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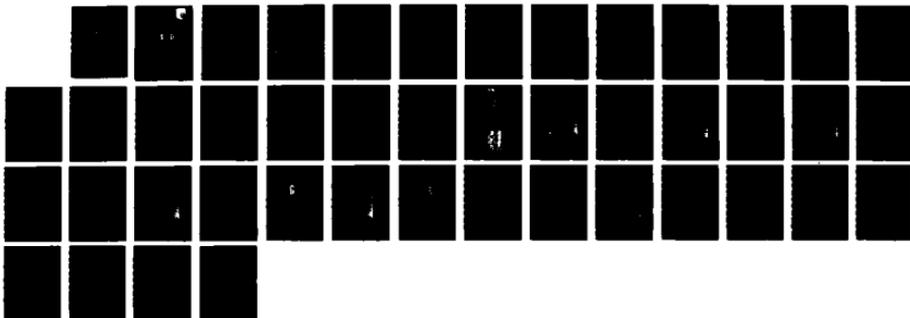
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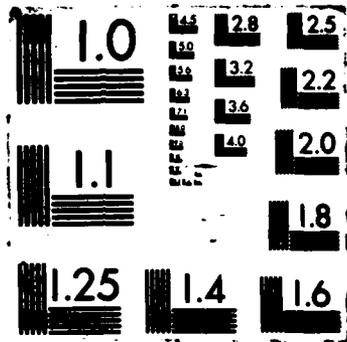
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CAPILLARY GC DETECTION METHODS FOR NITROGEN AND SULFUR COMPOUNDS IN SHALE-DERIVED JET PROPULSION FUELS

ELLEN M. STEWARD
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Experimental Support Branch
Fuels and Lubrication Division

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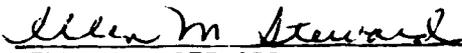
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This technical report has been reviewed and is approved for publication.


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FIELD	GROUP	SUB. GR.										
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19. ABSTRACT (Continue on reverse if necessary and identify by block number) <p>Correlations have been drawn between nitrogen and sulfur content in jet propulsion fuel and poor fuel performance. Recent studies have suggested that certain nitrogen and sulfur compound classes are more detrimental to fuel performance than others. This report emphasizes the importance of knowing which nitrogen and sulfur compound classes are present in jet propulsion fuel and demonstrates the ability of several capillary gas chromatographic (GC) detectors to selectively detect individual nitrogen and sulfur compounds in these fuels. <i>(Keywords: ...)</i></p>												
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1. Nitrogen and Sulfur Compounds in Shale-Derived Jet Propulsion Fuels.

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LIST OF ABBREVIATIONS

ABBREVIATION/SYMBOL	DEFINITION
GC	Gas Chromatograph
ml/min	milliliters/minute
DB-1	Dura Bond, Cross Linked Methyl Silicone
ppm-N	parts per million - Nitrogen
ppm-S	parts per million - Sulfur
FTID	Flame Thermionic Detector
TSD	Thermionic Specific Detector
TID-2-H2/Air	Thermionic Detector - H2/Air
CLD	Chemiluminescent Detector
TID-1-N2	Thermionic Detector-1-N2
FPD	Flame Photometric Detector
FID	Flame Ionization Detector
ng-N	nanograms - Nitrogen
ng-S	nanograms - Sulfur
nm	nanometers
Kb	Base Dissociation Constant
RRF	Relative Response Factors
SD	Standard Deviation
ASTM	American Society for Testing and Materials

SECTION I

INTRODUCTION

The determination of total nitrogen and total sulfur content in aviation turbine fuels is of great importance when predicting the performance of these fuels. With the introduction of non-petroleum fuels (i.e. shale oil, coal liquefaction products, tar sand bitumen), the interest in this area has grown.

Several correlations have been drawn between nitrogen and sulfur contents in fuels and poor fuel performance. Tar sand bitumens, shale oils and coal-derived liquids contain large amounts of sulfur and nitrogen compounds. Emissions from these compounds may be toxic and should be reduced to a minimum for environmental concerns (1,2,3,10). Nitrogen and sulfur compounds play a major role in the formation of gum and sediments (3,4) and greatly contribute to fuel instability during storage (3,6,9,10). Sulfur is responsible for the corrosion of certain metals and synthetic rubbers in the fuel system (11). Nitrogen compounds poison catalysts during the hydrotreating process making refining more expensive than necessary (5,6,7,8,10).

Several methods are available for determining total nitrogen and total sulfur content in fuels. Recently, there has been speculation as to whether certain nitrogen and sulfur compound classes are more detrimental to fuel performance than others.

Anilines, along with phenolic compounds, are believed to be responsible for most of the toxicity in coal liquefaction products (2). Pyrroles have long been suspected to be the major cause of gum formation in fuel (3). Studies carried out by Exxon indicate that some nitrogen compounds produce no sediment in fuel, whereas alkyl-substituted pyrroles and indoles produce significant quantities of sediment in fuel under the same conditions (4). It is the more basic nitrogen compounds that are

suspected of causing deactivation of the catalyst during the hydrotreating process (5).

There are several classes of sulfur compounds in propulsion fuels. It is the free sulfur that causes metal corrosion and the mercaptan compounds that cause deterioration of the synthetic rubber in fuel systems (11). Although there is an ASTM procedure for the determination of mercaptans in fuel, elemental sulfur and hydrogen sulfide may interfere with the procedure, resulting in inaccurate data (12).

The above examples emphasize the importance of knowing which nitrogen and sulfur compound classes are present in jet propulsion fuels rather than relying on total levels which are not predictive of fuel performance. The purpose of this report is to demonstrate the ability of several capillary GC detectors to detect individual nitrogen and sulfur compounds in jet propulsion fuels.

SECTION II

EXPERIMENTAL

1. Overview

The abilities of the following detectors to detect nitrogen or sulfur compounds in jet propulsion fuels were investigated and compared to a flame ionization detector (FID):

FTID - Flame Thermionic Detector

TSD - Thermionic Specific Detector

TID-2-H₂/Air - Thermionic Detector

CLD - Chemiluminescent Detector

TID-1-N₂ - Thermionic Detector

FPD - Flame Photometric Detector

A Varian 3700 gas chromatograph equipped with a split/splitless injector and a fritted glass injector liner was used. The column used was a DB-1, wide-bore, thick-film column.

Since argon was required for the operation of the CLD, argon was used as the carrier gas throughout the experiment. When comparing argon to helium, argon provided increased responses for all detectors investigated.

Table 1 lists common operating conditions and individual detector operating conditions.

2. Sample Preparation

Chromatographic comparisons between the detectors of interest and the FID were carried out on standard solutions containing known quantities of nitrogen

TABLE 1

OPERATING CONDITIONS

COMMON CHROMATOGRAPHIC CONDITIONS

GC VARIAN 3700

COLUMN 60M DB-1, WCOT, 0.32 ID,
1.0uM Film Thickness, 80,000 Effective
Theoretical Plates

INJECTOR Glass Frit, Split (1:2), 280 Deg. C

COLUMN FLOW 8.8ml/min Ar @ 46 PSIG
and 40 Deg. C

TEMPERATURE PROGRAMMING 40 to 240 Deg. C @ 5 Deg. C/min

SAMPLE 2 to 5 ul Manual Injection of Neat
Jet Propulsion Fuel

INDIVIDUAL DETECTOR CONDITIONS

	GAS 1 ml/min	GAS 2 ml/min	M/U ml/min	amps	volts	Deg. C
FTID	AIR 150	H2 20	N2 20	2.76	-45	320
TSD	AIR 175	H2 3.28	N2 20	2.80	-4	320
TID-2- H2	AIR 50	H2 3.04	N2 20	3.20	-5	320
CLD	OXYGEN (PYR) 260	OXYGEN (OZO) 120	Ar 100	N/A	N/A	1050
FPD	AIR 170	H2 140	N2 20	N/A	N/A	320
TID-1- N2	N2 40	N2 60	N/A	2.50	-45	320

(Solutions 1, 2, 3) or sulfur (Solutions 4, 5) compounds prepared in a shale-derived jet fuel previously determined to have no nitrogen or sulfur containing species. Each solution contained an internal standard. Tables 2,3,4,5 and 6 list the compounds used in each solution, their concentrations, and their relative response factors (RRF).

Solutions of n-undecane vs 2-methylindole in toluene for the nitrogen detectors and n-undecane vs phenylsulfide in toluene for the sulfur detectors were used for selectivity determinations.

The standard solutions of nitrogen or sulfur compounds in a shale-derived jet propulsion fuel were used to determine the chromatographic detection limits. The determinations were made using 2-methylindole for the nitrogen detectors and 2,5-dimethylthiophene for the sulfur detectors.

All solutions were gravimetrically prepared.

