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FTIR Analysis of Aviation Fuel Deposits

Larry S. Helmick and Gary T. Seng
Lewis Research Center
Cleveland, Ohio

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Larry S. Helmick* and Gary T. Seng

National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135

SUMMARY

Five modes of operation (absorption, emission, single reflectance, attenuated total reflectance, and photoacoustic) of a Nicolet 7199 Fourier Transform Infrared Spectrophotometer have been investigated in order to determine which modes were most suitable for qualitative analysis of jet fuel deposits. The absorption and emission modes were found to be the most advantageous for investigation of the bulk and surface properties of accelerated storage/thermal deposits where relatively large quantities of deposit are generally available.

The general effects of fuel type, stress temperature, stress time, type of spiking agent, spiking agent concentration, fuel flow, and postdepositional treatment on the chemical nature of accelerated storage/thermal deposits were then investigated by FTIR by systematically varying these parameters.

A correlation of the infrared spectra and chemical structure of model fuel storage/thermal deposits has been attempted.

INTRODUCTION

Jet fuels undergo chemical reactions which ultimately result in sediment/deposit formation when subjected to high temperatures in the presence of oxygen. Temperatures of 100° to 300° C are presently encountered in the heat exchangers, fuel lines, and nozzles of jet aircraft under normal operating conditions. Accumulation of deposits in these areas reduces the rate of heat and fuel flow, thus adversely affecting the operation of the aircraft. With increased use of higher temperature, advanced design turbines, and the potential use of broadened-properties fuels and synfuels, thermal degradation problems are expected to increase in future years. Knowledge of the chemical structure of the deposit is necessary in order to identify the chemical reactions involved in its formation. Suitable modification of fuels, handling techniques, or materials may then be possible in order to eliminate these reactions and minimize the deposits.

Several approaches have been taken in recent years to obtain information concerning the chemical structure of fuel deposits. These include photoacoustic spectroscopy, electron spectroscopy for chemical analysis, scanning electron microscopy, energy dispersive analysis of X-rays, secondary ion mass spectroscopy, Fourier transform infrared spectroscopy, Raman spectroscopy, and pyrolysis/gas chromatography-mass spectrometry. Much of this research has been supported by NASA and has recently been summarized (ref. 1).

*Cedarville, College, Cedarville, Ohio 45314 and NASA-ASEE Faculty Fellow.

The purposes of this investigation were (1) to evaluate five modes of operation of a Nicolet 7199 FTIR spectrophotometer and determine which modes would be most valuable in a qualitative investigation of the surface and bulk chemical structure of jet fuel accelerated storage/thermal deposits; (2) to use Fourier transform infrared spectroscopy (FTIR) to qualitatively determine the effects of the type of fuel, stress temperature, stress time, type of spiking agent, spiking agent concentration, fuel flow, and post-depositional treatment on the nature of the accelerated storage/thermal deposit; and (3) to determine whether low temperature storage deposits contained precursors which could be converted into thermal deposits by additional post-depositional heating under nitrogen or air.

To accomplish these objectives, Fourier transform infrared absorption, emission, single reflectance, attenuated total reflectance, and photoacoustic spectra were obtained for deposits produced on stainless-steel foil by heating fuel samples containing selected spiking agents. The advantages and disadvantages of each mode were then evaluated. The absorption and emission modes were selected for analysis of fuel deposits. The type of fuel used, stress temperature, stress time, type of spiking agent, spiking agent concentration, fuel flow, and post-deposit treatment were then systematically varied to determine which factors affect the nature of the deposit and thus the FTIR spectrum. Finally, post-depositional heating of accelerated storage deposits was conducted to determine whether they could be converted into thermal deposits.

EXPERIMENTAL PROCEDURE

Instrument Description

Infrared spectra were obtained on a Nicolet 7199 Fourier Transform Infrared Spectrophotometer equipped with a liquid nitrogen cooled mercury-cadmium-telluride detector, model NIC-E7000 Emission Accessory, model NIC-AT7000 Variable Angle Attenuated Total Reflectance Accessory with a 50 mm KRS-5 crystal, and a single External Reflectance Accessory constructed in-house. Photoacoustic spectra were obtained on the same instrument with a helium filled Nicolet Photoacoustic Cell.

Sample Preparation and Instrument Operation

Absorption spectra. - Samples were prepared by carefully scraping approximately 0.1 mg of deposit off the metal foil and grinding it with 200 mg of spectroscopic grade potassium bromide in a Wig-L-Bug ball mill for 30 sec. The powder was then placed in a die, evacuated, and pressed into a transparent pellet. After collecting between 20 and 100 scans employing a suitable set of instrumental parameters, the single beam spectrum was ratioed against the spectrum of a blank potassium bromide pellet and plotted as percent transmittance versus wave number. Proper instrument adjustment, calibration, and operation was verified using a polystyrene standard.

Emission spectra. - Samples were prepared by cutting a 0.5 cm disk from the stainless-steel foil coated with the deposit. The sample was placed in the thermostatted sample holder well of the Nicolet emission attachment which

had previously been calibrated with a YSI (Yellow Springs Instrument) thermistor thermometer. Using a suitable set of instrumental parameters, 400 background scans were collected at 30° C. The temperature was then increased to the desired value and 400 sample scans were collected. The background was subtracted from the sample and the difference spectrum so produced was ratioed against the difference spectrum of a powdered charcoal blackbody produced in the same manner at the same temperatures. The resulting spectrum was plotted as emission intensity versus wave number. To insure proper operation of the instrument, polystyrene was run in the emission mode and the spectrum was compared with that obtained using the absorption mode.

Photoacoustic spectra. - Samples were prepared by cutting a 0.5 cm disk from the stainless-steel foil coated with the deposit. Using a dry bag, the sample was sealed in the Nicolet photoacoustic attachment under helium. Between 300 and 500 scans were collected using an appropriate set of instrumental parameters and ratioed against the spectrum of powdered charcoal which was similarly obtained. A spectrum of polystyrene was obtained and compared with an absorption spectrum to insure proper operation of the instrument.

Attenuated total reflectance spectra. - Three clean stainless steel foils and one foil coated with the thermal deposit were clamped (two on each side) to an ultrasonically cleaned and vacuum dried crystal of KRS-5, and mounted in the instrument at an angle of 46°. Approximately 100 scans were collected using a suitable set of instrumental parameters and ratioed against four blank foils identically attached to the crystal. However, optimum results were obtained when the contact surface area was increased by using four identical samples. Since four identical samples were generally not available, and since the roughness of the thermal deposit prevented good surface contact with the crystal, it was difficult to obtain spectra of satisfactory quality in this mode. Proper instrument operation was verified using a Teflon sample.

Single reflectance spectra. - The stainless-steel foil coated with the deposit was mounted on the single reflectance attachment which had been aligned in the instrument. The sample was scanned 200 times using a suitable set of instrumental parameters and ratioed against an ultrasonically cleaned stainless-steel blank.

Control spectra. - Absorption spectroscopy reveals information concerning the bulk of the material, while emission spectroscopy is a surface analysis technique (ref. 2). For material in which the surface and bulk are similar, essentially identical spectra should be obtained, providing that in the emission mode, reabsorption due to temperature gradients within the sample does not occur. Polystyrene spectra (fig. 1) exhibit this similarity, indicating that no reabsorption is occurring to alter the emission spectra.

Since photoacoustic and emission spectroscopy are both surface analysis techniques, they should produce spectra of the surface material which exhibit similar frequencies (although relative band intensities may vary somewhat.) Actual observation of spectra with similar band frequencies for polystyrene (fig. 1) as well as for fuel deposits indicates that this is the case and that again no reabsorption is occurring in the emission mode which might seriously alter the spectra of the material.

