

WL-TR-93-2015

AD-A269 035



**ANALYSIS OF DEPOSIT PRECURSORS IN JET FUELS USING FOURIER
TRANSFORM INFRARED SPECTROSCOPY**

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January 1993

Interim Report for Period April 1991-August 1991

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REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
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1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE January 1993	3. REPORT TYPE AND DATES COVERED Interim April 1991 to August 1991		
4. TITLE AND SUBTITLE ANALYSIS OF DEPOSIT PRECURSORS IN JET FUELS USING FOURIER TRANSFORM INFRARED SPECTROSCOPY		5. FUNDING NUMBERS PE: 62203F PR: 3048 TA: 05 WU: AF C: F33615-87-C-2714		
6. AUTHOR(S) William Schulz and David Bryan Shehee				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Department of Chemistry Eastern Kentucky University Richmond, Kentucky 40475		8. PERFORMING ORGANIZATION REPORT NUMBER		
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Steven Anderson 513/255-3190 Aero Propulsion and Power Directorate (APPD) Wright Laboratory Wright-Patterson Air Force Base, OH 45433-6563		10. SPONSORING / MONITORING AGENCY REPORT NUMBER WL-TR-93-2015		
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for Public Release; Distribution is Unlimited.		12b. DISTRIBUTION CODE		
13. ABSTRACT (Maximum 200 words) Thermal oxidation products from jet fuels will be formed in the presence of fuel and oxygen at elevated temperatures. Development of fuels that will not form solid residues depends on the development of a method to analyze the rate of oxidation of fuels. Gravimetric determination of fuel residues was imprecise and time consuming. Gas Chromatography - Mass Spectrometry (GC-MS) of oxidation products yields a great deal of fundamental information but is too specific to be used as a rapid method for determining the rate of oxidation. Fourier Transform Infrared (FTIR) Spectrometry is non-specific and gives integrated signals for classes of oxidation products that will give rapid analytical results for rates of oxidation as well as the ability to study the effectiveness of chemical additives.				
14. SUBJECT TERMS Thermal Stability Thermal Oxidation FTIR Oxidation Products			15. NUMBER OF PAGES 54	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT Unlimited	

ABSTRACT

Thermal oxidation products from jet fuels will be formed in the presence of fuel and oxygen at elevated temperatures. Development of fuels that will not form solid residues depends on the development of a method to analyze the rate of oxidation of fuels. Gravimetric determination of fuel residues was imprecise and time consuming. Gas Chromatography - Mass Spectrometry (GC-MS) of oxidation products yields a great deal of fundamental information but is too specific to be used as a rapid method for determining the rate of oxidation. Fourier Transform Infrared (FTIR) Spectrometry is non-specific and gives integrated signals for classes of oxidation products that will give rapid analytical results for rates of oxidation as well as the ability to study the effectiveness of chemical additives.

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FOREWORD

This report was prepared as a part of the requirements for a masters degree in Chemistry from Eastern Kentucky University. The study described herein was performed under task 26 of the Scholarly Research Program, F33615-87-C-2714 which was funded by the Aero Propulsion and Power Directorate, Wright Laboratory, Wright-Patterson Air Force Base, Ohio 45433. Mr. Steve Anderson (WL/POSF) was the technical monitor for this program.

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SECTION 1.0

INTRODUCTION

The problem of fuel instability exists from the time it is refined until the time it is consumed. The concern for the instability of jet fuels is evident in a great body of scientific literature. A 1974 Russian article (1) lists 122 references. A 1986 review by Taylor and Frankenfield (2) contains 55 "representative, rather than all inclusive" references. The latest article (3), a 1991 review on fuel stability studies, lists 140 references. The increasing concern regarding fuel stability, particularly thermal stability, is a direct result of using fuel as a heat exchange fluid in modern aircraft. It is evident from the amount of literature written on the topic that the instability of jet fuels is a growing concern, yet, in a 1989 paper Reddy (4) states: "Although considerable effort has been devoted to understanding and solving fuel degradation problems, knowledge of the detailed chemistry is lacking."

The use of the word stability in describing fuel has many implications. For example, fuel stability refers to a fuel's general resistance to change, (5) but stability may also refer to a fuel's storage stability or its thermal stability. Storage stability refers to the ability of a fuel to be stored in ambient conditions for extended periods of time without experiencing appreciable deterioration. Thermal stability can be defined as "the ability of a fuel to withstand relatively high temperature stress for short periods of time, without appreciable deterioration" (6) (appreciable deterioration refers to oxidation products, such as color change, soluble and/or insoluble gum, particulate matter, surface deposits, coke and fouling materials). Of the two, "Thermal stability is the most important jet fuel property considering impact on maintenance cost." (7)

There are several definitions used to describe fuel gums and particulates depending on the preference of the individual doing the investigating. The following are

used by some research groups in the US Air Force, and are consequently used in this report:

Soluble Gums - Oxidation products soluble in fuel or hexane.

Insoluble Gums - Oxidation products insoluble in fuel or hexane, but soluble in acetone.

Particulates - Oxidation products insoluble in acetone.

Acetone was chosen as the "gum solvent" by the WL/POSF group because it is easily removed for subsequent weighing or other analytical procedures. Other recipes often used are mixtures of solvents such as methanol, toluene and acetone or methanol, methylene chloride and toluene or benzene.

Although color change is relatively unimportant in fuel quality, it is often used as a general indication of instability. The development of soluble or insoluble gum is what begins to inhibit gasoline, diesel or turbine engine performance, (8) and although soluble gum is not directly responsible for any particular engine difficulties, very high values can lead to clogging in filters and/or screens. Soluble gum can be used as an indication of the current and future behavior of the fuel during storage (9). Insoluble gum, because it must be filtered before passing to the combustion chamber, clogs screens and filters rapidly, which leads to malfunctions in injection systems and oil burner nozzles. When particulates form (followed by sediment formation) fuel filters get plugged. Particulates can also bind with corrosive products such as water, dirt and rust. Engine difficulties arise from the presence of coke and other fouling materials which form varnishes on heat exchangers and deposit solids in combustion nozzles. This results in reduced efficiency of the heat transfer surface areas in heat exchangers, which in turn leads to the malfunction of the fuel system (10). Difficulties which have been cited as problems due

to diesel injector coking include engine noise, excessive smoke, loss of power (due to reduced fuel spray), poor fuel economy, degraded emissions and poor handling (11).

In aircraft systems, synthetic seal and o-ring failure may occur in the fuel system as a result of attack by peroxides or hydroperoxide oxidation products (12). Aircraft failure has been attributed to this cause. Other problems include filter, heat exchanger and afterburner feed tube clogging.

The stability of a fuel depends on the hydrocarbon composition, the source of the crude oil, the boiling range, the type of refining and the conditions under which it was stored. Stability decreases with increasing order of paraffins, naphthenes, aromatics, olefins and diolefins (5). Trace impurities such as the following metals significantly influence fuel stability: copper, zinc or aluminum. Oxygen containing compounds as well as thiols, thiophenes, polysulfides, pyrroles, pyridines, indoles and isoquinolines will also cause fuel instability.

The conditions under which the fuel is stored play a major role in determining a particular fuel's stability. Things such as temperature, pressure, storage time, oxygen content, the type of storage vessel and the environment to which the fuel is exposed are some of these conditions. Poor stability results from extended storage times, high temperature and high oxygen content.

The problems associated with fuel instability are complex. Although there may be no single explanation, most agree that fuel instability is a result of oxidation and/or autoxidation reactions. Other chemical reactions may also be responsible for fuel instability. Polymerization reactions involving unsaturated hydrocarbons and several reactive organic compounds of sulfur, nitrogen and oxygen are among these reactions. These reactions may be catalyzed by trace amounts of dissolved metals (3). Although each fuel has its own degradation mechanism, the overall process of fuel instability is shown in Figure 1.

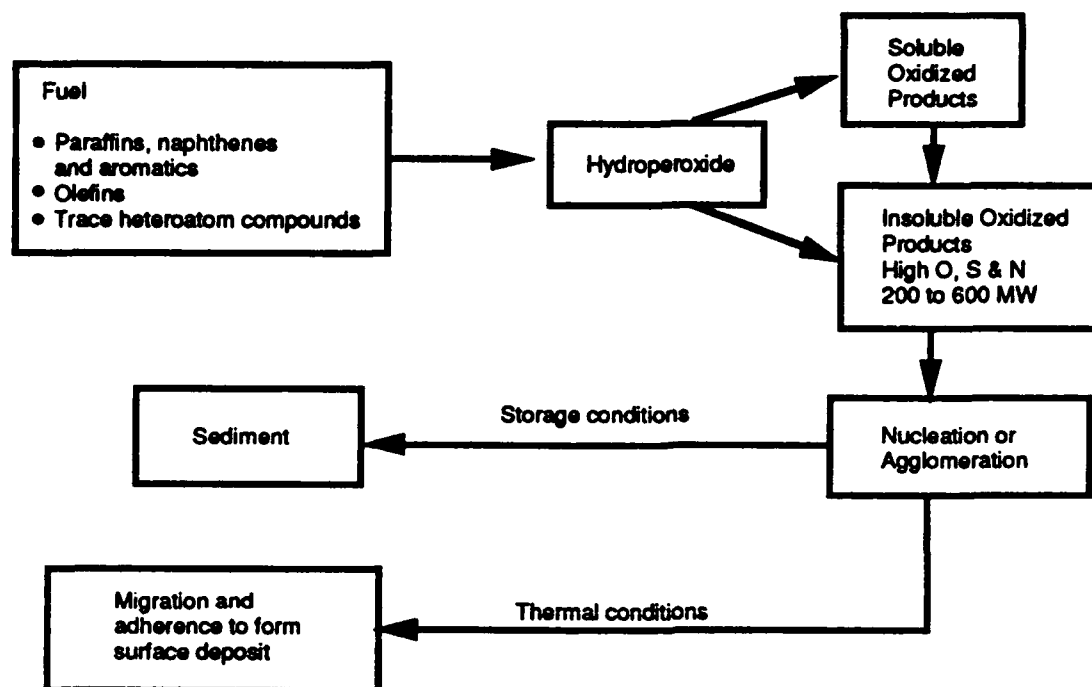


Figure 1. A Suggested Scheme for Fuel Instability.

