Variability of Major Organic Components in Aircraft Fuels
Volume I: TECHNICAL DISCUSSION
(Volume I of III)

B.M. HUGHES, G.G. HESS, K. SIMON, S. MAZER, W.D. ROSS, and M.T. WININGER
MONSANTO CO, DAYTON LAB
DAYTON, OH 45407

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This report summarizes qualitative and quantitative data on the chemical variability of approximately 300 features (chemical components or mixtures of components) with concentrations greater than 0.1 mg/ml in Air Force distillate fuels obtained from over 50 sources. These data were obtained to better understand the environmental effects of possible fuel spills and to serve as a data baseline in photochemical smog and soot formation studies.

Fifty-four petroleum-derived JP-4 fuels, one shale-derived JP-4 fuel, and one petroleum-derived JP-5 fuel were analyzed. The variability of the absolute concentrations in mg/ml was assessed for each feature in the capillary GC/FID (gas chromatography/flame ionization detection) analysis of the 54 fuels. Data base management programs developed and used in this assessment included the calculation of averages, ranges, standard deviations, and percent relative standard deviations of the 300 chromatographic feature concentrations in duplicate analyses of almost all of the fuels. The variability of the data acquisition and data analysis phases of the study was also assessed by calculating the
averages, ranges, standard deviations, and percent relative standard deviations for the 300 feature concentrations of one JP-4 fuel, which was used as the Reference Fuel and analyzed 14 times.

This report is presented in three volumes. Volume I contains the technical discussion, Volume II consists of illustrations, and Volume III contains the sample data package for JP-4 reference fuel.
EXECUTIVE SUMMARY

This report summarizes qualitative and quantitative data on the chemical variability of approximately 300 features (chemical components or mixtures of components) with concentrations greater than 0.1 mg/ml in Air Force distillate fuels obtained from over 50 sources. These data were obtained to better understand the environmental effects of possible fuel spills and to serve as a data baseline in photochemical smog and soot formation studies.

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The Reference Fuel also served as the calibration standard for a portion of the capillary GC/FID data analysis and all of the capillary GC/MS (gas chromatography/mass spectrometry) data analysis. For the GC/FID data analysis, each of the 300 feature concentrations was calibrated relative to the Reference Fuel concentrations of the 300 features. For the GC/MS data analysis, the Reference Fuel was used in a similar manner except that characteristic ions of specific features were used instead of the total ion chromatograms. The major components in the Reference Fuel were also characterized as completely as possible with regard to compound class and exact compound identification to correlate the variability of GC/FID features with mass spectrometer-identified features. This latter analysis resulted in the identification of approximately 200 GC/MS features and correlation with approximately 150 GC/FID features above a concentration of 0.4 mg/ml. All concentrations of major components
relative to the Reference Fuel were determined from GC/MS data using a calibration curve which extended over a 40-fold Reference Fuel concentration range. Because of sample dilution in the preparation of the calibration curves, only 84 of the major GC/MS features could be quantified relative to the Reference Fuel. However, comparison of the variability of the 84 GC/MS features with the corresponding GC/FID features demonstrates that the variability and quantitation as measured from GC/FID data do represent those compounds or mixtures of compounds identified from the GC/MS analysis.

The following general conclusions can be drawn from the results of this study:

- The ability of the automated GC/FID laboratory data system to reproducibly identify fuel features is very good.

- The ability of the automated GC/FID laboratory data system to generate precise Kovats Indices is very good.

- The ability of the automated GC/FID laboratory data system to reproducibly quantify the identified fuel features is very good.

- The total amounts of chromatographable components in the 54 fuels were constant and in agreement with the total amount in the Reference JP-4 Fuel, within the precision of the analyses.

- Significant variabilities were found in the concentrations of individual features (i.e., in the composition) in individual fuels.

- The Reference JP-4 Fuel chosen for this study appears to be a good qualitative standard for the 54 fuels.

- Most features identified by the automated GC/FID laboratory data system can be correlated with those obtained in a GC/MS analysis.
A large number of individual components in the Reference JP-4 Fuel features could be identified by manually assisted computer library search techniques from the GC/MS data, the use of relative boiling point indices (RBPI) and Kovats Indices proved surprisingly valuable in making the identifications.

The fuel component identifications in this study agree well with those in other studies.

In most cases the variability of GC/FID features is caused by the specific compound identified for that feature by GC/MS. Thus, owing to the long-term stability of the instrumentation, one-time identification of features by GC/MS can be used in conjunction with the automated GC/FID analyses for a large number of samples, to specify which particular components are varying notably in concentration.

Because the variability of fuel features by automated GC/FID analysis is highly reproducible with respect to Kovats Index and concentration, and because the feature variabilities correlate well with specific compound variability measured via GC/MS, the automated GC/FID system is a rapid, inexpensive, and reliable method of identifying the specific components causing fuel variabilities. This information may be used to establish correlations between fuel components and specific fuel properties.

Based on the results of this study, the following recommendations are offered:

1. The method of automated identification and quantitation of GC/FID features developed in this program should be used industry-wide to characterize the petroleum-derived distillate fuels being supplied to the Air Force.
• The approach of chemical feature identification should be exploited to the fullest to improve the physical properties and performance characteristics of the fuels.

• The method of automated feature identification and quantitation developed in this study should be used from the outset to evaluate all shale-derived fuels proposed as substitutes for the petroleum-derived fuels.

• All tables and figures referred to in this volume are published separately in Volume II of this report. Volume III is a sample data package for the reference JP-4 fuel.
PREFACE

This research was conducted by Monsanto Company, Dayton Laboratory, 1515 Nicholas Road, Dayton, Ohio 45407 under contract No. F08635-83-C-0067, and JON 19002027 for the Headquarters Air Force Engineering and Services Center, Engineering and Services Laboratory, Envirornics Division, Tyndall AFB, Florida 32403. Thomas B. Stauffer was the AFESC/RDVC Project Officer.

The work was begun in December 1982 and completed in November 1983. This Interim report covers the analysis of 54 different JP-4 fuel samples, one JP-5 sample and one shale-derived JP-4 sample.

This report is presented in three volumes. Volume I contains the technical discussion, Volume II consists of illustrations and Volume III contains the sample data package for JP-4 reference fuel.

This report has been reviewed by the Public Affairs Office and is releasable to the National Technical Information Service (NTIS). At NTIS it will be available to the general public, including foreign nations.

This report has been reviewed and is approved for publication.

THOMAS B. STAUFFER
Sr. Research Chemist

ROBERT E. BOYER, COL, USAF
Director, Engineering and Services Laboratory

JIMMY M. FULFORD, Lt Col, USAF
Chief, Envirornics Division
# VOLUME I - TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Title</th>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>I</td>
<td></td>
</tr>
<tr>
<td></td>
<td>INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>A. GOALS OF THE STUDY</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>B. GENERAL APPROACH</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>EXPERIMENTAL METHODS</td>
<td></td>
</tr>
<tr>
<td></td>
<td>A. GC/FID ANALYSES</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>1. Feature Selection for Reference JP-4 Fuel</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>2. Sample Analysis of Petroleum- and Shale-Derived Fuels</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td>B. GC/MS ANALYSES</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td>1. Instrumental Parameters</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td>2. Identification of Features: Sequence of Operations</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td>3. Identification of Features: Logic of Specific Identification</td>
<td>29</td>
</tr>
<tr>
<td></td>
<td>4. Reproducibility of Chromatograms</td>
<td>33</td>
</tr>
<tr>
<td></td>
<td>5. Method of GC/MS Quantitation</td>
<td>34</td>
</tr>
<tr>
<td></td>
<td>III</td>
<td>37</td>
</tr>
<tr>
<td></td>
<td>RESULTS AND DISCUSSION</td>
<td></td>
</tr>
<tr>
<td></td>
<td>A. QUALITATIVE IDENTIFICATION OF GC/FID FEATURES FROM GC/MS DATA</td>
<td>37</td>
</tr>
<tr>
<td></td>
<td>1. Identification of GC/MS Features</td>
<td>37</td>
</tr>
<tr>
<td></td>
<td>2. Correlation of GC/FID with GC/MS Features</td>
<td>39</td>
</tr>
<tr>
<td></td>
<td>3. Relationship Between Kovats Indices (KI) of Correlated Features in GC/FID and GC/MS</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>4. Comparison of Calculated Boiling Points with Those Cited in Literature</td>
<td>41</td>
</tr>
<tr>
<td></td>
<td>5. Comparison of MC KI Values with Those Cited in Literature</td>
<td>41</td>
</tr>
<tr>
<td></td>
<td>B. VARIABILITY OF GC/FID FEATURES IN DISTILLATE FUEL SAMPLES</td>
<td>43</td>
</tr>
<tr>
<td></td>
<td>1. Sources of Fuels</td>
<td>43</td>
</tr>
<tr>
<td></td>
<td>2. Petroleum-derived JP-4 Fuels (54 Samples)</td>
<td>43</td>
</tr>
</tbody>
</table>
VOLUME I - TABLE OF CONTENTS (concluded)

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>C.</td>
<td>VARIABILITY OF GC/MS FEATURES IN DISTILLATE FUELS</td>
<td>47</td>
</tr>
<tr>
<td>D.</td>
<td>DESCRIPTION OF A SAMPLE DATA PACKAGE FOR THE REFERENCE JP-4 FUEL AND</td>
<td>49</td>
</tr>
<tr>
<td></td>
<td>OTHER DELIVERABLES WHICH ARE SUPPLIED UNDER SEPARATE COVER</td>
<td></td>
</tr>
<tr>
<td>IV</td>
<td>CONCLUSIONS AND RECOMMENDATIONS.</td>
<td>53</td>
</tr>
<tr>
<td>A.</td>
<td>CONCLUSIONS</td>
<td>53</td>
</tr>
<tr>
<td>B.</td>
<td>RECOMMENDATIONS</td>
<td>57</td>
</tr>
<tr>
<td>REFERENCES</td>
<td></td>
<td>61</td>
</tr>
</tbody>
</table>
GLOSSARY OF TERMINOLOGY

AN - LAS Command used to analyze a raw or processed data file with one of the LAS Methods containing named features.

BIPxxx - Designation for the LAS file containing data processed to replace retention times in minutes, with Kovats Indices divided by 10 for each feature of the processed data file DFPxxx. Feature concentrations are in percent relative to the Reference Fuel.

BKPxxx - Designation for LAS the file containing data processed to replace retention times in minutes, with Kovats Indices divided by 10 for each feature of the processed data file DFPxxx. Feature concentrations in absolute amounts (mg/ml).

Calibration Peaks - Subsection of the Data Analysis section of the LAS Method, in which retention time, response factor and compound name information is stored relative to the naming and quantitation of peaks.

CALB - Name given to a particular sample when retention time - Kovats Index information is to be used to update the parameters in the LAS Parameter File, FILEA.

DFPxxx - Designation for the LAS file containing processed data from the raw data file DFRxxx.

DFRxxx - Designation for the LAS file containing raw data from distillate fuels analysis xxx.

DFANME - LAS Method used to create BKPxxx files with retention times replaced by the Kovats Index divided by 10.

DFABME - LAS Method used to name all features in the BKPxxx files and calculate all feature concentrations in absolute units (mg/ml).
GLOSSARY OF TERMINOLOGY (continued)

DFPCNT - LAS Method similar to DFLaE which is used to produce BIPxxx files and calculate all feature concentrations relative to the Reference Fuel.

Feature - Peak in a chromatogram identified by the computer according to criteria incorporated into the peak detection algorithm. A feature may consist of one or more components.

FILEA - LAS File in which the relationships between retention times and Kovats Indices are stored.

Harmonic Mean Temperature ($T_{hm}$) - The absolute temperature lying between a lower absolute temperature ($T_e$) and an upper absolute temperature ($T_u$), which is defined by the relationship: $T_{hm} = 2T_e T_u / (T_e + T_u)$.

Image-1000 - Name of the Hewlett-Packard Data Base Management System used by Monsanto Company (HC) in this study.

KOCAME - LAS Method used to calibrate the retention time-Kovats Index relationship.

Kovats Index - Retention index for a specific component in a mixture, obtained by interpolation between the retention times of the next earlier and next later eluting normal alkane. Retention index for n-butane is 400, for n-pentane is 500, and for n-hexane it is 600, etc.

Kovats Program - See description of KOVPG1

KOVLPG1 - Basic Program that operates on a processed data file, DFPxxx, to correlate the Kovats Index with the retention time for each named feature in the data file. Features with names beginning with a "$" are normal hydrocarbon marker compounds and are used to calibrate parameters in FILEA when the sample name is CALB. When the sample name is other than CALB, KOVPG1 Calculates Kovats Indices of all detected peaks, using the Kovats Index-retention time relationship stored in FILEA.
GLOSSARY OF TERMINOLOGY (continued)

L/S - Hewlett-Packard Model 3356 - Laboratory Automation System.

Micropipette - Rainin (Gilson) variable volume micropipette, Model P-200, with disposable tip.

Marker Compounds - Normal hydrocarbons which are interpolation end points used to calculate Kovats Indices.

