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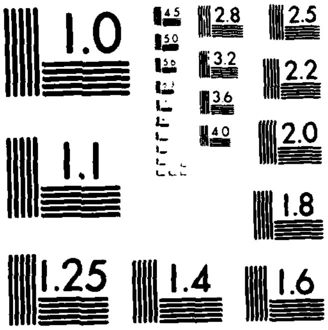

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Part II

TANDEM MASS SPECTROMETRIC ANALYSIS (MS/MS) OF JET FUELS
PART II: QUANTITATIVE ASPECTS OF DIRECT MS ANALYSIS

H.L.C. Meuzelaar, W.H. McClennen

Biomaterials Profiling Center
391 S. Chipeta Way, Suite F, Research Park
Salt Lake City, Utah 84108

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Paul C. Hayes Jr.
Paul C. Hayes Jr.
Project Scientist

A.V. Churchill
A.V. CHURCHILL, Chief
Fuels Branch

FOR THE COMMANDER

Robert D. Sherrill
ROBERT D. SHERRILL, Chief
Fuels and Lubrication Division
Aero Propulsion Laboratory

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cts of the direct mass spectrometry (MS) determination of
es in jet fuels are discussed. Low energy ionization and
over the complete sample vaporization process are found to be
ent parameters for direct MS analysis of liquids with boiling
an 250°C and high naphthenic compound content. The derivation
mixtures from complex fuel samples by liquid chromatography
extraction techniques is shown to be a viable alternative
and costly production of appropriate standards from individual

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compounds. As discussed in this report, advanced computer techniques in pattern recognition and multivariate statistical analysis provide powerful options for data processing beyond the procedures of ASTM method D2789-81 for gasoline analysis.

FOREWORD

This is Part II, "Quantitative Aspects of Direct MS Analysis", of a larger study, "Tandem Mass Spectrometric Analysis (MS/MS) of Jet Fuels", that investigated the feasibility of tandem mass spectrometry (MS/MS) as a direct MS technique for the determination of hydrocarbon classes in high naphthenic jet fuels. Part I dealt with the qualitative capabilities of these techniques.

The research effort was sponsored under the United States Air Force contract F33615-84-C-2412 and Project Funds 24801200, with Geo-Centers, Inc., Newton Upper Falls, Massachusetts (GC-416-84-004). This work was administered through the Scholarly Research Program of the Fuels and Lubrication Division, Aero Propulsion Laboratory (AFWAL/POSF), Air Force Wright Aeronautical Laboratories, Wright-Patterson Air Force Base, Ohio. Ms Eva M. Conley was the Air Force contract manager and Mr Paul C. Hayes, Jr was the Air Force task project scientist.

This work reported herein was conducted in the Biomaterials Profiling Center (BPC) of the University of Utah, Salt Lake City, Utah under the direction of Dr Henk L.C. Meuzelaar The research was performed during the period of July 1984 through September 1984 and the report released in January 1985.

Biomaterials Profiling Center wishes to express their appreciation to Dr Herbert R. Lander for his assistance with this project. The authors gratefully acknowledge the samples and related information supplied by P.C. Hayes, Jr, Lt R.C. Striebich and Tim L. Dues in the Aero Propulsion Laboratory at Wright-Patterson Air Force Base, Ohio. We further acknowledge the contributions of: J.M. Richards, Q.D. Lee, and T.R. Sharp for their assistance in instrument operation; W. Windig and T. Schurtz for invaluable aid in the data analysis; and other BPC personnel for cooperation in the preparation of this report.

Geo-Centers, Inc. wish to express their appreciation to Ms Eva M. Conley for her help and assistance in overcoming administrative problems with this Task 4 of Contract F33615-84-C-2412.

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SECTION I

INTRODUCTION

The purpose of this project has been to develop and partially evaluate a fast, simple, and direct mass spectrometric method for the determination of compound classes in various jet fuels. Our previous report (1) described the basic experimental techniques and discussed primarily qualitative aspects of the data analysis. This report is an extension of the previous report and focuses on quantitative aspects of the data processing with some further discussion of pertinent procedures and instrumental parameters. The conclusions and recommendations derived from the entire project are presented at the end of this report.

SECTION II

EXPERIMENTAL

1. SAMPLE PREPARATION

The origin and nomenclature of the samples was presented earlier (1). The shale derived JP-4 fuel (SH4) (Sample Number #83-POSF-056) was perhaps the most complex mixture of aliphatic and aromatic hydrocarbons and is therefore used as an example several times in this report. Sample SH4 was fractionated on a milligram scale by open column liquid chromatography (LC) using ideas adapted from a thin layer chromatography (TLC) separation by Harvey et al. (2).

The small column was made from a Pastuer type disposable pipet of approximately 2 ml total volume dry packed with 0.8 gm silica gel (<125 µm) sieved from 60-200 mesh ("Baker Analyzed" reagent). The silica gel had been activated at 175°C overnight prior to use. The tip of the pipet was flame drawn to form a short (2 mm) capillary of approximately 0.1 mm i.d. at the bottom of the column. Two layers of about 0.1 gm washed and ignited sea sand (Fisher Chemical S-25) were placed at the top and bottom of the silica gel to prevent clogging of the outlet and minimize the solvent disturbance of the top of the column bed. The 24 mg of SH4 was placed on the top of the dry column and eluted with approximately 2 ml pentane followed by approximately 1.5 ml of pentane and ethyl ether (5/1 v/v). Fractions 1 through 5 comprised the sequential pentane eluant of approximate volumes 0.4, 0.15, 0.25, 0.37 and 0.56 ml. Fraction 6 contained the rest of the eluted solvents.

2. MS ANALYSIS

A schematic diagram of the basic mass spectrometer as described in our first report (1) is shown in Figure 1. For the project, described herein, the Curie-point pyrolysis MS was adapted for simple direct probe analysis of the jet fuel liquids as shown in Figure 2. General heating of the inlet is provided by the heated ceramic tube which is maintained at 220°C. However, this source alone heated the sample in the glass capillary holding tube too slowly, requiring more than 5 minutes for

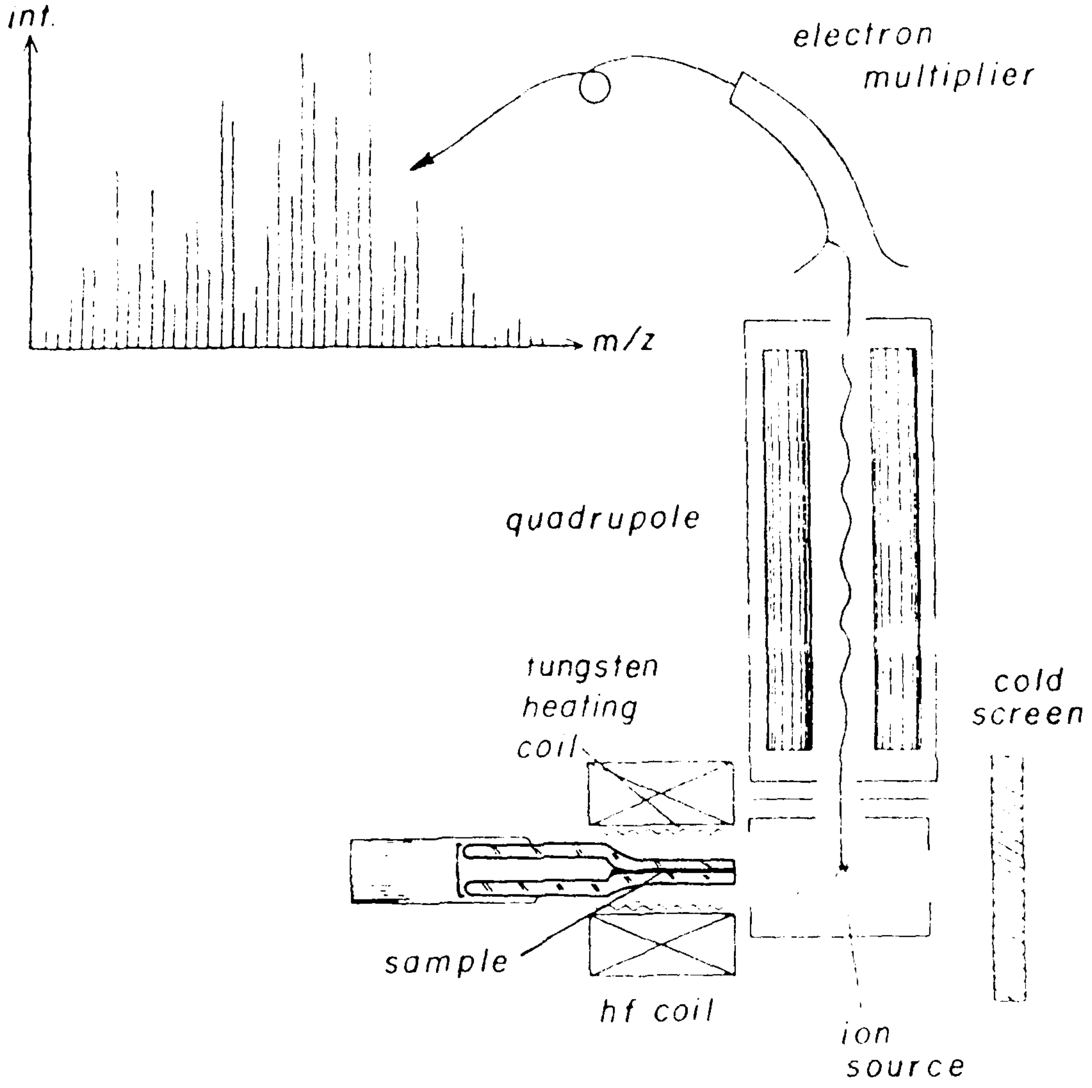


Figure 1. Schematic diagram of MS instrument for direct liquid analysis.

