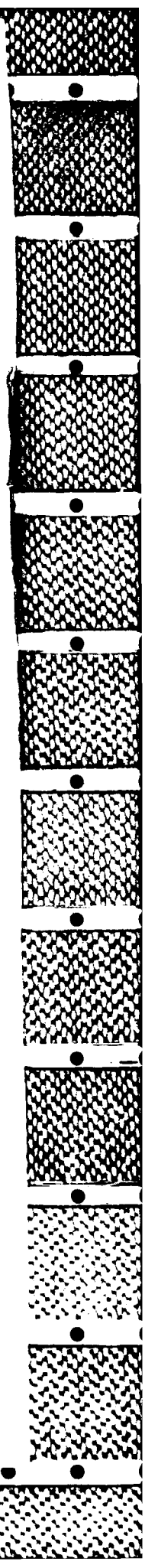




COPY RESOLUTION TEST CHART



DTIC FILE COPY

TRW (4)

TRW Space & Technology
Group
Applied Technology
Division

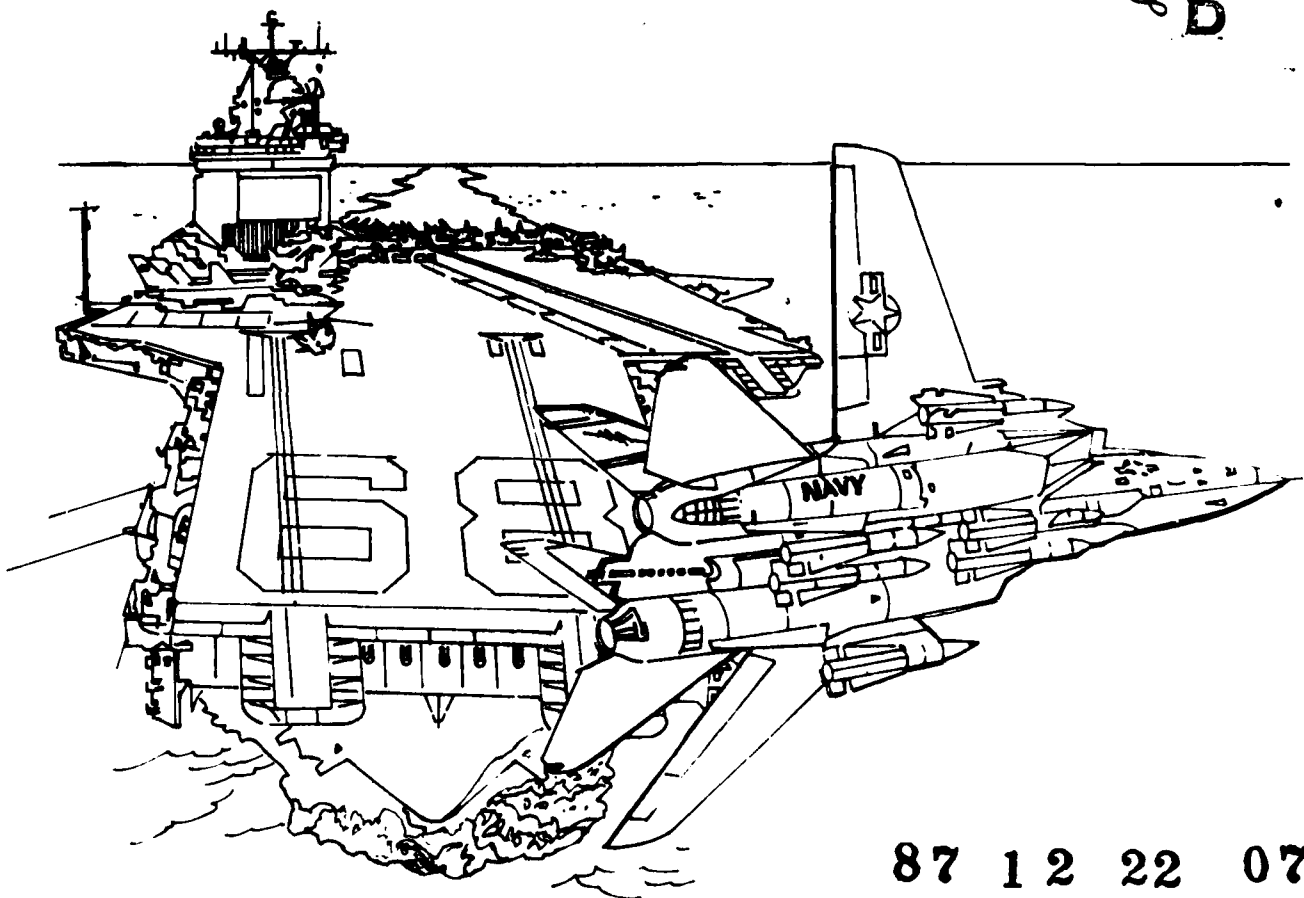
AD-A189 457

Navy Fuels Analytical Chemistry

Final Report
December 24, 1987

Contract No. N00014-86-C-2509
Report No. 47946-6005-UT-00

DTIC
ELECTE
DEC 30 1987
S **D**



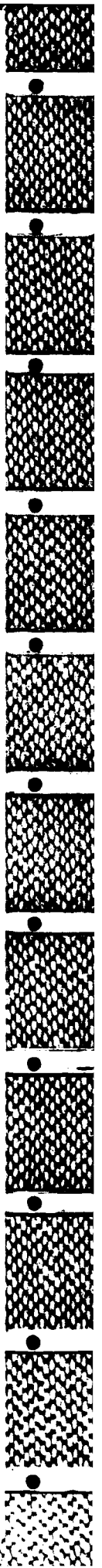
87 12 22 077

Prepared by
TRW Space & Technology Group
One Space Park
Redondo Beach, CA 90278

Prepared for
Naval Research Laboratory
Washington D.C. 20275
Attention: Code 6180

DISTRIBUTION STATEMENT A
Approved for public release
Distribution Unlimited

413409



REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION Unclassified		1b. RESTRICTIVE MARKINGS	
1c. SECURITY CLASSIFICATION AUTHORITY		3. DISTRIBUTION/AVAILABILITY OF REPORT Unlimited	
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE		5. MONITORING ORGANIZATION REPORT NUMBER(S)	
4. PERFORMING ORGANIZATION REPORT NUMBER(S) 47946-6005-UT-00		7a. NAME OF MONITORING ORGANIZATION Naval Research Laboratory	
6a. NAME OF PERFORMING ORGANIZATION TRW Applied Technology Division	6b. OFFICE SYMBOL <i>(If applicable)</i>	7b. ADDRESS (City, State and ZIP Code) Washington, D.C. 20375	
6c. ADDRESS (City, State and ZIP Code)		9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER Contract No. N00014-86-C-2509	
8a. NAME OF FUNDING/SPONSORING ORGANIZATION Naval Research Laboratory	8b. OFFICE SYMBOL <i>(If applicable)</i>	10. SOURCE OF FUNDING NOS.	
8c. ADDRESS (City, State and ZIP Code)		PROGRAM ELEMENT NO. 63724-N	PROJECT NO. R0838
11. TITLE (Include Security Classification) Naval Fuels Analytical Chemistry (U)		TASK NO.	WORK UNIT NO. NRL-61-00-85
12. PERSONAL AUTHOR(S) Martin H. Mach			
13a. TYPE OF REPORT Final	13b. TIME COVERED FROM 86/11/10 TO 87/11/16	14. DATE OF REPORT (Yr., Mo., Day) 87/12/20	15. PAGE COUNT 36
16. SUPPLEMENTARY NOTATION			
17. COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	JP-5, Sulfur Compounds, High Performance Liquid Chromatography, Gas Chromatography, Mass Spectrometry, Hall Detector.	
	SUB. GR.		
19. ABSTRACT (Continue on reverse if necessary and identify by block number)			
<p>The objective of this program was to develop analytical methods for the separation, quantitation, and identification of sulfur compounds in JP-5 turbine fuels. The principal accomplishments were 1) HPLC methods to separate benzothiophenes and sulfide/disulfides from as-received fuel, 2) the development of the Integrated Sulfur Detector, a modification of the Hall GC detector, permitting the quantitation of nanogram amounts of sulfur in HPLC fractions, 3) preliminary GC/MS analysis of the separated fractions.</p> <p><i>(Keywords)</i></p>			
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS <input type="checkbox"/>		21. ABSTRACT SECURITY CLASSIFICATION Unclassified	
22a. NAME OF RESPONSIBLE INDIVIDUAL Dr. Dennis Hardy		22b. TELEPHONE NUMBER <i>(Include Area Code)</i> (202) 767-3559	22c. OFFICE SYMBOL Code 6180

TABLE OF CONTENTS

	<u>PAGE</u>
Foreword and Acknowledgment.....	iii
Abstract.....	iv
1.0 SUMMARY	1
2.0 INTRODUCTION	2
3.0 EXPERIMENTAL	4
4.0 RESULTS AND DISCUSSION	5
4.1 HPLC Separation of the Sulfide/Disulfide Fraction..	5
4.2 The Integrated Sulfur Detector (ISD).....	7
4.2.1 System Blanks	8
4.2.2 ISD Response to Different Sulfur Compounds..	10
4.2.3 Linearity of ISD Response	10
4.2.4 Automation of the ISD	10
4.2.4.1 System Modifications	10
4.2.4.2 Results	15
4.3 GC and GC/MS Analysis	18
4.3.1 GC-FID Analysis	18
4.3.2 GC/MS Analysis	25
4.0 REFERENCES	29
5.0 ACRONYM LIST	30
Appendix A: Sample Fuel Designations	A-1



Accession For	
NTIS CRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution/	
Availability Codes	
Dist	Availability for Special
A-1	

FOREWORD AND ACKNOWLEDGEMENTS

This is the final report of a 12 month program performed by TRW's Chemistry Laboratory, a part of the Applied Technology Division under the Space and Technology Group.

Dr. Martin Mach, Program Manager and Principal Investigator, would like to acknowledge the technical contributions made by Kevin B. Patzkowsky for the development of HPLC separation methods and the Integrated Sulfur Detector, and Christopher J. Murphy for the GC/MS analyses.

We are pleased to acknowledge the interest and participation of Drs. Dennis Hardy, COTR, and Dr. Robert Hazlett, conversations with whom added to the technical strengths of the program.

ABSTRACT

The objective of this program was to develop analytical methods for the separation, quantitation, and identification of sulfur compounds in JP-5 turbine fuels. The principal accomplishments were 1) HPLC methods to separate benzothiophenes and sulfide/disulfides from as-received fuel, 2) the development of the Integrated Sulfur Detector, a modification of the Hall GC detector, permitting the quantitation of nanogram amounts of sulfur in HPLC fractions, 3) preliminary GC/MS analysis of the separated fractions.

1.0 SUMMARY

The objectives of the Navy Fuels Analytical Chemistry Program are to separate, identify, and quantitate organosulfur compounds in JP-5 turbine fuels. To these ends, TRW developed the following methods:

- * A technique to separate the benzothiophene/dibenzothiophene (BT/DBT) and sulfide/disulfide (S/D) fraction using high performance liquid chromatography (HPLC) with a silver nitrate/silica gel normal phase column.
- * A modification of the Hall gas chromatograph (GC) detector, our so-called Integrated Sulfur Detector (ISD) for the quantitation of nanogram amounts of sulfur compounds in small (1.0 ul) fuel samples, and
- * Preliminary GC and gas chromatography/mass spectrometry (GC/MS) identification of some of the compounds in the isolated fractions.

These methods can be used to characterize the changes in sulfur compound distribution in JP-5 fuels arising from different crudes, refining conditions, aging, and thermal, mechanical, and oxidative stress.

