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IMPROVED ANALYSIS OF PETROLEUM AND SHALE-DERIVED FUEL DISTILLATES BY ALTERING GC PROGRAMMED TEMPERATURE RATES

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Overlapping chromatographic peaks of components from different hydrocarbon classes can be disengaged by exploiting their shifts in relative retention behavior with changes in linear rates of programmed temperature. Many co-eluting species in complex chromatograms of shale- and petroleum-derived jet fuels can be resolved without varying stationary phase, column length, or initial column temperature.

Retention indices were simultaneously determined on two bonded phase, fused silica capillary columns of slightly different polarities at three different linear programmed temperature rates. For certain hydrocarbon types, no change in index values was observed with an alteration in programming rate. However, the indices of other hydrocarbon classes shifted uniformly with programmed temperature rates on each of the two stationary phases. When applied, this phenomenon could help resolve coeluting members of different or even the same hydrocarbon type and elucidate their probable structure. The overall precision of the retention indices, i.e., the mean standard deviation at the 95% confidence levels, was less

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than +/- 0.13 for either column at any of the three programming rates. Since the above technique is automated, it could also be a useful screening tool to search for specific hydrocarbons in a myriad of unknown components of a complex hydrocarbon mixture.

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FOREWORD

This technical report describes work performed under the In-House Work Unit 30480591 administered by the Fuels Branch (POSF), Fuels and Lubrication Division (POS), Aero Propulsion Laboratory (AFWAL/PO), Air Force Wright Aeronautical Laboratories. Project scientists for this program were Mr. Paul C. Hayes, Jr. and Edward W. Pitzer, both of whom also prepared this report.

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INTRODUCTION

1. THE CHALLENGE

Hydrocarbon feedstocks and distillate products require ever-increasing analytical scrutiny due to the continual rise in costs and fall in availability of high quality petroleum crudes. Modern feedstocks are including lower grade crudes, materials from alternate sources of energy, e.g., shale oil, tar sands, coal liquids, biomass, etc. and may eventually become totally synthetic. The petrochemical engineer must have timely and reliable analytical results to economically optimize processing operations and monitor product integrity. Thus, a greater burden is then placed on the analytical chemist to respond faster with more pertinent compositional detail on samples of a variable nature. This is no easy task.

Commercial hydrocarbon products such as gasoline, kerosene, and aviation turbine fuels are blends of literally thousands of hydrocarbons. The detailed hydrocarbon distribution of petroleum- and shale-derived jet fuels is far too complicated to be unraveled by even the most efficient ultra high resolution capillary column. However, multi-dimensional gas chromatography appears most promising in determining selected individual components and in clarifying hydrocarbon-type classifications. Heart-cut segments of the total hydrocarbon profile can be diverted automatically from one capillary column to another having greater selectivity.

The objective of this report is to expound on a versatile technique to disengage hydrocarbon solutes that is applicable not only to single but also

multi-dimensional analysis strategies. Searching for the best column to produce a given separation need not proceed through an entire raft of capillary columns of widely different lengths or stationary phases. The same capillary column usually employed for similiar analyses could be used once again but under different isothermal or programmed temperature regimes.

2. SIMULTANEOUS DUAL COLUMN CHROMATOGRAPHY

To date, no ultra high efficiency capillary column can resolve all components of a complex sample in a single analytical run. The practice of dual capillary column chromatography allows different selectivities to alter relative elution behavior and hopefully permit newer separations in nearly the same analysis time. Several publications [References 1-6] detail the advantages of simultaneous analysis using two capillary columns of different polarities. The recent papers of Wright [Reference 7] and Levy [Reference 8] are particularly noteworthy. The benefits of the technique include: confirmation of the presence or absence of individual components, an increase in the reliability of assignments (particularly where isomers are possible co-eluants), and a convenient check on peak purity. Yet as before, it is still possible for components to emerge as one peak on a single capillary column using one set of run parameters.

3. BACKGROUND: "RETENTION INDEX SYSTEM" (RIS)

In their foundational article on gas-liquid partition chromatography, James and Martin [Reference 9] proposed that both the retention volume and the retention time of a solute can be characteristic and aid in its identification. The "retention idex"concept introduced by Kovats [Reference 10] calculates

the logarithmetic retention of a solute interpolated between those of two standard compounds. Any homologous series of organic compounds can be the standards. Ettre is credited with coining the expression "retention index system" (RIS) and for ardently promoting it for the uniform expression of retention data. Having recently celebrated its silver anniversary [Reference 11], the RIS has been studied and utilized in over 1500 journal articles!

Van den Dool and Kratz [Reference 12] demonstrated that for a programmed temperature gas chromatographic run, the logarithmetic relationship which existed under isothermal operation is replaced by the approximately linear relationship:

$$I^{c}_{pt,s} = 100 \left[\frac{T_r(s) - T_r(z)}{T_r(z+1) - T_r(z)} \right] + 100\,z \qquad (1)$$

where: $I^{c}_{pt,s}$ represents the retention index of substance "s" determined by linear programmed temperature "pt" on column "c", and where "$T_r(s)$" is the absolute retention time of substance "s", "$T_r(z)$" and "$T_r(z+1)$" are the absolute retention times of the n-alkane standards which bracket the substance of interest, "z" is the number of carbon atoms in the n-alkane standard that elutes just prior to substance "s", and "z+1" is the number of carbon atoms in the n-alkane that elutes just after substance "s".

Traditionally, Air Force JP-4 jet fuels exhibit a wide boiling range, i.e., 20-250 ℃, and a preponderence of normal paraffins (see Figure 1) regardless of the crude source. Consequently, JP-4 fuels lend themselves handily to gas chromatographic analysis employing retention indices under linear programmed temperature conditions.

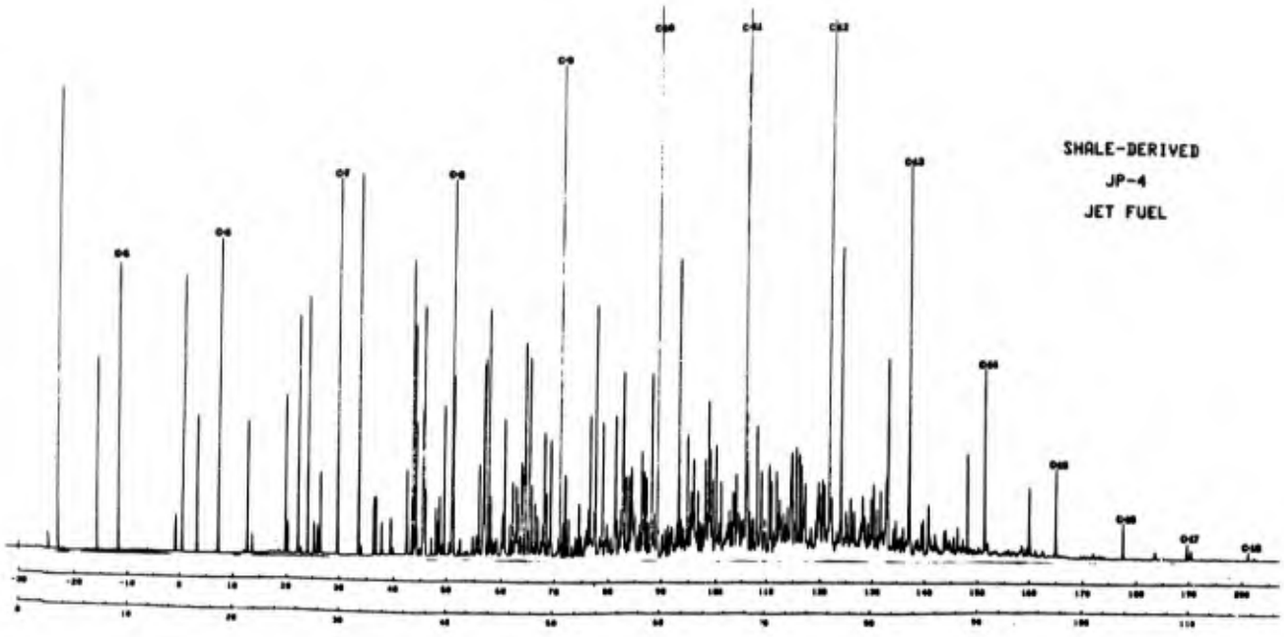

Figure 1. FID Chromatogram of Shale-Derived Jet Fuel Programmed at 2°C/min on Methyl Silicone Column as Per Table 1 Run Parameters

4. RETENTION INDICES, POLARITY, AND TEMPERATURE

A recent review of the RIS [Reference 11] discloses a rich bibliography specifically on the analyses of complex hydrocarbon mixtures. The literature is replete with temperature coefficients of Kovats indices (isothermal) and the use of temperature in distinguishing different classes of hydrocarbons [References 13-25]. The notion of modifying column polarity by altering column temperature was elegantly exploited by Bertsch, Pretorius, Kaiser, and Rieder [References 26-28] in a tandem column gas chromatographic system, i.e., "SECAT". Given independent temperature control of series-coupled columns each with stationary phases of different polarity, a powerful handle was now available for manipulating relative retention behavior. The effective polarity of the entire gas chromatographic system could be shifted conveniently anywhere between the polarities of the two pure stationary phases simply by adjusting the individual temperatures (isothermal) of each column. In this way, relative retention values of solutes could easily and dramatically be fine tuned for optimum resolution and elution order even reversed. Kaiser and Rieder [Reference 27] tracked quantitatively the polarity change afforded by the tandem columns, as a function of temperature, in terms of isothermal retention indices. Smuts et al. [References 29-31] formulated and confirmed the basic relationships of the chromatographic parameters of the technique. However, Kaiser et al. [Reference 28] point out that the "SECAT" method does not significantly improve the resolution of a sample having apolar solutes of interest (such as the jet fuels studied in the present paper).

Analogous work on apolar samples using programmed temperature indices has not been extensively investigated. Only a few researchers have reported characteristic shifts in retention indices of different hydrocarbon types as a

function of programmed temperature rate. Schulz and Reitemeyer [Reference 32] noted that the retention indices for branched paraffins, n-olefins-1, and n-olefins-2 displayed negligible variations. According to them, alkyl naphthalenes showed only a slight shift. Alkyl benzenes, on the contrary, exhibited a sizeable index change that could reverse peak elution order with different heating rates. The retention behavior of over 70 polycyclic aromatic hydrocarbons (PAHs) with different programming rates was reported by Beernaert [Reference 33]. Huynh and Vu Duc [Reference 34] also exploited the programmed temperature dependency of the retention indices of PAHs. In analyzing PAHs in samples cleaned up prior to chromatography, spurious interferences, primarily the normal alkanes, remained in the final extracts. For their application, varying the rate of temperature programming was a simple means of ensuring the purity of a suspected PAH peak. Though not reporting data via the RIS, several research groups effectively used programmed temperature to alter relative retention in hydrocarbon matrices. Schutjes, Vermeer, Rijks, and Cramers [Reference 35] demonstrated that ultra high resolution columns can allow separation of overlapping hydrocarbon types by a change in elution temperature of only 10 °C. Consequently, reliable information on solute purity could also be garnered. Similarly, Ettre [Reference 36] showed how optimizing a multi-step temperature program for the analysis of gasolines can separate once-coeluting solutes of different hydrocarbon types. By altering the programmed temperature rate for the analysis of a petroleum fraction, the Grobs [Reference 37] placed naphthalene in a less crowded region of the chromatogram for more accurate quantitation.

Improved reproducibility of programmed temperature retention indices is at hand with the commercial availability of inert, fused silica columns

[References 38,39] having permanently bonded stationary phases exhibiting excellent thermal stability [Reference 40]. Sadtler Research Laboratories has, in fact, introduced a "Gas Chromatography Retention Index Library" [Reference 41] of chemical compounds measured on fused silica capillary columns under several sets of conditions that include two different linear programmed temperature rates on four different stationary phases. Indeed, Knoppel et al. [Reference 42] confirmed the increasing use of such programmed indices for the analysis of complex mixtures. Knoppel standardized crucial chromatographic parameters to ensure reproducible programmed temperature retention indices from column to column. If one keeps the same stationary phase, phase ratio, and initial column temperature, then subtle adjustments in column inlet pressure or carrier flow rate, temperature programming rate, or column geometry can effectively reproduce indices from column to column for all components of a mixture. As Knoppel succinctly reported [Reference 42], "As long as the elution temperatures do not change, the retention indices do not change either."

What is newly reported here is a programmed RIS study that includes selected n-alkyl cyclohexanes, certain branched paraffin homologues, 5-alkyl indans, and 1-alkyl tetralins. These along with other hydrocarbon classes were all chromatographed at three different rates of linear programmed temperature simultaneously on two fused silica columns of different stationary phases. Fundamentally, we exploited the effect column temperature has on stationary phase polarity to improve peak disengagement. According to the Grobs, changing relative retention behavior by altering elution temperature can be versatile in improving solute separations and in verifying peak purity. Unfortunately such tactics are "virtually unused in practical gas chromatography" [Reference 37].