Preparation of Static Accelerated Storage/Thermal

Deposits at 60° and 125° C

Deposits were prepared employing a procedure developed by Daniel (ref. 3). A specific amount of spiking agent was added to 20 ml of fuel in a wide-mouth, 4 oz, glass jar containing two weighed stainless-steel foils and sealed with a Teflon-lined cap. The jars were placed in an oven set at the test temperature ($60 \pm 1^\circ$ or $125 \pm 3^\circ$ C). After a suitable amount of deposit had formed, the jar was opened and the foil removed, rinsed with hexane, dried at room temperature and atmospheric pressure or at 80° C under vacuum (60 torr), and weighed. Fuels which were slow to produce deposits were saturated with oxygen by opening the jar and bubbling oxygen through the solution for 5 min, resealing, and replacing the jar in the oven. A summary of conditions employed is given in table I.

Preparation of Static Accelerated Thermal Deposits at 250° C

Thermal deposits were prepared under static fuel conditions by adding an appropriate amount of the spiking agent to 10 ml of oxygen-saturated fuel in a 35 ml high-pressure stainless-steel capsule containing a preweighted stainless-steel foil. The capsule was placed in a muffle furnace at $250^\circ \pm 20^\circ$ C for 7 to 10 days. After cooling to room temperature, the capsule was opened and the fuel and foil removed. The foil was rinsed with hexane and dried at atmospheric pressure and room temperature. The fuel was centrifuged to obtain the suspended sediment for analysis. This sediment was washed with hexane and dried at room temperature and 0.05 torr. A summary of conditions employed for preparation of static accelerated thermal deposits is also included in table I.

Preparation of Modified JFTOT Accelerated Thermal Deposits

Thermal deposits were produced by stressing 700 ml of air-saturated fuel containing the appropriate amount of spiking agent on the Modified JFTOT Flat Sample Rig (MJFSR) at 260° C (ref. 4). After stressing, the preweighted stainless-steel foil containing the deposit was rinsed with hexane, dried at 80° C under vacuum (60 torr) and weighed.

RESULTS AND DISCUSSION

FTIR Mode Selection

The Nicolet 7199 Fourier Transform Infrared spectrophotometer offers five modes of operation: absorption, emission, single reflectance, attenuated total reflectance, and photoacoustic. All of these modes were investigated in order to determine which modes of operation were most suitable for qualitative analysis of fuel deposits. Modes for both bulk and surface analyses were desired. Although the absorption mode required relatively large quantities of deposit, it was selected for continued use because it was the only mode which provided bulk analyses. Of the surface analysis techniques, attenuated total reflectance (ATR) was not practical for continued use because the hardness and roughness of the thermal deposits prevented good contact between the deposit

and the ATR crystal. Consequently, four identical samples were required in order to obtain satisfactory spectra, and generally only one or two samples were available. Photoacoustic spectroscopy lacked adequate signal to noise ratio, particularly at the lower frequencies. The single reflectance mode was rapid to use and provided good quality spectra. However, it did not afford the opportunity to do in situ post-deposit stressing of samples. The emission mode afforded adequate sensitivity and resolution, and was the only mode which also provided the ability to do in situ post-deposit thermal stressing of samples. Consequently, it was selected for continued use as a surface analysis technique. The results of this portion of the investigation are briefly summarized in table II.

Unspiked Fuel Deposits

All commercial fuels contain small amounts of a large variety of compounds which readily undergo free radical air oxidation. Regardless of the fuel, the products obtained from the oxidation reactions presumably contain similar functional groups (alcohols, ketones, peroxides, carboxylic acids, etc.), although their exact individual structures may vary. These relatively polar compounds would then tend to separate out of the relatively nonpolar fuel, producing deposits containing compounds with similar functional groups (ref. 5). Since infrared spectroscopy detects the functional groups of compounds, the infrared spectra of most fuel deposits should be similar in the functional group region from approximately 1300 to 2000 cm^{-1} . However, the fingerprint region from 400 to 1300 cm^{-1} is dependent upon the exact chemical structure. Therefore, differences in band frequencies should exist in the fingerprint region. This can be seen for fuel deposits from a variety of fuels (Jet A, ERBS, JP-4, JP-5) in figure 2. These spectra are comparable to spectra of deposits already in the fuels literature (refs. 6 and 7).

However, a model fuel prepared from purified dodecane and tetralin does not contain the large variety of compounds presumably important in deposit formation in actual fuels. Consequently, the deposit produced from this model fuel might be expected to be somewhat different than deposits produced from actual fuels, as is seen by the differences in band frequencies in the spectra in figure 2.

Stress Temperature

Although it is generally recognized that the fuel stress temperature affects the rate of oxidation as well as rate of deposit formation, it is not known whether it also affects the type of functional groups produced or the degree of oxidation or polymerization which occurs when fuels produce deposits. The differences in the spectra of figure 3 at 1180 cm^{-1} and 1450 to 1650 cm^{-1} for deposits obtained from ERBS spiked with pyrrole and stressed at 60°, 125°, and 250° C under static conditions (as well as differences in spectra for deposits from ERBS spiked with 1 percent shale extract, and unspiked ERBS) suggest that stress temperature may be important in determining the type of functional groups present. At this time, it is not possible to determine what factors are significant in determining the effects of the stress temperature on the nature of the deposit, although some suggestions have recently been made (ref. 8).

Length of Stress Time

The similarity of band frequencies in spectra for deposits from dodecane/tetralin spiked with thiophene (fig. 4) as well as ERBS spiked with pyrrole obtained after different lengths of stress time indicate that the length of stress time has little effect on the type of functional groups in the deposit.

In order for precipitates to form, compounds must undergo sufficient oxidation and/or polymerization to become insoluble in the relatively nonpolar fuel. Apparently, the major changes in chemical structure occur before, rather than after, separation has occurred, with the introduction of several new types of oxygen containing functional groups. That is not to say that no further reaction (i.e., "aging", crystallization, or polymerization) is occurring in the deposit after it has formed (ref. 8). However, any further reaction may simply be introducing more of the same types of functional groups, rather than new types of functional groups, into the deposit. Consequently, the "age" of the deposit would have little effect upon the infrared spectrum. Thus, infrared data obtained on fuels which have had sufficient stress time to produce enough deposit to give a reasonable spectrum should still be comparable, even though the stress times are different.

Spiking Agents

Since commercial fuels already contain low concentrations of a broad variety of compounds containing heteroatoms, the addition of a small amount (175 ppm or less) of nitrogen or sulfur in the form of a heterocycle such as pyrrole or thiophene might not change the chemical composition of the fuel enough to appreciably alter the chemical reaction paths leading to deposit formation. Therefore, it is not surprising that it is difficult to detect significant differences in band frequencies or relative intensities in the spectra of the deposits from ERBS spiked with pyrrole or thiophene (fig. 5), or Jet A spiked with quinoline, thiophene, or shale extract, regardless of the spiking agent, as long as the concentration is low. However, the model fuel prepared from purified dodecane and tetralin does not contain appreciable concentrations of compounds containing heteroatoms. Consequently, addition of even low concentrations of pyrrole or thiophene apparently alters the chemical reaction paths sufficiently to significantly affect the chemical nature of the deposit, as seen by the differences in the 500 to 900 cm^{-1} region of the spectra of figure 6.

At higher concentrations (500 ppm or more), however, the spiking agent detectably affects the nature of the deposit as seen by the differences in band frequencies in figure 7 for ERBS spiked with pyrrole, thiophene, fuel oil, and shale extract. (Concentrations between 175 and 500 ppm were not investigated.) However, the effect of a high concentration of spiking agent is generally not sufficient to totally dominate the reaction paths leading to deposit formation, and thus the nature of the deposit itself, regardless of the fuel employed. The deposit produced by fuels such as ERBS, Jet A, dodecane, or dodecane/tetralin spiked with pyrrole, shale extract, thiophene, or fuel oil is dependent on the fuel used.

Fuel Flow

Although it is difficult to obtain deposits under the flowing fuel conditions of the Modified JFTOT Flat Sample Rig which are heavy enough to be analyzed by commercial FTIR absorption or emission techniques, results on two deposits (ERBS spiked with shale extract, and dodecane/tetralin spiked with pyrrole at 250° C) providing marginal spectral quality have been obtained. Comparison of their spectra with the spectra of deposits produced under stationary fuel conditions at 250° C (fig. 8) suggests that fuel flow probably has an effect on the nature of the deposit, as has previously been suggested (ref. 8). However, spectra of better quality must be obtained before this conclusion can be substantiated.