2.0 INTRODUCTION

The objective of this program is to quantify and identify the sulfur compounds in JP-5 fuels so that changes in their composition resulting from thermal, mechanical, and oxidative stress could be linked to specific chemical reactions. Because of their low concentration relative to hydrocarbons, methods had to be developed to separate the several classes of sulfur compounds from the hydrocarbons and permit successful GC and GC/MS analysis, quantitation, and compound identification.

This report summarizes work performed under Contract No. NM00014-86-C-2509, "Navy Fuels Analytical Chemistry" for the Naval Research Laboratory. This is the third contract in a continuing effort to elucidate the role of sulfur compounds in JP-5 fuel instability. A brief summary of the accomplishments during the course of these studies is given below.

1.1 First Contract Period ("Navy Mobility Fuels Evaluation", Contract No. N00014-82-C-2370, 9/82 to 5/84)

Experiments performed during this period (Ref. 1) focused on the role of sulfur compounds in fuel lubricity and elastomer compatibility, and initiated efforts to isolate and identify the individual sulfur compounds. The sulfur compounds were isolated via an oxidation/reduction scheme that verified the presence of BTs and DBTs, but which led to incomplete reactions and artifacts, e.g., the formation of dihydro-BTs from the reduction step.

1.2 Second Contract Period ("Navy Fuels Analytical Chemistry", Contract No. N00014-84-C-2267, 9/84 to 3/86)

During the second contract period (Ref. 2), efforts concentrated on the analytical chemistry associated with the isolation and identification of the native sulfur compounds in JP-5. A new method of separating the different sulfur classes was developed based on selective adsorption of sulfur compounds relative to polycyclic aromatics (the principal interference in other HPLC methods) using a silica gel (normal phase) column impregnated with 20% silver nitrate. This method was a good deal faster than the oxidation/reduction technique, and did not suffer the disadvantages of incomplete reactions and artifact formation.

In addition to improved class separations, sulfur mass balance of the HPLC fractions was initiated via the development of the ISD, a modified Hall electrolytic conductivity detector in the sulfur mode (HECD-S) in which the total sulfur response comes off as a single, easily integrated peak.

1.3 Third (present) Contract Period ("Navy Fuels Analytical Chemistry", N00014-86-C-2509, 11/86 to 11/87)

Work performed during the current contract period was aimed at a) extending the HPLC separation method beyond BTs and DBTs to the more polar sulfides and disulfides, b) optimizing the ISD to perform mass balance determinations of the isolated sulfur fractions, and c) identification of the isolated sulfur compounds by GC and GC/MS.

Details of the current studies are provided in the following sections.

3.0 EXPERIMENTAL

3.1 Samples. Fuel samples are designated NFP-xx ["Navy Fuels Program"], and are described in Appendix A.

3.2 Capillary Gas Chromatography

Samples were analyzed on either a Tracor 560 GC (HECD-S, ISD) or Varian 3700 as follows:

FID runs: J&W inlet splitter with flow reversing quartz liner packed with HMDS/DMCS treated glass beads, heated to 280C. Helium carrier to give a flow rate of 25 cm/sec (methane) at 60C, split flow at 30 ml/min.

Column: J&W 30m x 0.25 mm i.d. fused silica, 0.25 um coating thickness

Program: 60C (2 min hold) to 280C at 8C/min and hold if necessary.

Detectors:

FID: 280C

HECD-S:

Base: 280C

Reactor: 850C

Methanol flow: knob at 12 o'clock

3.3 ISD operation: See Fig. 2

3.4 GC/MS: VG 30-253 with Hewlett-Packard 5890A GC. Same column and conditions as for GC-FID.

3.5 HPLC: Dupont 850 with UV and RI detectors

Column: 250 mm x 10 mm i.d. 20% silver nitrate on R-Sil-5 (Applied Sciences)

3.6 Data System: Nelson model 3000

4.0 RESULTS AND DISCUSSION

Our research philosophy has been to develop an integrated approach using

- * HPLC to isolate sulfur class fractions
- * the ISD to quantitate sulfur in the isolated fractions, and
- * GC and GC/MS to identify and quantitate individual sulfur compounds

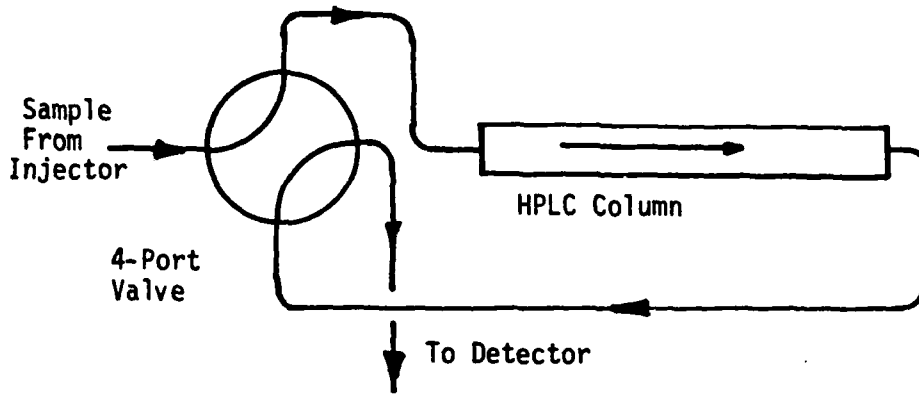
4.1 HPLC Separation of the Sulfide/Disulfide (S/D) Fraction

Separation of BT from polycyclic aromatic hydrocarbons (PAH) has been accomplished on a silica gel/silver nitrate column using 10% benzene in pentane. More polar sulfides and disulfides should, at least in principle, be eluted using more polar solvents once the PAHs and BTs have been collected. Because essentially all hydrocarbons and PAHs are removed prior to isolation of the BT fraction, they would not be present in the S/D fraction and complicate GC/MS quantitation and identification. Thus, it was felt that sulfides and disulfides could be collected as one fraction and the individual compounds identified by GC/MS.

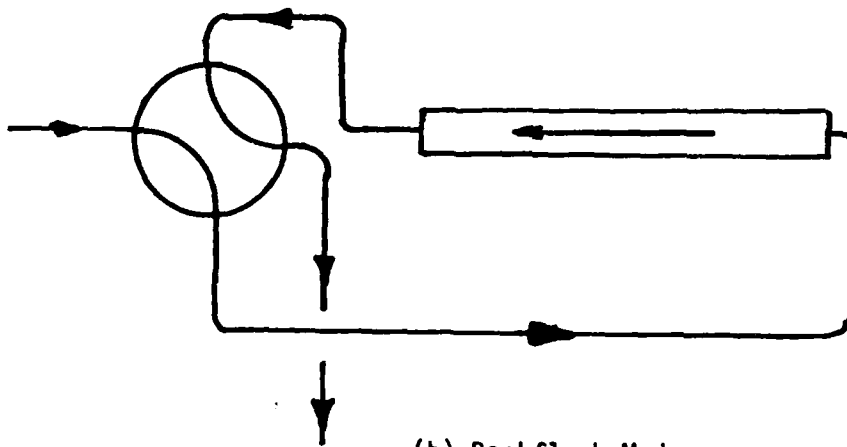
Initial experiments employed model sulfides and disulfides to determine HPLC conditions under which these materials would elute from the silver nitrate/silica gel column. N-octyl sulfide (NOS) and n-butyl disulfide (NBDS) were not eluted using up to 100% benzene. Therefore, a more polar solvent, i.e., ethyl acetate, at varying concentrations in benzene, was used. It should be noted that the choice of polar solvents was limited to those that would not dissolve significant amounts of silver nitrate (as shown by a lack of precipitate when aqueous chloride ion is added to the spent eluant), e.g., solvents other than alcohols or acetonitrile. Ethyl acetate gives only a slight precipitate, but even this slight amount of dissolution appears sufficient to clog the column, leading to increased back pressure and eventual pump shutdown.

This problem was remedied somewhat by disconnecting the column and reconnecting it backwards to reverse the solvent flow. However, back pressure on the reversed column crept up as the run progressed. In order to avoid the troublesome job of connecting and reconnecting the column whenever the back pressure became too high, a 4-port backflush valve was plumbed into the system to reverse solvent flow, as shown in Fig. 1. However, rather than use the backflush valve to simply alleviate the pressure buildup, it was decided to use the new configuration to collect fractions via backflush, instead of having to elute the more polar materials completely through the column.

Tests with NOS and NBDS confirmed that these compounds elute by backflushing with 30% ethyl acetate in benzene, a solvent



(a) Normal Flow Mode



(b) Backflush Mode

Fig. 1

Flow Diagram for HPLC Normal and Backflush Modes

mixture that did not lead to pressure anomalies during individual runs.

This backflush method has the following advantages over normal mode operation:

- * Separations are rapid because the compounds of interest do not have to traverse the entire length of the column,
- * High concentrations of ethyl acetate which lead to pressure problems are not required, and, most important,
- * Column plugging and back pressure problems are eliminated because the column packing is "conditioned" during normal/backflush switching.

For a single fuel sample, HPLC separation into benzothiophenes and sulfides/disulfides would be accomplished as follows:

- * Elution of hydrocarbons followed by BTs using 10% benzene in pentane.
- * Switch to 100% benzene to elute the last traces of more polar PAHs.
- * Switch to backflush with 30% ethyl acetate in benzene to elute the sulfides and disulfides.

Using this technique, the S/D fraction has been isolated from four fuel samples, viz., NFP-1, -3, -12, -13, and their GC and GC/MS analysis described in Section 4.3. [A description of the each of the "Navy Fuels Program" (NFP) fuels is presented in Appendix A.]

4.2 The Integrated Sulfur Detector (ISD)

A method has been developed for the quantitation of nanogram amounts of sulfur in small (1 ul) fuel samples based on gas chromatography with a modified HECD-S. Sulfur dioxide formed by the oxidation of sulfur compounds in the combustor tube is trapped on heated copper oxide and released as a pulse after the chromatographic run is over. Thus, all of the sulfur compounds are integrated as a single peak, hence its designation of the "integrated sulfur detector", or "ISD". This is a modification of a microcoulometric technique for trace sulfur detection (Ref. 3), but adapted for use on a commercial GC.

Initial experiments with the ISD showed that while it should work in principle, it was quite finicky. Blanks varied from day to day and even hour to hour, in spite of substantial efforts to remove contaminants from all gases and surfaces that might come in contact with the GC effluent or otherwise find their way into the copper oxide trap. However, sample size considerations caused us to persevere in developing this device to the point

where it was a reliable laboratory instrument. In our original setup, the oxidant gas, as specified by the manufacturer (Tracor), was air. In this configuration, the data were variable, with non-reproducible blanks, detector spikes, and drastic changes in sensitivity. Efforts were made to improve the results by scrupulously cleaning parts in contact with the gas streams, removing fines from the copper oxide, regularly changing the nickel oxidizer tube, etc., but without consistent success.

Finally, some thought was given to the process by which the sulfur compounds are oxidized in air. It seemed possible that nitrogen in the air could be oxidized in the 850 C nickel tube, and that non-reproducible amounts of nitrogen oxides might give rise to a signal in the HECD-S. Accordingly, research grade oxygen was used instead of air, and the gases adjusted to give an approximately 7:5 ratio of helium (carrier plus make-up) to oxygen. This change led to a dramatic change in the blank peak, making it both sharper and smaller, and reducing noise. Furthermore, day to day reproducibility was improved compared to data for air.

