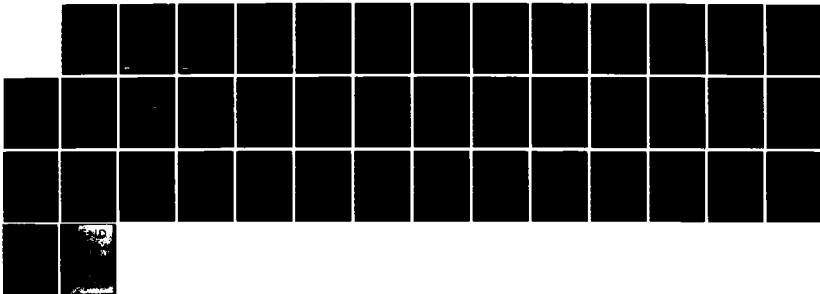
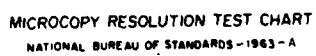


AD-A147 724 ANALYSIS OF MIDDLE DISTILLATE FUELS BY HIGH RESOLUTION 1/1
FIELD IONIZATION MASS SPECTROMETRY(U) SRI INTERNATIONAL
MENLO PARK CA R MALHOTRA ET AL. 29 OCT 84
UNCLASSIFIED N00014-81-K-2032 F/G 21/4 NL





MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

6

ANALYSIS OF MIDDLE DISTILLATE FUELS BY HIGH RESOLUTION FIELD IONIZATION MASS SPECTROMETRY

AD-A147 724

Annual Report

Covering Period from June 1, 1982, through August 31, 1984

By: Ripudaman Malhotra, Michael J. Coggiola,
Steven E. Young, Doris Tse, and S. E. Buttrill, Jr.
Mass Spectrometry Program

Prepared for:

Robert N. Hazlett
NAVAL RESEARCH LABORATORY
Code 6180
Washington, DC 20375

Naval Research Laboratory
Contract N00014-81-K-2032
SRI Project PYU 3554

DTIC
EXTRACTED
NOV 23 1984
E

SRI International
333 Ravenswood Avenue
Menlo Park, California 94025
(415) 326-6200
TWX: 910-373-2046
Telex: 334 486

84 11 06 06 6

DTIC FILE COPY



This document has been approved
for public release and sale; its
distribution is unlimited.

SRI International



ANALYSIS OF MIDDLE DISTILLATE FUELS BY HIGH RESOLUTION FIELD IONIZATION MASS SPECTROMETRY

Annual Report

Covering Period from June 1, 1982, through August 31, 1984

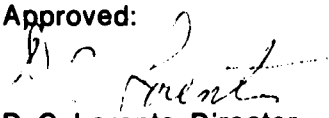
By: Ripudaman Malhotra, Michael J. Coggiola,
Steven E. Young, Doris Tse, and S. E. Buttrill, Jr.
Mass Spectrometry Program

Prepared for:

Robert N. Hazlett
NAVAL RESEARCH LABORATORY
Code 6180
Washington, DC 20375

Naval Research Laboratory
Contract N00014-81-K-2032
SRI Project PYU 3554

Approved:


D. C. Lorents, Director
Chemical Physics Laboratory

G. R. Abrahamson
Vice President
Physical Sciences Division

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED			1b. RESTRICTIVE MARKINGS		
2a. SECURITY CLASSIFICATION AUTHORITY			3. DISTRIBUTION/AVAILABILITY OF REPORT UNLIMITED		
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE					
4. PERFORMING ORGANIZATION REPORT NUMBER(S)			5. MONITORING ORGANIZATION REPORT NUMBER(S)		
6a. NAME OF PERFORMING ORGANIZATION SRI INTERNATIONAL		6b. OFFICE SYMBOL (If applicable) 410281	7a. NAME OF MONITORING ORGANIZATION NAVAL RESEARCH LABORATORY		
6c. ADDRESS (City, State and ZIP Code) Menlo Park, California 9r025			7b. ADDRESS (City, State and ZIP Code) Washington, DC 20375		
8a. NAME OF FUNDING/SPONSORING ORGANIZATION Naval Air Propulsion Center		8b. OFFICE SYMBOL (If applicable) 393808	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-81-K-2032		
8c. ADDRESS (City, State and ZIP Code) Trenton, New Jersey 08628			10. SOURCE OF FUNDING NOS.		
			PROGRAM ELEMENT NO. 62765N	PROJECT NO. WF65-511- 000	TASK NO. - - -
			WORK UNIT NO. 61-0085		
11. TITLE (Include Security Classification) ANALYSIS OF MIDDLE DISTILLATE FUELS . . .					
12. PERSONAL AUTHOR(S) Ripudaman Malhotra, Michael J. Coggiola, Steven E. Young, Doris Tse, and S. E. Buttrill, Jr.					
13a. TYPE OF REPORT Annual		13b. TIME COVERED FROM 1 Jun 82 TO 31 Aug		14. DATE OF REPORT (Yr., Mo., Day) 1984 October 29	
				15. PAGE COUNT 33	
16. SUPPLEMENTARY NOTATION					
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP	SUB. GR.	Distillate Fuel Analysis, Jet Fuel, Diesel Fuel, Mass Spectrometry, Field Ionization, High Resolution z-Series Analysis		
19. ABSTRACT (Continue on reverse if necessary and identify by block number)					
A method for the rapid and detailed chemical characterization of distillate fuels has been developed using high resolution field ionization mass spectrometric (HR-FIMS) techniques. A vintage AEI MS-9 mass spectrometer has been modified to house a volcano-style field ionizer and has been equipped with a high-temperature batch inlet system. Field ionization is particularly useful in this regard because it produces only molecular ions for most compounds and because different compound types do not differ in their ionization efficiencies by more than a factor of four. The mass spectrometer is operated at a resolution of 3000, which is adequate to resolve all the different types of hydrocarbons likely to be present in the fuel sample. continued....					
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT. ☐ DTIC USERS ☐			21. ABSTRACT SECURITY CLASSIFICATION UNCLASSIFIED		
22a. NAME OF RESPONSIBLE INDIVIDUAL G. R. Abrahamson, Vice President.			22b. TELEPHONE NUMBER (Include Area Code) 415/859-3131		22c. OFFICE SYMBOL VP-Physical Sciences

Although the successful operation of the mass spectrometer for the analysis of fuels was demonstrated, for routine operation, a number of additional modifications were necessary. These included replacement of magnet power supply, electric sector power supply, and ion gauge controllers. Software has been written to present the mass spectrum intensities in a matrix where the various columns represent the different z-series of the hydrocarbons and the rows represent the number of carbon atoms in any given component. Analysis of a stable and an unstable jet fuel showed that the unstable fuel had a substantially higher naphthalene content.

CONTENTS

INTRODUCTION AND BACKGROUND.....	1
DESCRIPTION OF EQUIPMENT AND SOFTWARE.....	5
Field Ionization Mass Spectrometer.....	5
High Temperature Batch-Inlet.....	12
High Resolution Mass Spectrometry Data System.....	13
Software for Generating Z-Tables.....	14
ANALYSIS METHOD.....	17
Sample Introduction.....	17
Ionization and Data Acquisition.....	18
Data Processing.....	19
TECHNICAL RESULTS.....	21
Analysis of a Stable and an Unstable Fuel.....	21
Standardization of the Analytical Procedure.....	27
CONCLUSIONS.....	32
REFERENCES.....	33

Accession For	
NTIS GRA&I	☒
DTIC TAB	☐
Unannounced	☐
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	



LIST OF ILLUSTRATIONS

Figure

1	Cross Section of Source Housing for MS-9.....	6
2	Detail Showing the Use of Batch Inlet with the Volcano-Style Field Ionization Source.....	8
3	Detail Showing the Use of Direct Insertion Probe for Solid Samples with the Volcano-Style Field Ionization Source.....	9
4	Example of the Resolving Power of MS-9 Equipped with Volcano-Style Field Ionizer Source.....	10
5	High-Resolution Field Ionization Mass Spectrum of Stable Fuel Sample NRL-81-5.....	22
6	High-Resolution Field Ionization Mass Spectrum of Unstable Fuel Sample NRL-81-6.....	23
7	High-Resolution Field Ionization Mass Spectrum of Test Mix 2.....	29
8	High-Resolution FIMS Data of Test Mix 2.....	30

LIST OF TABLES

Table

1	Resolving Power Required to Separate Possible Mass Doublets at m/z 300.....	3
2	Relative Field Ionization Sensitivities for Hydrocarbons.....	24
3	Composition of Stable Fuel NRL-81-5 by Carbon Number and z-Series.....	25
4	Composition of Unstable Fuel NRL-81-6 by Carbon Number and z-Series.....	26
5	Composition of Test Mix 2 and Relative Field Ionization Efficiencies of its Constituents.....	31

INTRODUCTION AND BACKGROUND

During the decade following the Arab oil embargo, an increase occurred in both the variety and variability of petroleum feedstocks for the production of middle distillate fuels. As a result, the variability and the chemical constitution of currently used middle distillate fuels are different from those used before 1970. Problems have arisen in the use of specifications developed empirically from experience with fuels of the older composition. In a few instances, a fuel that met specification on delivery quickly became so unstable in storage as to become unusable. Therefore, new fuel specifications based more directly upon the chemical constitution of the fuel are needed. This requires the development of new methods for distillate fuel analysis capable of providing rapid and detailed information on the chemical composition of the distillate fuels.