TABLE 2

SOLUTION 1

FTID CHROMATOGRAPHIC DATA

<u>COMPOUND</u>	<u>ppm-N</u>	<u>FTID RRF</u>
PYRROLIDINE	112.96	0.8552
PIPERIDINE	91.94	1.0173
4-METHYL PYRIDINE	52.09	0.9643
2-METHYL PYRIDINE	48.14	0.7076
2,5-DIMETHYL PYRROLE	53.68	•
2,2,6,6-TETRA METHYLPIPERIDINE	59.45	0.9260
3,4-DIMETHYL PYRIDINE	44.40	0.9210
2,4-DIMETHYL-3- ETHYLPYRROLE	62.49	1.3166
1-METHYL INDOLE	37.82	0.9795
2-METHYL INDOLE	39.78	0.9402

•INTERNAL STANDARD

TABLE 3

SOLUTION 2

TSD and TID-2-H2/AIR CHROMATOGRAPHIC DATA

COMPOUND	ppm-N	TSD		TID-2-H2-AIR	
		RRF (mean)	SD (3)	RRF (mean)	SD (3)
PYRROLIDINE	11.42	1.0306	0.01	1.2777	0.14
PIPERIDINE	9.26	0.7299	0.02	0.7138	0.37
4-METHYL- PYRIDINE	5.27	1.7251	0.03	0.8560	0.02
2-METHYL- PYRIDINE	4.87	0.7348	0.01	0.6492	0.01
2,5-DIMETHYL- PYRROLE	5.43	•	•	•	•
2,2,6,6-TETRA- METHYLPIPERIDNE	6.01	0.7958	0.05	0.7953	0.03
3,4-DIMETHYL- PYRIDINE	4.49	0.6216	0.01	0.7940	0.02
2,4-DIMETHYL- 3-ETHYLPYRROLE	6.32	0.7175	0.03	1.4214	0.04
1-METHYL- INDOLE	3.82	0.5636	0.01	0.9349	0.41
2-METHYL- INDOLE	4.02	1.1270	0.06	0.8766	0.04

•INTERNAL STANDARD

TABLE 4
SOLUTION 3
CLD CHROMATOGRAPHIC DATA

COMPOUND	ppm-N	CLD	
		RRF (mean)	SD (3)
1-METHYLPYRROLIDINE	9.88	1.0480	0.03
PIPERIDINE	8.36	1.2929	0.00
2-METHYLPYRROLIDINE	4.63	1.0929	0.02
3-METHYLPYRROLIDINE	6.64	1.7969	0.14
4-METHYLPYRROLIDINE	11.50	1.0258	0.14
2,5-DIMETHYL- PYRROLE	8.96	•	•
3,5-DIMETHYL- PYRROLIDINE	9.54	1.0357	0.03
2,3,6-TRIMETHYL- PYRROLIDINE	6.27	1.0664	0.05
1-METHYLINDOLE	4.22	1.0697	0.04
5-METHYLINDOLE	4.57	1.0050	0.02

•INTERNAL STANDARD

TABLE 5

SOLUTION 4

FPD CHROMATOGRAPHIC DATA

COMPOUND	ppm-S	FPD	
		RRF (mean)	SD (3)
THIOPHENE	28.58	1.3250	0.04
2-METHYL- THIOPHENE	25.49	1.4568	0.10
2,5-DIMETHYL- THIOPHENE	27.22	1.3296	0.04
ETHYL- SULFIDE	24.80	0.9259	0.04
THIOPHENOL	21.18	0.8420	0.08
BUTYL- SULFIDE	28.66	•	•
PHENETHYL- MERCAPTAN	25.40	1.5136	0.24
THIANAPHTHENE	25.18	0.8373	0.01
sec-BUTYL- DISULFIDE	14.12	0.8901	0.12
PHENYL- SULFIDE	22.43	0.6643	0.01

•INTERNAL STANDARD

TABLE 6

SOLUTION 5

TID-1-N2 CHROMATOGRAPHIC DATA

COMPOUND	PPM-S	TID-1-N2 RRF
ETHANE- THIOL	22.51	2.3909
2-PROPANE- THIOL	25.37	2.0517
THIOPHENE	24.17	+ ND
1-BUTANE- THIOL	23.96	3.5127
2,5-DIMETHYL- THIOPHENE	24.55	+ ND
ETHYL- DISULFIDE	24.82	0.8880
THIOPHENOL	24.85	0.2236
BUTYL- SULFIDE	25.89	+ ND
PHENETHYL- MERCAPTAN	25.24	*
sec-BUTYL- DISULFIDE	23.95	2.6559
3,4-DIMERCAPTO- TOLUENE	23.32	1.9981
PHENYL- SULFIDE	24.48	+ ND

+ ND - COMPOUND NOT DETECTED BY TID-1-N

*INTERNAL STANDARD

SECTION III

DETECTORS

1. Flame Thermionic Detector (FTID)

The FTID is manufactured by Detector Engineering Technology, Inc. It was designed as a nitrogen and electronegative specific detector. The FTID tower (Fig.1) is divided into two portions. The lower portion of the tower contains the H₂/Air flame and the flame ion suppress electrode. The upper portion of the tower is a self-contained TID transducer that houses the TID source. The source is comprised of a surface layer containing a high concentration of Cs in a ceramic matrix and a sub-layer of Ni-ceramic.

The flame is used solely for sample decomposition. Ions produced in the flame are suppressed by applying an ion suppress voltage. The neutral products travel up the tower where the electronegative constituents are selectively reionized by the electrically heated thermionic source (13).

Figure 3 shows comparative chromatograms of solution 1 using the FTID and FID. The peaks in the upper chromatogram are in the 50 ng-N range. The FTID chromatogram exhibits considerable sample matrix interference.

2. Thermionic Specific Detector (TSD)

The TSD is manufactured by Varian Associates, Inc. The detector was designed as a nitrogen and phosphorus specific detector. The tower (Fig. 2) contains an electrically heated bead made of a ceramic alkali material surrounded by a fuel-poor H₂ plasma. This low temperature source suppresses the normal flame ionization