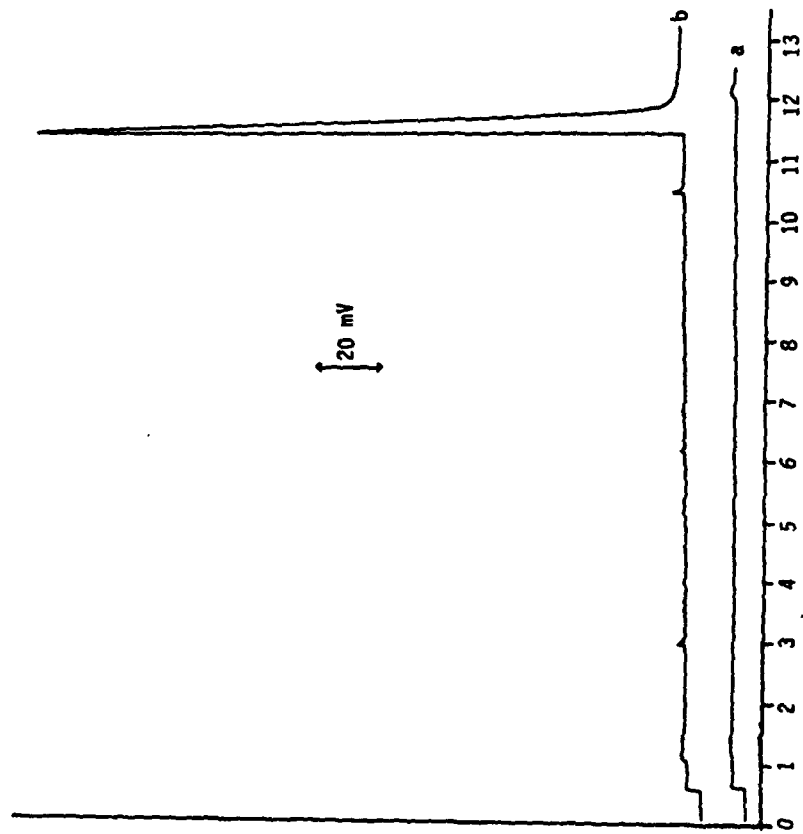
Details of these experiments, plus data on ISD response as a function of compound class, and linearity data are presented below.

4.2.1 System Blanks

The use of oxygen instead of air as the oxidant gas significantly reduces the system blank, in addition to making the peaks sharper. Fig. 2 is a typical chromatogram, showing the response of the ISD to 142 ng of sulfur (from BT, upper trace) and a system blank (hexane, lower trace) under the same conditions. In this case the area of the sulfur and blank peaks were 1,840,000 and 11,635, respectively, the blank being 0.6% of the sulfur peak.

While the use of oxygen led to a major improvement in ISD response, other changes in system configuration resulted in higher blanks, increased noise, etc. For example, it was found that the lowest blanks were obtained when the helium and oxygen gases were controlled using needle valves and rotameters, rather than the neoprene diaphragm flow controllers supplied with the GC. Although standard GC practice calls for flow controllers because viscosity/temperature effects will slow the helium carrier at elevated temperatures, the small amount of presumably sulfur contamination in standard flow controllers led to an unacceptably high blank.

A second example was the use of a data system controlled solenoid valve to shut the oxygen on and off during a run. We used a valve from another GC that had seen many years of service with clean gases, but this valve also introduced significant contamination into the system. Additional data on the



a. BLANK ISD CHROMATOGRAM
b. BENZOTHIOPHENE STANDARD CHROMATOGRAM, 142 ng SULFUR

Fig. 2 Typical ISD Chromatograms

sensitivity of the ISD to different components is presented in Section 4.2.4.

4.2.2 ISD Response to Different Sulfur Compounds

The ISD was challenged with four different classes of sulfur compounds to determine whether its response is a function of the type of sulfur present. Four compounds, each within the retention time range of JP-5, were tested: BT, dodecanethiol (DDT), NBDS, and NOS. Data over the range of 50 - 200 ng (as sulfur) injected, Fig. 3, show that all of the compounds give approximately the same normalized ISD response (Table 1)

4.2.3 Linearity of ISD Response

Linearity of response was determined using standard solutions of BT in hexane. Injections spanned the range of from 55 to 51,000 ng (as sulfur) injected. Detector response versus amount of sulfur injected was plotted using either peak area (Fig. 4) or peak height (Fig. 5), the response being linear when plotted as peak area or height versus log (S injected).

4.2.4 Automation of the ISD

In its initial configuration, most of the timed events of the ISD, e.g., oxygen on/off, trap heat/cool, were manually controlled. In order to improve reproducibility, several functions were automated using a combination of the timed events relays of the data system along with new heating and gas flow controllers. The results are described in the following sections.

4.2.4.1 System Modifications

Operation of the ISD involves four different timed functions:

- * Vent open/close. When the vent is open, solvent from the GC column is vented. This function is used at the beginning of the run to vent solvent so that it does not contaminate the nickel oxidizing oven.
- * GC oven program. The ISD uses a packed column since the only separation required is the dilution solvent (with HPLC fractions) from the fuel components. A temperature program is necessary to permit solvent/fuel separation (low temperature) while keeping the total run time short (high temperature) to reduce the system blank.
- * Trap temperature. The copper oxide trap is kept at 500C to allow evolved carbon dioxide to pass through while retaining the sulfur dioxide, and then rapidly heated to 850C to desorb the sulfur dioxide.
- * Oxygen on/off. Oxygen is added to the column effluent during

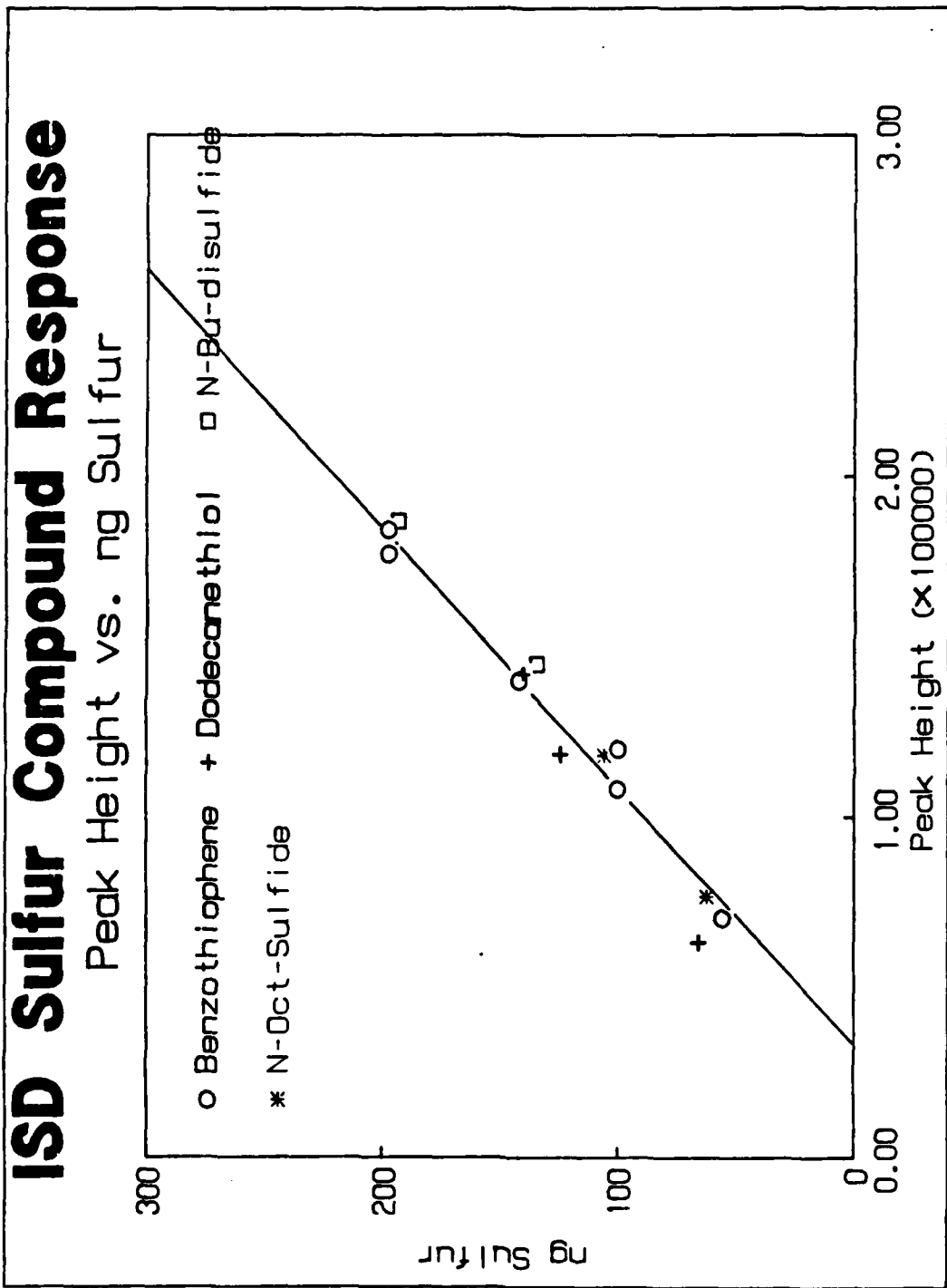


Fig. 3 ISD Response to Sulfur Compounds

Table :
Normalized ISD Response Data
for Different Sulfur Compounds

Compound	ng Sulfur Inj.	Height/ng	Area/ng
BT	99.9	1081	14314
	142	1201	15015
DDT	125	952	11840
	141	1000	11915
NBDS	134	1169	12612
NDS	106	1113	13962
Average		1073	13231
% Std. dev.		8.8	9.3