For the past several years, SRI International's unique Field Ionization Mass Spectrometer (FIMS) has provided detailed quantitative information on the composition of diesel and jet fuels derived from oil-shale, coal, and petroleum. Because field ionization is a very soft technique of ionization, it produces molecular ions only for most of the fuel components, with very little fragmentation, and this makes analysis by FIMS relatively simple. Complete and quantitative molecular weight distributions on all of the types of hydrocarbon compounds present in these fuels previously required a time consuming chromatographic separation of the fuel into several fractions. Each of these fractions was then analyzed separately by FIMS. The purpose of the current effort (NRL Contract No. N00014-81-K-2032) is to develop a high resolution FIMS facility capable of providing a

rapid and complete quantitative analysis of distillate fuels without the need for a chromatographic separation step.

A low resolution mass spectrometer, which is capable of separating ions differing by a full mass unit, is not capable of resolving many of the different components present in a hydrocarbon fuel. Compound classes such as saturates and naphthalenes have the same nominal masses, but different molecular formulae and correspondingly different mass defects. Thus, for both nonane (C_9H_{20}) and naphthalene ($C_{10}H_8$), the molecular ions would result in a single peak at m/z 128 with a low resolution mass spectrometer, but would appear as a doublet in a high resolution instrument because the exact masses of these compounds are 128.1565 and 128.0626, respectively.

The resolving power ($M/\Delta M$) necessary to separate all saturates from the naphthalenes up to mass 300 is 3,200. The saturates/naphthalenes pair is one of the several examples of $C-H_{12}$ doublets. Others in this category include tetralins/pyrenes, tricycloalkanes/phenanthrenes. In all these cases, the latter compound, which is of the same nominal mass as the former, has one more carbon and twelve less hydrogens. In each case, a resolving power of 3,200 is sufficient to resolve the doublets up to mass 300.

As the resolution of the mass spectrometer increases, it becomes possible to separate, detect, and quantitate minor components of a fuel containing heteroatoms such as oxygen, nitrogen, and sulfur. Table 1 shows the resolving power that is required to separate possible mass doublets at m/z 300, the molecular weight of the heaviest components expected in a middle distillate fuel. The mass doublets in Table 1 were selected as those most likely to be encountered in a field ionization mass spectrum, which consists almost entirely of molecular ions. The doublets are listed in decreasing

Table 1

RESOLVING POWER REQUIRED TO SEPARATE POSSIBLE
MASS DOUBLETS AT m/z 300

<u>Mass Doublet</u>	<u>$\Delta M \times 1000$</u>	<u>Required Resolving Power at m/z 300</u>
C-H ₁₂	93.9	3,200
S-C ₂ H ₈	90.6	3,300
O-CH ₄	36.4	8,200
N ₂ -C ₂ H ₄	25.1	11,900
S-O ₂	17.8	16,900
³⁴ SH ² -C ₃	16.5	18,200
¹³ CO-N ₂ H	15.7	19,100
CO-N ₂	11.2	26,700
¹³ C ₂ -C ₂ H ₂	8.9	33,600
N- ¹³ CH	8.11	37,000
C ₃ -SH ₄	3.37	89,000

Note to Table 1: The resolving power tabulated is that necessary to separate two peaks of equal intensity such that the valley between them is 10% of their height. If one peak is very much smaller than the other, the resolving power required to quantitate the smaller peak increases by an amount that depends on the details of the mass spectrometer peak shape.

order of mass difference or increasing values of the resolving power required to separate them. The separation of $S-C_2H_8$ doublet is only slightly more difficult than the $C-H_{12}$ doublet requiring a resolving power of 3,300. However, there is another doublet involving sulfur that is much more difficult to separate. The last entry in Table 1 shows that a resolving power of 89,000 is required to separate the C_3-SH_4 doublet. However, the corresponding doublet for the sulfur-34 isotope can be separated at only 18,200 resolving power. Because sulfur-34 is present at the level of 4.2% natural abundance, there is at least the possibility of detecting major sulfur components from the presence of this isotope peak. It is unlikely that a resolving power of 89,000 will be obtained in the foreseeable future with the high resolution FIMS.

Nitrogen is the most abundant and most important heteroatom found in refined middle distillate fuels from shale. In a molecular ion spectrum, the $N-^{13}CH$ doublet will be encountered, which requires 37,000 resolving power to separate at m/z 300.

Increased resolution can be attained only at the expense of sensitivity. To date we have been operating the spectrometer at a resolving power of 3,300 to 4,000--our primary goal being to resolve the $C-H_{12}$ doublet.

This report describes the work performed during the period June 1982 to August 1984. Before this period, a used high-resolution mass spectrometer had been procured, refurbished, equipped with an SRI volcano-style field ionizer, and interfaced with a Kratos DS 55C data system for high resolution mass spectrometry, and these aspects are discussed only briefly.

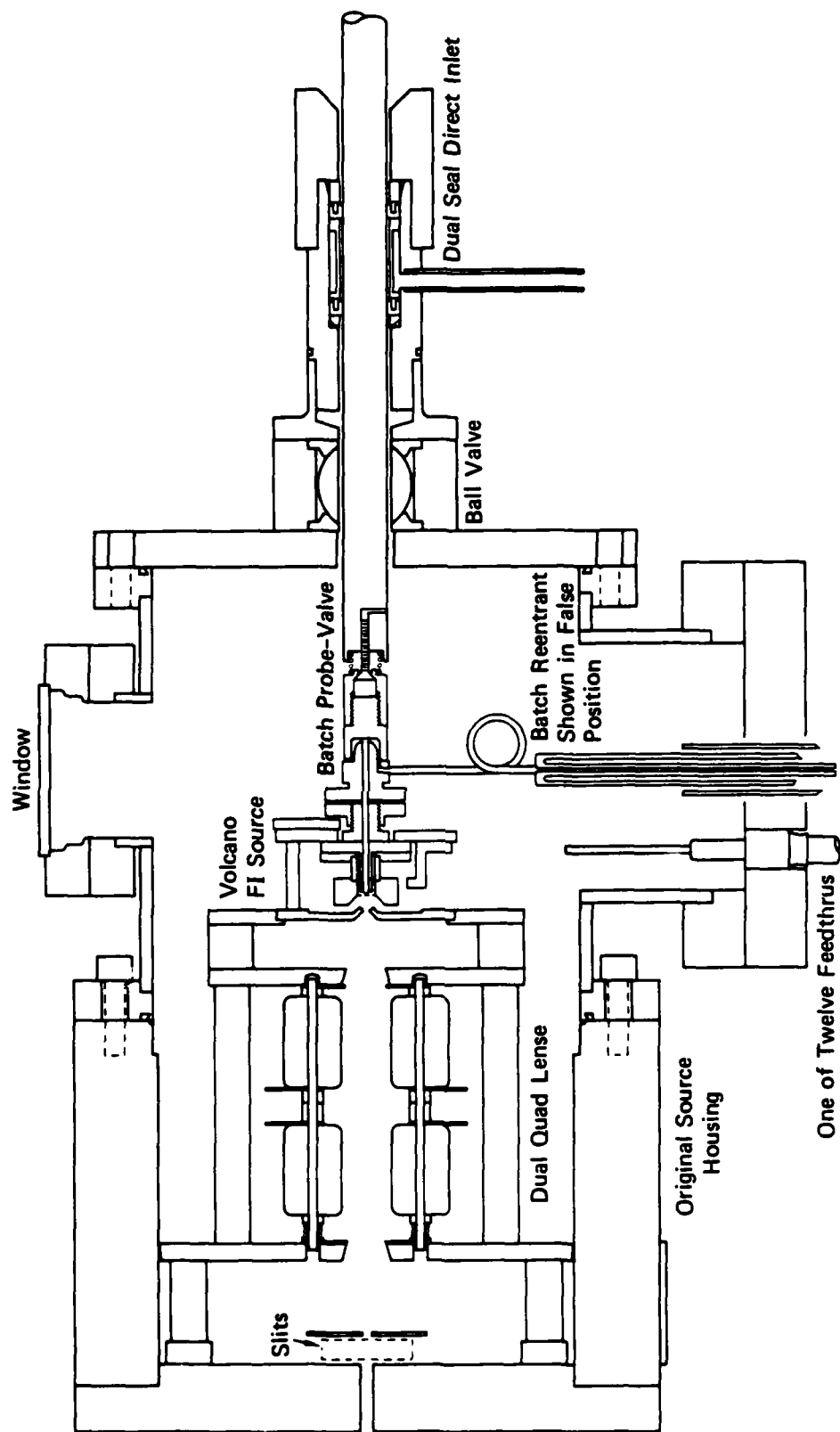
DESCRIPTION OF EQUIPMENT AND SOFTWARE

Each of the major elements of the high resolution FIMS analysis system for distillate fuels is considered separately in this section.

Field Ionization Mass Spectrometer

The mass spectrometer used in this work is an MS-9 manufactured by AEI, Ltd., of Manchester, England. It is a double-focusing mass spectrometer with 90-degree electric and magnetic sectors. This instrument was delivered to its original owner in 1964 and at that time had a specified mass resolution of 15,000. When received at SRI, the mass spectrometer had been out of service for several years. It was completely disassembled, cleaned, and reworked to bring it into good operating condition. In the electron-impact ionization mode using the original ion source, a mass resolution of 30,000 was eventually obtained.