Merge Feature - Property of the LAS Methods which corrects peak splitting; i.e., which combine all peaks with retention time differences of 0.05 minutes or less into a single feature.

Method - LAS file which controls the data analysis of raw or processed data files. This file contains variable parameters which control the integration, identification, and concentration calculation of features as well as post-analysis programming and report generation.

Master Method - LAS Methods DFABME and DFPCnt, which name all features in the Reference Fuel with concentrations greater than 0.1 mg/ml and calculate feature concentrations either in absolute or relative amounts, respectively.

NAMER - FORTRAN program which incorporates the Kovats Index of each feature into the name of that feature.

Parameter File - File used for storing data associated with Method postanalysis programs. This file was used in the present report to correlate retention times (minutes) with Kovats Indices.

PREPARE - LAS Command used to prepare a Method.

Processed Data File - LAS file which contains retention time, concentration and compound name information obtained from analyzing a Raw Data File with an appropriate LAS Method.
GLOSSARY OF TERMINOLOGY (continued)

REP1 - FORTRAN program which reports (outputs) all of the data in a given data base, in the order in which it is stored.

REP4 - FORTRAN program that statistically summarizes the feature concentration distributions, as in REP6, and reports a histogram of the concentration distribution for each feature in a data base.

REP5 - FORTRAN program that statistically summarizes the feature Kovats Index distribution for each feature in a data base, as in REP7, and reports a histogram of the Kovats Index distribution for each feature.

REP6 - FORTRAN program that statistically summarizes and reports the concentration values for each feature in a data base.

REP7 - FORTRAN program that statistically summarizes and reports the Kovats Index for each feature in a data base.

REP8 - FORTRAN program that reports (outputs) all of the data in a given data base, in order according to the first four characters in the sample name.

Raw Data File - LAS File which contains the digital values representing the analogue output voltages from the 5880 Flame Ionization Detector. For the present study, these values are stored at a rate of 8 values/second.

Relative Response Factor - Response of a given component relative to the internal standard.

Response Factor - Factor which indicates the signal intensity that is produced by a given amount of a substance in the FID detector.
GLOSSARY OF TERMINOLOGY (continued)

RC - Updates response factors of the named peaks in the LAS Method during recalibration; used to adjust the factors in DFPCT so that the concentration of each feature in the Reference Fuel was 100 percent.

RTE-IV - Real Time Executive-IV Operating System used on the 3356-LAS.

RU - RTE-IV Command used to run FORTRAN programs.

TOMB - FORTRAN program that summarizes the status of a given data base.

Windowing - Selecting a retention time or Kovats Index range in which a given feature will be detected and properly identified.
SECTION I
INTRODUCTION

A. GOALS OF THE STUDY

This program is being completed to determine the chemical variability of Air Force aircraft fuels. The objective was to obtain quantitative and qualitative data on the variability of major and minor chemical components of Air Force distillate fuels. These data are necessary to better understand the environmental effects of possible fuel spills. Results will also serve as a data baseline in photochemical and soot formation studies.

The major goals of this study were met by dividing the work into three phases. In the first phase (detailed in this report) the variability of concentrations of the major organic components in liquid aircraft fuels was studied. The second phase will determine the variability of concentrations of water-soluble components present in liquid aircraft fuels. The third phase will focus on the variability of concentrations of the gas phase components in equilibrium with the liquid fuel.

With respect to the first part of the study, the complexity of typical petroleum- and shale-derived distillate fuels dictates the maximum use of sophisticated computer-operated data acquisition and data interpretation systems. In addition, to complete the study within the cost constraints, the implementation of an analysis approach should yield variability data within the constraints of existing analytical and computer instrumentation commercially available and onsite in the contractor's laboratory.

On a more technical level, the study of the variability of organic component concentrations in fuel samples consists of two elements: (1) the identification of the components in the fuels to be studied, and (2) the quantitation of these components in a given set of fuel samples. Superimposed upon both of these technical elements are the instrumentation and resource constraints mentioned above. Successful completion of the present study required a
continual balancing of resource availability with the technical requirements for measuring and reporting the variability of hundreds of components in over 50 aircraft fuels.

To study the variability of the components of fuels, the following goals were achieved:

- The major organic components of aircraft fuels were identified.
- These components were quantified in a set of samples from known supplier, lot number, etc.
- The distributions of these components were determined in this well-characterized set of samples.

The approach used for this complex study is described, in general terms, in Section 1B. Technical details are provided in Section II, Experimental Methods, and in Section III, Results and Discussion.

B. GENERAL APPROACH

At first, the three goals listed in Section 1A may not seem particularly difficult to achieve. However, when they are to be achieved for samples with hundreds of components present, the goals become very challenging. In this work, extensive use of capillary chromatography, combined with flame ionization and mass spectrometric chromatographic detection, was required due to the large number of components present.

Petroleum- and shale-derived aircraft fuels are so complex that complete chromatographic resolution is impossible even when using state-of-the-art chromatographic instrumentation. Often analytical systems yield one chromatographic peak per component of interest; however, in some cases, one chromatographic peak may actually represent several components of interest.
Instead of referring to the "components" of aircraft fuels when actually referring to recognizable chromatographic peaks, we will refer to the "features" of a fuel. This terminology adds precision to the meaning of a chromatographic peak. When flame ionization detection is used, only a retention time identifies a chromatographic peak. Because it is possible that several components may have identical retention times (within the present resolution capability of capillary chromatographic separations), it is imprecise and incorrect to refer to a chromatographic peak as a single component. To emphasize that fact, each peak is referred to as a "feature" of the chromatogram.

Mass spectrometric detection adds another dimension to the analysis. Instead of relying on retention time to distinguish adjacent or co-eluting components, available mass information gives a much higher certainty that a measured chromatographic peak, when detected with a mass spectrometer, can be correlated with a certain compound. However, this is true only if no other compounds (or isomers of compounds) give similar mass spectra. Many isomers of certain compounds are expected to be found in petroleum- and shale-derived fuels produced from the distillation of biologically derived materials held at equilibrium for millions of years at elevated temperatures and pressures. Therefore, using the mass spectrometer as a detector does not yield an unequivocal definition of a GC/FID or GC/MS feature due to mass spectra similarities.

To better define GC/FID and GC/MS features, additional information can be easily derived from the capillary chromatographic analyses of complex mixtures. This information can be derived by using normal hydrocarbons to develop a retention index to define the unknown components or features of aircraft fuels. In the present study, Kovats Indices (Reference 1) were calculated to replace the absolute retention time (in minutes) of eluting features with a number calculated from the linear interpolation of normal hydrocarbon retention time data. Methane is assigned an index of 100, ethane an index of 200, propane an index of 300, etc.; interpolation between these markers yields Kovats Indices of all the chromatographic features detected that are relatively independent of slight fluctuations in GC conditions. Petroleum- and shale-derived fuels
are natural mixtures of hydrocarbons that contain these normal hydrocarbons as major features in the chromatograms. Therefore, this approach is easily implemented for each analysis of each distillate fuel.

Other information can be derived from the capillary chromatographic analysis of complex mixtures by using the same calibration technique as that described for the Kovats Index calculation, but calculating the predicted boiling points of all eluting features, based on the boiling points of the normal hydrocarbons in the fuel mixture. This boiling point data must be used carefully because the elution order of all compounds is not based solely on boiling points. However, these data, along with the feature Kovats Index and the feature mass spectra, can be used to determine which compound or groups of compounds constitute a single GC/FID feature.

Two additional reasons for defining features revolve about the need to process over 50 samples in duplicate, using the GC/FID analysis system, and to measure and correlate approximately 300 features in each of these analyses. This means that approximately 30,000 numbers must be manipulated and reported. Reporting would require approximately 170 pages of data, if typed with a four-column, 44-line format. This amount of data is prohibitive, particularly when considering that feature distributions must be determined and statistics calculated from these 30,000 data points. Hence, the concept of features was used so that the computer system that collected the GC/FID data could also be used to generate tables that identify eluting chromatographic species. Therefore, a feature is defined not only by the presence of a chromatographic peak, which the experienced scientist can detect, but also by the manner in which the data analysis computer program measures and detects the presence of chromatographic peaks. When chromatographic resolution is not identical for all analyses, the method used for integrating the chromatograph detector response vs. elution time data can cause certain features to merge or produce new features where only one existed. Therefore, the initial choice of the features to be studied must be based on a study of the variability of how the overall analytical system replicates the analysis of a standard fuel.
An additional reason for using the concept of a feature deals with the finite number of characters that can be used to name a given compound. As will be shown later, only approximately 22 ASCII characters may be used for naming compounds or features on the existing computer system. However, the number of characters required to name a compound exactly or to include a description of the presence of multiple compounds for a specific feature easily exceeds this number. Therefore, the feature is a very simple way of assigning complex descriptions to a single chromatographic peak within the peak name data storage field. For the present study, Kovats Indices and consecutively numbered features are used exclusively in lieu of exact proper compound names. A three-digit number can then be used to represent a feature (chromatographic peak) that may require several lines of text to describe the feature's actual components. This more complicated description of the feature is reserved for the tables in the GC/MS results section, which describe in detail each feature for which variability data is presented.

This feature-naming approach also was used to expedite the checking of large amounts of data where only a number needed to be remembered for a specific feature, and not the positional substitution of methyl groups on a naphthalene fused ring, or some other more complex compound designation. Using feature numbers for feature identification also allowed the GC/FID variability study to proceed in parallel with the GC/MS qualitative identification of features; this improved the efficiency of this phase of the study.

After the features for which variability would be assessed were identified, each feature was quantified using two different FID approaches. GC/FID data were used extensively in the present study as the primary source of quantitative data because over 95 percent of the compounds are closely related and exhibit very similar flame-ionization detector responses. Therefore, responses relative to an internal standard do not vary over long periods of time. This is not the case for GC/MS data, because ion source focus elements adjustment may significantly vary the total amount of ionization which the mass spectrometer detection system measures, depending upon the masses of the major fragment ions. In addition, the present mass spectrometer data system does not allow easy development of specialized programs for file and data manipulation, as is
the case for the data system used to acquire the GC/FID data. This latter data system also has a very extensive data base management system that is not available on the mass spectrometer system. Feature concentrations were determined in absolute amounts (mg/ml) by using an internal standard analysis technique that references all of the detected features to the internal standard (anthracene-d\textsubscript{10}) peak area.

The second method of assessing feature concentrations consists of using the Reference JP-4 Fuel as a calibration standard and deriving relative response factors for each of the 300 features present in the JP-4 Reference Fuel. This set of response factors was calculated so as to normalize each feature in the Reference JP-4 Fuel to 100 percent. The value for each feature, when calibrated with respect to the Reference Fuel, indicates whether that particular feature is above or below the concentration of the feature in the Reference Fuel.

As described earlier, GC/MS data served as the primary qualitative tool for characterizing the general compound class or specific compound identification of GC/FID features. In this role, it was used to detect mixtures of components in GC/FID features above 0.4 mg/ml. Although GC/MS was not the system on which the primary quantitative information was determined, GC/MS data were used in a quantitative manner similar to that employed for determining the concentration of features relative to the Reference Fuel. In this GC/MS quantitative analysis, each of the GC/FID features above 4 mg/ml was identified using retention time and up to three characteristic masses. Calibration curves were then generated for each of these features (86 discrete compounds), with the Reference Fuel yielding 100 percent for the amount of each feature. As was the case for GC/FID data, the concentration relative to the Reference Fuel was determined for each of the sample fuels. This GC/MS quantitative analysis is redundant because it generates a set of concentrations relative to the Reference Fuel that have been calculated in a much more accurate way from GC/FID data. However, it is not redundant when one considers the standpoint that, because the variabilities of the GC/FID features prove to be very similar to the variabilities based on GC/MS characteristic mass quantitations, the 86 features in the Reference Fuel being measured by GC/FID are shown to be properly represented
by the identifications based on the maccs spectra of those features. By extrapolation, one may also assume that the variability measured for the additional 75 to 100 features that fall between 0.4 and 4 mg/ml is most likely caused by those compounds identified from qualitative GC/MS analyses.

This approach to the quantitative and qualitative analysis of distillate fuels was developed to maximize the quality of data obtained and minimize the resources required to obtain the data. The following points summarize this overall approach:

- It relies heavily on GC/FID for quantitative analysis, yielding data on duplicate fuel sample analyses with the incorporation of a data base management approach for the measurement of a large number of features.

- It produces an output that can be easily interpreted. If a feature is named, then it is present in the Reference Fuel and its quantity, relative to the Reference Fuel, can be determined from the appropriate normalized output. If a feature number is missing, then that feature which was present in the Reference Fuel is below the detection limit in the sample fuel analysis. If a feature is unnamed, then it is present in the fuel and absent (or below the detection limit) in the Reference Fuel.

- It incorporates mass spectrometric qualitative analyses for over two-thirds of the features present in the Reference Fuel. These analyses assume that all fuels will contain the same features, although at different concentrations.