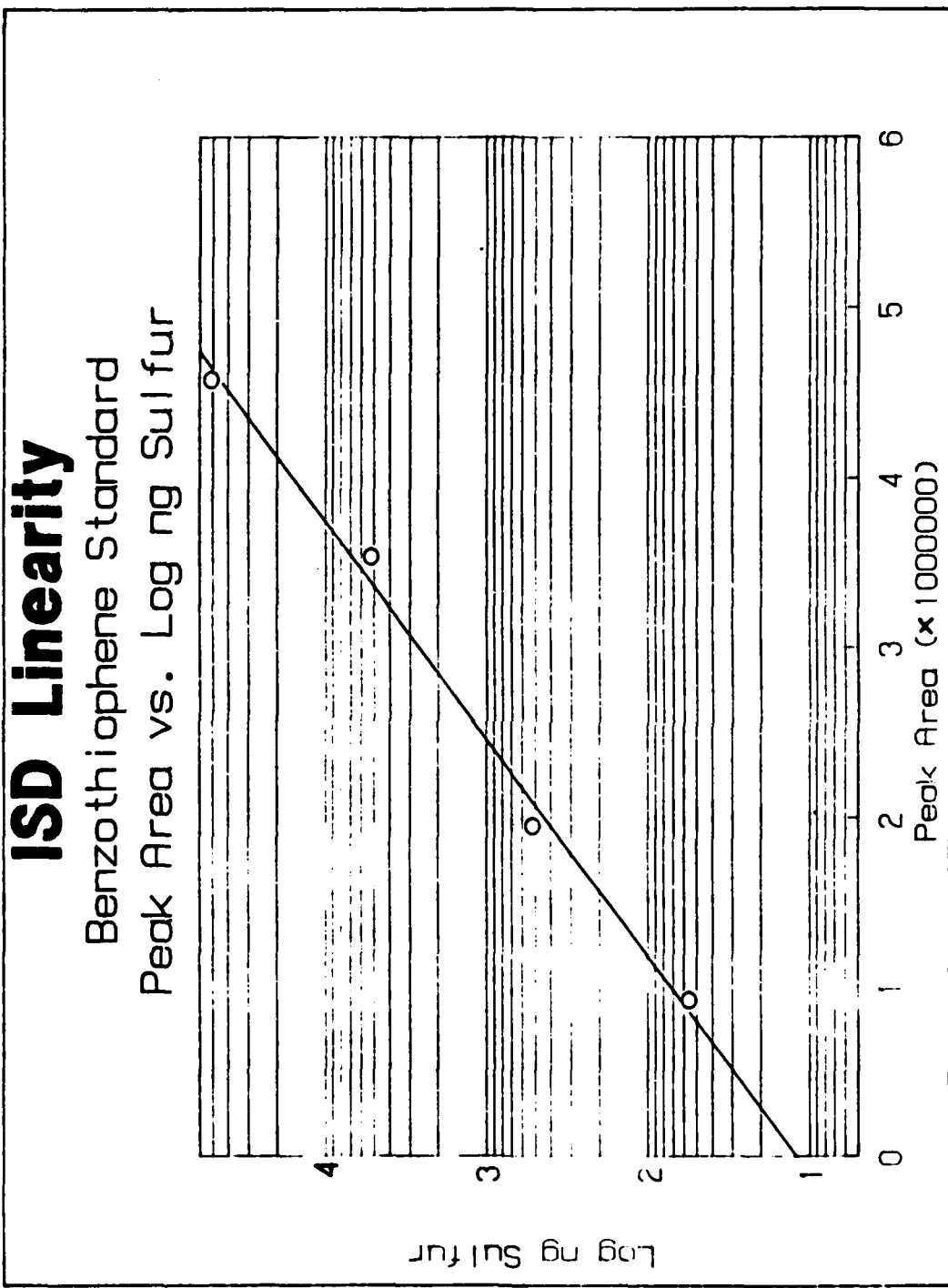


Fig. 4 ISD Linearity Based on Peak Area

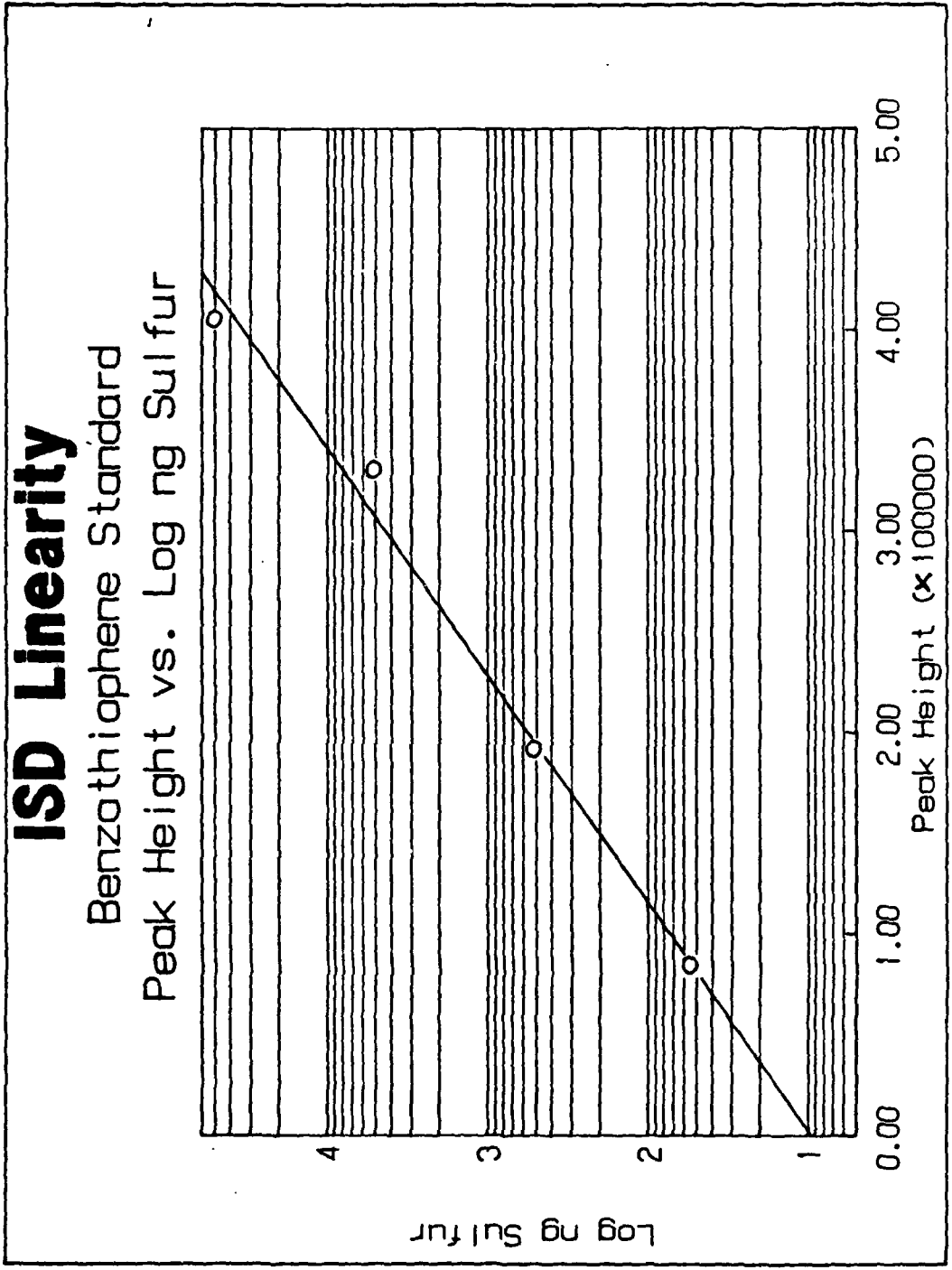


Fig. 5 ISD Linearity Based on Peak Height

the run to oxidize the column effluent in the furnace. It is shut off when the trap temperature is ramped to 850C to reduce detector noise and other artifacts.

These timed event functions are shown schematically in Fig. 6.

Automating the system necessitated several changes from the original configuration. In particular:

- * The trap is now heated with an Omega Corp. "Ramp and Soak" (RS) controller, allowing very fast cycling between 500C and 850C. The initiation of the heat, hold, and cool cycles is controlled by the chromatography data system. Previously, the trap was heated manually using a Variac.
- * The oxygen flow is controlled with a stainless steel diaphragm flow controller and a small on/off solenoid valve, with the on/off functions controlled by the data system. Previously, the oxygen was controlled with a needle valve and rotometer.
- * The copper oxide trap is fabricated from a 5" length of 1/4" o.d. alumina tubing containing 1" of copper oxide between quartz wool plugs, and terminated with stainless steel Swagelok 1/4" to 1/16" reducing unions. The trap temperature is monitored by a chromel/alumel thermocouple placed midway along its 5" length, and separated from the alumina body by the insulating wrap. The RS was adjusted to provide a fast ramp from 500C to 800C with minimum overshoot and minimum cycling around the set point.

4.2.4.2 Results

Fig. 7 shows a trace of the trap temperature during an ISD run, along with the ISD trace for a blank run. The peak at 16 minutes is the system blank, with an area of 500,000. The large peaks at 19 minutes are due to the electrical switching of the RS controller and can be eliminated with a special noise suppressor.

Once the event times and RS parameters were established, efforts were made to reduce the size of the system blank from over a million to around the 15,000 - 20,000 needed to insure good quantitation of the sulfur fractions. Unfortunately, this was not achieved, principally because the origin of these high blanks is not well understood.

In the past, specific changes in the system significantly reduced noise and blank problems. For example, changing the oxidizing gas from air (manufacturer's recommendation) to oxygen greatly reduced noise and led to a sharper total sulfur peak. However, other changes led to ambiguous results, as the following examples will attest:

