807.93	0.06	0.14	0.18
2,4-Dimethylheptane	821.03	820.88	0.03	0.08	0.24	812.35	812.25	0.01	0.02	0.24
2,6-Dimethylheptane	827.06	827.01	0.06	0.15	0.21	816.99	816.92	0.05	0.14	0.13
2,5-Dimethylheptane	833.18	833.09	0.05	0.14	0.44	825.03	824.98	0.10	0.26	0.41
3,3-Dimethylheptane	834.68	834.35	0.03	0.07	0.15	830.23	830.12	0.02	0.04	0.08
Ethylbenzene	843.07	842.99	0.02	0.06	0.60	944.10	944.04	0.04	0.11	0.51
<i>cis,trans,trans</i> -1,2,4-Trimethylcyclohexane	844.82	844.85	0.02	0.06	0.09	861.39	861.27	0.04	0.09	0.08
<i>m</i> -Xylene	851.82	851.75	0.02	0.06	1.25	950.03	950.04	0.04	0.09	1.52
<i>p</i> -Xylene	852.80*	852.79	0.04	0.10	0.75	948.54	948.54	0.04	0.10	0.46
2,3-Dimethylheptane	853.26	852.79	0.04	0.10	(852.80)*	849.82	849.76	0.03	0.07	0.31
4-Methyloctane	861.46	861.41	0.03	0.08	0.49	856.49	856.26	0.03	0.08	1.09
3-Methyloctane	869.43	869.38	0.03	0.06	0.66	865.52	865.42	0.08	0.20	0.78
<i>o</i> -Xylene	874.53	874.44	0.05	0.13	0.87	981.56	981.73	0.02	0.06	0.76
<i>cis</i> -1-Ethyl-3-methylcyclohexane	881.29	881.34	0.05	0.12	0.11	906.01	906.00	0.01	0.02	0.15
Cumene	908.92	908.83	0.00	0.01	0.23	1006.06	1006.19	0.04	0.09	0.26
2,6-Dimethyloctane	933.62	933.61	0.01	0.03	0.21	925.44	925.44	0.06	0.15	0.18
3,4-Diethylhexane	937.44	937.02	0.02	0.06	0.29	936.07	936.24	0.05	0.12	0.14
1,3,5-Trimethylbenzene	952.83	952.76	0.02	0.05	0.50	1051.36	1051.54	0.04	0.09	0.43
4-Ethylcyclohexane	961.30	961.39	0.02	0.04	(961.45)*	956.33	956.34	0.03	0.08	0.15
1-Ethyl-2-methylbenzene	961.45*	961.39	0.02	0.04	0.57	1070.46	1070.63	0.04	0.09	0.41
2-Methylnonane	963.97	963.97	0.03	0.09	0.21	957.96	958.06	0.03	0.08	0.18
3-Methylnonane	970.32	970.38	0.05	0.12	0.18	966.96	967.06	0.03	0.07	0.18
1,2,4-Trimethylbenzene	976.91	976.86	0.01	0.02	1.62	1080.84	1081.02	0.08	0.19	1.55
Isobutylbenzene	992.48*	992.49	0.04	0.10	0.05	1082.90	1083.25	0.04	0.09	0.08
3-Ethylbenzene	992.53	992.49	0.04	0.10	(992.48)*	1064.57	1064.75	0.04	0.09	0.07
1,2,3-Trimethylbenzene	1003.68	1003.65	0.00	0.01	0.48	1120.33	1120.56	0.00	0.00	0.14
1-Methyl-3-isopropylbenzene	1006.59	1006.61	0.03	0.08	0.14	1103.84	1104.03	0.04	0.09	0.12
Indan	1013.44	1013.39	0.02	0.06	0.08	1147.39	1147.75	0.04	0.09	0.07
<i>n</i> -Butylcyclohexane	1025.65	1025.71	0.02	0.05	0.08	1054.03	1054.12	0.08	0.19	0.08
1-Methyl-3-propylbenzene	1035.51	1035.57	0.02	0.06	0.47	1134.57	1134.80	0.04	0.09	0.05
1,4-Diethylbenzene	1038.88	1039.11	0.01	0.04	0.33	1142.00	1142.30	0.04	0.09	0.14
<i>n</i> -Butylbenzene	1039.90	1039.96	0.01	0.03	0.11	1139.89	1140.16	0.07	0.19	0.21