Post-depositional Treatment of Deposit

Deposits are coated with a thin film of fuel when they are removed from the preparation apparatus. In order to be able to analyze the deposit without interference from the fuel, it is necessary to remove the film. This is generally done by rinsing the deposit with hexane followed by drying at 80° C and 60 torr for 2 hr. The deposit must remain unaltered under these conditions if accurate and reliable data are to be obtained on the nature of the deposit as it is produced in the fuel.

The similarity of band frequencies and relative intensities in the absorption spectra shown in figure 9 for dodecane/tetralin spiked with pyrrole indicates that heating under vacuum, as described above, does not drastically affect the bulk of the deposit. However, differences in the 500 to 1100 cm^{-1} region of the emission spectra (fig. 10) on the same deposits suggest that some type of change may have occurred on the surface of these deposits. That not all deposits undergo these surface changes can be demonstrated by the similarity of the emission spectra (not shown) for ERBS spiked with pyrrole and Jet A spiked with shale extract.

If the differences are due solely to loss of low molecular weight volatile components from the surface, then room temperature vacuum drying of the deposit at 0.05 torr would be expected to produce emission spectra which are different than emission spectra obtained on deposits dried at room temperature and atmospheric pressure. Comparison of such spectra, for example, dodecane/tetralin spiked with pyrrole, (fig. 11) indicates that generally this is not the case. These findings suggest that the surface of the deposit does not always contain the same functional groups or distribution of functional groups as the bulk, and that the changes in the surface or bulk which occur with heating might also be ascribed to the loss of volatile components produced by oxidation, condensation, or pyrolysis reactions induced by this heating. This hypothesis is supported by the observation that on heating of the sample from 100° to 250° C at atmospheric pressure, the emission spectrum becomes weaker and loss of material from the deposit is visibly apparent. Scanning electron microscope photographs show loss of material from the deposit as well. Furthermore, emission spectra obtained as the temperature is increased from 100° to 250° C indicate that some samples, such as the deposit from dodecane/tetralin spiked with pyrrole, which have been dried at atmospheric pressure and room temperature undergo relatively major changes both in band frequencies and relative intensities as material is lost (fig. 12).

Spectra obtained after reducing the sample temperature to 100° are not identical to the original 100° spectra, indicating that the changes are indeed irreversible and not simply an artifact of the temperature at which the spectrum was run.

In comparison, emission spectra of several deposits, for example, ERBS spiked with pyrrole, which have been dried at 60 torr and 80° C for 2 hr appear to undergo relatively minor changes or no changes detectable by infrared spectroscopy (fig. 13) on heating from 100° to 250° C. This suggests that these deposits either are less susceptible to changes induced by heating or that part of the volatile material responsible for the changes has already been removed.

Finally, rinsing of the model fuel deposit with "trisolvant" (prepared by mixing equal volumes of acetone, isopropyl alcohol and toluene) containing 4 percent diacetone alcohol or with methyl alcohol visibly dissolves some of the material. Emission spectra of the remaining material (fig. 14) are significantly different than spectra of the original deposit, demonstrating that some components have again been selectively removed. Emission spectra of the remaining deposit as it is heated from 100° to 250° C again show relatively little change, indicating that the material which has been removed is somehow involved in the thermal reactions. (The improved signal to noise ratio in spectrum C is due to the fact that it was obtained at 250° C rather than 60° C.)

Similarities in the final spectra of figures 12 and 14 further suggest that the material which is selectively removed by methyl alcohol may be the same material which is removed on heating the deposit to 250° C. Similar treatment of the deposit from Jet A spiked with shale extract gave analogous results.

Further characterization and identification of these compounds may be possible through the use of pyrolysis gas chromatography and/or triple quadrupole mass spectroscopy. This possibility is presently being investigated.

There was also some question of whether the heating of an accelerated storage deposit to 250° C under an inert atmosphere or in air might convert it to an accelerated thermal deposit similar in chemical structure to one produced under flowing fuel in the Modified JFTOT Flat Sample Rig. However, this does not seem to be the case. Although spectra of deposits such as the one from Jet A spiked with fuel oil number 4, which have been heated, may begin to resemble spectra of MJFSR deposits, they do not appear to become identical (fig. 15).

Spectral Absorption and Emission Band Assignments

Analysis of infrared absorption and emission band frequencies shows that deposits prepared from purified dodecane and tetralin contain a complex variety of aliphatic and aromatic oxygen-containing compounds. Comparison of spectra for deposits formed from this simple model fuel system may allow some bands to be assigned (table III and fig. 16). Real fuels appear to produce deposits containing conjugated and unconjugated carbonyls as ketones, aldehydes, esters, carboxylate salts, as well as aromatic groups, and ethers.

Heterocycles such as pyrroles and thiophenes may also be present. However, actual fuel deposits are generally too complex to be able to make specific band assignments with any degree of certainty.

CONCLUSIONS

The Nicolet 7199 Fourier Transform Infrared Spectrophotometer offers five modes of operation: absorption, emission, single reflectance, attenuated total reflectance, and photoacoustic. The absorption and emission modes were found to be the most suitable for qualitative analysis of bulk and surface properties of accelerated storage/thermal deposits produced under static fuel conditions.

Real fuels produce similar but not identical accelerated storage/thermal deposits. These deposits can readily be distinguished from deposits produced by a model fuel consisting of dodecane and 10 percent tetralin. The nature of the deposits appears to be dependent upon the stress temperature, but independent of the length of stress time.

Low concentrations (175 ppm or less) of spiking agents appear to have little, if any, effect on the nature of the deposit for real fuels. High concentrations (500 ppm or more), on the other hand, appear to have a major effect on the nature of the deposit.

Accelerated storage/thermal deposits produced under static fuel conditions at 250° C appear to be different than accelerated thermal deposits produced on stainless steel foil under flowing fuel conditions in the Modified JFTOT Flat Sample Rig.

Generally, changes occur in the FTIR emission spectra on heating the accelerated storage/thermal deposits under nitrogen, or in the presence of oxygen. Comparison of absorption spectra (a bulk property technique) and emission spectra (a surface property technique) as well as vacuum drying experiments and solvent extraction experiments indicate that these changes may be due to loss of volatile components produced by oxidation, condensation or pyrolysis reactions induced by heating. However, these storage/thermal deposits do not appear to be converted to accelerated thermal deposits on heating.

Because of the relatively small number of possibilities, limited infrared band assignments may be made on deposits from simple model fuel systems. However, deposits from real fuels have the potential of being much more complex. Consequently, for these deposits specific band assignments are difficult to make.

Additional information concerning the chemical structure of fuel deposits may be obtainable from more sophisticated FTIR instruments such as the polarization-modulated Fourier infrared emission microspectrophotometer presently being operated by Lauer (refs. 8 and 9). Preliminary work also suggests that identification of specific compounds present in deposits from the model fuel may be possible using gas chromatography/triple quadrupole mass spectroscopy.

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TABLE I. - FTIR SAMPLE PREPARATION MATRIX^a

Fuels:	Dodecane, Dodecane and 10 vol % tetralin, Jet A, ERBS (Experimental Referee Broadened Specification Fuel, ref. 10), JP-4, JP-5
Spiking agents:	Pyrrole, pyridine, quinoline, thiophene, cumene, acid extract of shale oil, fuel oil # 4
Spiking agent concentrations: ^b	30 ppm, 175 ppm, 500 ppm, 1000 ppm, 1.0 wt % , 2.0 wt %
Stress times:	static fuel at 60° C: 4 to 13 months at 125° C: 1 to 6 weeks at 250° C: 7 to 10 days flowing fuel at 250° C: 2.5 to 8 hrs
Post-deposit stress temperatures:	100°, 125°, 170°, 250° C in nitrogen and in air

^aSamples were not prepared using all possible combinations of conditions.

^bFor pure compounds, values denote heteroatom concentration. For the final two agents, values denote "whole mixture" concentration.