Programmed Functions for the ISD

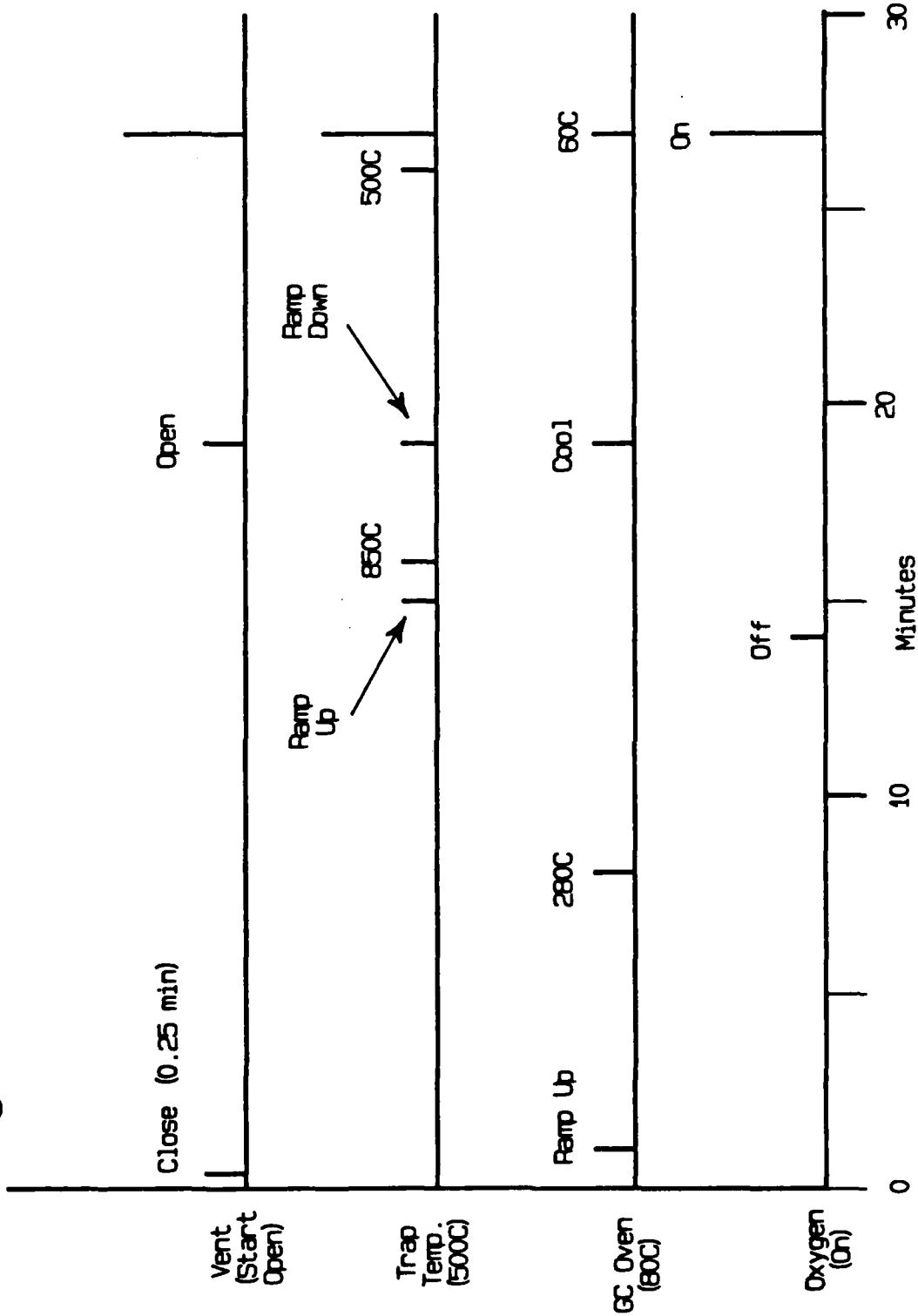


Fig. 6 Time Programmed Functions for the ISD

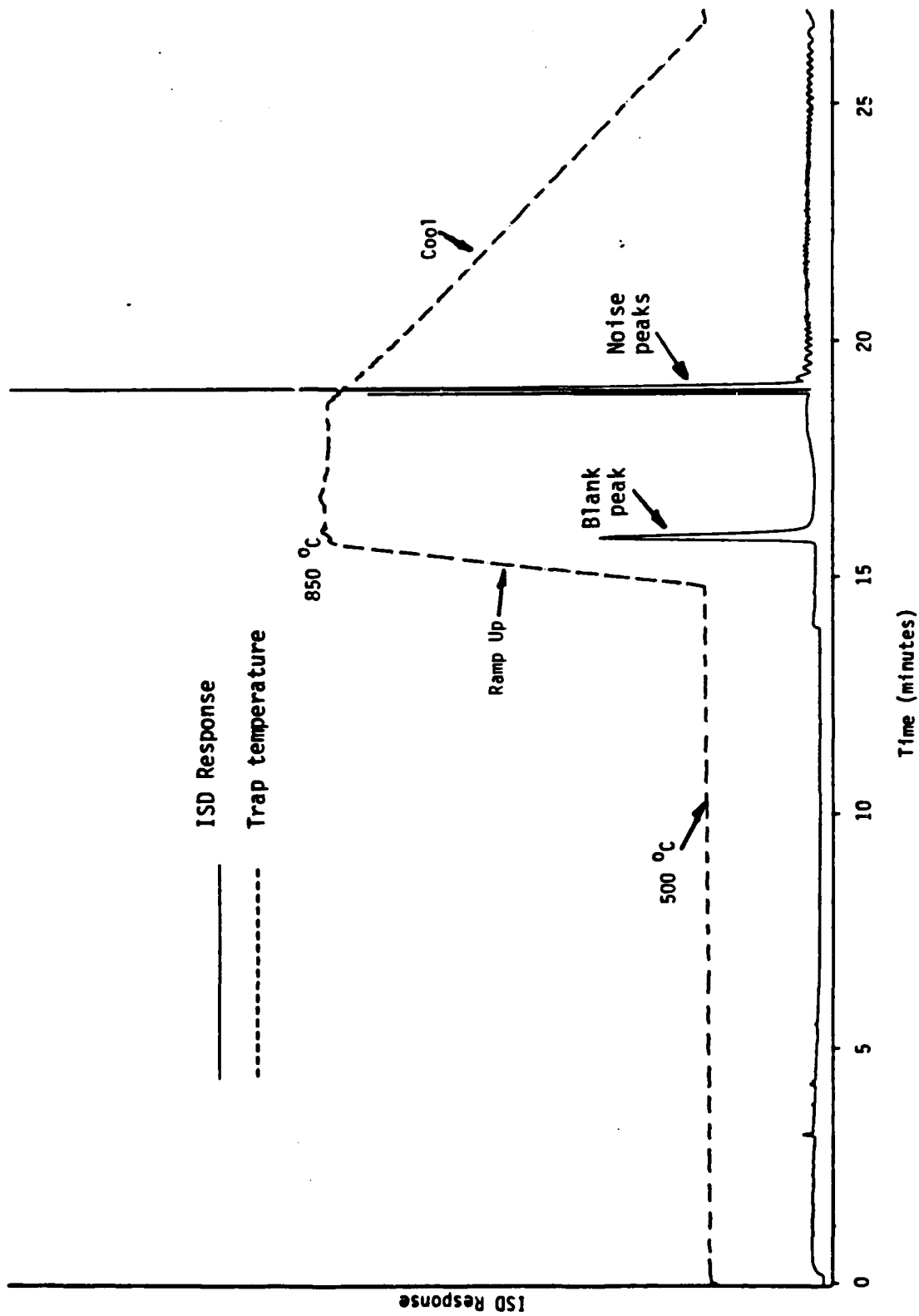


Fig. 7 ISD trace for a System Blank (No Sample Injected)

- * Replacing a damaged rotometer tube (which had been in the GC since it was new) with an identical new one led to a large increase in the blank. Efforts to remedy this problem were to no avail, and the solution was to remove the new tube from the system.
- * A special stainless steel flow controller and low internal solenoid valve were installed to better control the oxygen flow. These "clean" components increased the system blank.
- * Small traps packed with activated molecular sieves were added to the helium (carrier gas) and oxygen lines downstream from all flow control devices and valves in an attempt to adsorb whatever might outgas from these components. The traps were further positioned so that they could be activated in place using a Bunsen burner. These new components decreased the system blank by 75%, but the blank was still too high for good sample quantitation.

4.3 GC and GC/MS Analysis

These studies focused on three fuels:

- * NFP-1 and -3: high sulfur, conventional, single distillation cut fuels, covering the boiling point range of roughly naphthalene to phenanthrene (or BT to DBT), and
- * NFP-13 (Sun B): a blended fuel with significantly more high boiling components, covering the boiling point range of from naphthalene to chrysene.

In addition to the examination of as-received fuels, it was decided to examine a thermally stressed fuel by HPLC and GC to determine if significant changes occurred in the BT/DBT or S/D fractions. Consequently, NFP-13 was thermally stressed for 24 hours at 150C in sealed ampules in the presence of air. This fuel was chosen because 1) its low boiling range contains the BT/DBT fraction found in the single-cut fuels, and 2) additional information would be obtained on the higher boiling fractions.

4.3.1 GC-FID Analysis

The GC curves of the S/D fractions from NFP-1 and -3 are shown in Figs. 8 and 9, respectively. Except for slight differences in the absolute GC retention times, the curves appear qualitatively identical in all major respects, similar to the case for the BT/DBT fractions of these fuels (Ref. 4).

Figs. 10 and 11 show the GC curves for the BT/DBT and S/D fractions, respectively, of as-received NFP-13. The corresponding curves for the stressed fuel are shown in Figs. 12 and 13. Comparison of Figs. 10 and 12 versus 11 and 13 shows that the BT/DBT fraction is a good deal more stress resistant than the S/D fraction. [Because these tests were

DATA FILE=msv99 FROM 0.00 MIN. TO 26.00 MIN. LOW SCALE= 0.000 MV. HIGH SCALE= 40.000 MV.
NFP-1 EtOAc Fraction