1-Methyl-2-propylbenzene	1049.75	1049.78	0.04	0.09	0.25	1154.98	1155.12	0.07	0.19	0.15
4-Methyldecane	1061.06*	1060.60	0.03	0.07	0.47	1056.61	1056.72	0.08	0.19	0.18
1,4-Dimethyl-2-ethylbenzene	1060.58	1060.60	0.03	0.07	(1061.06)*	1166.50	1166.69	0.04	0.09	0.41
1,3-Dimethyl-4-ethylbenzene	1062.14	1062.15	0.04	0.10	0.29	1168.99	1169.12	0.07	0.19	0.30
2-Methyldecane	1064.77	1064.84	0.02	0.06	0.26	1059.14	1059.20	0.04	0.09	0.22
1,2-Dimethyl-4-ethylbenzene	1068.04	1068.12	0.02	0.06	0.46	1176.59	1176.73	0.00	0.00	0.44
1,2-Dimethyl-3-ethylbenzene	1086.88	1086.72	0.02	0.06	0.16	1206.44	1206.60	0.04	0.11	0.17
1-Ethyl-3-isopropylbenzene	1088.54	1088.70	0.03	0.06	0.13	1187.05	1187.22	0.07	0.19	0.06
1,2,3,5-Tetramethylbenzene	1102.85	1102.78	0.07	0.19	0.34	1216.82	1217.00	0.06	0.16	0.44
2,6-Dimethyldecane	1119.35	1119.29	0.02	0.06	0.13	1109.50	1109.61	0.07	0.19	0.18
Tetralin	1136.43	1136.65	0.07	0.17	0.21	1288.39	1288.54	0.11	0.26	0.18
n-Pentylbenzene	1141.13	1141.25	0.06	0.15	0.05	1242.74	1242.57	0.33	0.83	0.08
Naphthalene	1156.25	1156.71	0.07	0.16	0.30	1344.95	1345.32	0.04	0.09	(1345.67)*
1,4-Di-isopropylbenzene	1157.71	1157.98	0.04	0.10	0.10	1256.77	1257.66	0.04	0.11	0.32
2-Methylundecane	1164.88	1164.95	0.03	0.07	0.32	1159.30	1159.51	0.07	0.19	0.08
1,2,4-Triethylbenzene	1223.09	1223.42	0.05	0.11	0.13	1334.53	1334.77	0.08	0.20	0.06
n-Hexylbenzene	1243.89	1243.81	0.03	0.09	0.09	1345.67*	1345.32	0.04	0.09	0.19
2-Methylnaphthalene	1267.22	1267.29	0.07	0.18	0.23	1458.02	1458.01	0.02	0.04	0.18
1-Methylnaphthalene	1281.76	1281.81	0.03	0.08	0.26	1484.30	1484.28	0.04	0.09	0.07
Butane					0.32					0.31
Pentane					0.82					0.86
Hexane					3.72					3.88
Heptane					7.26					7.17
Octane					3.04					3.34
Nonane					1.17					1.13
Decane					1.03					0.91
Undecane					1.92					2.20
Dodecane					2.42					2.36
Tridecane					2.17					1.98
Tetradecane					1.47					1.30
Pentadecane					0.63					0.57
Hexadecane					0.17					0.17
Heptadecane					0.05					0.05
Total					79.45					79.30

* 95% Confidence limit for three determinations = $\frac{4.303 \sigma}{1.732}$

one unit. Therefore a tentative assignment interval of ± 0.5 Kováts index unit was used for matching indices.

After all peak assignments were complete, a precision survey was performed on Fuel 15B (Table IV). The resulting deviations of assignments from the true library values, ± 0.127 for the OV-101 and ± 0.180 for the OV-17, indicate that the assignments were well within the ± 0.5 assignment interval.

The preceding tables list the two jet propulsion fuels selected for this article. The peaks tentatively identified in each fuel are listed numerically by their OV-101 library indices. "K.I.-samp." represents the mean Kováts index for the three runs of a sample on the particular column and is accompanied by the standard deviation and 95% confidence level for three determinations. "K.I.-101" and "K.I.-17" represent library Kováts index values for the known reference standards. "A%" indicates the area percent of an identified peak from the first run of the fuel sample. Area percent is not intended to determine quantitatively the component but is used merely as a comparison tool to aid in the qualitative identification of peaks. For example, in shale-derived JP-4 Fuel 15B (see Table IV), the area percent of the peak thought to be 2-methylhexane is 0.45 A% on the OV-101 column and 0.44 A% on the OV-17 column. This comparative relationship lends additional credibility to the Kováts index matching process.