To install an SRI volcano-style field ionization (FI) source on the MS-9, the original source and mounting flange were removed along with the original solid sample probe and reentrant connection for the batch inlet system. To make room for the field ionization source and some new ion lenses, an extension of the original source housing was designed and built. Figure 1 shows a scale drawing of a cross section through the modified MS-9 source housing. The new housing also includes provision for introducing solids via a heated direct insertion probe. When the batch inlet is used,



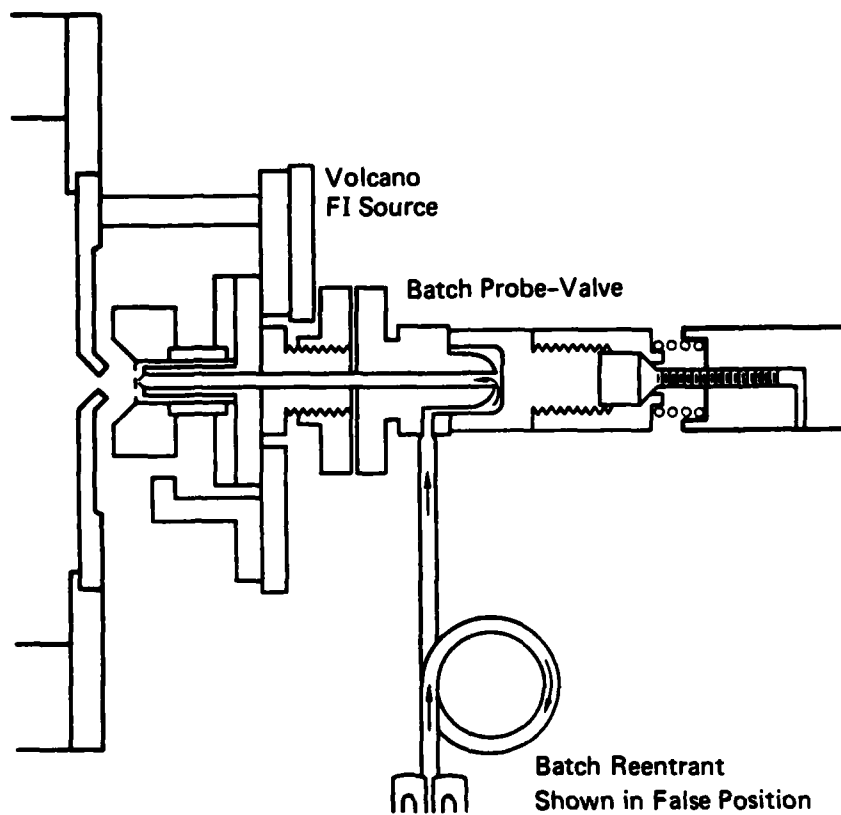
JA-3554-1

FIGURE 1 CROSS SECTION OF SOURCE HOUSING FOR MS-9

a dummy probe is inserted that caps the end of the ionizer to prevent escape of gases from the batch inlet into the source housing; instead, the gases go through the ionizer. This is shown in Figure 2. Figure 3 shows a detail of the volcano-style ionizer when used in conjunction with a solids probe.

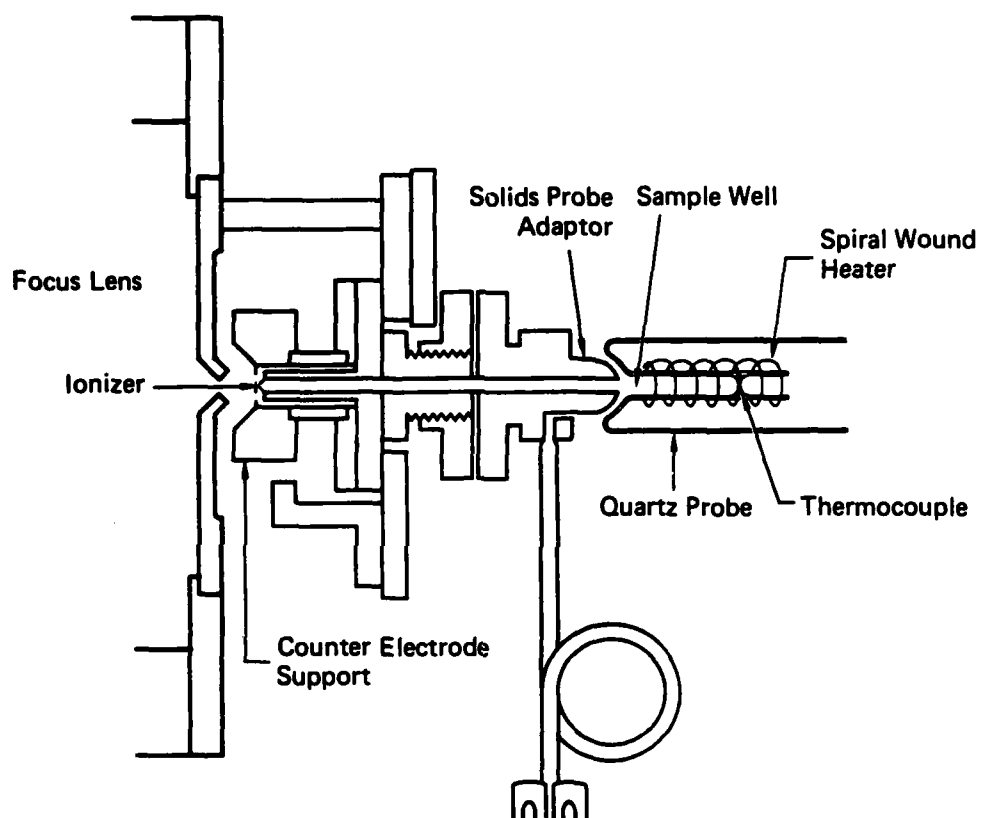
The volcano-style FI source used in this project was designed at SRI by Aberth and Spindt.¹ The ionizer is described in detail in the Final Technical Report for Contract N000173-79-C-0462 entitled, "Analysis of Middle Distillate Fuels by Field Ionization Mass Spectrometry." Ions produced by the field ionization of fuel molecules are accelerated to 6 kV and focused into a small-diameter, round beam. The ions then pass through a dual electrostatic quadrupole lens assembly that provides: (1) strong focusing of the ion beam onto the entrance slit of the MS-9 mass spectrometer, and (2) a means of transforming the round ion beam into a more nearly ribbon-shaped beam that better matches the shape of the entrance slit to the mass spectrometer.

The resolution of the MS-9 equipped with the FI source was tested with a mixture of hydrocarbons containing both saturates and naphthalenes in the molecular weight range 128 to 156. The instrument could easily resolve the molecular ions of these two classes of compounds, indicating a resolution of greater than 1600. With a mixture of benzene and pyridine, it was possible to resolve the molecular ions of pyridine and benzene containing a single carbon-13 atom; furthermore, the instrument resolved the doublet due to the latter ion and the 1% of protonated benzene that is present in this system. The separation of this minor ion from the molecular ion of benzene with one carbon-13 requires a resolving power of 18,800; as shown in Figure 4, this power has been slightly exceeded.



JA-3554-2

FIGURE 2 DETAIL SHOWING THE USE OF BATCH INLET WITH THE VOLCANO
STYLE FIELD IONIZATION SOURCE



JA-3554-3

FIGURE 3 DETAIL SHOWING THE USE OF DIRECT INSERTION PROBE
FOR SOLID SAMPLES WITH THE VOLCANO-STYLE FIELD
IONIZATION SOURCE

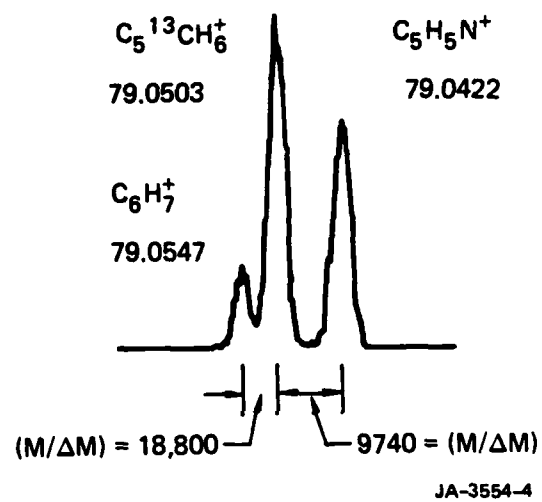


FIGURE 4 EXAMPLE OF THE RESOLVING POWER OF MS-9 EQUIPPED
 WITH VOLCANO STYLE FIELD IONIZER SOURCE
 Mixture of Benzene and Pyridine.

These results demonstrated that the MS-9 could be interfaced with an FI source and that the particular instrument has the needed resolving power. However, for routine use of the spectrometer, a number of alterations were required. These modifications are discussed below.

The magnet current regulation unit in the MS-9 was found to become unstable, and thus successive scans were not reproducible. The scan-to-scan variation was so large that the data system could not produce a valid calibration for the entire run. The problem was found to be a weak vacuum tube in the magnet current regulator. The tube was one of a matched set of three high power vacuum tubes that would have cost \$900 to replace. Rather than invest money in an obsolete unit, we designed, built, tested, and installed a new solid state magnet current regulator that uses power MOSFET transistors. The unit has been operating reliably for more than 18 months now.

