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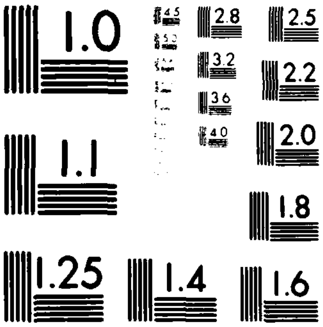

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Part I

TANDEM MASS SPECTROMETRIC ANALYSIS (MS/MS) OF JET FUELS
PART I: EXPERIMENTAL PROCEDURES AND QUALITATIVE DATA ANALYSIS

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July 1985

FINAL REPORT FOR PERIOD June 1984 - July 1984

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WRIGHT-PATTERSON AIR FORCE BASE, OH 45433-6563

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

This technical report has been reviewed and is approved for publication.

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UNCLASSIFIED
SECURITY CLASSIFICATION OF THIS PAGE

AD-A170 221

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION
Unclassified

1b. RESTRICTIVE MARKINGS
N/A

2a. SECURITY CLASSIFICATION AUTHORITY
N/A

2b. DECLASSIFICATION/DOWNGRADING SCHEDULE
N/A

3. DISTRIBUTION/AVAILABILITY OF REPORT
Approved for Public Release;
Distribution Unlimited

4. PERFORMING ORGANIZATION REPORT NUMBER(S)
GC-FR-416-84-0001

5. MONITORING ORGANIZATION REPORT NUMBER(S)
AFWAL-TR-85-2047 Pt. 1

6a. NAME OF PERFORMING ORGANIZATION
Biomaterials Profiling Center

6b. OFFICE SYMBOL (If applicable)

7a. NAME OF MONITORING ORGANIZATION
Geo-Centers, Inc.

6c. ADDRESS (City, State and ZIP Code)
391 S. Chipeta Way, Suite F, Research Park
Salt Lake City, Utah
84108

7b. ADDRESS (City, State and ZIP Code)
320 Needham Street
Newton Upper Falls MA
02164

8a. NAME OF FUNDING/SPONSORING ORGANIZATION
Aero Propulsion Laboratory

8b. OFFICE SYMBOL (If applicable)
AFWAL/POSF

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
F33615-84-C-2412

8c. ADDRESS (City, State and ZIP Code)
Air Force Wright Aeronautical Laboratories
Wright-Patterson Air Force Base
OH 45433-6563

10. SOURCE OF FUNDING NOS.

PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT NO.
63215F	2480	12	00

11. TITLE (Include Security Classification)
TANDEM MASS SPECTROMETRIC ANALYSIS (MS/MS) OF

12. PERSONAL AUTHOR(S)
Henk L.C. Meuzelaar and William H. McClennen

13a. TYPE OF REPORT
Final

13b. TIME COVERED
FROM 6/1/84 TO 7/31/84

14. DATE OF REPORT (Yr., Mo., Day)
July 1985

15. PAGE COUNT
38

16. SUPPLEMENTARY NOTATION
Report prepared under contract to Geo-Centers, Inc. via the AFWAL/POS Scholarly Research Program.

17. COSATI CODES

FIELD	GROUP	SUB. GR.
07	01	03
21	04	05

18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
jet fuel analysis; mass spectrometry; tandem mass spectrometry MS/MS; low voltage ionization; liquid sample inlet; GC/MS Naphthenic fuels; multivariate statistics; factor analysis; discriminant analysis; alkyl decalins; alkyl tetralins

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

A fast, direct mass spectrometry (MS) determination of hydrocarbon classes in jet fuels is presented. A novel inlet technique using 0.1 mm i.d. micropipet glass capillaries for sampling the liquid fuels and reproducibly placing the 10 to 20 ug samples in the MS vacuum for analysis is demonstrated. Low voltage electron ionization is shown to produce molecular ion series characteristic of alkyl substituted naphthalenes, tetralins, and decalins. Structurally specific fragment ions for several hydrocarbons, as determined by gas chromatography - mass spectrometry, are used to help identify compound classes by tandem mass spectrometry (MS/MS). As discussed, MS/MS can add a dimension of separation to overlapping molecular ion series while maintaining the greater speed of direct MS over GC/MS. In addition, multivariate statistical analysis is demonstrated to be a powerful method for comparison of MS spectra from complex jet fuels to chemical class standards.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT
UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT. ☐ DTIC USERS ☐

21. ABSTRACT SECURITY CLASSIFICATION
UNCLASSIFIED

22a. NAME OF RESPONSIBLE INDIVIDUAL
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22c. OFFICE SYMBOL
AFWAL/POSF

DD FORM 1473, 83 APR EDITION OF 1 JAN 73 IS OBSOLETE.

UNCLASSIFIED
SECURITY CLASSIFICATION OF THIS PAGE

FOREWORD

This is Part I, "Experimental Procedures and Qualitative Data 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 II will deal with the quantitative aspects 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-416-84-001). This work was administrated 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 June 1984 through July 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 Mr 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 1 of Contract F33615-84-C-2412.

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SECTION I

INTRODUCTION

The primary purpose of this project was to develop a fast, simple and direct method for the determination of compound classes present in various jet fuels. This effort was prompted by the growing interest in and approaching usage of coal-, shale- and tar sand-derived fuels as alternatives to conventional oil supplies. These synthetic fuels are known to have compositionally dependent characteristics and properties which can differ significantly from conventional oil products. These differences involve the bulk hydrocarbon structures as well as the heteroatomic "impurities" from the alternate crude sources and can even represent improvement in energy content as in the case of denser naphthenics. The utility of the bicyclic decalins is further demonstrated by their presence in the Russian jet fuel recovered from the MIG flown by its defecting pilot to Japan in the mid 1970's. Thus, the alkyldecalins and their hydrogenation precursors, alkylnaphthalenes and alkyltetralins, were specially targeted for the direct mass spectrometry (MS) study. The structures and terminology used in this report for these three classes of bicyclic compounds are shown in Figure 1. The complete series of alkyl homologs for each of these compounds is indicated by the simple addition of an R to the indicated structure as shown in Figure 1b. In this report, the isomeric 5-carbon ring structures are generally not distinguished from the 6-carbon ring compounds shown.

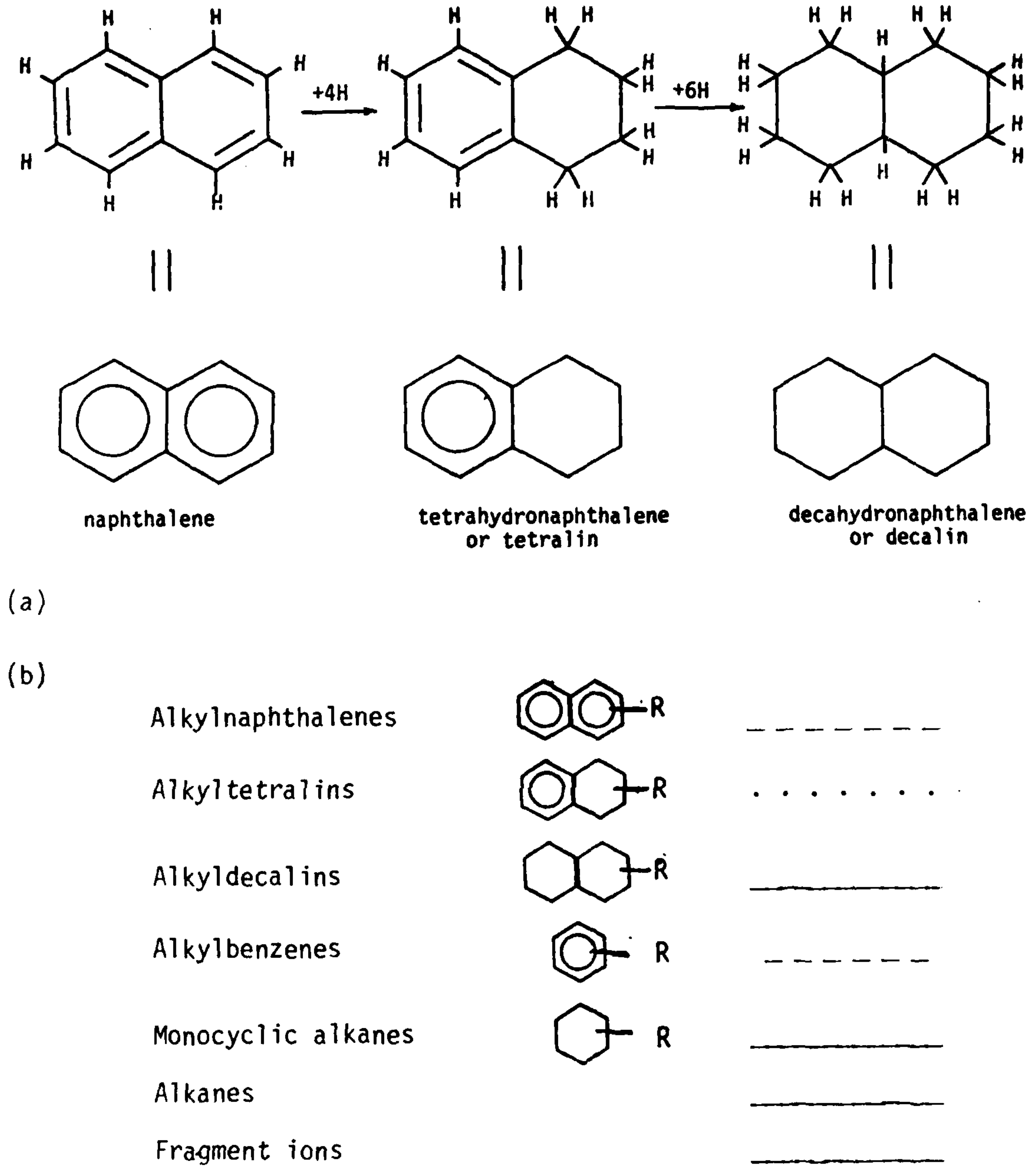

Figure 1. Nomenclature of (a) bicyclic structure and (b) homologous ion series in mass spectra.

The initial plan was to use direct electron ionization (EI) tandem MS (MS/MS) to determine the amounts of each of these compound classes in the fuel mixtures. In this "hyphenated" technique, the first MS performs a separation of compounds (as ions) based on molecular weight while the second MS identifies the ion structures by the fragments formed through collision induced dissociation (CID). Thus, this combined separation-identification technique has much of the analytical power of gas chromatography MS (GC/MS) coupled with the high speed and ease of digitization of direct MS and without the often long chromatographic separation time.