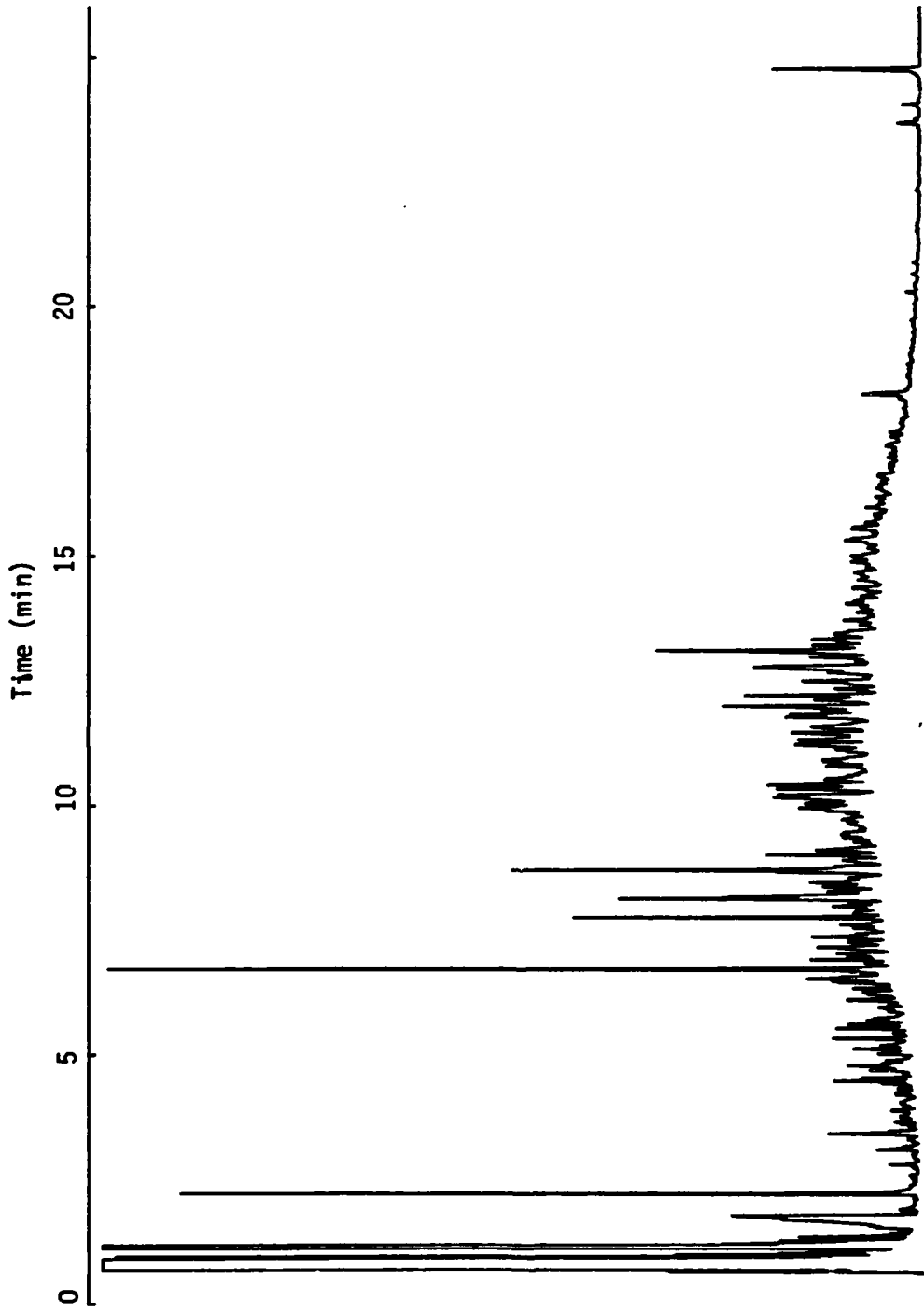


Fig. 8

GC-FID Trace of NFP-1, Sulfide/Disulfide Fraction

DATA FILE=nbv11 FROM 0.00 MIN. TO 24.00 MIN. LOW SCALE= 0.000 MV. HIGH SCALE= 20.000 MV.
NFP-3 ESDAC Fraction

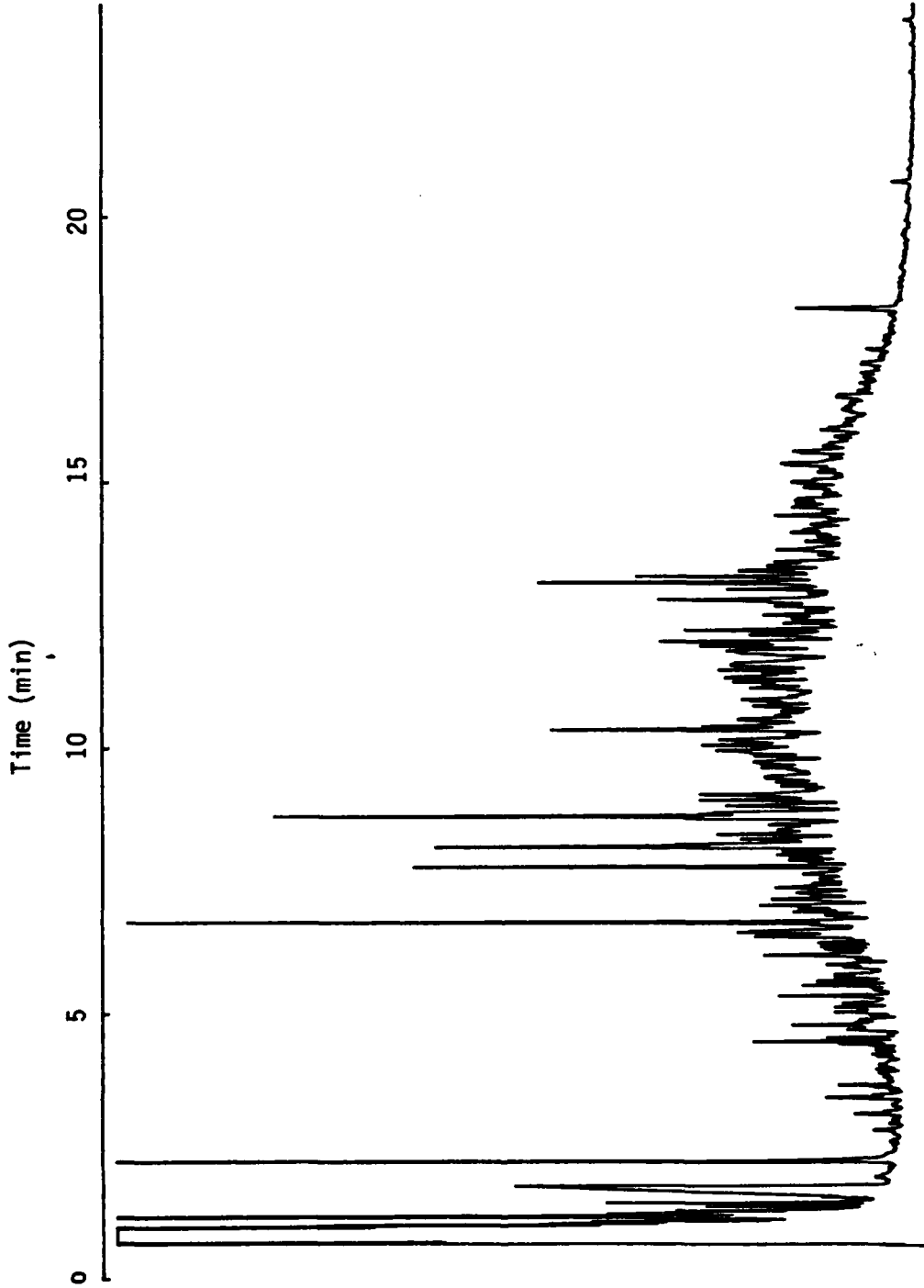


Fig. 9
GC-FID Trace of NFP-3, Sulfide/Disulfide Fraction

DATA FILE=nbvy2 FROM 0.00 MIN. TO 26.00 MIN. LOW SCALE= 0.000 MV. HIGH SCALE= 100.000 MV.
NFP-13 BT Fraction

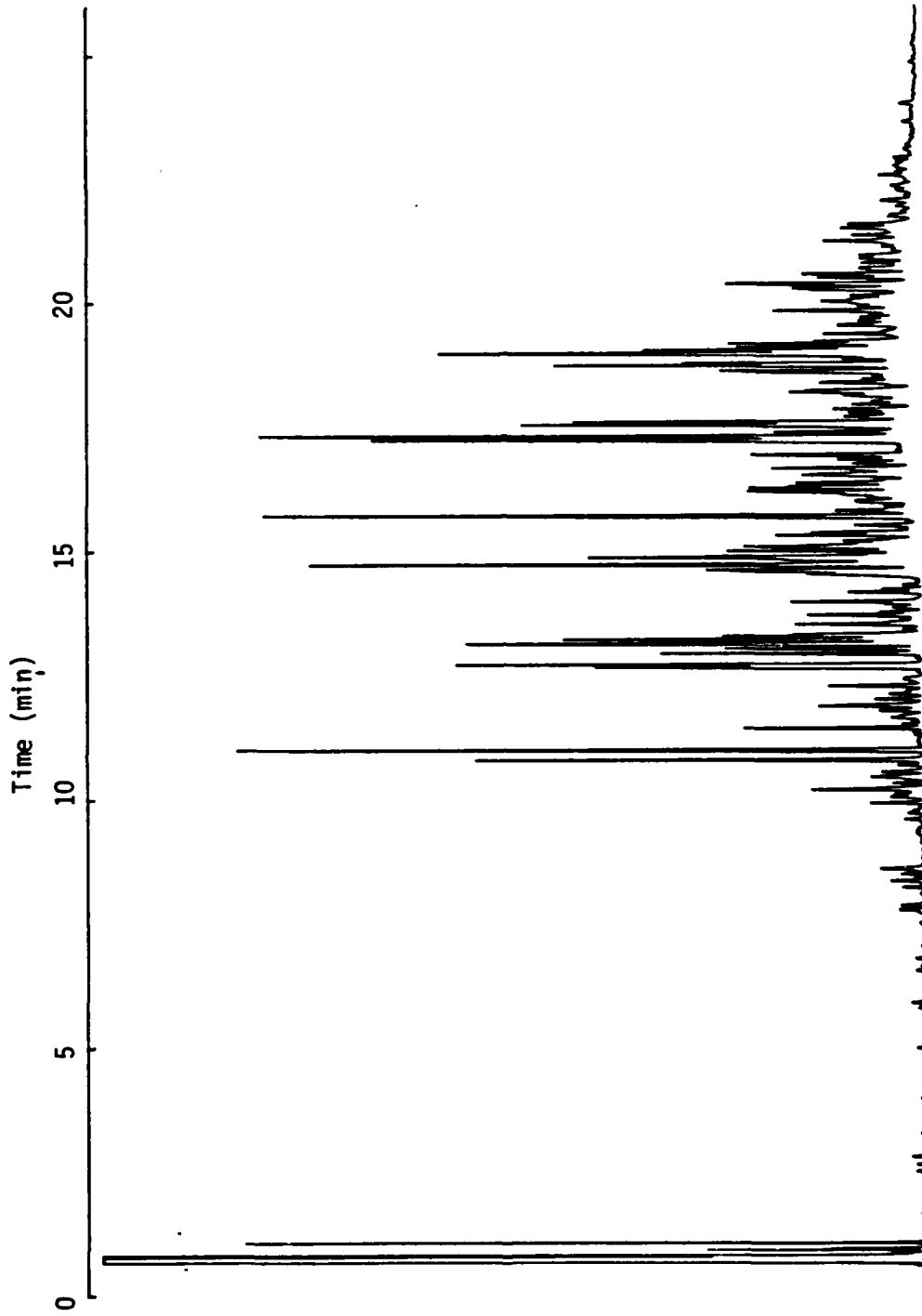


Fig. 10
GC-FID Trace of NFP-13, BT Fraction (Unstressed)

DATA FILE-NAVY4 FROM 0.00 MIN. TO 26.00 MIN. LOW SCALE= 0.000 Mv. HIGH SCALE= 10.000 Mv.
NFP-13 EtOAc Fraction

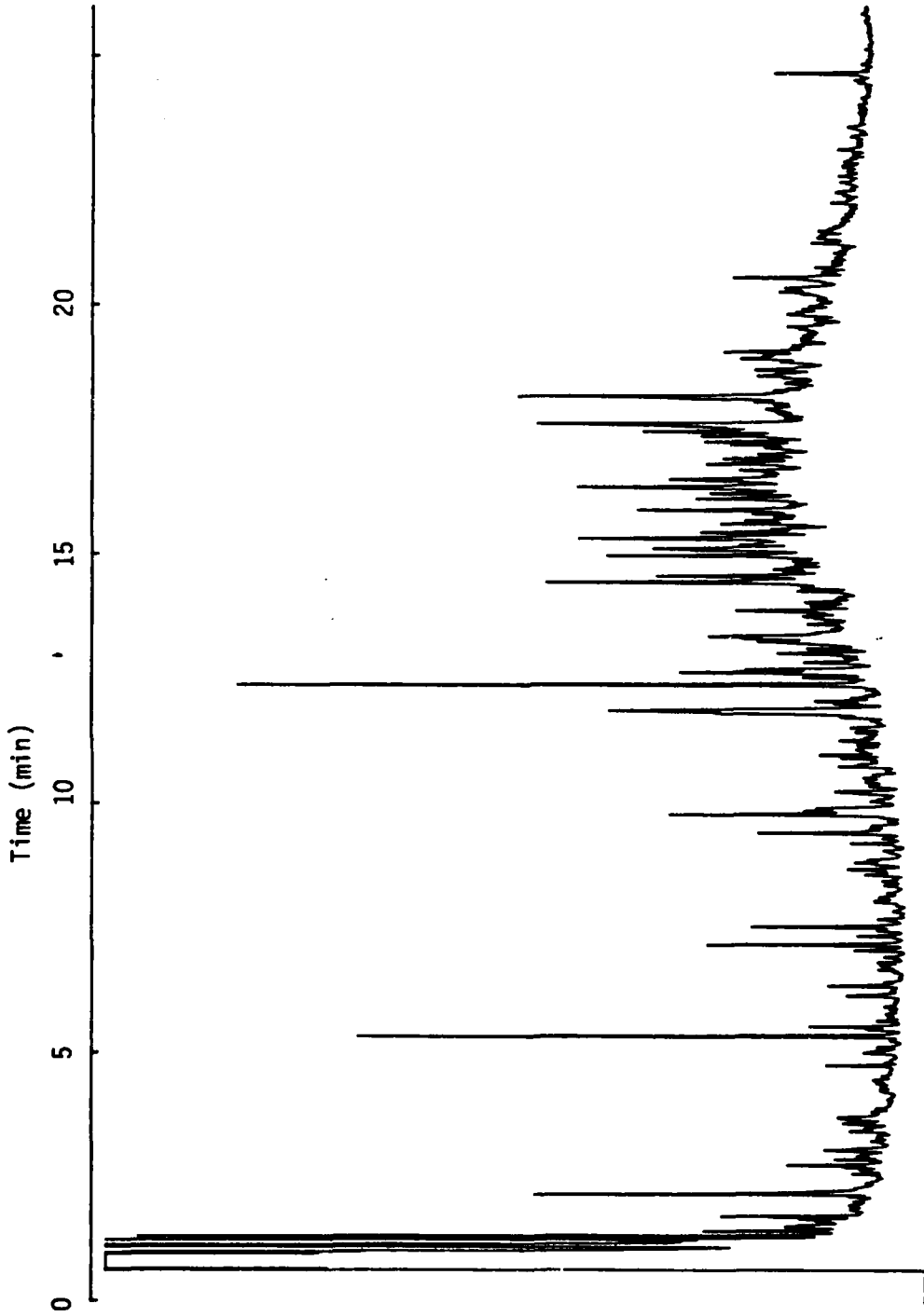


Fig. 11
GC-FID Trace of NFP-13, Sulfide/Disulfide Fraction (Unstressed)

DATA FILE=mvys FROM 0.00 MIN. TO 26.00 MIN. LOW SCALE= 0.000 MV. HIGH SCALE= 200.000 MV.
NFP-13 BT Fraction Stressed