A series of twelve 45-V batteries provided the necessary potential for the electric sector. A fraction of this voltage was also used as a reference for the 6-kV ion acceleration power supply. The batteries needed frequent replacement, and often it was noticed that the time centroids of a given peak would change during a run, indicating fluctuations in the battery voltage. The problem was rectified by installing a custom-designed 530-V DC power supply that is isolated from the ground by better than 10^{10} ohms. Drift is less than 10 ppm/°C.

The two ion gauge controllers on the MS-9 also proved to be too unreliable for routine use. The calibration of the ion source pressure gauge varied by a factor of two or more from day to day. The analyzer gauge frequently failed, causing the entire spectrometer to shut itself off. Again, rather than invest time and money in obsolete vacuum tube technology, we

replaced the original ion gauge controllers with two Granville-Phillips Model 260 controllers. This required the modification of the vacuum system of the MS-9 to accept the modern-style ion gauge tubes and construction of a relay interface unit to enable the new ion gauge controllers to operate the vacuum interlocks; the latter protect the high voltage power supply, ion source controls, and the ion multiplier from possible damage due to loss of high vacuum.

Noise in the signal line caused many peaks to be split into two or more peaks. Therefore a two-stage, low-pass RC filter (1 KHz) was installed in the signal line to remedy this problem.

High Temperature Batch-Inlet

The MS-9 was originally equipped with a glass batch-inlet system connected to the electron-impact source by a metal, four-way valve. The four-way valve was designed to allow connection of either the batch inlet or a separate gas inlet to the electron-impact ion source. In addition, the ion source could be isolated from the two inlet systems and the high vacuum could be applied to the lines leading from the two inlet systems to the four-way valve. It was desirable to remove this valve because it provided a source of cross-contamination between samples, its metal construction could cause selective chemical degradation of the fuel molecules, and the large dead-volume required for the permanent connection to the FI source.

The inlet system has been completely rebuilt and connected directly with the volcano-style FI source by means of a heated glass and quartz transfer line. The sample holder is sealed to the batch inlet using a gold gasket seal. This seal was not reliable and has allowed air to leak into the

system on a few occasions. Careful polishing of all the mating surfaces has improved the performance considerably. Although currently usable, the batch inlet system may need to be replaced in the future. The batch inlet has been operated up to 300°C, however, usually it is operated around 225°C, which is sufficient to get a normal signal for compounds as large as C₂₆H₅₄ (MW 366).

High Resolution Mass Spectrometry Data System

A number of commercially available data systems for high resolution mass spectrometry were evaluated; the Kratos DS-55C was chosen, based on its superior quality and low cost. The system hardware consists of a NOVA-4C computer, a Lear Siegler ADM5 monitor, a 12-Megabyte Winchester disk, and an 8-inch floppy drive. Also included is a fast preprocessing board for rapid data acquisition. The software package consists of an integrated and interrelated set of programs for the various aspects of high resolution mass spectrometry. These include routines for:

- Control of the mass spectrometer
- Data acquisition
- Time-to-mass conversions
- Peak averaging
- Quantitation of peaks
- Plotting of spectra
- Computation of molecular formulae from accurate mass data
- Report production.

The DS-55C system was purchased and interfaced with the mass spectrometer with Government funds. With internal funds, SRI purchased and installed a Versatec V-80 printer-plotter and the interface for the Nova-4C computer for use on this project.

Routine use of the mass spectrometer with the data system was impeded by several problems with the data system hardware; the most elusive problem was the occasional failure of the system to detect signals from the spectrometer. A thorough check of the components of the preprocessor unit revealed three instances where the components on the board did not match the specifications in the circuit diagrams. The necessary changes were made and the problem was solved. The data system then ran automatically for ten days continuously without a single failure.

Software for Generating Z-Tables

Jet fuels are likely to contain anywhere between 50 and 150 components. A list of masses and their intensities would be a cumbersome way to present the information on the composition of these fuels. A more manageable representation would be a matrix in which homologous series of different compound classes are sorted into different columns. Because most of the fuel components are hydrocarbons, the obvious choice of compound classification is that according to the z-number, where z is defined by expressing the molecular formula of the hydrocarbon as C_nH_{2n+z} .

A mass scale that defines the mass of the CH_2 unit as 14.0000 can be used to sort the different compound classes, since in this scale the mass defect of any given class will be the same throughout the mass range. Rather than writing a new computer code to generate a z-table from the raw data, we modified an existing DS-55C program. The original program was designed to calculate the elemental composition corresponding to each peak in the spectrum. An added advantage of this approach is that the intensities of ^{13}C satellite peaks can also be easily added to the intensity of the parent peak.

As originally written, the DS-55C program used a combinatorial method to calculate all of the possible molecular compositions that would have an exact mass within some specified range about an experimentally measured mass. Thus, for a measured mass of 128.0643 (naphthalene), the program would determine that either $C_{10}H_8$ (with a deviation of 1.7 millimass units), or $C_9^{13}CH_7$ (with a mass deviation of 6.1 millimass units) were possible elemental compositions. If a heteroatom such as sulphur were included in the combinatorial search, then two additional compositions would be found: $C_7H_{12}S$ (-1.7 millimass units), and $C_6^{13}CH_{11}S$ (2.8 millimass units). Once these formulae are determined, the corresponding z-number is easily found as:

$$z\text{-number} = (\text{number of hydrogen atoms}) - 2 \times (\text{number of carbon atoms}).$$

In this way, the four compositions given above would yield z-numbers of -12, -13, -2, and -3, respectively. By assuming that the first elemental composition having an even z-number is the most likely choice, it is then a simple matter to enter the corresponding measured intensity into a table where the rows are labeled by carbon number and the columns are labeled by the z-number. In the present case of naphthalene, the measured intensity of the peak at mass 128.0643 would be included in the table entry for carbon number 10, and z-number -12. A naphthalene molecule with a single ^{13}C substitution with a measured mass of 129.0674 would yield elemental compositions of $C_{10}H_9$ (mass compositions of $C_{10}H_9$ (deviation = -3.1 millimass unit, z-number = -11), and $C_9^{13}CH_8$ (deviation = 1.4 millimass units, z-number = -12). Because the ^{13}C composition has the even z-number, it would be assumed as the correct formula. Note that it too has a carbon number of 10, and a z-number of -12. Therefore, its intensity would be added to the intensity of the unsubstituted naphthalene already included in the table.

Once all of the entries in the table have been computed, their intensities are summed, and renormalized to a total intensity of 100.0. The resulting table of percentages can then be printed, plotted, or stored for future reference. In addition, a second program has recently been written that could retrieve the stored z-tables from different runs, and compute the average and standard deviation for each entry. This procedure is useful in evaluating the reproducibility of the analysis method.

ANALYSIS METHOD

In general, the quantitative chemical analysis of a complex mixture requires the separation of that mixture by one or more means into individual components or groups of components. The amounts of each of the separated fractions or components are then determined. In earlier work, samples of jet or diesel fuels were separated using a liquid chromatography procedure. Each of the chromatographic fractions was then analyzed further by gas chromatography, or FIMS or other means. The method being developed for this project is based on simultaneous separation and quantitation of fuel mixtures by high resolution FIMS. The general procedure is described below.

Sample Introduction

Approximately 1-2 μL of liquid fuel together with 0.5-1 μL of a mixture of benzene, toluene, and isooctane, which serve as mass markers, are introduced into a high temperature, glass batch-inlet system attached to the high resolution FIMS instrument. To minimize loss of volatile components during sample introduction, the fuel and the standard mass-marker mixture are taken in micro-pipettes (Microcaps, Drummond Scientific Company, Broomall, PA) and placed inside the sample holder. Inside the evacuated glass batch-inlet system, the fuel sample vaporizes completely. A portion of the fuel sample vapor flows into the ion source of the mass spectrometer. Because all of

the fuel sample is vaporized at the same time, the number of molecules of a specific type flowing into the ion source is directly proportional to the number of molecules of that type present in the original fuel.

Ionization and Data Acquisition

The field ionization source in the mass spectrometer ionizes sample molecules into molecular ions. The molecular ions are separated according to their mass by the spectrometer, which is operated at a mass resolution of 3000 or greater, sufficient to completely separate the molecular ions of the different hydrocarbon types present in the original fuel. The mass spectrometer is scanned at a speed of 120 seconds per decade. A scan time of 110 seconds plus a magnet settling time of 10 seconds allows one scan to be completed every 2 minutes. Typically, 10 to 15 scans are collected, although the amount of sample used is sufficient to allow two to three times as many scans if so desired.

The Kratos DS-55C data system requires the presence of a large number of reference peaks in the high resolution mass spectrum. These reference peaks are normally produced by introducing perfluorokerosene (PFK) into the electron impact ion source together with the sample. Because of their negative mass defect, the numerous fragmentation peaks of PFK are easily resolved from most of the sample peaks and provide good mass calibration. However, field ionization produces little fragmentation and most of the commonly used reference compounds, including PFK, are unsuitable for use as internal mass references for our purpose. We have solved this problem by using added compounds and the common fuel components as references. A mixture of benzene, toluene, and isooctane is added together with the fuel

sample. Isooctane is one of the few compounds that even under field ionization undergoes complete fragmentation to give t-butyl ions. This is advantageous since the molecular ion of isooctane would be in the mass range of interest. At the same time, isooctane boils at a high enough temperature to allow easy handling. The fragment t-butyl ion produced from isooctane and the molecular ions of benzene and toluene serve as the autostart masses for the time-to-mass conversion software. A combination of saturated hydrocarbon and alkylbenzene peaks are used as reference masses for the rest of the mass range. Several sets of reference peak masses have been tabulated and different ones are used for different types of fuels.

