

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

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**INTRODUCTION AND BACKGROUND**

During the decade following the Arab oil embargo, there has been an increase 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 the 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. There have even been a few instances in which a fuel which 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 will require the development of new methods for distillate fuel analysis capable of providing rapid and detailed information on the chemical composition of the distillate fuels.

A number of methods for the analysis of fossil fuels by mass spectrometry have been reported. Many of them, including the ASTM standard, D2425-67 (1978), use electron-impact (EI) ionization. This mode of ionization causes extensive fragmentation and precludes obtaining any information on the molecular-weight distribution of the sample. To circumvent this problem, many investigators have used low-energy electron-impact ionization, and other softer modes of ionization, such as field ionization (1,2) and field desorption (3). Both field desorption, and low-energy EI display a wide range of response factors for different classes of compounds and field ionization appears to be a method of choice, at least for distillate fuels (4).

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. 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 followed by FIMS analysis of each of these fractions. In this paper we describe the development of 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.

By using high resolution, it will be possible to distinguish between molecular ions belonging to different hydrocarbon classes that share the same nominal mass. To resolve pairs of hydrocarbons differing by a C-H<sub>12</sub> doublet, e.g., nonane and naphthalene, a resolving power of 3,200 is sufficient for all molecules of molecular weight 300 amu or less.

## DESCRIPTION OF EQUIPMENT AND SOFTWARE

### Field Ionization Mass Spectrometer

A vintage MS-9 mass spectrometer (AEI, Ltd.) was completely disassembled, cleaned, and reworked to bring it into good operating condition. In the EI ionization mode using the original ion source, a mass resolution of 30,000 was eventually obtained. The spectrometer has been interfaced with a Kratos DS-55C data system.

In order 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 (5). Figure 1 shows a scale drawing of a cross-section through the modified MS-9 source housing.

The volcano-style FI source used in this work was designed at SRI by Aberth and Spindt (6). 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) focusing of the ion beam on to 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. Furthermore, with a mixture of benzene and pyridine, it was possible to resolve besides the molecular ions of pyridine and benzene containing a single carbon-13 atom 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 the inset of Figure 1, this power has been slightly exceeded.

### Software for Generating z-Tables

Distillate fuels are likely to contain anywhere between 50 and 150 constituents. A list of masses and their intensities would be a very 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 were sorted into different columns. Since 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 which defines 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 (7). Rather than writing a new computer code to generate a z-table from the raw data, an existing DS-55C program was modified. 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.

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 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, and any fuel composition-property correlations.

## **ANALYTICAL PROCEDURE**

### Sample Introduction

Approximately 1-2  $\mu\text{L}$  of liquid fuel together with 0.5-1  $\mu\text{L}$  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 PIMS instrument. To minimize loss of volatile components during sample introduction, the fuel and the standard mass-marker mixtures 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 ten seconds allows one scan to be completed every two 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 which 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 is sufficiently high boiling 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 alkybenzene 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.

## **RESULTS AND DISCUSSION**

### Determination of Response Factors

Relative ionization efficiencies were determined by using a number of test mixes containing up to 30 components. The various test mixes were designed to study possible matrix effects and to determine the efficiencies of isomeric compounds. These studies also helped in developing the analytical technique. Ionization efficiencies of the various compounds were measured relative to 1-phenylheptane. Response factors were determined for several homologs within a compound class. We observed that ionization efficiencies for the various classes of compounds varies only slightly over the molecular weight range encountered with distillate fuels; 100 to 300 amu. Branching lowers the observed intensity of the molecular ion because of some fragmentation, but this effect is serious only in the case of molecules containing quaternary carbons. Polycyclic aromatics have the highest ionization efficiency and straight chain aliphatics the least.

For the purposes of analyzing fuel samples we used an average of the response factors of the various homologs belonging to that class. We had not expected compounds more unsaturated than biphenyls in diesel and jet fuels and therefore had not determined the response factors of phenanthrenes and dihydrophenanthrenes. However, we did encounter them and have used the same response factors for them as naphthalenes. The response factors used for the various classes are given in Table 1.

### Analysis of Some Distillate Fuel Samples

We had earlier reported on the analysis of a stable and unstable fuel sample and shown that the unstable fuel had a substantially greater amount of naphthalenes (5). This result is in concert with the findings of Mayo and Lan (8).

Several other diesel fuel marine and experimental jet fuel samples have been analyzed by HR-FIMS. Results of the analysis of a very stable fuel (NRL-83-14) are shown in Table 2. The table gives the mole percent of the various constitu-

ents by their carbon number and z-series. The fuel contains 27.8% acyclic and 14.4% monocyclic saturates. No bicyclic or tricyclics were detected. This fuel is also very rich in alkyl benzenes and tetralins. It is interesting to note that the distribution of the compounds within any z-series is fairly uniform for all compound classes except naphthalenes. The compound at m/z 212.0712, identified as C<sub>17</sub>H<sub>8</sub> (z = -26, M.W. 212.0626) is most likely ethyl (or dimethyl-) dibenzthiophene (M.W. 212.0660). Composition of a model fuel used for engine tests, NRL-82-15, is given in Table 3. The fuel is less stable relative to NRL-83-14 and has somewhat of a higher naphthalene content.