There are three processes used to improve fuel stability--removing the precursors that cause deterioration, changing the chemical composition of the fuel and eliminating sediment precursor effects. Current methods to effect these processes include hydrotreating, caustic scrubbing, clay treatment or the use of additives. These treatments may also be combined for added efficiency.

Hydrotreating can be described as the interaction of a fuel with hydrogen gas. The reaction is performed at high temperatures in the presence of a catalyst. Hydrotreatment is expected to rid the fuel of unsaturation and lower the sulfur content. It is the most effective treatment for eliminating stability problems (13). The inherent problem with hydrotreatment is that while being the most effective, it also remains the most expensive.

Caustic scrubbing increases a fuel's stability by removal of compounds such as thiophenols. Though this method is less expensive than hydrotreating, it is also less effective as it does not always produce a stable product. Additionally, caustic scrubbing does not remove copper or pyrrolic nitrogen compounds which also produce instability (13).

Fuel stability may also be increased by clay treatment. Polar materials, generally heteroatomic and unsaturated, are readily removed by this technique. The basic problem with this method is the loss of product by extraction.

The chemistry of alkanes (12) and less stable species such as cycloalkanes and tetralins is fairly well defined (14). In the presence of oxygen, even the purest aliphatic compounds will oxidize to form insoluble gums at temperatures as low as 100°C. This implies that when subjected to temperatures ranging from 100°C to 400°C in the presence of air, even the most stable fuels can only reach thermal oxidative stability by the use of additives.

There are four different types of chemical additives: antioxidants, stabilizers, dispersants and chelating agents. Antioxidants, as their name implies, inhibit the

formation of oxidation products. Although dispersants do not prevent oxidation products from forming, they will suspend them in a fine form and allow them to pass through filters and screens. Chelating agents, also known as metal deactivators, chelate metal ions to prevent any catalysis by them. The common practice is to use two or more of these additives together, for additional effectiveness.

For several years, both industry and the military have been searching for a rapid, reproducible method to characterize and predict the stability of liquid fuels. Presently, there is no universally accepted method that accomplishes this. The goal of this research was to develop a method which would adhere to these demands, while remaining relatively inexpensive.

To date, the two methods for testing storage stability are long term and accelerated stability tests. The long term stability test is not practical to use because of the time involved. Accelerated stability tests attempt to speed up chemical reactions by exposure of fuels to elevated temperatures in the presence of air. Generally, these techniques are used as well as those which show appropriate color changes in the fuel.

Analysis of color changes are performed using the ASTM D1500 color test, whereas the analysis of sediment formation is carried out by volumetric or gravimetric analysis, colorimetry or filtering methods. Instrumental analysis can be performed using gas chromatography-mass spectrometry, infrared spectrometry, liquid chromatography, atomic absorption, inductively coupled plasma emission spectrometry, nuclear magnetic resonance, electron spin resonance spectrometry and emission microscopy. Again, there is no universally accepted analysis procedure, a problem that this research attempts to eliminate.

In the initial stages of this research, insoluble oxidation products were studied using the aforementioned techniques. Accelerated methods were used due to the development of a rapid, reproducible, inexpensive thermal stress apparatus (14). The test is very similar to the British flask test (15) for thermal oxidation, and seems to be suited

for both the study of thermal oxidation and for the development of methods to analyze thermal oxidation. Sediment formation was studied using filtering techniques coupled with the analysis of insoluble oxidation products using gas chromatography-mass spectrometry (GC-MS) and pyrolysis gas chromatography-mass spectrometry. The inherent problems with this method were centered around time consumption and specificity. Since the GC-MS method was so specific, a 12-component surrogate fuel was developed, which closely resembled a real JP-8 fuel. Even with the surrogate fuel, extraction of oxidation products and analysis by GC-MS yields dozens of peaks which had to be integrated for quantitation of the extent of oxidation and would not necessarily be representative of, or transferable to, any real fuels.

Because of the overwhelming amount of information from GC-MS analysis, attention was shifted to studying the precursors to insoluble oxidation products by a non-specific method. The idea was that the tendency of a fuel to form insoluble oxidation products could be studied by looking at the formation of precursor oxidation products. Fourier transform infrared (FTIR) analysis provides a means of determining the amount of such products formed from the integration of absorbances caused by O-H, C=O and C-O stretching. The integration gives a quantitative measure of compound group (alcohol, carbonyl), rather than specific compounds found by using GC-MS. FTIR spectroscopy is also amenable to automated programmed analysis of a reaction with accessories such as attenuated total reflectance (ATR) flow cells or in situ probes coupled to the spectrometer by fiber optics. The method can be further developed to give oxidation rates quickly and with high precision. Presently, the method has given promising results for quantitatively studying the extent of oxidation of different fuels under varying conditions, as well as analyzing the effectiveness of certain additives.

SECTION 2.0

EXPERIMENTAL

2.1 SPECIFICATIONS OF INSTRUMENTATION, EQUIPMENT, CHEMICALS, AND FUELS

The following represents the specifications of the instruments, the equipment, the apparatus and the chemicals, including the additives and fuels used for analysis. A schematic of the flask test is provided in Figure 2.

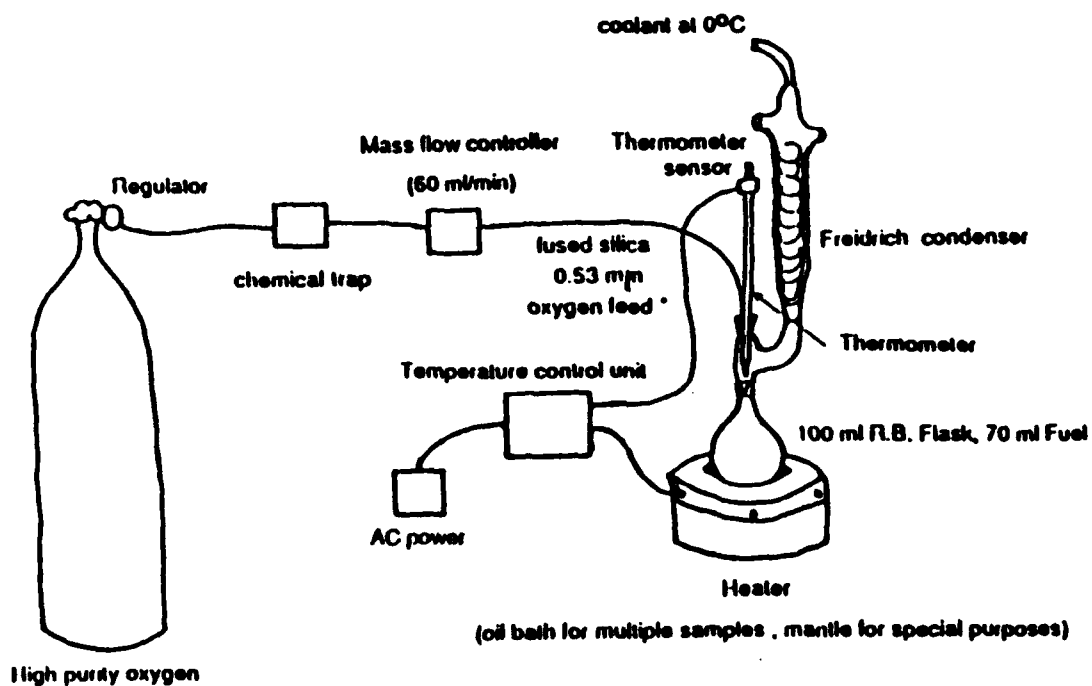
1) Instrumentation.

The infrared spectra were obtained using a Mattson Galaxy 4020 model FTIR with MS DOS based data station, using First and Advanced First software. All samples were in solution and were run through a 0.025 mm KBr Potassium Bromide flow cell.

2) Equipment

a) There were three different heating sources used. Initially, the fuel was stressed using a silicon hot oil bath and an electrical unit prepared by Dr. Schulz. Another heating source used was a glas-col 100 mL heating mantle with a maximum of 90 volts for a dry flask. The last type of heating source used was a 100 mL thermowell with a maximum of 140 watts.

b) All heating sources were used with an I²R Therm-o-watch^(TM), model L7-1100SA. The purpose of the Therm-o-watch^(TM) was to control the temperature to $\pm 1^{\circ}\text{C}$.