It was soon observed, however, that large compound class differences were evident in simple low voltage electron ionization mass spectrometry (EIMS) even without the added dimension of the second MS and the complexity and reduced sensitivity which accompany it. Thus, the main focus of this initial effort has been the direct MS analysis of a set of carefully blended mixtures of naphthalenes, tetralins, and decalins to evaluate the determination of these three compound classes in unknown fuels. One significant accomplishment was the development of a simple and reproducible sample introduction procedure for liquids with the boiling range of jet fuels. Multivariate statistical analysis of the MS data through the application of routines from the Statistical Package for the Social Sciences (SPSS) [1], permitted the use of all the various fragment and molecular ions of each compound class in measuring the relative composition of two unknown fuels. In addition to the direct MS and MS/MS, other techniques utilized in this project included open column liquid chromatography to isolate a series of alkyltetralins from one of the supplied samples and capillary GC/MS to confirm the presence and identity of many different isomers in each of the hydrocarbon classes examined. Further multivariate statistical analyses, discussions, and conclusion are included in Part II of this report [2].

SECTION II

EXPERIMENTAL

1. SAMPLE ORIGIN AND PREPARATION

Six separate samples were obtained from the Aero Propulsion Laboratory (POSF) at Wright-Patterson Air Force Base (WPAFB) for analysis. The first three were oil derived mixtures of naphthalenes with different degrees of hydrotreatment as indicated by three levels of aromatic content: 95, 30, and 2%. The fourth sample was the high naphthenic content "unknown" fuel from the Russian MIG. The fifth sample was an oil shale-derived JP-4 type fuel chosen for its high monocyclic aliphatic content. The last sample examined was the lower boiling distillate fraction of the 2% aromatic sample. The identifying numbers, descriptive sample names, and our three-digit designations are listed in Table 1.

Approximately 0.5 gm of a seventh primary sample enriched in alkyltetralins was made from 3 gm of the 30% aromatic sample by elution from silica gel using a solution of pentane and cyclohexane (60/40 v/v). The 60-120 mesh (125-250 μm) silica gel had been sieved from Baker 60-200 mesh and activated at 175°C in air for three hours. The 1.5 cm i.d. x 30 cm long open column was packed with approximately 20 gm of silica gel suspended in pentane. The eluting solution was periodically sampled through a 0.075 mm i.d. fused silica capillary into the source of an EI mass spectrometer as described below (the MS/MS instrument) to monitor the m/z 152 methyl decalin peak and the m/z 148 methyl tetralin peak. The solutions exiting the column had the following approximate

TABLE 1

PRIMARY SAMPLES FROM WRIGHT-PATTERSON AIR FORCE BASE

Sample Code	Sample - Description	BPC Name
83-POSF-0994	Light pyrolysis fuel oil/95% aromatics	95%
83-POSF-0801	Light pyrolysis fuel oil/30% aromatics	30%
82-POSF-0162	Flash point 80°C/2% aromatics	2%A
83-POSF-1028	Project Stablemate (Russian MIG fuel)	STB
82-POSF-0561	Shale-derived JP-4	SH4
84-POSF-1949	2% aromatics HD1 (distillate of sample #3 cut off at 500°F)	DC2

compositions: 0-25 ml solvent, 25-42 ml clean decalins, 42-56 ml mixture of decalins and tetralins, and 56-80 ml clean tetralins. The clean tetralin fraction was then mixed in integer multiples of 100 μl aliquots with the naphthalenes (95% aromatics) and decalins (2% aromatics) to produce the binary and ternary solutions shown in Figure 2. Table 2 lists the mixture numbers and compositions along with the direct MS analysis numbers for the four WPAFB samples not used in making the ternary blends.

2. GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS) ANALYSIS

The first five samples from WPAFB (#1, 3, 17, 18, 19 in Table 2) were analyzed by GC/MS on a Hewlett-Packard 5840 GC coupled to a VG-Micromass 7050 MS (electrostatic and magnetic sector instrument). Split injection (90% vented) of approximately 1 μl of 10% solutions in hexane isomers was used on the 0.3 mm i.d. X 30 m methyl silicon coated fused silica capillary column with temperature programming as follows: 2 min isothermal hold at 100°C, 100 to 250°C at 7°C/min, isothermal hold at 250°C for 10 min. The EI mass spectrometer source was operated at 17.5 electron volts (eV) rather than the usual 70 eV to reduce fragmentation of the cyclic aliphatics. The MS was scanned from m/z 500 to 20 at 1 s/decade (total 2 s/scan) with a nominal resolution of 700. Several other analyses were performed on neat samples and at 70 eV with less useful results due to detector saturation.

3. DIRECT MS ANALYSIS

The direct EIMS was performed on an Extranuclear 5000 quadrupole MS using pulse counting ion detection with signal averaging of 600 scans

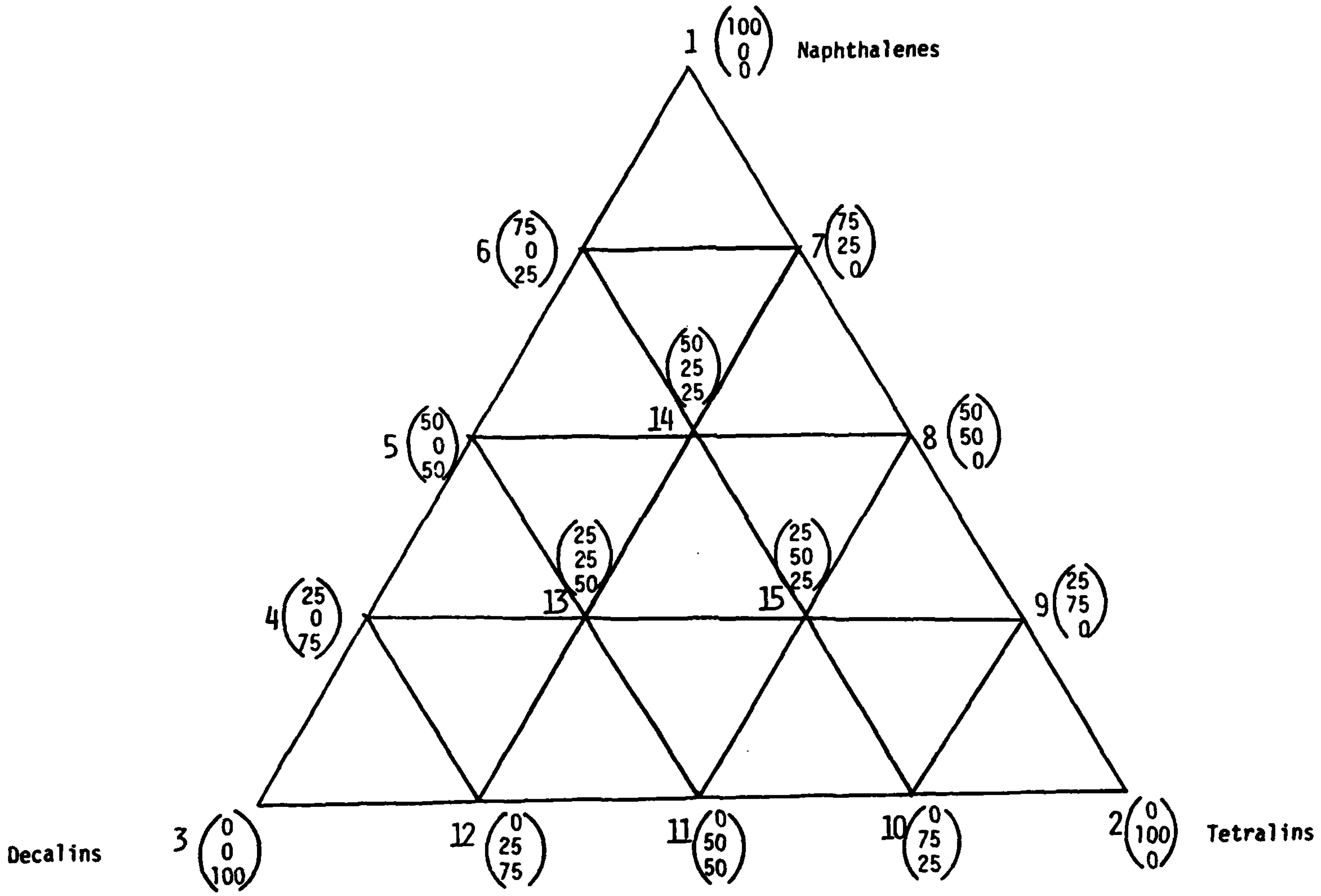

Figure 2. Ternary composition diagram corresponding to sample numbers in Table 2.

TABLE 2

DIRECT MS MIXTURE ANALYSIS SAMPLE COMPOSITIONS

Sample Number	Sample Name	Mixture Composition (Volume %) Naphthalenes	Tetralins	Decalins
1	Naphthalenes (95% aromatics)	100	0	0
2	Tetralins (separated from 30% aromatics)	0	100	0
3	Decalins (2% aromatics)	0	0	100
4	Diblend of naphthalenes and decalins	25	0	75
5	Diblend of naphthalenes and decalins	50	0	50
6	Diblend of naphthalenes and decalins	75	0	25
7	Diblend of naphthalenes and tetralins	75	25	0
8	Diblend of naphthalenes and tetralins	50	50	0
9	Diblend of naphthalenes and tetralins	25	75	0
10	Diblend of tetralins and decalins	0	75	25
11	Diblend of tetralins and decalins	0	50	50
12	Diblend of tetralins and decalins	0	25	75
13	Ternary Blend	25	25	50
14	Ternary Blend	50	25	25
15	Ternary Blend	25	50	25
16	2% aromatics distillate cut (<500°F)			
17	30% aromatics			
18	Project Stablemate			
19	Shale JP-4			

from m/z 20 to 260 at a rate of 1000 amu/s and total scan time of 3 min with unit mass resolution. The EI source was operated at 12 eV electron energy to minimize fragmentation of the aliphatic compounds and maximize the proportion of molecular ions. The liquid samples in micropipettes (see Sample Inlet System below) were held next to the ion source in a glass tube on the end of a direct insertion probe as indicated in Figure 3.

A schematic diagram of the system is shown in Figure 3. Data were taken on a Hewlett Packard (HP) 5933A data system. The contour plot spectra were converted to bar plots and normalized on an HP 2100 MX computer and then run through SPSS for the multivariate statistical analysis on a DEC 20 computer. It should be noted that mechanical difficulties encountered during the direct MS mixture analysis twice required full shut-down and venting of the instrument between the triplicate sets of analysis. The high degree of spectral reproducibility is especially impressive in view of the drastic nature of the interruptions on these analyses.