The asterisks in the "K.I.-101", "K.I.-17", and "A%" columns indicate compounds that appear to have coeluted. The asterisked number in the "A%" column is actually the library index (*i.e.* "K.I.-101" or "K.I.-17") of the other compound with which that compound has appeared to coelute. For example, benzene and methylcyclohexane coelute on the OV-17 column. Furthermore, their OV-17 library indices, 739.24 and 739.15 respectively, both fall within the ± 0.5 assurance limit for the sample peak in petroleum derived JP-4 Fuel 1B-792009 (see Table III) having an index 739.18.

To clarify this situation, the area percents of the Fuel 1B suspect constituents, benzene and methylcyclohexane, on the OV-101 were added and compared to the area percent of the OV-17 peak suspected to be coeluting benzene and methylcyclohexane. The resulting 1.48 A% on the OV-101 compared to the 1.44 A% on the OV-17, once again indicating the usefulness of area percent when matching peaks by Kováts indices.

It must be pointed out, however, that these area percent relationships become increasingly difficult to observe in the middle of the distillation range of any given fuel sample. This is due primarily to the increased number of isomeric compounds existing in that boiling range and the present inability of the GLC system to resolve all of these compounds.

Figs. 1-4 are chromatograms from both the OV-101 and OV-17 columns for the fuels selected for display in this report. Other petroleum derived JP-4 fuels not reported here¹⁴ illustrated a need for the detailed characterization of jet fuels. Those fuels supposedly represented the same fuel only sampled at different points in a fuel handling system. Inspection of the chromatograms readily indicated that the samples were indeed different. Extensive Kováts index libraries enable one to discern exactly how fuel samples differ.

Due to the countless number of compounds existing in a complex hydrocarbon mixture such as jet propulsion fuel, it is necessary to have a method better than

TABLE IV
SHALE-DERIVED JP-4 FUEL 15B-792009

Hydrocarbon name	OV-101						OV-17					
	K.I.-101	K.I.-SAMP.	σ	95% C.L.*	A%	K.I.-17	K.I.-SAMP.	σ	95% C.L.*	A%		
2-Methylbutane	464.94	464.98	0.24	0.59	0.52	462.44	462.15	0.77	1.92	0.50		
Benzene	642.11	642.08	0.13	0.32	0.14	739.24	739.18	0.06	0.16	(739.15)*		
Cyclohexane	650.27	650.22	0.00	0.00	0.51	687.73	687.99	0.26	0.64	0.51		
2-Methylhexane	659.24	659.19	0.00	0.00	0.45	638.62	639.08	0.53	1.32	0.44		
3-Methylhexane	669.11	669.06	0.00	0.00	1.02	655.49	655.84	0.39	0.96	1.03		
3-Ethylpentane	681.54	681.39	0.00	0.00	0.06	678.53	678.85	0.26	0.64	0.05		
Methylcyclohexane	715.63	715.63	0.04	0.11	1.90	739.15*	739.18	0.06	0.16	2.00		
Ethylcyclopentane	725.43	725.50	0.05	0.12	0.23	749.43	749.35	0.05	0.13	0.35		
2,5-Dimethylhexane	726.53	726.51	0.03	0.07	0.06	717.54	717.57	0.12	0.30	0.07		
2,4-Dimethylhexane	728.30	728.28	0.07	0.17	0.21	720.98	720.99	0.08	0.20	0.43		
Methylbenzene	747.63	747.58	0.06	0.14	1.26	845.42	845.70	0.02	0.05	0.86		
2,3-Dimethylhexane	754.03	754.07	0.04	0.10	0.28	751.82	751.66	0.05	0.12	0.22		
2-Methylheptane	760.60	760.48	0.09	0.23	1.03	753.77	753.63	0.05	0.12	1.11		
4-Methylheptane	762.04	762.05	0.05	0.13	0.45	757.35	757.25	0.13	0.32	0.49		
3-Methylheptane	768.75	768.65	0.02	0.06	0.55	765.12	765.04	0.04	0.09	0.79		
3-Ethylhexane	769.84	770.10	0.03	0.06	(769.96)*	768.08	767.90	0.03	0.08	0.45		
cis-1,3-Dimethylcyclohexane	769.96*	770.10	0.03	0.06	1.26	794.50	794.59	0.21	0.52	1.24		
cis-1,2-Dimethylcyclohexane	820.39	820.45	0.04	0.10	0.44	851.27	851.31	0.03	0.07	0.34		
cis,cis-1,3,5-												
Trimethylcyclohexane	825.38	825.26	0.02	0.06	0.91	838.47	838.38	0.01	0.02	0.08		
2,6-Dimethylheptane	827.06	827.04	0.02	0.05	0.61	816.99	816.94	0.03	0.07	0.61		
1,1,3-Trimethylcyclohexane	830.35	830.32	0.02	0.05	0.86	846.55	846.53	0.02	0.06	1.39		
3,3-Dimethylheptane	834.68	834.14	0.06	0.16	0.07	830.23	830.03	0.01	0.01	0.03		
Ethylbenzene	843.07	843.11	0.01	0.02	0.41	944.10	944.16	0.08	0.19	0.17		
cis,trans-1,2,4-												
Trimethylcyclohexane	844.82	844.83	0.00	0.01	0.51	861.39	861.34	0.11	0.27	0.49		
cis,cis,trans-1,3,5-												
Trimethylcyclohexane	848.69	848.66	0.05	0.12	0.11	868.09	868.01	0.11	0.26	0.08		