TABLE II. - COMPARISON OF FTIR ANALYSIS MODES FOR FUEL DEPOSITS

Mode	Conditions	Findings
Emission	Sample temperature employed is 87° C	Distinguishable spectra obtained at 50 μ G. Quality improves substantially at 300 μ G. Deposits $\geq$ approximately 300 μ G required (at stated temp.). Post-deposit stressing possible.
Reflectance	"Single" mode	Generally better quality spectra than obtained by emission at 87° C for same samples. Simplest of the modes to employ for sample analysis.
Attenuated total reflectance	KRS-5 crystal	Generally lower quality spectra than obtained by emission or "single" reflectance using same samples. However, using the mode capability of handling 4 identical samples, distinguishable spectra obtained at 64 μ G (8 μ G/cm ²).
Absorption	KBr pellet	Good quality spectra obtained for all samples analyzed. However, deposit quantities must be sufficiently high to permit removal without removing metal substrate. General observations indicate amounts $\geq$ approximately 100 μ G/cm ² are required, depending on deposit nature.
Photoacoustic	Under helium	Lower quality spectra than obtained by emission due to marginal signal to noise ratio at lower frequencies.

TABLE III. - CORRELATION OF INFRARED SPECTRA AND
MOLECULAR STRUCTURE OF MODEL FUEL DEPOSITS (SEE FIG. 15)

Model fuel system	Frequency, cm ⁻¹	Possible structure
Dodecane, tetralin	1780 1730 1670 1600 1600,1580,1490,750 1470,1450,750 1260,1150 1080 820,690,630,570 720	Peroxide or anhydride carbonyl 2-tetralone, unconjugated carbonyl 1-tetralone, conjugated carbonyl Conjugated alkene Ortho-disubst. benzene Aliphatic C-H Phthalate carboxyl Ether, ester, alcohol C-O Vinylic C-H Aliphatic CH ₂ or <u>cis</u> -alkene
Dodecane, Tetralin, Thiophene	1710 1670 1600 1600,1580,1490,750 1460,750 1260,1150 1080 760 650	2-tetralone, unconjugated carbonyl 1-tetralone, conjugated carbonyl Conjugated alkene Ortho-disubst benzene Aliphatic C-H Phthalate carboxyl Ether, ester, alc. C-O 3-subst. thiophene or 2-tetralone Vinylic C-H
Dodecane, Tetralin, Pyrrole	1710 1650 1420 1270 1100 800-650	2-tetralone, unconjugated carbonyl 1-tetralone or 2-pyrrolone Aromatic C=N, pyrroles Phthalate carboxyl Ether, ester, alc. C-O Ortho-disubst. benzene, 2,5-disubst. pyrroles, 3-subst. pyrroles, vinylic C-H

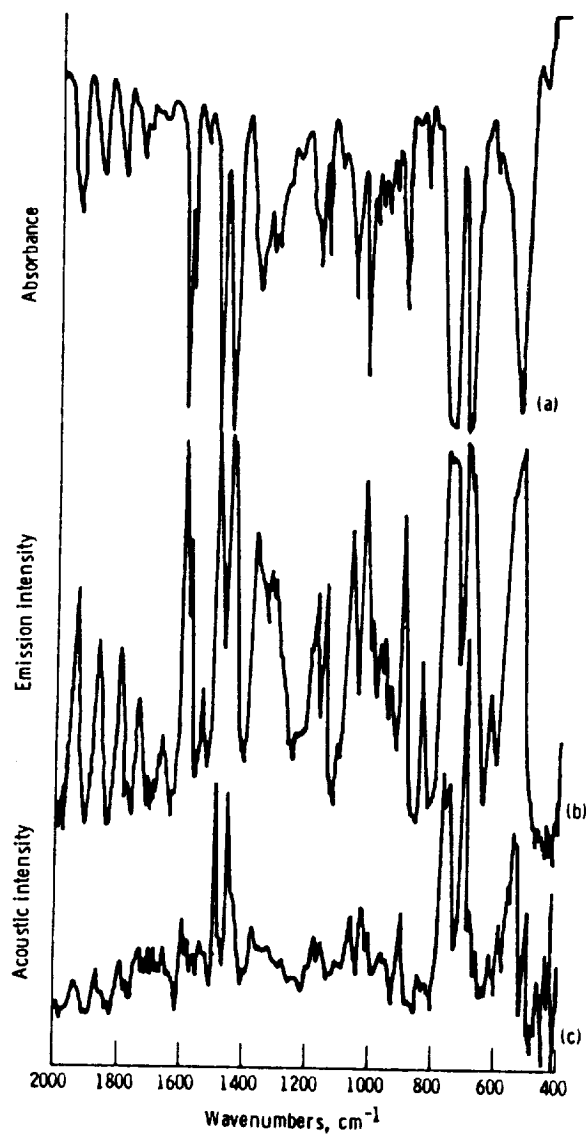


Figure 1. - Spectra of polystyrene film; (a) absorption, (b) emission (1000°C), and (c) photoacoustic.

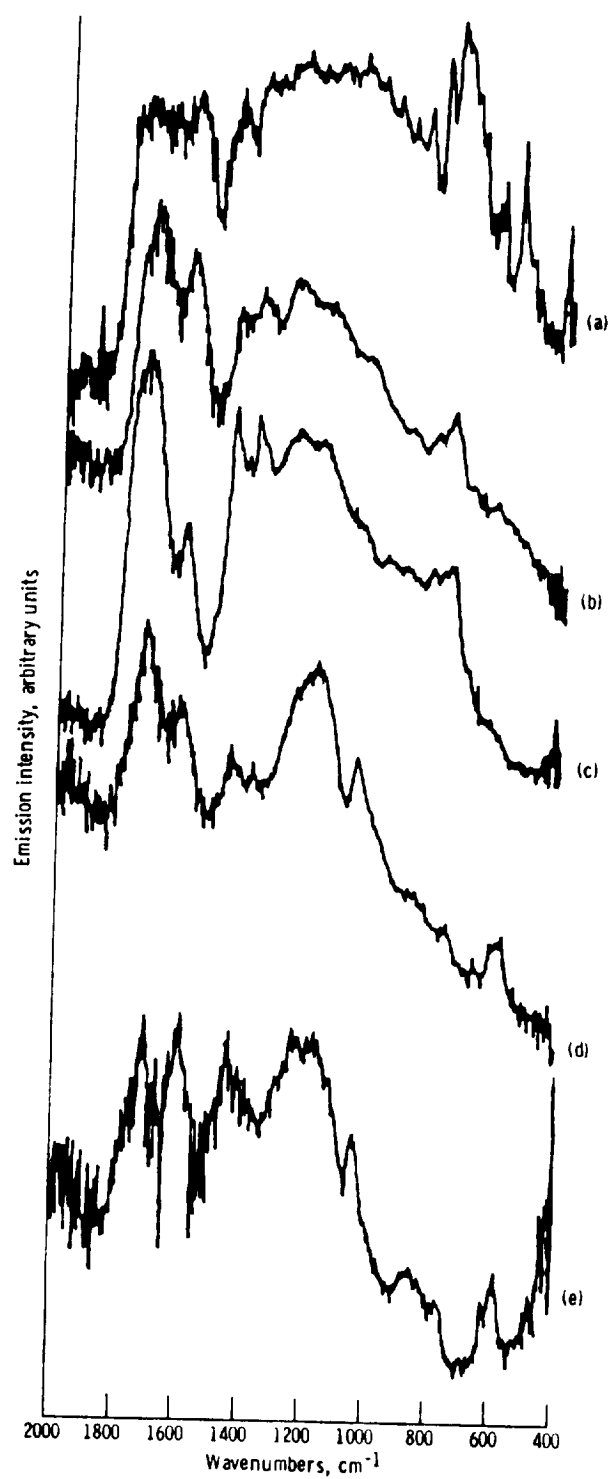


Figure 2 - Emission spectra (100°C) of accelerated storage/thermal deposits produced at 125°C by neat (a) dodecane/tetralin, (b) ERBS, (c) JP-4, (d) JP-5, and (e) Jet A.