SECTION II

EXPERIMENTAL

1. CAVEATS

No concerted effort was made at determining either individual hydrocarbon response factors or the degree of split discrimination with solute molecular weight. Normalized area percentages were used solely as a tool in tracking the progress of the peak disengagements. Of course, all such qualitative judgements on compound identity were tentative and will later be checked by GC-MS.

A word of caution: there is no guarantee that a compound disengaged by a change in the temperature programming rate will not then coelute with a different compound in another part of the chromatogram. According to Delaney [Reference 43], "No chromatographic analysis method can be guaranteed to quantitate a particular substance and only that substance." Hence, the possibility exists that at least two components could be contained under some of the peaks reported in the present work. Davis and Giddings [Reference 44] emphasize the severe degree of peak overlap that can occur in complex chromatograms from a purely random consideration. Special detectors can, in principle, increase the specificity of the analysis and thus raise the reliability of identification and subsequent quantitation. However, the theme of this paper is improving but not proving peak purity.

2. EQUIPMENT AND CONDITIONS

The gas chromatograph utilized in this study was a Varian Model 3700. It was equipped with a split-splitless capillary column inlet system, dual flame ionization detectors, a Varian Model 8000 automatic liquid sampler, and

cryogenic (liquid nitrogen) capability. Two analog-to-digital (A/D) converters fed raw data simultaneously to a Hewlett-Packard 3356D Lab Automation System, where a BASIC program automatically calculated retention indices referenced to the normal paraffins. Table 1 details the pertinent capillary parameters.

The injection port ends of two fused silica columns were threaded through a two-holed graphitized Vespel ferrule and inserted into the same injection port of the capillary inlet system. The detector port ends, however, were connected to two separate flame ionization detectors, each monitored by its own A/D device. Each hole in the ferrule measured 0.4 mm in internal diameter. Care was taken to ensure that the ends of both silica columns terminated side by side and the same distance from the glass frit of the injector insert. No special modifications of the injector body were necessary.

To avoid potential contamination problems, ultra-high-purity helium (99.999%) was used as the carrier gas. The helium was subsequently 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 regulators [Reference 45].

Column capacity also had to be considered. Progressive column overloading can cause typical "leading" peak shapes and a shifting in retention index values. Symmetrical peaks can be obtained by lowering the sample load. Schomburg and Dielmann [Reference 46] 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 and

TABLE 1
CHROMATOGRAPHIC OPERATING CONDITIONS

DETECTOR	FLAME IONIZATION DETECTOR (FID)
DETECTOR TEMPERATURE	250 °C
INJECTOR	FRITTED GLASS INSERT (NORMAL SPLIT MODE)
INJECTOR TEMPERATURE	250 °C
SEPTUM PURGE FLOW-RATE	15 ml/min
DETECTOR MAKE-UP FLOW-RATE	30 ml/min (HELIUM)
DETECTOR HYDROGEN FLOW-RATE	30 ml/min
DETECTOR AIR FLOW-RATE	300 ml/min
LIQUID SAMPLE VOLUME	0.3 ul SPLIT 1:50 (DILUTED 1:100 PRIOR WITH CS_2)
ELECTROMETER	10^{-12} A/mv
COLUMN #1	ULTRA-1, CROSS-LINKED METHYL SILICONE (MS), 0.33 um FILM, 0.22 mm I.D. X 50 m FUSED SILICA
HELIUM CARRIER FLOW-RATE	2.91 ml/min at 40 psig, -30 °C (u = 25.4 cm/s at 143 °C)
COLUMN #2	ULTRA-2, CROSS-LINKED 5% PHENYL-METHYL SILICONE (PMS), 0.33 um FILM, 0.22 mm I.D. X 50 m FUSED SILICA
HELIUM CARRIER FLOW-RATE	2.42 ml/min at 40 psig, -30 °C (u = 23.1 cm/s at 143 °C)

jet fuels were diluted nearly 100:1 in a relatively non-interfering solvent (carbon disulfide) to limit the amount of the most predominant hydrocarbon species entering the columns to less than 10 ng each.

The alkyl-substituted indans and tetralins were synthesized by R. S. Smith, Chemistry Department, University of Wyoming, Laramie, Wyoming, while nearly all the other standards were purchased from Wiley Organics, Inc., Columbus, Ohio. All standards and samples were chromatographed simultaneously on both columns from -30 °C to 240 °C at a linear programmed temperature rate of either 1, 2, or 3 C/min.

The selection of the standard components used in this study were based on their tentative identification in petroleum- and shale-derived jet fuel samples previously studied in this laboratory [Reference 47]. The fuels analyzed in the present paper are, in fact, those same samples.

SECTION III

RESULTS AND DISCUSSION

1. DEFINITION

The objective of this paper is to re-focus attention on the merits of optimizing relative retention behavior by gently perturbing the polarity of the stationary phase of a capillary column. Of the several techniques available [Reference 6], only altering the linear programmed temperature rate of the analysis will be discussed here.

If a chromatographic run is performed at one programmed temperature rate, a certain set of retention indices will be generated for the components of the sample. If the analysis is repeated at a slightly higher or lower programming rate, a different set of indices may result for some but not all of the hydrocarbons. This phenomenon of changing retention indices with linear programmed temperature rates will hereafter be referred to as the "delta I-pt" effect, i.e. :

$$\delta I^{c}_{pt(m-n),s}$$

i.e., the change in retention index "I" for a solute "s" on a column of stationary phase "c" chromatographed at two different linear programmed temperature rates "pt(m)" and "pt(n)".

Using the "delta I-pt" effect and simultaneous dual column chromatography, one compound could, for example, be described by four unique retention index values, i.e., one for each column polarity (2) at each programmed temperature rate (2). Tables 2 and 3 list the retention indices of standard compounds chromatographed simultaneously on two columns of different polarity at three different linear programmed temperature rates. The corresponding shifts in the indices are also calculated for a change from 1 °C/min to 2 °C/min or from 1 °C/min to 3 °C/min.

TABLE 2

RETENTION INDICES GENERATED ON METHYL SILICONE (MS) COLUMN AT THREE DIFFERENT LINEAR PROGRAMMED TEMPERATURE RATES

COMPOUND NAME	I^{ms} pt,s (1 C/min)	SD	95% C.L.	I^{ms} pt,s (2 C/min)	SD	95% C.L.	I^{ms} pt,s (3 C/min)	SD	95% C.L.	δI^{ms} pt(1-2),s	δI^{ms} pt(1-3),s
2,3-DIMETHYLBUTANE	556.31	.05	.13	558.82	.02	.05	560.33	.00	.01	2.50	4.02
2,2,3-TRIMETHYLBUTANE	627.97	.08	.20	630.06	.01	.01	631.28	.13	.33	2.09	3.31
BENZENE	640.61	.04	.09	643.07	.00	.00	644.46	.03	.09	2.46	3.85
CYCLOHEXANE	647.36	.07	.18	650.41	.03	.08	652.19	.01	.01	3.05	4.83
2,3-DIMETHYLPENTANE	664.78	.05	.12	666.38	.00	.01	667.28	.07	.17	1.60	2.50
3-ETHYLPENTANE	683.88	.07	.17	684.72	.01	.03	685.24	.06	.14	.84	1.36
1-HEPTENE	689.01	.04	.10	689.10	.05	.11	689.22	.03	.07	.09	.21
2,2,3,3-TETRAMETHYLBUTANE	710.35	.02	.05	712.98	.00	.00	714.69	.02	.05	2.63	4.34
METHYLCYCLOHEXANE	710.40	.05	.12	713.04	.01	.02	714.82	.03	.07	2.63	4.42
1-c-2-DIMETHYLCYCLOPENTANE	710.76	.00	.01	713.09	.02	.06	714.60	.01	.02	2.33	3.84
2,2,3-TRIMETHYLPENTANE	727.92	.02	.04	729.78	.01	.03	730.95	.04	.10	1.86	3.03
METHYLBENZENE	746.99	.02	.06	749.29	.02	.06	750.81	.03	.07	2.30	3.82
2,3-DIMETHYLHEXANE	758.65	.02	.04	759.59	.02	.04	760.14	.04	.09	.94	1.49
3-ETHYL-3-METHYLPENTANE	763.06	.01	.03	765.47	.02	.06	766.94	.01	.02	2.41	3.88
3,4-DIMETHYLHEXANE	766.04	.03	.08	767.33	.03	.08	768.12	.01	.04	1.29	2.08
2-METHYLHEPTANE	766.78	.02	.06	766.99	.02	.06	767.12	.02	.06	.21	.34
c-1,3-DIMETHYLCYCLOHEXANE	767.70	.02	.05	770.50	.02	.05	772.28	.04	.09	2.80	4.58
4-METHYLHEPTANE	767.75	.03	.07	768.05	.07	.18	768.28	.03	.07	.03	.53
3-METHYLHEPTANE	773.42	.03	.09	773.79	.06	.15	774.07	.03	.07	.37	.65
3-ETHYLHEXANE	774.01	.01	.02	774.57	.01	.01	774.94	.03	.07	.56	.93
1-OCTENE	789.04	.03	.07	788.99	.01	.02	789.05	.01	.02	-.05	.01
2,2,3-TRIMETHYLHEXANE	820.18	.02	.04	821.86	.02	.06	822.87	.02	.05	1.68	2.69
ETHYLCYCLOHEXANE	821.60	.04	.10	824.96	.02	.04	827.15	.04	.11	3.35	5.55
ETHYLBENZENE	841.26	.02	.05	844.05	.00	.01	845.90	.03	.07	2.79	4.64
m-XYLENE	850.24	.04	.10	852.98	.03	.06	854.72	.02	.05	2.74	4.48
p-XYLENE	851.35	.03	.07	854.04	.04	.11	855.80	.03	.08	2.69	4.45
2,3-DIMETHYLHEPTANE	856.05	.02	.06	856.89	.01	.03	857.42	.01	.03	.84	1.37
c,t,c-1,2,3-TRIMETHYLCYCLOHEXANE	863.57	.01	.04	867.65	.02	.05	870.20	.01	.04	4.08	6.63
4-METHYLOCTANE	865.16	.03	.06	865.34	.02	.05	865.43	.02	.05	.18	.27
2-METHYLOCTANE	866.36	.04	.09	866.49	.01	.03	866.60	.03	.08	.13	.24
3-ETHYLHEPTANE	870.74	.03	.06	871.27	.04	.09	871.59	.01	.02	.53	.85
o-XYLENE	870.77	.04	.09	874.14	.02	.05	876.31	.02	.05	3.37	5.54
3-METHYLOCTANE	872.35	.02	.05	872.61	.02	.06	872.89	.01	.01	.26	.54
2,4,6-TRIMETHYLHEPTANE	876.19	.02	.05	876.71	.08	.19	877.12	.03	.07	.52	.93
1-NONENE	888.92	.02	.05	888.92	.02	.06	888.98	.04	.10	.00	.06
PROPYLCYCLOHEXANE	920.09	.02	.05	923.67	.02	.06	925.93	.02	.05	3.58	5.84
PROPYLBENZENE	934.43	.04	.09	937.74	.01	.03	939.69	.04	.09	3.32	5.26
1-ETHYL-3-METHYLBENZENE	943.22	.04	.10	946.06	.03	.07	947.75	.02	.04	2.84	4.53
2,3-DIMETYLOCTANE	954.65	.03	.07	955.54	.01	.03	955.88	.03	.08	.89	1.23
5-METHYLNONANE	961.48	.01	.03	961.76	.04	.10	961.62	.02	.05	.28	.14
4-METHYLNONANE	963.12	.08	.21	963.33	.03	.08	963.34	.04	.10	.21	.22
2-METHYLNONANE	965.96	.02	.04	966.07	.02	.05	966.05	.01	.02	.11	.09
3-ETHYLOCTANE	968.42	.03	.08	968.93	.01	.03	969.13	.06	.14	.51	.71
3-METHYLNONANE	971.80	.03	.09	972.15	.05	.13	972.23	.02	.04	.35	.43
tert-BUTYLBENZENE	972.82	.03	.08	976.53	.06	.16	978.96	.06	.14	3.71	6.14
1,2,4-TRIMETHYLBENZENE	972.82	.03	.08	976.75	.13	.32	978.96	.06	.14	3.93	6.14
1-DECENE	988.74	.08	.21	988.81	.01	.03	988.83	.05	.13	.06	.09
ISOBUTYLBENZENE	988.86	.06	.14	992.41	.04	.10	994.66	.03	.08	3.55	5.80
2,2,4,6,6-PENTAMETHYLHEPTANE	990.04	.01	.03	992.84	.03	.07	994.39	.03	.07	2.80	4.35
1,2,3-TRIMETHYLBENZENE	997.82	.04	.10	1002.62	.03	.07	1005.67	.02	.04	4.80	7.85
1-METHYL-3-ISOPROPYLBENZENE	1003.40	.05	.12	1006.35	.06	.15	1008.12	.01	.03	2.95	4.73
INDAN	1007.28	.02	.04	1013.03	.03	.07	1016.71	.03	.06	5.75	9.43
BUTYLCYCLOHEXANE	1023.13	.08	.21	1026.83	.03	.08	1029.30	.05	.12	3.70	6.17
1,4-DIETHYLBENZENE	1036.33	.03	.06	1039.17	.15	.36	1042.04	.01	.01	2.84	5.71
1-METHYL-4-PROPYLBENZENE	1036.49	.03	.08	1039.82	.02	.06	1042.19	.05	.11	3.33	5.70