Time centroid data are usually collected because they can be conveniently reprocessed in the event of an incomplete or unsatisfactory time-to-mass conversion. This can sometimes be a problem because of the highly variable fuel composition of distillate fuels from different sources. Reprocessing of the time-centroid data with a different set of reference peaks is necessary in such cases.

Data Processing

Each of the scans of ion peak intensity is stored in a computerized high resolution mass spectrometer data system, which averages these individual scans and calculates the accurate masses and the elemental composition (chemical formulas) of each of the peaks in the field ionization mass spectrum of the fuel sample. This information enables the peak intensities to be sorted by compound type (z-series) and the number of carbons present in the molecule. The final result of the analysis is a table showing the relative amounts of the various compounds present in the fuel mixture, organized

by z-series and carbon number. The relative field ionization signals of each component of the fuel can be converted into mole fraction of that component present in the original fuel sample by using measured relative field ionization efficiency data for known compounds. This step, as yet, has only been performed manually, but it will be incorporated into the data system shortly.

TECHNICAL RESULTS

Analysis of a Stable and an Unstable Fuel

Two marine diesel fuel samples, NRL 81-5 and NRL 81-6, have been analyzed by HR-FIMS. Fuel 81-5 was typical of marine diesel fuels and behaved normally in use and in storage. Sample 81-6 was from a lot that had passed all the normal specification tests, but began producing large amounts of deposits after only a few weeks of storage.

High resolution FI mass spectra of the two fuels are shown in Figures 5 and 6. Both fuels span a similar mass range, roughly 100 to 300 amu. The intense signal at m/z 260 is due to 1-phenyltridecane, which was added to the fuel to assist in the mass calibration. These analyses were performed before we began using isooctane in the mass marker mixture. The z-series analysis of the two fuels was performed manually using ionization efficiencies that were developed during the previous contract (N00173-79-C-0462). Ionization efficiencies used in this analysis of the different classes of compounds are given in Table 2, and the composition of the fuels according to the z-series and carbon number are presented in Tables 3 and 4. The fuels have similar composition for most classes of compounds; the main difference is the relatively large amount of $z = -12$ (i.e., naphthalenes) and a correspondingly smaller amount of $z = +2$ (i.e., saturates) in the unstable fuel. This result is in concert with the findings of Mayo and coworkers,² who have implicated alkyl naphthalenes in the production of gum and other residues.

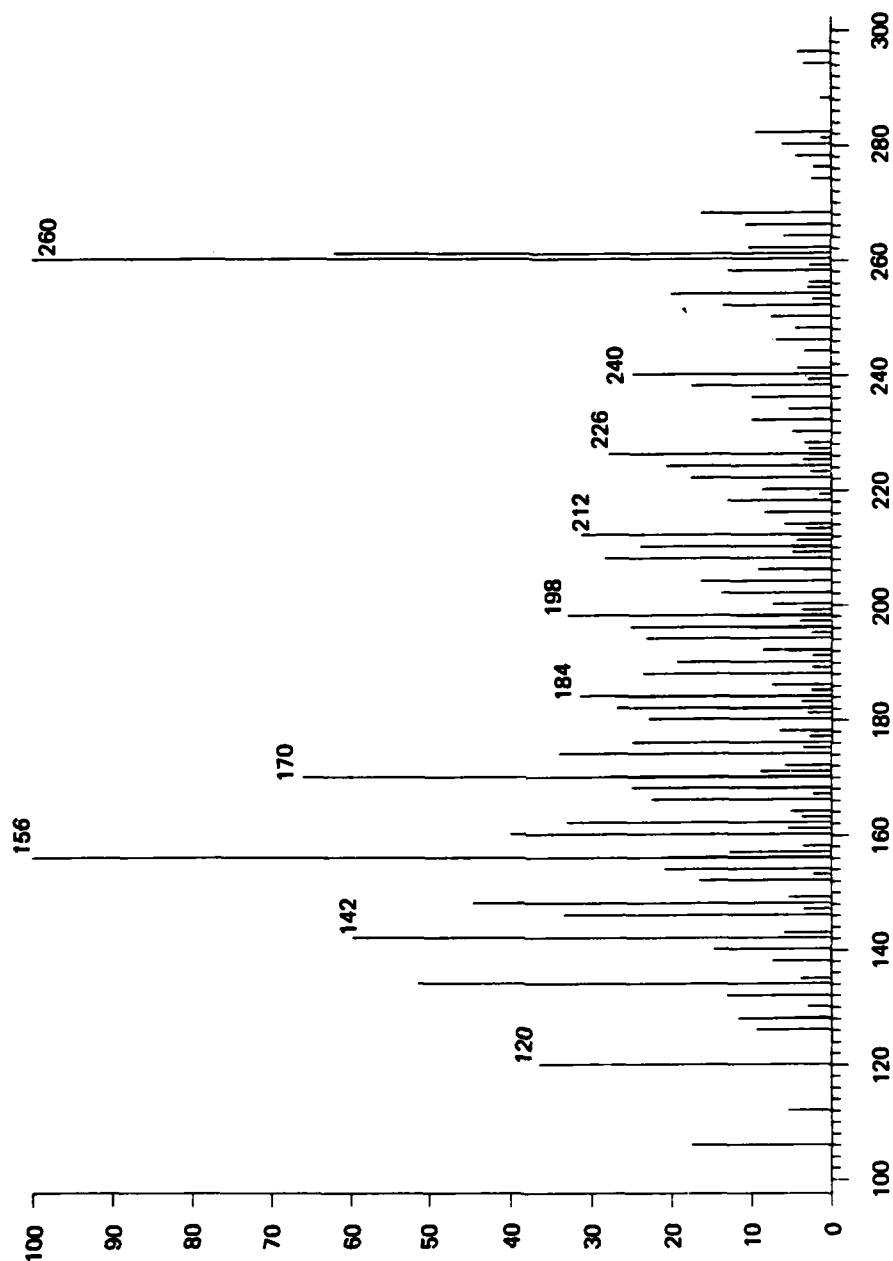


FIGURE 5 HIGH RESOLUTION FIELD IONIZATION MASS SPECTRUM
OF STABLE FUEL SAMPLE NRL-81-5

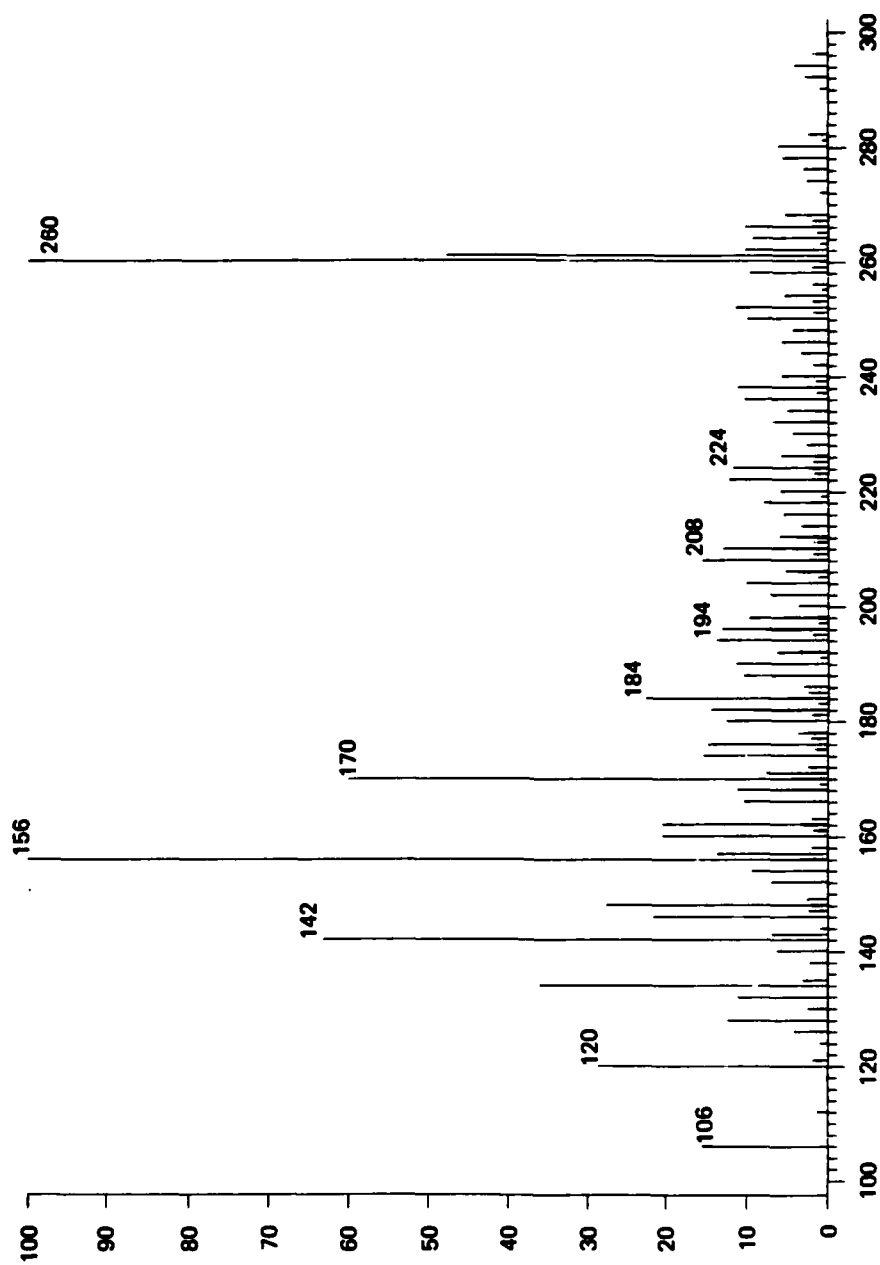


FIGURE 6 HIGH RESOLUTION FIELD IONIZATION MASS SPECTRUM
OF UNSTABLE FUEL SAMPLE NRL-81-6

Table 2

REALTIVE FIELD IONIZATION
SENSITIVITIES FOR HYDROCARBONS

z	Sens.	z	Sens.
2	0.45	-10	1.40
0	0.50	-12	1.40
-2	0.70	-14	1.20
-4	0.70	-16	1.10
-6	1.20	-18	1.40
-8	1.30	-20	1.10