(Continued on p. 192)

TABLE IV (continued)

Hydrocarbon name	OV-101					OV-17				
	<i>K.I.-101</i>	<i>K.I.-SAMP.</i>	σ	95% C.L.*	<i>A%</i>	<i>K.I.-17</i>	<i>K.I.-SAMP.</i>	σ	95% C.L.*	<i>A%</i>
<i>m</i> -Xylene	851.82	851.67	0.05	0.12	0.87	950.03*	950.16	0.04	0.11	2.10
<i>p</i> -Xylene	852.80	852.95	0.00	0.01	0.57	948.44	948.68	0.08	0.19	0.08
2-Methyloctane	862.66	862.52	0.04	0.09	0.32	856.17	856.22	0.07	0.18	0.76
<i>cis,trans-cis</i> -1,2,3-Trimethylcyclohexane	867.35	867.39	0.02	0.04	0.37	892.49	892.41	0.11	0.26	0.34
<i>cis,trans,cis</i> -1,2,4-Trimethylcyclohexane	869.09	869.30	0.04	0.10	(869.43)**	894.23	894.06	0.11	0.27	0.42
3-Methyloctane	869.43*	869.30	0.04	0.10	0.92	865.52	865.33	0.00	0.01	1.24
<i>o</i> -Xylene	874.53	874.44	0.02	0.06	0.67	981.56	981.81	0.04	0.11	0.60
<i>cis</i> -Ethyl-3-methylcyclohexane	881.29	881.30	0.02	0.04	0.53	906.01	905.98	0.04	0.11	1.55
<i>trans</i> -1-Ethyl-2-methylcyclohexane	901.06	901.23	0.00	0.00	0.50	927.63	927.41	0.04	0.11	1.03
<i>cis</i> -1-Ethyl-4-methylcyclohexane	903.98	903.97	0.00	0.01	0.17	930.25	930.12	0.04	0.11	0.12
Cumene	908.92	908.76	0.01	0.01	0.06	1006.00	1005.74	0.04	0.10	0.08
Isopropylcyclohexane	912.85	912.79	0.01	0.02	0.25	943.24	943.10	0.00	0.00	0.19
<i>cis</i> -1-Ethyl-2-methylcyclohexane	920.98	920.95	0.05	0.13	0.17	954.58	954.53	0.04	0.11	0.36
2,7-Dimethyloctane	929.14	929.53	0.02	0.06	0.20	919.33	919.27	0.04	0.11	0.08
2,6-Dimethyloctane	933.62	933.61	0.02	0.06	0.98	925.44	925.42	0.09	0.22	1.09
3-Ethyl-3-methylheptane	940.32	940.20	0.02	0.05	0.55	946.53	946.82	0.09	0.22	0.02
1-Ethyl-3-methylbenzene	944.83	944.71	0.02	0.05	0.45	1046.12	1046.02	0.06	0.14	1.34
1,3,5-Trimethylbenzene	952.83	952.76	0.02	0.05	0.51	1051.36	1051.63	0.02	0.05	0.07
4-Methylnonane	954.97	954.83	0.02	0.05	0.25	950.20	950.16	0.04	0.11	(950.03)*
4-Ethylcyclohexane	961.30*	961.24	0.02	0.05	0.69	956.33	956.19	0.04	0.11	0.65
1-Ethyl-2-methylbenzene	961.45	961.24	0.02	0.05	(961.30)*	1070.46	1070.72	0.01	0.03	0.10
2-Methylnonane	963.97	963.86	0.02	0.05	0.36	957.96	957.80	0.00	0.00	0.83
3-Ethylcyclohexane	966.99	966.74	0.02	0.06	0.17	964.56	964.33	0.04	0.11	0.05
3-Methylnonane	970.32	970.18	0.02	0.05	0.55	966.96	966.84	0.00	0.00	1.09
1,2,4-Trimethylbenzene	976.91	976.72	0.03	0.07	0.67	1080.84	1081.01	0.07	0.17	1.37
<i>cis</i> -1-Methyl-4-isopropylcyclohexane	983.78	983.77	0.03	0.08	0.21	1012.55	1012.37	0.04	0.11	0.12
3-Ethylnonane	992.53	992.43	0.04	0.11	0.08	1064.57	1064.49	0.01	0.03	0.44
1,2,3-Trimethylbenzene	1003.68	1003.48	0.04	0.10	0.36	1120.33	1120.49	0.07	0.17	0.35
<i>p</i> -Cumene	1009.38	1009.32	0.00	0.01	0.18	1104.61	1104.64	0.03	0.08	0.53
Indan	1013.44	1013.29	0.01	0.01	0.14	1147.39	1147.63	0.04	0.09	0.03
<i>n</i> -Butylcyclohexane	1025.65	1025.59	0.03	0.07	0.49	1054.03	1053.98	0.06	0.15	0.54