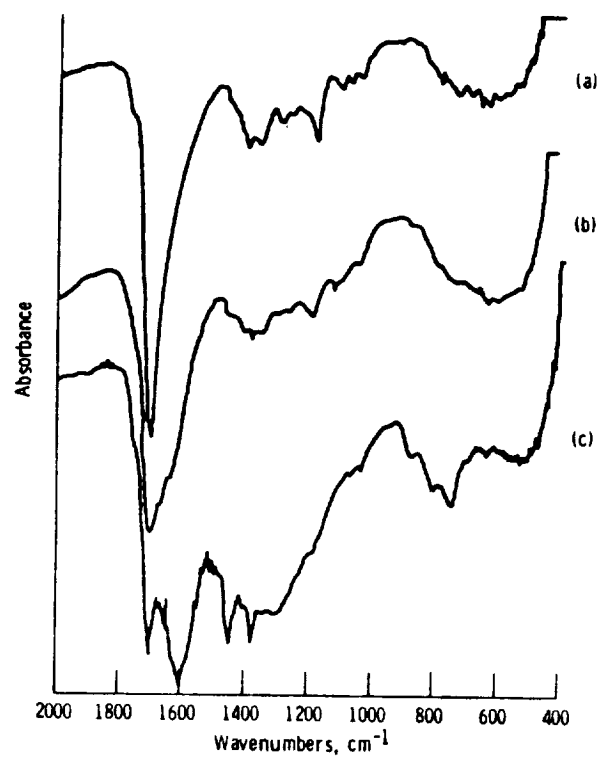


Figure 3. - Absorption spectra of accelerated storage/thermal deposits produced by ERBS spiked with 0.1% pyrrole and stressed at (a) 60°C, (b) 125°C, and (c) 250°C.

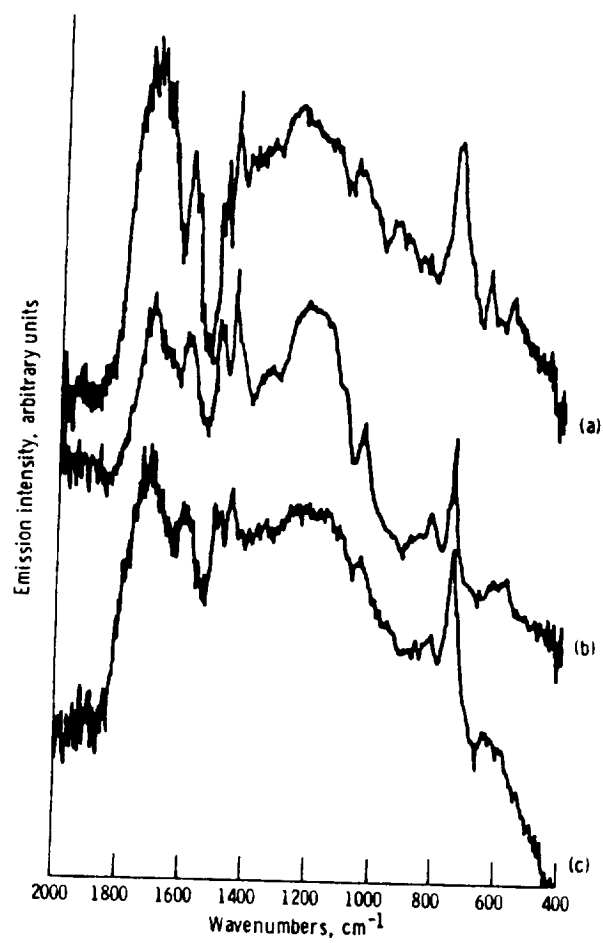


Figure 4. - Emission spectra (100^o C) of deposits produced at 125^o C by dodecane/tetralin spiked with 2 percent thiophene after (a) 6 days, (b) 13 days, and (c) 24 days.

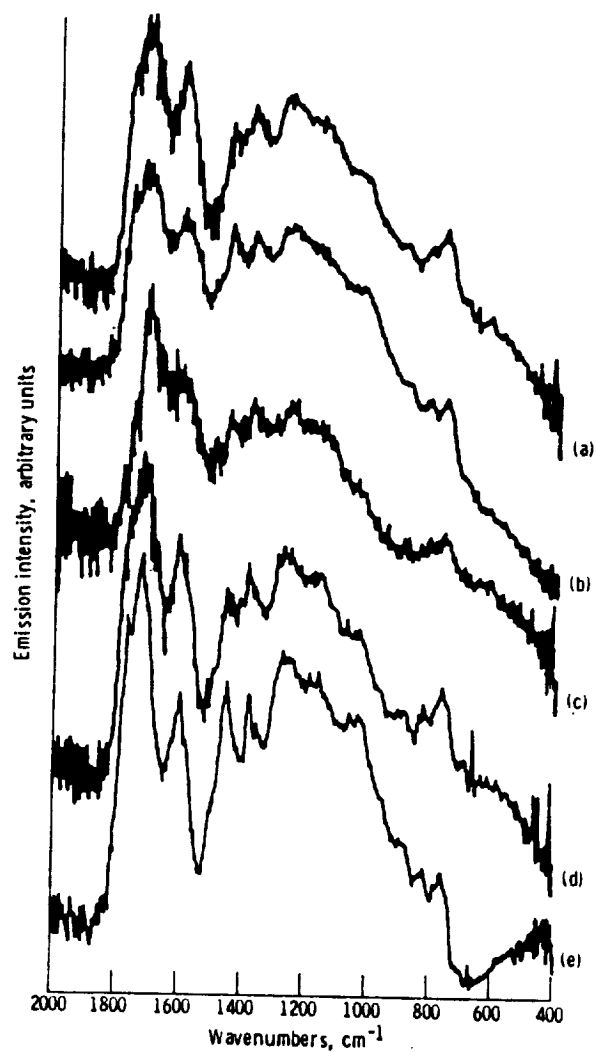


Figure 5. - Emission spectra (100⁰ C) of deposits produced at 125⁰ C by (a) unspiked ERBS, and ERBS spiked with (b) 30 ppm pyrrole, (c) 175 ppm pyrrole, (d) 30 ppm thiophene, and (e) 175 ppm thiophene.

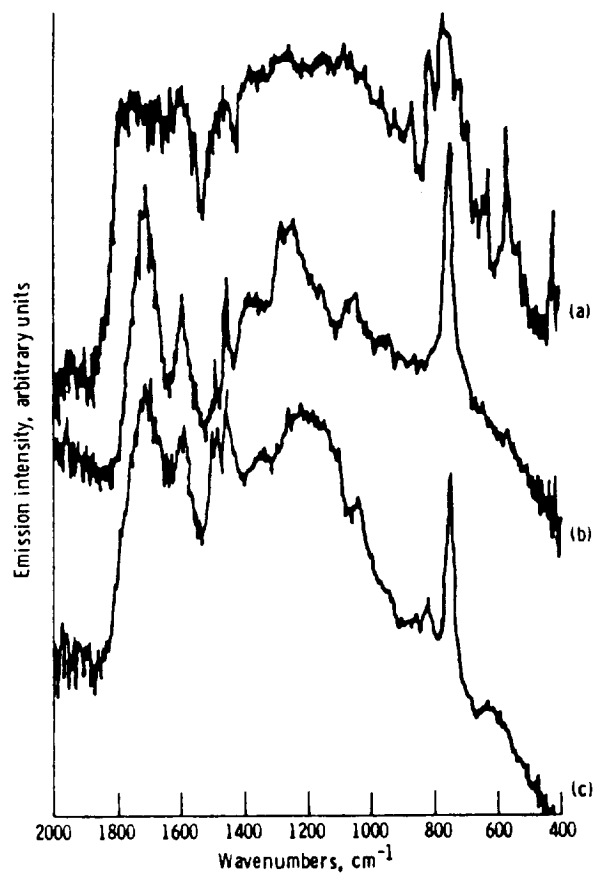


Figure 6. - Emission spectra (100⁰ C) of deposits produced at 125⁰ C by (a) unspiked dodecane/tetralin, and dodecane/tetralin spiked with (b) 30 ppm pyrrole, and (c) 30 ppm thiophene.