Table 3
COMPOSITION OF STABLE FUEL NRL-81-5 BY CARBON NUMBER AND z-SERIES

n	z	2	0	-2	-4	-6	-8	-10	-12	-14	-16	-18
8			0.5			0.7						
9		0.5	1.0			1.5						
10		1.2	1.5	0.5		2.2	0.5		0.4			
11		2.4	2.1	1.2		1.9	1.3		2.1			
12		3.1	2.5	1.6	0.4	1.4	1.5	0.1	3.6	0.2		
13		3.5	2.7	1.6	0.5	1.0	1.3	0.2	2.4	0.4		
14		3.7	2.5	1.7	0.6	0.8	0.9	0.3	1.0	0.6		0.1
15		3.5	2.4	2.0	0.7	0.7	0.5	0.3	0.4	0.4		0.2
16		3.1	2.1	1.3	0.5	0.5	0.3	0.2	0.2	0.2		0.1
17		2.8	1.8	0.7	0.4	0.4	0.2	0.1	0.1			
18		2.2	1.4	0.5	0.3	0.3	0.1		0.1			
19		1.8	1.1	0.4			0.5	0.1				
20		1.1	0.6	0.3	0.2	0.1						
21		0.5	0.3									
SUM		29.4	22.4	12.0	3.6	11.6	7.2	1.3	10.3	1.8	0.0	0.4

Table 4
COMPOSITION OF UNSTABLE FUEL NRL-81-6 BY CARBON NUMBERS AND Z-SERIES

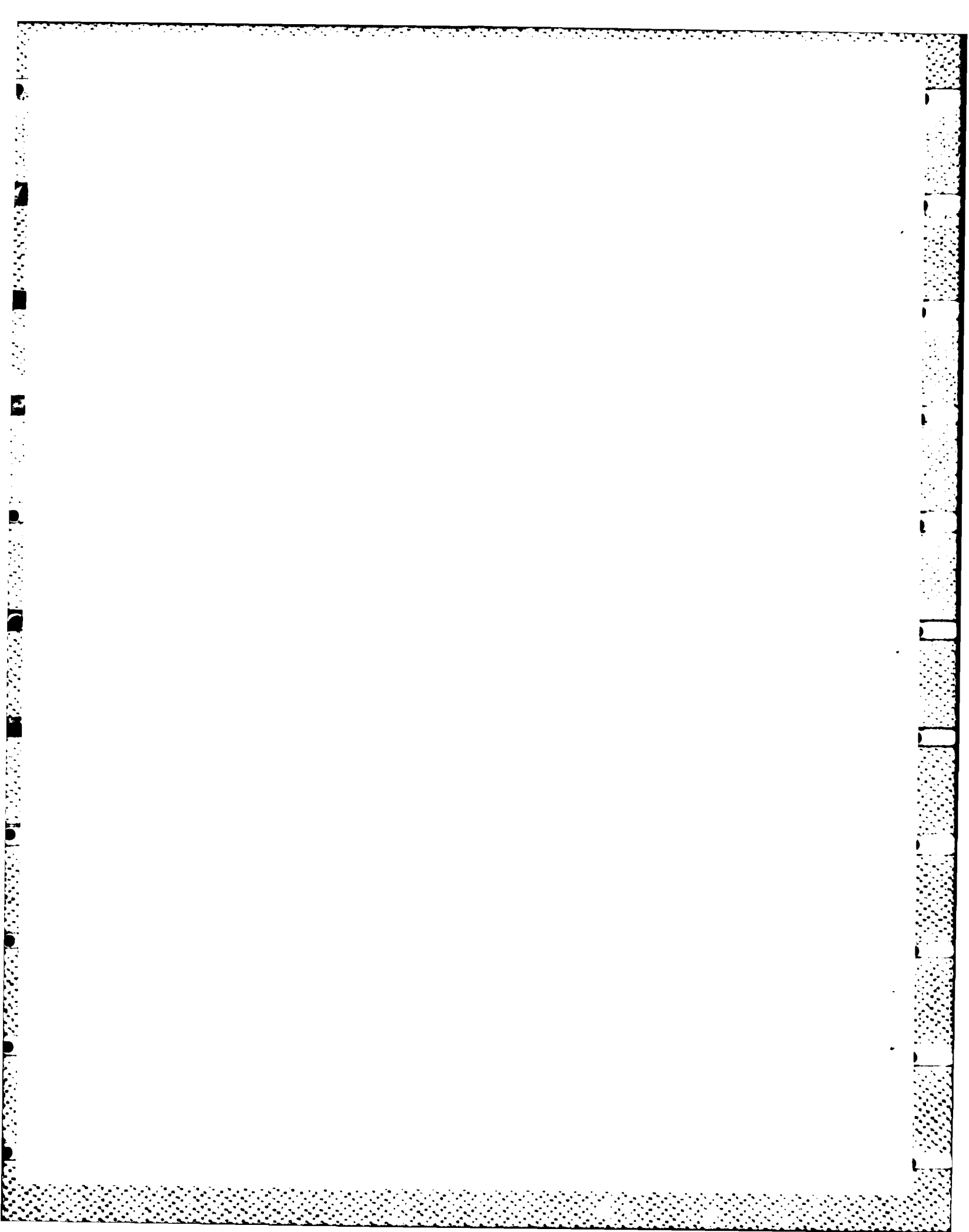
n	z	2	0	-2	-4	-6	-8	-10	-12	-14	-16	-18
8			0.3			1.2						
9			0.8			2.3						
10		0.4	1.2	0.4		3.0	0.9		0.9			
11		0.8	1.9	1.0		2.3	1.7	0.1	4.5			
12		0.9	2.2	1.4		1.7	1.6	0.1	7.2	0.1		
13		1.0	2.3	1.7	0.3	1.0	1.2	0.2	4.3	0.5		
14		1.1	2.1	1.6	0.4	0.7	0.8	0.2	1.3	0.8		0.3
15		1.4	2.1	2.1	0.6	0.7	0.6	0.3	0.7	0.7		0.5
16		1.2	2.0	1.4	0.7	0.5	0.4	0.2	0.3		0.1	0.3
17		1.2	2.2	1.2	0.6	0.5	0.3	0.2	0.1	0.2		
18		1.1	2.3	1.2	0.6	0.4	0.3	0.1				
19		1.1	1.7	1.1			0.8	0.1				
20		0.5	1.2	0.8	0.4	0.2						
21		0.3	0.9	0.4								
SUM		11.0	23.3	14.4	3.7	14.5	8.4	1.6	19.2	2.3	0.1	1.0

The above analysis was made on the assumption that only hydrocarbons are present in the fuel. The resolution of the instrument does not permit separation of oxygen, nitrogen, and sulfur peaks from the corresponding hydrocarbon peaks. We are currently planning installation of a larger capacity diffusion pump for the source housing; this pump will permit introduction of larger amounts of sample, and we hope to then have enough signal intensity to increase the resolving power to about 10,000. This will permit resolution of oxygen compounds from hydrocarbons.

Standardization of the Analytical Procedure

Analysis of fuel samples NRL 81-5 and 81-6 demonstrate the feasibility of using high resolution FIMS for chemical characterization of distillate fuels. However, for routine application it is necessary to standardize the procedure and optimize the operating conditions. As a part of this project, considerable effort was expended on this aspect as well. For this work several test mixes were prepared and analyzed repeatedly. One test mix (Test Mix 2) containing 34 pure compounds has been analyzed more than 50 times. The test mixes were prepared by accurately weighing out the pure compounds and storing them in Teflon-sealed vials. Several of the instrumental problems discussed in an earlier section were detected during this process of repeated analysis.

Standardization of the procedure was time consuming because of the many alterations needed in the instrument. Furthermore, on several occasions the volcano FI sources were deactivated or burnt and had to be replaced. The ion currents obtained from the newer sources were often weak, resulting in poor signal-to-noise ratio and wide variability in the analysis. We have



now been using Ta-coated volcano FI sources, which are proving to be very resilient and also give strong ion currents.