*Deactivated fused silica oxygen feed reaches bottom of fuel in R.B. flask

Figure 2. Schematic Diagram Modified Flask Test for Thermal Oxidation of Fuels.

c) The cooling source for the apparatus was a Hotpack refrigerated bath circulator that was filled with a mixture of water and ethylene glycol. The temperature was held at approximately 0-5°C.

d) Ten milliliter Mohr pipets were used to take samples.

e) All samples taken were collected in 15 mL culture tubes made of borosilicate glass.

f) A Mettler AC 100 was used for analytical samples, and a Fisher Scientific XL300 was used for heavier samples.

g) The type of tubing used for oxygen and nitrogen feed was 0.53 mm id deactivated fused silica quartz capillary column (normally used in a GC).

3) Glassware

a) All glassware used was Pyrex and was 19/22 or 24/40 in size.

b) The glassware used for the thermal stress apparatus was as follows: Friedrichs condensers, 24/40 to 19/22 Claissen adapters, drying tubes filled with dryerite and 100 mL round bottom flasks.

4) Chemicals

a) The solvents used were commercially obtained. Solvents used included acetone, methanol and methylene chloride. The alcohol and ketone used in the method development were both reagent grade and purchased, not prepared. The alcohol used was 1-dodecanol and the ketone was 2-octanone.

b) The fuels used in the analysis were all obtained from the United States Air Force, with the exception of the surrogate JP-8 (called JP-8S), which was prepared as previously described. Fuels used in analysis were: JP-8S, JP-8, JP-7, JP-TS, Jet A-1 (90-POSF-2747), Jet A-1 (91-POSF-2813) and Jet A-1 (91-POSF-2814).

c) The additives used in the analysis were all obtained from the United States Air Force. Additives used included JFA 5 (85-POSF-2284), which was composed of 3 high molecular weight tertiary aliphatic amines, a metal deactivator (N,N-disalicylidine-1,2-propanediamine), and a polyacrylamide (approximately 20,000 MW), which is used as an anti-coagulant. Two pure compounds were also investigated as antioxidants: The first was a hindered phenol type, "AO-29," also called "BHT" (butylated hydroxy toluene), or by IUPAC nomenclature di-tert-butyl-4-methyl-phenol. The second antioxidant was a tertiary aromatic amine type designated UOP #5 (90-POSF 2781), or by IUPAC nomenclature, N,N'-di-sec-butyl-p phenylenediamine.

2.2 PREPARATION OF SOLUTIONS FOR QUANTITATIVE ANALYSIS

The first step in developing a quantitative method for the FTIR was to prepare solutions of the surrogate JP-8 fuel spiked with varying concentrations of known oxidation products, one alcohol and one ketone. This was necessary in order to test the validity of the quantitative package on the FTIR and ultimately for use in preparing a method. The oxidation products chosen were 1-dodecanol and 2-octanone. These two chemicals were chosen because they are typical oxidation products, readily available, low in volatility.

Quantitative techniques were used in preparing solutions for their ultimate use as standards. 1-dodecanol and 2-octanone were weighed into a 10 mL volumetric flask on an analytical balance and the flask was filled to the calibration mark with JP-8S. The concentrations of the solutions used in the methods are given in tables 1 a, b, and c.

2.3 DEVELOPMENT OF A METHOD FOR QUANTITATIVE ANALYSIS

After the samples were prepared, they were run on the FTIR and saved on the computer as a method for quantitative analysis. Windows were then created which contained only those areas which gave absorbances uncharacteristic in the fuel (i.e., oxidation products). The windows were chosen by overlapping spectra of the surrogate JP-8 and sola, which had the largest concentration of alcohol and ketone. The samples were then run four times each in order to test the predictions of the quantitative package. Although the predictions of the instrument were fairly accurate, they were not as accurate as expected. Upon advice from Mattson, two separate methods were prepared, one that was specific for O-H and C-O stretching, which was named alcohol; and one that was specific for C=O stretching, which was named ketone. After the method was developed, each solution (for each of the four times it was run), was saved on the computer for predictions of concentrations. After each spectrum was run, the solution that gave the best prediction results was used in the method until the accuracy of the instrument was acceptable. The precision of the instrument was tested by putting sola spectra in all of the available spaces (a total of eight concentration predictions can be performed at a time) of the alcohol and ketone methods and letting the FTIR predict the concentration. The results were accurate; the FTIR had an average deviation of zero for the alcohol and ketone methods (it predicted the exact same concentration every time and gave the exact same sum square of errors). The spectra of the solutions chosen to represent the alcohol method can be seen overlaid on each other (Figure 3). The spectra of those solutions chosen for the ketone method are shown in Figure 4. Notice that all colors shown on the

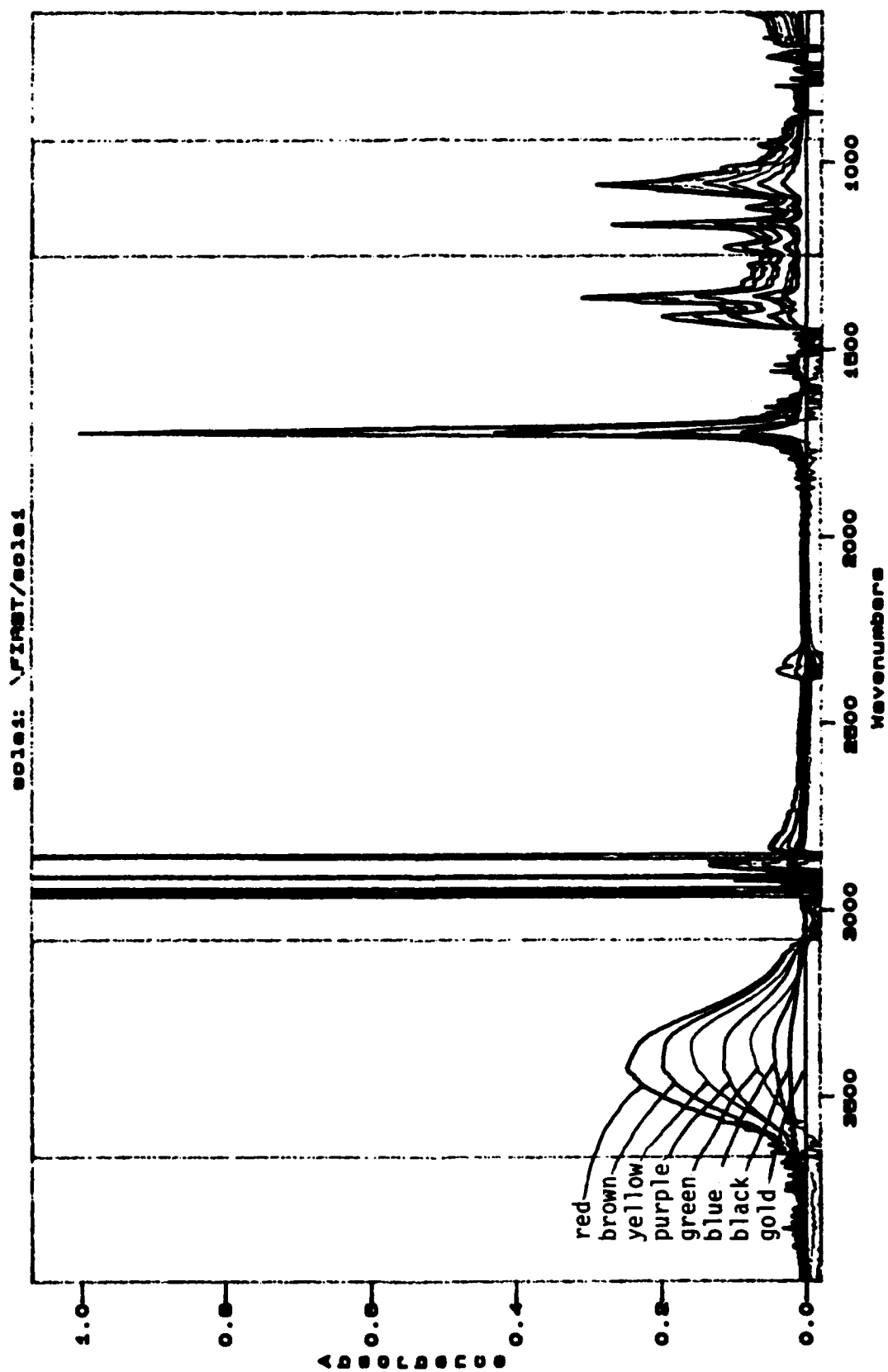


Figure 3. FTIR Spectrum of Surrogate JP-8 Spiked With 1-Dodecanol and 2-Octanone (Alcohol Method Samples)