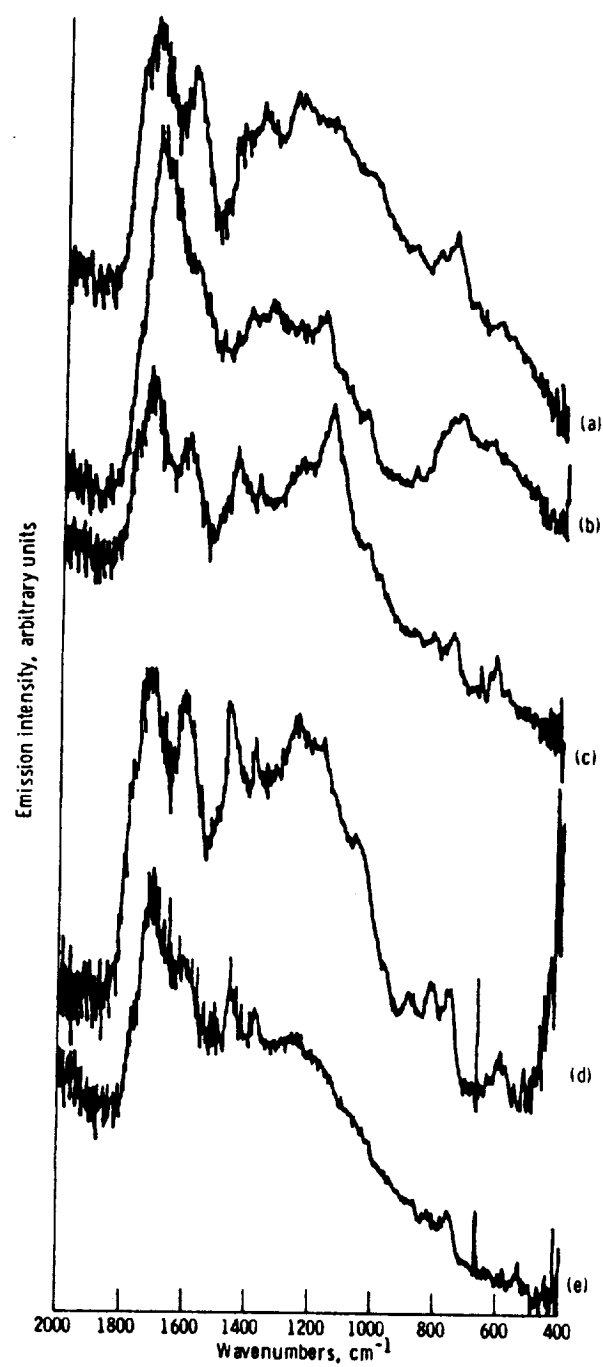


Figure 7. - Emission spectra (100°C) of deposits produced at 125°C by (a) unspiked ERBS, and ERBS spiked with (b) 0.1% pyrrole, (c) 1% thiophene, (d) 1% fuel oil, and (e) 1% shale extract.

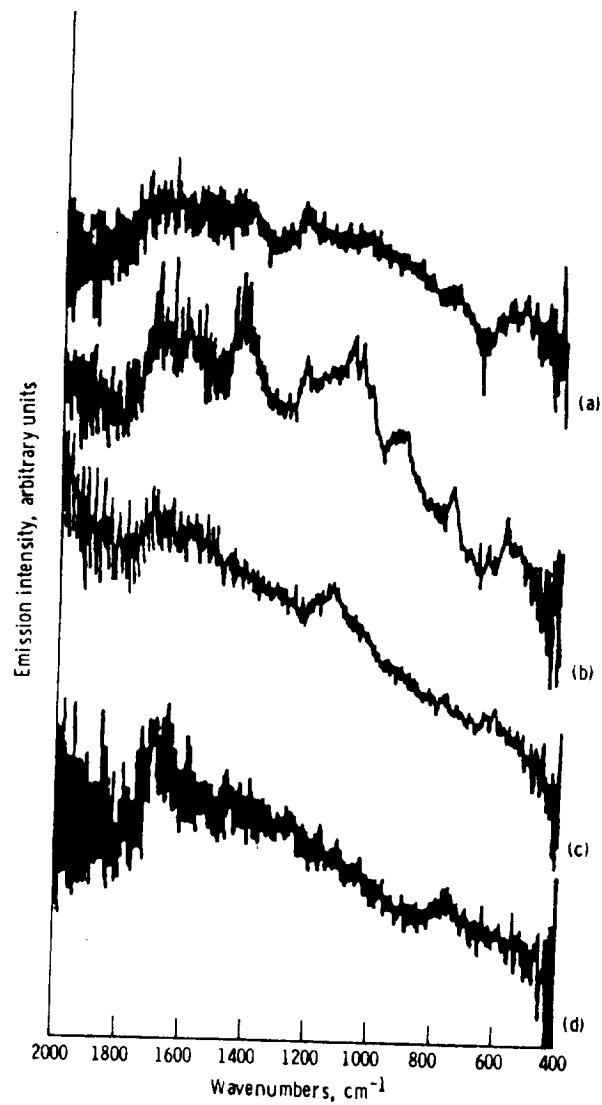


Figure 8. - Emission spectra (1000°C) of accelerated storage/thermal deposits produced at 250°C by ERBS spiked with 1% shale extract under (a) flowing fuel, (b) stationary fuel, and by dodecane/tetralin spiked with 0.1% pyrrole under (c) flowing fuel, (d) stationary fuel.

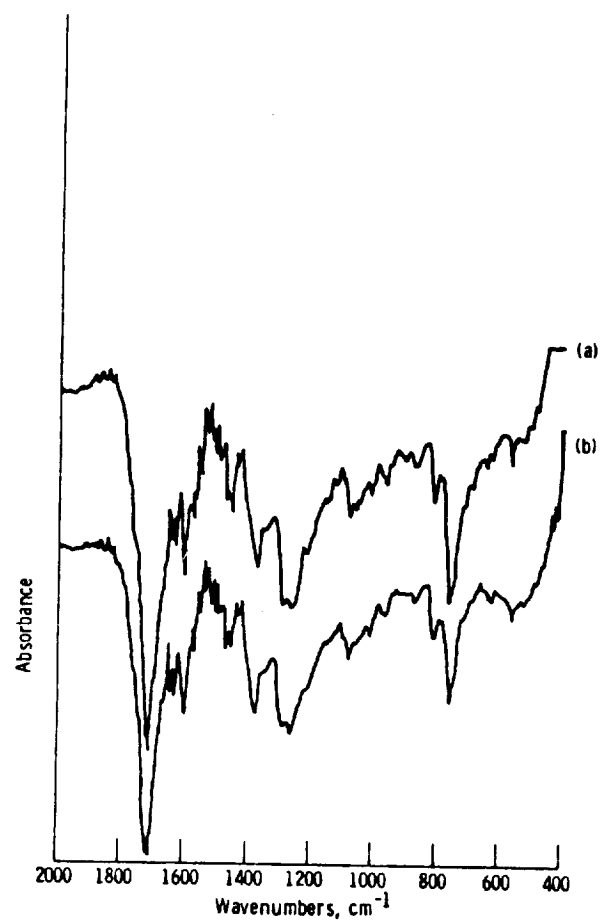


Figure 9. - Absorption spectra of the deposit produced at 125°C by dodecane/tetralin spiked with 175 ppm pyrrole after drying at (a) room temperature and atmospheric pressure, and (b) 80°C and 60 torr.