With these changes accomplished, a systematic study was conducted to determine the effect of various operating parameters on the mass spectrum; this was done to allow determination of conditions that give reproducible analyses even when all the operating parameters are not exactly the same. A representative FI mass spectrum of Test Mix 2 is shown in Figure 7. Figure 8 shows the same data in a tabular form as generated by the data system. As can be seen from doublets at masses 112, 142, 168, and 196, the mass spectrometer is operating with sufficient resolution. The molar amounts of each of the components of Test Mix 2, together with their ionization efficiencies relative to 1-phenylheptane, are given in Table 5. The various compounds have been grouped according to their z -values, where z is determined from the chemical formula of the compound when expressed in the form C_nH_{2n+z} .

The ionization efficiencies of saturated hydrocarbons generally vary between 25% and 40% relative to 1-phenylheptane. Monocyclic alkanes ionize more efficiently than the saturates; their efficiencies range from 30% to 70%. Other polycyclics ($z = -2$ and -4) also fall within this range. Ionization efficiencies of the various alkylbenzenes are around 100%, with the exception of *p*-xylene and *n*-propylbenzene, which are around 70%. The reduced ionization efficiency for the lighter components may reflect some losses during the freeze-pump-thaw cycle.

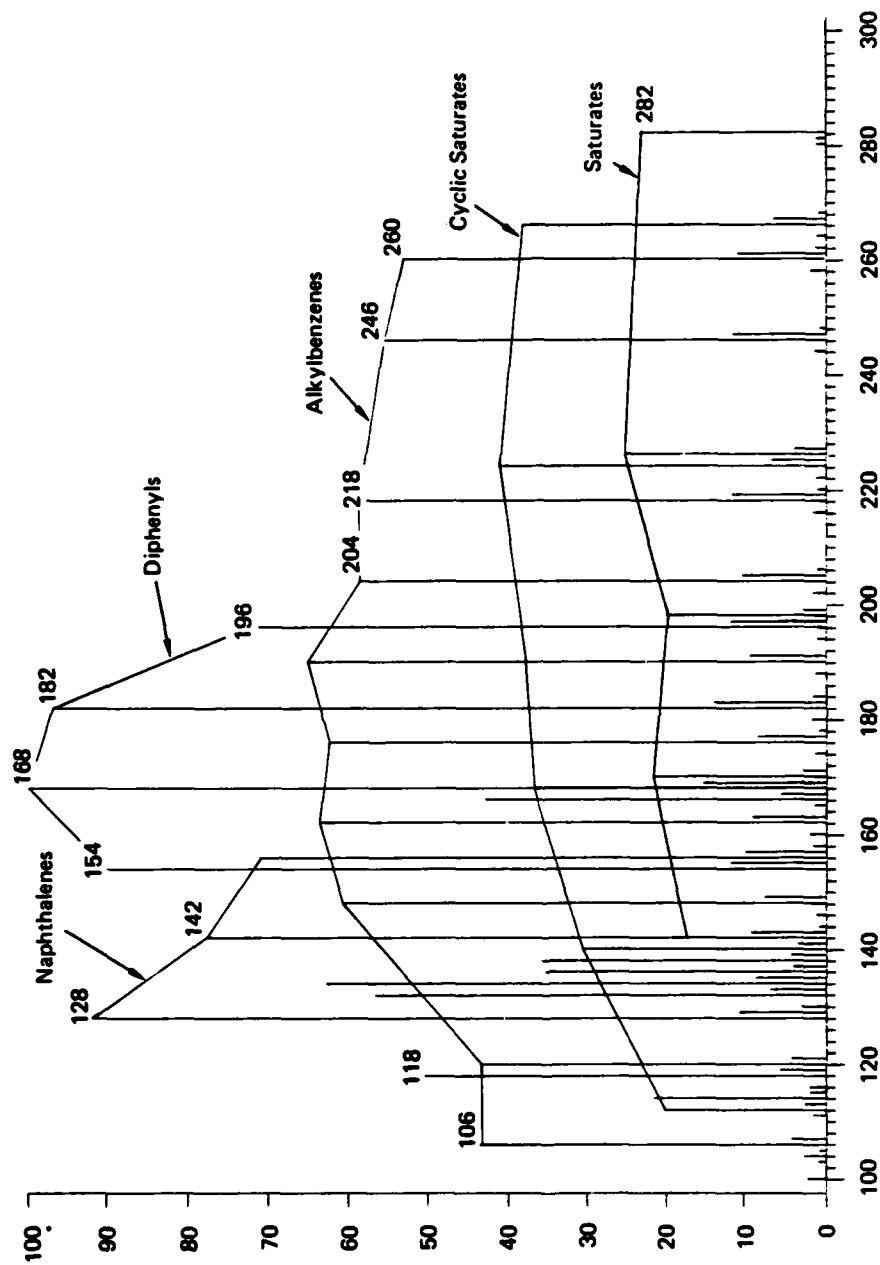


FIGURE 7 HIGH RESOLUTION FIELD IONIZATION MASS SPECTRUM
OF TEST MIX 2

DPB12V0V6.MS
SCAN: 1. 6/21/84 15.7
IONISATION: EI
NO. PEAKS: 132
BASE/REF INT: 67948./ 16475.
TIC: 510384.
MASS RANGE: 57.0784 - 282.3286
RETN TIME/MISC: 8.7 8.7 8.7

PEAK NO.	MEASURED MASS	NO. POINTS	ABSOLUTE INTENSITY	X INT. BASE	X INT. MREF	X INT. 176	X TOT. ION
1	32.1276	21	3787.	5.6	1.2	36.9	6.7
2	34.1277	12	301.	0.3	0.3	2.6	0.6
3	36.1153	18	306.	0.3	1.3	2.6	0.6
4	38.1124	18	165.	0.2	1.6	1.6	0.6
5	37.3019	25	1054.	1.6	10.3	18.3	0.2
6	36.1958	25	635.	9.2	61.1	61.1	1.2
7	34.2886	18	105.	0.3	2.6	2.6	0.6
8	32.1645	18	238.	2.3	1.2	2.6	0.6
9	31.2548	29	1761.	12.9	12.7	17.2	0.3
10	30.1582	14	8336.	2.6	1.2	17.2	0.3
11	28.1433	14	324.	0.5	2.6	3.2	0.6
12	28.1463	10	135.	0.2	0.8	1.3	0.6
13	27.2371	21	1957.	2.7	11.3	18.9	0.4
14	26.2347	21	9123.	13.4	11.3	18.9	0.4
15	24.2250	12	242.	0.4	1.6	2.4	0.6
16	22.1714	14	4139.	1.6	4.6	6.4	0.1
17	20.1668	21	1655.	6.1	4.6	10.3	0.9
18	20.1543	17	6768.	1.6	5.4	10.3	0.2
19	22.1373	25	218.	10.8	41.1	66.8	0.8
20	22.1373	18	179.	0.3	1.3	2.6	0.6
21	20.1222	18	1862.	2.8	11.4	13.4	0.4
22	21.1209	21	9637.	1.2	1.2	53.9	1.9
23	21.1209	29	172.	3.3	1.8	1.7	0.6
24	21.1126	18	172.	0.4	1.7	2.8	0.1
25	21.1084	18	288.	0.4	1.7	2.8	0.1
26	21.1030	0	152.	0.4	1.7	1.9	0.6
27	20.1321	21	1555.	2.5	18.1	16.2	0.3
28	20.1321	25	9634.	14.2	1.6	2.6	0.1
29	22.1746	12	263.	0.4	1.6	4.6	0.6
30	19.1393	17	4.2.	0.4	2.5	31.9	0.6
31	19.1347	12	3277.	0.4	1.5	2.5	0.6
32	19.1347	12	562.	1.4	5.8	9.4	0.2
33	17.1356	21	1922.	2.8	10.7	18.7	0.4
34	16.1199	21	6193.	9.1	37.6	60.4	1.2
35	16.1255	25	11717.	1.2	114.2	114.2	2.3
36	15.1316	18	174.	0.3	1.1	1.7	0.6
37	15.1316	18	194.	0.3	1.2	1.9	0.6
38	14.1898	12	1516.	2.2	9.2	14.8	0.3
39	13.1762	17	18699.	1.7	2.2	184.2	2.1
40	13.1762	25	238.	0.4	1.4	2.3	0.6
41	13.1535	18	276.	0.4	1.7	2.3	0.6
42	12.1159	12	2336.	0.4	13.9	22.3	0.1
43	12.1134	21	15346.	2.5	96.8	155.4	3.1
44	12.1121	21	371.	0.4	1.8	2.3	0.6
45	10.1918	12	155.	0.2	1.8	1.6	0.6
46	10.1632	18	1482.	1.1	0.5	13.7	0.3
47	10.1624	29	18561.	15.1	1.8	188.8	2.8
48	10.1624	29	249.	0.7	2.3	4.6	0.6
49	11.1353	12	3544.	5.2	2.3	34.5	0.7
50	10.1836	14	255.	0.4	1.6	2.6	0.6
51	10.1836	14	255.	0.4	1.6	2.6	0.6
52	10.1836	14	255.	0.4	1.6	2.6	0.6
53	10.1836	14	255.	0.4	1.6	2.6	0.6
54	10.1836	14	255.	0.4	1.6	2.6	0.6
55	10.1836	14	255.	0.4	1.6	2.6	0.6
56	10.1836	14	255.	0.4	1.6	2.6	0.6
57	10.1836	14	255.	0.4	1.6	2.6	0.6
58	10.1836	14	255.	0.4	1.6	2.6	0.6
59	10.1836	14	255.	0.4	1.6	2.6	0.6
60	10.1836	14	255.	0.4	1.6	2.6	0.6
61	10.1836	14	255.	0.4	1.6	2.6	0.6
62	10.1836	14	255.	0.4	1.6	2.6	0.6
63	10.1836	14	255.	0.4	1.6	2.6	0.6
64	10.1836	14	255.	0.4	1.6	2.6	0.6
65	10.1836	14	255.	0.4	1.6	2.6	0.6
66	10.1836	14	255.	0.4	1.6	2.6	0.6