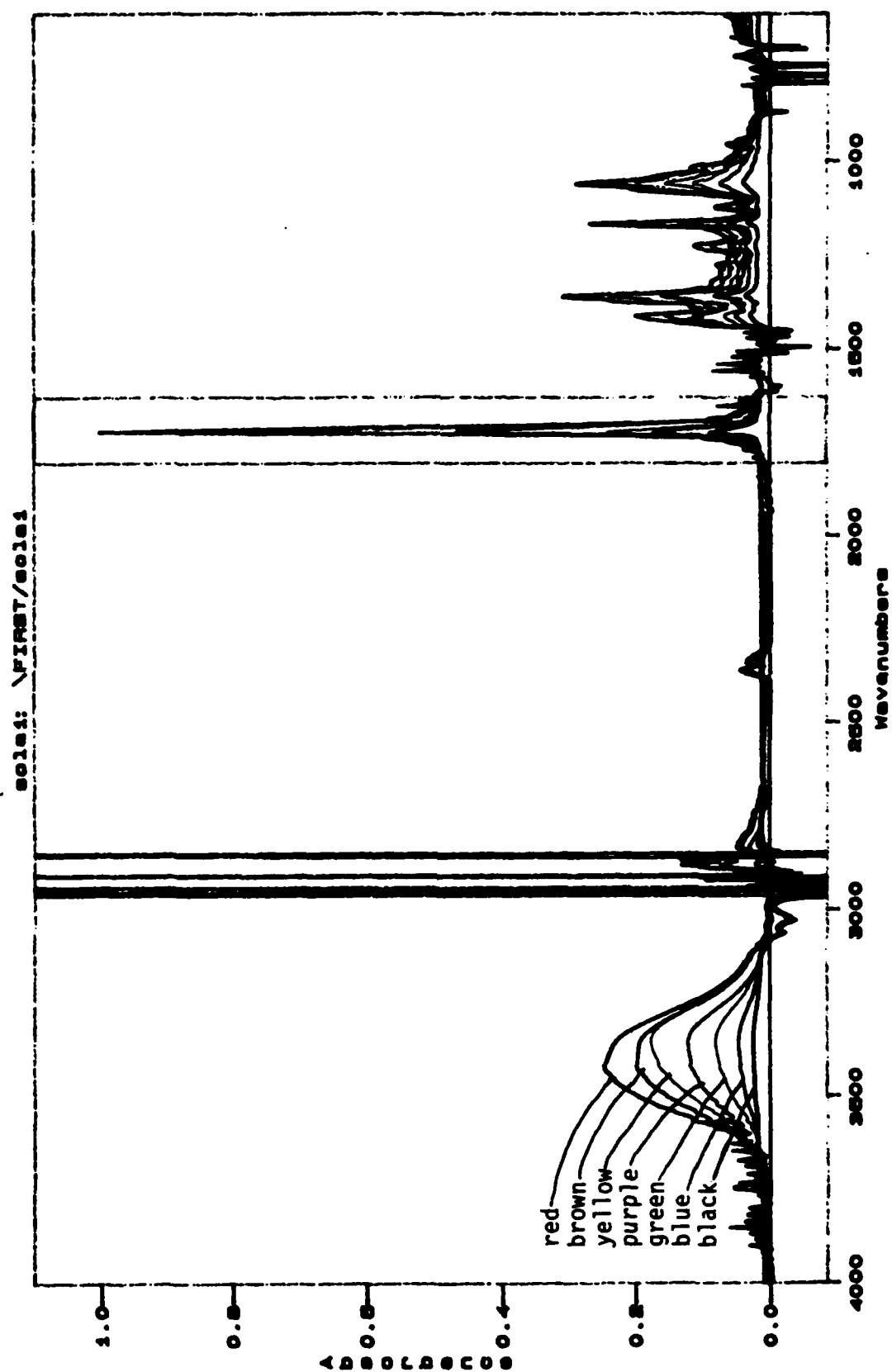


Figure 4. FTIR Spectrum of Surrogate JP-8 Spiked With 1-Dodecanol and 2-Octanone (Ketone Method Samples).

TABLE 1a

METHOD SOLUTIONS

		Transmission FTIR Analysis of Alcohol(1) and Ketone(2)		Spiked Surrogate JP-8			
		Actual Concentration					
		In Moles/Liter					
SAMPLE		ALCOHOL	KETONE	Predicted Concentration in Moles/Liter			
				ALCOHOL	SSE (3)	KETONE	SSE
SOLA 1		1.353	1.341	1.348	0.002	1.348	0.001
SOLA 2		1.353	1.341	1.369	0.012	1.117	0.029
SOLA 3		1.353	1.341	1.37	0.01	1.128	0.032
SOLA 4		1.353	1.341	1.391	0.01	1.145	0.035
SOLB 1		1.131	1.005	1.129	0.002	1.005	0.002
SOLB 2		1.131	1.005	1.219	0.011	0.883	0.012
SOLB 3		1.131	1.005	1.206	0.005	0.878	0.011
SOLB 4		1.131	1.005	1.222	0.01	0.88	0.012
SOLC 1		0.904	0.66	0.945	0.019	0.712	0.005
SOLC 2		0.904	0.66	0.992	0.054	0.664	0.001
SOLC 3		0.904	0.66	0.903	0.004	0.595	0.008
SOLC 4		0.904	0.66	1.037	0.023	0.627	0.004
(1) ALCOHOL as 1-dodecanol							
(2) KETONE as 2-octanone							
(3) Sum Square of Errors from Mattson, INC. Advanced First Software							
(4) Solutions in boldface type are those used in the method							

TABLE 1b
METHOD SOLUTIONS

		Transmission FTIR Analysis of Alcohol(1) and Ketone(2)				
		Spiked Surrogate JP-8				
		Actual Concentration				
		In Moles/Liter				
SAMPLE	ALCOHOL	KEONE	ALCOHOL	SSE (3)	KEONE	SSE
SOLD 1	0.675	0.655	0.685	0.001	0.597	0.007
SOLD 2	0.675	0.655	0.737	0.011	0.654	0.001
SOLD 3	0.675	0.655	0.754	0.008	0.603	0.008
SOLD 4	0.675	0.655	0.825	0.02	0.607	0.011
SOLE 1	0.452	0.334	0.453	0.003	0.299	0.019
SOLE 2	0.452	0.334	0.55	0.023	0.377	0.004
SOLE 3	0.452	0.334	0.558	0.006	0.329	0.001
SOLE 4	0.452	0.334	0.563	0.005	0.334	0.001
SOLF 1	0.319	0.248	0.249	0.001	0.212	0.004
SOLF 2	0.319	0.248	0.305	0	0.243	0.002
SOLF 3	0.319	0.248	0.383	0.008	0.233	0.002
SOLF 4	0.319	0.248	0.414	0.015	0.238	0.004
(1) ALCOHOL as 1-dodecanol						
(2) KETONE as 2-octanone						
(3) Sum Square of Errors from Mattison, INC. Advanced First Software						
(4) Solutions in boldface type are those used in the method						

TABLE 1c
METHOD SOLUTIONS

Transmission FTIR Analysis of Alcohol(1) and Ketone(2)						
Actual Concentration in Moles/Liter			Spiked Surrogate JP-8			
SAMPLE	Actual Concentration in Moles/Liter		Predicted Concentration in Moles/Liter			
	ALCOHOL	KETONE	ALCOHOL	SSE (3)	KETONE	SSE
SOLG 1	0.166	0.119	0.095	0.001	0.093	0.005
SOLG 2	0.166	0.119	0.171	0.001	0.115	0
SOLG 3	0.166	0.119	0.248	0.012	0.117	0.001
SOLG 4	0.166	0.119	0.222	0.006	0.118	0
JP-8S	0	0	0.001	0	0.003	0.004
JP-8S1	0	0	-0.002	0	0.005	0.004
JP-8S2	0	0	-0.001	0	0.005	0.005
JP-8S3	0	0	-0.007	0	0.002	0.004
(1) ALCOHOL as 1-dodecanol						
(2) KETONE as 2-octanone						
(3) Sum Square of Errors from Mattson, INC. Advanced First Software						
(4) Solutions in boldface type are those used in the method						

spectra range from the JP-8S that gave the best zero value for each method (shown by the color orange), to the sola that gave the most accurate determination for each method (shown by the color red). The "background" spectrum of each fuel was obtained and subtracted from the spectra of each corresponding stressed fuel.

2.4 TESTING THE METHOD

The next step in developing the method was to test it by stressing some of the surrogate JP-8 and looking at prediction results. Although there was no way of telling how much oxidation should occur at any given time, the sample was acceptable if it gave good qualitative results and if the Mattson SSE (sum square of errors) was relatively small. The SSE tells how much of the predicted results could not be accounted for by the quantitative method. More specifically, if there is something present in the designated windows which the computer does not recognize, it will be part of the SSE. A good example of this is hydrogen bonding, which is not accounted for in the method, but does occur in stressed fuel.