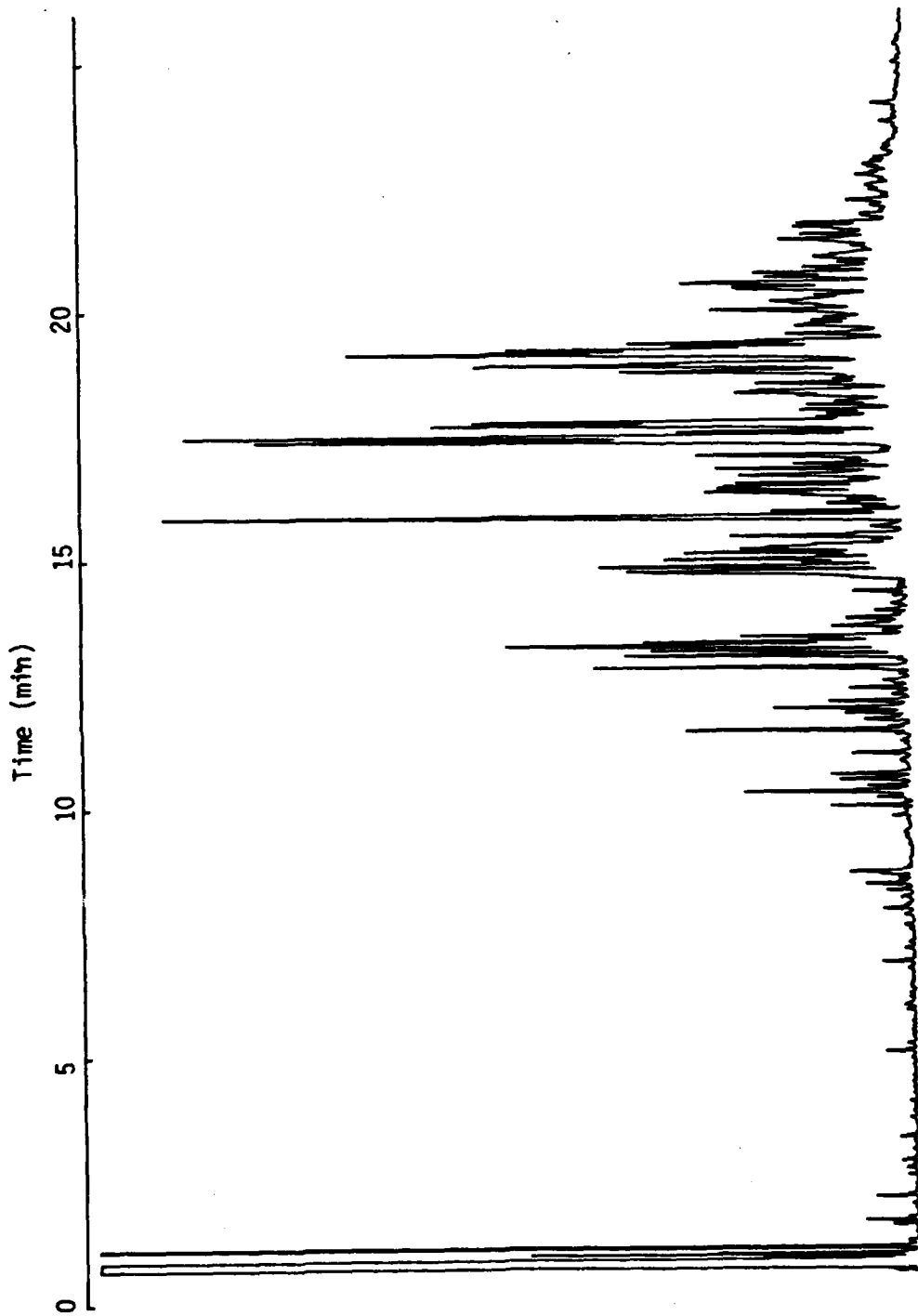


Fig. 12
GC-FID Trace of NFP-13, BT/DBT Fraction (Stressed)

DATA FILE=nevy6 FROM 0.00 MIN. TO 26.00 MIN. LOW SCALE= 0.000 MV. HIGH SCALE= 20.000 MV.
NFP-13 ESCOAC Fraction Stressed

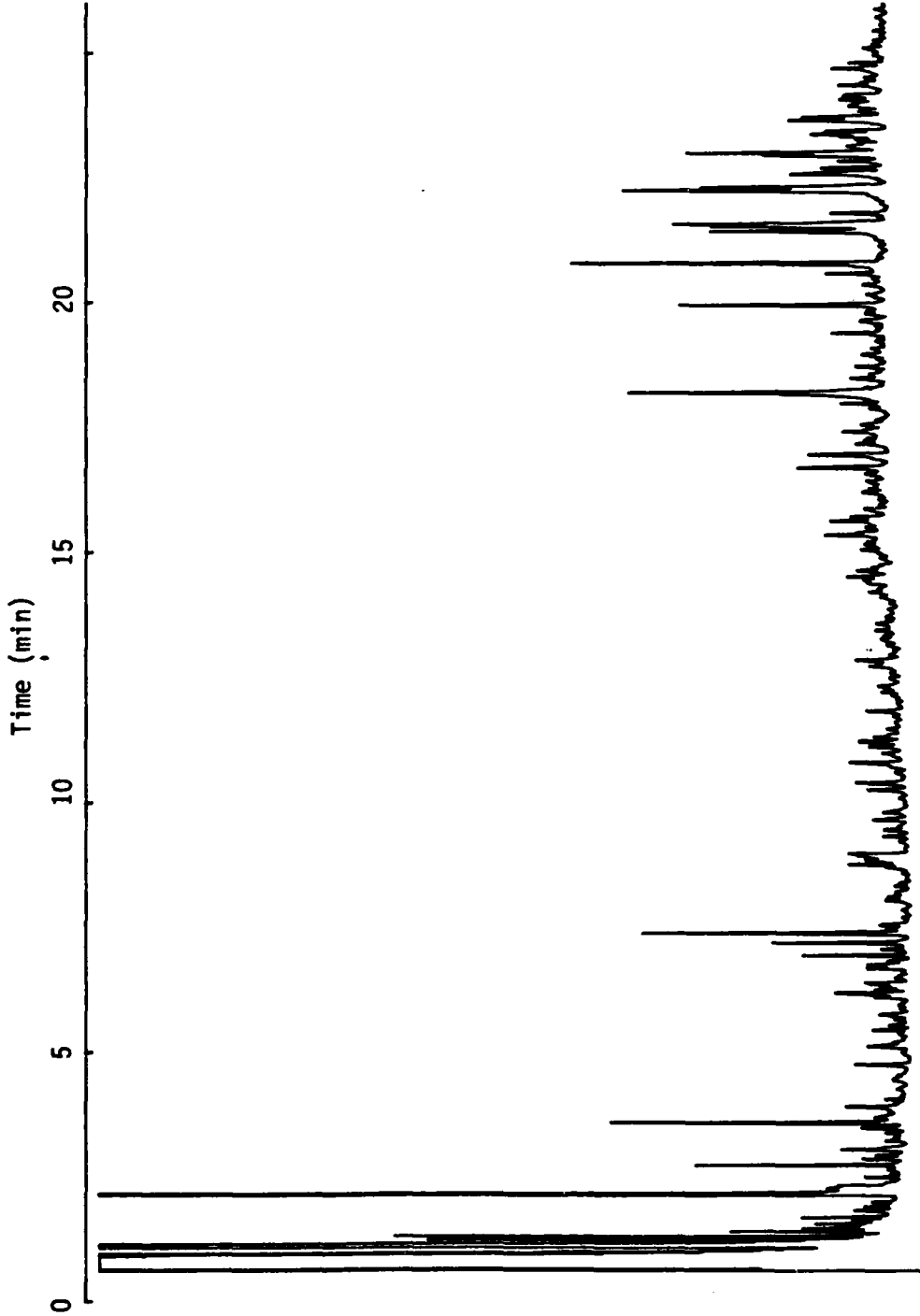


Fig. 13

GC-FID Trace of NFP-13, Sulfide/Disulfide Fraction, Stressed

performed without an internal standard, the absolute intensities of the peaks cannot be used to determine the amount of sample loss due to stress. Note that the chromatograms of the stressed fuels, Figs. 12 and 13, are presented at a display sensitivity twice that of Figs. 10 and 11.]

4.3.2 GC/MS Analysis

While time limitations of the program did not allow for extensive GC/MS analysis of all of the collected fractions, preliminary data are presented below.

The GC/MS chromatogram of the S/D fraction from NFP-1 is shown in Fig. 14, along with selected mass spectra of major peaks "A" - "D" (Fig. 15). The chromatogram of as-received fuel is shown in Fig. 16 for comparison. Standards have not been examined at this time, so the class and structural assignments are preliminary. For example, peak "A" could be a C-10 sulfide, with M+ at 172, and alkyl loss ions at 157 ($-\text{CH}_3$) and 129 ($-\text{C}_3\text{H}_7$).

GC/MS analyses of the S/D fraction from NFP-13 reveals high concentrations of PAH that tend to overwhelm the traces of sulfides and disulfides. Although experiments with model compounds shows that the PAH should be eluted during the benzene foreflush part of the separation, it appears that some PAHs remain on the column and are desorbed during the ethyl acetate/benzene backflush. Since these compounds are present in much higher concentrations than the sulfides and disulfides, even "traces" of retained material can severely contaminate the S/D fraction. [Unfortunately, it was not possible to run a simultaneous FID/HECD-S chromatogram to determine which compounds contained sulfur because the capillary GC/Hall detector was modified for use as an ISD]. This problem could likely be reduced by an additional foreflush or backflush step with low percentages of ethyl acetate in benzene to remove the last traces of PAH without eluting the sulfides and disulfides.

SST: 3044
TRACE: A
SCAN: 563

Sigs: E11

Run:

3-JUL-87 07:32:30-250

Chromatogram Identifiers: A: RTTC

Text: NFP-1 SAMPLE INJESS LINE228

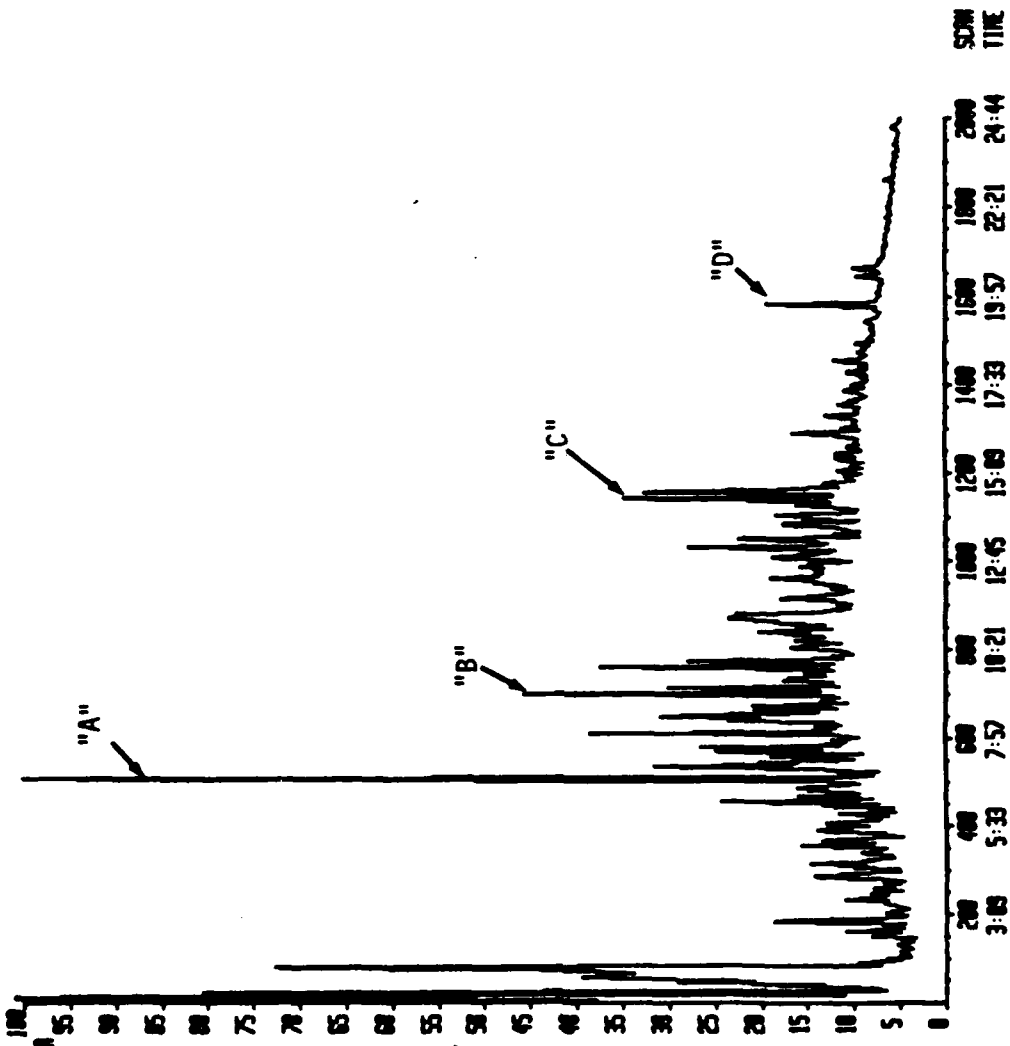
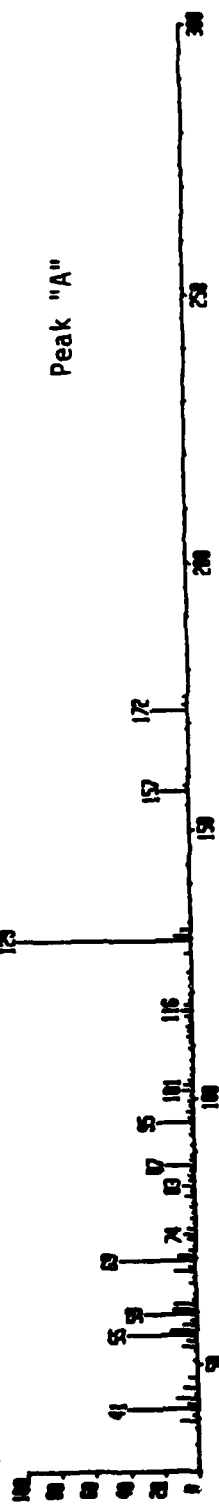
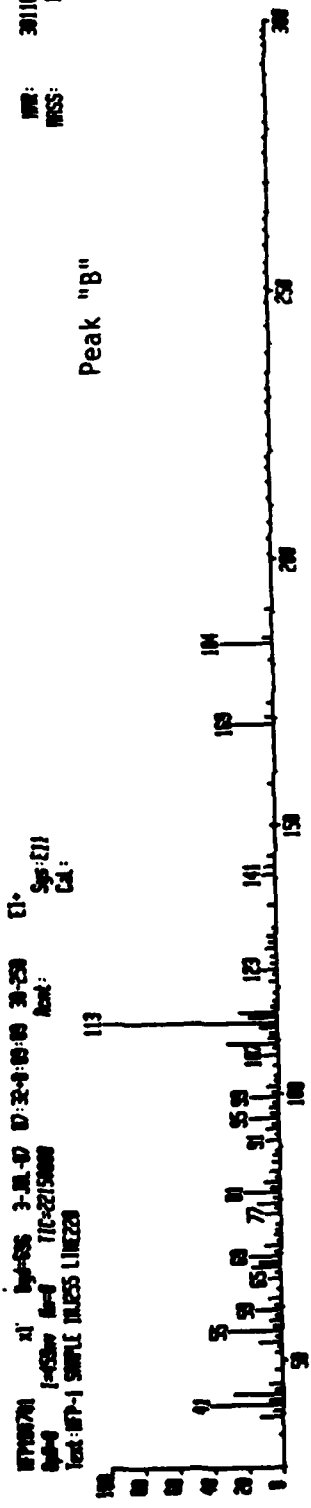