TABLE 2 (con't)

BUTYLBENZENE	1037.42	.08	.19	1040.68	.03	.07	1043.02	.07	.16	3.26	5.60
t-DECALIN	1037.52	.09	.22	1044.69	.02	.04	1049.50	.04	.09	7.17	11.98
2,2,7,7-TETRAMETHYLOCTANE	1038.54	.04	.09	1039.44	.10	.25	1039.50	.02	.05	.90	.96
1,3-DIMETHYL-5-ETHYLBENZENE	1040.64	.03	.06	1043.33	.02	.06	1045.32	.05	.13	2.69	4.68
NEOPENTYLBENZENE	1040.69	.02	.04	1049.08	.04	.10	1052.19	.03	.08	4.39	7.50
5-METHYLDECANE	1059.03	.01	.02	1058.91	.05	.11	1059.06	.02	.04	-.12	.03
4-METHYLDECANE	1062.01	.02	.05	1061.91	.07	.17	1062.10	.03	.06	-.10	.09
2-METHYLDECANE	1065.78	.04	.10	1065.56	.03	.07	1065.83	.01	.03	-.23	.05
3-ETHYLNONANE	1067.34	.08	.20	1067.56	.01	.03	1068.00	.04	.09	.22	.66
3-METHYLDECANE	1071.41	.07	.17	1071.58	.10	.24	1071.88	.04	.09	.17	.47
tert-PENTYLBENZENE	1072.17	.04	.09	1077.18	.04	.09	1080.48	.01	.03	5.01	8.31
p,tert-BUTYLTOLUENE	1073.37	.03	.08	1077.11	.01	.02	1079.53	.02	.04	3.74	6.16
c-DECALIN	1078.85	.05	.11	1086.83	.04	.10	1092.00	.06	.15	7.98	13.15
1-UNDECENE	1088.79	.06	.15	1088.78	.03	.07	1088.91	.01	.03	-.01	.12
5-METHYLINDAN	1112.54	.03	.07	1118.91	.05	.13	1123.00	.02	.04	6.37	10.46
PENTYLCYCLOHEXANE	1126.52	.03	.07	1130.60	.01	.01	1133.26	.03	.08	4.08	6.74
TETRALIN	1130.46	.05	.13	1138.09	.02	.05	1142.95	.03	.06	7.63	12.49
PENTYLBENZENE	1138.36	.10	.25	1142.28	.05	.13	1144.71	.05	.11	3.93	6.35
NAPHTHALENE	1146.97	.18	.45	1155.82	.05	.11	1161.44	.03	.08	8.85	14.47
5-METHYLUNDECANE	1157.14	.04	.10	1157.29	.07	.16	1157.24	.04	.10	.15	.10
4-METHYLUNDECANE	1160.82	.05	.11	1161.04	.04	.04	1161.03	.05	.13	.22	.21
2-METHYLUNDECANE	1165.25	.07	.17	1165.41	.05	.12	1165.39	.04	.10	.16	.14
1-DODECENE	1188.76	.10	.24	1188.93	.05	.12	1189.04	.01	.02	.17	.28
1-METHYLTETRALIN	1194.51	.08	.20	1202.17	.03	.07	1207.37	.02	.05	7.66	12.86
5-ETHYLINDAN	1206.07	.02	.05	1212.73	.08	.19	1217.04	.01	.03	6.66	10.97
HEXYLCYCLOHEXANE	1231.08	.01	.01	1235.37	.04	.09	1238.08	.05	.12	4.29	7.00
HEXYLBENZENE	1241.23	.17	.42	1245.30	.04	.09	1248.08	.05	.12	4.07	6.85
5-METHYLDODECANE	1255.93	.04	.09	1255.93	.04	.09	1255.85	.02	.05	.00	-.05
4-METHYLDODECANE	1260.48	.03	.07	1260.29	.06	.15	1260.60	.05	.12	-.19	.12
3-METHYLDODECANE	1271.05	.06	.16	1271.47	.06	.14	1271.70	.03	.07	.42	.65
1-METHYLNAPHTHALENE	1272.66	.07	.17	1283.05	.06	.14	1289.57	.12	.31	10.39	16.91
1-TRIDECENE	1288.97	.04	.10	1289.08	.08	.19	1289.22	.07	.16	.10	.25
1-ETHYLTETRALIN	1293.93	.09	.21	1302.33	.07	.16	1308.09	.08	.20	8.40	14.16
5-PROPYLINDAN	1298.54	.07	.18	1305.58	.05	.13	1310.08	.08	.21	7.04	11.54
2,2,4,4,6,8,8-HEPTAMETHYLNONANE	1323.66	.16	.39	1329.26	.03	.08	1332.64	.08	.19	5.60	8.98
HEPTYLCYCLOHEXANE	1335.38	.07	.17	1339.99	.07	.17	1342.75	.09	.21	4.61	7.37
HEPTYLBENZENE	1344.62	.08	.20	1349.17	.07	.18	1351.94	.06	.14	4.55	7.32
4-METHYLTRIDECANE	1359.82	.20	.50	1359.92	.12	.29	1359.99	.07	.18	.10	.17
1-ETHYLNAPHTHALENE	1359.14	.17	.42	1369.60	.04	.10	1376.32	.08	.20	10.46	17.18
2-METHYLTRIDECANE	1364.94	.15	.37	1365.01	.10	.25	1365.08	.12	.30	.19	.14
3-METHYLTRIDECANE	1371.23	.08	.20	1371.66	.15	.37	1371.68	.03	.08	.43	.45
1-TETRADECENE	1389.08	.04	.09	1389.35	.01	.03	1389.46	.03	.08	.27	.38
1-PROPYLTETRALIN	1389.24	.06	.16	1397.65	.14	.35	1403.17	.05	.12	8.41	13.93
1,4-DIMETHYLNAPHTHALENE	1399.47	.22	.55	1411.24	.05	.12	1419.17	.05	.11	11.77	19.70
5-BUTYLINDAN	1403.33	.11	.26	1410.65	.11	.27	1415.33	.10	.24	7.32	12.00
OCTYLCYCLOHEXANE	1439.90	.04	.10	1444.49	.06	.15	1447.56	.07	.17	4.60	7.66
OCTYLBENZENE	1448.08	.04	.11	1452.71	.05	.11	1455.83	.01	.02	4.63	7.75
5-METHYLTETRADECANE	1454.18	.01	.03	1454.31	.05	.13	1454.27	.01	.02	.13	.09
4-METHYLTETRADECANE	1459.27	.01	.01	1459.71	.02	.06	1459.66	.03	.08	.44	.39
2-METHYLTETRADECANE	1464.89	.04	.10	1464.87	.06	.14	1464.95	.04	.09	-.02	.06
3-METHYLTETRADECANE	1471.07	.03	.06	1471.79	.14	.36	1471.39	.09	.22	.72	.32
1-BUTYLTETRALIN	1489.19	.08	.20	1497.72	.10	.25	1503.26	.02	.04	8.53	14.07
NONYLCYCLOHEXANE	1544.32	.06	.16	1549.04	.02	.04	1552.36	.02	.05	4.72	8.04
6-METHYLPENTYLDECANE	1550.23	.03	.06	1550.20	.05	.11	1550.11	.01	.03	-.03	-.12
NONYLBENZENE	1552.20	.13	.32	1556.98	.03	.08	1560.39	.04	.10	4.79	8.19
2-METHYLPENTADECANE	1564.80	.12	.29	1564.89	.08	.19	1564.84	.09	.23	.09	.04
3-METHYLPENTADECANE	1571.46	.02	.05	1571.82	.12	.30	1572.06	.02	.06	.36	.60
DECYLCYCLOHEXANE	1648.54	.03	.07	1653.53	.03	.08	1656.86	.14	.36	4.99	8.32
DECYLBENZENE	1655.82	.15	.37	1661.14	.03	.08	1664.63	.07	.18	5.33	8.81
2-METHYLHEXADECANE	1664.72	.11	.26	1664.77	.11	.27	1664.63	.07	.18	.05	-.09
1,3,5,8-TETRAMETHYLNAPHTHALENE	1668.42	.02	.04	1682.69	.01	.01	1691.83	.13	.33	14.27	23.41
UNDECYLBENZENE	1760.12	.05	.12	1765.33	.03	.07	1769.12	.05	.12	5.21	9.00
AVERAGE 95% C.L.			.13			.11			.10		

NOTE: "SD"
"95% CL" means +/- 95% confidence limits for triplicate runs calculated via:

$$95\%\ CL = \frac{SD(4.303)}{1.732}$$

TABLE 3
RETENTION INDICES GENERATED ON PHENYL-METHYL SILICONE (PMS) COLUMN AT THREE DIFFERENT LINEAR PROGRAMMED TEMPERATURE RATES

COMPOUND NAME	I^{pms} pt,s (1 C/min)	SD	95% C.L.	I^{pms} pt,s (2 C/min)	SD	95% C.L.	I^{pms} pt,s (3 C/min)	SD	95% C.L.	δI^{pms} pt(1-2),s	δI^{pms} pt(1-3),s
2,3-DIMETHYLBUTANE	556.20	.01	.02	558.70	.02	.05	560.20	.01	.02	2.50	4.00
2,2,3-TRIMETHYLBUTANE	628.44	.05	.11	630.41	.00	.01	631.53	.01	.02	1.97	3.09
CYCLOHEXANE	653.15	.07	.17	656.24	.01	.02	658.10	.02	.05	3.09	4.95
BENZENE	655.57	.01	.03	658.13	.02	.05	659.63	.01	.02	2.56	4.06
2,3-DIMETHYLPENTANE	665.13	.05	.12	666.68	.01	.02	667.50	.01	.03	1.55	2.37
3-ETHYLPENTANE	684.11	.03	.07	684.98	.03	.09	685.47	.00	.01	.87	1.36
1-HEPTENE	691.74	.02	.06	691.87	.01	.02	691.94	.02	.04	.13	.20
2,2,3,3-TETRAMETHYLBUTANE	712.25	.03	.06	714.80	.01	.03	716.46	.02	.04	2.55	4.22
METHYLCYCLOHEXANE	715.22	.03	.07	718.06	.01	.02	719.89	.03	.08	2.84	4.67
1-c-2-DIMETHYLCYCLOPENTANE	715.40	.03	.07	717.85	.01	.03	719.43	.01	.02	2.45	4.03
2,2,3-TRIMETHYLPENTANE	728.57	.03	.07	730.36	.02	.04	731.52	.02	.06	1.79	2.95
2,3-DIMETHYLHEXANE	758.63	.03	.06	759.55	.02	.06	760.10	.01	.02	.92	1.47
METHYLBENZENE	761.89	.01	.01	764.46	.01	.01	766.26	.02	.05	2.57	4.37
3-ETHYL-3-METHYLPENTANE	764.38	.02	.04	766.76	.01	.02	768.22	.00	.00	2.38	3.84
2-METHYLHEPTANE	765.99	.03	.08	766.21	.01	.02	766.26	.02	.05	.22	.27
3,4-DIMETHYLHEXANE	766.33	.03	.07	767.70	.02	.04	768.60	.08	.21	1.37	2.27
4-METHYLHEPTANE	767.16	.01	.03	767.53	.07	.17	767.77	.03	.07	.37	.61
c-1,3-DIMETHYLCYCLOHEXANE	771.53	.01	.03	774.44	.03	.07	776.29	.01	.02	2.91	4.76
3-METHYLHEPTANE	773.02	.03	.06	773.47	.06	.15	773.76	.03	.06	.45	.74
3-ETHYLHEXANE	773.78	.00	.01	774.37	.02	.04	774.75	.01	.02	.59	.97
1-OCTENE	791.72	.03	.08	791.76	.02	.05	791.77	.01	.03	.04	.05
2,2,3-TRIMETHYLHEXANE	820.26	.04	.11	821.85	.01	.04	822.87	.03	.06	1.59	2.61
ETHYLCYCLOHEXANE	827.11	.05	.12	830.63	.01	.04	832.99	.00	.00	3.52	5.80
2,3-DIMETHYLHEPTANE	855.86	.03	.08	856.70	.01	.03	857.24	.01	.03	.84	1.38
ETHYLBENZENE	857.33	.02	.05	860.40	.04	.10	862.45	.04	.09	3.07	5.12
4-METHYLOCTANE	864.58	.03	.07	864.75	.02	.05	864.91	.04	.11	.17	.33
m-XYLENE	865.16	.02	.04	868.16	.04	.09	870.12	.01	.03	3.00	4.96
2-METHYLOCTANE	865.63	.02	.04	865.75	.01	.03	865.92	.04	.10	.12	.29
p-XYLENE	865.82	.04	.10	868.78	.03	.06	870.79	.02	.05	2.96	4.97
c,t,c-1,2,3-TRIMETHYLCYCLOHEXANE	867.92	.02	.04	872.06	.03	.06	874.78	.04	.09	4.14	6.86
3-ETHYLHEPTANE	870.44	.01	.02	870.98	.02	.04	871.37	.02	.05	.54	.93
3-METHYLOCTANE	871.93	.05	.12	872.24	.03	.09	872.56	.05	.13	.31	.63
2,4,6-TRIMETHYLHEPTANE	874.05	.02	.04	874.49	.04	.10	874.86	.04	.10	.44	.81
o-XYLENE	887.70	.02	.05	891.29	.02	.06	893.63	.05	.03	3.59	5.93
1-NONENE	891.78	.04	.10	891.75	.02	.05	891.84	.02	.04	-.03	.06
PROPYLCYCLOHEXANE	925.46	.02	.04	929.15	.03	.06	931.59	.02	.04	3.69	6.13
PROPYLBENZENE	950.62	.06	.16	954.04	.01	.03	956.30	.01	.03	3.42	5.68
2,3-DIMETHYLOCTANE	954.40	.02	.06	955.21	.02	.05	955.61	.01	.03	.81	1.21
1-ETHYL-3-METHYLBENZENE	958.89	.04	.10	962.63	.01	.03	964.24	.02	.06	3.74	5.35
5-METHYLNONANE	960.91	.06	.15	961.01	.03	.07	960.97	.03	.08	.10	.06
4-METHYLNONANE	962.48	.01	.04	962.63	.01	.03	962.67	.05	.14	.15	.19
2-METHYLNONANE	965.23	.06	.15	965.28	.01	.03	965.28	.02	.05	.05	.05
3-ETHYLOCTANE	968.10	.03	.07	968.53	.05	.14	968.75	.03	.07	.43	.65
3-METHYLNONANE	971.40	.04	.11	971.74	.01	.02	971.85	.03	.08	.34	.45
2,2,4,6,6-PENTAMETHYLHEPTANE	987.85	.01	.02	990.16	.04	.10	992.02	.01	.03	2.31	4.17
tert-BUTYLBENZENE	989.31	.06	.15	993.20	.18	.44	995.68	.24	.61	3.89	6.33
1,2,4-TRIMETHYLBENZENE	989.41	.02	.06	993.40	.01	.03	996.08	.12	.31	3.99	6.67
1-DECENE	991.63	.06	.14	991.76	.02	.06	991.73	.03	.06	.13	.10
ISOBUTYLBENZENE	1004.03	.03	.07	1007.86	.12	.30	1010.66	.01	.01	3.83	6.63
1,2,3-TRIMETHYLBENZENE	1017.96	.02	.04	1023.11	.03	.08	1026.55	.03	.06	5.15	8.59
1-METHYL-3-ISOPROPYLBENZENE	1019.92	.04	.09	1023.11	.03	.08	1025.18	.01	.03	2.07	5.26
BUTYLCYCLOHEXANE	1028.77	.04	.09	1032.57	.01	.02	1035.27	.05	.13	3.80	6.50
INDAN	1030.81	.01	.02	1036.70	.11	.26	1041.08	.01	.01	5.89	10.27
2,2,7,7-TETRAMETHYLOCTANE	1035.93	.03	.06	1036.70	.11	.26	1036.75	.01	.01	.77	.82
t-DECALIN	1048.56	.06	.14	1056.17	.05	.11	1061.35	.04	.09	7.61	12.79