1-Methyl-3-propylbenzene	1035.51	1035.43	0.02	0.06	0.38	1134.57	1134.66	0.01	0.03	0.42
<i>trans</i> -Decalin	1042.88*	1042.88	0.07	0.17	1.00	1102.07	1102.01	0.00	0.00	0.83
1,3-Dimethyl-5-ethylbenzene	1042.81	1042.88	0.07	0.17	(1042.88)*	1144.78	1144.87	0.04	0.10	0.05
1,4-Dimethyl-2-ethylbenzene	1060.58	1060.88	0.09	0.22	0.54	1166.50	1166.52	0.05	0.12	0.06
1,3-Dimethyl-4-ethylbenzene	1062.14	1062.01	0.01	0.04	0.13	1168.99	1169.09	0.01	0.04	0.05
1,2-Dimethyl-4-ethylbenzene	1068.04	1067.96	0.03	0.06	0.23	1176.59*	1176.70	0.02	0.04	0.05
<i>tert</i> -Pentylbenzene	1076.00	1076.37	0.03	0.07	0.08	1176.49	1176.70	0.02	0.04	(1176.59)*
<i>cis</i> -Decalin	1084.51	1084.49	0.01	0.01	0.41	1158.23	1158.11	0.04	0.11	0.36
1-Undecene	1088.37	1088.14	0.00	0.01	0.33	1106.67	1106.86	0.01	0.01	0.03
1,2,3,5-Tetramethylbenzene	1102.85	1102.65	0.04	0.09	0.07	1216.82	1217.15	0.04	0.10	0.24
2,6-Dimethyldecane	1119.35	1119.17	0.08	0.20	0.28	1109.50	1109.40	0.07	0.17	0.35
Tetralin	1136.43	1136.37	0.06	0.14	0.60	1288.39	1288.71	0.00	0.00	0.29
<i>n</i> -Pentylbenzene	1141.13	1140.86	0.04	0.10	0.29	1242.74	1243.07	0.04	0.10	0.14
2-Methylundecane	1164.88	1164.79	0.03	0.08	0.31	1159.30	1159.25	0.01	0.02	0.59
1- <i>tert</i> -Butyl-4-ethylbenzene	1165.62	1166.13	0.07	0.17	0.06	1266.63	1266.76	0.04	0.10	0.06
Butane					0.94					0.94
Pentane					0.91					0.88
Hexane					1.22					1.34
Heptane					1.58					1.75
Octane					2.50					1.71
Nonane					2.42					2.87
Decane					3.76					4.32
Undecane					5.55					4.71
Dodecane					3.84					4.12
Tridecane					2.03					2.13
Tetradecane					0.81					0.84
Pentadecane					0.32					0.37
Hexadecane					0.15					0.14
Heptadecane					0.07					0.06
Octadecane					0.03					0.03
Total					56.93					61.03