- It provides the concentration of features relative to the JP-4 Reference Fuel, based on GC/MS analysis. Therefore, comparison of GC/MS relative amounts with the GC/FID relative amounts for the same feature indicates how well the GC/FID variability data for the feature represent the variability of the actual component identified from mass spectral data interpretation.
SECTION II

EXPERIMENTAL METHODS

The experimental methods used to acquire and summarize data that measure the variability of approximately 300 features in over 50 aircraft fuels can be divided into three major areas: GC/FID Analyses, Data Base Management System, and GC/MS analyses. In this report, the Data Base Management is described in the GC/FID Analyses section (Section II A), because the computer system used to acquire GC/FID data also was used for the development of the Data Base Management System. However, the details of the Data Base Management System are computer-specific and will be discussed only with respect to the types of data displayed and results obtained. Complete computer program documentation is beyond the scope of this project.

Figure 1 provides an overall flow diagram of the logic and steps that were used to obtain the final feature distribution data for the fuels studied. The two major analytical instrumentation techniques shown at the top of the flow diagram were used more or less in parallel fashion, as shown. Each major element below the two parallel analytical approaches will be described in detail in the discussion of each major technique. Therefore, Section II, Experimental Methods, is divided and subdivided in a manner similar to that shown in Figure 1. To simplify this section, other more detailed flow diagrams or descriptions of instruments, computer programs, naming conventions, etc., have been included in the appropriate subsection where such information is needed.

A. GC/FID ANALYSES

All samples were analyzed using a Hewlett-Packard 5880 capillary GC/FID analysis system. A detailed description of this system and the operating parameters used are shown in Table 1. Instead of using the 5880 chromatographic integration system for producing tables of retention time and raw area counts for discrete peaks, the 5880 was interfaced to the Hewlett-Packard 3356-Laboratory Automation System (LAS) for this purpose. The analogue voltage output from the flame-ionization detector was converted to the digital value
eight times per second and stored as raw data on the LAS disc storage system. These raw data files were then processed further, using various analysis methods that produced tables of retention times and area counts. These were also stored on the LAS as processed data files.

Processed data files were used in two ways so that the distributions of chromatographic features could be related to components in a preselected Reference JP-4 Standard fuel. The first use of processed data files was to assign Kovats Indices to known chromatographic peaks, which were primarily normal hydrocarbons from $C_4$ through $C_{20}$. These marker hydrocarbons were assigned values of 400, 500, ..., 2,000 for $n-C_4$, $n-C_5$, ..., $n-C_{20}$ hydrocarbons by using a Kovats calculation program, KOVPG1, and the naming capability of the processed data files. These markers were identified in the processed data file compound name field with a special first character. Because all $n$-hydrocarbons from $C_4$ through at least $C_{14}$ were present in all fuels analyzed, Kovats Indices for all detected features could be calculated from calibration data obtained from the same fuels raw data file. The Kovats calculation program interpolated all features between the normal hydrocarbon marker compounds, and it generated a table of Kovats Indices, retention times, and peak areas for all samples analyzed. In addition, the Kovats program created a second processed data file in which all retention time data (in minutes) were replaced by the calculated Kovats Index divided by 10. (Division by 10 was required because no values greater than 540 minutes could be stored in this data field in the processed data file.)

The processed data file was used to produce a file in which an alphanumeric name was assigned to each feature and the elution times were replaced by the Kovats Indices (divided by 10). Hence, the processed file contained an almost invariant digital value for the elution time of each feature, which the gas chromatographic analysis program could use to assign alphanumeric feature names that could be easily understood by the scientist. This alphanumeric feature name also was used as an item in the Data Base Management System that could be easily correlated for all samples in a given data base. An example of this procedure is provided in the next section on the determination of features to be quantified for the Reference JP-4 Fuel.
1. Feature Selection for Reference JP-4 Fuel

In order to explain the manner in which features were initially identified for the Reference JP-4 Fuel, several details of file-naming conventions had to be described. A six-character alphanumeric name was used to identify raw and processed data files (described above) and analysis Methods (described later) used to create processed data files from raw data files. A detailed file-naming convention was essential to manage the large number of samples and types of data generated. The first convention relates to the names of raw and processed files generated from the initial injection of a distillate fuels sample. Of the six characters available for file naming, the first three were alphabetic to aid in identifying the type of file being referenced. The last three characters were numeric and referred to a specific injection made by the automatic GC/FID sample injection system. Raw data were assigned a file name DFRxxx (Distillate Fuels Raw data xxx), and processed data were assigned a file name DFPxxx (Distillate Fuels Processed data xxx). To be of acceptable quality, the processed data file was required to: (1) contain raw peak areas of the anthracene-d\textsubscript{10} internal standard which varied by less than 20 percent for a set of analyses; (2) yield total concentrations that were between 400 mg/ml and 800 mg/ml; (3) contain no peaks with retention times within 0.05 minute of each other; and (4) identify all marker compounds properly. Multiple peaks within 0.05 minute were interpreted as peak-splitting detected by the LAS and were considered analytical artifacts. This was a severe problem for the sample solvent and a small problem for the actual components of the distillate fuel samples. Peak-splitting was corrected by reanalyzing raw data with the "Merge" feature of the LAS integration method to be described later.

Once a processed file had been created to meet the above quality criteria, the Kovats calculation program was used to prepare a processed data file with the name BKPxxx (BKovats Processed file xxx). (xxx is a three-digit number from 001 through 999 that identifies the raw data file which was created for a specific sample at a specific time.) Additional naming conventions will be described later in this report, as needed.
A detailed flow diagram for distillate fuel feature selection is shown in Figure 2. The file-naming conventions and descriptions of data analysis given above are shown in the figure up to the dagger (#). At this point, the BKPxxx file had been created with named Kovats marker compounds, methylene chloride solvent, system impurities, and anthracene-d10 internal standard. An example of the first page of this file is shown in Table 2. Only a small portion of the chromatographic peaks have been named. To use the correlation properties of the MC Data Base Management System, each peak must be named. However, for the initial Reference JP-4 Fuel analyses, no unique identification can be made, based only upon GC/FID retention times, except those named features in the BKP file. Therefore, a FORTRAN program called "NAMER" was developed to incorporate each feature Kovats Index into the name of every detected feature. This was accomplished by converting the Kovats Index/10 number (which is stored in the retention time field of the processed file) into its ASCII representation and placing this representation into the 22-column peak name field of the BKPxxx file. Table 3 provides an example of the same file output shown in Table 2 after executing the program NAMER. The "P" at the end of the compound name indicates that the name was assigned directly from Kovats Index data stored in processed file, and the "M" indicates that the name was assigned using a LAS method which uses a predefined window for naming. BKPxxx now contains information in each peak name field that can be correlated with similarly named peaks in BKPyyy, BKPzzz, etc., generated from the 14 replicate analyses of the Reference JP-4 Fuel.

To help the reader understand the work completed, the MC data base management system is described in the following subsection.

a. Data Base Management System

The MC Data Base Management System (DBMS) used for the correlation of data from the analysis of distillate fuels was centered on the Hewlett-Packard IMAGE-1000 Data Base Management System. The MC system used IMAGE-1000 subroutines to store and correlate all named features in processed data files in a given data base. In addition to feature names, feature concentrations,
feature Kovats Indices/10, sample names, processed file names and total concentrations also were stored in the MC DBMS. Programs were developed to add, subtract, and summarize all of the above parameters for a given data base. The data base size was designed for inclusion of up to 500 different features in 500 discrete samples. In practice, the MC DBMS actually was developed for use with a number of discrete data bases. Separate data bases were assembled to meet the requirements of various studies. Data bases were used to correlate data from duplicate analyses of each distillate fuel, data from 14 replicate analyses of Reference JP-4 Fuel, and all data from the analyses of petroleum-derived JP-4 fuels. This latter data base consisted of 52 fuels, each analyzed in duplicate, and two fuels analyzed singly. Various types of data correlation programs were written for specific types of output. The following descriptions and examples show the types of correlation programs developed.

- REP1 and REP8. Programs output all data present in a given data base. REP8 orders the output by the first four characters in the sample name. Table 4 shows a typical output for a data base containing replicate analyses of a particular distillate fuel.

- REP6. Program statistically summarizes the concentration values for each feature. The output (presented in Table 5) shows the feature name, feature concentration average, feature concentration range, feature concentration standard deviation, feature concentration percent relative standard deviation, and the number of processed data files in which that feature was detected.

- REP7. Program statistically summarizes the Kovats Index values for each feature. The output (presented in Table 6) shows the feature name, feature Kovats Index average, feature Kovats Index range, feature Kovats Index standard deviation, feature Kovats Index percent relative standard deviation, and the number of processed files in which that feature was detected.

- REP4. Program summarizes the feature concentration distributions as REP6 but also provides a visual histogram display of the concentration distribution for each feature. This display shows the number of times that each
feature was detected in a predetermined concentration interval. The total number of intervals is determined at the time of data output, and REP4 shows the number of times that a concentration value occurs between the "LOW VALUE" and "HIGH VALUE" for the number of intervals specified. The actual concentration intervals are determined from the RANGE of concentration values, the lowest and highest concentration values in the range, and the number of intervals selected. An example of one feature output is shown in Table 7. This output requires one page per feature.

• REP5. Program summarizes the feature Kovats Index distribution as REP7, but also provides a histogram display of the Kovats Index distribution for each feature similar to that in REP4. An example of one feature output is shown in Table 8. This output requires one page per feature.

• TOMB. Program summarizes the status of a given data base. Table 9 provides an example of the type of detailed file information that this utility program provides.

With the preceding brief description of the NC-developed Data Base Management System and correlation programs, discussion of the method of feature identification in the Reference JP-4 Fuel will be continued. As shown at the point of the dagger (#) in Figure 2, each feature in each of the BKPxxx files of Reference JP-4 Fuel was named using the FORTRAN program called "NAMER." This program produced feature names for each detected peak that included the Kovats Index in the feature name. After running NAMER, each file was added to a data base, and REP6 and REP7 were used to statistically evaluate the various features that were named; Tables 10 and 11 provide these initial data base outputs.

As shown in Tables 10 and 11, each feature named by NAMER includes a "P" at the end of the feature name to indicate that it was named from the BKPxxx processed file. From these two outputs, initial identification of the Kovats Indices of all detected features was made. However, these tables emphasize a problem when only the Kovats Index measured in a single processed data file produced from each analysis is used to name a distillate fuels feature. A
Feature whose Kovats Index is half integral values, will be assigned the lower Kovats Index at one time, but it may be assigned the higher Kovats value at another time because of chromatographic variability. Therefore, because the Kovats Index is not an integer value but a real value, another method that includes using a window to name features is more appropriate. This problem can be seen in Table 11 where the Kovats Index 677 is detected 14 times, and the index 678 is detected twice. The actual value of the Kovats Index for this feature is between 677 and 678. Therefore, using integer values for assigning Kovats Indices causes the data base management programs to treat this one feature as two different features with two different names.

At this point, Laboratory Automation System (LAS) methods will be described to show how the LAS uses windows to assign feature names rather than assign a real value to determine the name. Naming conventions employed for the various Methods will also be discussed.

a. LAS Integration Methods

Methods KOCAME and DFANME, shown in the third and fourth blocks of Figure 2, were used, respectively, to calibrate the retention time-Kovats Index relationship, and to create BKPAxxx files with the retention times replaced by Kovats Index/10. The Methods are almost identical; therefore, only one Method (shown in Table 12) will be discussed.

The LAS Method is divided into four sections: DATA INPUT; DATA ANALYSIS; USER PROGRAMS; and REPORTS. The DATA INPUT section is used to control important parameters in the peak detection algorithm of the Method. The subsection entitled "INTEGRATOR EVENTS" causes all artifact peaks to be merged. Table 12 shows the Method when the solvent peaks between 8.58 and 10.4 minutes are merged into one value. The DATA ANALYSIS section contains the important parameters associated with the detection and naming of the features, along with the type of standardization used, report output formats, and labels for the concentration units. The REFerence Retention Time Window of 0.05 indicates the absolute window that is used to detect the internal standard, which is defined with an "&" in the first character of the name. The percent Retention Time
Window of 1.0 percent corresponds to a window of 0.5 minute for a peak with retention time of 50 minutes. This latter window is used for identifying all named peaks other than the internal standard. The Response Factor-Unknown is the response factor assigned to all unnamed peaks. This factor was chosen to be the same as the factors for all named peaks. The factor, 1.0, was chosen after analysis of an analytical standard of \(n\text{-C}_5\) through \(n\text{-C}_{20}\) hydrocarbons resulted in a range of factors from 1.0 to 1.3, with 1.3 corresponding to \(n\text{-C}_5\) hydrocarbon.