4. TANDEM MASS SPECTROMETRY (MS/MS) ANALYSIS

The MS/MS experiments were run on a similar instrument based on Extranuclear quadrupoles but largely designed and built in-house and shown schematically in Figure 4. The EI source was operated in the range of 14 to 90 eV depending on the particular need of less fragmentation or more sensitivity. The collision induced dissociation (CID) was performed between the two quadrupole MS with ion energies of approximately 40 eV using argon as the target gas. The argon was metered through a 0.025 mm i.d. x 3 mm long fused silica capillary into the

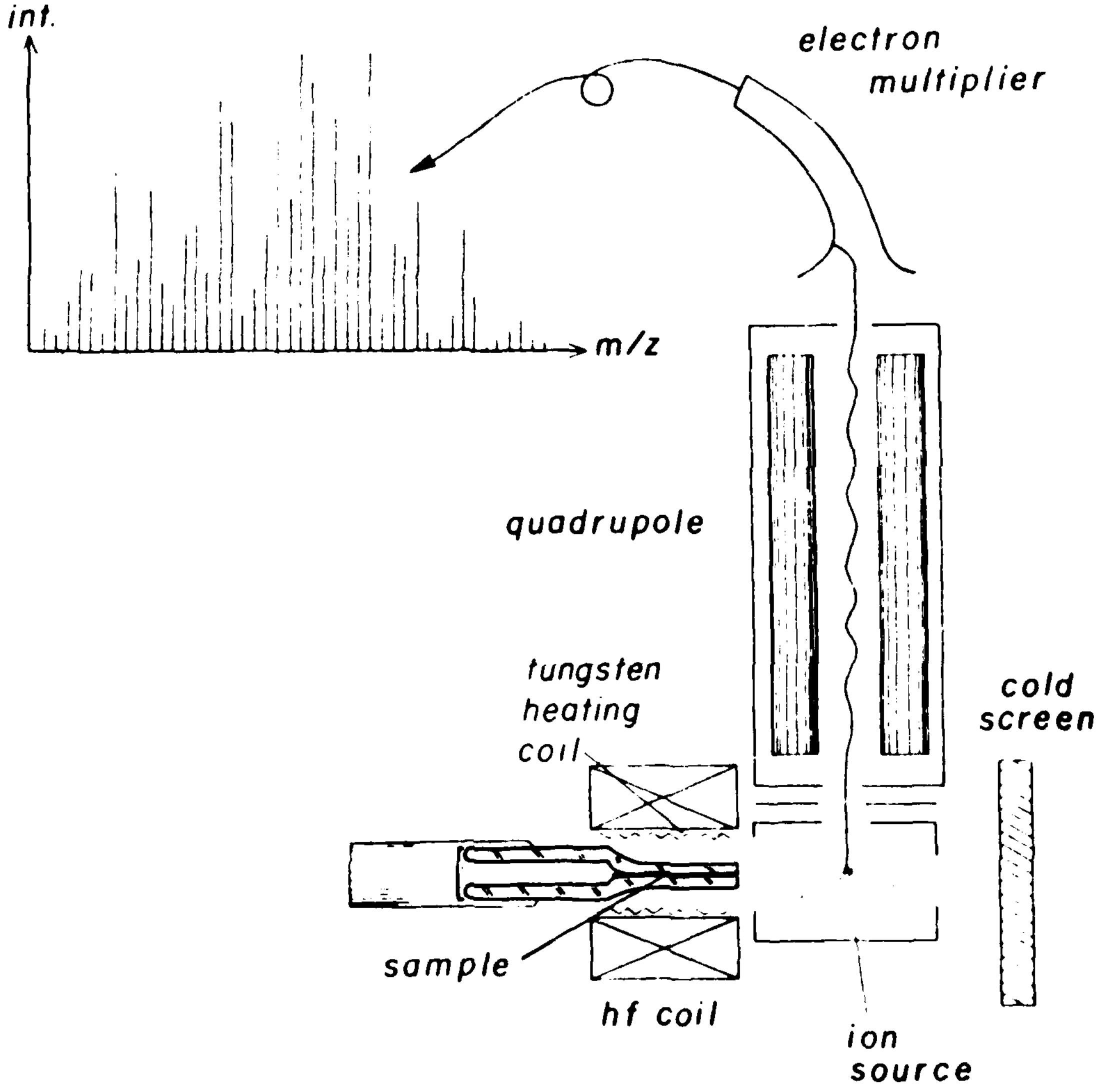

Figure 3. Schematic diagram of electron ionization mass spectrometer (EIMS) for direct liquid analysis.

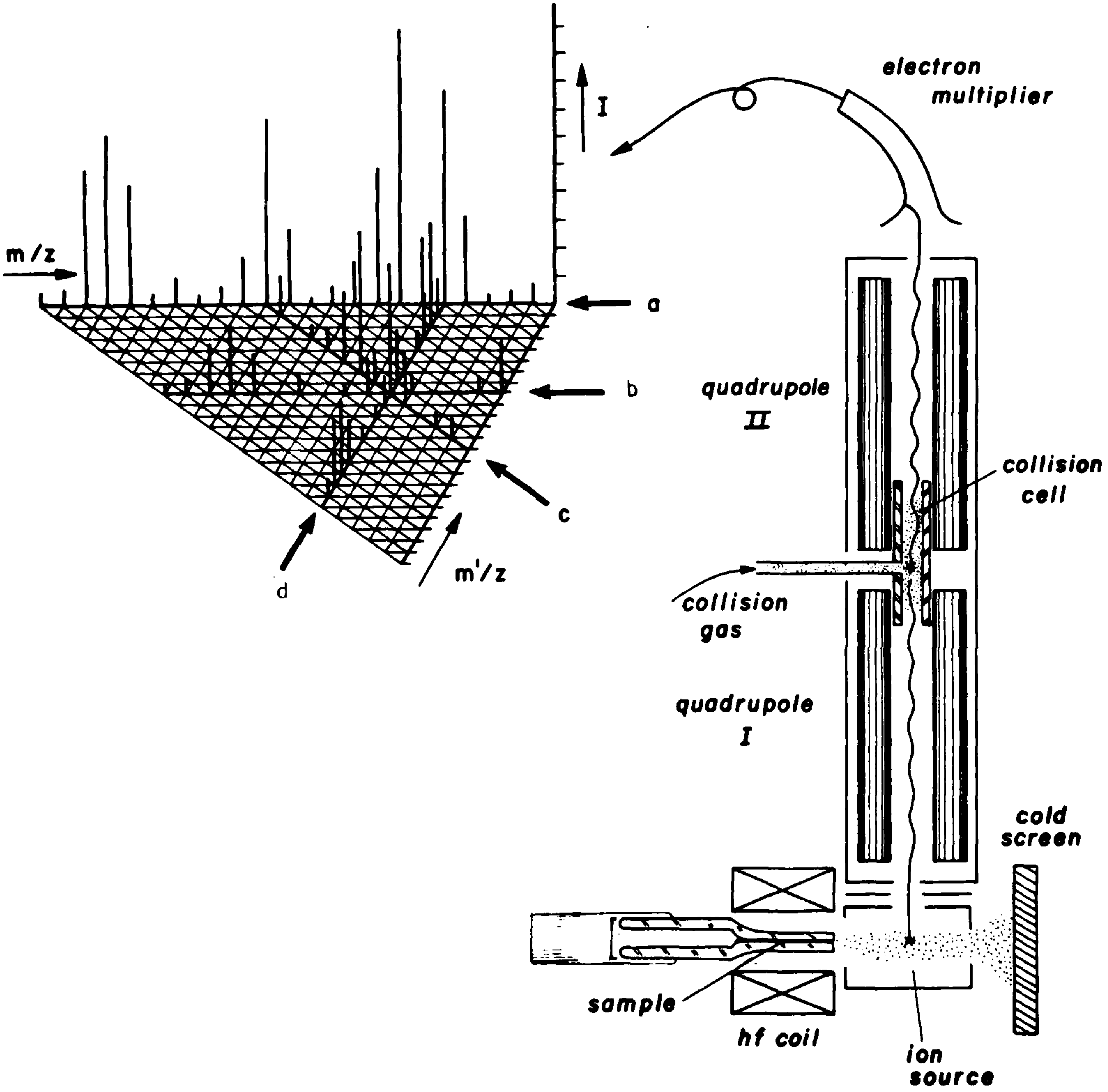

Figure 4. Schematic diagram of tandem mass spectrometer (MS/MS) system. Different modes of operation are represented by (a) single MS, (b) daughter ion, (c) parent ion, and (d) constant loss spectra as explained in the text.

collision region to give an overall vacuum system pressure of 6-7 X 10^{-6} torr (9 x 10^{4} Pa). The total pumping speed of the vacuum system is over 1100 l/sec using a Balzer TPH 110 turbomolecular pump in the ion source region and a Varian VK-12 cryopump below the CID region.

The signal averaged spectra were taken on an IBM 9000 computer interfaced to the instrument. Data were taken over a variety of mass ranges and total scan times depending on the particular MS/MS experiment being performed. Several general types of analysis are illustrated in the spectral portion of Figure 4 showing ion intensities plotted above a 2 dimensional mass grid. The two mass scales, m/z and m'/z, indicate scanning of quadrupoles I and II, respectively. A routine single MS experiment is represented by scanning along line (a). For a daughter or fragment ion spectrum, the first MS was used to select a single mass ion from the ion source and the second MS scanned the fragments produced from this ion in the CID region as indicated by direction b in Figure 4. The mode thus obtained a fingerprint spectrum of one fragment or molecular ion in the direct MS spectrum. In parent ion spectra the second quadrupole was tuned to select only one mass CID fragment ion and the first MS scanned to show which parent ions could produce this daughter as indicated by line C in Figure 4. This mode was used to examine the class composition of a sample by measuring the direct MS ions which produced a fragment ion characteristic of a certain hydrocarbon class. A constant loss spectrum, represented by line (d) in Figure 4, involved scanning both quadrupoles simultaneously with a constant offset of m'/z less than m/z. This mode would detect, for instance, similar alkyl substituents, but was not investigated for this project.

5. MS SAMPLE INLET SYSTEM

A somewhat novel method of sample introduction was used for the direct MS of these complex volatile liquid fuels with boiling point ranges from 100 to nearly 300°C at atmospheric pressure. The liquid samples were placed in 1/4, 1/2, or 1 μl Drummond Microcaps disposable pipettes sealed at one end and then allowed to evaporate from the open end directly into the MS ion source. The unique aspects of this direct probe technique involved the use of the very small internal diameter (i.d.) capillary tubes, 0.1 mm i.d. for the 1/4 μl and 0.2 mm i.d. for the 1 μl, and the simple way in which reproducible samples were taken. In general, the micropipette was briefly touched to the liquid surface to partially fill it by capillary action, the opposite end quickly flame sealed and the sample centrifuged into the closed end. The small i.d. severely limited the rate of evaporation from tube at room temperature and allowed the sample volume to be accurately measured simply by the length of the liquid column. For small representative sampling the 1/4 μl capillaries were filled to approximately 2 mm length or approximately 16 nl volume and then heated to about 200°C in the MS inlet to totally evaporate the sample in less than three minutes. This allowed fast and very reproducible analyses of the total sample. For relatively constant long-term signals from samples or standards, the larger tubes were used with little or no heating in the MS vacuum. These conditions facilitated the sometimes lengthy initial optimization of all instrument parameters for MS/MS analysis.