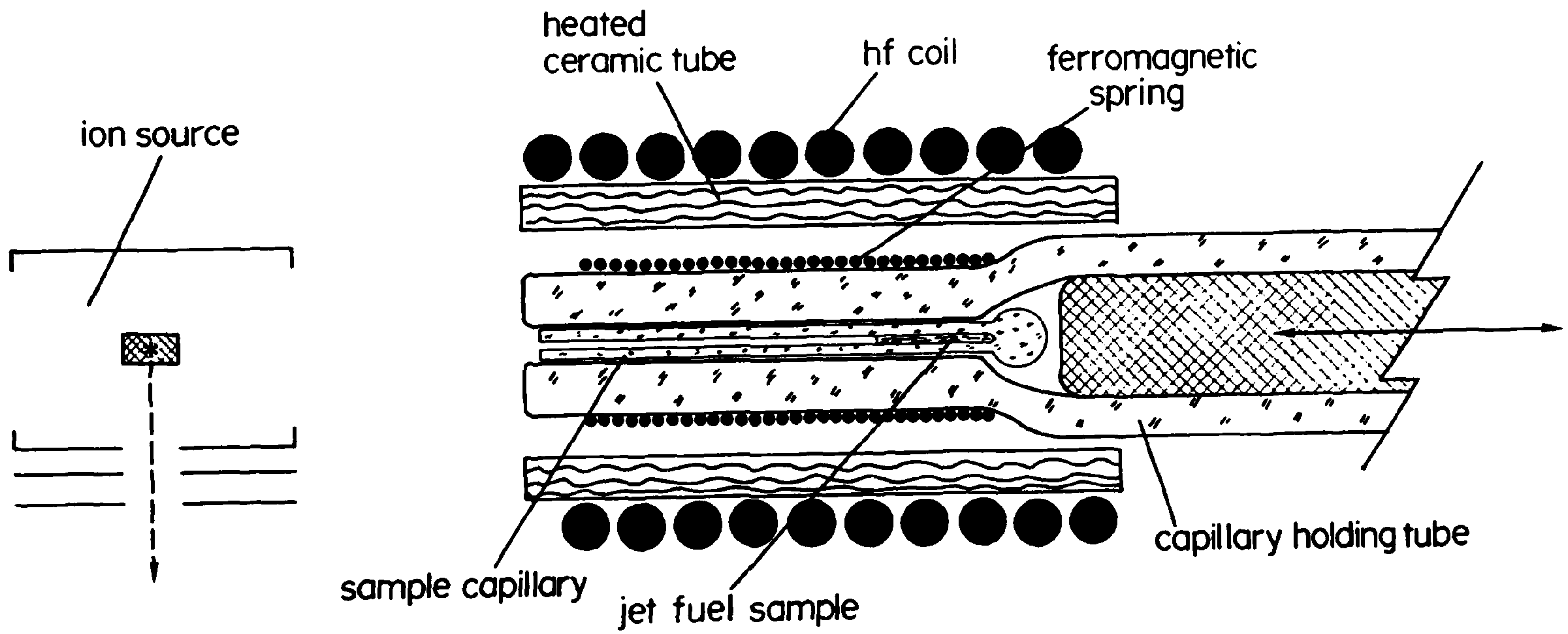


Figure 2. Detailed schematic drawing of the capillary inlet system adapting the Curie-point pyrolysis MS for use with liquid jet fuels.

total sample evaporation. Thus the ferromagnetic spring, which could be heated very quickly by the Curie-point high frequency, was placed on the capillary holding tube. As shown in the previous report, this enabled complete evaporation of 16 nl of jet fuel in less than 3 minutes. The insulating effect of the glass capillary holding tube makes the exact temperature profile of the jet fuel sample unclear. However, since the ferromagnetic spring is heated most intensely by the high frequency at the center of its length, it seems most likely that the liquid column is heated from its vapor interface end toward the closed end of the capillary. This sample introduction technique was used on nearly all of the direct MS (not MS/MS) analyses previously reported and is discussed later in this report as an important part of a general MS procedure. Other data sets specifically discussed in this report were run somewhat differently.

The analyses run at different electron energies were all performed on a single larger sample without heating. A 0.7 μl sample in a 0.2 mm i.d. capillary at ambient temperature provided an essentially constant vapor composition for varying the ionization energy. Similar sized samples were run with heating for the MS/MS analyses to give higher intensity signals over still reasonably short analysis times (10 to 20 min.).

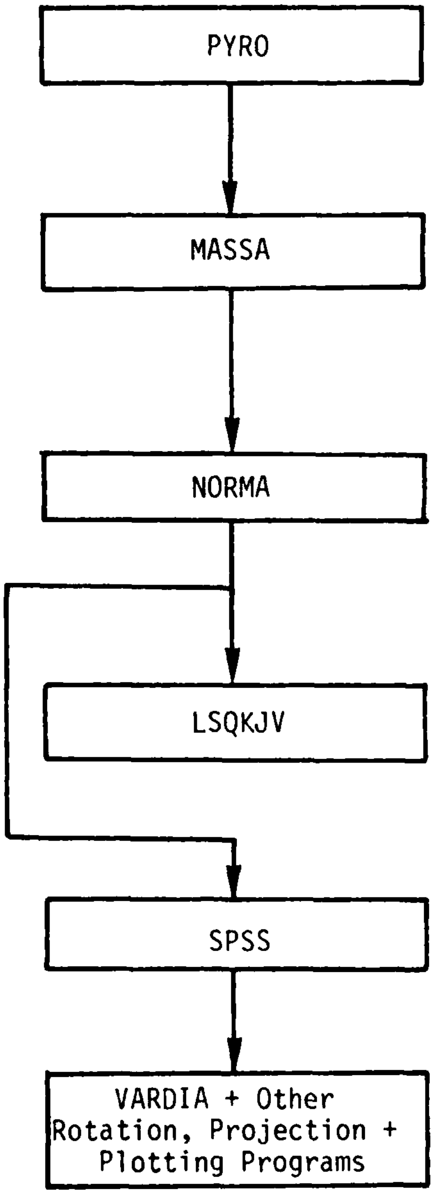
The fractionated silica gel LC samples were often run with significant amounts of solvents. Solutions even as dilute as 5% or less were effectively run to assay the relative amounts of various compound classes present in eluted fractions. The technique was also used for detecting the presence of residual solvent during efforts to produce a pure tetralin fraction from the 30% aromatic sample (30%) (83-POSF-0801). Dilute pentane solutions were generally too volatile to easily sample with the micropipette capillaries. The SH4 pentane fractions described above were thus evaporated nearly to dryness and then redissolved in hexanes for direct MS analysis via the capillaries.

3. DATA PROCESSING

Some of the computer programs used for processing the mass spectrometric data are described in Table 1. PYRO, MASSA, NORMA and VARDIA

TABLE 1

FLOW OF DATA PROCESSING OPERATIONS FOR DIRECT PROBE MASS SPECTRA OF JET FUELS



PROGRAMS	FUNCTIONS
PYRO	Start Pyrolyzer. Scan mass spectrometer. Count ions. Sum spectrum scans. Plot raw spectra.
MASSA	Identify peak maxima. Calibrate mass scale. Correct mass scale slope and offset. Plot bar graphs.
NORMA	Change object status. Change feature status. Calculate normalization factors. Calculate variances. Plot feature/feature diagrams. Format file for SPSS.
LSQKJV	Set mass range. Eliminate unwanted peaks. Read sample and reference spectra. Compare sample and reference spectra. Minimize sum of squares of residuals. Normalize to 100% composition.
SPSS	Factor analysis. Discriminant analysis. Plot discriminant scores.
VARDIA + Other Rotation, Projection + Plotting Programs	Calculate and plot variance diagrams. Calculate and plot component spectra. Calculate ternary composition planes. Project outside mixtures onto ternary plane.

were developed at the University of Utah Biomaterials Profiling Center and are described elsewhere (3,4). LSQKJV was obtained from the Colorado School of Mines (5) and operates on the theory and techniques of Fausett and Weber (6). SPSS stands for the Statistical Package for the Social Sciences (7) and presently serves as our main source of multivariate statistical analysis (MVSA) routines.

Preliminary or exploratory MS analyses such as MS/MS spectra or many LC fractions merely proceeded through the first two programs to the production of bar plots. Simple visual evaluation was generally sufficient from that point.

Samples for quantitative or more careful qualitative work were taken through more extensive data processing. The spectra of 19 samples analyzed in triplicate and described in the previous report went through two different iterations of NORMA followed by numerous runs through SPSS and a great variety of further calculations.

Spectra from all 19 samples were run through the LSQKJV program using the three "pure" components (naphthalenes, tetralins and decalins) as the reference spectra. The 12 blended mixtures and four "unknowns" were each compared to the reference compounds both as individual spectra and as spectra averaged from the three replicate analyses. The LSQKJV program was limited to a 150 mass range which was chosen as from m/z 66 to m/z 215. This range included nearly all of the 100 NORMA "most specific peaks" along with some peaks of zero intensity.

The LSQKJV program works by minimizing the sum of the squares of the residuals (z) or as explained by Fausett and Weber (6), by minimizing

$$z = \sum_{j=1}^{m} \left(\sum_{i=1}^{n} x_i r_{ij} - s_j \right)^2$$

subject to:

$$\sum_{i=1}^{n} x_i = 1$$

where m is the number of m/z's used; n is the number of reference compounds; r_{ij} is the relative abundance of the ions at the jth m/z in the normalized standard spectrum of the ith reference compound; s_j is the relative abundance of the ions at the jth m/z in the normalized sample spectrum; and x_i is the relative concentration of the ith reference compound ≥ 0. In the process of solving this matrix a kind of dummy reference spectrum is generated which carries along a relative abundance of unaccounted for mass intensities. After normalization of these r_{ij}'s, the optimized relative concentration of this dummy spectrum is another kind of "residual" which is a measure of the correlation or goodness of fit of the solution. This "residual", which is the meaning used later in the discussion, has (at least) three possible sources. The first is other components, or compounds in the sample which were not included in the reference spectra. The second source is statistical noise which is always present in all experimental spectra mass intensities and makes a perfect fit impossible. A third source is systematic errors in sample or reference spectra which may reduce the goodness of fit and the result accuracy in some explainable manner. In the situation where the sample has ion intensities totally absent from the reference spectra, case one of other components probably applies. Otherwise however, evaluation of whether a "residual" represented an additional component or simply a measure of correlation was subject to educated interpretation.