Information relating to the naming of peaks and calibration of the retention time/Kovats Index relationship is stored in the CALIBRATION PEAKS subsection of the DATA ANALYSIS section. The peak names are used by the KOVPG1 POST ANALYSIS USER PROGRAMS, and FILEA PARAMETER FILE shown in the third section of the Method in Table 12. Names that begin with "$" are defined in KOVPG1 as marker compounds; the value following "$" and terminated with a "-" determines the actual values of the Kovats Indices for the marker compounds. To calibrate the retention time-Kovats Index relationship stored in FILEA, the DFRxxx data file is analyzed with a sample name of "CALB". This tells the KOVPG1 program to update the parameters in the FILEA PARAMETER FILE. The raw data file is then reanalyzed with the proper sample name (other than CALB), and Kovats Index calculations are performed by interpolation for all peaks that are not designated as Kovats marker compounds (all unnamed peaks and those named peaks that do not contain a "$" as their first character). Each peak name in the Method also is terminated with an "M" to distinguish that the name was derived from method "windowing" and not from the NAMER program. (The NAMER program places a "P" as the last character of the named peaks in the resulting processed data file.) The same type of calculation described above for the determination of Kovats Indices also was performed to calculate boiling points for all of the features in the Reference Fuel. In this case, however, the Kovats Index value for the marker compounds was replaced with the marker compound boiling points times 100. The last section of the LAS Method includes information used to route the processed data file outputs to a particular output terminal.
An example of the first page of the output produced by analyzing a DFPxxx file with DFANHE is shown in Table 13; the first page of output from the post analysis program "KOVPG1" is shown in Table 14; and the first page of output from listing the BKPxxx file created by the KOVPG1 post analysis program is shown in Table 15. This demonstrates that the feature retention times have indeed been replaced by the correct Kovats Index calculated from the KOVPG1 program, and the BKPxxx is now properly constructed to produce the final desired data output.

At this time, feature assignment from the statistical summaries of REP6 and REP7, shown in Table 10 and 11 and referenced in Figure 2, will be discussed. As noted in the statistical summary headings of Tables 10 and 11, 16 Reference JP-4 Fuel analyses were included in the data base summarized in these tables. However, several small features were detected only in less than one-half of the 16 samples or produced Kovats Indices that caused NAMER to assign two different consecutive values to the same feature's index. Inspection of the REP8 output (not shown) for this data base revealed that two processed data files were responsible for most of these variations; these were deleted from the data base. From this data base of 14 Reference JP-4 Fuels analyses, average Kovats Indices were determined and assigned to all detected features in the data base. Several features were later eliminated due to poor replicability. All of these features were in the 0.1 to 0.2 mg/ml absolute concentration range and were poorly replicated due to the presence of shoulders or poor peak-shape replication.

In order to correlate each feature identified in the Reference JP-4 Fuel with the actual chromatographic peaks measured, Figure 3 shows an expanded chromatogram obtained from the analysis of the Reference JP-4 Fuel. In this figure, the features numbered from 001 through Impurity No. 3 are written near the baseline of each feature. This chromatogram, generated on the LAS using an Extended Method, also shows how each feature was integrated. The dotted line at the base of each chromatographic peak shows how the baseline was calculated to measure the peak area for the corresponding peak. Many baselines are calculated properly with the exception of those for features 131
through 135 and 150 through 295. Due to the complex nature of these regions of the chromatogram, valley-to-valley calculations were made to estimate where the proper baseline lies for these peaks. However, this approach tends to cause the calculated areas to be less than those calculated if a fixed baseline value were used. This explains why an average value of approximately 800 mg/ml (the theoretical value) was not reported for the total concentrations of all components in many of the distillate fuels samples.

The deviations from 800 mg/ml measured for the total concentrations of components can be used to determine which fuel samples contained large numbers of poorly resolved components that resulted in underestimating the quantities of those components present. This underestimation does not cause a serious problem in a feature-by-feature comparison. As noted in Figure 3, this error is on the order of 10 to 20 percent for major components in these retention time regions; this is the same order of magnitude of replication as that of the Reference JP-4 Fuel. However, when this difference is summed over a larger number of features, it causes the total amounts measured to be low by 10 to 20 percent, a significant factor in the measurement of the total concentrations of components in the fuels. In addition, values for the total concentrations of components reported for each fuel may include this systematic error which would not be corrected by normal random error statistics.

A master method named DFABME (Distillate Fuels ABsolute MEthod) was prepared using the LAS program called PREPARE (PREPARE Method). A listing of this method is shown in Table 16. The method contains the same information as described above for the DFANME; and is used to integrate the original raw data obtained from capillary GC/FID sample injection. However, because this method must be used with BKPxxx files that contain Kovats Index/10 for the retention times, all time information in DFABME must be in Kovats Index/10 units rather than minutes. This applies to the run time, reference retention time window, percent retention time window, and the feature retention times. Feature concentrations are calculated according to the formula shown in Equation (1).
\[ C_i = \frac{F_i A_i \times R \times D}{F_s A_s} \times 100 \]

where \( C_i \) = concentration of component \( i \)
\( F_i \) = relative response factor for component \( i \)
\( F_s \) = relative response factor for internal standard
\( A_i \) = area of component \( i \)
\( A_s \) = area of internal standard
\( R \) = true ratio of standard to sample, obtained by dividing "STD-AMT" by "SAMP-AMT"
\( D \) = parameter "% Dilution Factor," normally 100 percent

The relative response factor for the methylene chloride solvent was set at zero so that its area was not included in the total concentration value. Response factors for the fuels hydrocarbons relative to the anthracene-\( d_{10} \) internal standard were determined for each of the carbon number ranges. In regions where the majority of the components eluted (C-9 to C-13) the average response factor was 1.0. In the ranges C-7 to C-9 and C-13 to C-20 the response factor was 1.1. Only in the C-5 to C-6 and C-6 to C-7 ranges, where very few of the components elute, were the response factors greater than 1.1; they were 1.3 and 1.2, respectively.

For simplicity the relative response factor, \( F_i \) was adjusted to equal the response factor for anthracene-\( d_{10} \) for the entire analysis (except for the methylene chloride). Two considerations prompted this choice. First, since the major objective was to determine variabilities of fuel components, the exact response factor would not affect the outcome of the variability analysis. Second, since the response factors determined for each carbon number range were average values for all the components in the range, a person interested in the exact concentration of a particular component would have to determine the response factor unique to that component, regardless of what the average value was for that range. Thus, using the response factor equal
to that of anthracene-d$_{10}$ for all compounds gives quantitative results very close (within 10 percent in most cases) to the true values, which can be readily modified for specific compounds.

The feature names that appear in the CALIBRATION PEAKS subsection of the DATA ANALYSIS section of the method are those used for the remainder of the present study. The names are designed to transmit a maximum amount of data to the MC Data Base Management System and to the researcher (within the limitations of the 22 characters of the feature name field). All Kovats Index marker compounds retain the index assigned to that feature, along with its compound designation; the methylene chloride solvent and system impurities are so designated. All other features have their exact calculated Kovats Index (obtained from the REP7 output of the data base of the 14 replicate Reference JP-4 Fuels analyses) included in the first 10 characters of the feature name. The last six characters of the name for all JP-4 features (including the marker compounds) are assigned a unique feature number from 001 through 297. Feature numbers 101, 111, 121, 172, 197, 252, 261, and 284 do not appear in this master method, having been eliminated due to their poor reproducibility when the Reference JP-4 Fuel was analyzed. All of these features were present at concentrations less than 0.5 mg/ml.

Table 17 shows the REP6 output of a data base in which the 14 replicate Reference JP-4 Fuel BKPx files were analyzed, using DFABME. All features with concentrations above 0.5 mg/ml (with the exception of features 161, 260, and 266) give percent relative standard deviations that are typically 10 percent or less. This shows that percent relative standard deviations greater than this value in the data base summary statistics for the data base, including all petroleum-derived JP-4 samples, indicate variability caused by real feature concentration variability in the set of samples and not by analytical uncertainties in obtaining and analyzing the data.

To facilitate easy interpretation of large amounts of data, a second master method was prepared in which each feature concentration was assigned an arbitrary value of 100 percent for the Reference JP-4 Fuel, and
the feature relative response factors were calibrated using the 14 Reference JP-4 Fuel BKPxxx processed data files. In effect, this replaces the highly variable absolute concentration amounts in the data display with a less varying number calculated relative to the Reference JP-4 Fuel. This uses relative concentration values to easily assess how a given sample feature pattern compares with the Reference JP-4 Fuel feature pattern. This data analysis approach does not require reinjection of the sample, but only reanalysis of the same BKPxxx data file used to generate absolute concentrations. To develop this type of data, the DFABME Method was copied to another LAS method named DFFCNT (Distillate Fuels PerCENT), and the amounts of each feature were modified to be 100.00. As shown in Figure 2, this method was Recalibrated using the 14 Reference JP-4 Fuels. The relative response factors, calculated by rearranging Equation (1), are shown for all features in the DFFCNT method (shown in Table 18). Table 19 shows the summary statistics for the data base of samples analyzed using this method. To save this data for inclusion into the data base, without writing over the absolute concentration data in the BKPxxx file, this data file type was assigned a new name, BIPxxx.

The previous discussion on the two methods used for analyzing distillate fuel samples defines how features are treated and quantified if these features are present in the Reference Fuel. Equally important is the determination of which features are present in a given fuel sample but not present in the Reference Fuel. Features not present in the Reference Fuel are identified from the DFABME and DFFCNT method outputs by those features that contain no name in the feature name field. The absence of names for features can easily be detected by visual inspection of the various outputs. The concentration reported for these unnamed peaks is calculated using a Relative Response Factor of 1.0 (the same as that for all named features), and the Kovats Index is obtained by multiplying the number in the Retention Time column by 10. If unnamed peaks are very near a Reference Fuel named feature, the unnamed feature may actually correspond to the named feature but fall just outside the window criterion for the naming of peaks. Therefore, careful interpretation of unnamed peaks is required.
2. Sample Analysis of Petroleum- and Shale-Derived Fuels

The previous section described how GC/FID features are identified, how the LAS data reduction programs quantify GC/FID data, and how the MC Data Base Management Programs provide a statistical evaluation of feature variability data. This section shows how the various elements described above were used to develop data bases containing petroleum-derived JP-4 fuels analysis data, petroleum-derived JP-5 fuel analysis data, and shale-derived JP-4 fuel analysis data.

a. Solvent Selection

The general complexity of aircraft fuels requires a state-of-the-art separations technique to reproducibly quantify and identify the large number of features present. This dictates the use of a capillary gas chromatographic separation technique in all phases of the study. One major disadvantage of this separation technique, however, is the very thin coating of bonded liquid phase on the narrow fused silica column material that causes serious overloading when absolute amounts of any given component approach 500 nanograms. For a typical JP-4 fuel, major component concentrations are in the 20 to 30 mg/ml range. GC/FID autosampler systems can reproducibly inject 1 μl sample volumes. Use of the system described in Table 1, in the split injection mode with a 1:100 split ratio, results in the injection of approximately 0.01 μl of a sample. For the typical JP-4 fuel, these injection parameters, when using undiluted fuel, result in injecting 300 ng of the major components in the fuel. This value is very close to 500 ng when column overloading becomes serious; however, even injection of 300 ng for the major components reduces chromatographic resolution. Using the undiluted fuel also does not allow maximum chromatographic resolution for nontypical fuels that may contain components at concentrations greater than 30 mg/ml. To analyze for a wider range of major component concentrations, the present study required that all fuel samples be diluted and that split injection capillary chromatographic techniques be used. A dilution factor of 1:10 was chosen to obtain good chromatographic resolution for samples that may contain up to 300 mg/ml (or approximately 38 percent by
weight) of any given component, while maintaining the ability to accurately quantify minor components in the 0.1 to 1.0 mg/ml range.

Any diluting solvent introduces an additional problem in the analysis of fuel samples. No matter which solvent is chosen, several minutes of the chromatogram are obscured due to the flame-ionization detector response to the solvent. Therefore, before any solvent system is chosen, one must determine to what extent the loss of fuel component data in this elution time region affects the overall study. Methylene chloride and n-nonane were chosen as most probable candidates for the diluting solvent. A comparison of the elution time of methylene chloride with the elution times of fuel components in the n-C₅ to n-C₆ region of the Reference JP-4 Fuel indicated that this compound would be an ideal solvent. To determine if any significant features were present in the methylene chloride retention time region, all 56 fuels were diluted with n-nonane, and the retention time region corresponding to the eluting methylene chloride solvent (if methylene chloride were used) was screened visually. Initial selection of methylene chloride was fortuitous because only two fuels contained components (one each) in this region, and no fuel contained any components greater than 0.4 mg/ml in this region.

The fuel screening analysis using n-nonane also was used to determine the distribution of features at the high-molecular-weight region of all of the fuels to select an appropriate internal quantitating standard. Only two samples contained compounds as high as n-C₁₈. Because this compound can be chromatographically resolved from anthracene-d₁₀, which is useful for mass spectrometric analysis due to its unique mass spectrum, anthracene-d₁₀ was chosen as the internal standard for both GC/FID and GC/MS quantitation.