6. MS TIME PROFILE ANALYSIS

A time profile direct MS analysis was performed on a 1/4 μl capillary sample of ternary standard #13 to aid in evaluation of the sampling techniques. In this analysis, the MS was independently scanned repetitively over a narrow mass range of m/z 151 to 160 while the computer was programmed to take one long slow scan. In this way the intensity of several peaks was recorded as a function of time during their evolution from the sample. In this case the computer scan took nearly three minutes.

The time profile analysis of mixture #13 is shown in Figure 5 as ion intensity versus time in seconds. The intensities of the m/z 152, 156, and 160 ions are seen to rise smoothly as the sample evaporates more and more rapidly with increasing temperature. All three peaks also drop very rapidly together when the sample is exhausted at about 130 s. The C_2 naphthalenes (m/z 156) have atmospheric pressure boiling points ranging from 251 to 263°C which are probably 40 to 60°C higher than the methyl decalins (m/z 152). Except for the higher initial signal from m/z 152, the two sets of compounds evaporate together for the most part rather than showing fractional distillation. Thus the geometry of the sample enclosed in the long thin capillary seems to minimize the extent to which lower boiling components can be lost from the sample, thereby accounting for the reproducibility of the liquid sampling technique.

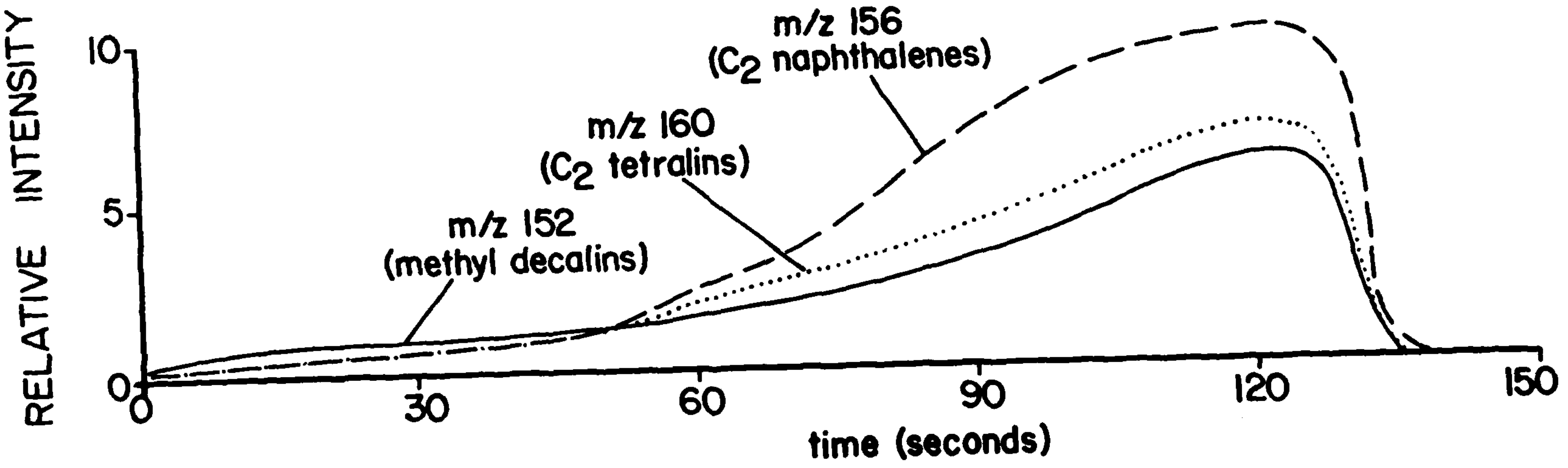

Figure 5. Intensity versus time profiles of ions at m/z 152, 156 and 160 during analysis of ternary blend #13.

SECTION III

RESULTS AND DISCUSSION

Examples of the GC/MS data are shown in Figure 6. The total ion current chromatogram indicates the overall distribution of compounds eluting from the GC by using MS as a kind of universal detector. However, the mass chromatogram of m/z 180 acts as a compound specific detector which responds primarily to the C_3 alkyldecalin isomers eluting between scans 130 and 220. Individual peaks are not as well resolved as might be expected because of the relatively long time per scan (2 s) and the fast temperature program (7°C/min). These two factors caused many peaks to be only one or two scans wide, therefore, they are quite poorly defined. Scanning only the range of m/z 300 to 20 and a 2-3 °C/min heating rate would both greatly improve the data quality. Alternatively, the data could be obtained on a faster scanning quadrupole MS. However, the GC/MS data did provide the necessary information on compound class fragmentation patterns, as seen in the individual spectra and on the different isomer distributions in the molecular ion chromatograms. For example, the spectra of simple decalins demonstrated both their extensive fragmentation, even at low electron energies, and the presence of strong characteristic even mass fragments at m/z 82, 96, 110. These were considered to be important possible daughter ions for parent spectra of the decalins in MS/MS analysis. The m/z 180 molecular ion chromatograms showed that the 2% and 30% aromatic samples both had quite similar isomer distributions for the C_3-decalins while the Project Stablemate fuel pattern was rather different. This variation could be caused simply by different distillation conditions or

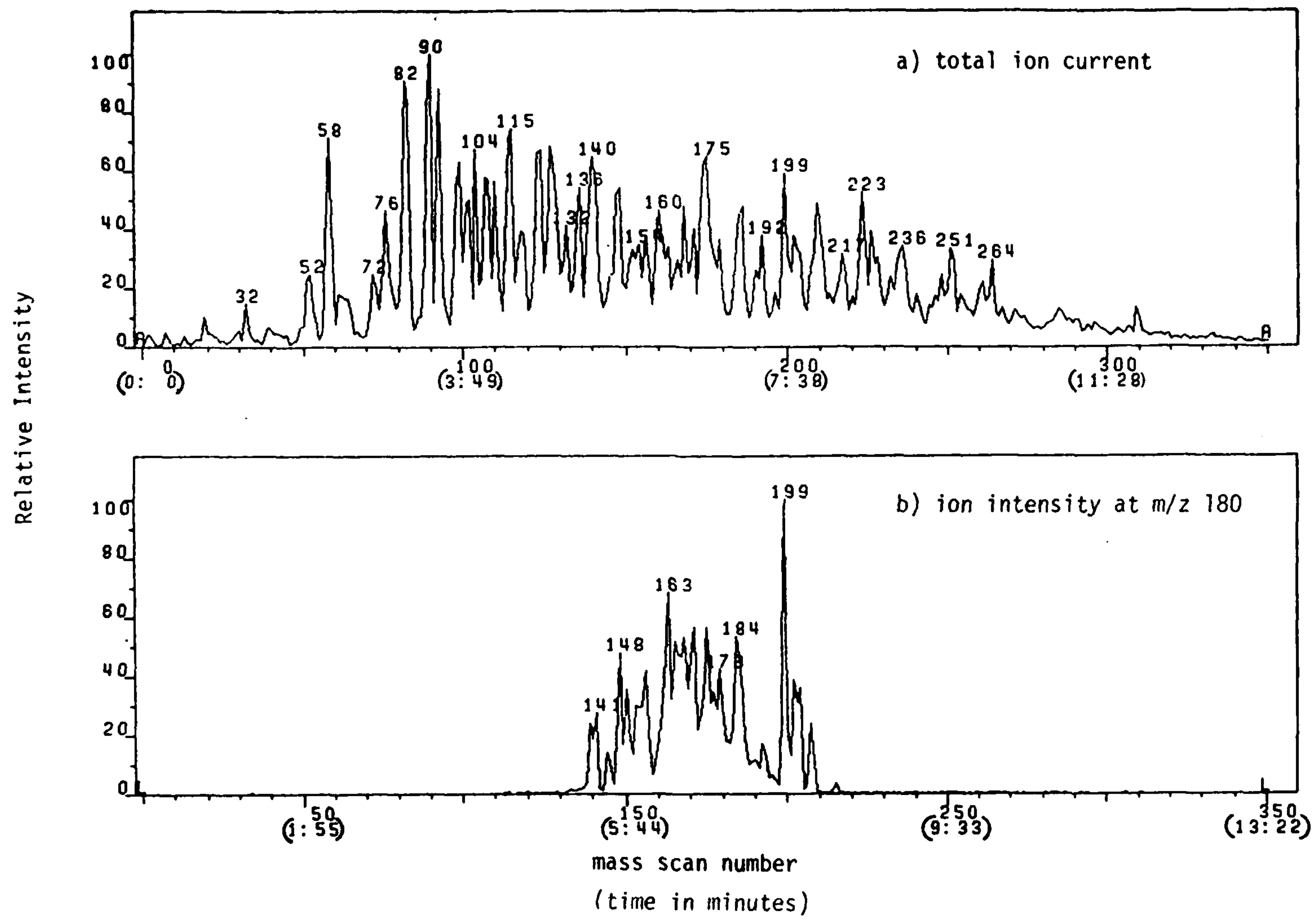

Figure 6. Reconstructed chromatogram of (a) the total ion current and (b) m/z 180 from GC/MS analysis of the 30% aromatics #17 (Table 2).

might indicate an important difference in the fuel feedstocks. In either event, this change in isomer content should be manifest in a subtle way in the MS/MS class analysis.

The direct low voltage mass spectra of the initial five samples are shown in Figures 7 and 8. It can readily be seen that the three compound classes, alkylnaphthalenes, alkyltetralins, and alkyldecalins, are primarily represented in the three corresponding samples, i.e., 95%, 30%, and 2% aromatics, as indicated by the lines connecting their molecular ions. This is especially clear in the first and third spectra of Figure 7 where the 95% and 2% samples are comprised predominantly of naphthalenes and decalins, respectively. The sample hydrotreated to the extent of 30% aromatics remaining is seen to be a mixture of tetralins and decalins. It should be noted that the decalins are easily fragmented even at the low electron energies to give the abundant series of both odd and even mass fragment ions extending from m/z 137 down to m/z 68 in addition to the molecular ion distribution over m/z 138, 152, 166, 180, 194, and 208.