SECTION III

RESULTS AND DISCUSSION

1. INSTRUMENT PARAMETERS

Several aspects of the direct MS analyses performed in this project are perhaps different enough from routine analyses by others to warrant some discussion. In particular, these areas include the method of sample introduction, signal averaging of repetitive individual scans, and the use of low energy electron ionization. Although not specifically discussed, these operating differences are within the general scope of the "Standard Test Method for Hydrocarbon Types in Low Olefinic Gasoline by Mass Spectrometry" ASTM D2789-81 (8). The new procedures would require independent calibration but should result in more accurate analysis of the higher boiling and chemically more complex jet fuels.

Sample introduction is critical to any MS analysis and the ASTM method D2789-81 does caution against possible large errors with small concentrations of naphthenics. Even in the typically used heated expansion volume (HEV), samples with broad boiling ranges might vary significantly in the vapor composition seen by the ionization source during the course of complete sample removal from the expansion volume. The higher boiling and especially more aromatic naphthenics would tend to initially be reduced in vapor concentration due to a higher amount of adsorption on the HEV walls. The capillary tube technique we used minimized the surface area for sample interaction but still showed a change in relative peak intensity from the initial low temperature vapor to the maximum sample evaporation rate as shown in the time profile of Figure 3. In both cases it would appear critical that the final spectrum be the signal average of repetitive scans taken over the full volume of sample vapor or liquid. The general HEV single scan technique might attempt to compensate by only sampling the initial HEV vapor of both unknown and standard and allowing identical calibration conditions to compensate for vapor and liquid composition differences. However, many much higher boiling compounds would have to be added to the list of standards used for gasoline in D2789-81 to allow accurate HEV analysis

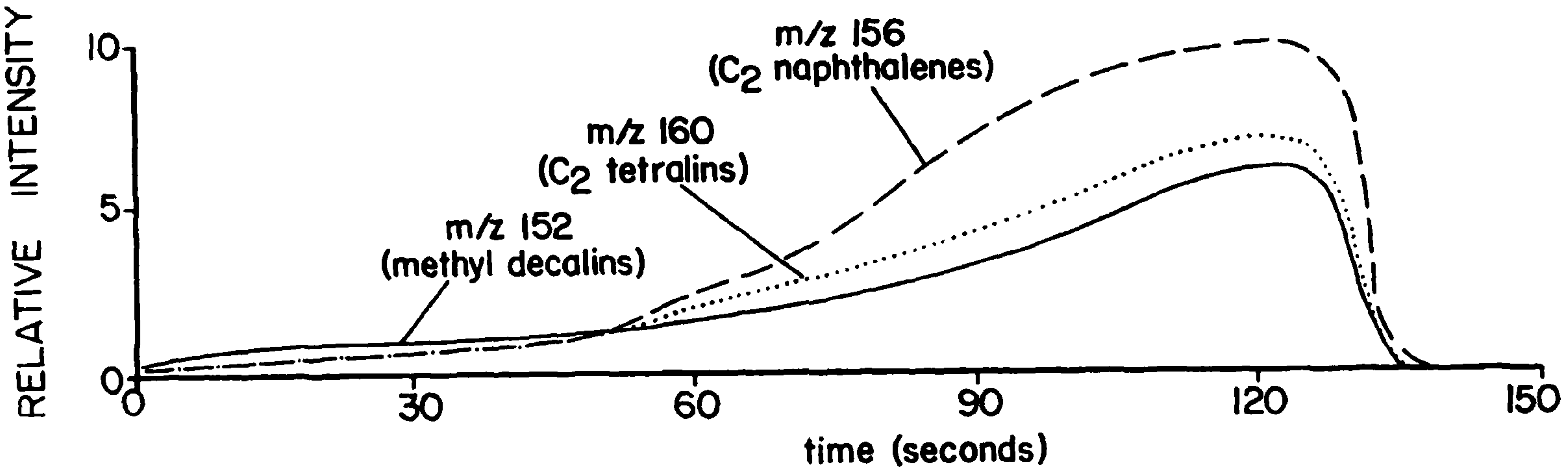


Figure 3. Time profile of ions at m/z 152, 156, and 160 from analysis of 50% decalins, 25% tetralins and 25% naphthalenes liquid sample.

of the higher boiling fuels. Since our technique utilized signal averaging over the evaporation of the complete sample liquid, sample and standard boiling range differences could well be less critical as long as pre-analysis liquid evaporation is minimized. Time zero in Figure 3 indicates the start of MS scanning and sample heating after taking 15-20 s to introduce the sample into the MS high vacuum. As can be seen from the total signal area of the ions in Figure 3, the pre-analysis sample losses by this technique are relatively insignificant.

Figure 4 shows three steps in the variation of the SH4 spectrum with electron energy. The increase in relative intensity of the highest peak from 10 to 50 to 200 arbitrary units at the 10, 12, and 20 eV ionization energies in our instrument could be seen. The energy related increase in sensitivity levels off at between 50 and 70 electron volts which is why most electron ionization spectra are run at these energies. However, besides overall intensity, the most prominent change is the dramatic increase in the ionization of aliphatic compounds relative to aromatics. At 10 eV the aromatic alkylbenzene series m/z 92, 106, etc. and indan/tetralin series at m/z 132, 146, 160, etc. dominate the spectrum because of their greater ease of ionization. As the energy increases, the aliphatics, as shown by the monocyclic series of m/z 56, 70, 84, etc., begin to ionize more efficiently and quickly take over the spectrum because of their higher concentrations. However, the higher energies produce higher amounts of fragmentation as well as ionization as seen in the accelerated increase in odd mass ions at m/z 57, 69, 91, 105, and 131 relative to the primarily molecular ions at m/z 56, 70, 92, 106, and 132. Although the higher energies may not actually reduce most of the molecular ions, their smaller relative heights make them harder to detect and complicate the calculation of carbon numbers and average molecular weights. This can be seen in the change in relative peak heights within each series, e.g., monocyclics maximum changing from m/z 112 to 70 to 56 and the alkylbenzenes from 120 to 106 are both due to increasing fragmentation. Although these effects are somewhat compensated for in ASTM method D2789-81, the fragmentation effects are made worse by the higher boiling ranges of the jet fuels.

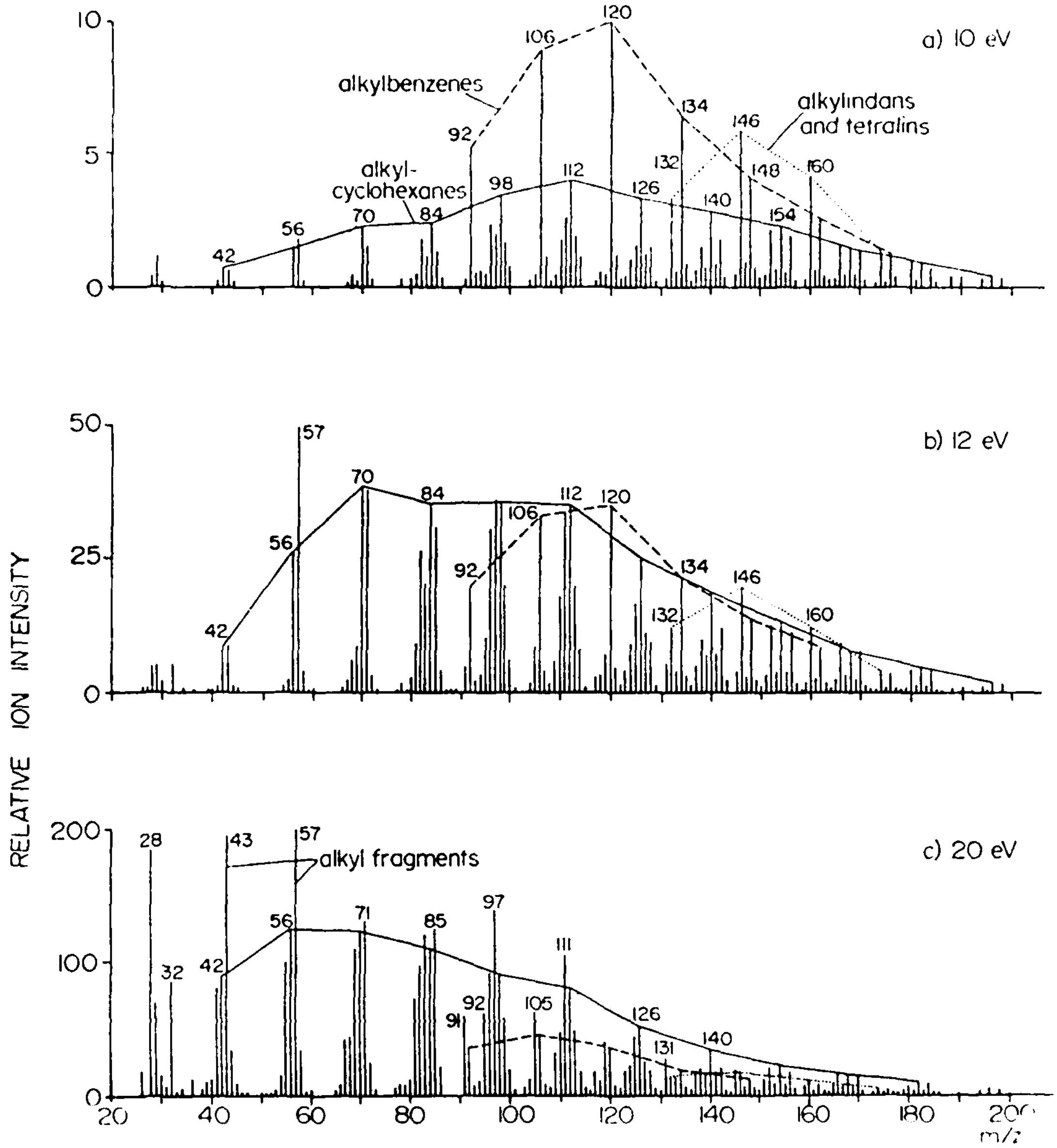


Figure 4. Mass spectra of the shale derived JP-4 (SH4) at electron ionization energies of a) 10 eV, b) 12 eV and c) 20 eV.