**SOURCE: SURFACE LAYER CONTAINING
A HIGH CONCENTRATION OF C_2 IN
A CERAMIC MATRIX AND A SUB-
LAYER OF Ni-CERAMIC**

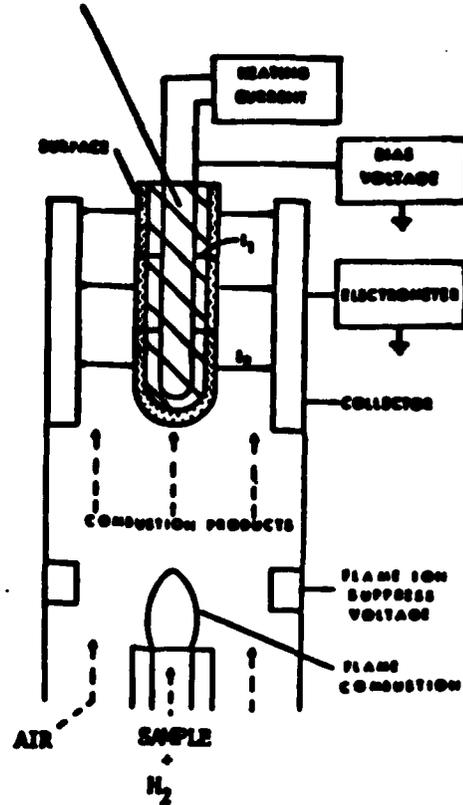


Figure 1. FTID Tower

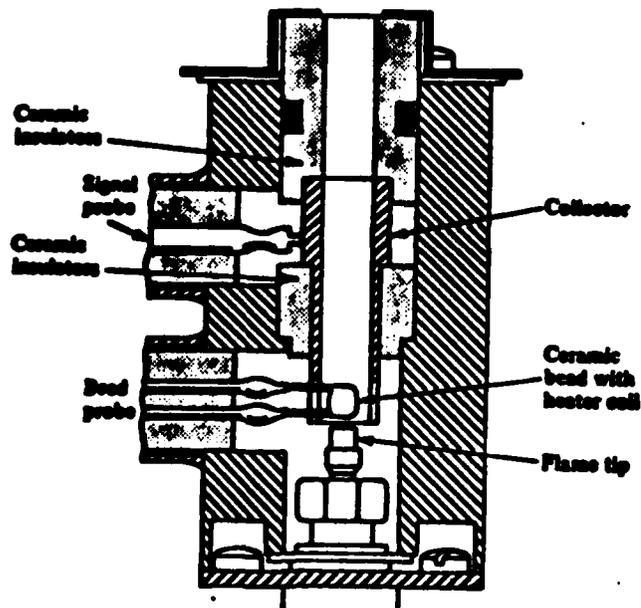
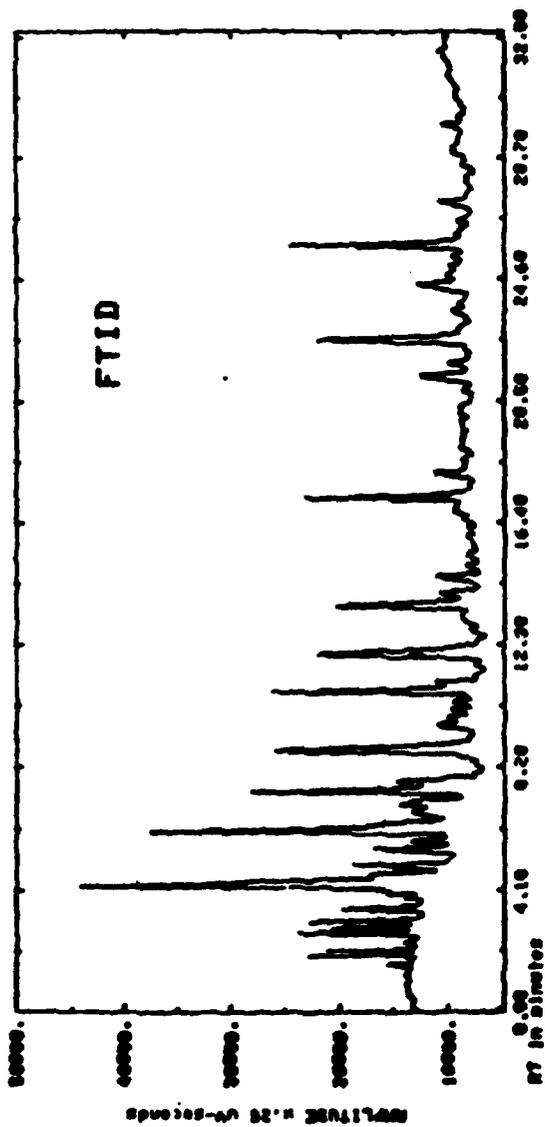
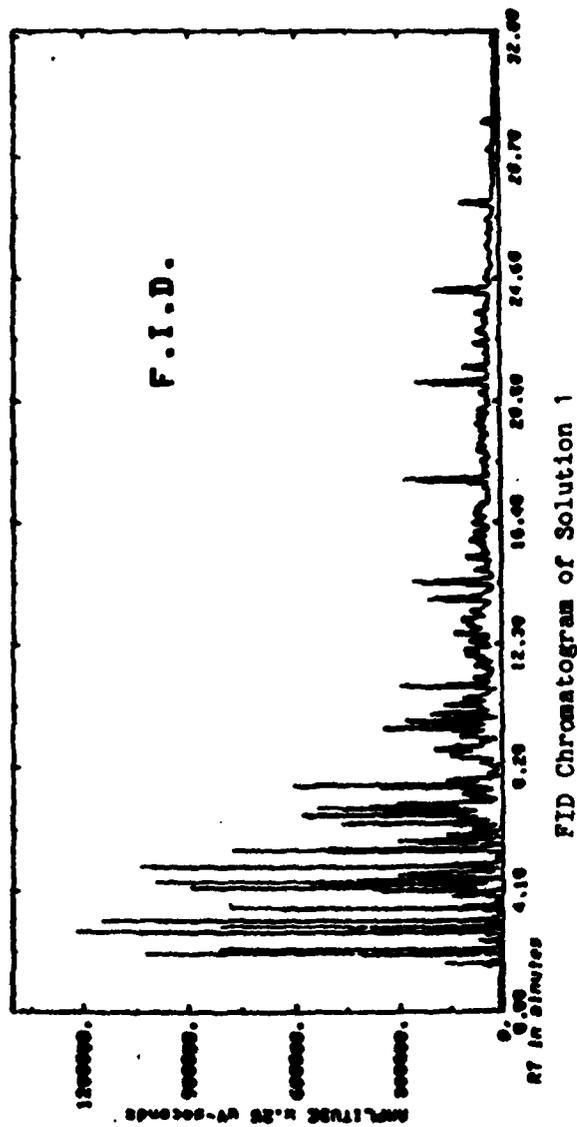


Figure 2. TSD Tower



FTID Chromatogram of Solution 1



FID Chromatogram of Solution 1

Figure 3. FTID vs FID Comparative Chromatograms of Solution 1

response of compounds not containing nitrogen or phosphorus (14). The fuel-poor plasma provides an environment in which nitrogen and phosphorus compounds decompose to form ions. The ions are then measured with a standard electrometer.

Figure 4 shows comparative chromatograms of solution 2 using an FID and TSD. The peaks in the upper chromatogram are in the 4 to 5 ng-N range. There is very little matrix interference in the TSD chromatogram. If the FID and TSD chromatograms were superimposed and drawn to the same scale, the nitrogen peaks in the TSD chromatogram would be below an acceptable signal level.

3. Thermionic Detector (TID-2-H2/AIR)

The TID-2-H2/Air is manufactured by Detector Engineering Technology, Inc. It was designed as a nitrogen and phosphorus specific detector. The tower (Fig. 5) houses a thermionic source comprised of multiple layers of Cs and Sr in a ceramic matrix with a sub-layer of Ni-ceramic. The source is surrounded by a dilute H2/Air, chemically reactive gas boundary layer. Sample compounds impact the source and boundary layer and are decomposed. Nitrogen and phosphorus compounds then form highly electronegative decomposition products which are ionized by the extraction of electrons from the thermionic source. The resultant ion current provides the detection signal (13).

Figure 6 shows comparative chromatograms of solution 2 using an FID and TID-2-H2/Air. The peaks in the upper chromatogram are in the 4 to 5 ng-N range. The TID-2-H2/Air chromatogram shows very little matrix interference. If the FID and TID-2-H2/Air chromatograms were superimposed and drawn to the same scale, the peaks in the TID-2-H2/Air chromatogram would be below an acceptable signal level.

Figure 7 shows comparative chromatograms from the TID-2-H2/Air and a GC-MS. The upper chromatogram is a neat injection of a shale-derived Jet A propulsion fuel using

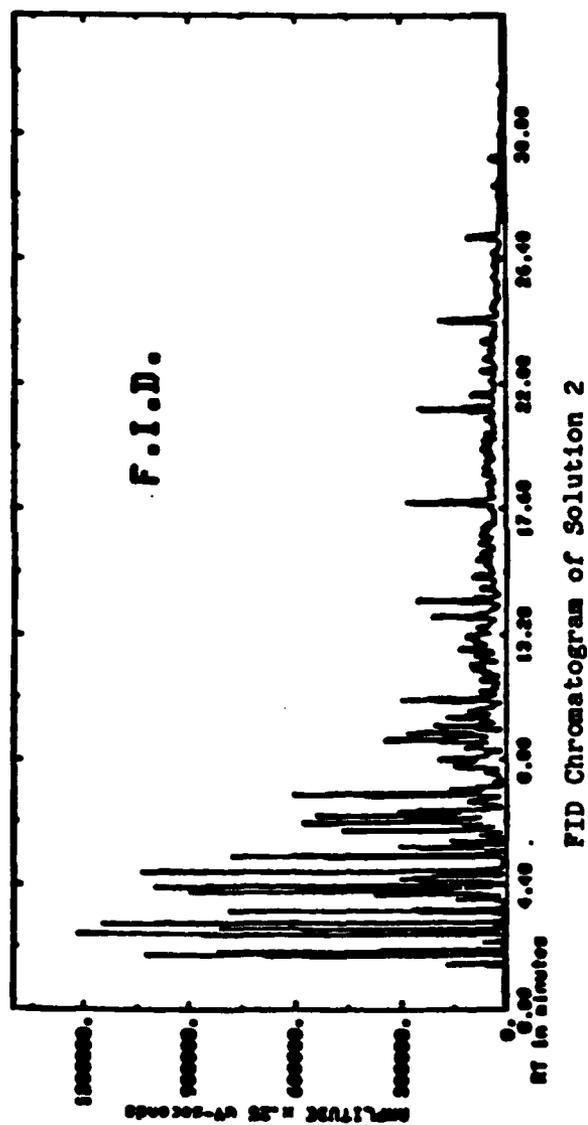
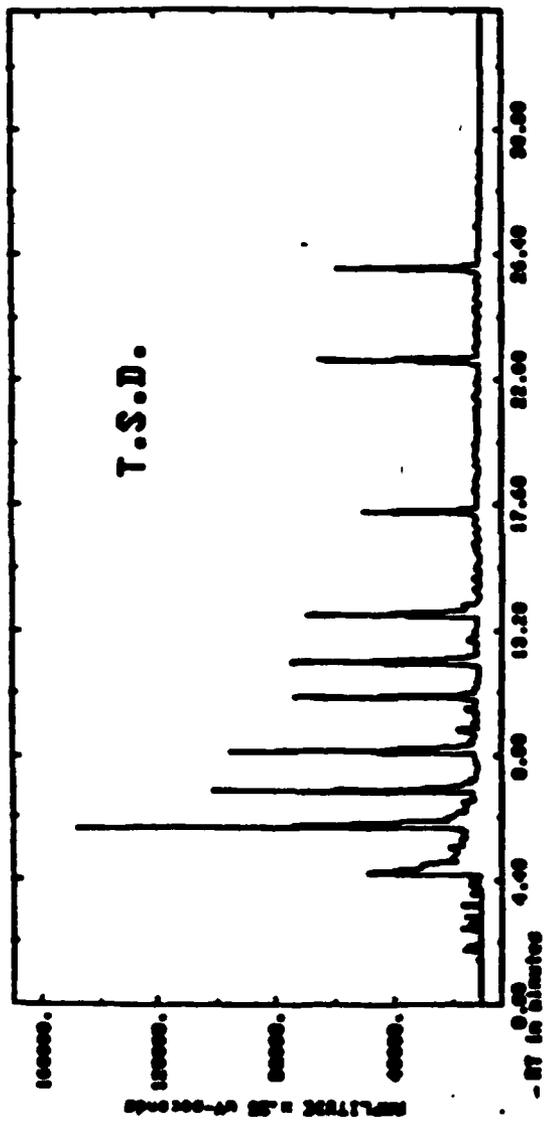