TABLE 3 (con't)

1-METHYL-4-PROPYLBENZENE	1052.90	.04	.09	1056.46	.03	.08	1059.10	.05	.13	3.56	6.20
1,4-DIETHYLBENZENE	1053.74	.03	.07	1057.31	.01	.02	1060.01	.01	.02	3.57	6.27
BUTYLBENZENE	1054.18	.01	.02	1057.89	.02	.04	1060.55	.04	.10	3.71	6.37
1,3-DIMETHYL-5-ETHYLBENZENE	1056.96	.04	.09	1060.10	.01	.01	1062.45	.02	.05	3.14	5.49
5-METHYLDECANE	1058.23	.02	.04	1058.15	.04	.09	1058.28	.04	.10	-.08	-.05
NEOPENTYLBENZENE	1060.23	.04	.09	1064.88	.03	.08	1068.02	.10	.24	4.65	7.79
4-METHYLDECANE	1061.22	.02	.05	1061.18	.02	.05	1061.42	.07	.18	-.04	.20
2-METHYLDECANE	1064.98	.01	.02	1064.93	.03	.08	1065.01	.04	.09	-.05	.03
3-ETHYLNONANE	1067.02	.05	.13	1067.23	.09	.23	1067.71	.03	.08	.21	.69
3-METHYLDECANE	1070.96	.01	.03	1071.31	.05	.12	1071.49	.02	.05	.35	.53
p-tert-BUTYLTOLUENE	1089.21	.08	.19	1093.17	.03	.07	1095.91	.03	.07	3.96	6.70
tert-PENTYLBENZENE	1089.28	.02	.04	1094.66	.04	.10	1098.17	.04	.11	5.38	8.89
1-UNDECENE	1091.72	.07	.17	1091.85	.07	.18	1092.00	.02	.04	.13	.28
o-DECALIN	1092.50	.05	.12	1101.09	.02	.05	1107.06	.10	.25	8.59	14.56
PENTYLCYCLOHEXANE	1132.42	.03	.07	1136.64	.06	.14	1139.51	.10	.24	4.22	7.09
5-METHYLINDAN	1135.50	.04	.09	1142.55	.05	.12	1147.03	.07	.17	7.05	11.53
PENTYLBENZENE	1155.95	.03	.08	1160.10	.02	.05	1162.94	.04	.09	4.15	6.99
5-METHYLUNDECANE	1156.30	.05	.11	1156.62	.04	.11	1156.52	.01	.02	.32	.22
TETRALIN	1157.79	.07	.17	1166.27	.04	.09	1171.51	.06	.15	8.48	13.72
4-METHYLUNDECANE	1160.03	.02	.05	1160.34	.05	.11	1160.35	.04	.10	.31	.32
2-METHYLUNDECANE	1164.40	.05	.12	1164.52	.05	.12	1164.69	.04	.10	.12	.29
NAPHTHALENE	1178.80	.12	.29	1188.47	.06	.15	1194.63	.10	.24	9.67	15.83
1-DODECENE	1191.75	.05	.11	1191.82	.04	.10	1192.15	.02	.05	.07	.40
1-METHYLTETRALIN	1222.02	.08	.20	1230.71	.06	.14	1236.24	.06	.15	8.69	14.22
5-ETHYLINDAN	1231.25	.02	.04	1238.62	.05	.11	1243.34	.03	.06	7.37	12.09
HEXYLCYCLOHEXANE	1237.21	.08	.20	1241.62	.04	.09	1244.73	.13	.33	4.41	7.52
5-METHYLDODECANE	1255.27	.02	.05	1255.07	.08	.21	1255.16	.07	.17	-.20	-.11
HEXYLBENZENE	1259.18	.05	.11	1263.43	.04	.09	1266.48	.08	.20	4.25	7.30
4-METHYLDODECANE	1259.69	.07	.18	1259.75	.09	.21	1259.86	.09	.23	.06	.17
3-METHYLDODECANE	1270.83	.05	.13	1271.24	.13	.33	1271.15	.02	.04	.41	.32
1-TRIDECENE	1292.10	.03	.08	1292.16	.02	.06	1292.37	.11	.27	.06	.27
1-METHYLNAPHTHALENE	1307.25	.05	.11	1319.04	.08	.20	1326.55	.06	.16	11.79	19.30
2,2,4,4,6,8,8-HEPTAMETHYLNONANE	1321.86	.13	.32	1327.20	.07	.18	1330.80	.15	.37	5.34	8.94
1-ETHYLTETRALIN	1321.92	.08	.19	1331.29	.15	.37	1337.31	.07	.17	9.36	15.39
5-PROPYLINDAN	1324.30	.14	.35	1331.98	.06	.16	1336.96	.05	.11	7.68	12.66
HEPTYLCYCLOHEXANE	1341.77	.08	.19	1346.47	.01	.01	1349.58	.07	.18	4.70	7.81
4-METHYLTRIDECANE	1359.17	.04	.09	1359.12	.03	.07	1359.17	.04	.11	-.05	.00
HEPTYLBENZENE	1362.93	.13	.32	1367.67	.05	.12	1370.87	.06	.15	4.75	7.94
2-METHYLTRIDECANE	1364.21	.09	.22	1364.21	.10	.25	1364.21	.03	.06	.00	.00
3-METHYLTRIDECANE	1370.88	.01	.03	1371.14	.06	.15	1371.32	.13	.32	.26	.44
1-TETRADECENE	1392.25	.13	.32	1392.49	.10	.24	1392.68	.05	.12	.24	.43
1-ETHYLNAPHTHALENE	1394.60	.03	.07	1406.41	.05	.12	1413.99	.03	.07	11.81	19.39
1-PROPYLTETRALIN	1417.18	.13	.31	1426.61	.07	.17	1432.88	.05	.11	9.43	15.70
5-BUTYLINDAN	1430.24	.08	.20	1438.14	.12	.29	1443.20	.19	.48	7.90	12.96
1,4-DIMETHYLNAPHTHALENE	1436.73	.02	.04	1450.12	.09	.22	1458.67	.14	.34	13.39	21.94
OCTYLCYCLOHEXANE	1446.58	.07	.16	1451.58	.05	.12	1454.77	.08	.20	5.00	8.19
5-METHYLTETRADECANE	1453.25	.04	.09	1453.31	.00	.00	1453.28	.10	.24	.06	.03
4-METHYLTETRADECANE	1458.66	.04	.10	1458.78	.07	.17	1458.78	.12	.29	.12	.12
2-METHYLTETRADECANE	1463.92	.07	.17	1464.09	.04	.09	1464.24	.06	.14	.17	.32
OCTYLBENZENE	1466.64	.09	.21	1471.90	.03	.09	1475.03	.10	.24	5.26	8.39
3-METHYLTETRADECANE	1471.08	.03	.07	1471.21	.04	.10	1471.39	.09	.22	.13	.31
1-BUTYLTETRALIN	1517.57	.05	.12	1527.06	.01	.02	1533.35	.09	.21	9.49	15.73
6-METHYLPENTADECANE	1549.33	.15	.38	1549.21	.03	.07	1549.11	.11	.26	-.12	-.22
NONYLCYLOHEXANE	1551.07	.07	.18	1556.36	.11	.27	1559.54	.06	.16	5.29	8.47
2-METHYLPENTADECANE	1563.71	.09	.22	1564.10	.07	.17	1564.13	.07	.18	.39	.42
3-METHYLPENTADECANE	1570.93	.03	.06	1571.48	.02	.04	1571.51	.07	.18	.55	.03
NONYLBENZENE	1570.95	.20	.49	1576.27	.10	.26	1579.75	.21	.52	5.32	8.80
DECYLCYCLOHEXANE	1655.41	.07	.18	1660.95	.09	.22	1664.11	.08	.19	5.54	8.70
2-METHYLHEXADECANE	1663.61	.08	.19	1663.85	.17	.41	1664.11	.08	.19	.24	.50
DECYLBENZENE	1675.02	.05	.12	1680.77	.13	.32	1684.34	.16	.40	5.75	9.32
1,3,5,8-TETRAMETHYLNAPHTHALENE	1708.95	.16	.39	1725.11	.11	.27	1735.38	.07	.18	16.16	26.43
UNDECYLBENZENE	1779.75	.15	.38	1785.43	.07	.17	1789.05	.17	.42	5.68	9.30
AVERAGE 95% C.L.			.12			.11			.13		

NOTE: "SD"
"95% CL" means +/- 95% confidence limits for triplicate runs calculated via:

$$95\%\ CL = \frac{SD(4.303)}{1.732}$$

Recall that the potential energy of interaction between a solute and a stationary phase in gas-liquid chromatography is a sum of electrostatic, inductive, and dispersive energies. Golovnya and Misharina [48] define GC polarity as the "capacity of a sorbent for various intermolecular interactions (of a physical and chemical nature) with the analyzed substance as determined by the partial molar free energy." Each contribution has its own temperature dependence. It would be folly to assume that different molecular interactions would have identical responses to the same variation in temperature. Herein lies the roots of the "delta I-pt" effect. The scope of this paper, however, does not encompass the theoretical explanations why a particular change in programmed temperature rate generates a given "delta I-pt" shift for a certain hydrocarbon structure. For our work, the practicality of the "delta I-pt" effect rests in disengaging solutes originating from different hydrocarbon types and even some isomers within the same hydrocarbon class in apolar sample matrices.

2. USING "delta I-pt"

The "delta I-pt effect can be an extremely powerful tool in helping to confirm the identification of compounds in a complex hydrocarbon mixture such as a jet propulsion fuel. The retention index system, in general, standardizes raw retention times. The "delta I-pt" effect offers an extra dimension to the information contained in retention index data. By merely changing the linear programmed temperature rate of an analysis, compounds that coeluted as a single peak can often times be disengaged. This disengaement can occur with an increase as well as a decrease in the linear temperature rate.