In all, low energy electron ionization should give better representation of molecular ions but with serious loss of signal. However, since the hydrocarbon group-types in these liquid samples have no sensitivity problem, the reduced signal intensity at lower energy is not a deterrent. Another potential problem is the loss of spectrum reproducibility due to small changes in the electron energy at low settings. This was apparently a significant problem in our test data set when the instrument was twice shut down and not allowed to fully reequilibrate in the course of replicate analyses. Better regulation of a low energy ion source may become possible within the near future through the use of photoionization techniques.

Another group of instrument parameters which should be discussed are those involved in MS/MS analysis. Figure 5 shows a daughter ion spectrum of the molecular ion at m/z 152 in the 2% aromatic sample compared to the low voltage GC/MS spectra of individual GC peaks from the same sample (analyses described further in the first report). The MS/MS spectrum can be seen to be a composite of these two compounds plus others of mass 152 minus the impurities present at m/z 134 and 154 in the GC peak of Figure 5b. This suggests again the tremendous qualitative power of MS/MS in adding a separation dimension to the direct MS technique. This MS/MS capability is quite useful in distinguishing between overlapping compound classes such as the alkanes, which show abundant lower mass MS/MS fragmentation, and the naphthalenes which show almost no major daughter peaks other than simple loss of alkyl substituents. However, we currently lack the advanced data system which would permit the level of data processing we have done on the simple direct MS spectra of this report. Thus, discussion of MS/MS in this report is limited to a brief comparison to other class separation techniques such as LC in the data processing section.

2. STANDARDS

An essential requirement for direct MS quantitation is a set of accurately known standards for calibration of the instrument response. Ideally the standards would be known mixtures of compounds or classes of compounds either identical to those in the unknown or at least of very

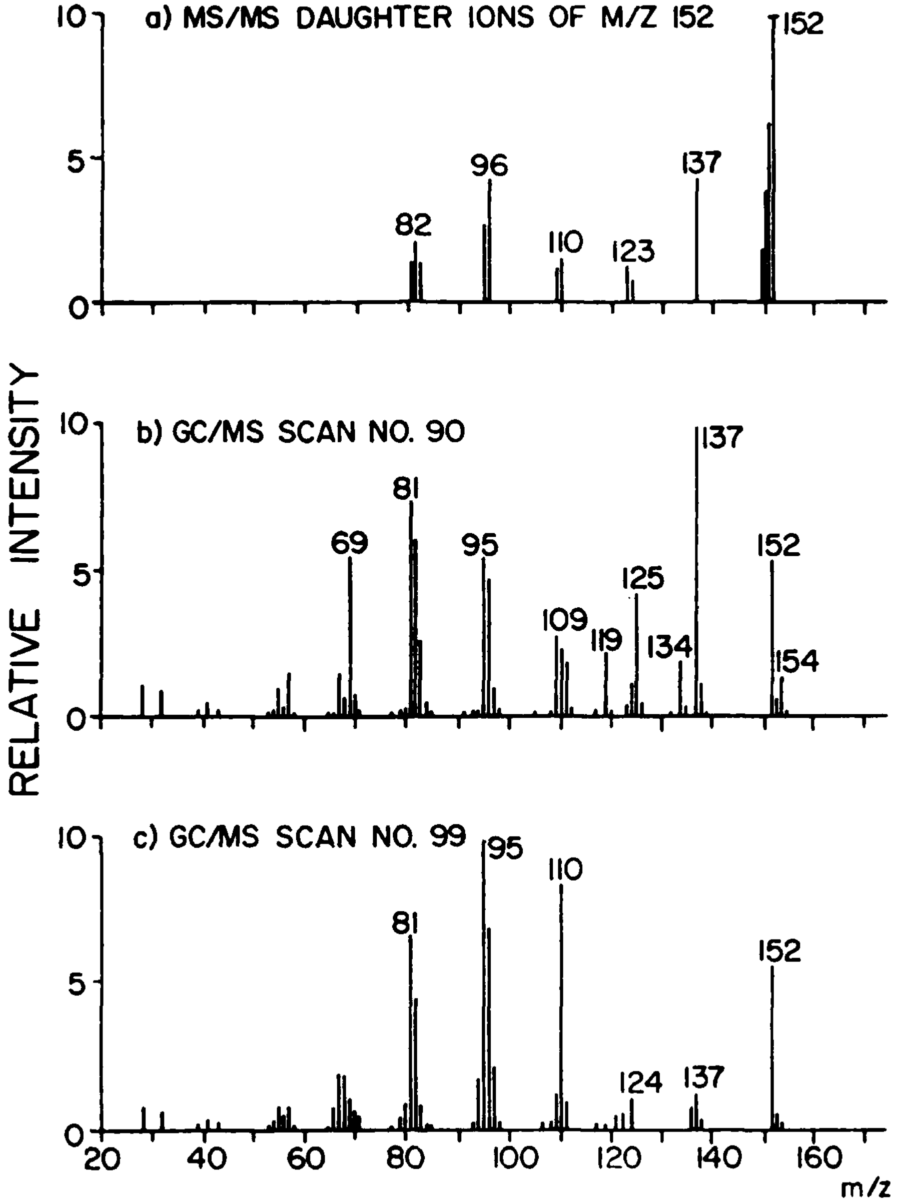


Figure 5. Comparison of the MS/MS daughter ion spectrum of m/z 152 to two low voltage GC/MS spectra. Note that the MS/MS fragmentation pattern of the methyldecalin molecular ion mixture contains features from each of the individual isomer patterns while excluding the impurity ions at m/z 119, 134, and 154.

similar response. In the ASTM method D2789-81 for gasoline (8) a mixture of nine pure compounds is used as a direct reference standard with basic response calibration factors generated using 79 compounds with up to nine carbons. However, gasolines typically only have compounds of up to 12 carbons while jet fuels may have compounds with 15 or more carbon atoms. The higher molecular weight range brings with it a very rapidly broadening variety of compounds and classes of compounds with overlapping series of molecular ions. Although a reference standard mixture of pure compounds is a useful idea, the relative number of possible hydrocarbons which are available as pure chemicals decreases dramatically above 9 or 10 carbons. Thus, general calibration mixtures of pure compounds become more and more difficult to extend from the gasoline to fuel oil ranges, especially when the more widely varied feedstocks are considered. These arguments seem to lead to the utility of class standards derived from the fuels themselves.

The fundamental tool for the isolation of classes of compounds is liquid chromatography (LC). Several ASTM methods (9,10) describe procedures for assaying and separating fractions of saturates, olefins, and/or aromatics using activated silica gel open columns. These procedures enhance their compound class resolution through the use of very long thin columns and essentially do not use any carrying solvent. However, the microscale procedure described in this report was a crude version of the thin layer chromatography (TLC) method (2) which seems to demonstrate the ultimate silica gel chemical class separation. The TLC method using non-polar n-pentane as the eluting solvent claims essentially complete separation of the following 7 fractions: n-alkanes, branched and cyclic hydrocarbons, alkenes, monoaromatics, hydroaromatics, diaromatics, and polyaromatics.

The 12 eV spectrum of the complex SH4 sample is shown in Figure 6 with the main molecular ion series indicated. Figures 7a-f show the spectra for the six SH4 fractions eluted from silica gel with pentane and some pentane/ether. From these spectra it can be seen that the aliphatic series in fraction 1 (Figure 7a) are clearly separated from the aromatics in the rest of the samples even though the various aromatics are not fully separated from each other. The variation in the

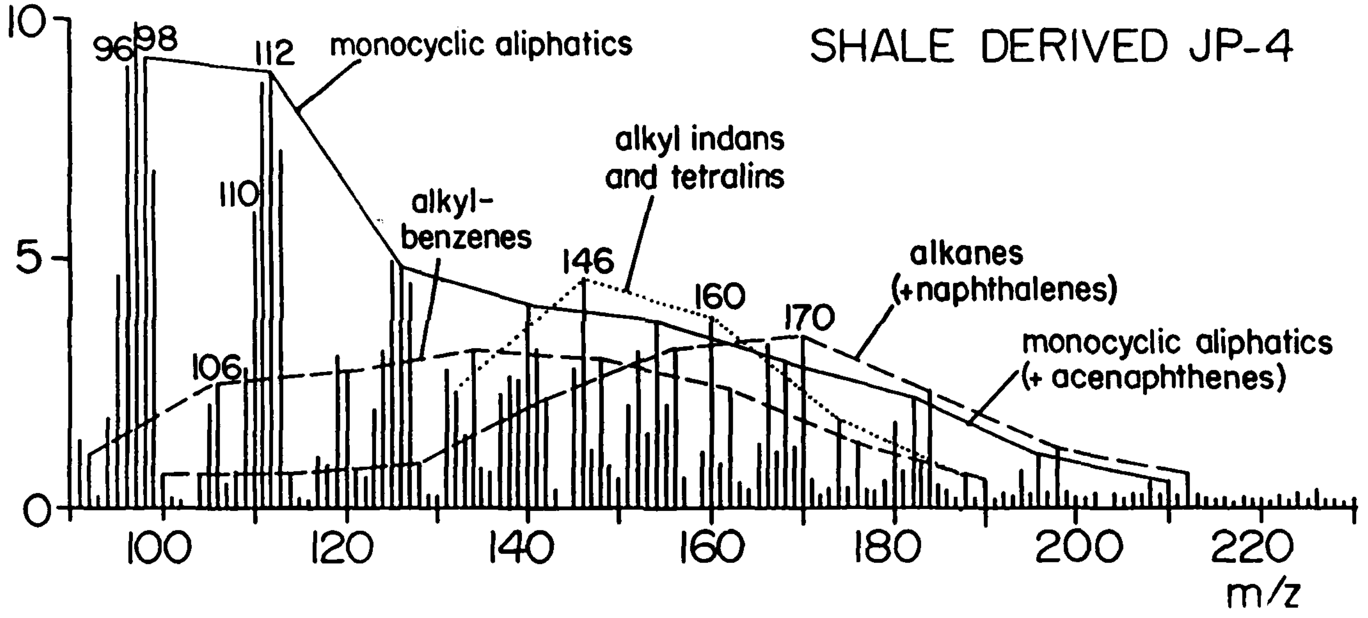


Figure 6. Mass spectrum 12 eV of the shale-derived JP-4 (SH4) dissolved in hexane.