Figure 4. TSD vs FID Comparative Chromatograms of Solution 2

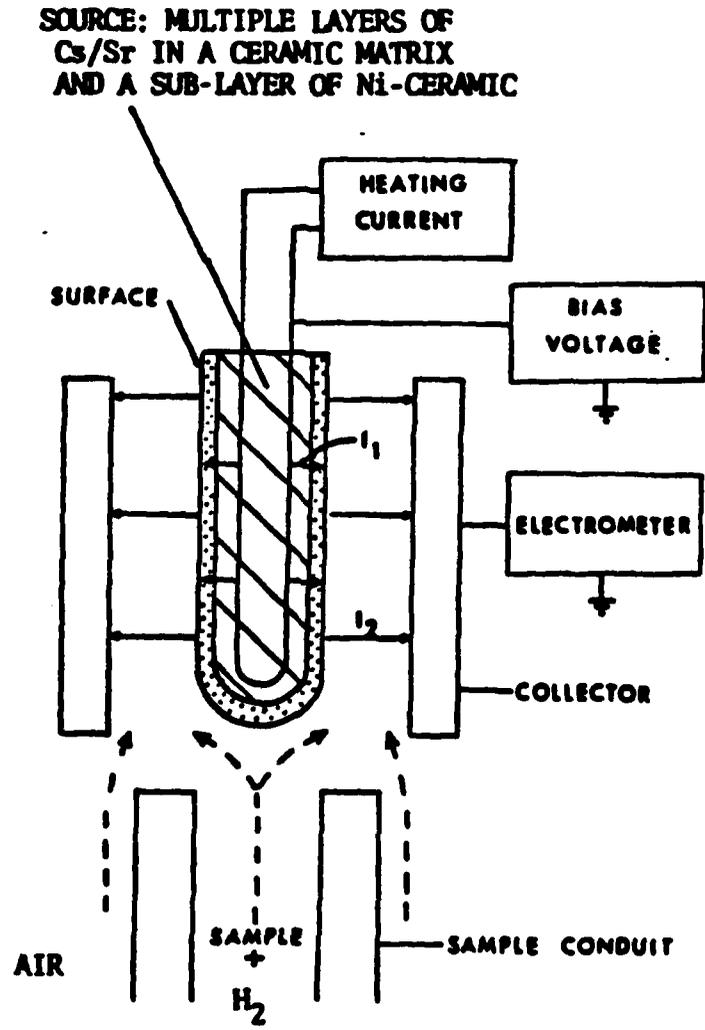
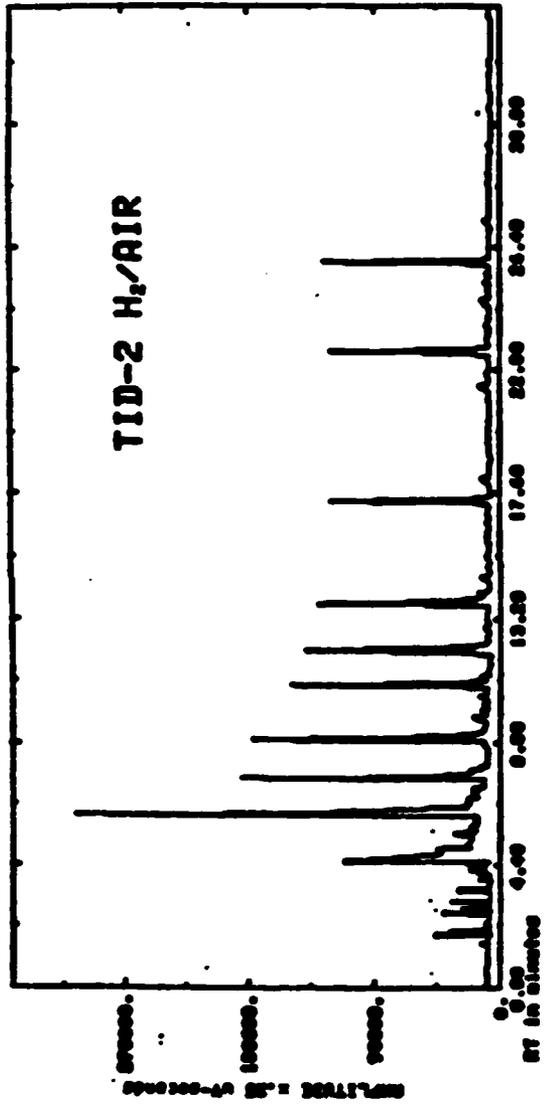
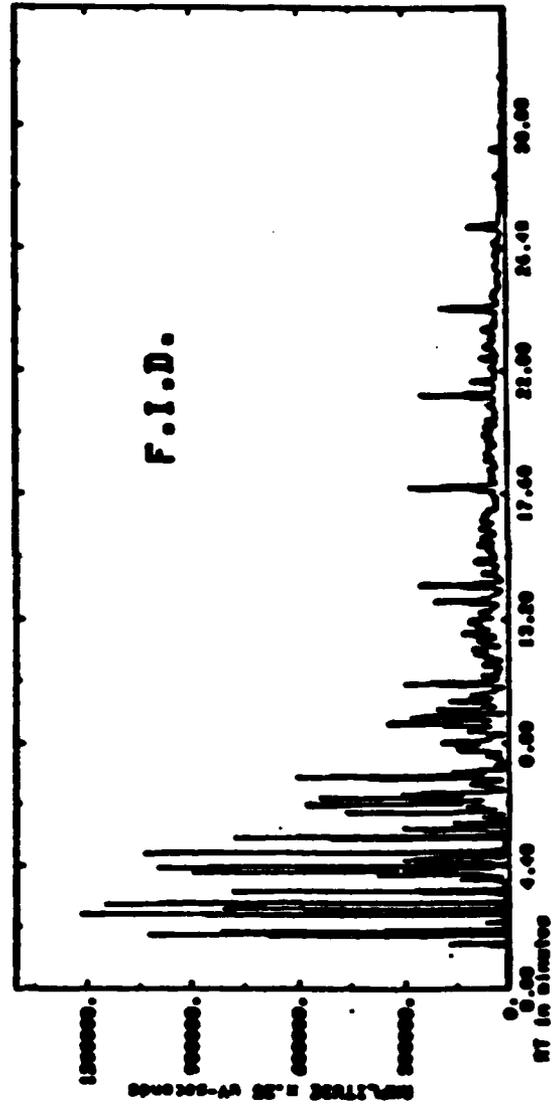


Figure 5. TID-2-H₂/Air Tower



TID-2-H2/Air Chromatogram of Solution 2



FID Chromatogram of Solution 2

Figure 6. TID-2-H2/Air vs FID Comparative Chromatograms of Solution 2

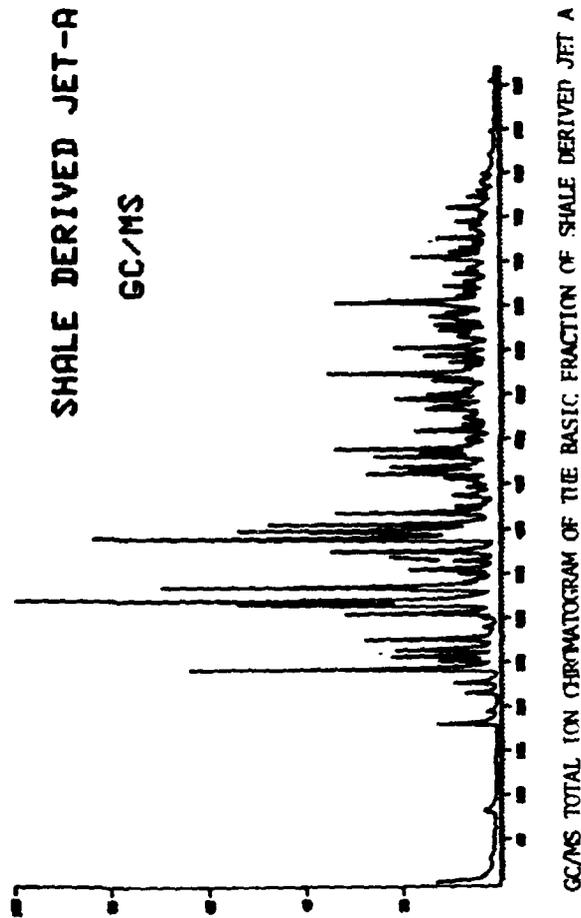
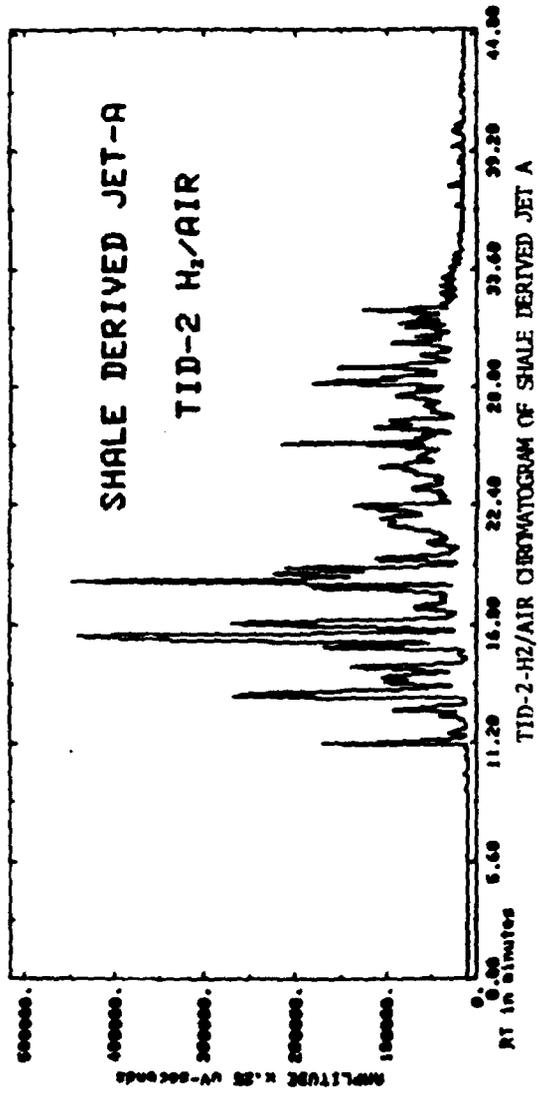


Figure 7. TID-2-H2/Air Chromatogram of Shale-Derived Jet A vs a GC-MS Total Ion Chromatogram of the Basic Fraction of Shale-Derived Jet A

a TID-2-H2/Air detector. The lower chromatogram is a GC-MS total ion chromatogram of the basic fraction from the same fuel. The MS tentatively identified nearly all components of the basic fraction as nitrogen-containing compounds (15). The chromatographic patterns of the two chromatograms are similar, indicating that an extraction process is not necessary when analyzing fuels for nitrogen content using a TID-2-H2/Air detector.