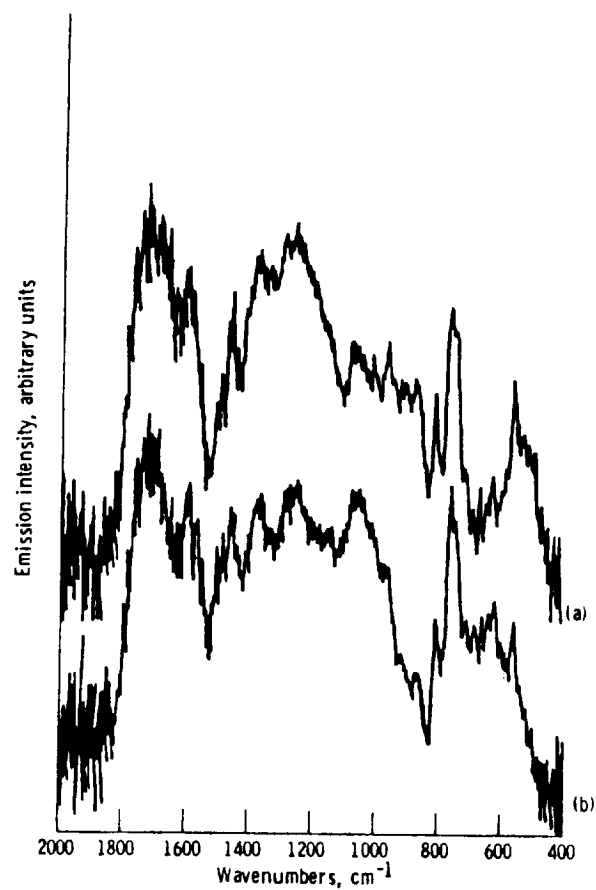


Figure 10. - Emission spectra (60^o C) of the deposit produced at 125^o C by dodecane/tetralin spiked with 175 ppm pyrrole after drying at (a) room temperature and atmospheric pressure and (b) 80^o C and 60 torr.

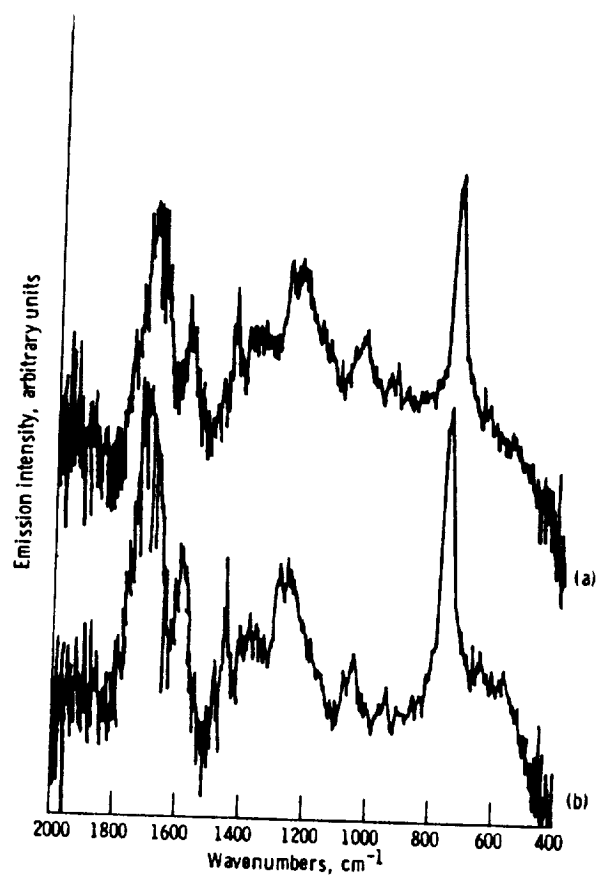


Figure 11. - Emission spectra (60° C) of the deposit produced at 125° C by dodecane/tetralin spiked with 30 ppm pyrrole and dried at room temperature and (a) atmospheric pressure (b) 0.05 torr.

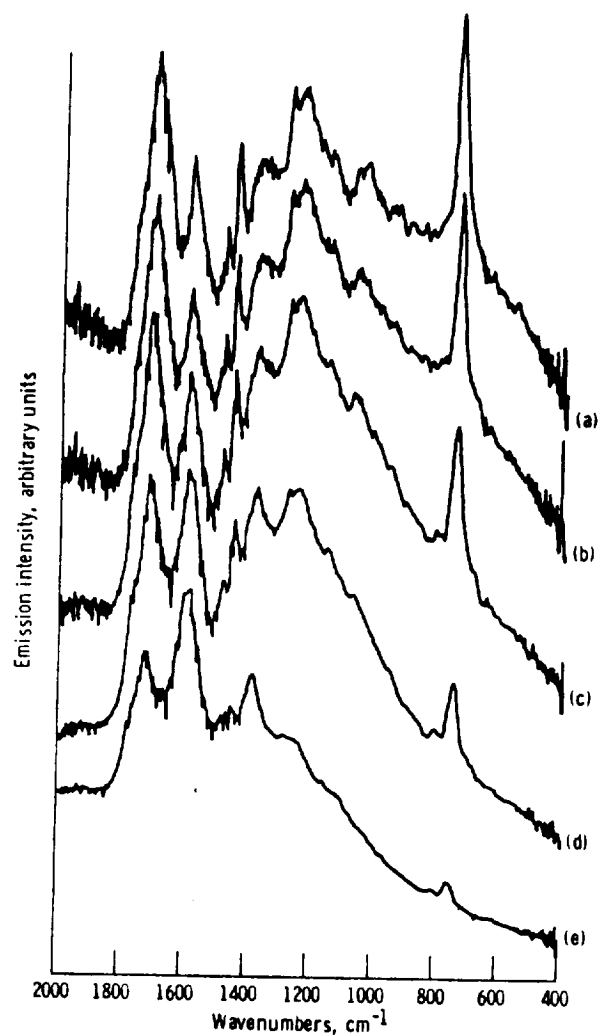


Figure 12. - Emission spectra (100^o C to 250^o C) of the deposit produced at 125^o C by dodecane/tetralin spiked with 30 ppm pyrrole and dried at room temperature and atmospheric pressure (a) immediately after heating to 100^o C at atmospheric pressure under nitrogen, (b) after 30 min at 100^o C, (c) after 15 min at 125^o C, (d) after 15 min at 170^o C, and (e) after 20 min at 250^o C.

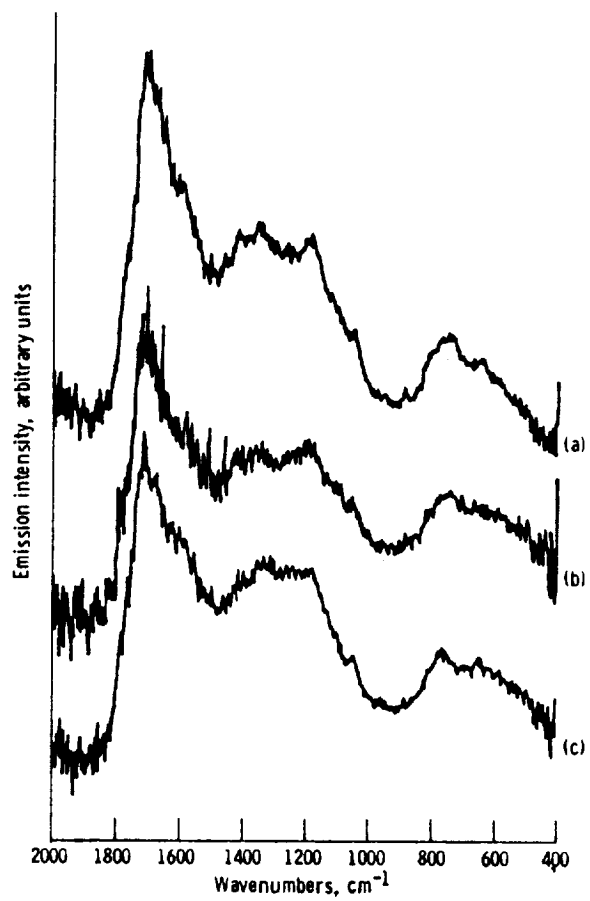


Figure 13. - Emission spectra (100^o C to 250^o C) of the deposit produced at 125^o C by ERBS spiked with 0.1% pyrrole and dried at 80^o C and 60 torr (a) immediately after heating to 100^o C at atmospheric pressure under nitrogen, (b) after 30 min at 170^o C, and (c) after 30 min at 250^o C.