A final consideration concerning solvent and/or system impurities also was addressed in this screening phase. A stock solution of anthracene-d₁₀ was prepared at a concentration of 1 mg/ml in methylene chloride (Burdick and Jackson, distilled in glass). This internal standard solution was analyzed using the chromatographic conditions to be employed for the Distillates Fuels analysis to assess the internal standard solution impurities. Three minor components, other than methylene chloride and anthracene-d₁₀, were detected.
in the chromatogram. These three components were identified as system impurities and were distinguished from distillate fuel components by not assigning Kovats Indices or feature numbers in the names for these components in the DFABME and DFPCNT methods shown in Tables 16 and 18. This action was taken so that the feature name would show that these features are due to our analytical system and are not components of the fuel.

b. Sample Analysis Protocol

To obtain quantitative data on the absolute concentrations of features detected in capillary GC/FID and GC/MS analyses, a strict analysis protocol was developed and verified for the replicate analysis of Reference JP-4 Fuel samples. Validation included placing processed data files of 10 Reference JP-4 Fuel samples, each analyzed in duplicate, into a single data base and using REP6 to display the percent Relative Standard Deviation for each of the normal hydrocarbons in the data base. The Reference JP-4 Fuel samples were analyzed after approximately every seven fuel samples, and therefore covered an elapsed time of 1 to 2 weeks. Percent Relative Standard Deviations of all n-hydrocarbons were in the 5 percent to 10 percent range. Analytical system variability also was assessed in a similar manner by analyzing 10 replicate injections of a single Reference JP-4 Fuel sample. The data base statistics for this set of analyses showed percent Relative Standard Deviations between 3 percent and 5 percent for the n-hydrocarbon concentrations in the Reference JP-4 Fuel sample.

To determine what changes, if any, occurred in the chromatographic resolution over the entire period of acquisition of GC/FID data, a comparison chromatogram of the Reference JP-4 Fuel analysis was generated as shown in Figure 4. This figure shows the data obtained from an early injection of the Reference Fuel (DFR062, solid lines) and a later injection of the Fuel (DFR226), dotted lines). Between these two analyses, approximately 150 injections (extending over 1 1/2 months) of all of the distillate fuels were made. As noted in the figure, these two chromatograms are virtually identical. The patterns and peak heights of all features in the two analyses are identical. The only difference in the two analyses appears to be in retention time. All
features in the later analysis are displaced to earlier retention times. However, this difference is less than one peak width and would easily be compensated for by our data analysis protocol, because these same changes also occur for all marker compounds and the internal standard.

The following sample-handling and sample analysis protocols were followed to assure that the variability measured in the Distillate Fuels data bases was caused by real variability in the feature distributions and not by variability in the GC/FID and data analysis of the fuels:

- **Sample Receipt and Storage.** All samples were received in 1-gallon shipping containers supplied by Tyndall Air Force Base personnel. Samples were assigned a unique log number when received and were refrigerated at 5°C.

- **Sample Dilution.** Each fuel sample was diluted in a 14 ml Pierce vial with Teflon®-lined septum by combining 1 ml of the fuel with 9 ml of methylene chloride (Burdick and Jackson, distilled in glass). One-ml micropipettes, with disposable pipette tips, and disposable serological 10 ml TD pipettes were used for volume measurement.

- **Internal Standard Addition.** Each diluted fuel sample was spiked with anthracene-d$_{10}$, immediately prior to analysis, in the autosampler vial used for GC/FID and GC/MS analysis. The 200 µl Gilson Pipetman®, with disposable pipette tips, was used to combine 200 µl of the diluted fuel sample and 200 µl of a 1 mg/ml anthracene-d$_{10}$ standard in a 1-ml autosampler vial. Teflon®-lined crimp-top vials were used.

- **Standards Storage.** Due to the high volatility of the major components of JP-4 and the methylene chloride solvent, all diluted samples and standard solutions were refrigerated at 5°C at all times except during the preparation of samples for analysis.

Figure 5 shows the overall flow diagram used to process the 56 fuel samples received from various Air Force suppliers.
B. GC/MS ANALYSES

1. Instrumental Parameters

The Reference Fuel was analyzed by GC/MS using the following conditions:

- Column head pressure: 4 psi
- Temperature program:
  - TEMP1 -30
  - TIME1 13
  - RATE3
  - RATE2 TIME 26.33
  - RATE10 TIME 110
  - TEMP2 300
  - TIME2 0

- Column: 30 m x 0.322 mm J & W fused silica capillary coated with 0.25 μM DB-5 liquid phase.

- MS/DS: Hewlett-Packard 5985B with Revision E multidrive operating system.

The GC oven temperature profile plotted in Figure 6 is exactly the same program as that used for the GC/FID analyses up to 110 minutes. Because the anthracene-d10 internal standard eluted in 98 minutes during the GC/MS analyses and no later peaks appeared, it was unnecessary to continue the 2°C/minute temperature ramp up to 225°C. Thus, the rate was changed to 10°C/min at 110 minutes and maintained at that rate until the 300°C temperature limit was reached to clear the column of residual traces of high-boiling compounds.

Nearly all of the mass spectral identification was performed using data in File Reference Number 17396 (FRN 17396). For that analysis, the scan time was 12.5 minutes and the scan delay was 12.0 minutes. The latter should have been 6.75 minutes to begin acquiring data for components in the fuel eluting immediately after the methylene chloride solvent. A subsequent Reference Fuel analysis using the 6.75-minute scan delay (FRN 17449) was used to determine
the components eluting between 6.75 and 12.0 minutes, and another analysis (FRN 17455) identified the four features that could be detected by GC/MS prior to the solvent peak.

The mass spectrometer parameters were as follows:

- Multiplier 1800 V
- Threshold 25 counts
- ADC 4/0.1 amu
- Mass range 10-250 amu
- Scan delay 6.75 min.

When the mass spectrometer threshold was set at 25, 14 percent of the space on a disc cartridge was used for data storage by the analysis, whereas a threshold of 10 used 41 percent of the cartridge. The lower threshold was essential in generating spectra with maximum information for library search and identification purposes. The higher threshold was satisfactory for the quantitation of the individual fuel samples, and it avoided excessive consumption of disc storage space.

2. Identification of Features: Sequence of Operations

The mass spectral identification of the features proceeded as follows:

- All features exceeding the 0.4 mg/ml (0.05 percent) threshold were identified from the 14 replicate GC/FID reference fuels analyses. Of the 288 features identified by GC/FID, 203 exceeded the threshold for mass spectral identification, and 192 followed the solvent peak in the GC/MS analyses.

- Identification of features was performed on a 100-unit range in Kovats Index; i.e., all of the features between n-heptane and n-octane were identified as a group. This was an arbitrary decision for the sake of simplicity.
Within each Kovats Index range, the ID numbers of the features to be identified were assigned to peaks on the GC/MS total ion chromatogram that corresponded as closely as possible to the features in a GC/FID chromatogram of the Reference Fuel.

The correlation between features observed in the GC/FID and the GC/MS chromatograms was based primarily on visual inspection of the groupings and intensities of the features appearing in each Kovats Index range. Minor differences in the GC/FID and the GC/MS Kovats Indices were not considered when the correspondence of the patterns was obviously correct. In fact, later examination of the GC/FID and GC/MS KI values revealed that small differences exist between the GC/FID and GC/MS KI values for some classes of compounds. (See discussion in Section III, Results and Discussion.)

In some of the higher molecular weight ranges, the pattern correlation between GC/FID and GC/MS chromatograms was very difficult; in those cases, the similarity of KI values for the feature in GC/FID with that in the GC/MS analysis was used to determine which GC/MS peak should be associated with which GC/FID feature. Peaks in the GC/MS total ion chromatogram below 0.4 mg/ml, based on the GC/FID-determined concentration, were ignored. In a few cases a rather large GC/MS peak did not seem to correspond to any GC/FID feature. In those cases, the GC/MS peaks were given names other than those assigned for the GC/FID analysis.

On the whole, the correspondence between the chromatograms obtained by GC/FID and GC/MS was good, so that the assignment of feature numbers to peaks in the GC/MS total ion chromatogram was straightforward. However, the correspondence was ambiguous in a number of cases. In those instances, the feature numbers were asterisked in the identification tables (to be described later) so that they could be scrutinized separately.

- The mass spectrum for each feature was printed and labeled. These mass spectra, along with all GC/MS raw data, are supplied under separate cover.
A table was prepared, listing the following information about each feature: feature number, GC/FID retention time, GC/FID Kovats Index, GC/MS retention time, GC/MS scan number, GC/MS Kovats Index, the difference between the GC/FID and the GC/MS Kovats Indices, and feature characteristic masses. An asterisk was used to denote those features for which correlation between GC/FID and GC/MS was difficult.

A second table was prepared in which tentative identifications were made for each feature, and the characteristic ions were tabulated.

A careful analysis of each tentative identification was performed, leading to the final identification, along with an identification of the class of compound present. Estimates of the confidence of each identification also were made.

All the information indicated in the three preceding paragraphs was compiled into a single large table for each Kovats Index Range for presentation in this report (see Tables 21-28).

3. Identification of Features: Logic of Specific Identifications

The considerations involved in the specific identification of features is shown schematically in Figure 7. The scheme is discussed in the following paragraphs.

a. Comparison of Reported Mass Spectral Data with Scan Numbers of Interest

The first step in determining which molecule(s) was (were) present in a given feature was to perform an automated search of the mass spectral library vs. the scan number of interest. In cases where partial overlapping of peaks was evident, the search was performed on a "background-subtracted" spectrum, where the "background" was the earlier or later eluting component in the mixture.
The Hewlett-Packard Probability Based Search (PBS) was used to list likely candidates for the identification of all unknown components in the Reference JP-4 Fuel. The search algorithm measures the significance of a match between a given mass spectral peak in an unknown compound in the Reference JP-4 Fuel sample with the corresponding mass spectral peak in all standard compounds in the NBS/NIH Mass Spectral Library which contains more than 30,000 compounds. The significance of such a match is expressed in terms of the probability that such a match would occur by chance. This probability is expressed as one chance in 10 to the K power. For low mass numbers (such as 43) and small abundance peaks, K is low, indicating that it is easy to obtain matches on such peaks. For large mass numbers (such as 112) and large abundances, K is large, because very few peaks are in this category.

If the probability of getting a match at mass M1 (expressed as one in 10 to the K1 power) is independent of the probability of getting a match at mass M2 (expressed as one in 10 to the K2 power), then the probability of getting both matches is the product of the individual probabilities, or one in 10 to the (K1 + K2) power. Under the same assumptions, the probability of obtaining n matches is one in 10 to the (K1 + K2 + ... + Kn) power. In PBS searching, the similarity of two spectra is judged by the sum of the K values associated with matching peaks, and by the ratio of this K value to the maximum attainable K value. Once a list of likely compounds for a given unknown compound is printed out, a trained mass spectroscopist visually compared the unknown compound spectrum with each of the most likely compounds. From this comparison, the unknown compound was assigned an identification, using logic described elsewhere in this section.

b. Consideration of Possible Structures

The mass spectra of the top several matches obtained from the PBS Search were compared visually with that of the feature to decide which were the best choices. This decision included a comparison of the large (i.e., high intensity) peaks in the feature and library spectrum to see whether their intensity ratios were approximately correct, and whether one or more large
peaks in one spectrum were missing in the other. These problems would usually indicate either an incorrect match or the presence of two or more components in the feature mass spectrum.

The apparent molecular ions in the feature were checked against the molecular weight (MW) of the library spectra to see whether some of the library spectra could be ruled out or considered to be more likely candidates. In some cases, additional library searches were performed to locate other possibilities more consistent with the high mass ions in the feature spectrum.

Numerous feature spectra exhibited masses characteristic of two classes of compounds -- most noticeably aromatic hydrocarbons and branched alkanes. In these cases, either a manual search was performed to identify the component not found by the library search (typically, the lower molecular weight aromatic component), or an additional library search was performed in which the molecular weight range was restricted to the mass of the apparent unidentified component (aromatic hydrocarbon) forcing appropriate candidate matches to be generated.

c. Boiling Point Comparison

Whenever possible, the boiling points of the best matches were examined to see whether they were reasonable for the retention time observed. This comparison was facilitated by substituting the exact boiling points of the normal alkanes for their Kovats Indices in one (arbitrarily selected) analysis of the Reference Fuel. The Kovats Index computer program was then used to calculate a set of "relative boiling point indices," analogous to the Kovats Indices, based on the retention times of the features. These values are the ones reported in the Calculated Boiling Point column of the feature identification tables in this report. The literature boiling points were obtained mainly from Ferris [Reference 2] and Rappoport [Reference 3]; the boiling points of the normal alkanes were taken from the latter source.
d. Kovats Index Comparison

Kovats Indices of the features were compared with the available published Kovats Indices of the tentatively identified components to see whether they were reasonable. Four sources of Kovats Indices were used:

- Hayes and Pitzer [Reference 4]. The OV-101 column was immediately programmed from the initial 35°C temperature to 200°C at 1°C/minute.

- Schröder [Reference 5]. The value at the lowest of various isothermal temperatures on a squalane column was selected in each case.

- Bredael [Reference 6]. The value at the lowest of various isothermal temperatures was selected in each case.