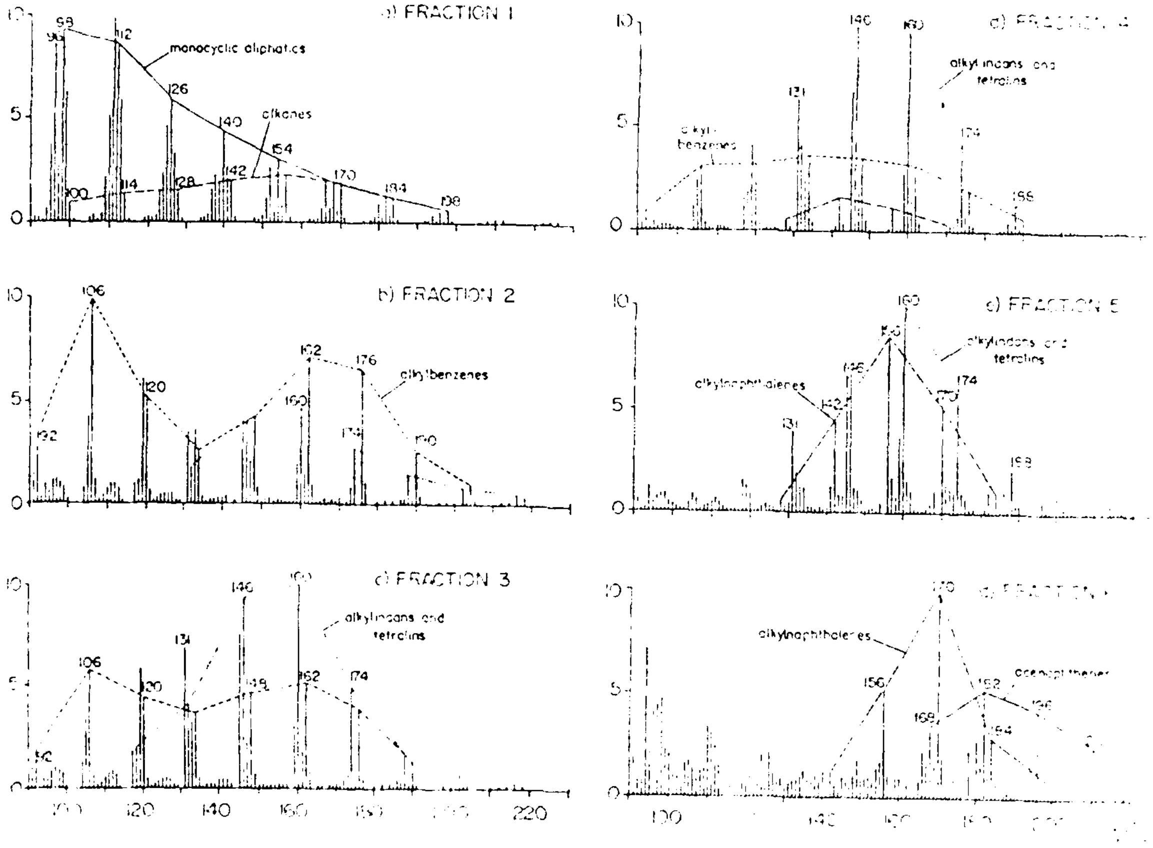


Figure 7a-f. Direct MS spectra of six LC fraction solutions separated from the SH4 sample on a silica gel open column using pentane and pentane/ether solvents. Compare to the original SH4 sample spectrum in Figure 6.

alkylbenzene distribution is probably due to the elution of long chain alkyl substituents before shorter multiply substituted compounds. It is also important to note the slight decrease in the higher mass members of the monocyclic and alkane series between the whole sample (Figure 6) and the first fraction (Figure 7a) as a result of removal of the underlying aromatics (Figure 7d-f). The extent of the separation of eight different compound classes in these samples is better represented by the bar graphs of Figure 8. The class relative abundances were calculated by simply summing the molecular ion intensities for each series in the spectra of Figure 7. Though far from perfect, this crude fractionation does demonstrate some of the potential of the technique.

Other chemical methods to isolate compound classes can be combined with LC to optimize effectiveness. Thus, the 95% aromatics sample of nearly pure alkylnaphthalenes was apparently obtained from a high naphthenic crude by fractional distillation. The 30% and 2% aromatics samples of primarily tetralins and decalins were then obtained through the synthesis route of hydrotreatment of the naphthalenes. Finally, as partially done with the tetralins and described in the first report, these samples can be cleaned up into even purer class standards by LC.

3. DATA PROCESSING

The most conventional method for working up direct MS data on liquid fuels is the ASTM method D2789 for gasoline (8). Basically, the total analysis can be done on a single sample by summing characteristic series of fragment and molecular ions and using previously determined calibration factors to obtain the relative amounts of each compound class. Although this method may be adequate for most gasoline samples, it requires some modification for extension to the higher boiling range jet fuels. Aside from the instrument parameter suggestions, an essential change for accurate jet fuel data would be the addition of standard compounds to cover the new classes and higher molecular weight compounds. Since virtually all of our analyses were at low electron energies which would require totally new calibration constants, we did not evaluate D2789-81 to determine what sort of compounds should be added. However, the method already has "cautions" and advises other

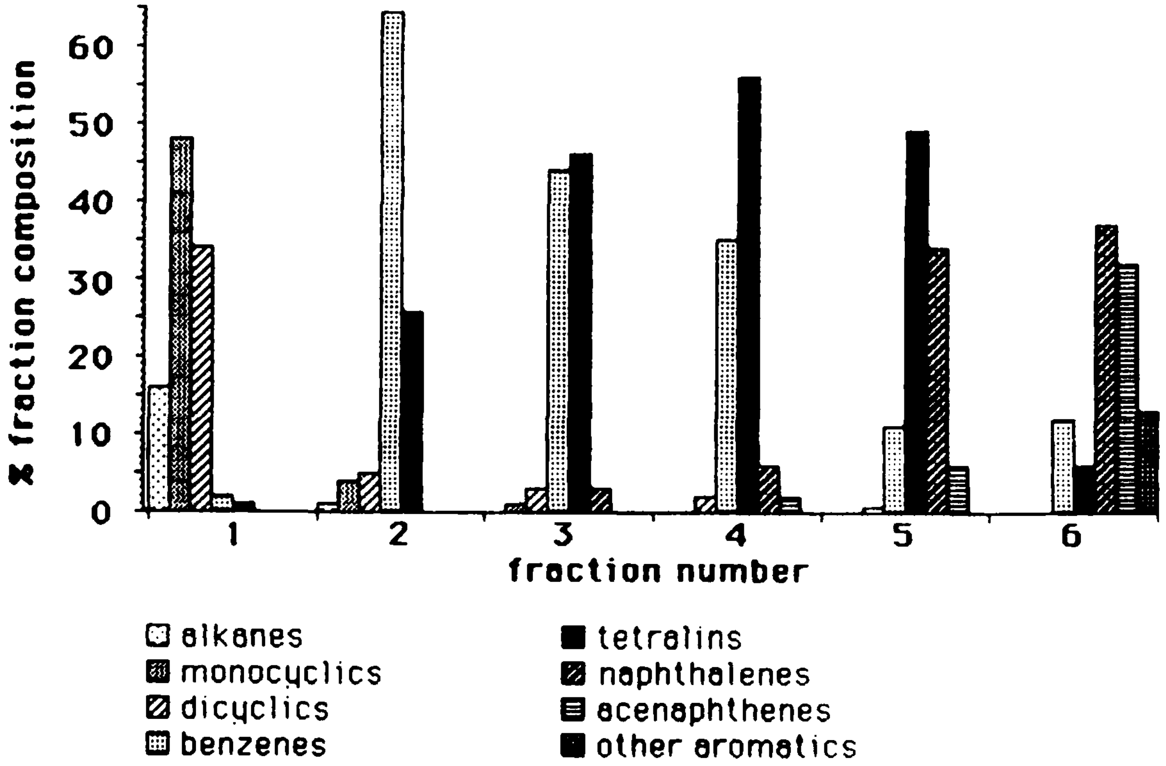


Figure 8. Bar graph representing the relative distribution of compound classes among the six LC fractions of sample SH4 shown in Figures 7a-f.

experiments for gasolines which might have olefins or naphthalenes overlapping with the monocyclics and alkanes, respectively. These problems will, of course, be much worse in the high naphthenic jet fuels. Simple direct low resolution MS by itself is not enough for complete and accurate spectral data workup; separate measurements, added dimensionality, and/or multivariate computer analysis are necessary.