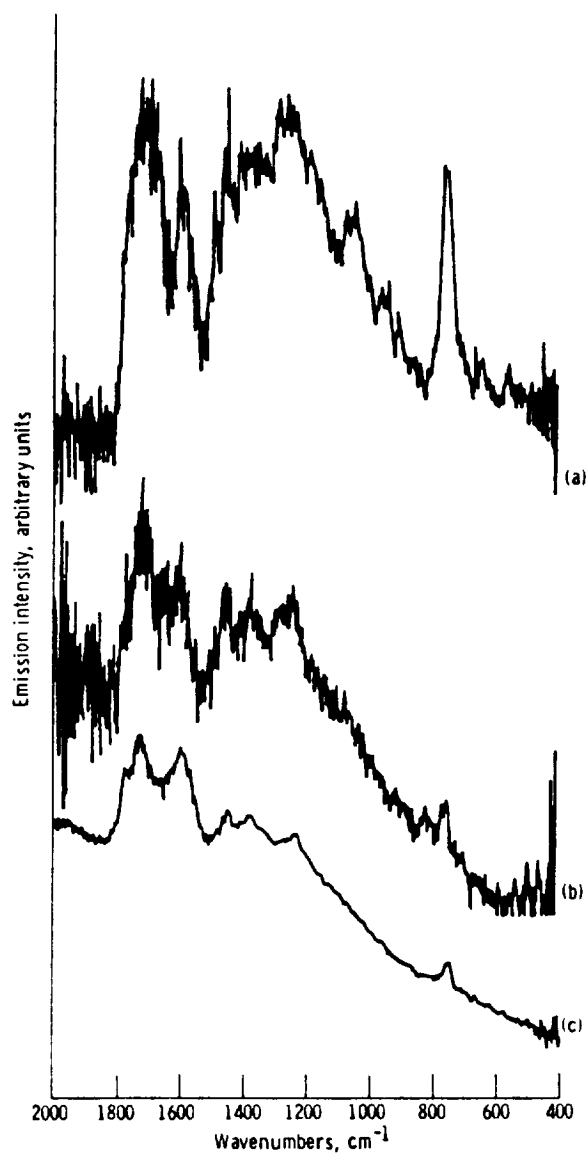


Figure 14. - Emission spectra (60^o C and 250^o C) of the deposit produced at 125^o C by dodecane/tetralin spiked with 30 ppm pyrrole and dried at room temperature and atmospheric pressure (a) initially, (b) after rinsing with methyl alcohol, (c) after heating remaining material to 250^o C for forty min at atmospheric pressure under nitrogen.

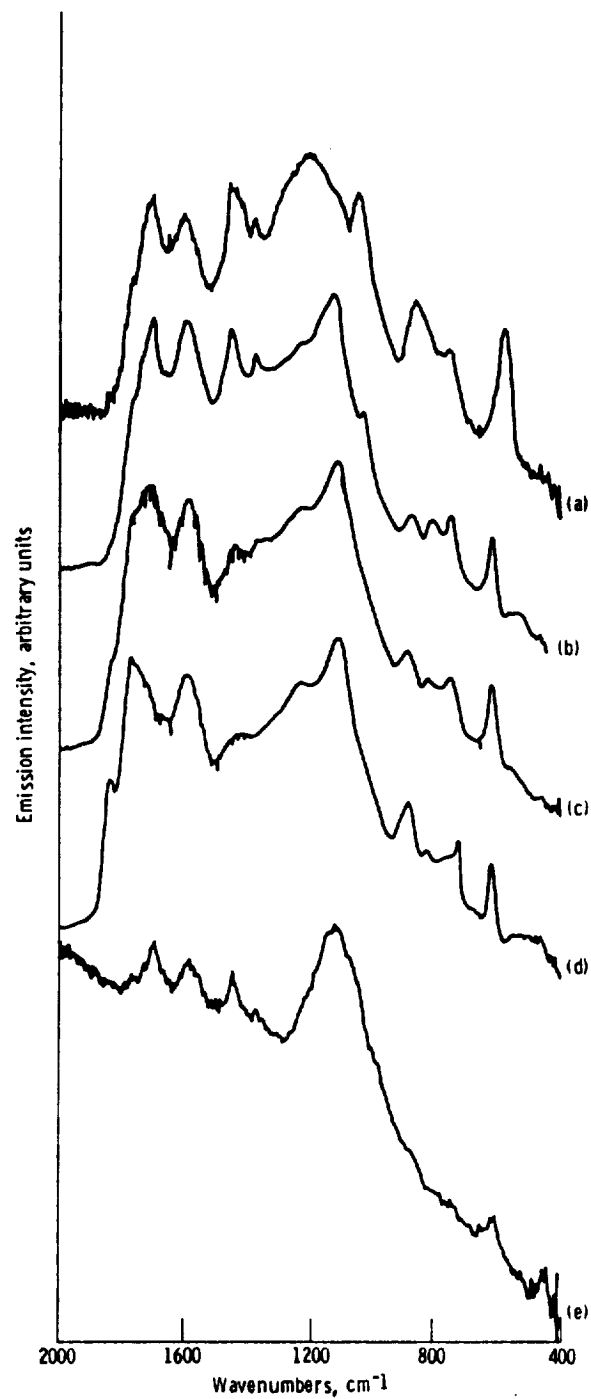


Figure 15. - Emission spectra (125°C and 250°C) of the accelerated storage deposit produced at 125°C by Jet A spiked with 2% fuel oil No. 4 after (a) 5 min at 125°C under nitrogen, (b) 5 min at 250°C under nitrogen, (c) 10 min at 250°C in air, and (d) 4 hr at 250°C in air. (e) Emission spectrum (250°C) of the accelerated thermal deposit produced in the MJFSR at 250°C by the same spiked fuel.

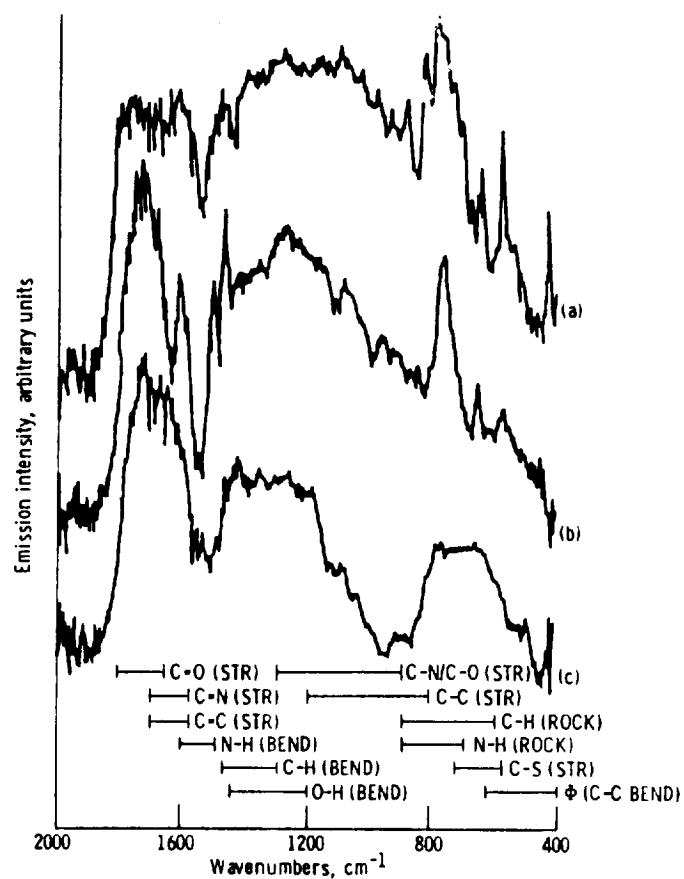


Figure 16. - Correlation of Infrared spectra and molecular structure for deposits produced by (a) unspiked dodecane/tetralin, and dodecane/tetralin spiked with (b) 2% thiophene, and (c) 0.1% pyrrole.

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16. Abstract Five modes of operation of the Nicolet 7199 Fourier Transform Infrared spectrophotometer have been evaluated for application in analysis of the chemical structure of accelerated storage/thermal deposits produced by jet fuels. Using primarily the absorption and emission modes, the effects of fuel type, stress temperature, stress time, type of spiking agent, spiking agent concentration, fuel flow, and post-depositional treatment on the chemical nature of fuel deposits have been determined.					
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