Obviously a major reason for the ease of distinguishing the three classes of bicyclic compounds is the fact that their homologous ion series involve non-interfering sets of ions. In Figure 8 the MIG fuel and the shale-derived JP-4 type fuel are seen to include several classes of compounds in addition to the three main series in Figure 7. The three most significant additional classes are the alkanes and the two monocyclic hydrocarbon series, the aromatic alkylbenzenes and the aliphatic alkylcyclohexanes. Note that the alkane molecular ion series, seen in Figure 8b, overlaps the naphthalene series, as seen in Figure

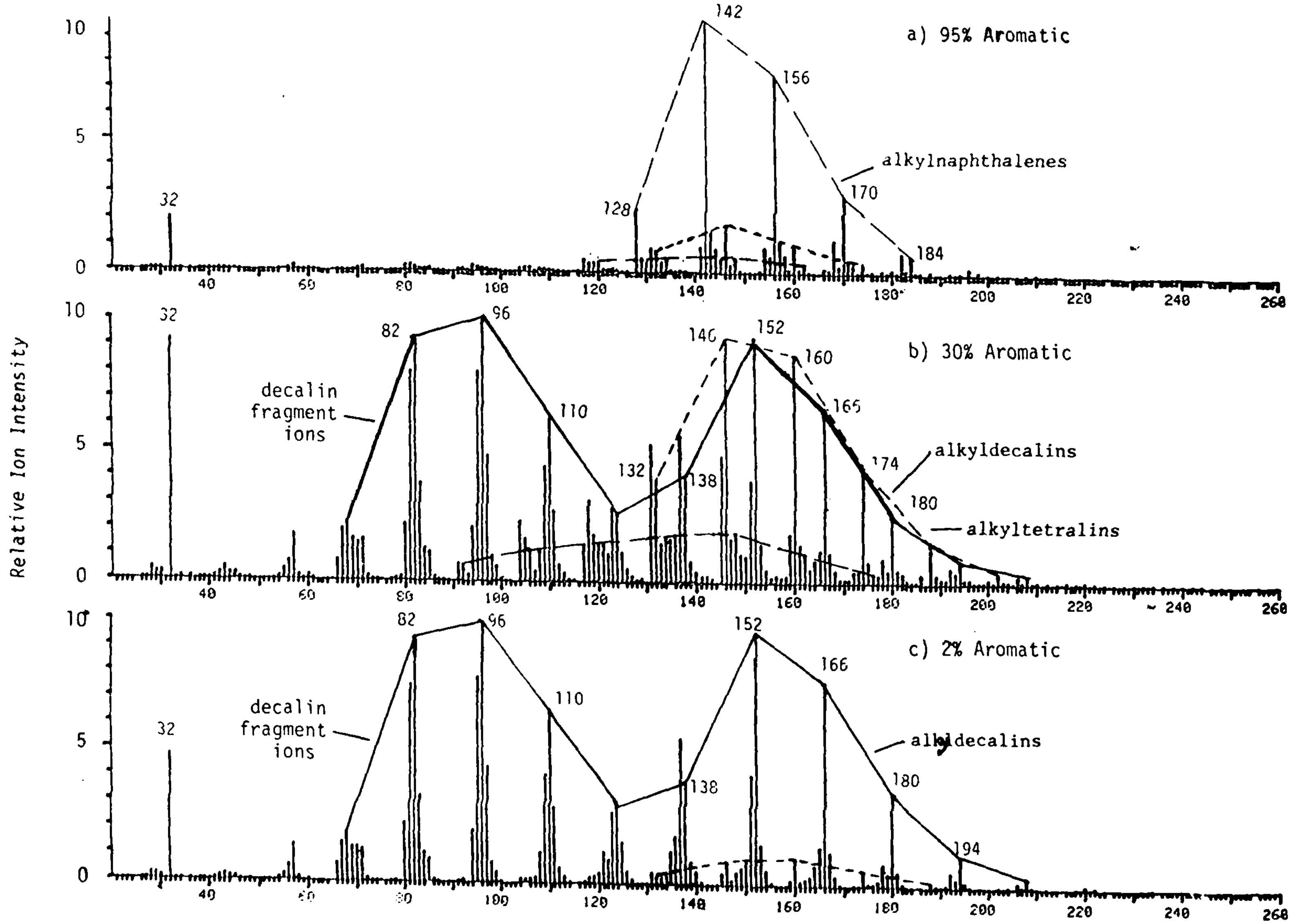

Figure 7. Low voltage mass spectra of the 95%, 30% and 2% aromatics samples (#1, 17, and 3 in Table 2). The ion at m/z 32 is due to O_2 in the air background of the instrument with N_2 essentially not ionized at the <14 eV electron energy.

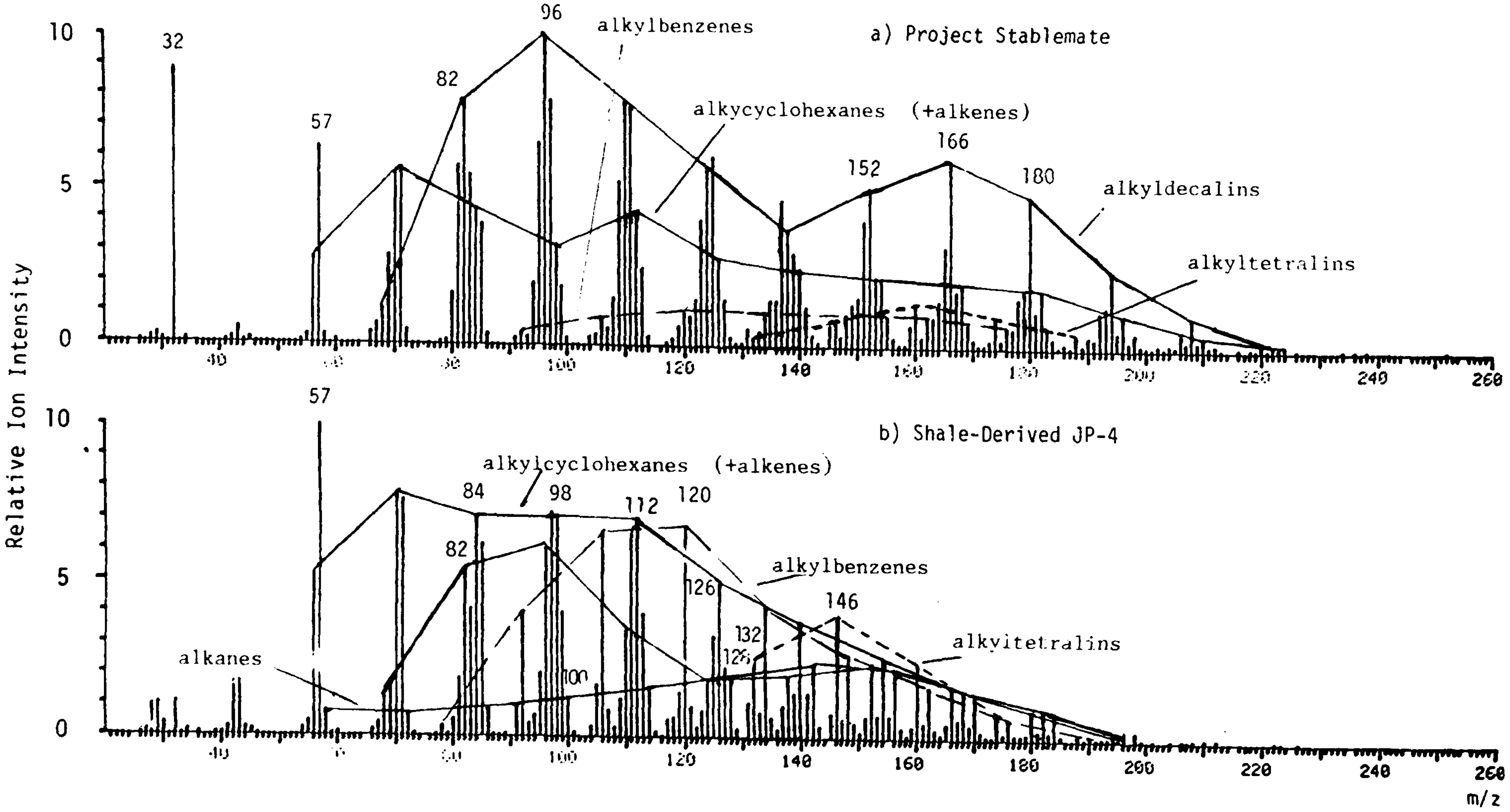

Figure 8. Low voltage mass spectra of the (a) Project Stablemate (#18) and (b) shale-derived JP-4 (#19) samples.

7a, starting with m/z 128 and continuing through the higher homologous ion series. The alkanes can be distinguished from the aromatic series by the fact that their molecular ion peaks continue smoothly below m/z 128 to m/z 114, 100, and 86 and also by the intense odd mass alkyl fragment ions especially at m/z 57, 71, 85, and 99. However, the possible presence of a minor series of naphthalenes beneath the alkanes in Figure 8b cannot be excluded on the basis of this spectrum alone but could readily be determined using MS/MS.

MS/MS daughter ion spectra of m/z 152 and 166 from the 2% aromatic sample are shown in Figure 9. These examples represent the fingerprint fragmentation or daughter ion spectra from collision induced dissociation (CID) of two prominent alkyl decalin molecular ions in Figure 7c by the process illustrated in Figure 4b. These daughter ion spectra show a composite of all the possible fragments from the various methyldecalin (Figure 9a) and C_2 alkyldecalin (Figure 9b) isomer parent ions at these collision energies. Note the abundance of even mass rearrangement ions at m/z 82, 96, and 110 as also observed in the decalins of Figure 7c.