Fig. 14
GC/MS Chromatogram of the Sulfide/Disulfide Fraction
from NFP-1

MR: 211000
MSS: 123



MR: 301100
MSS: 113



MR: 173000
MSS: 63



MR: 91100
MSS: 43

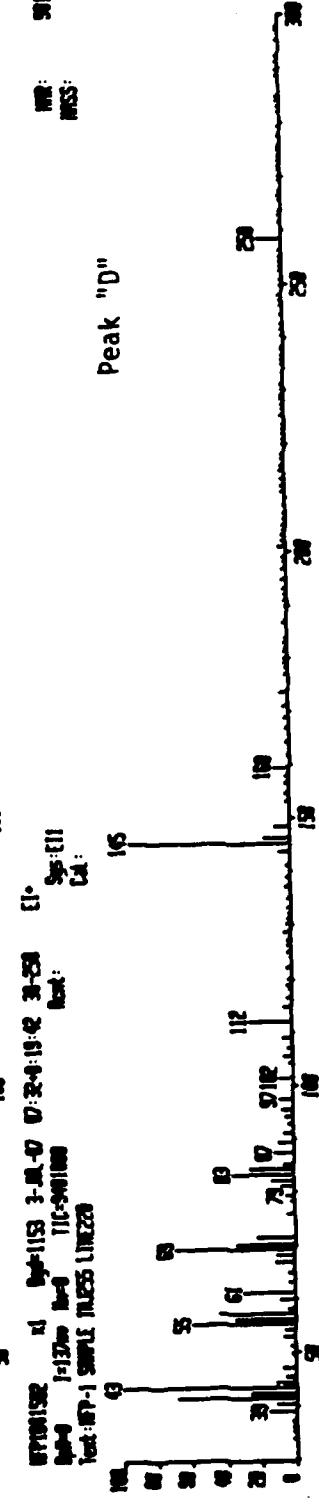


Fig. 15 Selected Mass Spectra of Peaks in Fig. 14

NFP11 01-2383 9-JUL-07 04:36:30-250 Rent: Sps:ELI IMP #: 44606
Chromatogram Identifiers : A :HTIC
Text:300 00-5, WE AT 142 SECONDS, SPLIT 60

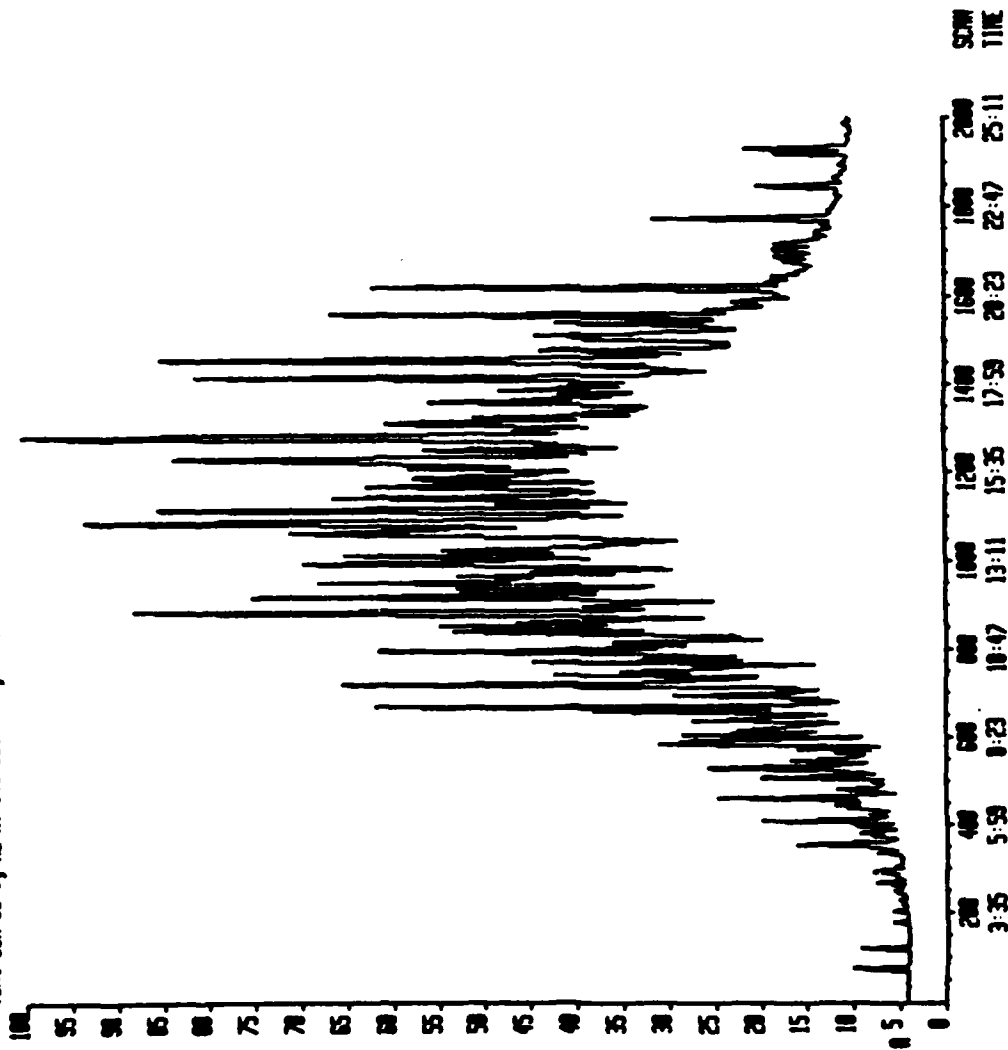


Fig. 16
GC/MS Chromatogram of NFP-1, As-Received

4.0 REFERENCES

1. E. Fishman, M. H. Mach, L. M. Fraser, and D. P. Moore, "Navy Mobility Fuels Evaluation", Final Report, July 20, 1984, Contract No. N00014-82-C-2370 for the Naval Research Laboratory.
2. M. H. Mach, "Navy Fuels Analytical Chemistry", Final Report, May 3, 1986, Contract No. N00014-84-C-2267 for the Naval Research Laboratory.
3. I. J. Oita, "Coulometric Determination of Sub Parts-Per-Million Levels of Sulfur in Volatile Liquids", Anal. Chem., 55, 2434 - 2436 (1983).
4. M. H. Mach, "Navy Fuels Analytical Chemistry", Second Quarterly Report, March 26, 1985, Contract No. N00014-84-C-2267 for the Naval Research Laboratory.

5.0 ACRONYM LIST

BT	Benzothiophene
DBT	Dibenzothiophene
DDT	Dodecanethiol
FID	Flame Ionization Detector
GC	Gas Chromatography
GC/MS	Gas Chromatography/Mass Spectrometry
HECD-S	Hall Electrolytic Conductivity Detector - Sulfur Mode
HPLC	High Performance Liquid Chromatography
ISD	Integrated Sulfur Detector
NBDS	n-Butyl Disulfide
NOS	n-Octyl Sulfide
PAH	Polycyclic Aromatic Hydrocarbon
RS	Omega Corp. "Ramp and Soak" temperature controller

APPENDIX A

Sample Fuel Designations

Fuel No.	Refinery	Date Rec'd	Comments
NFP-1	Powerine	10 Oct 1982	One gallon, high sulfur JP-5 shipped from NRL, designated 80-5
NFP-2	Exxon Banicia	15 Oct 1982	Five gallons JP-5 distilled from 90% North Slope 10% San Joachin Valley crude. Heavily hydrotreated. No AO-35 added
NFP-3	Powerine	10 Nov 1982	One gallon JP-5 picked up at refinery. Designated TL-88 by Powerine
NFP-4	Mobil	5 Sept 1981	One pint JP-4, picked up at refinery
NFP-5	Nat. Bur. of Stds.	-	NBS Std. 1624a, Sulfur in Diesel Fuel Oil
NFP-6	n.a.	10 Dec 1982	1 gallon JP-5 from NAPC
NFP-7	Powerine	-	5 gallons JP-5
NFP-8	Ashland	8 Mar 1983	Ashland 140 solvent, 5 gallons, similar b.p. range to JP-5, no additives
NFP-9	Shell	9 Mar 1983	Shell solvent 71, 5 gallons, similar to NFP-8
NFP-10	Beacon	10 May 1983	5 gallons JP-5

Fuel No.	Refinery	Date Rec'd	Comments
NFP-11	Mobil	10 May 1983	5 gallons JP-5, picked up at refinery in glass gallon jugs
NFP-12	Sun	Oct 1984	1 pint Suntech A from NRL
NFP-13	Sun	Oct 1984	1 pint Suntech B from NRL
NFP-14	n.a.	10 April 85	1 pint NAPC 81-9A, JP-5
NFP-15	n.a.	10 April 85	1 pint NAPC 81-19A, high aromatic JP-5
NFP-16		5 Aug 85	50 ml NRL 83-57 Exxon Baton Rouge
NFP-17		5 Aug 85	50 ml NRL 83-60 Gulf Port Arthur
NFP-18		5 Aug 85	50 ml NRL 83-62 Mobil Torrance
NFP-19		5 Aug 85	50 ml NRL 83-63 Fletcher Oil

END
DATE
FILMED
MARCH
1988
DTIC