The next level in sophistication in jet fuel direct MS data analysis comes through computerized pattern recognition techniques. The method used in this project to determine the best linear combination of standard spectra to duplicate an unknown spectrum was the minimization of the sum of the squares of the residuals (least squares approximation or LSQKJV). Though the program was originally developed and tested for standard spectra of individual compounds, it was also found suitable for compound class mixture standards (6). Table 2 lists the results of the program using the three fractionated samples (#1 - naphthalenes, #2 - tetralins, and #3 - decalins) as standards for analysis of all the blended mixtures (nos. 4 through 15) and the unknowns (DC2, 30%, STB, and SH4). The table lists the volume % of each standard used in preparing the blended mixtures as well as the calculated values and "residuals". In the case of the binary and ternary mixtures, the residual is taken to be simply a relative measure of the goodness of fit with zero being perfect. The tabulated results were chosen from multiple calculations based on the smallest residual. The results in Table 2 were plotted on a triangular diagram shown in Figure 9 to elucidate any obvious trends in the errors. Although there are tendencies for the experimental points to pull away from the corners and toward standard no.1 (naphthalenes), the explanation was not immediately apparent. Several hypotheses were explored. The impurities in each of the class standards, even those that were from other classes, e.g., tetralins in the naphthalenes, could not be at fault because the mass spectra should still be perfectly additive. The mixtures were all carefully made from the same class standards and the portion of tetralins from the naphthalenes standard should be proportional to the naphthalene peaks even when they were in addition to the intensities from the tetralin standard. The pattern of errors had to be

TABLE 2

VOLUME % COMPOSITION OF STANDARD MIXTURES AND UNKNOWN SAMPLES USING THE LSQKJV PROGRAM

Sample Name	Prepared (% v/v)			Calculated (% v/v)				
	Naphthalenes	Tetralins	Decalins	Naphthalenes	Tetralins	Decalins		Residual
4	25	-	75	32.5	0.2	67.3		0.3
5	50	-	50	49.9	3.2	46.8		12.4
6	75	-	25	72.7	3.0	24.2	*	15.4
7	75	25	-	72.2	24.3	3.4	*	22.7
8	50	50	-	56.4	43.6	0.0		3.4
9	25	75	-	31.0	66.2	2.8	*	15.3
10	-	75	25	0.9	73.1	26.0	*	11.8
11	-	50	50	0.3	50.3	49.4		4.0
12	-	25	75	0.3	28.4	71.3		4.5
13	25	25	50	29.8	23.2	47.0		0.3
14	50	25	25	54.3	24.5	21.2		0.002
15	25	50	25	29.7	44.8	25.6		0.01
DC2				0.0	0.4	99.6		1.1
30%				0.0	36.0	64.0		1.0
STB				10.1 (4.0	9.0 3.6	80.8 31.9		153 60.5%)**
SH4				15.2 (5.6	19.7 7.2	65.1 23.8		173 63.4%)**

* Results from average spectra rather than individual spectra chosen because of lower residual values.

** Normalized results including the residuals as portion of sample not defined by naphthalene, tetralin, and decalin standards.

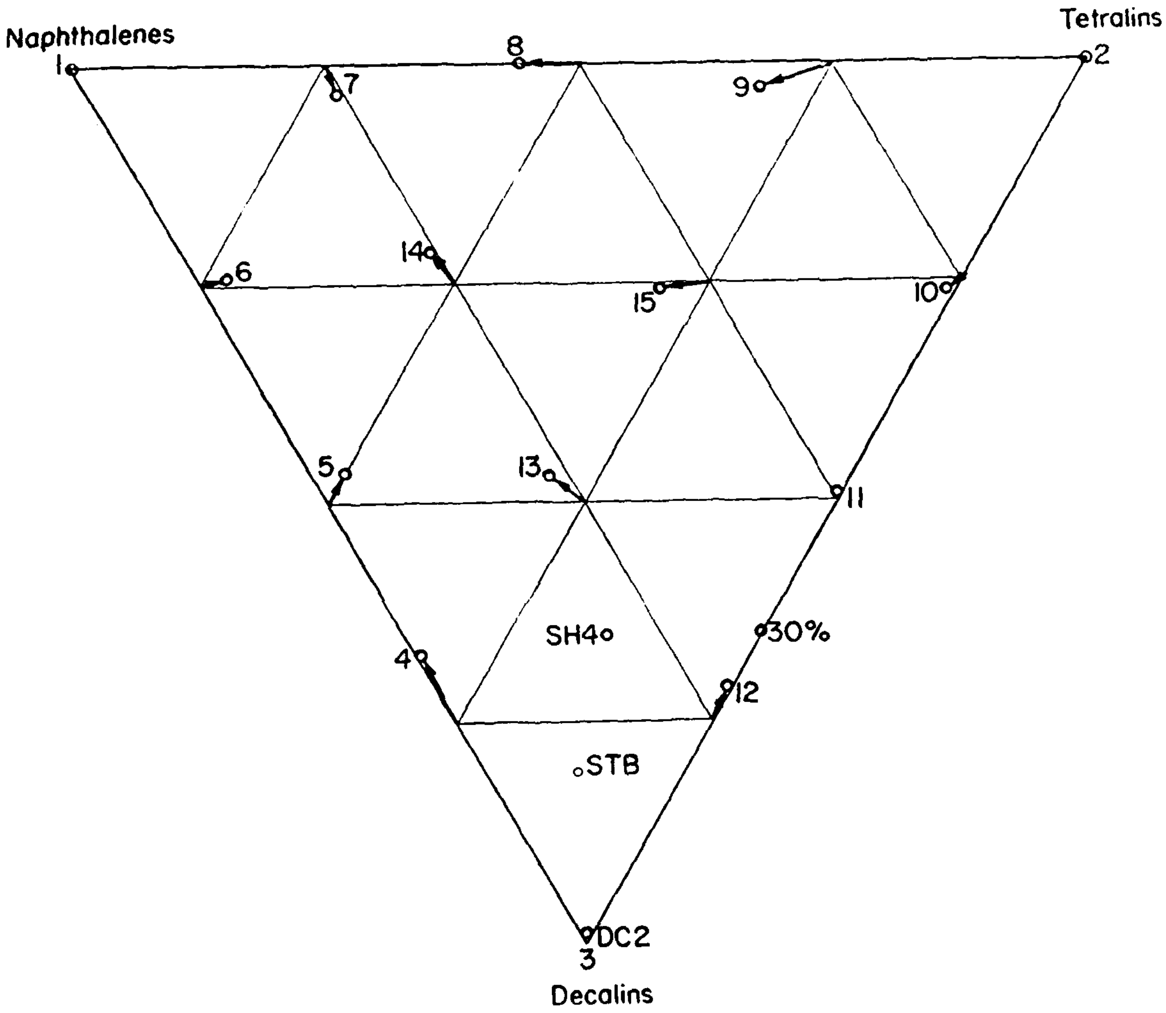


Figure 9. Triangular composition diagram of pattern recognition analysis results from LSOKJV program as tabulated in Table 2.

related to some systematic difference between the way compounds were represented in the naphthalenes standard versus mixtures of that class.

The error trends observed in Figure 9 are virtually all explained by a logarithmic attenuation of the tallest peaks in the spectra due to detector saturation. This effect was most serious for the naphthalenes sample 1 because the major composition of the liquid was represented in the intensities of relatively few different ions. Whereas, in samples with more aliphatic structures, such as the decalins or even tetralins, a similar total ion intensity was distributed over many more m/z's including both molecular and fragment ions. Thus, samples 4, 13, 15 and 9 all indicate more than their actual 25% naphthalenes because sample 1 has naphthalene peaks which are attenuated to less than their 4 x 25% intensity. This problem was anticipated and partially compensated for by running slightly smaller amounts of sample 1, but the pattern of the results suggests that some attenuation still occurred. Samples 6 and 7 (75% naphthalenes) were not compensated for the potential problem and apparently were attenuated even more than sample 1, thus offsetting their results toward too little naphthalenes. Considering the possible validity of this systematic error explanation, the average absolute error for all of the calculated values of only 3.0% seems quite acceptable.

Of course, the LSQKJV results of real interest were the four unknowns, the samples which were not simply mixtures of the three standards. These are listed in Table 2 and plotted in Figure 9. Sample 16, DC2, was simply a distillate fraction of the decalins standard and therefore produced an expectedly low residual (1.1) along with its nearly complete (99.6%) standard 3 composition. Apparently, the distillation cut changed the DC2 decalin distribution in such a way that the proportion of tetralins could now be better fit by 0.4% of standard 2. The 30% aromatics sample, number 17, which was the LC source of the tetralins standard after removal of the decalins, also gave an expectedly low residual and a 36% tetralins, 64% decalins composition.

The very high residuals in the STB and SH4 samples indicate that major portions of their compositions are not represented in the three dicyclic class standards. These two samples are seen to contain as much as 60.5 and 63.4% other compounds, respectively, by renormalizing the percent composition to include the residual. Thus it can be seen that the originally calculated values for the three components, those plotted in Figure 9, are the relative compositions of the approximately 40% portions represented in the ternary diagram plane. Of the analyzed portion, the decalins are obviously predominant in both with much smaller amounts of naphthalenes and tetralins. This is certainly the case in the SH4 sample where, as seen in FIgures 6 and 7, the alkanes may contribute to nearly half the intensity of ions at m/z 142, 156, and 170.

The factor and discriminant data analysis results were briefly discussed in the first report (1). Another set of SPSS calculations without the SH4 and STB samples is shown in Figure 10 for comparison to the LSQKJV results. This graph is a scatter plot of the first two discriminant function scores showing the points averaged from the triplicate analyses of each sample. The triangular grid is based on use of the three corner points as standards and shows the deviation of each of the determined values from the synthetic volume % composition. In this case the average absolute error in each component was only 1.7% or about 0.6 of the LSQKJV error and also still includes the systematic error of naphthalene peak attenuation. The reduction in error is due to the use of triplicate spectra for each sample and the maximization of the difference between samples relative to the difference within each set of replicates. Of course, the real errors for both methods are dependent on the accuracy of the mixtures and ultimately on the purity of the standards. Thus, the approximate 40% tetralin composition of the 30% aromatic sample no. 17 in Figure 10 indicates 40% of standard #2 which might include as much as 10% decalins and alkyl benzenes.