2.5 THERMAL STRESS APPARATUS

All fuels were stressed using the modified thermal stress apparatus (14). A schematic diagram of this apparatus was shown in Figure 2. Freidrich's condensers were supplied with coolant refrigerated at 0-5 °C to condense volatile compounds. The condensers were attached to 100 mL round bottom flasks by Claissen adapters, and the center opening of the adapters were used as the entrance ports for both the thermometer and the fused quartz 0.53 mm internal diameter capillary oxygen feed line. The Thermo-watch(TM) sensor was clipped onto the thermometer and adjusted for a sensitivity to give $\pm 1^{\circ}\text{C}$ temperature control. The gas delivery system was valved to deliver either nitrogen or oxygen to two mass flow control units adjustable from 0-100 mL/min flow rate. One feed line could be shut off, allowing either single or dual fuel stressing. The

0.53 mm fused quartz gas feed lines were inserted through the "Viton B" thermometer seals of the Claissen adapter to within about 2 mm of the bottom of the round bottom flasks and connected directly to the mass flow controllers at the other end. The gas feed lines were about 2 meters in length.

2.6 STRESSING THE FUEL

1) JP-8S

The first fuel stressed was JP-8S, which was stressed at 175°C and 160°C, respectively. The flow rate of oxygen to both the 175°C and the 160°C stress flasks was set at 48 mL/min., determined by a flow meter. To insure that the fuel oxidation stress was uniform, the fuel was purged with nitrogen until the desired stress temperature was reached. Initially, 60 mL of fuel were stressed at a time; this would later be increased to 70 mL at a time. Ten milliliter samples were taken every 30 minutes for 2 hours, starting 30 minutes after the desired temperature was reached. After the samples were taken, they were quenched in an ice water bath. The ice water was poured off after cooling and the beaker which contained all of the samples was wrapped with aluminum foil to block light from the samples. Because of heat and humidity problem caused by defective air-handling systems in the building, the time between the moment the samples were taken until the time they were run on the FTIR varied from 1 day to 4 weeks. Before these particular samples were run on the FTIR it was apparent that they had coagulated; consequently, they were ultrasonicated before being run. The spectra of all four samples for each stressing temperature can be seen superimposed in Figure 5. Notice the different colors--red indicates sample number one which was taken after 30 minutes of stress; brown represents the second sample taken at 60 minutes; yellow is indicative of the third sample, which was taken at 90 minutes; and purple depicts the fourth and final sample of the fuel, taken after 120 minutes of stress. The windows for absorbance are

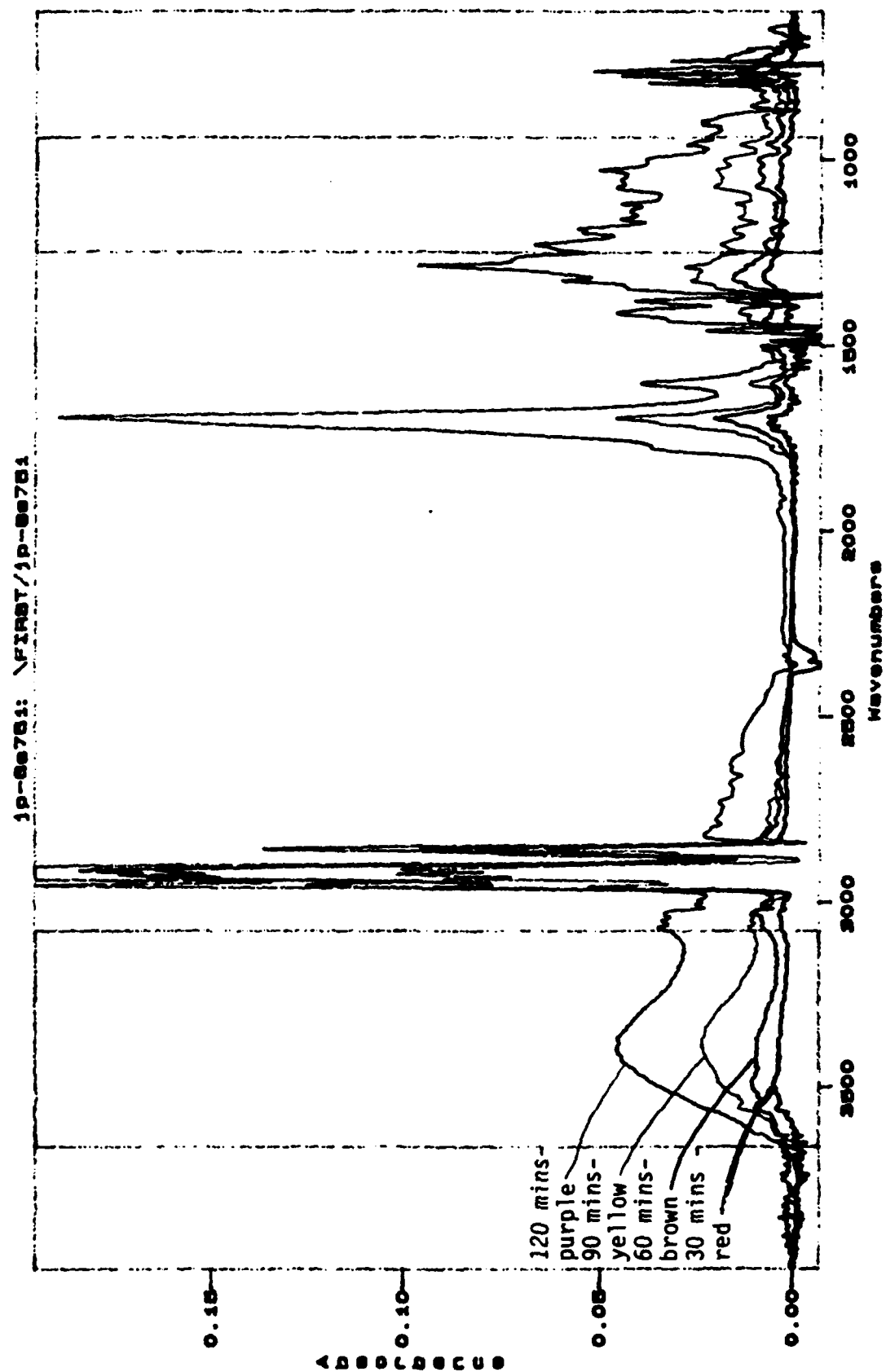


Figure 5. FTIR Spectrum of JP-8S Stressed at 175°C With Oxygen Flow at 48 mL/min.

also shown in Figure 5, the reason for their presence in the figures will be described in the results and discussion section.

Two additional samples of JP-8S were stressed at 150°C and 140°C, respectively. This time, 60 mL of the fuel were stressed and it must be noted that the flow rate of the oxygen was not checked; it was assumed that the flow rate would not change from the aforementioned 48 mL/min. The same procedures were followed as with the previous samples.

2) Jet A-1 (90-POSF-2747)

The next fuel to be stressed was Jet A-1 (90-POSF-2747). The fuel was stressed under the same conditions as the JP-8S and again the flow rate of the oxygen was assumed to be 48 mL/min. The fuel was stressed at 175°C and 160°C. The spectra for the 175°C stressed 2747 is shown in Figure 6 on page 22. Notice the deviance from the aforementioned color scheme in the O-H portion of the alcohol window in the spectrum. The expected sequence of colors should be red, brown, yellow, then purple, with the red being the least stressed sample. In the 175°C spectrum, however, the sequence of colors in the O-H portion of the alcohol window goes from purple to yellow to red to brown. This will be discussed in the next section of this work.

3) JP-8 (UN 1863)

JP-8 (UN 1863 lot) was stressed under the same conditions as the 175°C and 160°C JP-8S and the flow rate was assumed to be 48 mL/min.

4) Jet A-1 (91-POSF-2813)

Jet A-1 (91-POSF-2813) was stressed under the exact same conditions as the JP-8. The flow rate of the oxygen was not checked, it was assumed to be 48 mL/min.