4. Chemiluminescent Detector (CLD)

The CLD is a free-standing Antek model 703-C nitrogen analyzer modified in the Aero Propulsion Laboratory at Wright Patterson AFB as a capillary GC detector (16). The fused silica capillary column enters the pyrolysis tube of the nitrogen analyzer from the GC oven through a heated transfer line and standard high temperature septum (Fig. 8). The high temperature of the pyrolysis tube (1000+ C), and a preponderance of oxygen permit oxidation of the entire sample, converting chemically bound nitrogen to nitric oxide. The nitric oxide enters the reaction chamber which is also supplied with ozone by an ozone generator. The nitric oxide reacts with the ozone to form a metastable nitrogen dioxide (NO_2^*). Upon relaxation to its stable state, the nitrogen dioxide emits a photon of light in the 700 to 900nm range, which is directly proportional to the amount of bound nitrogen in the eluting compound. This photon is then measured by a photo-multiplier tube (17).

Figure 9 shows comparative chromatograms of solution 3 using the CLD and FID. The peaks in the upper chromatogram are in the 20 to 40 ng-N range. In order to increase the sensitivity of the detector, the voltage applied to the photo-multiplier tube was increased to the maximum suggested by the manufacturer. Because the detector responds only to NO_2^* , the active baseline in the CLD chromatogram can be attributed to this increase in voltage rather than matrix interference. If the CLD

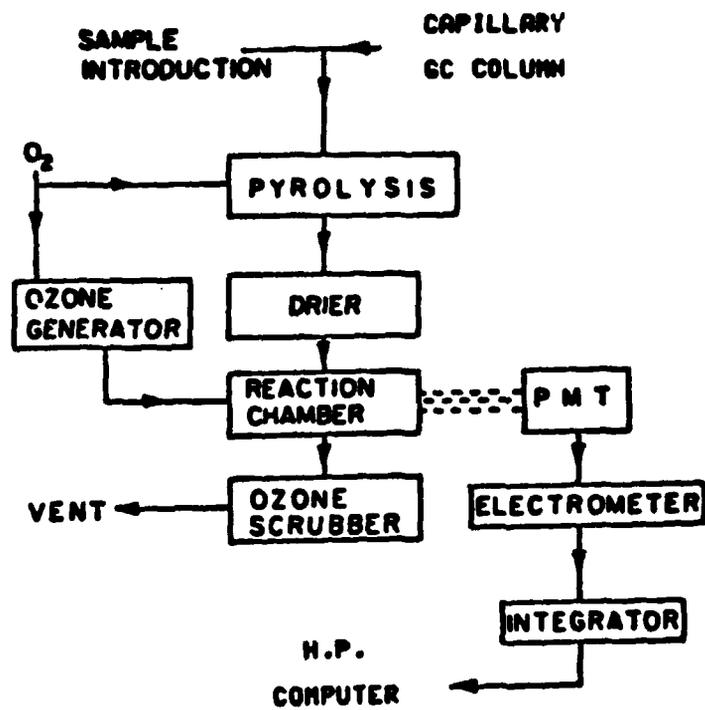


Figure 8. Block Diagram of CLD

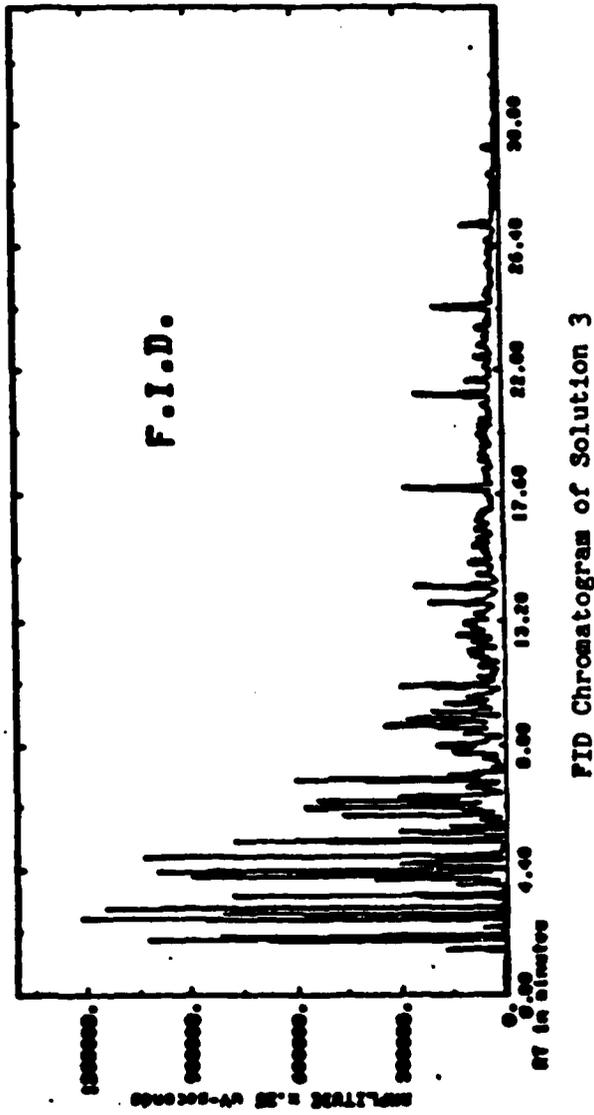
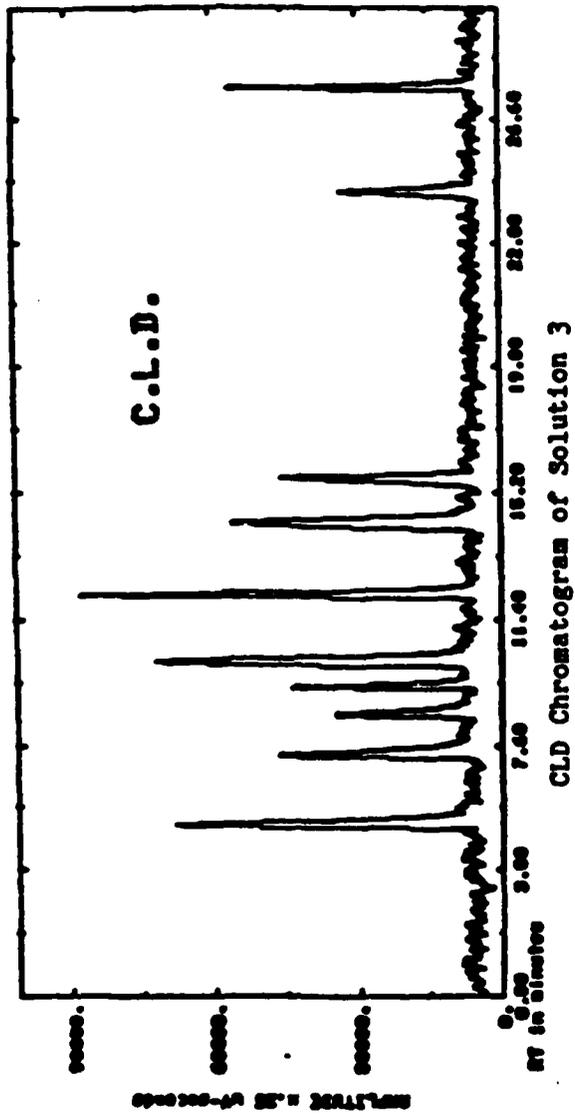


Figure 9. CLD vs FID Comparative Chromatograms of Solution 3

and FID chromatograms were superimposed and drawn to the same scale, the nitrogen peaks in the CLD chromatogram would be at the minimum acceptable signal level.

The preliminary interfacing of the Antek Nitrogen Analyzer to a high-resolution GC detector was performed as a feasibility study. It is obvious that additional modifications to the instrument are necessary. A smaller pyrolysis tube, reaction chamber, and slower flow rates will eliminate band-broadening and greatly increase the sensitivity of the detector (16).

5. Flame Photometric Detector (FPD)

The FPD is manufactured by Varian Associates, Inc. It was designed as a sulfur and phosphorus specific, packed column detector. The FPD was designed as a dual-flame detector (Fig. 10). The lower, hotter flame causes partial combustion and decomposition of the solute molecules into relatively simple species to prevent quenching of the sulfur emission by other organic compounds (14). Because this quenching phenomenon is not present when using capillary columns, the lower flame can be turned off. By operating the FPD in the single flame mode when using capillary GC columns, the detector's sensitivity is greatly increased.