- Smith, Harper, and Jaber [Reference 7]. After a 5-minute hold at the initial temperature of 10°C, the SE-30 column was programmed at 5°C/minute to 210°C.

e. Identification of Compound and Confidence Level

When all of the preceding factors had been considered, the specific identification of the compound was recorded, along with the code indicating the chemical class of the compound. In the class corresponding to the formula \( \text{C}_n \text{H}_{2n} \), which would indicate a cycloalkane or an alkene, the C or the E in the chemical class code was underlined if it was felt that the difference between the two possibilities was fairly well defined.

The level of confidence used to identify a specific compound was estimated by considering the questions indicated in Figure 7:

- Would the mass spectra of other isomers of this compound be very similar to, or reasonably distinct from, the proposed structure?
Would the other possibilities for this mass spectrum be numerous or few?

Could other classes of molecules have similar spectra, thereby greatly increasing the number of possible choices?

Would alternate compounds have very similar or easily distinguishable boiling points, and is the boiling point of the proposed compound close enough to the calculated value to be reasonable?

The confidence level for the compound class identification was determined using the following questions:

- Are the high mass ions -- particularly the apparent molecular ions -- appropriate for the class being proposed?

- Are the fragmentation patterns -- especially in the lower mass range -- characteristic of that class?

- What are the chances that a different class of compounds could yield a mass spectrum with these same general features?

4. Reproducibility of Chromatograms

As indicated in Section II.A, the reproducibility of the GC/FID chromatograms was determined by analyzing the reference fuel at various times throughout the project duration. Similarly, GC/MS chromatograms of the reference fuel were obtained at various times to show the high reproducibility of these results; this comparison is shown in Figure 8. Furthermore, the columns in the GC/FID and GC/MS instruments were interchanged, and the analyses were rerun to check the chromatogram variability due to both column and instrument.
5. Method of GC/MS Quantitation

All distillate fuels samples were analyzed using the same chromatographic and mass spectrometric conditions as outlined above in Section II.B.1. Quantitation was accomplished using a procedure very similar to the GC/FID quantitation where the Reference JP-4 Fuel was used as the standard reference material. Figure 9 shows the sample analysis and data reduction in flow diagram format. However, for mass spectrometric quantitation, characteristic mass responses for the major 84 features described in the qualitative identification section of Section III, Results and Discussion, were used in lieu of total ion responses. For this method of quantitation, the Hewlett-Packard-developed software package entitled "Internal Standard/Isotope Dilution" (HP 59821A) was used exclusively.

This approach produced five-point calibration curves over a 40-fold concentration range for each of the major 84 features in the Reference JP-4 Fuel. The correlation of the 84 features with GC/MS peaks is shown in Figure 8. Up to three characteristic masses were chosen for each feature quantified in this manner and appropriate dilutions of the Reference JP-4 Fuel were made. Figures 10 and 11 show examples of the calibration curve and the characteristic mass chromatograms used to determine the concentration of that particular feature in relation to the Reference Fuel.

To easily compare the feature concentrations in a fuel sample with concentrations in the Reference JP-4 Fuel, the concentration units are indicated in terms of the Reference JP-4 Fuel. Each feature relative response factor was calibrated to yield a value of 100 percent for that feature in the Reference JP-4 Fuel, and the output from this program (shown in Table 20) was compared to the DPPCNT Method output from analysis of the GC/FID data for that particular fuel. See Section III, C for an explanation of the handwritten numbers in the "CONC'N % REL" column in Table 20.

Theoretically, if the characteristic masses of all of the 84 features are correctly identified, and the 84 features are properly correlated with
GC/FID features, then the mass spectral output shown in Table 20 would be identical to the DFFCNT Method output, shown in Table 19. These outputs are included in Distillate Fuels Data Packages (which are transmitted to the Air Force under separate cover) for all 56 fuel samples analyzed for the present study. An example of the total data package for one fuel sample (chosen to be the Reference JP-4 Fuel) is discussed later and shown in Volume III. In Volume III, all of the outputs described in both the GC/FID and GC/MS Experimental Methods section of Section II are included for each fuel analyzed.
SECTION III

RESULTS AND DISCUSSION

A complete discussion of all phases of component variability is not feasible due to the complex nature of distillate fuels. However, the present section is designed to describe major results obtained from the present study and give the reader enough description of all generated data so that specific points not discussed can be addressed by further inspection of the data, which is supplied under separate cover. The first section addresses the mass spectrometric qualitative identification of the major features detected in the Reference JP-4 Fuel. A second section describes the sources of the 56 fuels analyzed and provides tables which describe the variability of almost 300 features in the fuel samples (based upon GC/FID analyses). The third section describes GC/MS results obtained on feature variability, where the mass spectrometric data are used in a quantitative manner to determine feature concentrations for those features quantified in the mass spectrometric analyses. The last section describes the detailed information included in Data Packages for each fuel analyzed. An example of a Data Package for the Reference JP-4 Fuel is shown in Volume III; the description of the organization of the Data Packages will use this package as an example.

A. QUALITATIVE IDENTIFICATION OF GC/FID FEATURES FROM GC/MS DATA

1. Identification of GC/FID Features

Tables 21 through 28 summarize the identifications of all major features detected in these GC/MS analysis of the Reference JP-4 Fuel. The following comments concerning the identification procedure may be helpful

Budzikiewicz, et al., [Reference 8] stated, "... it seemed reasonable to investigate initially these simplest of all organic compounds (i.e., the aliphatic hydrocarbons) because they would presumably show the most easily interpretable reactions. This ... assumption proved erroneous. Aliphatic
hydrocarbons were found to exhibit a characteristic and reproducible fragmentation pattern, which, however, could only with difficulty if at all, be correlated with their structures." This means that it is not generally possible to look at a hydrocarbon mass spectrum and deduce the structure from "first principles." Thus one is forced to rely heavily on spectral pattern matching, i.e., computer searching, for specific compound identification.

The mass spectra of different classes of compounds such as branched alkanes, cycloalkanes, aromatics, etc., present differences that are generally recognizable, without pattern matching, especially when molecular or parent ions are visible to assist in the assignment. Such molecular ions were present in a large number of the mass spectra obtained for the Reference Fuel features; hence, it was possible in most cases to be reasonably certain of the compound class, even when no specific molecule could be identified. Thus, the following simple scale was used to indicate the level of confidence with which the classes were identified:

++ = known standard  
+ = probably correct  
o = possibly correct  
- = just a guess

The confidence which one may have in the specific compound identification must necessarily decrease with increasing molecular weight of the compounds. Table 29 indicates the number of isomers possible for just two general carbon and hydrogen compositions. The problem of the geometric increase in the number of isomers is compounded by a corresponding decrease in the percentage of these isomers for which mass spectra have been recorded. For the higher molecular weight species, given the number of isomers possible, the similarity of some of their mass spectra, the relatively small temperature range over which they elute, and the paucity of mass spectra in the NBS/NIH Mass Spectral Library, it becomes simply a stroke of good fortune to correctly identify a particular isomer of a given elemental composition. The following scale was used to show the estimated confidence with which specific identifications are known:

38
4 = known standard
3 = "certain"
2 = probably correct
1 = possibly correct
- = specific identification not made

In the higher molecular weight ranges, the great majority of the identifications must be at confidence level 1 or -. In spite of this, it is frequently possible to make a reasonably confident assessment of the compound class for the feature.

In addition to the limitations on compound identification imposed by the inherent complexity of the system, other existing limitations are typical of any research project: time available for instrumental analyses, computer workup of the data, and analyst time. While a substantial increase in these categories would improve the accuracy of the identifications, the percentage of improvement would probably be substantially less than the percentage increase in time commitment. The mass spectrum of each feature, provided under separate cover, could be used to improve the accuracy or specificity of any particular assignment made.

2. Correlation of GC/FID with GC/MS Features

To a certain extent, the correlation between GC/FID and GC/MS features (discussed in Section II.3.2.) was more direct at shorter retention times. However, it was found that the n-undecane (C_{11} to C_{12}) region was the least well correlated, whereas the n-dodecane (C_{12} to C_{13}) region was readily correlated.

The difficulty in correlating GC/FID with GC/MS features in the C_{11} to C_{12} range was probably due to the large number of overlapping peaks (seen in the mass spectra). Slight shifts of some of the components relative to others would create rather different feature patterns in the two analyses.
Table 30 summarizes the number of features for which there were problems in correlating the GC/FID and GC/MS patterns; i.e., those features which are asterisked (*) in the Feature Identifications tables. It seems reasonable to assume that some of the correlations in question would actually prove to be correct, whereas some that are assumed to be correct might not be; hence, the figure indicated should be approximately correct. Thus, 75 percent of the number of features in the GC/FID chromatogram correlate with those in the GC/MS chromatogram. When considering the absolute concentrations of the components involved, however, this 75 percent of the number of components correspond to 85 percent of the absolute concentrations of the GC/FID features that correlate with GC/MS features.

3. Relationship Between Kovats Indices (KI) of Correlated Features in GC/FID and GC/MS

Examining only the KI values for those features that could be identified with relative certainty (i.e., specific I.D. confidence of 2 or 3), and for those features for which the correlation between the GC/FID and the GC/MS chromatograms did not appear to present any problem, the following observations were made:

- Using the most numerous compound class [branched alkanes (BA)] as a probe, it is obvious that the ΔKI (FID - MS) values are quite different up to the middle of the C7-C8 range from those after that point. The mean ΔKI (BA) value for the lower molecular weight range is -2.0 ± 0.9 (seven data points); the mean value for the upper molecular weight range is +0.8 ± 0.7 (19 data points). The lower molecular weight range corresponds to compounds eluting during the -30°C hold period and the initial 3°C/minute temperature range in the chromatograph ovens. The higher molecular weight range corresponds to the 2°C/minute temperature range in the chromatograph ovens. This corresponds to oven temperatures between 10°C and 280°C.

Because the majority of features in the fuel elute in the higher molecular weight group, only that range is considered in the subsequent discussion.

40
Table 31 summarizes the KI comparison.

Obviously, the KI (MS) values are always lower than the KI (FID) values, indicating that all of the components are eluting earlier, relative to the normal alkanes, in the GC/MS system than in the GC/FID. It also appears that one may expect the mean ΔKI value for cycloalkanes and substituted benzenes to be approximately twice as large as that for branched (acyclic) alkanes, although the relatively large σ values make this conclusion tenuous.

4. Comparison of Calculated with Literature Boiling Points

Relative Boiling Point Indices (RBPI) were calculated for the GC/FID features using the known boiling points [Reference 3] of the normal alkanes as reference points. These values were compared with the literature boiling points of the identified (specific I.D. code = 2 or 3) features, for which no problem was apparent in correlating the FID and the MS features. The results are shown in Table 32.

These data indicate that in the GC/FID system the retention times of the branched alkanes and cycloalkanes, relative to the normal alkanes, make them appear to have lower boiling points than the values reported for them in the literature; for substituted benzenes, the opposite behavior is observed. The standard deviations of the means of these differences are relatively large, so that only the means for the substituted benzenes and the cycloalkanes differ from ΔBP = 0 by more than approximately 1σ.

The reasonably close correlation between the calculated boiling points of the specifically identified compounds and their corresponding literature values lends credence to the proposed identifications.

5. Comparison of MRC KI Values with those Cited in Literature

It is readily apparent that exact correlations of literature KI values with each other or with the MRC results can not be made. This does not mean that they are of no value. Two major factors that affect KI values are the
stationary phase of the GC column and the temperature at which the components elute. Although the four stationary phases being compared here (SE-30, squalane, OV-101, and DB-5) are all "nonpolar," they have slightly differing individual characteristics that affect the elution times of the components differently. Because KI values are temperature-dependent, those obtained via isothermal analyses at different temperatures will not be comparable. For those components eluted in a temperature-programmed analysis, the harmonic mean of the injection temperature and the exit temperature (assuming constant linear programming and no initial hold time) should indicate the temperature to be used for comparison with an isothermally determined KI [Reference 9].

Most features of the reference fuel in this study eluted at harmonic mean temperatures considerably lower than any of the isothermally determined literature values. Nevertheless, by comparing the KI value corresponding to a proposed identification of a particular feature with literature KI values for that species, it was frequently possible to decide whether or not the proposed assignment was reasonable.

The Kovats Indices listed in Tables 21 through 28 in the column headed "Literature KI's, SE-30 [7]," are the Indices from the AFESC report by Smith [Reference 7] Table 5: Major Components of JP-4. In cases where the fuel component assignment is incorrect in that report or at variance with the Monsanto Company result, the KI values in the column SE-30 [7] are placed in the row of the correctly or differently named component.

The discrepancies between the AFESC report and the Monsanto Company results are summarized in Table 33. Components listed in the AFESC report with no obvious counterpart in the Monsanto Company study are identified in Table 34. Components listed as "Unidentified" in the AFESC report are not considered.