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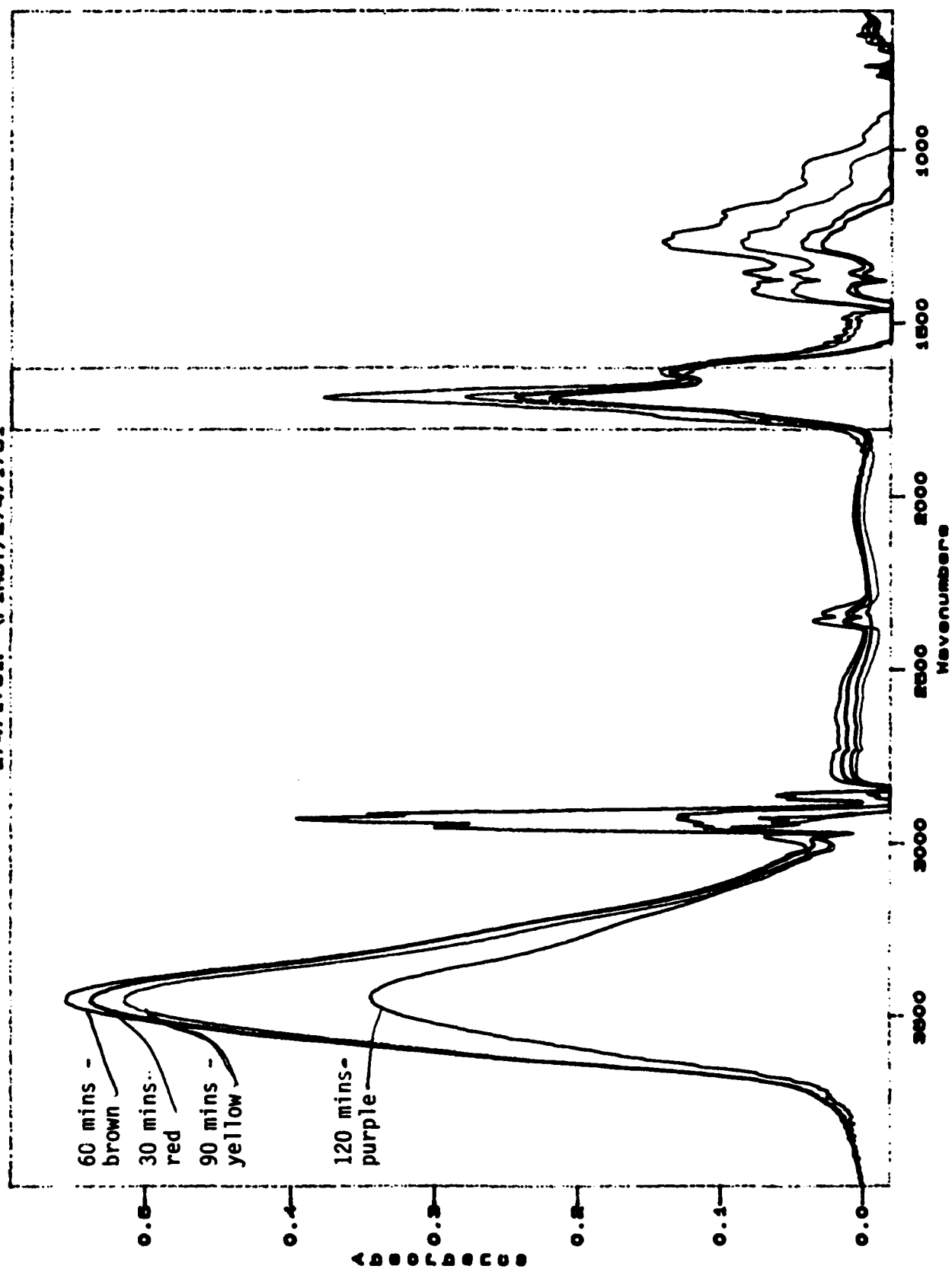


Figure 6. FTIR Spectrum of Jet-A-1 (90-POSF-2747) Stessed at 175°C With an Oxygen Flow Rate of 48 mL/min.

5) JP-TS

JP-TS was also stressed under the same conditions that were used in stressing the JP-8. The flow rate was assumed to be 48 mL/min.

6) JP-8S spiked with approximately 1 mg of copper

JP-8S samples spiked with approximately 1 mg of copper each were stressed at 140, 150, 160 and 175°C. The respective samples contained 0.0010, 0.0011, 0.0013, and 0.0015 mg of copper powder. The flow rate of oxygen was assumed to be 48 mL/min.

7) JP-7

Seventy milliliter samples of JP-7 were stressed at 140, 150, 160 and 175°C. The flow rate for oxygen was assumed to be 48 mL/min.

8) JP-8S spiked with 0.5% JFA-5 (85-POSF-2284)

Samples of JP-8S spiked with approximately 0.5% of JFA-5 (85-POSF-2284) were stressed at 140, 150, 160 and 175°C. JFA-5 was described earlier in the experimental section. The oxygen flow rate was assumed to be 48 mL/min. The amounts of JFA-5, respectively, were 0.264 g (0.49%), 0.274 g (0.51%), 0.270 g (0.50%) and 0.269 g (0.50%).

9) Jet A-1 (91-POSF-2814)

Jet A-1 (91-POSF-2814) was stressed at 170 and 175°C. Sample size was 70 mL with oxygen flow of 48 mL/min. There was another interesting switch in oxidation products as can be seen in the spectrum Figure 7. Again, the colors are expected to proceed from red (the least stressed fuel), to brown, to yellow to purple (the fuel stressed the longest).

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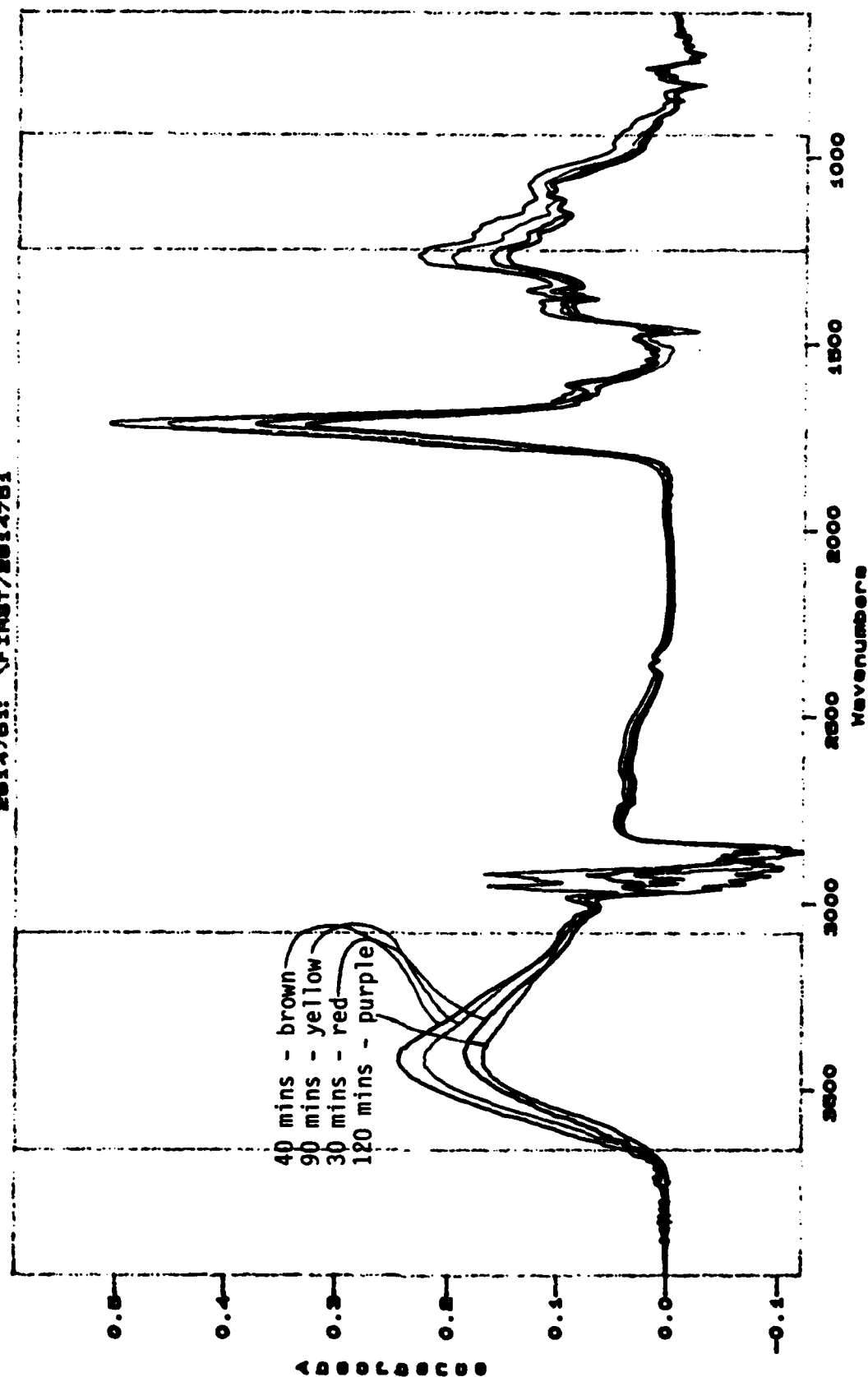


Figure 7. FTIR Spectrum of Jet-A-1 (91-POSF-2814) Stressed at 175°C With an Oxygen Flow Rate of 48 mL/min.

10) JP-8S spiked with 0.5% of AO-29 and UOP #5

The last samples to be stressed were both JP-8S and were both run at 175°C. The flow rate was checked and set at 48 mL/min. In one flask, 0.308 g or 0.501 % of AO-29 was added. In the other flask, 0.310 g or 0.506 % of UOP #5 was added. AO-29 and UOP #5 were previously described in the experimental section.

SECTION 3.0

RESULTS AND DISCUSSION

The results obtained for each fuel (including the spiked samples) under varying stress conditions are given in the charts on the following pages. It must be noted that for each sample run, the corresponding fuel was used as a background on the FTIR. Also, each time a fuel was run, a manual baseline correction was performed to insure that the baseline was on zero, in order for the quantitative predictions to be as accurate as possible. The baseline was chosen as the best representative straight line along the bottom of the spectrum. The charts that follow are labeled and are in an order that facilitates a comparison between fuels that were stressed with additives to those stressed without additives.