* 95% Confidence limit for three determinations = 4.303σ
 = 1.732

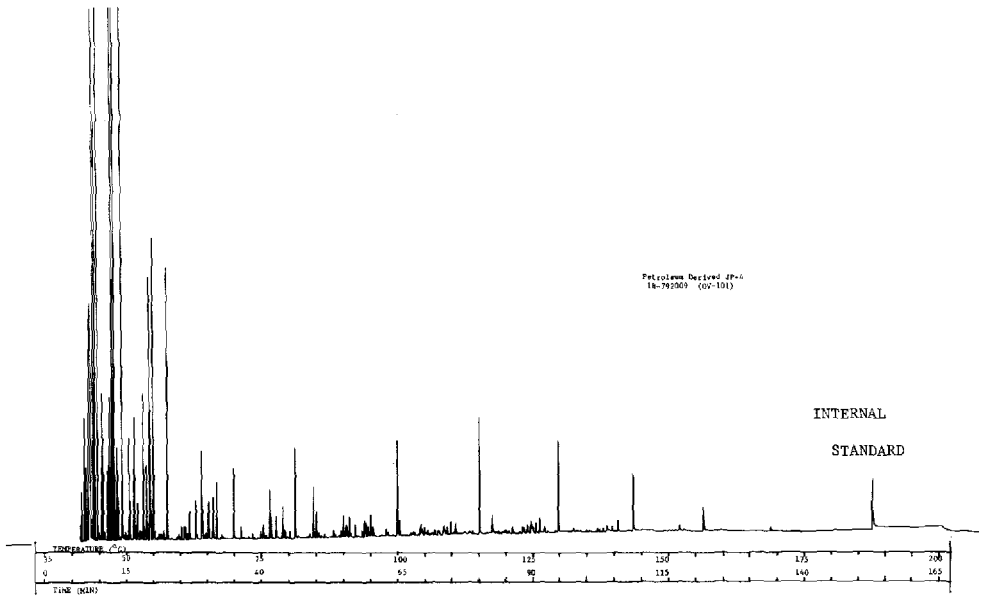


Fig. 1. Petroleum-derived JP-4 1B-792009 (OV-101).

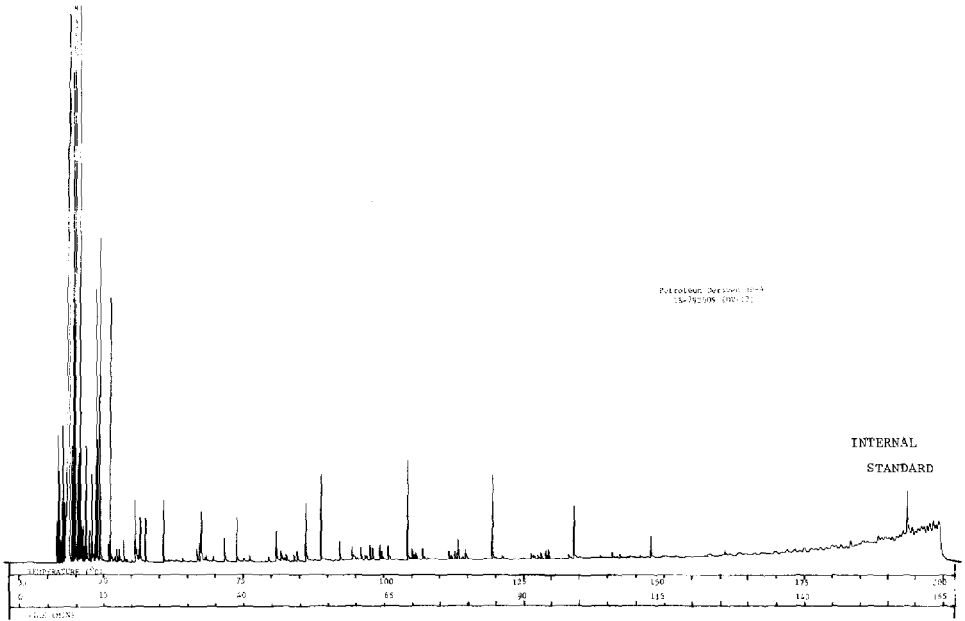


Fig. 2. Petroleum-derived JP-4 1B-792009 (OV-17).