It is evident that there is considerable agreement of results from the MRC study with the earlier work of Smith, et al. Even in those cases where the components are assigned differently in the two studies, the two structures are usually in the same chemical class, but simply isomers of each other.
B. VARIABILITY OF GC/FID FEATURES IN DISTILLATE FUELS SAMPLES

1. Sources of Fuels

Table 35 summarizes pertinent information concerning the sources and types of fuels analyzed. The first half of the table gives the unique three-digit number used to reference each fuel, followed by the source, source city and state, and a more complete MRC identifier. The second half of the table repeats the unique three-digit number and gives the POSF No. (if assigned), identification given by each supplier on the 1-gallon shipping container, a Laboratory Report No. (if known), and the sampling date. The POSF No. is assigned by the Fuels Branch, Fuels and Lubricants Division, Aeropropulsion Laboratory, Wright-Patterson Air Force Base, Ohio (AFWAL/POSF); it can be used to obtain additional sample information, if required. Sample number 607 is the Reference JP-4 Fuel used for compound identification and portions of the GC/FID and all of the GC/MS quantitation of the remaining samples. All samples in the table are petroleum-derived JP-4 fuels with the exception of number 606, which is a petroleum-derived JP-5 fuel, and number 640, which is a shale-derived JP-4 fuel.

2. Petroleum-Derived JP-4 Fuels

The 54 JP-4 petroleum-derived fuel samples described in Table 35 were analyzed as described in Section II.A, Experimental Methods. Table 36 summarizes the variability of the concentrations (in mg/ml) measured for all features. Table 37 summarizes the variability of the concentrations (relative to the Reference JP-4 Fuel concentrations) measured for all features. Table 38 summarizes the variability of the Kovats Indices measured for all features. The compound names given in these tables are correlated to compound identifications from mass spectrometric analysis of components in the Reference JP-4 Fuel. These identifications are given in Tables 21 through 28. The amounts, ranges and standard deviations shown in Tables 36 through 38 are in units of mg/ml, % Rel. and Kovats Index units, respectively. The percentage of relative standard deviation is obtained by dividing the standard deviation by the average value and multiplying by 100. Note that the percentages of relative
standard deviation for all features in Tables 36 and 37 are identical because the same raw data was used to obtain the information upon which these two tables are based. The information under the heading labeled "Number of Samples" gives the number of samples that contain the corresponding features named in the first column.

For the statistical summary of the data bases shown in Tables 36 through 38, 52 fuel samples were analyzed in duplicate and two fuels were analyzed singly, yielding a total of 106 sample analyses of 54 fuels. Fuel Numbers 612 and 627 were analyzed singly. The last two columns in Tables 36 and 37 can be used as measures of the variability of each of the features named in the 54 fuels. A total of 114 features were detected in at least 104 of the 106 samples. Percentage of relative standard deviations greater than 30 percent were measured for all features with the exception of Impurity Number 1, which had a value of 23.6 percent; Impurity Number 2, which had a value of 6.7 percent; FE=63, which had a value of 24.5 percent (and was present in 9 samples); FE=226, which had a value of 27.6 percent (and was present in 11 samples); FE=285, which had a value of 24.9 percent (and was present in 11 samples); anthracene-d_{10}, which had a value of 9.5 x 10^{-6} (and was made to be exactly 10.0 for this internal standard); Impurity Number 3, which had a value of 18.7 percent, and the Total Concentration, which had a value of 11.7 percent. All these low percentage relative standard deviation values are consistent with the fairly constant level of impurities in all analyses, and the fairly constant Total Concentration of all components in all samples. The low percentage of relative standard deviations for features 063, 226 and 285 are due to the small numbers of samples that contain these features. All percentage of relative standard deviations greater than approximately 15 percent are measures of the true variability of the features in the 54 fuel samples because values less than 15 percent were measured for almost all features when the Reference JP-4 Fuel was analyzed 14 times, as shown in Tables 17 and 19.

Another measure of the variability of the data obtained on the 54 petroleum-derived JP-4 fuels can be seen from careful inspection of the average amounts of feature concentrations shown in Table 37, where each feature has been normalized to the concentration of that feature in the Reference JP-4
Fuel. Of the 288 features quantified in the Reference JP-4 Fuel, only 52 features were less than 50 percent or greater than 150 percent, when normalized to the concentrations in the Reference JP-4 Fuel. Of these 52 features, 18 were present in less than 47 of the 106 samples in the data base. Therefore, the original choice of the Reference JP-4 Fuel is probably as representative a sample of the whole data base of petroleum-derived JP-4 fuels as one can obtain, without actually making an artificial mixture of all fuels. This is not very significant from a quantitation standpoint; however, from the standpoint of qualification, it shows that the detailed mass spectral analysis of major components in this one Reference JP-4 Fuel sample should contain information on the qualitative identification of all major components in most of the fuels shown in Tables 36 through 38.

The last conclusion that can be drawn from the data base containing results of analysis of 54 petroleum-derived fuels relates to the assignment of Kovats Indices for all of the 288 features analyzed. The percentages of relative standard deviations in the Kovats Indices measured for all features are shown in Table 38 to typically lie below 0.1 percent. The only significant exceptions to this are for the early eluting feature Numbers 001, 002 and 004 which have percentage of standard deviations of 0.27, 0.22 and 2.3 percent. This means that for compounds with Kovats Indices of 1000, the relative standard deviation is typically between 0.1 and 1 Kovats Index unit.

Many more correlations could be made from more detailed analyses of the 54 fuel samples summarized in Tables 36 through 38. A complete listing of all feature concentrations in all samples summarized in the tables has been submitted under separate cover (using REP8). In addition, histograms of all features (using REP4 and REP5) have been supplied. However, this documentation contains more than 1000 pages and can not be made a part of this Final Report. In addition, 54 Data Packages have been supplied under separate cover that show chromatograms and tables generated from the GC/FID and GC/MS analysis of all petroleum-relative JP-4 Fuels. Section III.D. and Appendix A describe these data packages in detail, if further correlations are necessary.
One important element of the REP8 listings of the 54 fuels is summarized in Table 39. For each analysis, the percentage of named peaks is calculated relative to the total number of peaks detected, and the percent concentration of named peaks is calculated relative to the total concentration of all peaks detected in each analysis. By comparing these values for replicate analyses, one can obtain qualitative information on how each sample replicates and how it compares to the Reference JP-4 Fuel. Because peaks used to identify named peaks in all samples are based upon the Reference JP-4 Fuel, the comparison of these two percentages gives a measure of how many peaks were unnamed and, therefore, presumably not present in the Reference JP-4 Fuel, and what percentage of the total concentration these unnamed peaks represent in the total fuel sample. Fuel number 607 is the Reference JP-4 Fuel and Table 39 shows that the percent Number is very nearly the same as the percent Concentration for duplicate analyses of this fuel sample. Similarly, Samples 588, 590, 591, 593, 595-597, 599-605, 608, 610, 611, 614, 616-621, 623-631, 634, 635, 637, 638, 643 and 644 all contain between 95 and 100 percent of the number and concentration of named versus total peaks. Most other petroleum-derived JP-4 samples lie between 89 and 95 percent for these two values. Table 39 shows that the lowest percentage of Number and Concentration of named peaks is contained in Sample 606 is the one JP-5 sample. This sample has values of approximately 75 percent for the number of named peaks and 85 percent for the concentration of named peaks. This shows that there are significant numbers of components in this one JP-5 fuel that are not present in the Reference JP-4 Fuel. The next most different sample shown in Table 39 is Sample 640, is a shale-derived JP-4. This sample has values of approximately 88 percent for a number of named peaks and 92 percent for the concentration of named peaks. Details of these two non-petroleum-derived JP-4 fuels are described in the next section.


Only one sample each of a shale-derived JP-4 (No. 640) and a petroleum-derived JP-5 (No. 606) fuel were received for analysis. Tables 40 and 41 give a REP8 total listing of a database that contained duplicate analyses of these two samples. Only impurity peaks are detected in the JP-5 fuel before n-C₈-ane;
only 25 percent of the Reference JP-4 Fuel features are present between n-C₈-ane and n-C₉-ane. By contrast, over 75 percent of the features in the Reference JP-4 Fuel are present in the shale-derived JP-4 fuel. Even with these widely different samples, however, approximately 600 mg/ml was measured for the total amount present in each sample. A comparison of the two duplicate analyses using concentrations relative to the Reference JP-4 Fuel (see Table 33) show even more striking differences in the two samples.

REP6 and REP7 outputs of a data base containing only duplicate shale-derived JP-4 samples are shown in Tables 42 through 44, and the same outputs for a data base containing only duplicate petroleum-derived JP-5 samples are shown in Tables 45 through 47. These statistical summaries show how well the concentration and Kovats Index values are replicated in the duplicate analyses. A comparison of feature concentrations in each sample with feature concentrations in the Reference JP-4 Fuel can be obtained from Tables 43 and 46, which report the concentrations in terms of the concentration in the Reference JP-4 Fuel. A value of 100 for a feature in each of these two tables means that the feature measured had the same concentration as the Reference JP-4 Fuel. A more complete comparison of these two fuels can be made from data packages included under separate cover.

C. VARIABILITY OF GC/MS FEATURES IN DISTILLATE FUELS

The assessment of variability of features quantified from GC/MS data is much more difficult than the same assessment of GC/FID features because data base management programs could not be developed on the data system used for acquisition of the GC/MS data. Table 48 gives such an assessment for 10 replicate analyses of the Reference JP-4 Fuel, using this fuel as the standard reference material for quantitation. This table required approximately 16 hours to generate and type manually, where the similar assessment of GC/FID features shown in Table 19 for over three times the number of features required approximately 2 minutes for the analyst to generate. Table 48 uses the same feature names as those assigned from the GC/FID analysis, when the GC/FID and GC/MS total ion chromatogram patterns are similar. For GC/MS features that could not be correlated to a corresponding GC/FID feature, yet were estimated
to be greater than 1 mg/ml from the GC/MS chromatogram, no feature number is assigned in the feature name. Table 48 shows the average concentration of the GC/FID feature from Table 36, and the average concentration (relative to the Reference JP-4 Fuel) from quantitative GC/MS analysis of the Reference Fuel. This latter concentration is reported in units of percent relative to the Reference Fuel; therefore, each feature should have a value of 100 percent. The deviation from 100 percent and the value for the GC/MS Range, GC/MS standard deviation, and GC/MS percent relative standard deviation are measures of the reproducibilities of GC/MS feature quantitation using this approach. As can be seen from the table, values less than 10 percent are reported for most features for the percent standard deviations.

The purpose for feature quantitation using GC/MS data is not for the study of feature variability, per se, but for the confirmation that variability assessed from GC/FID data is for those features identified in Tables 21 through 28 from the detailed GC/MS analysis of the Reference JP-4 Fuel. In order to easily compare the results from GC/MS quantitation with GC/FID quantitation, the values for each feature (relative to the Reference JP-4 Fuel) determined from GC/FID data were manually written in the GC/MS quantitation tables (an example is shown in Table 20). Each of these GC/MS quantitation tables with GC/FID values is included with each fuel analysis in each fuel data package. To summarize any significant differences detected between these two outputs, a list of GC/MS quantitation ID numbers that were poorly replicated for all fuels was compiled; these are summarized in Table 49. Approximately one-half of the samples showed good correlations for over 90 percent of the features quantified by GC/MS. All fuels, with the exception of the JP-5 fuel and No. 629, showed good correlations for over 85 percent of the features. The correlation for Fuel Number 629 was good for approximately two-thirds of the features quantified.

The data for replicate analyses of fuels shown in Table 49 also indicate how serious these discrepancies are; the data can be used to estimate which ID numbers are difficult to reproducibly quantify using this approach. In general, over 90 percent of the poor correlations listed in Table 49 are
probably not real but are caused by difficulties in automatically quantifying these features from GC/MS data. A more detailed analysis of this data can be obtained from the GC/MS quantitation outputs given in the data packages for each fuel.

D. DESCRIPTION OF A SAMPLE DATA PACKAGE FOR THE REFERENCE JP-4 FUEL AND OTHER DELIVERABLES WHICH ARE SUPPLIED UNDER SEPARATE COVER

A reporting of all data obtained from this study can not be included in this final report. However, the following list shows all data that has been transmitted to the Air Force; it may be helpful in a more detailed study of the 56 fuels analyzed under this phase of this contract.

- REP8 listing of all absolute concentrations and % Rel. concentrations data for the 54 petroleum-derived JP-4 fuels data base.

- REP4 and REP5 histograms of absolute concentrations and % Rel. concentrations for all features in the 54 petroleum-derived JP-4 fuels data base.

- All mass spectra of features identified in the Reference JP-4 Fuel.

- All raw data from GC/MS analyses.

- Data packages for all 56 fuels.