The photo-multiplier tube in the FPD measures characteristic light emissions from excited S₂ molecules through a specific bandpass filter (324nm). Therefore, the detector's response to compounds containing a single atom of sulfur is proportional to the square of the compound concentration. This mode of detection and integration makes accurate quantitation very difficult. Therefore, we recommend that an FID be used in tandem with the FPD to overcome the problem of accurate quantitation.

Figure 11 shows comparative chromatograms of solution 4 using an FPD and FID. The peaks in the upper chromatogram are in the 20 to 30 ng-S range. The FPD chromatogram shows no matrix interference. Because the FID and FPD use different

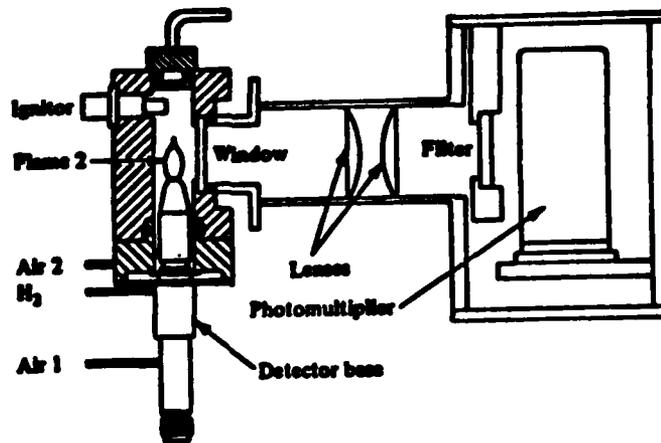


Figure 10. FPD Tower

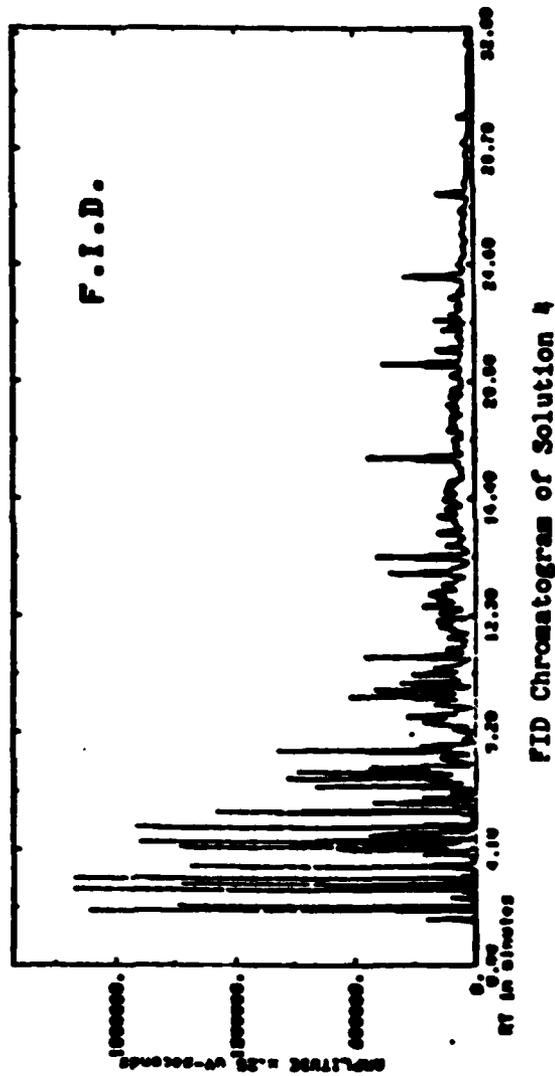
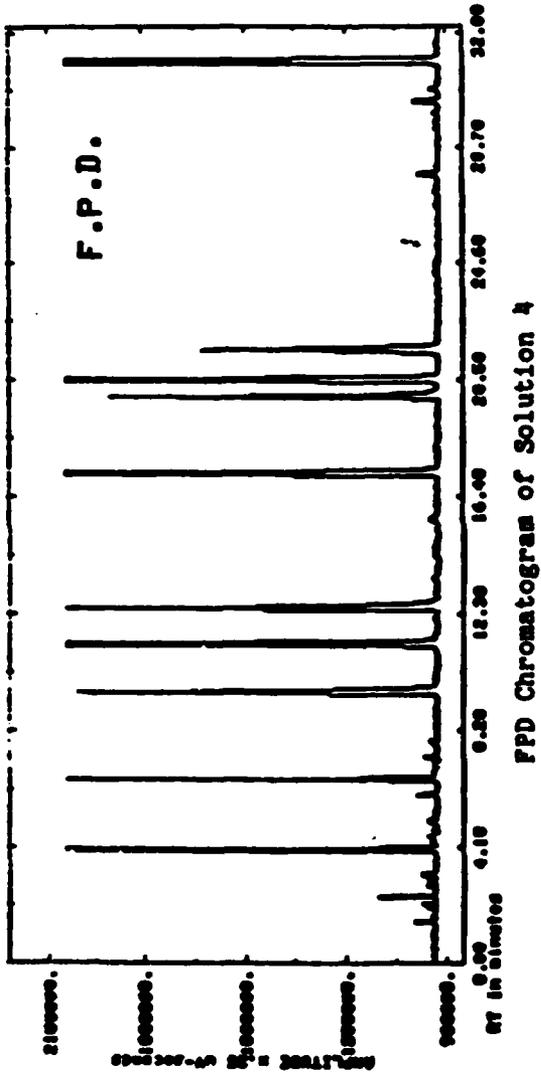


Figure 11. FPD vs FID Comparative Chromatograms of Solution 4

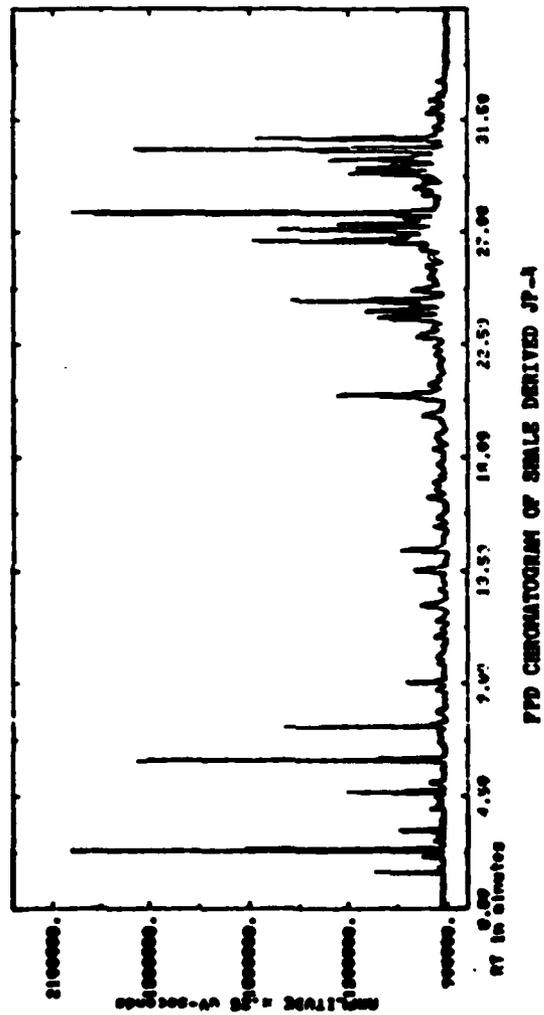


Figure 12. SHALE DERIVED JP-4
0.04 WT % SULFUR BY X-RAY FLUORESCENCE

electrometers and different modes of integration, comparing peak amplitudes between the two chromatograms is not valid.

Figure 12 is a chromatogram of a shale-derived JP-4 using an FPD. The fuel was determined to have 0.04 wt.% total sulfur by X-Ray fluorescence (ASTM D 2622). The number and size of peaks in the chromatogram for 0.04 wt.% total sulfur and the lack of matrix interference is an indication of the FPD's high sensitivity and selectivity to sulfur compounds.

6. Thermionic Detector (TID-1-N2)

The TID-1-N2 is manufactured by Detector Engineering Technology, Inc. It was designed as a nitro group and electronegative specific detector. The tower (Fig.13) houses a thermionic source comprised of a surface layer containing a high concentration of Cs in a ceramic matrix with a sub-layer of Ni-ceramic. The source is surrounded by a chemically inert gas boundary layer of nitrogen. The sample compounds are ionized by the extraction of electrons from the heated source to form negative ions. The negative ion current provides the detection signal (13).

Due to the low electronic work function of the thermionic source and the detector's specificity for electronegative compounds, the TID-1-N2's potential as a sulfur detector was investigated.

Figure 14 shows comparative chromatograms of solution 5 using a TID-1-N2 and an FPD. The FPD responds to all sulfur compounds added to the solution, whereas the TID-1-N2 responds mainly to the mercaptan compounds with some response to the disulfides. The feasibility of the TID-1-N2 being developed as a mercaptan specific detector seems promising. Since mercaptans are believed to be detrimental to fuel systems, further research and development of this detector as a mercaptan detector would seem to be necessary for fuels research in the USAF.