PEAK NO.	MEASURED MASS	NO. POINTS	ABSOLUTE INTENSITY	X INT. BASE	X INT. MREF	X INT. 176	X TOT. ION
67	184.1716	18	143.	0.2	0.9	1.4	0.6
68	184.1716	29	143.	0.2	0.9	1.4	0.6
69	184.1716	29	143.	0.2	0.9	1.4	0.6
70	184.1716	29	143.	0.2	0.9	1.4	0.6
71	184.1716	29	143.	0.2	0.9	1.4	0.6
72	184.1716	29	143.	0.2	0.9	1.4	0.6
73	184.1716	29	143.	0.2	0.9	1.4	0.6
74	184.1716	29	143.	0.2	0.9	1.4	0.6
75	184.1716	29	143.	0.2	0.9	1.4	0.6
76	184.1716	29	143.	0.2	0.9	1.4	0.6
77	184.1716	29	143.	0.2	0.9	1.4	0.6
78	184.1716	29	143.	0.2	0.9	1.4	0.6
79	184.1716	29	143.	0.2	0.9	1.4	0.6
80	184.1716	29	143.	0.2	0.9	1.4	0.6
81	184.1716	29	143.	0.2	0.9	1.4	0.6
82	184.1716	29	143.	0.2	0.9	1.4	0.6
83	184.1716	29	143.	0.2	0.9	1.4	0.6
84	184.1716	29	143.	0.2	0.9	1.4	0.6
85	184.1716	29	143.	0.2	0.9	1.4	0.6
86	184.1716	29	143.	0.2	0.9	1.4	0.6
87	184.1716	29	143.	0.2	0.9	1.4	0.6
88	184.1716	29	143.	0.2	0.9	1.4	0.6
89	184.1716	29	143.	0.2	0.9	1.4	0.6
90	184.1716	29	143.	0.2	0.9	1.4	0.6
91	184.1716	29	143.	0.2	0.9	1.4	0.6
92	184.1716	29	143.	0.2	0.9	1.4	0.6
93	184.1716	29	143.	0.2	0.9	1.4	0.6
94	184.1716	29	143.	0.2	0.9	1.4	0.6
95	184.1716	29	143.	0.2	0.9	1.4	0.6
96	184.1716	29	143.	0.2	0.9	1.4	0.6
97	184.1716	29	143.	0.2	0.9	1.4	0.6
98	184.1716	29	143.	0.2	0.9	1.4	0.6
99	184.1716	29	143.	0.2	0.9	1.4	0.6
100	184.1716	29	143.	0.2	0.9	1.4	0.6
101	184.1716	29	143.	0.2	0.9	1.4	0.6
102	184.1716	29	143.	0.2	0.9	1.4	0.6
103	184.1716	29	143.	0.2	0.9	1.4	0.6
104	184.1716	29	143.	0.2	0.9	1.4	0.6
105	184.1716	29	143.	0.2	0.9	1.4	0.6
106	184.1716	29	143.	0.2	0.9	1.4	0.6
107	184.1716	29	143.	0.2	0.9	1.4	0.6
108	184.1716	29	143.	0.2	0.9	1.4	0.6
109	184.1716	29	143.	0.2	0.9	1.4	0.6
110	184.1716	29	143.	0.2	0.9	1.4	0.6
111	184.1716	29	143.	0.2	0.9	1.4	0.6
112	184.1716	29	143.	0.2	0.9	1.4	0.6
113	184.1716	29	143.	0.2	0.9	1.4	0.6
114	184.1716	29	143.	0.2	0.9	1.4	0.6
115	184.1716	29	143.	0.2	0.9	1.4	0.6
116	184.1716	29	143.	0.2	0.9	1.4	0.6
117	184.1716	29	143.	0.2	0.9	1.4	0.6
118	184.1716	29	143.	0.2	0.9	1.4	0.6
119	184.1716	29	143.	0.2	0.9	1.4	0.6
120	184.1716	29	143.	0.2	0.9	1.4	0.6
121	184.1716	29	143.	0.2	0.9	1.4	0.6
122	184.1716	29	143.	0.2	0.9	1.4	0.6
123	184.1716	29	143.	0.2	0.9	1.4	0.6
124	184.1716	29	143.	0.2	0.9	1.4	0.6
125	184.1716	29	143.	0.2	0.9	1.4	0.6
126	184.1716	29	143.	0.2	0.9	1.4	0.6
127	184.1716	29	143.	0.2	0.9	1.4	0.6
128	184.1716	29	143.	0.2	0.9	1.4	0.6
129	184.1716	29	143.	0.2	0.9	1.4	0.6
130	184.1716	29	143.	0.2	0.9	1.4	0.6
131	184.1716	29	143.	0.2	0.9	1.4	0.6
132	184.1716	29	143.	0.2	0.9	1.4	0.6

JA-3554-8

FIGURE 8 HIGH RESOLUTION FIMS DATA OF TEST MIX 2

Note doublets at m/z: 142, 168, and 196.

Table 5
COMPOSITION OF TEST MIX 2 AND
RELATIVE FIELD IONIZATION EFFICIENCIES OF ITS CONSTITUENTS

z	Compound	NW	Amount in Mixture (mmol)	Relative Field Ionization Efficiency
+2	n-Decane	142	1.00	0.27
	n-Dodecane	170	1.02	0.35
	n-Tetradecane	198	1.02	0.32
	n-Hexadecane	226	1.02	0.40
	Eicosane	282	1.00	0.37
0	Ethylcyclohexane	112	1.05	0.32
	n-Butylcyclohexane	140	1.06	0.49
	n-Hexylcyclohexane	168	1.01	0.58
	n-Octylcyclohexane	196	0.97	0.60
	n-Decylcyclohexane	224	0.99	0.66
	n-Tridecylcyclohexane	266	0.97	0.61
-2	Decalin	138	0.98	0.57
	Dicyclohexane	166	1.04	0.69
-4	Adamantane	136	1.01	0.56
-6	P-Xylene	106	0.95	0.70
	n-Propylbenzene	120	0.94	0.70
	Diethylbenzene	134	1.04	1.00
	n-Pentylbenzene	148	1.01	0.97
	1-Phenylhexane	162	1.03	1.02
	1-Phenylheptane	176	1.02	1.00
	1-Phenylloctane	190	1.02	1.04
	1-Phenylnonane	204	1.00	0.94
	1-Phenyldecane	218	1.01	0.94
	1-Phenyldodecane	246	1.02	0.89
	1-Phenyltridecane	260	0.99	0.85
-8	Indane	118	1.00	0.81
	Tetralin	132	1.03	0.91
-12	Naphthalene	128	1.01	1.48
	2-Methylnaphthalene	142	0.99	1.24
	2-Ethylnaphthalene	156	0.98	1.13
-14	Biphenyl	154	1.01	1.45
	4-Phenyltoluene	168	1.01	1.61
	Dimethylbiphenyl	182	1.01	1.55
	Diphenylpropane	196	0.96	1.14

CONCLUSIONS

Work performed under this contract demonstrates the applicability of high resolution FIMS as a powerful technique for the chemical characterization of middle distillate fuels. Most of the problems with the spectrometer have been remedied, and the instrument has been operating on a routine basis. The only weak point in the entire system appears to be the heated batch inlet system. The sample holder must be bolted onto the main body each time a new sample is introduced, and a user is never certain of a leak-free connection until after the freeze-pump cycle, during which time some of the volatiles may be lost in evaporation. Moreover, the batch inlet has several metal parts where certain fuel components may be selectively adsorbed or undergo chemical transformation--resulting in faulty analysis. An all-glass batch inlet, which uses optical flat plates for attaching the sample holder, is clearly desirable, but the cost of a commercial unit is quite prohibitive. We have been exploring other possible inexpensive alternatives, such as purchasing the optical flats and constructing the remaining setup at SRI.

An all glass batch inlet, while desirable, is certainly not essential to the successful completion of the remaining tasks. With the present arrangement replicate analyses show a variation of less than 20% for most of the peaks. We have determined the relative field ionization efficiencies for most of the commonly occurring hydrocarbons in these fuels. However, we

have not yet incorporated these factors in the computer program that generates the z-series analysis. We plan to do this in the near future and then begin analysis of the various fuel samples submitted to us by the Naval Research Laboratory.

References

1. W. Aberth and C. A. Spindt, Int. J. Mass Spectrom. Ion Phys., 1977, 25, 183.
2. F. R. Mayo and B. Y. Lan, Division of Petroleum Chemistry, Preprints, 1983, 28(5), 1209.

END

FILMED

12-84

DTIC