### CONCLUSIONS

This work demonstrates the applicability of high-resolution FIMS as a powerful technique for rapid chemical characterization of middle distillate fuels. We have fixed most of the problems with the spectrometer, and the instrument is now operating on a routine basis. The only weak point in the entire system appears to be the heated batch inlet system. Preliminary results have shown that this technique provides accurate and reproducible data. Data analyzed thus far are too scant to make definitive fuel composition-property correlations; such studies are currently underway.

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Table 1  
RELATIVE FIELD IONIZATION EFFICIENCIES OF VARIOUS HYDROCARBONS

<u>Compound Class</u>	<u>Z</u>	<u>Relative Response</u> *
Alkanes	2	0.34
Monocyclic alkanes	0	0.54
Bicyclic alkanes	-2	0.63
Tricyclicalkanes	-4	0.56
Benzenes	-6	0.91
Tetalins	-8	0.86
Octahydrophenanthrenes	-10	1.03
Naphthalenes	-12	1.03
Biphenyls or Tetrahydro- phenanthrenes	-14	1.44
Dihydrophenanthrenes	-16	1.44
Phenanthrenes or Anthracenes	-18	1.44

\*Relative to 1-phenylheptane.

Table 2

## COMPOSITION OF FUEL NRL-83-14\* BY CARBON NUMBER AND z-SERIES

n	z	2	0	-2	-4	-6	-8	-10	-12	-14	-16	-18	-26
10						2.58							
11						2.91	1.84	1.53					
12						2.08	2.47	5.15					
13			3.52			2.02	2.58	6.96	0.77				
14		4.89											
15		5.16	2.30			2.14							
16		5.34	2.87			1.59	2.11	1.54	1.26	0.79	0.98		
17		4.00	2.19			2.07	1.73	1.35	1.26	0.84	1.01		
18		4.74	1.31			2.04	1.94			0.86			
19		3.65	2.20			1.42							
20						1.94							
SUM		27.8	14.4			20.8	12.7	16.5	4.2	0.8	1.8	1.0	†

\*A very stable fuel sample.

†The compound is most likely ethyl (or dimethyl-) dibenzthiophene.

Table 3

## COMPOSITION OF FUEL NRL-82-15\* BY CARBON NUMBER AND z-SERIES

n	z	2	0	-2	-4	-6	-8	-10	-12	-14	-16	-18
8						0.63						
9						1.00						
10						0.89						
11		1.67	0.89			0.83	1.17	4.08				
12		6.95	1.52	1.96		1.30	2.02	6.54				
13			2.75			1.69	2.50	6.55				
14		4.60										
15		3.74	2.21	2.62	0.92	1.26						
16		3.61		2.09		1.04	1.55	1.23	1.57	0.89		
17		4.64	1.68	1.24	1.32	1.43	1.24	0.80	0.78	0.47		
18		3.07	2.16	0.70		0.62	1.07	0.69				
19		2.57	2.11	0.96		0.53		0.44				
SUM		30.9	12.5	9.6	2.2	11.2	9.6	2.7	20.0	1.4		

\*Relatively unstable fuel, but not the worst.

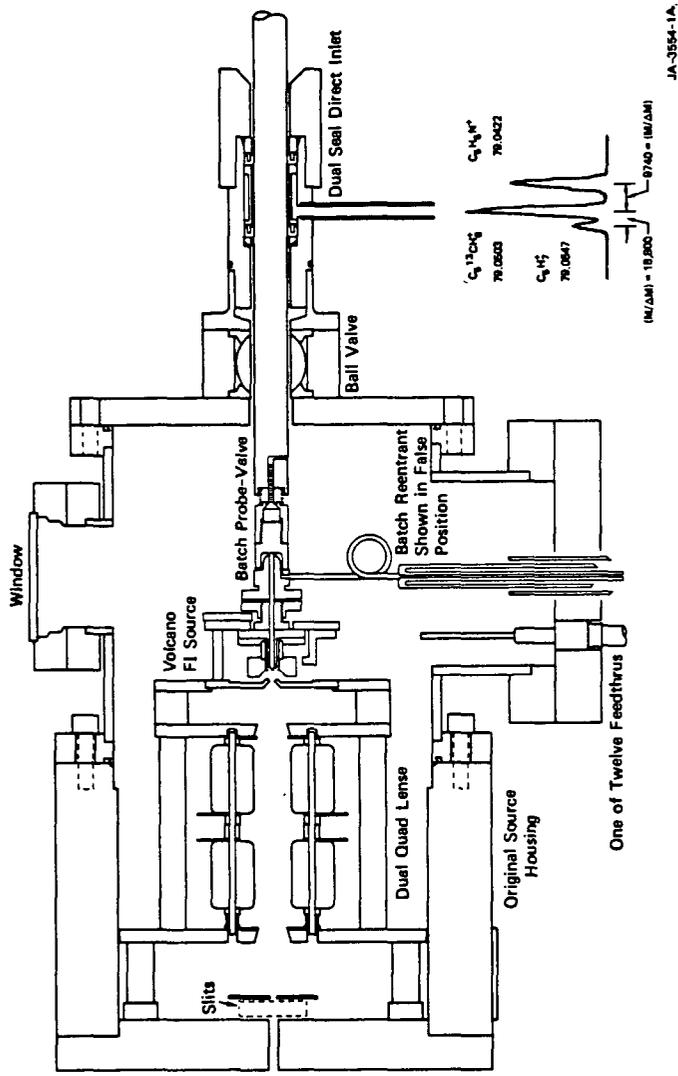


FIGURE 1 CROSS SECTION OF SOURCE HOUSING FOR MS-9