If all hydrocarbon species in a complex hydrocarbon matrix shifted, and by the same relative amount, elucidating the identity of a given unknown compound

would be futile. Fortunately, different hydrocarbon types display varying amounts of retention index shifts with a given change in linear programmed temperature rate. Those species that are structurally similar to the retention index markers. i.e., the normal paraffins in our work, characteristically shift only a negligible amount. Figures 2 through 9 are plots of the calculated "delta I-pt" shift as a function of carbon number for a particular hydrocarbon group-type from chromatographic runs made at 1 and 2 C/min. Note that for each compound there are two data points. One data point corresponds to the shift observed on the apolar column, the other point for the shift on the polar column. Figures 2 and 3 present the 1-olefins and the 2-methyl alkanes as typical examples of hydrocarbon types that remain relatively fixed in retention behavior with changes in programmed temperature rate. The elution of the 3-, 4-, and 5-methyl alkanes is likewise fixed under the same chromatographic conditions (see Tables 2 and 3). Here the "delta I-pt" shifts on the apolar column are indistinguishable from those on the polar column. Figures 4 through 9 introduce compound types exhibiting significant "delta I-pt" shifts. The highly branched paraffins, i.e., the tetra-methyl substituted, show pronounced shifts. Notice the "delta I-pt" shifts on the apolar column are consistently higher than those on the polar column. Not suprisingly, the magnitude of the shifts of the di-methyl and tri-methyl alkanes fall between those of the mono-methyl and the tetra-methyl alkanes (See Tables 2 and 3). Interestingly, in the remaining figures, the "delta I-pt" shift values on the polar column are always higher than those observed on the apolar column. The n-alkyl cyclohexanes and n-alkyl benzenes share almost the same shift values on a carbon number basis.

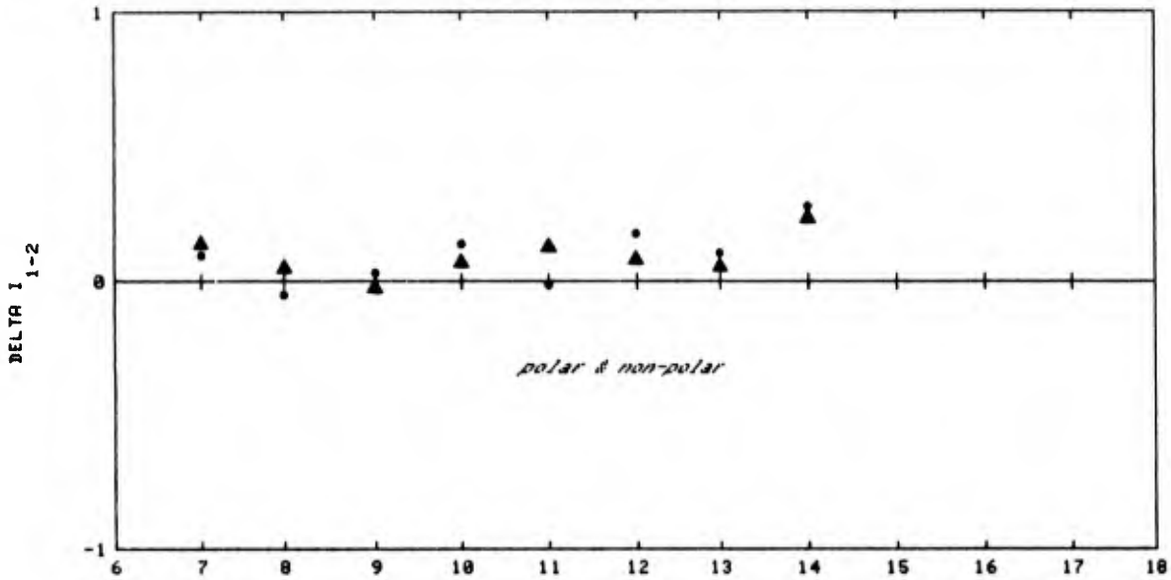

Figure 2. $\delta I^{c}_{pt(1\text{-}2),s}$ Values of the 1-olefins as a Function of Carbon Number (● = apolar; ▲ = polar)

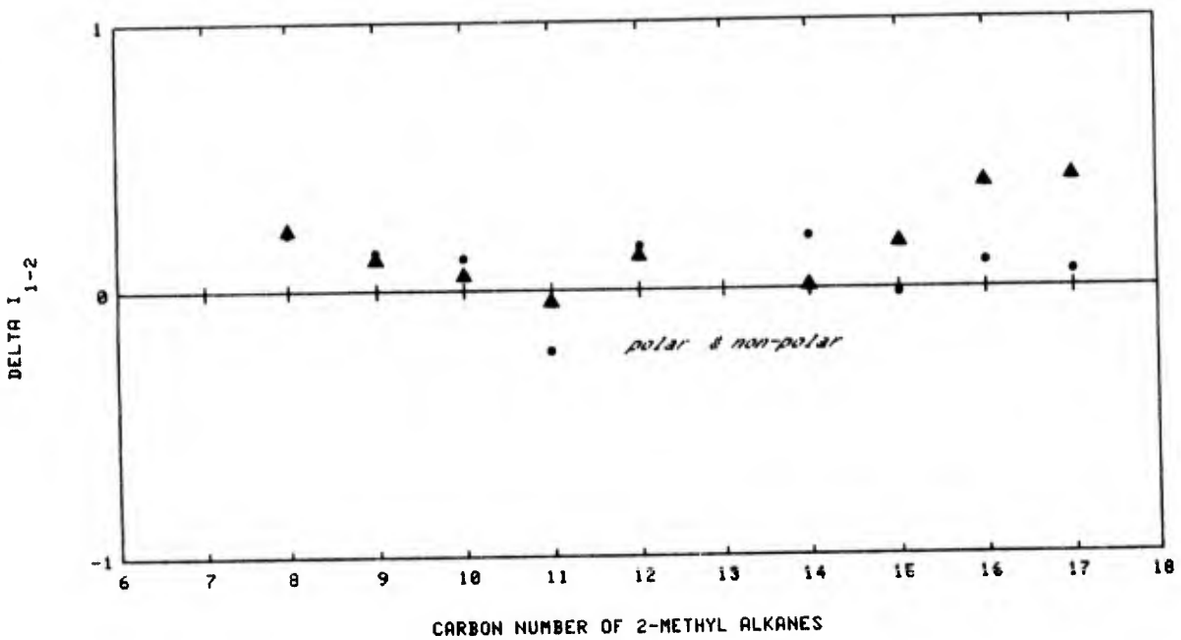

Figure 3. $\delta I^{c}_{pt(1-2),s}$ Values of the 2-methyl alkanes as a Function of Carbon Number (● = apolar; ▲ = polar)

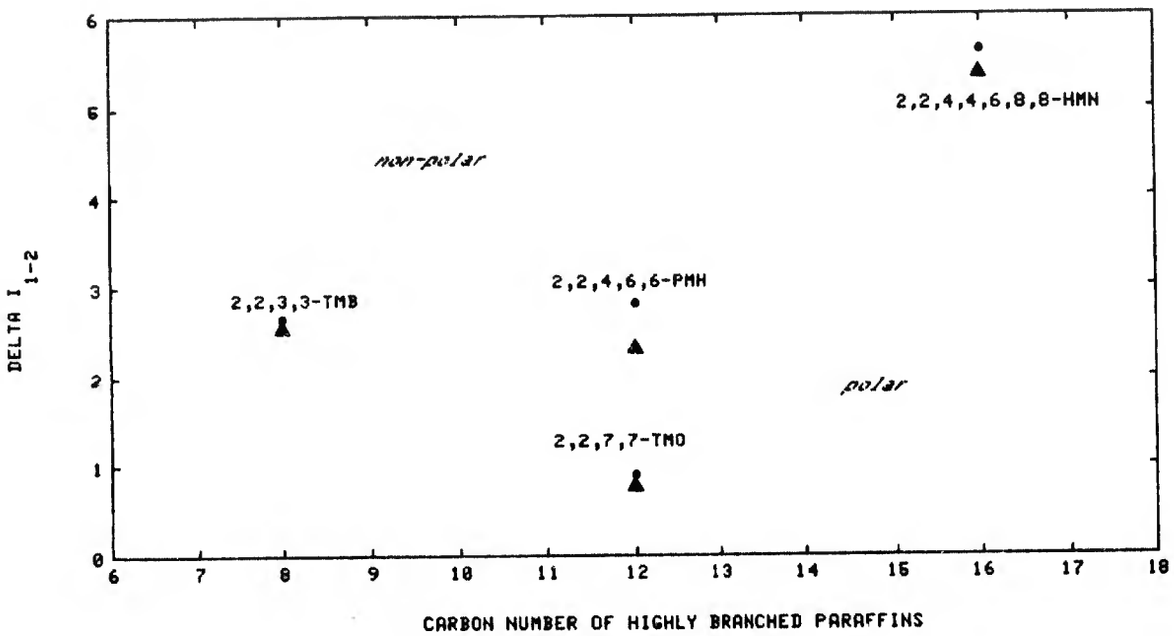

Figure 4. $\delta I^{C}_{pt(1-2),s}$ Values of Some Highly Substituted Paraffins as a Function of Carbon Number (● = apolar; ▲ = polar)

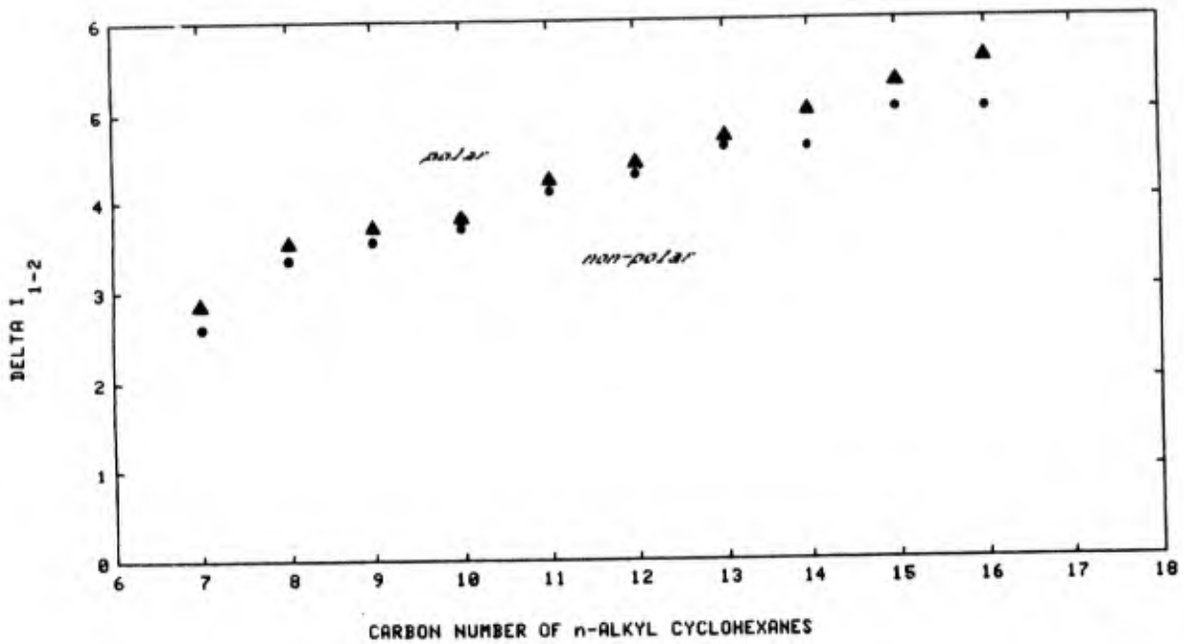

Figure 5. $\delta I^{C}_{pt(1\text{-}2),s}$ Values of the n-alkyl cyclohexanes as a Function of Carbon Number (● = apolar; ▲ = polar)

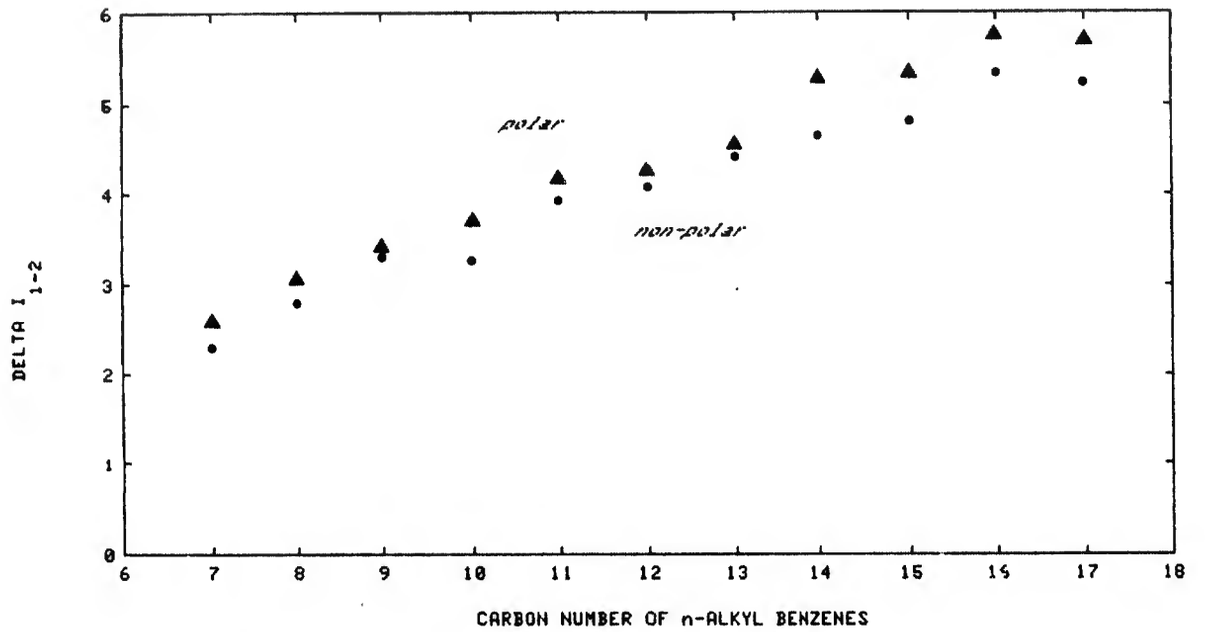

Figure 6. $\delta I^{c}_{pt(1-2),s}$ Values of the n-alkyl benzenes as a Function of Carbon Number (● = apolar; ▲ = polar)