Figure 10 gives examples of parent ion spectra for CID production of daughter or fragment ion m/z 95 from the 2% aromatic, 30% aromatic and Stablemate fuels. The spectra are almost identical for the very similar alkyldecalins in the 30% and 2% aromatics samples (#3 and 17) while the significant differences in the Stablemate spectrum of Figure 10c reflects the difference in decalin isomer distributions as shown by GC/MS single ion chromatograms or in Figure 8a. Thus, the MS/MS data confirm the anticipated capability for qualitative

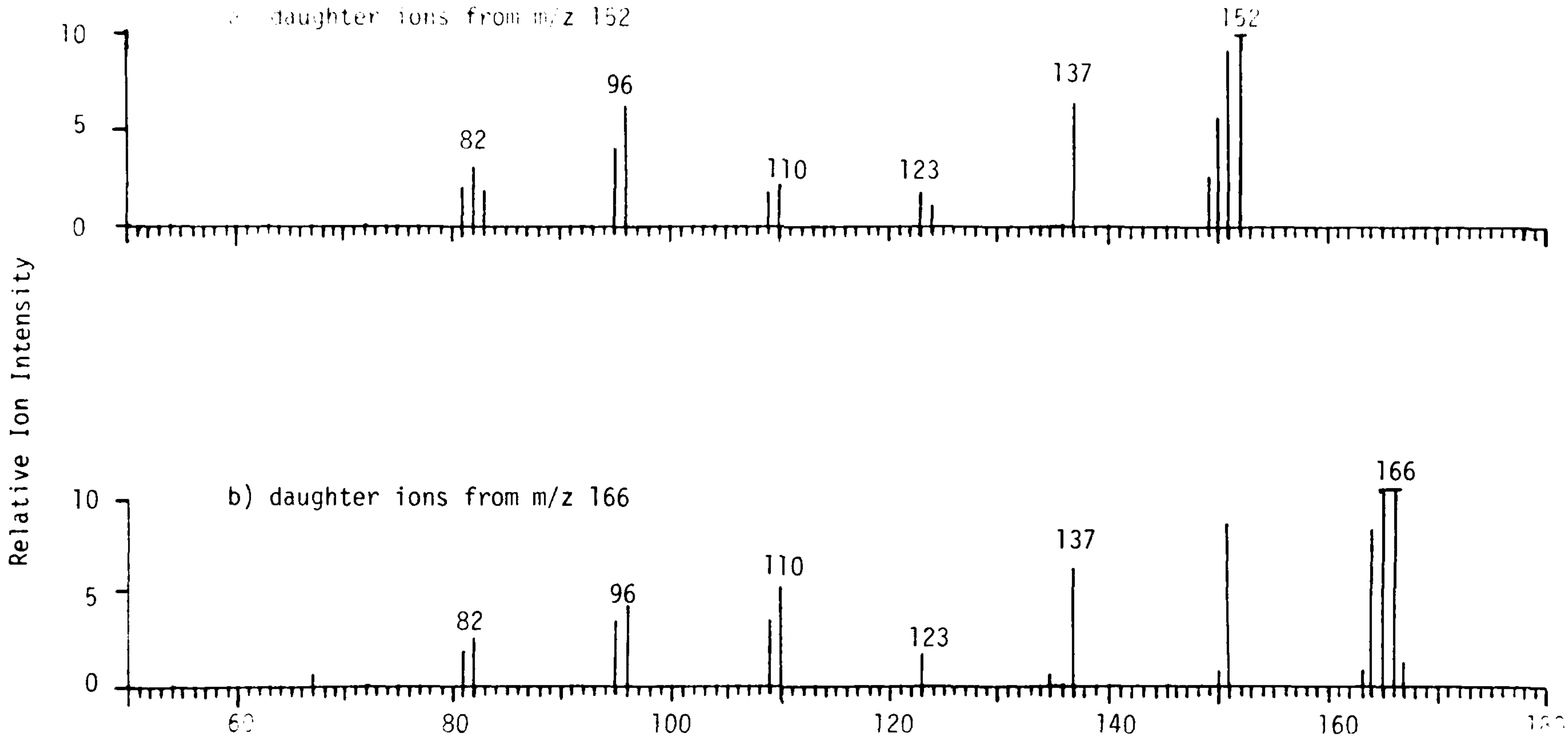

Figure 9. Daughter ion MS/MS spectra of molecular ions at (a) m/z 152 (methyl decalins) and (b) m/z 166 (C_2 decalins) from the 2% aromatic sample #3.

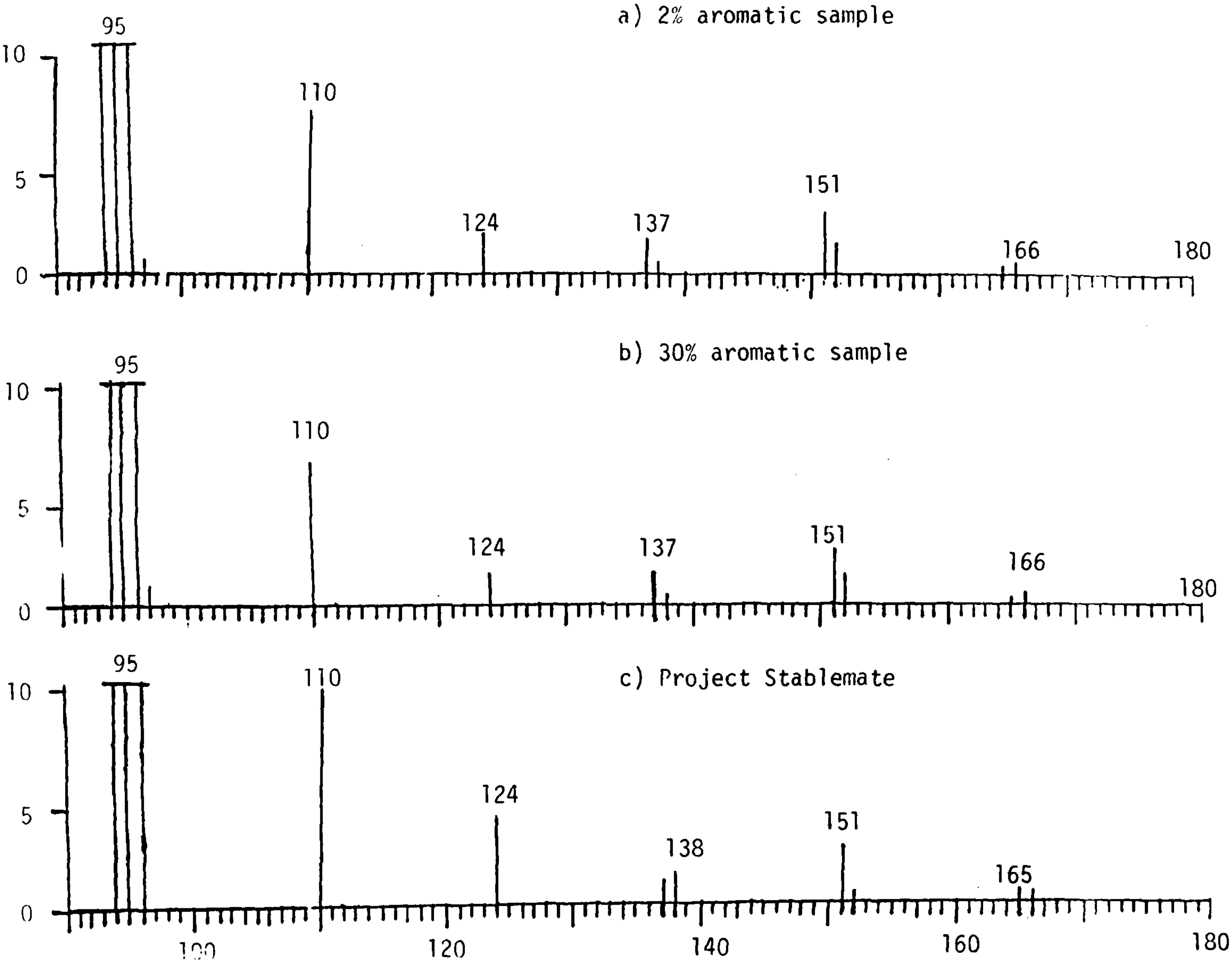

Figure 10. Parent ion MS/MS spectra of fragment ion m/z 95 from samples (a) #3, (b) #17, and (c) #18.

hydrocarbon class identification in the jet fuels with the problems of sensitivity and quantitation still remaining to be resolved. Although several possible MS/MS approaches to these problems can be envisaged, we were encouraged by the high degree of class delineation available in the direct low voltage MS. The simpler technique was pursued especially since resulting methods could later be applied to the MS/MS technique.

In Figure 11 the results of the open column LC separation on silica gel of the alkyltetralins from the 30% aromatic sample are shown. The spectrum of the hydroaromatic fraction (Figure 11b) is compared directly to the original 30% aromatics spectrum (Figure 11a and 7b) to demonstrate the attainable completeness of separation of the tetralins and alkylbenzenes from the earlier eluting decalins. Note the presence of cyclohexane peaks at m/z 56, 69, and 84 from incompletely removed solvent. An incompletely separated portion of the tetralins containing some decalins had to be added back into the cleaned tetralins to give enough volume for mixing the binary and ternary blends. Thus, after solvent removal, the "cleaned up" tetralins used as sample #2 produced the spectrum of Figure 11c.

The spectra of the three essentially pure samples in the ternary mixture analysis are shown again as mixture numbers 1, 2, and 3 in Figure 12. Note that the composition of the three compound class samples is not totally independent with the presence of tetralins in both the naphthalenes (#1 Figure 12a) and decalins (#3 Figure 12c) as well as the decalins in the tetralin sample. An extremely useful way of comparing the spectra from different samples is through bivariate plots of relative ion intensities as shown in Figure 13. The relative intensities of each peak in a spectrum are calculated from the normalization