A significant effort of this project both before and since the first report has been the application of the discriminant analysis to points not within the ternary composition plane. Thus, in Figure 14 of the first report (1), the STB and SH4 samples were orthogonally projected into the ternary diagram much as they appear in the LSQKJV analyses of Figure 9. However, recent experiments, including computer

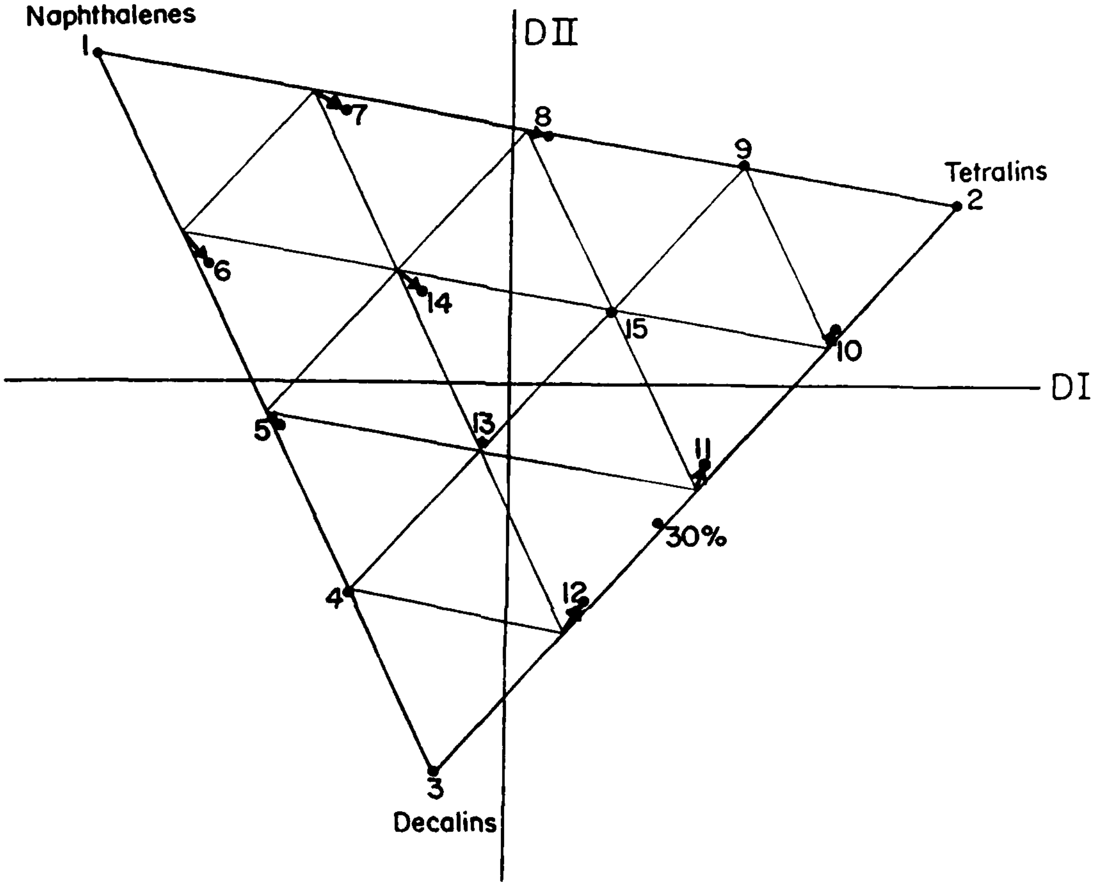


Figure 10. Scatter plot of the average scores for the first two discriminant functions obtained from the 17 samples made up of naphthalenes, tetralins and decalins.

analysis of a four component simulated data set,suggest a projection scheme as illustrated in Figure 11. In this model, points 1, 2 and 3, containing 75, 50 and 25% D respectively, are projected from the 100% D point to their relative ABC compositions on the bottom triangle. By contrast, orthogonal projects of these three points would all be focussed much closer to the center of the ABC ternary composition diagram. Confirmation of these ideas was beyond the scope of this preliminary project and continued study is necessary to develop a general quantitation method. One expectation which is demonstrated in Figure 11 is the fact that inaccuracies are increased as a direct function of the distance of projection onto a composition plane. Similarly, errors are expanded if the unknown is projected from an incorrect fourth component. This again emphasizes the need for class standards of compositions as close as possible to the unknown.

Another approach to the discriminant analysis was through the program VARDIA (4). This program, through unsupervised pattern recognition techniques, is able to mathematically extract principal component spectra from a set of mixtures. Thus, for example, the spectra for the three "pure" standards (nos. 1, 2 and 3) were deleted from the data set of Figure 10 and the job rerun through SPSS and VARDIA. The resulting computer extracted "standard" spectra shown in Figure 12 effectively reproduce the exact primary compound class compositions of the real standards shown again from the first report in Figure 13. Better than simply reproducing the real standard spectra however, the extracted spectra have been cleaned up by removal of the contaminations in each standard from the other two. Even more impressive, these same principal component spectra were extracted from a subsequent SPSS analysis of just the three central mixtures nos. 13, 14 and 15 (see Figure 10) which contained a maximum of 50% of each of the three standards. With proper normalization, the computer derived spectra could be added to the mixture data set and rerun through discriminant analysis to give a ternary composition triangle based on the "pure" standards. Since each of the experimental standards was in fact something of a mixture, the pure component triangle would be constructed slightly outside the

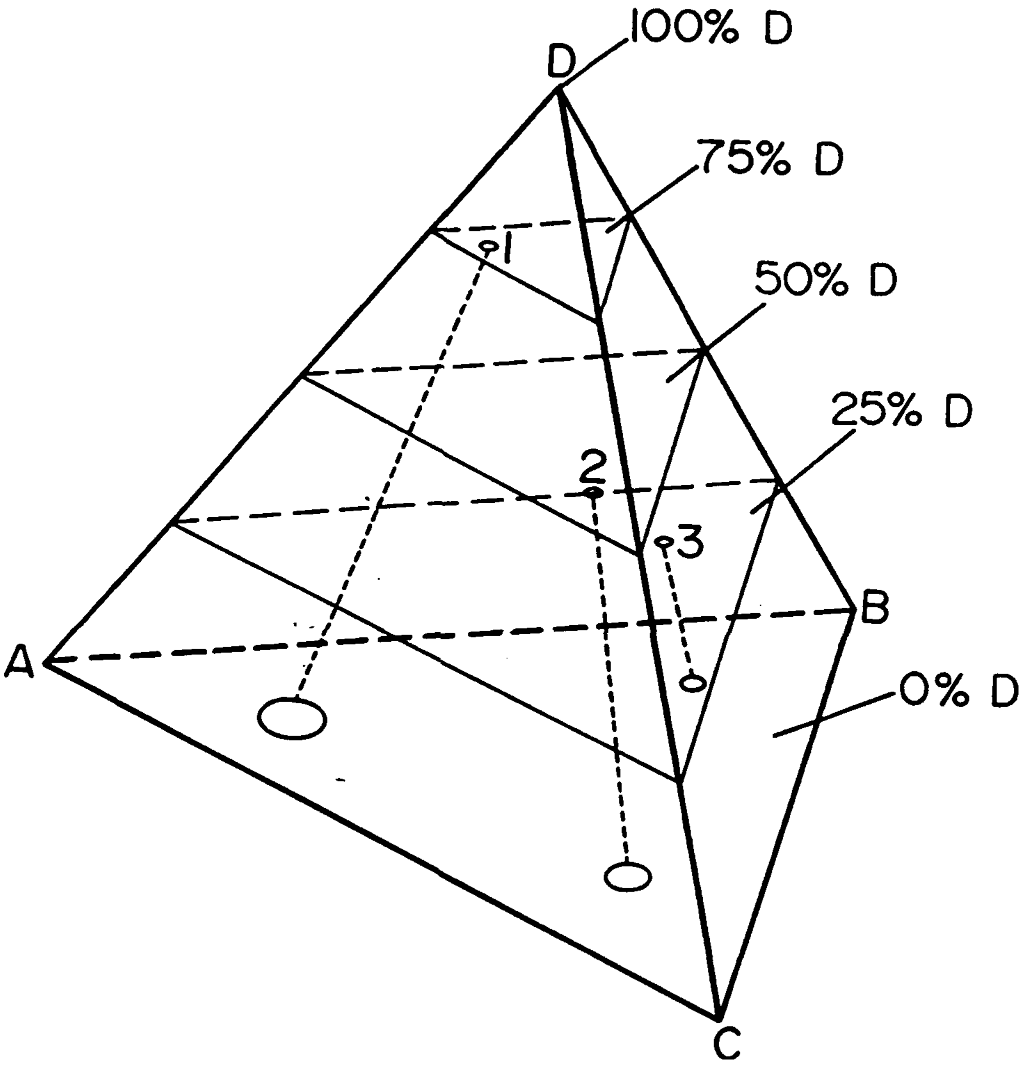


Figure 11. Quaternary (ABCD) mixture diagram depicting the projection of three mixtures containing different concentrations of component D onto a ternary (ABC) mixture diagram. Note that the absolute ABC error increases with larger projection distances.