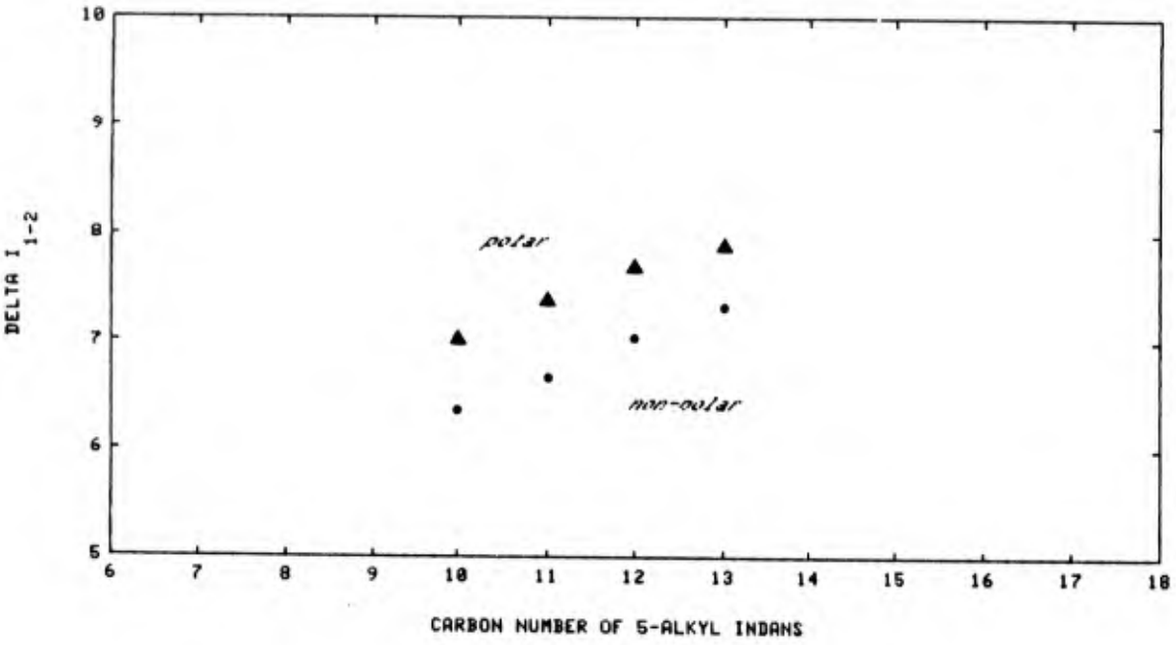

Figure 7. $\delta I^{c}_{pt(1-2),s}$ Values of 5-alkyl indans as a Function of Carbon Number (● = apolar; ▲ = polar)

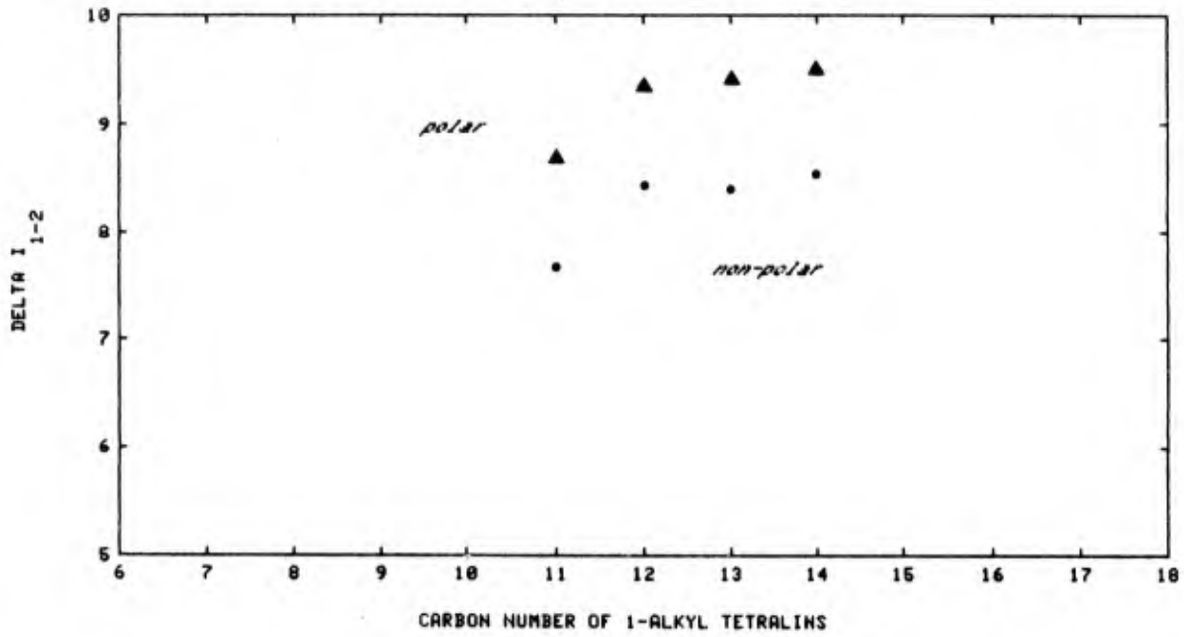

Figure 8. $\delta I^{C}_{pt(1-2),s}$ Values of 1-alkyl tetralins as a Function of Carbon Number (●= apolar; ▲= polar)

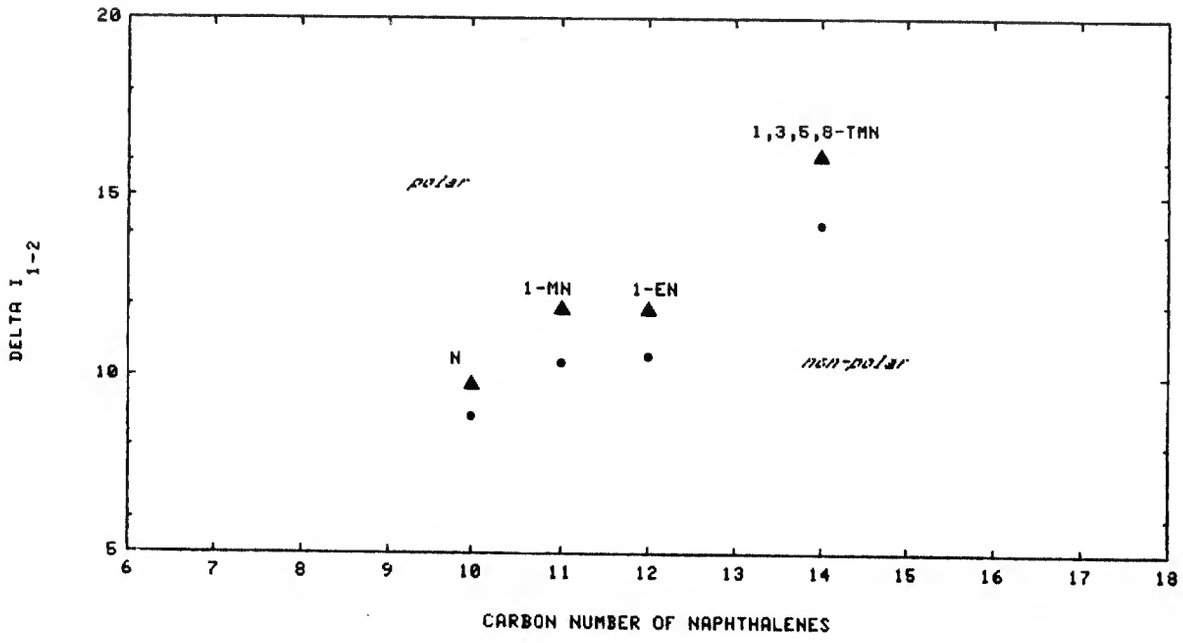

Figure 9. $\delta I^{C}_{pt(1-2),s}$ Values of Some alkyl naphthalenes as a Function of Carbon Number (● = apolar; ▲ = polar)

These shifts are, fortunately, far removed from the shifts of the branched paraffins, for a given programmed rate change. The alkyl indans and alkyl tetralins have "delta I-pt" displacements almost twice those of the n-alkyl cyclohexanes and n-alkyl benzenes. The alkyl naphthalenes have shifts of even greater magnitude.

Note that in all cases except one, the "delta I-pt" shifts are larger on the slightly more polar column than on the non-polar column when any shifts are indeed discernible. Of all the hydrocarbon types studied, only the di-, tri-, and, tetra-methyl alkanes have consistently greater shifts on the non-polar column than on the polar column. Of course, these non-polar species can interact more effectively with the non-polar, rather than with the polar stationary phase. Similarly, the cycloparaffinic and aromatic hydrocarbon types interact more effectively with the slightly polar phase than with the non-polar phase. The greater the degree of interaction of a solute on a particular stationary phase, the more pronounced the resultant shift in relative retention behavior. Table 4 is a compilation of the average range in "delta I-pt" shifts found for each hydrocarbon class on the two fused silica columns for a 1 °C/min to 2 °C/min programming rate change. The values (not shown) are naturally much more pronounced for the 1 °C/min to 3 °C/min rate change (see Tables 2 and 3).

Figures 10 through 12 illustrate both graphically and with retention indices how prominent hydrocarbon species found in actual jet fuels can be more reliably identified and quantified via exploiting the "delta I-pt" effect. For purposes of graphical clarity, the chromatograms shown in these figures are of

TABLE 4
"delta I-pt" EFFECT OF VARIOUS HYDROCARBON TYPES

COMPOUND CLASS	C# RANGE	RANGE OF "delta I-pt" VALUES	
		MS COLUMN 1-2 °C /min	PMS COLUMN 1-2 °C /min
1-OLEFINS	7 - 14	0.1 - 0.3	0.1 - 0.2
2-METHYL ALKANES	8 - 17	0.2 - 0.1	0.2 - 0.4
HIGHLY BRANCHED ALKANES	8 - 16	2.6 - 5.6	2.5 - 5.3
n-ALKYL CYCLOHEXANES	7 - 16	2.6 - 5.0	2.8 - 5.5
n-ALKYL BENZENES	7 - 17	2.3 - 5.2	2.6 - 5.8
5-ALKYL INDANS	10 - 13	6.4 - 7.3	7.1 - 7.9
1-ALKYL TETRALINS	11 - 14	7.7 - 8.5	8.7 - 9.5
NAPHTHALENES	10 - 14	8.9 - 14.3	9.7 - 16.2

ALKANE/AROMATIC HYDROCARBON SEPARATION

COELUTING PAIR	ms I pt, s (1 C/min) LIBRARY	ms I pt, s (1 C/min) SAMPLE	AREA %	ms I pt, s (2 C/min) LIBRARY	ms I pt, s (2 C/min) SAMPLE	AREA %	ms I pt, s (3 C/min) LIBRARY	ms I pt, s (3 C/min) SAMPLE	AREA %
3-ETHYLHEPTANE	870.74			871.27	871.38	0.25	871.59	871.55	0.22
		870.96	0.90						
o-XYLENE	870.77			874.14	874.30	0.68	876.31	876.47	0.67
		AREA % TOTAL	0.90		AREA % TOTAL	0.93		AREA % TOTAL	0.89