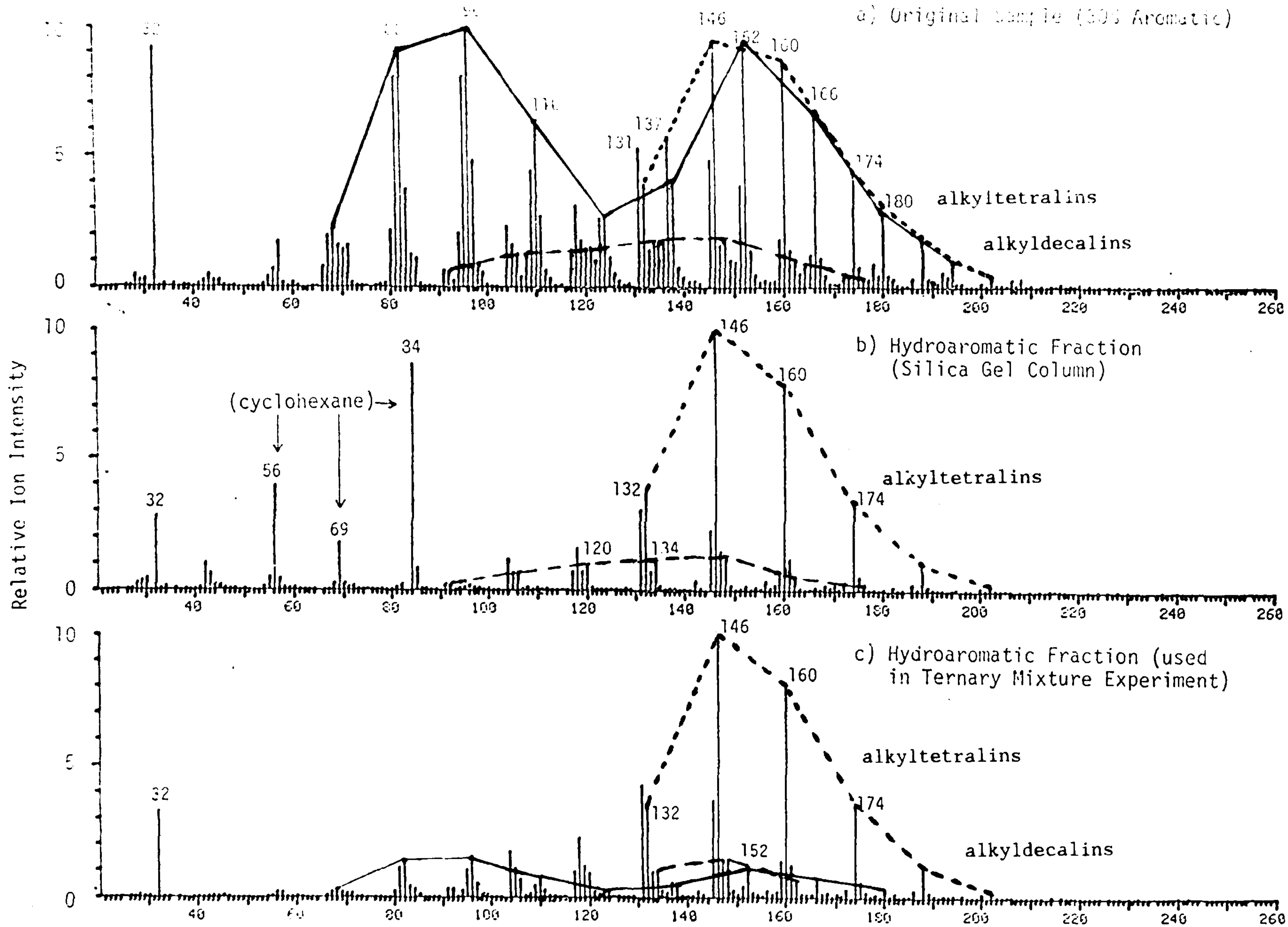

Figure 11. Low voltage mass spectra of (a) the 30% aromatic sample #17, (b) a hydroaromatic fraction of #17, and (c) sample #2.

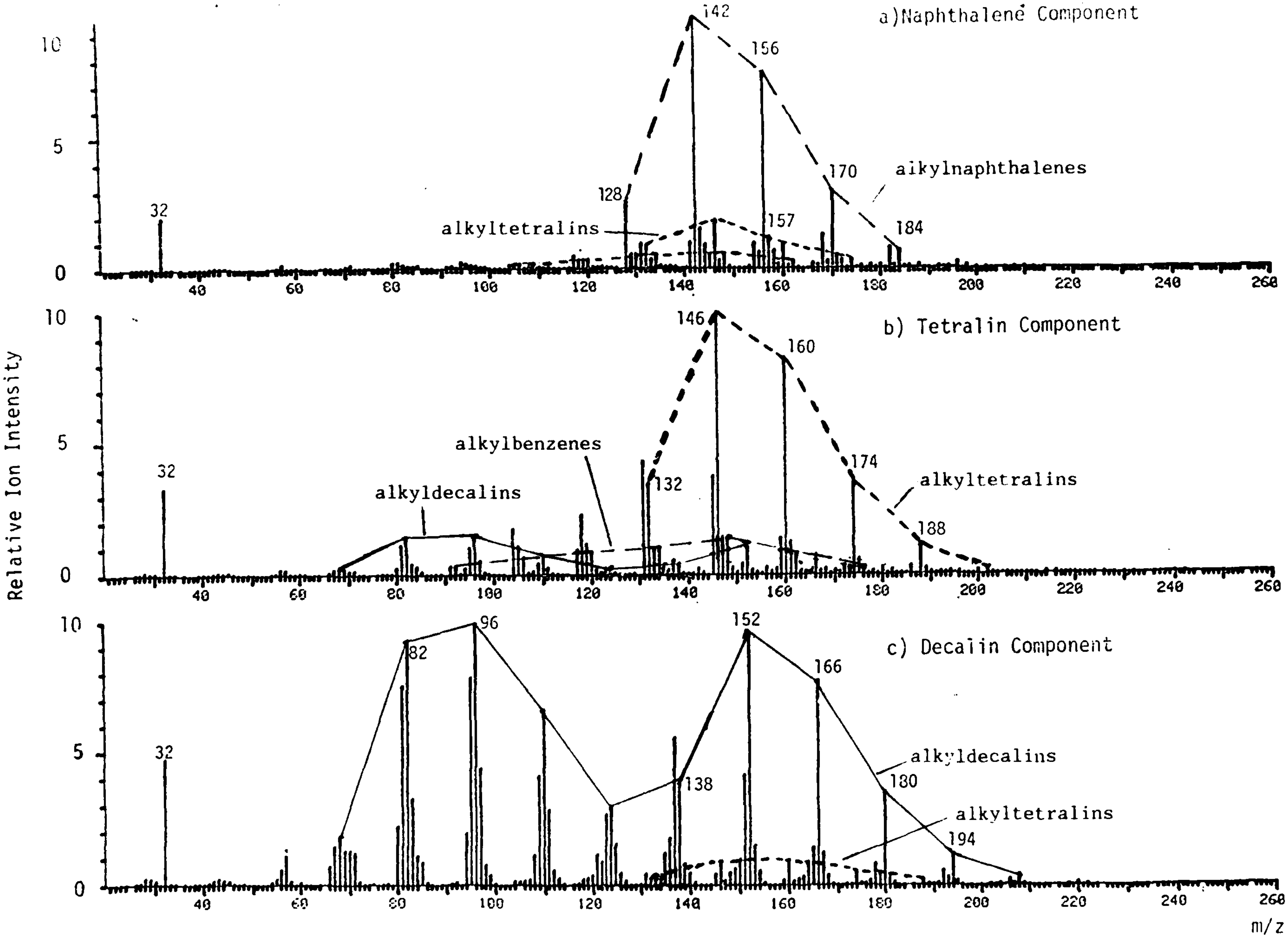

Figure 12. Low voltage mass spectra of three samples used in ternary mixtures: (a) naphthalenes #1, (b) tetralins #2, and (c) decalins #3.

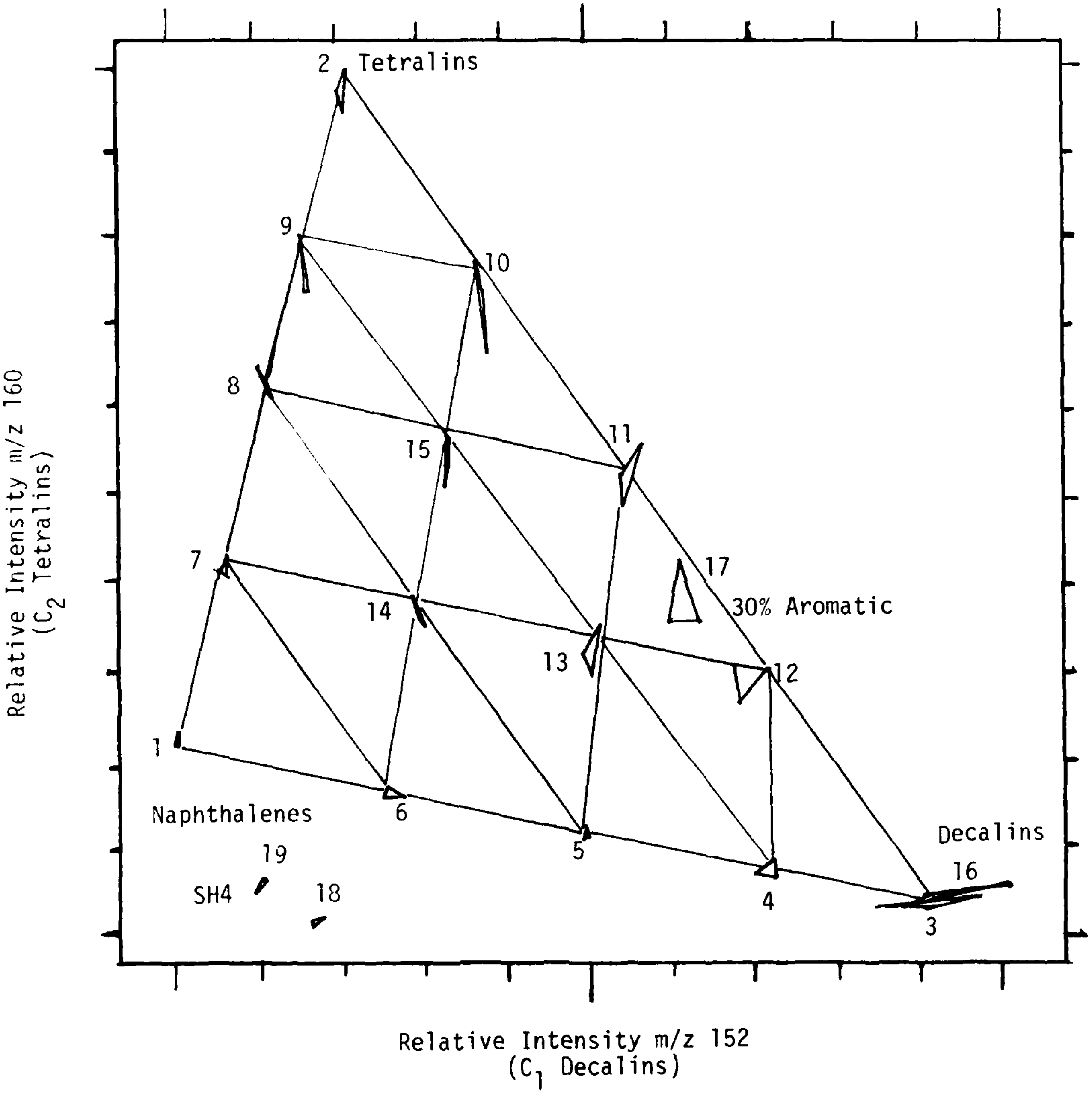

Figure 13. Bivariate plot of m/z 160 versus m/z 152 ion intensities from low voltage mass spectra of samples in triplicate.

of the total peak intensity to 100. The sample numbers are as designated in Table 2 and clearly represent the ternary mixture composition in the triangular diagram of Figure 2. The smaller, irregular triangles in Figure 13 connect the individual points from the triplicate analyses and graphically indicate the very good reproducibility of the technique despite the significant instrument problems encountered during this series of analyses. The venting of the mass spectrometer high vacuum, which occurred twice during the analysis series, could have caused slight changes in sensitive parameters such as the electron energies, reducing somewhat the normal instrument reproducibility.