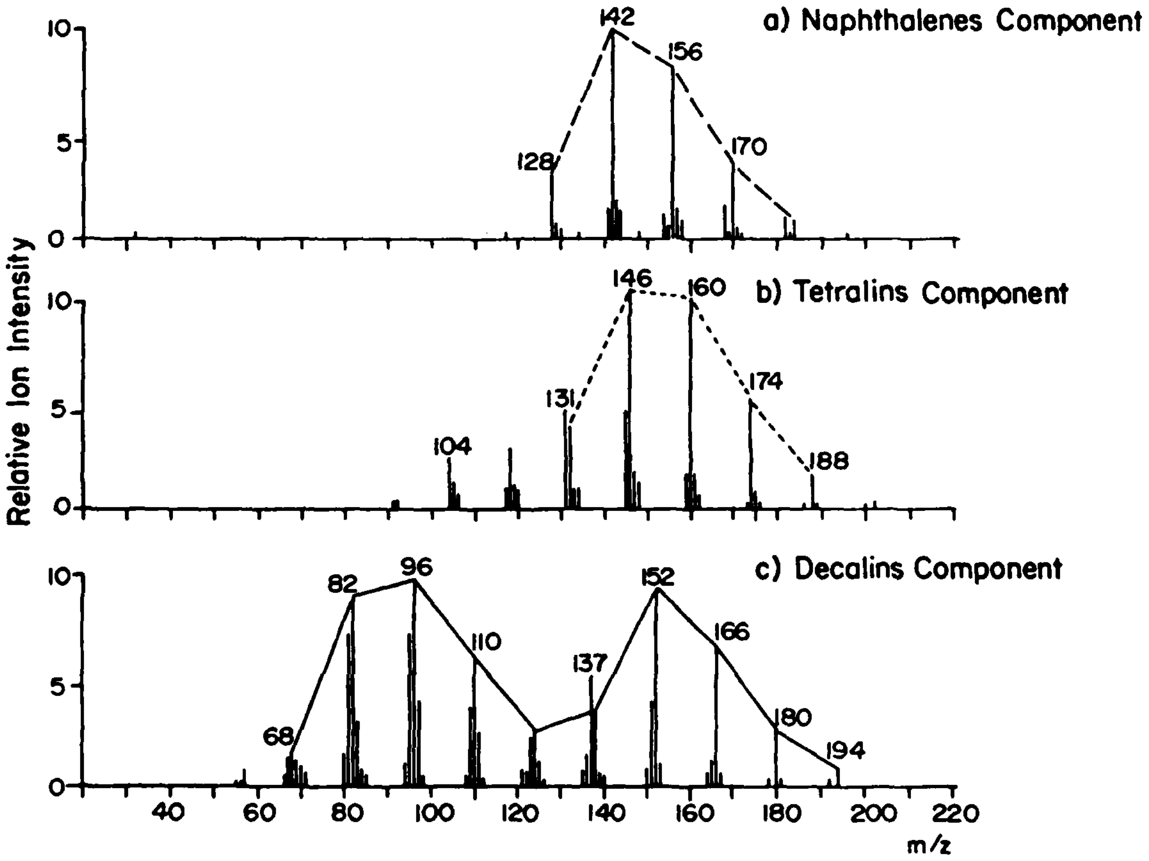


Figure 12. Principal component spectra mathematically extracted from the mixture spectra of samples 4 through 15 (see Figure 10) using the program VARDIA.

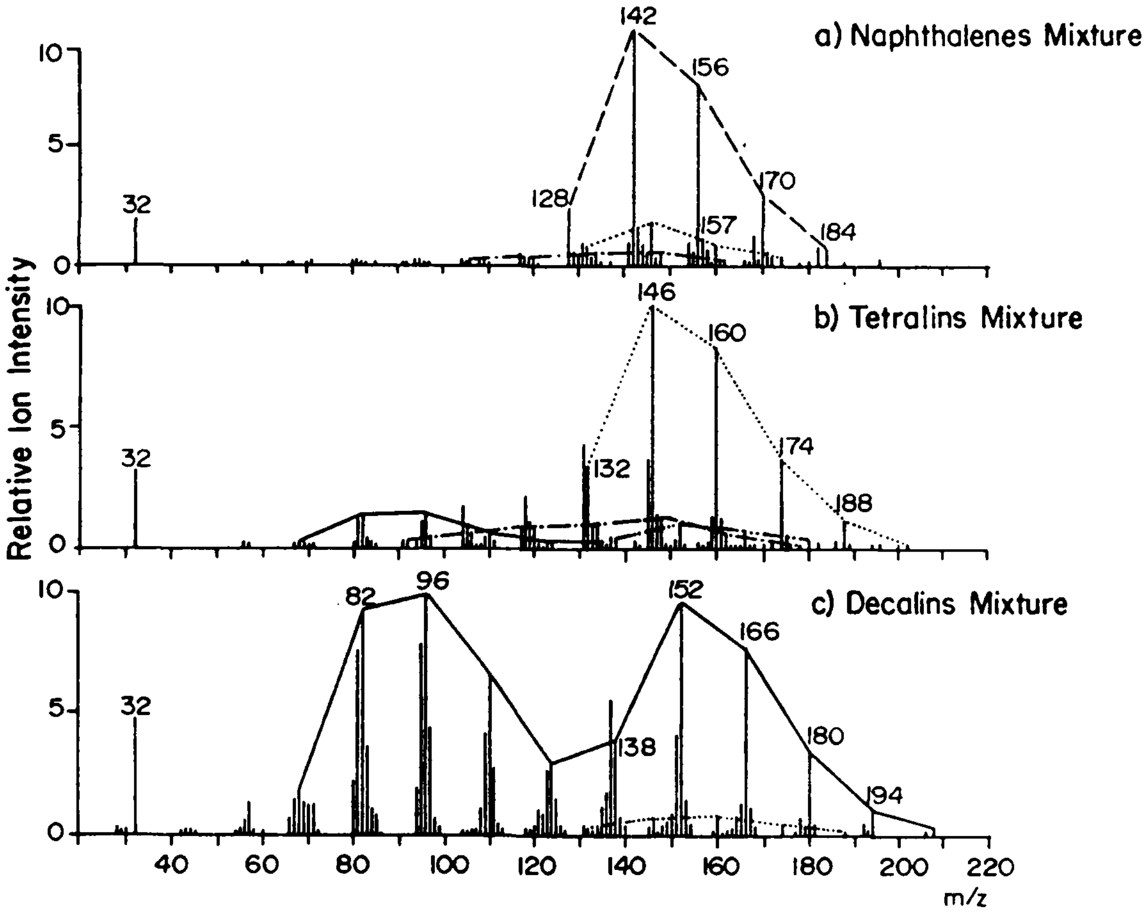


Figure 13. Actual spectra of class standards used to make the mixtures of Table 2 and Figures 9 and 10. Notice the impurities in each sample from the other classes.

diagram of Figure 10. Again, the full investigation of this prospect requires further study and program development.

Several of the topics discussed thus far now merge in the possibilities for more advanced work. Liquid chromatography (LC) could be used to separate an unknown into three or more fractions such as those shown in Figure 7 for direct MS analysis with the original sample. From the partially separated class mixtures, principal component spectra could be extracted and, with correct normalization, be used to quantitatively determine the hydrocarbon groups in the fractions and original sample. The fractions which contained more than one class, such as the alkanes, monocyclic and dicyclicaliphatic hydrocarbons in Figure 7a, might require comparison to true class standards. However, the combined LC and computer standard extraction would give the closest possible class compound distributions for comparison to the unknown while eliminating the need for a high resolution LC separation or individual compound mixing to produce a nearly exact standard match. Presently available open column LC technology would give sufficient fraction resolution to separate the otherwise overlapping molecular ion series, e.g., alkanes from naphthalenes and monocyclic aliphatics from olefins and acenaphthenes. The computer principal component extraction would largely eliminate the overlap of LC peak tails in adjacent fractions. The original mixture and/or its fractions could then be compared selectively to a subset of three or more appropriate standards, either single class external mixtures or the derived principal component spectra. The combined LC/MS computer analysis approach would still most likely be much quicker and simpler than a complete high resolution GC/MS computer experiment. Whereas LC/MS/computer analysis only separates homologous compounds within each compound class, GC/MS/computer analysis separates many isomeric compounds as well, creating a much more complex picture. This degree of complexity, although interesting from a purely analytical point of view, creates the need for very careful identification and summation of isomeric compounds in GC/MS before a quantitative group analysis can be performed. In complex jet fuels, such as obtained from hydrogenated and refined syncrudes, the GC/MS identification and summation procedure is far from trivial and may suffer from several possible sources of error. In contrast, the LC/MS approach provides more direct information on compound class analysis and alkyl substitution.

Finally, an aspect of data analysis mentioned in the first report but still not performed on these samples is the correlation of MS chemical analysis with more conventional fuel measurements. This type of analysis would most readily involve the intercomparison of a large set of different unknown fuels without detailed individual sample analysis as opposed to the detailed class determination on a single LC fractionated sample just discussed. This was not possible within the scope of this preliminary study with the limited number of samples and none of the other data. However, it could be performed on a fairly modest base of samples already tested by the other techniques (flashpoint, density, viscosity, smoke index, etc.) and properly stored since then. This correlation method has been demonstrated in a paper on the MS analysis of 100 coals with 25 conventional parameters (11).

SECTION IV

CONCLUSIONS

1. Direct low voltage mass spectrometry (MS) has been shown to be a suitable method for fast and simple characterization of the chemical class composition of liquid jet fuels. The present qualitative capability as well as the strong quantitative potential have been demonstrated.

2. Sample introduction for direct MS analysis of jet fuels is more critical than for lower boiling gasoline samples and a novel direct probe procedure has been developed.

3. Tandem mass spectrometry (MS/MS) shows long term promise for direct compound class analysis but requires a more advanced data system than currently available in our laboratory.

4. Open column liquid chromatography (LC) is a very useful technique for chemical separation and/or clean-up of compound classes suitable for subsequent use as standard mixtures.

5. Open column LC offers a currently available technology for adding a dimension of separation to the direct MS class analysis.

6. Single spectrum pattern classification techniques such as the least squares method tried here can be useful with appropriate standards and MS operating conditions.

7. Factor and discriminant analysis of direct MS data offer the most powerful options for quantitative compound class determinations.

8. Combined LC and MS techniques plus multivariate data analysis should provide for unambiguous class assignment as well as enable the optimization of standards for quantitative class determinations.

SECTION V

RECOMMENDATIONS

1. Further testing of the suggested instrument parameters should confirm their utility and general application. Initially, this would simply involve the comparison of the novel as well as the more routine techniques on two or more different MS instruments.

2. Preparation of appropriate standards for quantitative compound class analysis of jet fuels should consider the use of sample-derived standards representing each compound class as an alternative to procuring hundreds of individual hydrocarbons to cover the wide range of jet fuel composition.

3. Development of fast, user-friendly programs can optimize the processing of direct MS data by advanced computer methods. This should include further study of the quantitation techniques and the mathematical extraction of class standards, as discussed in this report.

4. Use of the direct MS technique with multivariate statistical analysis can possibly draw pertinent correlations between jet fuel chemical composition and performance characteristics. Application of this approach to a variety of samples with available conventional and performance data could theoretically predict the chemical composition for the "ideal" jet fuel for a given application or scenario.

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