The first two deliverables are described in Section II.A.1.a., Data Base Management System. All raw GC/MS raw data files were copied to an HP7920 disc cartridge supplied by MS Kyung O. Yu, Air Force Aerospace Medical Research Laboratory, Toxic Hazards Division, Toxicology Branch, Wright-Patterson Air Force Base, Ohio (AFAMRL/THT). The remainder of this section will be used to describe in detail the contents of data packages supplied for all fuels analyzed. An example of the data package for the Reference JP-4 Fuel (No. 607) is given in Volume III.
Each data package consists of approximately 80 pages, numbered consecutively. The first three digits of the page number is the Fuel Number, and the last three digits range consecutively from 001 through the last page number of the package. The first page contains a summary sheet describing the contents of the data package. This was used by MRC personnel to compile each data package; it includes the detailed file names associated with GC/FID and GC/MS data files. Each type of data is separated by variously colored sheets of paper to simplify finding particular sections. The following are contained in each fuel data package:

1. Duplicate GC/FID chromatograms.

2. Duplicate processed data file outputs obtained from the initial analysis of the duplicate raw data files.

3. Duplicate tables for retention time to Kovats Index correlations.

4. Duplicate processed data file outputs where concentrations of features are in absolute units (mg/ml).


6. Duplicate processed data file outputs where concentrations are in amounts relative to the Reference JP-4 Fuel.


8. GC/MS chromatogram.

9. GC/MS Quantitation output.

Each duplicate GC/FID chromatogram is shown in four pages so that the C_3-C_7 region is on one page, the C_7-C_10 region is on the next page, the C_10-C_13 region is on the next page, and the C_13 through impurity Number 3 region is shown on the final page. The broad square peak at approximately 8.5 minutes is
the CH₂Cl₂ solvent; the peak at approximately 106 minutes is the anthracene-d₁₀ internal standard. The duplicate processed data file outputs show all retention times, areas, and amounts of all peaks detected from processing the raw data shown in the GC/FID chromatograms. Only Kovats marker compounds (indicated with a "$" as the first character), CH₂Cl₂ solvent, impurities and the internal standard (indicated by a "#" as the first character) are named. Duplicate tables for retention time to Kovats Index correlation show the interpolated values of Kovats Indices for each detected peak, using Kovats Marker compounds identified with a "$" as the first character as end points of the interpolation.

The duplicate processed data file outputs that follow the retention time to Kovats Index correlation tables are produced by analyzing the raw data shown in the GC/FID chromatograms with the DFABME Method. This Method, described in Section II.A.1., Feature Selection for Reference JP-4 Fuel, uses the average Kovats Index from 14 replicate Reference JP-4 Fuel analyses to define the Kovats Index of each feature. The retention times printed out in this output are in units of Kovats Index/10, and the concentrations are calculated using a relative response factor of 1.0. This results in feature concentrations being calculated in absolute amounts (mg/ml).

The data base statistics for the concentrations measured in the duplicate analyses is the REP6 output. The percentage of standard deviations greater than 10 percent are circled to point out features that exhibit poor replicability.

The duplicate processed data file output, in which concentrations are calculated relative to the Reference JP-4 Fuel, uses the DFPCNT Method for analysis of the raw data shown in the GC/FID chromatograms. However, relative response factors for each feature in the Reference JP-4 Fuel were calculated so that a relative value of 100 percent would be obtained for the concentrations of each feature in the Reference Fuel. The data base statistics for the concentration of features in this pair of processed files also are output using REP6. The GC/MS chromatogram is output in four pages in such a way that the
C₈-C₇ region is shown on the first page, the C₇-C₁₀ region is shown on the second page, the C₁₀-C₁₃ region is shown on the third page, and the C₁₃-anthracene-δ₁₀ region is shown on the last page.

The last table in the fuel data package is the output from quantitative GC/MS analysis of the fuel. The relative response factors for each feature quantified in the GC/MS fuel analysis are chosen so that the concentration of each feature is 100.00 percent relative when the Reference JP-4 Fuel is analyzed. The corresponding average feature concentration values from GC/FID analysis of the fuel and normalized to the Reference Fuel (shown in Item 7 above), are manually written into this table to the right of the computer output value for concentration. GC/MS data which are manually calculated are shown in the table to the left of the calculated concentration value.
SECTION IV

CONCLUSIONS AND RECOMMENDATIONS

A. CONCLUSIONS

The following general conclusions can be drawn from the present study:

1. The ability of the automated GC/FID laboratory data system to reproducibly identify fuel features is very good.

2. The automated system identified 90 percent of the features in 12 or more of the 14 replicate Reference JP-4 Fuel analyses. In those cases where the feature was identified in fewer than 12 of the replicate analyses--typically in 2 to 6--the concentration of the individual feature was low (approximately 0.1 mg/ml) so that the sum of all such poorly identified features was 6.1 mg/ml, or only 1 percent of the total amount of material in the fuel.

3. The ability of the automated GC/FID laboratory data system to generate precise Kovats Indices is very good.

4. Typical values for percent relative standard deviations of Kovats Indices for the approximately 300 features in all of the JP-4 fuels data bases were in the $10^{-4}$ to $10^{-3}$ range. For the n-C10-ane region, this corresponds to a Kovats Index range of 0.1 to 1.0 KI unit. The n-C10-ane component elutes at a feature retention time of 54 minutes, and the value of $10^{-4}$ to $10^{-3}$ for percent relative standard deviation corresponds to a relative standard deviation of 0.005 to 0.05 minutes. This type of precision is not unusual from injection to injection; however, the fact that these values were obtained for a set of samples that were analyzed over a 6-week period of time shows the extent to which the present analysis protocol and capillary chromatographic instrumentation can be used to provide long-term stability in analyzing complex mixtures.
5. The ability of the automated GC/FID laboratory data system to reproducibly quantify the identified fuel features is very good.

6. For the 14 replicate analyses of the Reference JP-4 Fuel, the relative standard deviation of the feature concentrations was approximately 10 percent for over 95 percent of the nearly 300 features.

7. The total amounts of chromatographable components in the 54 fuels were constant and in agreement with the total amount in the Reference JP-4 Fuel, within the precision of the analyses.

8. For the Reference JP-4 Fuel, the average total amount of chromatographable components based on 14 replicate analyses was 607 mg/ml, with 4.1 percent relative standard deviation. For 54 fuels, the average of the total amounts was 601 mg/ml, with 11.7 percent relative standard deviation.

9. Significant variabilities were found in the concentrations of individual features (i.e., in the composition) in individual fuels.

10. Whereas the 14 replicate analyses of the Reference JP-4 Fuel yielded relative standard deviations of approximately 10 percent, the 54 petroleum-derived JP-4 samples produced relative standard deviations of 50 to 70 percent for the vast majority of the features. Thus, the latter variabilities are due to sample variations rather than analytical imprecision.

11. The Reference JP-4 Fuel chosen for this study appears to be a good qualitative standard for the 54 fuels.

12. Greater than 90 percent of the total numbers of features and greater than 98 percent of the total concentration of features could be accounted for in 38 of the 54 fuels when this Reference Fuel was used to identify which features to quantify. The two that deviated most significantly from this percentage were a petroleum-derived JP-5 and a shale-derived JP-4 fuel. The fact that it is also a good quantitative standard can be seen from the REP6 output which shows the average concentration of each feature when calibrated with respect to
the Reference Fuel. Approximately 236 features yielded values between 50 and 150 percent relative to the Reference Fuel. If all samples were the same as the Reference Fuel, this average amount would be 100 percent for each feature.

13. The majority of the features identified by the automated GC/FID laboratory data system can be correlated with features obtained in a GC/MS analysis.

14. Even though the GC/FID analysis occurs with atmospheric pressure at the end of the capillary column, in contrast to the $10^{-8}$ atm. pressure at the end of the column in the GC/MS analysis, approximately 75 percent of the features could be correlated in the two procedures. The biggest problem was the difficulty in correlating the remaining 25 percent of the features. This difficulty evidently arises because the different column end pressures in the two techniques caused different classes of compounds to have slightly different retention times (either longer or shorter) relative to the normal alkanes. When large numbers of closely spaced components are eluting as in the C-11 to C-12 region where the majority of the feature correlation problems occurred, slight shifts of partially overlapping components yield substantial differences in the feature pattern observed.

15. A large number of the individual components in the Reference JP-4 Fuel features could be identified by manually assisted computer library search techniques from the GC/MS data; the use of relative boiling point indices (RBPI) and Kovats Indices proved surprisingly valuable in making the identifications.

16. The computer search of the 30,000-compound library of 70-eV mass spectra provided the starting point. The possible matches were substantially narrowed by considering the calculated boiling points (RBPI) and the Kovats Indices in comparison with the literature values for the same or similar compounds. This information was combined with manual interpretation of the remaining mass spectra to make the final assignment. Specific compound identifications became increasingly difficult as the molecular weight ranges increased, but the identification of compound class (i.e., branched alkane,
substituted benzene, etc.) remained fairly certain until late eluting components were encountered. The use of 70-eV mass spectra throughout the study was preferred to other ionization procedures, such as chemical ionization or low-energy electron impact, for several reasons. First, 30,000 compounds are available in the 70-eV NBS/NIH library. Second, reproducibility, both quantitatively and qualitatively, is high with 70-eV spectra. Third, alternative procedures generate their own unique problems: low-energy electron impact leads to widely varying sensitivity from one compound to the next, which could completely distort the feature pattern in the GC/MS system relative to GC/FID; and chemical ionization leads to adduct ions (molecular ion + 15 amu, molecular ion + 29 amu, etc.) which can make interpretations more difficult, rather than simpler, when complex mixtures of unknowns are involved.

17. The fuel component identifications in this study agree well with those in other studies.

18. Aside from a very few obvious misidentifications in the study of Smith, et al., the present identifications differ from those reported by Smith in only a small number of cases, and then primarily in terms of the isomers involved, but not in the compound classes. All studies of hydrocarbon mixtures, like the present one, show increasing numbers of "unknown" or "unidentified" designations with increasing molecular weights. Even identifications of chemical class become very difficult toward the end of the chromatogram.

19. The variability of GC/FID features is actually caused by the specific compound identified for that feature by GC/MS. Thus, owing to the long-term stability of the instrumentation, one-time identification of features by GC/MS can be used in conjunction with the automated GC/FID analyses for a large number of samples, to specify which particular components are varying notably in concentration.

20. Eighty-five selected features were quantified in all of the fuels by GC/MS, using the intensities of two or more ions selected because they were characteristic of the components identified. The variations in concentrations
of these components based on ion intensities correlated well with the variations in GC/FID feature concentrations for over 85 percent of the features studied.

21. Because the variability of fuel features by automated GC/FID analysis is highly reproducible with respect to retention time (KI) and concentration, and because the feature variabilities correlate well with specific compound variations via GC/MS, the automated GC/FID system provides a rapid, relatively inexpensive and reliable method of identifying the specific components causing fuel variabilities. This information may be used to establish correlations between fuel components and specific fuel properties.

B. RECOMMENDATIONS

Based on the results of this study, the following recommendations are offered:

1. The method of automated identification and quantitation of GC/FID features developed in this program should be used industry-wide to characterize the jetoleum-derived distillate fuels being supplied to the Air Force.

2. Each supplier of distillate fuel should provide with each lot of fuel an analytical report of the type presented in this report for each fuel. The suppliers' reports would serve as ongoing documentation of the composition of the fuels and would therefore be a valuable quality control feature.

3. The approach of chemical feature identification should be exploited to the fullest to improve the physical properties and performance characteristics of the fuels.

4. The specific chemical components of the fuels, and the relative amounts of each present, are the sole factors determining the characteristics of the fuel. Such gross properties as engine performance, engine wear, fuel storage problems, environmental pollution, and any other concerns must be related to the individual components in the fuel. To correlate gross properties with
specific fuel components, factor analysis (pattern recognition) should be used. The variabilities in gross properties of interest should be examined for correlations with the variabilities in feature profiles, to find which features enhance desired characteristics or exacerbate problems. Multidimensional factor analysis has proven to be an extremely powerful tool in revealing key factors in very complicated environmental and medical problems, and it should prove equally valuable in this situation. Other data, such as infrared spectrum profiles, could be combined with the feature variability information to yield additional opportunities for correlations.

5. The method of automated feature identification and quantitation developed in this study should be used from the outset to evaluate all shale-derived fuels that are proposed as substitutes for the petroleum-derived fuels.

6. The shale-derived fuels will be even more complex than the already complicated petroleum-based fuels because of the oxygen-, sulfur-, and nitrogen-containing species that they may contain. In such a system, it will be critical to develop a data base on fuel feature variability that can pinpoint those components responsible for characteristics of concern.

7. The shale oil study would need to start from the beginning, with a complete characterization of the individual features by a detailed GC/MS analysis similar to the one conducted in this study. In the present study, the GC oven temperature program was established to afford maximum feature separation with a reasonable minimum of run time, especially in the earlier eluting features. The program worked well for that purpose. However, because of the possibility of obtaining excellent interlaboratory correlations of Kovats Indices and relative boiling point indices, it would be highly desirable to perform the shale oil (and any similar) analysis using a linear temperature program with no initial temperature hold. For a mixture with the approximate complexity and volatility of the JP-4 fuel, a heating rate of 1°C/min, starting from -30°C would provide excellent information. This would permit good comparisons with other linearly programmed analyses or isothermal analyses because the harmonic mean temperatures for eluting components would be readily calculated and meaningful.
The use of feature variability data to monitor newly developing shale oil sources could help to solve fuel performance problems at an early stage, and perhaps even suggest modifications in the shale oil recovery and refining processes while they are still being developed.
REFERENCES


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