3.1 METHOD AND ANALYSIS

The first three charts shown are of the surrogate JP-8, spiked with varying concentrations of alcohol (1-dodecanol) and ketone (2-octanone). The solutions that were used in the method as prediction models are in boldface type. The FTIR spectra of these solutions were previously given in the experimental section. Although discrepancies seem to exist in some of the predictions for certain solutions, it must be taken into consideration that these solutions were run on the FTIR at different times and under different conditions. In the warmer spring and summer months the humidity's effect on the FTIR caused difficulties with the accurateness of the spectra--the FTIR began to pick up water and carbon dioxide which gave interferences in the regions of interest. The spectra that were acceptable were used in the method. For a summary of the method solutions see Tables 1a, 1b, and 1c.

3.2 ANALYSIS OF JP-8S WITH AND WITHOUT ADDITIVES

3.2.1 Analysis of the Surrogate JP-8

The results for the stressing of JP-8S are shown in Figure 5. There seems to be some discrepancies between the 160 and 175°C stressed JP-8S. It must be noted that variations in results may be due to the presence of water and carbon dioxide caused by the humidity. Although samples were run at 140 and 150°C, the important trends in oxidation were observed in the 160 and 175°C samples. Observation of the alcohol concentrations for these two samples showed an interesting trend. As expected, the 175°C samples begin and end with a greater extent of oxidation than the 160°C samples. The second and third samples however show that the 160°C sample had a larger concentration of alcohol oxidation products than the 175°C samples. At first this seemed to be inconsistent with past studies. A possible explanation for the contradiction involved the mechanism associated with the oxidation of jet fuels. The general sequence for oxidation started with the fuel (some type of alkane, branched or normal) being oxidized to an alcohol, which was then oxidized to an aldehyde or ketone, which was in turn oxidized to a carboxylic acid, which was then oxidized to carbon dioxide, water, and a new carboxylic acid. It seems that at higher temperatures fuels go through this mechanism more rapidly than at lower temperatures (Figures 6 and 7). In fact, it seems that at lower temperatures (140 and 150°C), the sequence stayed in its initial stages. When temperatures of 160°C were obtained, the fuel seemed to move through the oxidation sequence slowly. In the 160°C samples, the concentration of both the alcohol and ketone increased at approximately the same rate. At first glance, this also seemed to be the case with the 175°C samples. However, by comparing the extent of oxidation of the 160°C sample to the 175°C sample, the reaction sequence became more evident. Although the 60 min sample taken at 160°C had a larger concentration of alcohol than did the 175°C sample, the concentration of ketone was larger in the 175°C sample. This suggests that although the 160°C sample was probably still in the initial stages of the

sequence, the 175°C sample had already been oxidized to aldehydes and ketones. The 90 minute sample at 160°C had a larger concentration of both alcohol and ketone. At this stage, the 160°C sample had probably been oxidized to aldehydes and ketones, while the 175°C sample had already been oxidized to carboxylic acids. At this stage it was possible that small molecules produced by oxidations cracking, such as formic or acetic acids could escape the system via the condensers. The possibility that some oxidation products could be lost by volatilization before analysis indicated another caution to be observed when using this method. After two hours of stressing, both the 160°C and 175°C samples seemed to have passed a region of anomalies and were producing soluble oxidation products that stayed in the fuel. For a complete summary of the data collected from these samples see Table 2.

3.2.2 Analysis of JP-8S Spiked with 1 mg of Copper

Comparison between stressed neat JP-8S and JP-8S spiked with copper indicated a caution that had to be observed in FTIR analysis of oxidation products. The amount of fuel stressed is an obvious difference; 60 mL of the neat JP-8S were stressed compared to 70 mL of the spiked surrogate. The neat JP-8S appeared to have been oxidized to a greater extent than was the spiked JP-8S. This was surprising considering the fact that metals have a catalytic effect in fuel. However, in the spiked samples (particularly the fourth samples at 150, 160 and 175°C), insoluble gum was present, while in the neat samples there were only color changes. This implied that the formation of insoluble gum decreased the extent of oxidation that can be monitored on the FTIR. Since only the fuel and any soluble gums could be put into a flow cell without the presence of a solvent, the results of the spiked surrogate JP-8 were not considered accurate. However, the data obtained from the stressing of the surrogate with copper can be seen in Table 3.

TABLE 2
JP-8S SAMPLE ANALYSIS

		Deposit Precursor Analysis of Surrogate JP-8 by Transmission FTIR							
SAMPLE	AMOUNT STRESSED	STRESS TEMP IN CELCIUS	STRESS TIME IN MIN.	Predicted Concentration in Moles/Liter				SSE	SSE(1)
				ALCOHOL	KEONE				
JP-8S	60mL	140	30	0	0.016	0.002			0.005
			60	-0.033	-0.001	0.002			0.005
			90	-0.009	0.003	0.001			0.003
			120	-0.001	0.004	0.002			0.003
JP-8S	60mL	150	30	0.002	0.008	0			0.003
			60	-0.01	0.001	0			0.003
			90	0	0.004	0			0.04
			120	0	0.005	0.001			0.003
JP-8S	60mL	160	30	0.008	0.006	0			0.003
			60	0.066	0.021	0.005			0.004
			90	0.155	0.074	0.012			0.029
			120	0.33	0.212	0.107			0.139
JP-8S	60mL	175	30	0.018	0.012	0			0.004
			60	0.054	0.026	0.001			0.006
			90	0.145	0.056	0.008			0.015
			120	0.352	0.253	0.1			0.162
(1) Sum Square of Errors from Mallison, INC. Advanced First Software									

TABLE 3

JP-8S ANALYSIS WITH 1 mg OF COPPER

		Deposit Precursor Analysis of JP-8S Spiked With 1mg of Copper by Transmission FTIR							
SAMPLE	AMOUNT STRESSED	STRESS TEMP IN CELCIUS	STRESS TIME IN MIN.	Predicted Concentration in Moles/Liter				SSE(1)	
				ALCOHOL	SSE	KEONE			
JP-8S	70mL	140	30	0.004	0	-0.001		0.003	
			60	0	0.001	0.01		0.005	
			90	0.001	0.001	0.01		0.004	
			120	0.005	0	0.007		0.003	
JP-8S	70mL	150	30	-0.004	0.001	0.01		0.005	
			60	-0.004	0.001	-0.002		0.003	
			90	0.001	0.001	0.013		0.006	
			120	0.071	0.004	0.035		0.011	
JP-8S	70mL	160	30	-0.002	0.001	0.014		0.005	
			60	-0.005	0.001	0.003		0.003	
			90	0.045	0.002	0.015		0.006	
			120	0.15	0.016	0.071		0.022	
JP-8S	70mL	175	30	0.013	0.003	0.011		0.002	
			60	0.001	0.002	0.034		0.012	
			90	0.054	0.004	0.069		0.024	
			120	0.17	0.021	0.079		0.025	
(1) Sum Square of Errors from Mallison, INC. Advanced First Software									

3.2.3 Analysis of JFA-5 as an Additive

In this analysis, the background solution for the spiked JP-8S is not representative of the actual samples. The concentration of JFA-5 in the samples were as follows: the 140°C sample contained 0.506 %, the 150°C sample contained 0.490 %, the 160°C sample contained 0.497 % and the 175°C sample contained 0.501 %. A sample should have been taken from each flask before stressing to use as a background, then it would have been representative of the samples taken. Alternatively, a background solution was prepared which contained 0.540 % of JFA-5. Although the quantitative analysis was not accurate, JFA-5 did seem to inhibit oxidation at or below 150°C and slowed down oxidation at 160°C. At or above 175°C, however, the effectiveness of JFA-5 decreased. The results obtained using JFA-5 as an additive were still better than those of the neat JP-8S. The general results from use of the additive are provided in Table 4.

3.2.4 Analysis of AO-29 as an Antioxidant

The major problem with investigating the effectiveness of AO-29 as an antioxidant is that it is a phenol type antioxidant. Thus, the background, which is subtracted from the sample to give only those areas in the spectrum that are new (i.e. oxidation products), contains C-O and O-H stretching. As the AO-29 was used up in the reaction, a negative absorbance was created, which ultimately gave a negative concentration prediction. However, this could be an asset in studying the rate of disappearance of an additive. Other than that, the AO-29 seems to be an effective antioxidant as seen in Table 5.

3.2.5 Analysis of UOP #5 as an Antioxidant

The analysis of UOP #5 seemed to be impossible on the FTIR. The major problem with analyzing UOP #5 is the large amount of C-N and N-H stretching present. The problems associated with C-N and N-H stretching were described previously in the

TABLE 4

JP-8S ANALYSIS WITH 0.5% OF JFA-5

		Deposit Precursor Analysis of JP-8S Spiked With 0.5% of JFA-5 by Transmission FTIR							
SAMPLE	AMOUNT STRESSED	STRESS TEMP IN CELCIUS	STRESS TIME IN MIN.	Predicted Concentration In Moles/Liter			SSE(1)		
				ALCOHOL	SSE	KESTONE			
JP-8S	70mL	140	30	0.002	0	0.001	0.004		
			60	0.002	0.001	0.005	0.004		
			90	-0.003	0	0.004	0.004		
			120	0.001	0	-0.001	0.004		
JP-8S	70 mL	150	30	0.002	0	0.004	0.004		
			60	-0.001	0.001	0.006	0.004		
			90	0.001	0	0.005	0.004		
			120	0.001	0.001	0.007	0.004		
JP-8S	70mL	160	30	-0.001	0	0.004	0.004		
			60	0	0	0.004	0.004		
			90	0.014	0	0.01	0.005		
			120	0.059	0.002	0.025	0.009		
JP-8S	70mL	175	30	0.008	0	0.001	0.004		
			60	0.031	0.001	0.011	0.005		
			90	0.07	0.001	0.023	0.008		
			120	0.098	0.005	0.052	0.019		
(1) Sum Square of Errors from Mattison, INC. Advanced First Software									

JP-8S ANALYSIS WITH 0.5% OF A0-29

(1) Sum Square of Errors from Mallison, INC. Advanced First Software

analysis of AO-29, in the discussion of the problems related to C-O and O-H stretching. The major difference in the analysis of the AO-29 is that it contained only one C-O/O-H group, whereas UOP #5 contains two C-N/N-H groups. The overall effect is a much larger negative absorption and correspondingly larger negative concentration. In addition, all samples contained a large amount of insoluble sediment which probably involved essentially all of the oxidation products. The information presented in Table 6. The UOP #5 was very counter-productive as an additive at 175°C.