The most useful information to be obtained from these data is the relative compositions of the "unknown", samples 16 through 19, compared to the known mixtures. Samples 16 and 17 are within the triblend triangles as would be expected from the fact that sample 16 is simply sample 3 minus the highest boiling components and sample 17, the 30% aromatic WPAFB liquid, is primarily just a combination of sample 2 and the decalins (as in sample 3) which were removed from it. However, the two true unknowns of rather different composition, #18 the Stablemate fuel and #19 the shale derived fuel, do not fall within the ternary mixture triangles because they have large amounts of other classes of compounds which therefore reduce the relative abundances of the class ions shown in Figure 12. A fundamental limitation of the bivariate plot is its inability to accurately represent three variables such as the concentrations of three different compound classes or even three single ions from each of the three bicyclic types. A simple solution used in the oral presentation of these data to the Aero Propulsion Laboratory at WPAFB on 22 June 1984 was a three-dimensional model using m/z 152, 160, and 157 as the x, y and z axes, respectively. The peak at m/z 157 was used instead of 156 for the C_2 alkylnaphthalenes because of the lower reproducibility of the very intense 156 ion. In this model the ternary mixtures made a nearly flat triangular plane connecting the three axes and enclosing the corner. The points for samples 18 and 19 were behind the triblend mixtures plane near the origin. For this simple 3 ion model the triangle corners of samples 1, 2 and 3 could be equated to essentially 100% samples of C_2-naphthalenes, C_2-tetralins, and methyldecalins with all of the triblend mixtures as linear combinations of these three to total 100%. Thus samples 18 and 19 which totaled much less than 100% of these compound classes (or the three representative ions) were off the plane toward the origin. However, the relative amounts of these three compound classes in the two samples could be measured by a straight line projection of the unknown points from the origin onto the mixture plane. For example, for the small fractions of numbers 18 and 19 from m/z 157, 160 and 152, the relative composition would be roughly 25, 25 and 50%, respectively.

The logical extension of the above discussion to include all the fragment and molecular ions of each of the compound classes through multivariate statistical analysis leads to the formation of a triangular plane in multidimensional space such as that shown in Figure 14. Again, samples 18 and 19 are off this plane but can be orthogonally projected onto it to give the points as indicated. For the representation shown, the optimal separation of all the samples (including the "unknowns" #18 and 19) was statistically found using three vectors which were linear

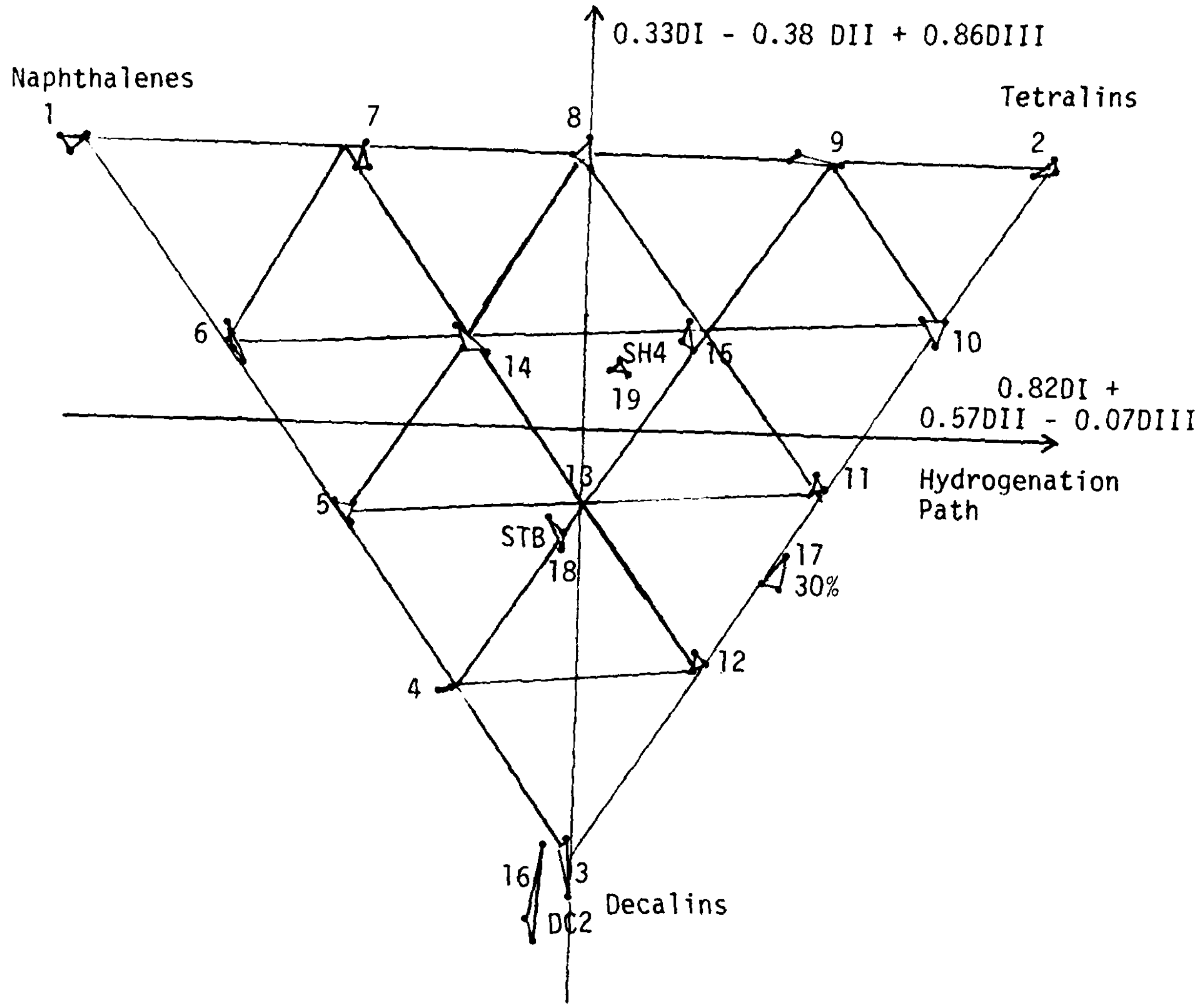

Figure 14. Scatter plot of modified discriminant function scores from multivariate statistical analysis of all sample spectra.

combinations of the intensities for the 100 ions listed in Table 3. The 100 ions listed were chosen as those most specific for separating all the planar samples (excluding 18 and 19) and the associated compound classes for each ion are also given in Table 3. The coordinates of the three "pure" components (samples 1, 2, and 3) in the three dimensional discriminant space were used to find the linear combinations for the planar representation or projection of Figure 14. The derived linear combinations of the three discriminant functions are shown on the two axes. An obvious improvement in reproducibility over that of Figure 13 is observed as a result of optimizing the differences between samples over the differences between replicates, using 100 masses instead of just 2.

A diagram such as shown in Figure 14 has several useful applications. First and foremost, it permits a compositional analysis of an unknown sample for the relative contribution of each of the components. This specific case analyzes for three classes of dicyclic compounds, naphthalenes, tetralins, and decalins, although other types of compounds or even more complex mixtures could be used. In our case, it can readily be seen that the 30% aromatics sample is roughly 40% tetralins and 60% decalins (as represented by samples 2 and 3, respectively). Similarly, the main components of typical crude oil based, shale derived, and coal derived fuels could be used to determine the most likely origin of an unknown fuel.

A second use, closely related to the first, and especially germane to the particular interest of the Air Force, is the measurement of the degree of hydrotreatment. A liquid such as the 95% aromatics sample

TABLE 3

100 MOST SPECIFIC PEAKS FOR SEPARATION OF TRIBLEND MIXTURE SAMPLES LISTING MOST LIKELY HYDROCARBON ASSIGNMENTS

	Naphthalenes	Tetralins	Decalins	Benzenes	Monocyclic Aliphatics	Alkanes	Other Aromatics		Naphthalenes	Tetralins	Decalins	Benzenes	Monocyclic Aliphatics	Alkanes	Other Aromatics		Naphthalenes	Tetralins	Decalins	Benzenes	Monocyclic Aliphatics	Alkanes	Other Aromatics		Naphthalenes	Tetralins	Decalins	Benzenes	Monocyclic Aliphatics	Alkanes	Other Aromatics
Ion m/z	1	2	3	B	C	A	0	Ion m/z	1	2	3	B	C	A	0	Ion m/z	1	2	3	B	C	A	0	Ion m/z	1	2	3	B	C	A	0
66								121								147				F				180			M				
67			F					122								148				M				182					M		M
68			F					123			F					150								183	F					F	
70					(F)			124			M/F					151			F					184	M					M	
80			(F)					125					F			152			M					185							
81			F					126					M			153					F		F	186							
82			F					127						F		154					M		M	188		M					
83			(F)	M	F			128	M					M		156	M					M		189				F			
92				M				129	+							157	+							190				M			
94			(F)					130								158								192							M
95			F					131		F						159		F						193			F				
96			F					132		M						160		M						194			M				
97			(F)		F			133				F				161				F				196					M		M
104		F						134				M				162				M				197	F					F	
105				F				135								164								198	M					M	
106				M				136								165			F					199							
108			(F)					137			F					166			M					200							
109			F					138			M					167					F		F	202		M					M
110			F					139					F			168					M		M	203							
111			(F)		F			141	F					F		170	M					M		206							M
112					M			142	M					M		171	+							210					M		M
117		F						143	+							172								212	M					M	
118		M/F						144								174		M						216		M					
119				F				145		F						175				F				224					M		M
120				M				146		M						176				M											

M = Molecular Ion
F = Fragment Ion
+ = $C^{13}M+1$ Ion

could be envisioned to follow a hydrogenation path such as that suggested in Figure 14 passing eventually through the 30% aromatic sample to the 2% aromatic sample. Different processes with different catalysts or feedstocks might follow slightly varying paths with different efficiencies to a desired endpoint. The present diagram would be of direct application in monitoring the transformations between the classes of dicyclic naphthenics.

It is strongly recommended that the best way to further refine and evaluate this technique would be through its application to additional unknowns. Other naphthenic samples with different degrees of hydrogenation would fit nicely into the present or a similar set of standards. A variety of samples from different sources would best demonstrate the possible range of chemical classes and the degree of quantitative accuracy which might be expected.

Finally, it is recommended that additional data on pertinent jet fuel properties accompany the additional samples wherever possible. One of the great advantages of multivariate statistical analysis is that there is almost no limit to the type of information that can be correlated to the chemical data. Thus, combustion efficiency, energy content, density, viscosity, storage stability, or any other parameters could be evaluated along with the chemical analysis. This type of multivariate analysis for performance trends might actually predict a better fuel concurrent with the compositional analysis and the analytical method evaluation.

SECTION V

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