SOURCE: SURFACE LAYER CONTAINING
A HIGH CONCENTRATION OF Cs IN
A CERAMIC MATRIX AND A SUB-
LAYER OF Ni-CERAMIC

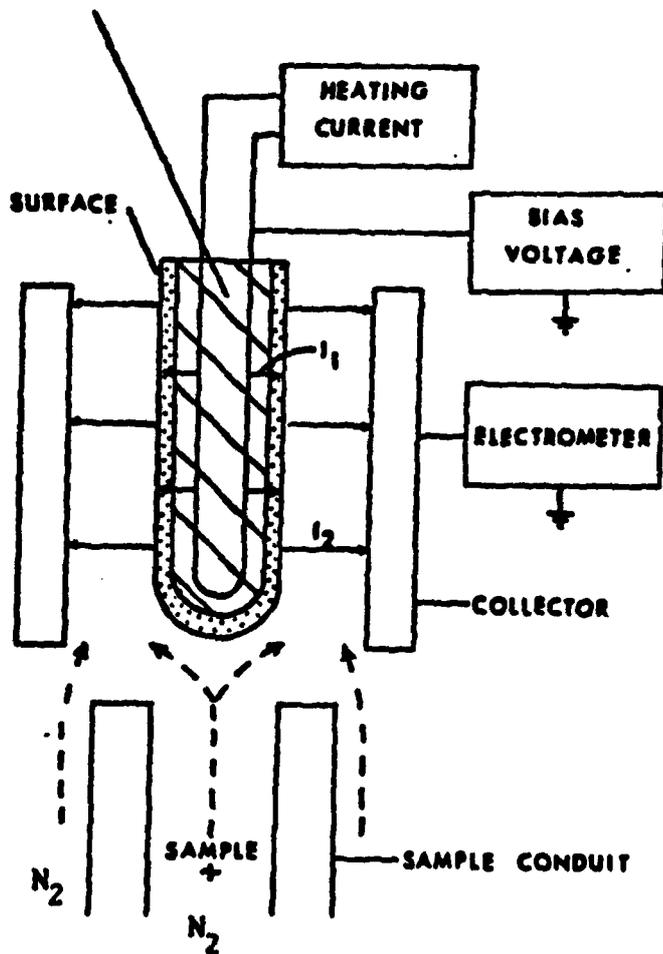


Figure 13. TID-1-N2 Tower

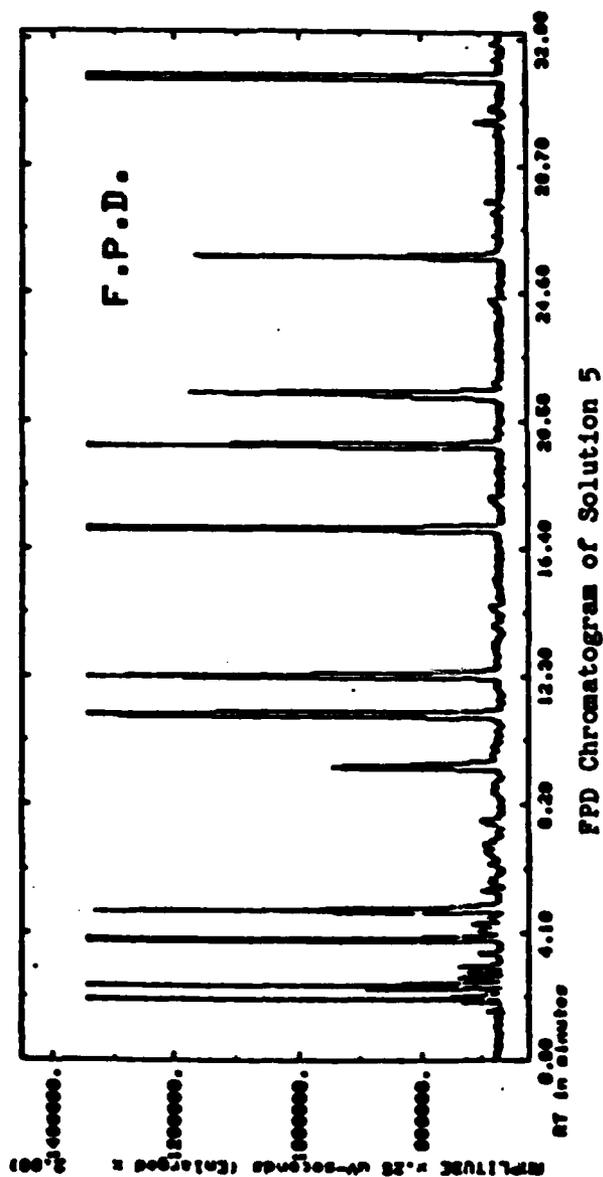
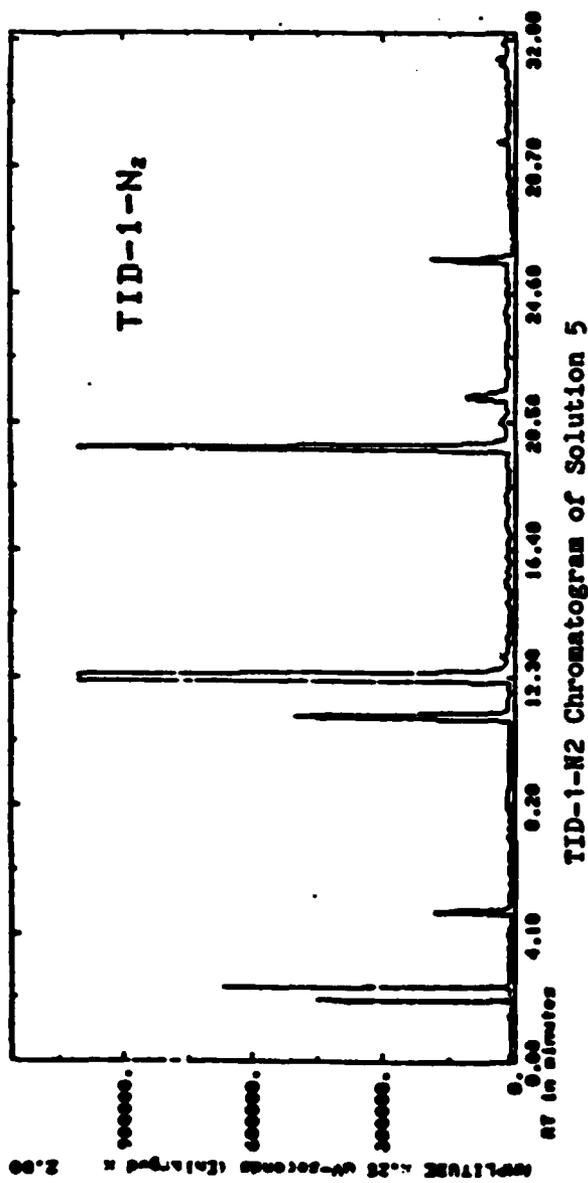


Figure 14. TID-1-N₂ vs FPD Comparative Chromatograms of Solution 5

SECTION IV

RESULTS

1. Relative Response Factors

Tables 2,3,4,5 and 6 list the relative response factors of individual compounds in each solution, and the detectors used for the analyses of these solutions. Standard deviations are listed for the detectors recommended for determination of nitrogen and sulfur in jet propulsion fuels.

Figure 15 graphically displays the relative response factor ranges for each detector investigated. Due to its specificity for mercaptans and disulfides over other sulfur compounds, the TID-1-N2 exhibits the widest range of relative response factors. The large physical separation between the point of sample decomposition and the detection of the signal permits the FTID to provide more uniform response factors irrespective of molecular structure of the sample compounds (13). Therefore, the FTID exhibits the narrowest range of relative response factors.

Figure 16 is a graphic display of relative response factor ranges for the nitrogen detectors. In the upper graph, all nitrogen compounds were considered in determining the relative response factor ranges. The lower graph displays relative response factor ranges using only the aromatic nitrogen compounds. When excluding the non-aromatic nitrogen compounds in determining relative response factor ranges, all detectors exhibit more uniform response factors with the CLD showing unity response. This is attributed to the difference in basicities between the aromatic and non-aromatic nitrogen compounds. It is known that non-aromatic nitrogen compounds are more basic than aromatic nitrogen compounds due to a resonance effect