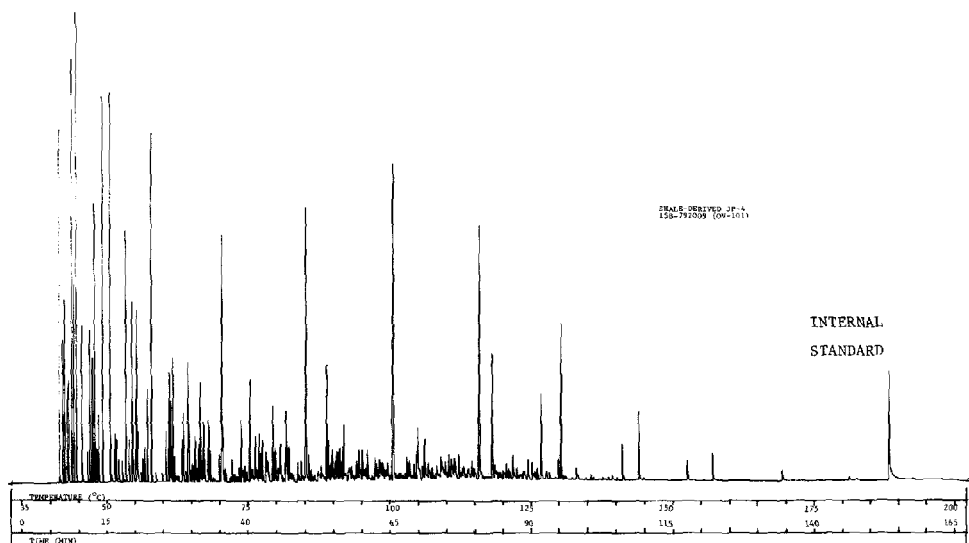


Fig. 3. Shale-derived JP-4 15B-792009 (OV-101).

random choice initially to select standards for a comprehensive library. The initial method used in this article was literature research of other glass capillary GC and detailed MS experiments performed on selected JP-4 jet propulsion fuels.

Next, the Kováts indices of members of homologous series generally varied in their Kováts indices by a set number of units. By generating linear graphs it was easy to estimate the Kováts index of a member of a homologous series given its carbon number or its boiling point. This method should by no means be used to identify components reliably, but can be used as a valuable tool in helping to choose reference compounds to extend an existing Kováts indices library. Table V demonstrates the usefulness in extrapolating the linear relationship of a homologous series to predict the presence of a member not among the reference standards. A fuel was selected at

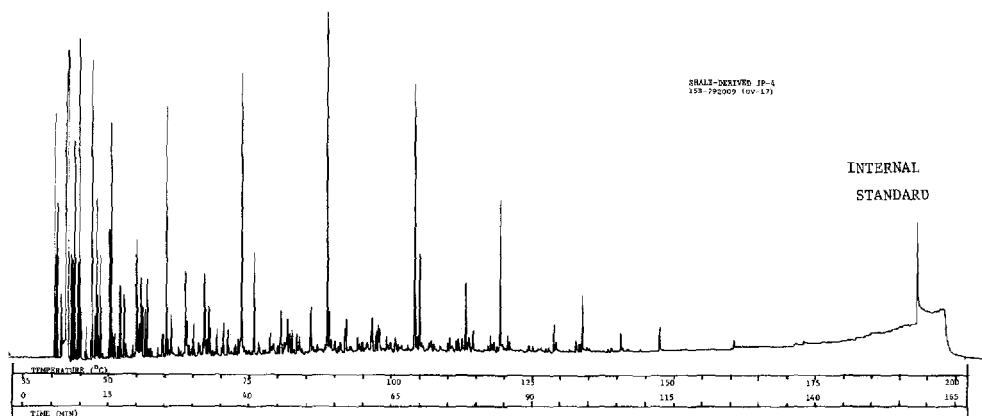


Fig. 4. Shale-derived JP-4 15B-792009 (OV-17).