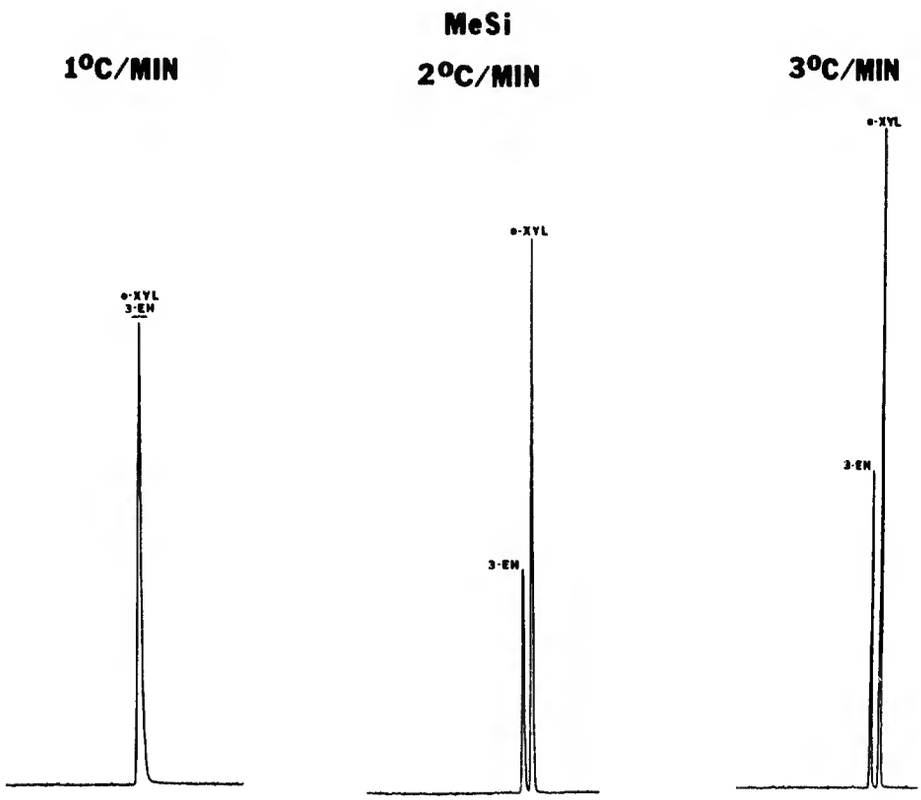

Figure 10. 3-ethylheptane and o-xylene Disengaged at 2°C/min and 3°C/min on the Methyl Silicone Column

ALKANE/ALKANE HYDROCARBON SEPARATION

COELUTING PAIR	ms I pt, s (1 C/min) LIBRARY	ms I pt, s (1 C/min) SAMPLE	AREA %	ms I pt, s (2 C/min) LIBRARY	ms I pt, s (2 C/min) SAMPLE	AREA %	ms I pt, s (3 C/min) LIBRARY	ms I pt, s (3 C/min) SAMPLE	AREA %
c-1,3-DIMETHYL-CYCLOHEXANE	767.70			770.50	770.49	1.14	772.28	772.25	1.10
		767.60	1.79						
4-METHYLHEPTANE	768.21			768.34	768.06	0.74	768.52	768.29	0.82
		AREA % TOTAL	1.79		AREA % TOTAL	1.88		AREA % TOTAL	1.92

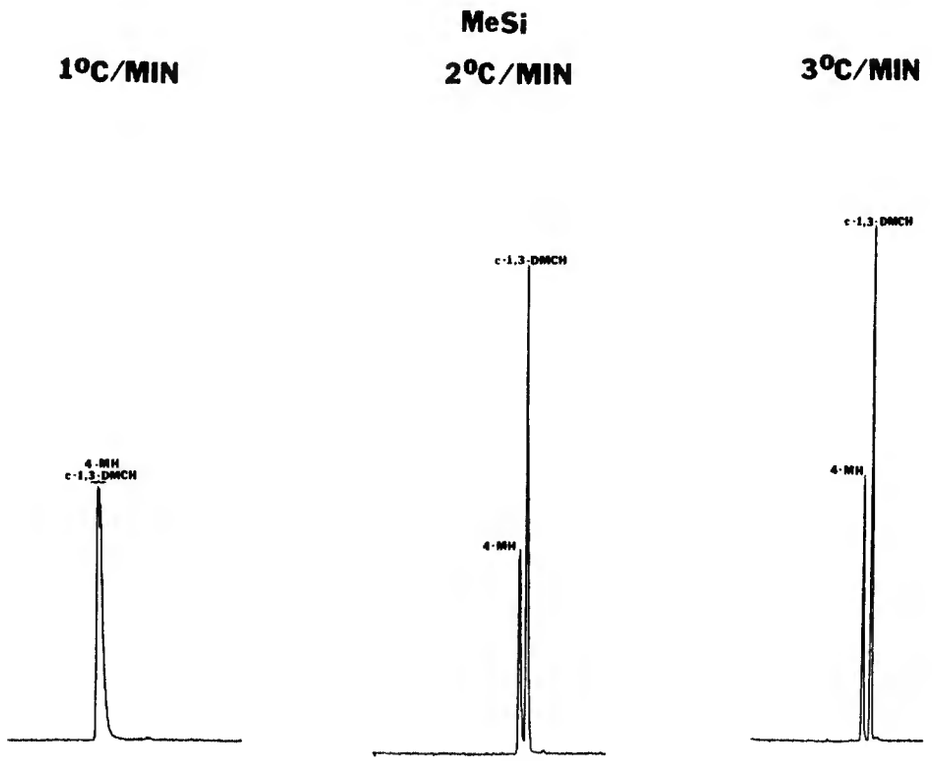

Figure 11. 4-methylheptane and cis-1,3-dimethylcyclohexane Disengaged at 2°C/min and 3°C/min on the Methyl Silicone Column

ALKANE/AROMATIC HYDROCARBON SEPARATION

COELUTING PAIR	pms I pt,s (1 C/min) LIBRARY	pms I pt,s (1 C/min) SAMPLE	AREA %	pms I pt,s (2 C/min) LIBRARY	pms I pt,s (2 C/min) SAMPLE	AREA %	ms I pt,s (3 C/min) LIBRARY	ms I pt,s (3 C/min) SAMPLE	AREA %
1-ETHYL-3-METHYL BENZENE	958.97	958.99	0.26	962.58			964.28	964.33	0.36
					962.59	1.05			
4-METHYLNONANE	962.45	962.61	0.71	962.58			962.70	962.60	0.92
		AREA % TOTAL	0.97		AREA % TOTAL	1.05		AREA % TOTAL	1.28

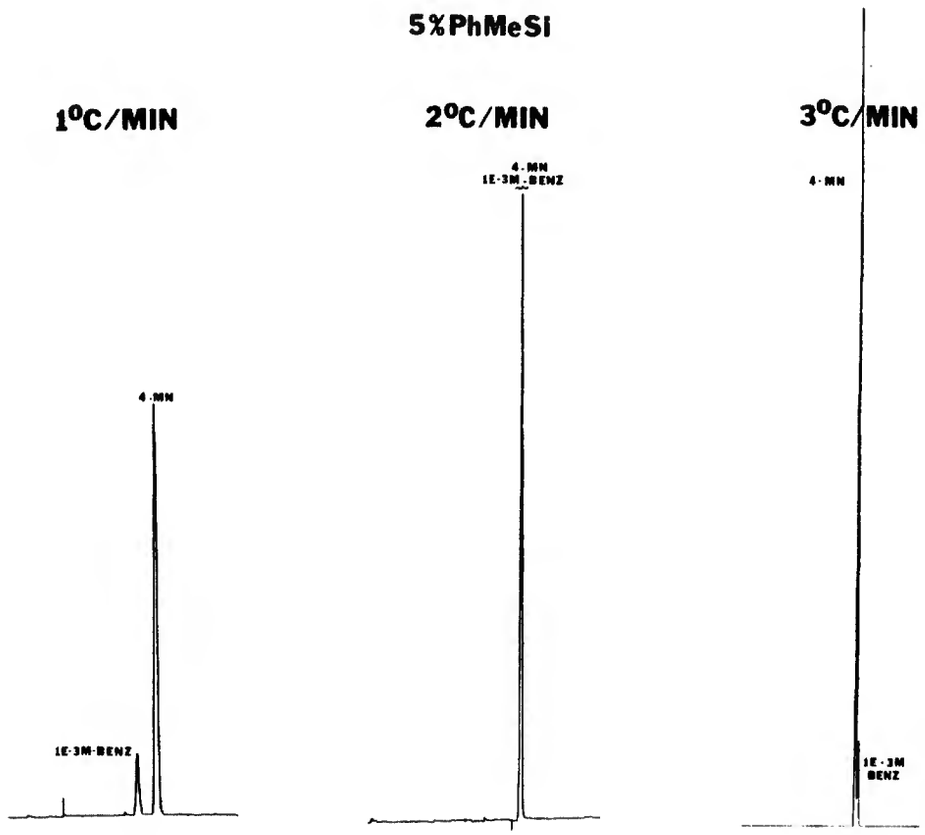

Figure 12. 1-ethyl-3-methylbenzene and 4-methylnonane Disengaged at 1°C/min and 3°C/min with Reversal of Elution Order on the Phenyl-Methyl Silicone Column

synthetic mixtures only. For a given hydrocarbon pair, each figure lists the reference library retention indices, actual fuel sample retention indices, and the corresponding peak area percentages from chromatographic runs at three different linear programmed temperature rates. A single entry in the "SAMPLE" and "AREA %" columns at one of the programmed temperature rates indicates coelution of the two example compounds. The comparison of the area percentages listed with each programmed temperature rate helps to corroborate the successful tracking and disengagement of the hydrocarbon pair. In Figure 10, a single chromatographic peak with a retention index of 870.96 and an area percentage of 0.90 at 1 C/min on the methyl silicone column was actually found to be 3-ethylheptane and o-xylene by simply increasing the programmed temperature rate. Note that the sum of the area percentages of the two hydrocarbons, when disengaged at 2 and 3 C/min, closely approximates the area percentage of their coeluted peak (at 1 C/min). In Figure 11, two saturated hydrocarbons were resolved on the apolar column by again increasing the programming rate from 1 C/min. In Figure 12, what was thought to be a single eluting compound at 2 C/min on the phenyl-methyl silicone column was actually shown to be both 1-ethyl-3-methylbenzene and 4-methylnonane by either raising or lowering the linear programmed temperature rate.

Figures 13 through 17 are chromatograms of some interesting manifestations of the "delta I-pt" effect but were not of compounds actually found in amounts exceeding 0.5 area percent in the particular jet fuels chosen for this study. In Figure 13, 1-propyltetralin and 1-tetradecene coeluted at 1 C/min on the apolar column. As the programmed temperature rate was increased, the

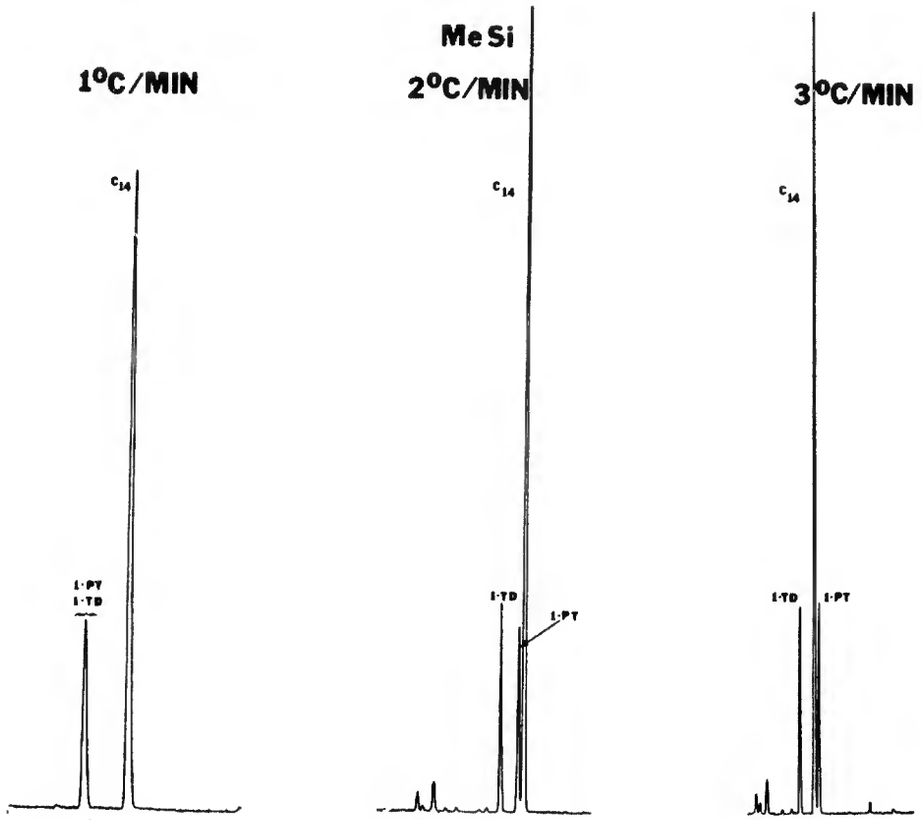

Figure 13. 1-tetradecene and 1-propyltetralin Disengaged at 2 °C/min and 3 °C/min with Reversal of Elution Order between 1-propyltetralin and the Standard n-C14 on the Methyl Silicone Column