3.2.6 Analysis of JP-8

The JP-8 appeared to be more stable than the surrogate JP-8. There was, however, insoluble gum present on the bottoms of the culture tubes, starting with the second 160°C sample and the first 175°C sample. For results of the analysis of the JP-8 see Table 7.

3.2.7 Analysis of JP-7

Although JP-7 was more expensive and supposedly more stable (due to hydrotreatment) than JP-8, JP-7 appears to be one of the most unstable fuel of those tested (with the exception of Jet A-1 90-POSF-2747). Although most of the fuels studied were fairly stable at or below temperatures of 150°C, the JP-7 began oxidizing after 90 minutes at 150°C. The large errors evident in the 90 minute and 120 minute samples stressed at 160 and 175°C are probably due to hydrogen bonding and/or ketone tautomerization, which were not accounted for in the method. The differences in the concentrations for the 160 and 175°C samples were due to the formation of insoluble gums/particulates at a faster rate in the latter. The analysis of JP-7 can be seen in Table 8.

TABLE 8

JP-7 SAMPLE ANALYSIS

		Deposit Precursor Analysis of JP-7					
		by Transmission FTIR					

3.2.8 Analysis of JP-TS

The concentration of oxidation products in the 160 and 175°C samples were nearly the opposite of what was expected. The third and fourth 160°C samples both show greater oxidation than the 175°C samples. Other fuels gave similar results, and those results were almost certainly due to the presence of insoluble gum/particulates in the higher temperature samples. The fourth 160°C sample of the JP-TS was the only sample of JP-TS in which any insoluble gum was observed. One explanation is the oxygen flow rate. The JP-TS was one of the last samples to be run and since the flow rates were not checked routinely for previous samples it was possible that the flow rates were not equal. However, since the first two samples taken followed the expected trend, another explanation was a possible mix-up in samples. The alarming fact was that JP-TS is typically a very stable fuel, and the results obtained from both JP-7 and JP-TS seem to indicate either that these fuels are more easily oxidized than JP-8 or JP-8S or that there has been a serious error in the course of this study. The most probable source of error is the loss oxidation products by formation of insoluble gums that are not observable. A possible explanation is that oxidation products from less stable fuels rapidly condense to clear gums that remain in the test flask or the collection tube, while the more stable fuels do not form such products as rapidly, and they then give greater oxidation absorbencies from the IR cell. For a complete analysis of oxidation products, see Table 9.

3.2.9 Analysis of Jet A-1 (90-POSF-2747)

Of all the fuels studied in this analysis, the 2747 Jet A-1 appeared to be the most unstable. The 2747 is oxidized greatly after only thirty minutes at 160°C. The large SSE errors can probably be attributed to hydrogen bonding and/or ketone tautomerization. After only thirty minutes at 175°C, the error was larger than the fourth sample taken at 160°C. Insoluble gum formation caused the extent of oxidation to decrease after the third sample for the alcohol stretching. A look at the spectrum of the

TABLE 9
JP-TS SAMPLE ANALYSIS

[illegible]

175°C 2747 (Figure 6) shown earlier, follows the fuel as it is proceeding through the degradation mechanism discussed earlier in the JP-8S discussion. Notice that the alcohol and ketone stretches are almost complete opposites.

3.2.10 Analysis of Jet A-1 (91-POSF-2813)

Although the concentration of alcohol oxidation products in the Jet A-1 (91-POSF-2813) were mostly negative, there were some present as ketone, which would explain the presence of soluble gums in the third and fourth samples of the 160°C and the second through fourth samples of the 175°C. The negative response for alcohol could be due to the humidity. For results of the 2747 and 2813 analysis see Table 10.

3.2.11 Analysis of Jet A-1 (91-POSF-2814)

The 2814 is another example of the fuel as it is going through the degradation mechanism. A look at the 175°C spectrum (Figure 7) in the experimental section will show this. The 2814 was another one of the most unstable fuels. Again, as was the case with the 2747, the sediment formation was extensive. This led to smaller concentration predictions for both the alcohol and ketone stretches. For the complete analysis of the 2814, see Table 11.

TABLE 10

JET A-1 (POSF-2813) SAMPLE ANALYSIS

		Deposit Precursor Analysis of Jet A1					
		by Transmission FTIR					
SAMPLE	AMOUNT STRESSED	STRESS TEMP IN CELCIUS	STRESS TIME IN MIN.	Predicted Concentration in Moles/Liter			SSE(1)
				ALCOHOL	SSE	KETONE	
POSF-2747	60mL	160	30	0.096	0.016	0.06	0.005
			60	0.358	0.164	0.184	0.025
			90	0.925	1.518	0.437	0.159
			120	1.892	3.509	0.951	1.06
POSF-2747	60mL	175	30	1.173	5.082	0.355	0.188
			60	1.267	4.894	0.406	0.214
			90	1.32	3.54	0.465	0.249
			120	1.14	1.469	0.636	0.414
POSF-2813	60mL	160	30	-0.013	0.002	0.002	0.004
			60	-0.012	0.002	0.002	0.003
			90	-0.007	0.001	0.003	0.003
			120	0.002	0.002	0.005	0.003
POSF-2813	60mL	175	30	-0.24	0.005	0.005	0.004
			60	0.014	0.001	0.007	0.004
			90	-0.001	0.003	0.01	0.003
			120	0.002	0.004	0.013	0.003
(1) Sum Square of Errors from Mallison, INC. Advanced First Software							

JET A-1 (POSF-2814) SAMPLE ANALYSIS

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SECTION 4.0

CONCLUSIONS

The use of the FTIR as a baseline method for studying the thermal-oxidative stability of fuels and the effectiveness of antioxidants is promising. In spite of questionable results when comparing the extent of oxidation of different fuels in this study, each individual stress test was self consistent. Experimental error was almost certainly responsible for the discrepancies observed in the oxidation of different fuels. One source of error is the operation of the flask test. Oxygen flow, temperature and fuel volume have to be identical in order to compare fuel stabilities. In addition, the experiment must be designed to preclude either the loss of volatile compounds or the formation of insoluble gum for any samples of fuels which are to be compared. The optimum conditions for such stressing should be determined experimentally.

Several factors handicapped this effort. One factor was extreme heat and humidity in the laboratories. Long purging of the sample compartment was necessary to obtain satisfactory spectra but even with purging it was difficult to obtain consistent baselines during certain time periods. Another factor was that, due to time and material limitations, all quantitation was done by reference to one set of spectra from external standards that were obtained and stored in computer memory over 2 months before some of the samples were analyzed. The external standards were in JP-8S, rather than in the fuel undergoing analysis. A third handicap is that the same IR cell was used for most of the samples and steadily deteriorated throughout the course of the work. The cell finally broke and the work was finished with a new cell. The stressed samples of JP-TS, JP-7, POSF-2747, -2814 and -2813 were all analyzed with the new cell. This, along with the fact that all of these samples had aged for at least 2 weeks after stressing was the most probable explanation for the contradicting results for different fuels. In retrospect, better results in this study could probably have been obtained by using only the O-H and C=O

windows. The C-O window contributing to the alcohol analysis had too many other absorbances present to obtain high precision. In addition, carbonyl absorbances from aldehydes and carboxylic acids should have been included in the method. The instrument used would not accommodate the additional window area for these absorbances, apparently because of limited memory.

Problems such as atmospheric humidity, cell thickness, cell deterioration and colloidal dispersion of particulates in samples should be eliminated by the use of attenuated total reflectance (ATR) flow cells, in situ ATR probes or even a "top loading" ATR sample holder. An ATR flow cell (which continuously circulates fuel directly from the stress flask) or an *in situ* ATR probe (which sits in the reaction flask), would also eliminate sample handling and coagulation problems.

FTIR appeared to be a method very worthy of development for the analysis of fuel oxidation. If used with enough computer memory, advanced quantitative analysis software, sophisticated sample cells and properly conducted experimental conditions, FTIR analysis should be a method of determining oxidation rates of fuel very quickly and with good precision. FTIR would be amenable to static or flowing stress situations and could provide insight to the nature of different oxidation products as well as a quantitative measures of the degree of oxidation.

SECTION 5.0

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