TABLE V
EXTRAPOLATED KOVÁTS INDICES: FUEL 15B-792009

<i>Homologous series</i>	<i>Hydrocarbon name</i>	<i>K.I.-101 extrap.</i>	<i>K.I.-101 sample</i>	<i>K.I.-17 extrap.</i>	<i>K.I.-17 sample</i>	<i>A% OV-101</i>	<i>A% OV-17</i>
2-Methyl-alkanes	2-Methyl: dodecane	1264.88	1264.92	1259.30	1259.85	0.28	1.18*
	tridecane	1364.88	1364.95	1359.30	1359.47	0.10	0.13
3-Methyl-alkanes	3-Methyl: decane	1071.32	1070.63	1067.96	1067.67	0.37	0.46
	undecane	1171.32	1170.98	1167.96	1167.99	0.27	0.38
	dodecane	1271.32	1271.05	1267.96	1268.24	0.18	0.49
	tridecane	1371.32	1371.29	1367.96	1367.58	0.08	0.29
4-Methyl-alkanes	4-Methyl: undecane	1160.06	1160.36	1156.49	1156.06	0.24	0.41
	dodecane	1260.06	1260.19	1256.49	1255.87	0.28	0.31
3-Ethyl-alkanes	3-Ethyl: nonane	1067.10	1066.69	1064.56	1064.49	0.16	0.43
	decane	1167.10	1167.52	1164.56	1164.11	0.25	0.07
	undecane	1267.10	1267.68	1264.56	1264.28	0.15	0.03
2,2-Dimethyl-alkanes	2,2-Dimethyl: nonane	1017.78	1017.51	1008.18	1008.28	0.28	0.08
	decane	1117.78	1117.70	1108.18	1107.96	0.20	0.08
	undecane	1217.78	1218.15	1208.18	1207.59	0.24	0.08
2,3-Dimethyl-alkanes	2,3-Dimethyl: nonane	1053.33	1053.56	1049.98	1050.27	0.07	0.12
	dodecane	1353.33	1353.15	1349.98	1350.30	0.06	0.11
2,6-Dimethyl-alkanes	2,6-Dimethyl: nonane	1033.62	1033.88	1025.44	1025.27	0.37	0.07
	dodecane	1315.87	1316.06	1305.25	1305.41	0.05	0.10
<i>n</i> -Alkyl-cyclohexanes	Cyclohexane: <i>n</i> -pentyl	1126.65	1127.14	1156.03	1156.06	0.29	0.41
Total						3.92	4.07

* Relatively large area percent here suggests this component co-eluted with another hydrocarbon.

random. Indices were calculated from the corresponding carbon number *versus* Kováts indices plot and compared with a sample component having nearly the same retention index. In all cases, a peak predicted on the OV-101 column was also successfully predicted on the OV-17 column.

From the existing Kováts libraries it was noted that there were some "gaps" in the tentative identification of components found in the fuel samples. By procuring compounds of classes common to jet propulsion fuel (*e.g.* branched alkanes, alkyl-benzenes, *etc.*) whose carbon numbers fall within these "gaps", the likelihood of identifying more compounds in the fuel could also be significantly increased. This is

particularly true for the shale-derived fuel consisting of nearly 30% by volume of cycloparaffins, as determined by MS.

Another useful feature of these Kováts libraries on different stationary phases is that an unknown compound, if sufficiently resolved on both columns could be assigned to a general hydrocarbon class by calculating its difference in index values, *i.e.* $\Delta K.I.$ values. In general, branched alkanes demonstrated a rather small negative $\Delta K.I.$ of *ca.* -3 to -10 units with substantial negative values for highly substituted alkanes. Cyclohexanes usually displayed a positive $\Delta K.I.$ of *ca.* $+24$ units for the standards included in the libraries. The dimethylcyclohexanes averaged *ca.* $+26$ units while the trimethylcyclohexanes averaged *ca.* $+18$ units. The 1-olefins examined showed a positive $\Delta K.I.$ of $+96$ units. However, certain substitutions gave $\Delta K.I.$ values in the $+110$ – 120 and higher range: three or more alkyl groups in the 1, 2 and 3 positions; or two alkyl groups in the 1 and 2 positions where one group was other than a methyl; or three or more alkyl groups in the 1, 2 and 4 positions. It appears that substituents that render the hydrocarbon molecule more spherical or spheroid in shape tend to exhibit higher positive $\Delta K.I.$ values. The few alkylate 1 naphthalenes investigated showed a positive $\Delta K.I.$ of almost $+201$ units.

CONCLUSIONS

The Kováts retention indices of nearly 200 reference hydrocarbons have been determined in a statistically reliable fashion on two open tubular GC columns of different stationary phases. The libraries are extremely valuable in characterizing jet fuel distillates derived from petroleum and shale oils.

Crucial to investigating hydrocarbon distribution in wide-boiling fuels is optimizing column resolution. A major stumbling block in GC-MS peak identification is the coelution of peaks¹⁸, especially in the middle of the distillation range of a jet propulsion fuel. Additional resolution of components on each of the stationary phases would greatly diminish this problem.

To this end, the future effort will be geared toward coating fused silica columns of relatively narrow bore, *i.e.* 0.10 mm I.D. Lower inherent chemical adsorptivity would be gained besides increased mechanical flexibility, which allows optimum positioning of the column in relation to the injector and detector. Furthermore, the decrease in internal diameter would translate into a proportional increase in the number of effective theoretical plates available (at the column's optimum flow-rate). Coupling improved open tubular gas chromatographic resolution to prior sample fractionation by preparative, high-performance liquid chromatography would constitute a powerful analytical approach to a detailed jet fuel characterization. However, all retention index identifications would be tentative and ultimately verified by GC-MS.

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