RESPONSE FACTOR RANGES

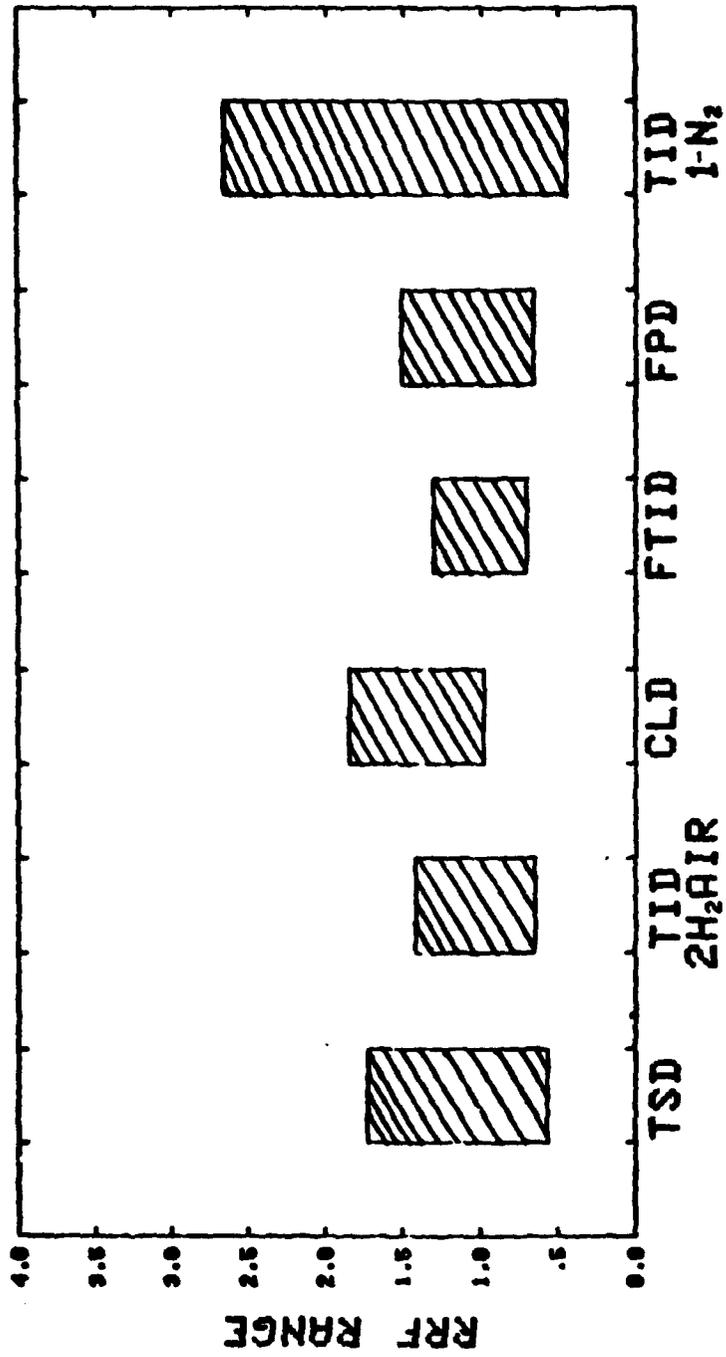
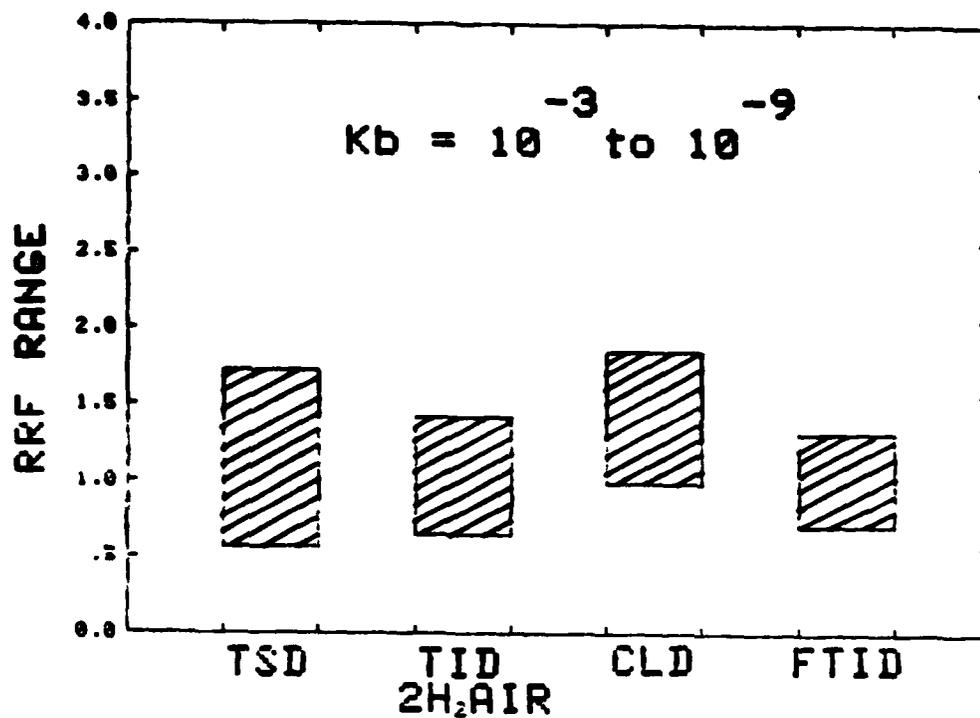
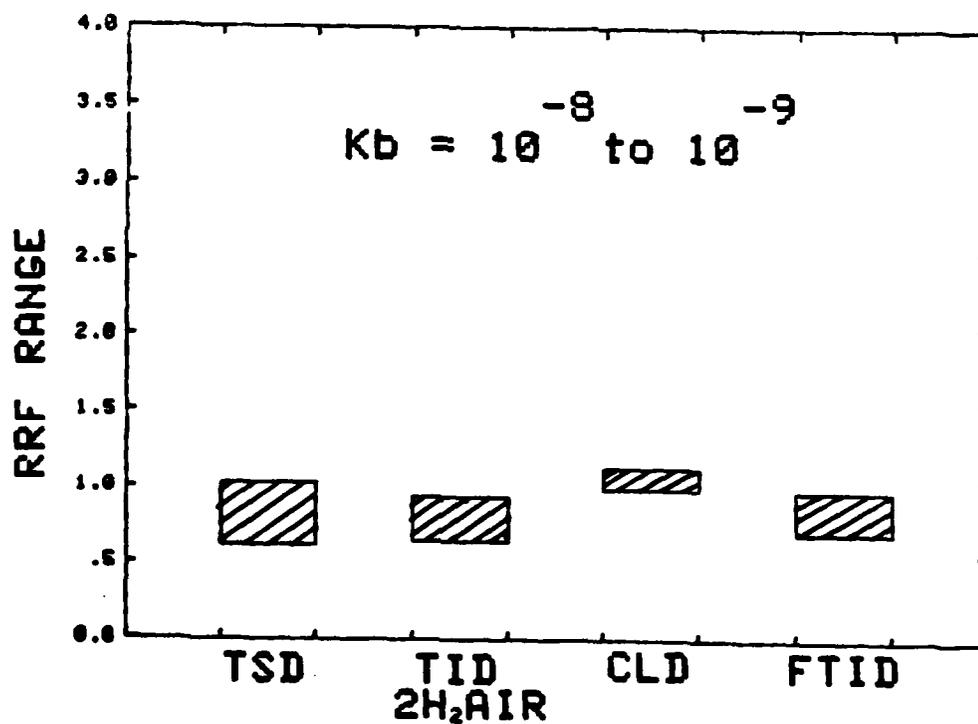


Figure 15. Graphic Display of Relative Response Factor Ranges for All Detectors



Relative Response Factor Ranges for Aromatic and Non-Aromatic Nitrogen Compounds



Relative Response Factor Ranges for Aromatic Nitrogen Compounds

Figure 16. Graphic Display of Relative Response Factor Ranges for Aromatic and Non-Aromatic Nitrogen Compounds vs Relative Response Factor Ranges for only Aromatic Nitrogen Compounds

(18). Non-aromatic nitrogen compounds can have basicity constants five to six orders of magnitude greater than their aromatic analogs (16). Comparison between the upper and lower graphs in figure 15 shows evidence that the non-aromatic compounds were being preferentially adsorbed onto the acidic sites of the column, injector and syringe. The use of an amine-deactivated column and silylation of the GC injector port and syringe will prevent sample compounds from being subjected to the many active sites usually present in these areas.

2. Selectivity

Selectivities of the detectors recommended for GC analysis of nitrogen and sulfur content in jet propulsion fuel are listed in table 7. Because the sample enters an atmosphere of total oxidative pyrolysis, the CLD is totally selective to nitrogen compounds in the sample. The selectivities of the TSD, TID-2-H₂/Air, and FPD are comparable to one another.

3. Chromatographic Detection Limit

Chromatographic detection limits for the detectors recommended for GC analysis of nitrogen and sulfur content in jet propulsion fuels are listed in table 8. Due to the complexity of jet propulsion fuels as a sample matrix, the concentration values listed are higher than those reported by the manufacturers of each detector.

The additional modifications recommended for the CLD (smaller pyrolysis tube and reaction chamber, and slower flow rates) will provide a much lower detection limit for the detector, making it comparable to, or lower than, the other detectors listed.

TABLE 7

SELECTIVITY DATA

CLD	TOTAL
	4
TID-2-H2/AIR	2 x 10 ⁴ gC/gN
	4
TSD	6 x 10 ⁴ gC/gN
	4
FPD	1 x 10 ⁴ gC/gS

TABLE 8

CHROMATOGRAPHIC DETECTION LIMIT

CLD	12 ng
TID-2-H2-AIR	1 ng
TSD	0.5 ng
FPD	1 ng

SECTION V

CONCLUSIONS

Of the six detectors investigated, four are recommended for GC analysis of nitrogen and sulfur compounds in jet propulsion fuels: the TSD, TID-2-H2/Air, CLD and FPD.

The FTID demonstrates uniform response factors as promised by the manufacturer. However, due to its lack of sensitivity and selectivity, the detector should not be used for trace analysis work for the determination of nitrogen in jet propulsion fuels.

The TSD is very sensitive and selective to nitrogen compounds in jet propulsion fuels. In order to obtain repeatable results on a day-to-day basis, bead current adjustments are necessary.

The TID-2-H2/Air is also very sensitive and selective to nitrogen compounds in a jet fuel matrix. Results are very repeatable, with little or no bead current adjustments.

The CLD is totally selective to bound nitrogen. A smaller pyrolysis tube and reaction chamber to accommodate compound loadings of capillary columns are necessary to increase the detector's sensitivity.

The FPD is very selective and sensitive to sulfur compounds in jet propulsion fuels. Because the detector's response is proportional to the square of the sulfur concentration in the sample, we recommend that an FID be used simultaneously with the FPD for quantitation purposes.

The TID-1-N2 is only selective to certain sulfur compound types in jet propulsion fuels. Modifications will be necessary to take advantage of its unique selectivity.

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