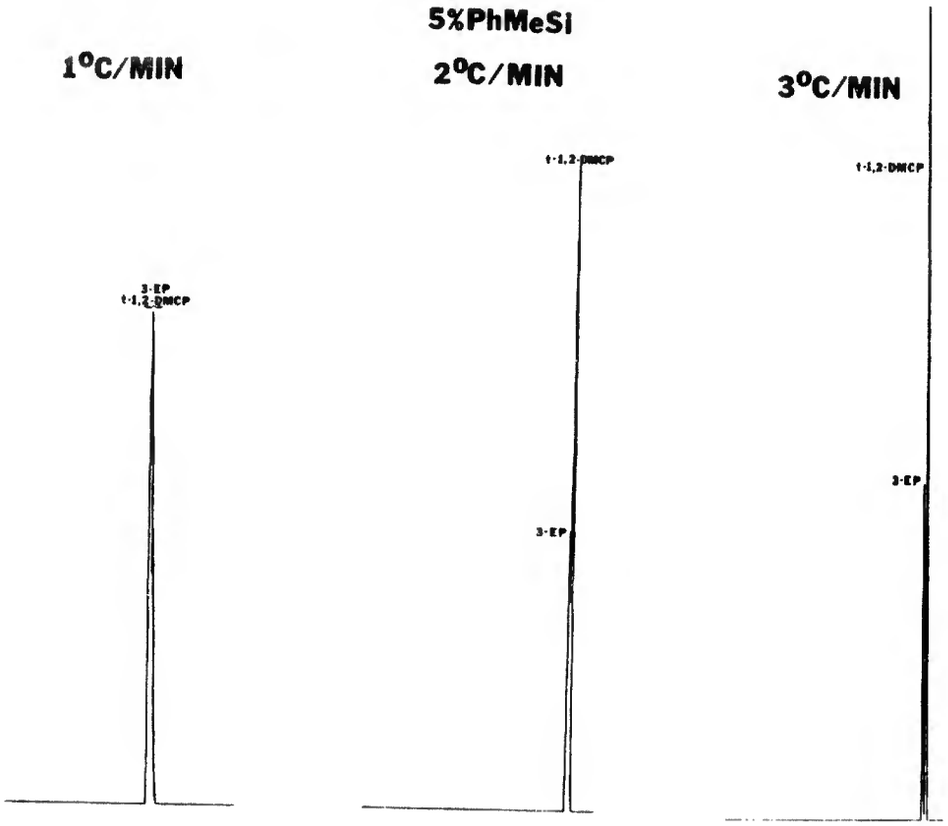

Figure 14. 3-ethylpentane and t-1,2-dimethylcyclopentane Partially Disengaged at 2 °C/min and Fully Disengaged at 3 °C/min on the Phenyl-Methyl Silicone Column

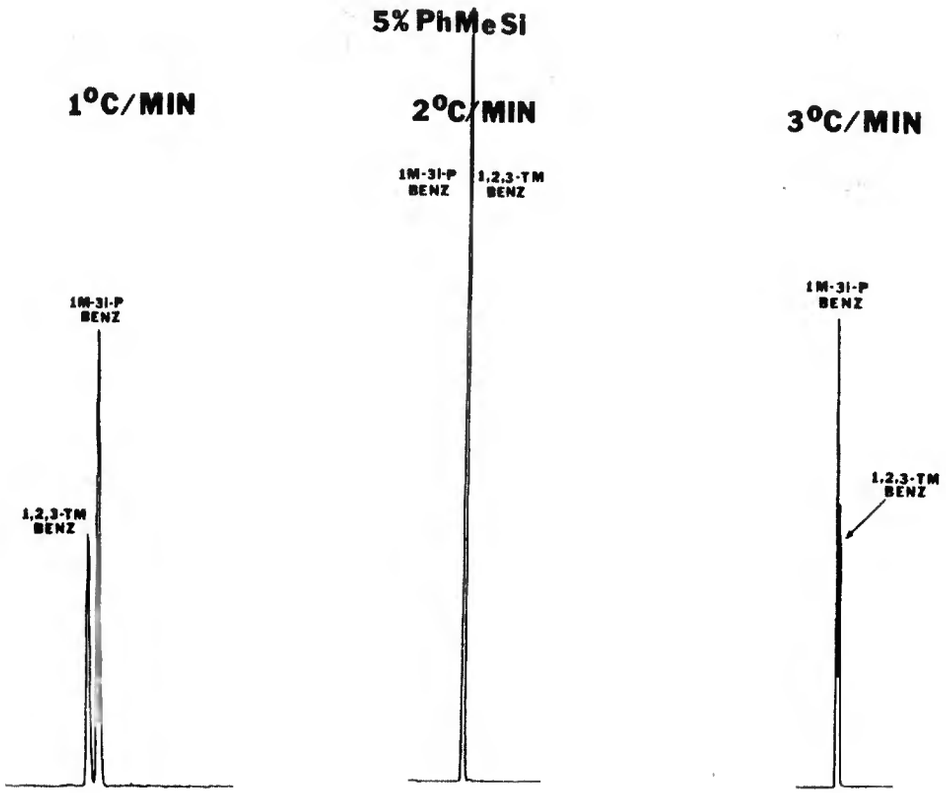

Figure 15. 1,2,3-trimethylbenzene and 1-methyl-3-isopropylbenzene Disengaged at 1 °C/min and 3 °C/min with Reversal of Elution Order on the Phenyl-Methyl Silicone Column

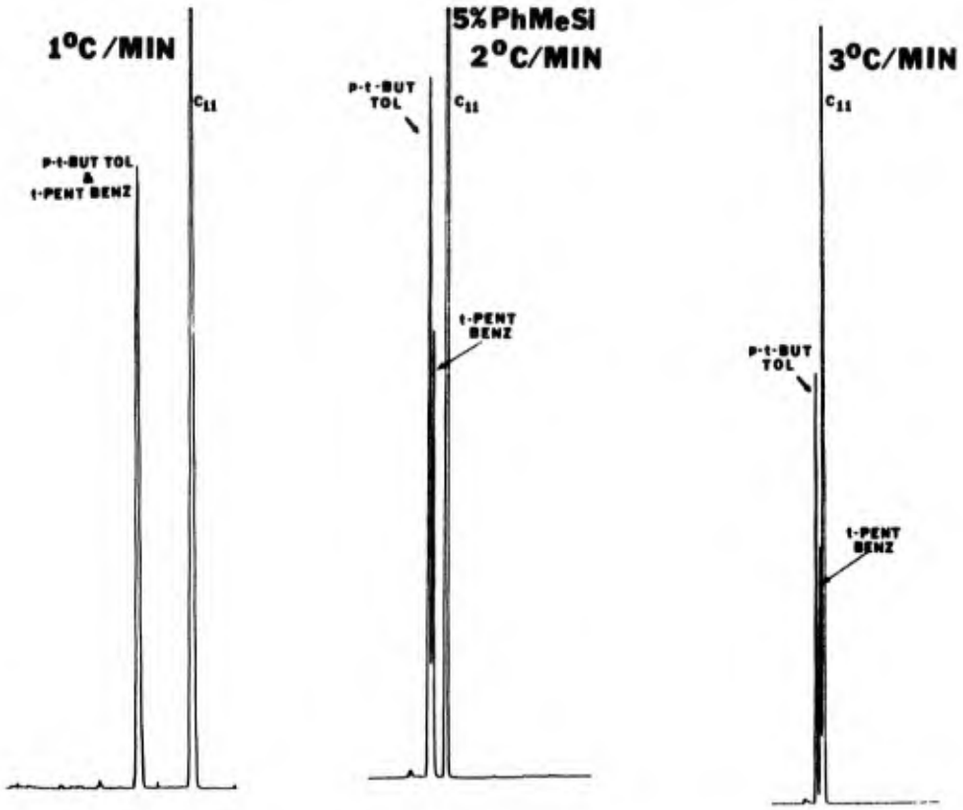

Figure 16. p-tert-butyltoluene and tert-pentylbenzene Disengaged at 2°C/min and 3°C/min on the Phenyl-Methyl Silicone Column

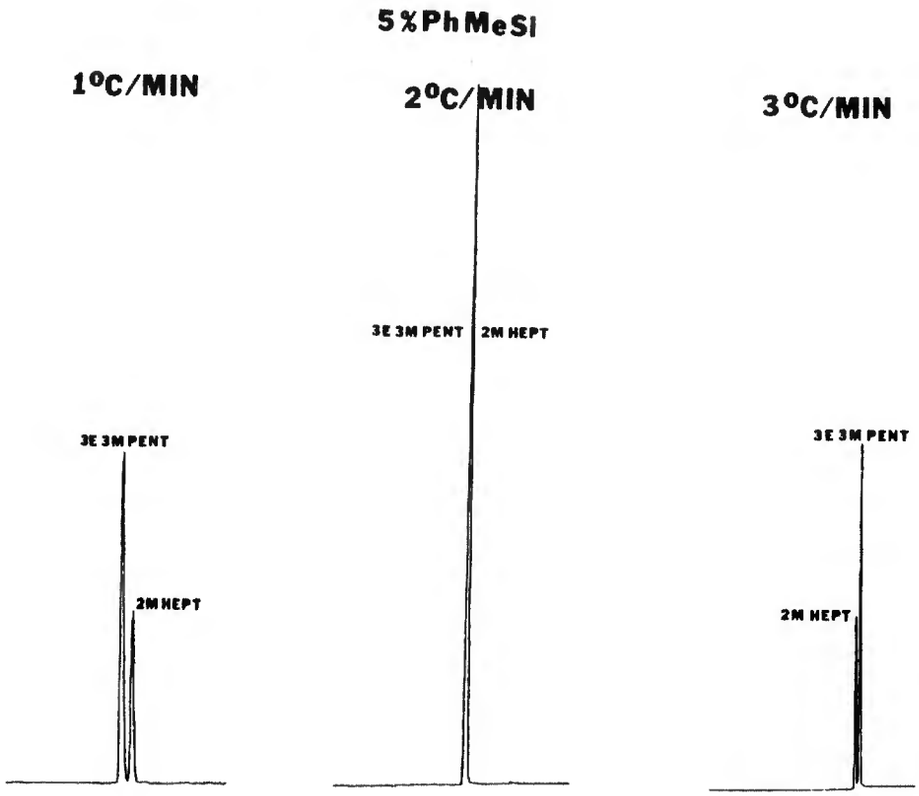

Figure 17. 3-ethyl-3-methylpentane and 2-methylheptane Disengaged at 1 °C/min and 3 °C/min with Reversal of Elution Order on the Phenyl-Methyl Silicone Column

significant "delta I-pt" character of the tetralin enabled it to pass the olefin at 2°C/min and even elute before the tetradecane reference at 3°C/min. In Figure 14, the resolution of two saturated hydrocarbons was improved on the phenyl-methyl column by raising the programming rate from 1°C/min (coelution) to 2°C/min (partial separation) and finally to 3°C/min (complete separation). In Figure 15, the separation of two alkyl benzenes was realized on the phenyl-methyl column. While both 1,2,3-trimethylbenzene and 1-methyl-3-isopropylbenzene exhibit sizeable "delta I-pt" shifts, the slightly larger value of the trimethylbenzene can aid in their disengagement. From coelution at 2°C/min, a reversal in elution order was observed between 1°C/min and 3°C/min programming rates. In Figure 16, a separation of two aromatic hydrocarbon isomers, p-tert-butyltoluene and tert-pentylbenzene, was performed on the phenyl-methyl column by just raising the programmed temperature rate. Finally, in Figure 17, two saturated hydrocarbon isomers, i.e., 3-ethyl-3-methylpentane and 2-methylheptane, were resolved on the phenyl-methyl column. By either raising or lowering the programmed temperature rate, the significantly larger "delta I-pt" shift characteristic of the more substituted paraffin enabled it to "migrate" away from the mono-methyl alkane.

SECTION IV

CONCLUSIONS AND SUGGESTIONS

Invoking the so-called "delta I-pt" effect in high resolution capillary gas chromatography can greatly increase the probability that an unknown peak will be identified and quantified correctly. Simultaneously injecting the sample into two fused silica columns of varied stationary phase composition and chromatographing the sample at two slightly different linear programmed temperature rates can quickly provide up to four unique retention indices for each detected species. For those species that display a "delta I-pt" shift, the greater the change in linear programmed temperature rates, the greater will be the resultant shift values. Likewise, the greater the polarity difference between any two fused silica capillary columns, the larger will be the difference in shift values at a particular programmed temperature rate for the more polar of two solutes. These individual retention indices coupled with the deduced shift behavior of the peak of interest, can be a helpful means of component confirmation, complementary to spectroscopy. With improvements in the reproduciblity of capillary column manufacturing and the application of specific detectors, programmed temperature retention indices and changes in the shift behavior of solutes as a function of elution temperature can greatly simplify the analysis of complex mixtures of a continously varying composition. The chromatographic bottom-line is: whatever it takes to alter the elution temperature of a solute, e.g., column length, initial temperature, column flow rate (or head pressure), programming rate, etc. can help resolve that solute from the sample matrix, even for apolar solutes in apolar samples.

Future work should entail incorporating a mass selective detector as one of the detectors on a dual column capillary system. This refinement would lend added credence to the assignments of compound identities. Furthermore, slightly altering the inlet pressure to the capillary columns should introduce a small shift in the retention indices and could also assist in clarifying compound identity.

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