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ENVIRONMENTAL DEGRADATION OF FUELS, FLUIDS, AND RELATED MATERIALS FOR AIRCRAFT

MONSANTO RESEARCH CORPORATION
DAYTON LABORATORY
DAYTON, OHIO 45407

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

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Investigations of the composition and properties of a number of hydrocarbon fuels are described. Fuel analyses for hydrocarbon types, trace metals content, trace organic contaminants and elemental composition are presented. Studies of the fluorescence spectral properties of aircraft exhaust emissions are described, as is an investigation of the feasibility of using fluorometric measurements on fuels to supplement coker thermal stability data. (cont'd)

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20. **ABSTRACT** (cont'd)

An investigation of the experimental parameters of the hot manifold flammability test is discussed along with test results for various hydraulic fluids.

Components recovered from aircraft crash sites have been examined to determine factors contributing to aircraft failure. Studies supporting Air Force programs for the formulation and specification development of high density fuels are presented.

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SECTION I

INTRODUCTION AND SUMMARY

This report describes work performed during a two-year program of research and development on the analysis and characterization of fuels, fluids and related materials. Many of the investigations and analytical studies under this program were conducted to aid in solving Air Force operational problems, to provide a data base for establishing realistic fuel specifications and to provide support for on-going in-house programs.

Major areas of investigation included:

- Aircraft exhaust emission studies, in which fluorescence spectral properties of jet engine exhaust were investigated, as well as the mass and size distribution of exhaust particulates.

- High density fuel investigations, wherein the properties of fuel components and blends were measured, air/fuel solubilities were determined and elemental and blend compositions were established. This work included a pilot plant scale distillation of 1100 gallons of fuel.

- Flammability tests, in which hydraulic fluids were tested for ignition on a hot surface under varying conditions. Components recovered from aircraft crash sites were also examined.

- Fuels analysis, by which fuel hydrocarbon types, metals content, elemental composition and trace organic contaminants were determined.

- Specialized support studies, in which such measurements as the mass of fuel deposits in B-1 fuel/oil cooler tubes, the composition of calibration gas mixtures, and the characterization of filter deposits were conducted.

SECTION II

FLUORESCENCE SPECTRAL STUDIES

A. EXAMINATION OF HYDROCARBONS IN JET ENGINE EXHAUST

The Air Force has sponsored the design and construction of a computer operated laser Raman spectrometer which has shown promise as a technique for the in-situ analysis of turbine exhaust gases. This sophisticated instrumentation has been demonstrated to function quantitatively for N_2, O_2, CO_2, smoke and temperature measurements (ref. 1). The device has the potential of allowing studies of combustion processes involving temperature and composition measurements which are not practical by other existing probe techniques. One limitation on the use of the system for exhaust gas analysis, however, has been broad-band fluorescence which is excited by the nitrogen laser. The strong fluorescence background seriously interferes with the relatively weak Raman signal. Studies were performed by Monsanto Research Corporation to aid in finding ways of circumventing the problem of fluorescence interference.

Full characterization of the fluorescence spectrum of hot jet engine exhaust, using the laser Raman spectrometer is not practical. Instead, a laboratory spectrophotofluorometer (Aminco Bowman SPF No. 4-8202) was used to evaluate the fluorescence of exhaust gases dissolved in a solvent at room temperature.

1. Literature Survey

In order to relate data obtained for solutions with data from hot exhaust gases, a literature survey was conducted to assess the effects on fluorescence of changes in temperature, pressure and physical state of the specimen.

An additional objective of the survey was to characterize the luminescence properties of compounds known to be present (ref. 2) in the exhaust gases. The literature survey findings were supplemented with laboratory fluorescence tests for some of the known constituents and are summarized in Appendix I. It was concluded that the general fluorescence spectral distribution of dissolved exhaust components in a solvent is similar to that which is observed directly in the hot exhaust. Temperature broadening is believed to account for much of the difference in spectral shape.

This conclusion was tested by spectral data obtained in the hot exhaust of a T-53 jet engine. Laser excited fluorescence was observed (ref. 1) when the engine was operated at idle power conditions. The fluorescence was believed to be due largely to

Mobil Jet Oil II which was suspected of entering the exhaust stream. The exhaust fluorescence was excited by a pulsed nitrogen laser operating at 337.1 nm. Fluorescence emission spectra excited at various wavelengths were recorded for the Mobil Jet Oil II and are presented in Figure 1. The exhaust spectrum and that of Mobil Jet Oil II are shown in Figure 2. The two spectra were normalized at 365.8 nm for ease of comparison. The close similarity is striking, the chief difference being a broadening at the higher wavelengths in the exhaust spectrum. This may be a temperature effect or be due to the presence of a different fluorescing species. The test is, of course, not conclusive but it suggests that fluorescence analysis in the laboratory can be used to predict the essential features of a fluorescence spectrum excited in hot exhaust gases.

2. Collection of Exhaust Combustion Products

Over the course of this work, exhaust combustion products from the T-56 Combustor located at the Air Force Aeropropulsion Laboratory, Wright-Patterson AFB were collected in three separate ways. The first approach involved the collection of a volume of gas (using a FEP sampling bag) which was then processed through a two-stage cryogenic trap. This trapping procedure was quite efficient, however its limitation lies in the transportation of the exhaust gases to the laboratory for processing. Sample bags, while being relatively inert, provide a surface for product condensation. Solvent rinses of the sample bags showed that fluorescing species were collected on the interior surface of the bag.

The fluorescence spectrum of the material washed from the bag was essentially the same as was obtained for the gaseous condensates. However, it is of interest to compare the excitation spectrum of this rinse with a similar spectrum of the vapor phase condensate shown in Figure 3. Both spectra are plots of the emission at 350 nm versus excitation wavelength. Both indicate that maximum fluorescence at 350 nm is obtained by excitation at approximately 290 nm. However, an excitation maximum is also shown at 240 nm for the condensate and 250 nm for the hexane rinse. The intensity ratios of the two peaks in these excitation spectra differ greatly, indicating that the fluorescence at 350 nm results from more than one component.

The second sampling method involved the more direct approach of passing the exhaust gases through a bubbler containing a measured volume of spectroscopically pure hexane, which had been cooled to prevent evaporation. Though the collection efficiency of this method has not been established, a linear relationship between total hydrocarbon content (THC) and fluorescence was obtained as is shown by data plotted in Figure 4. The last sample of the bubbler-collected series, 4AL04, shows a THC content of 675 ppm but does not exhibit a linear increase in

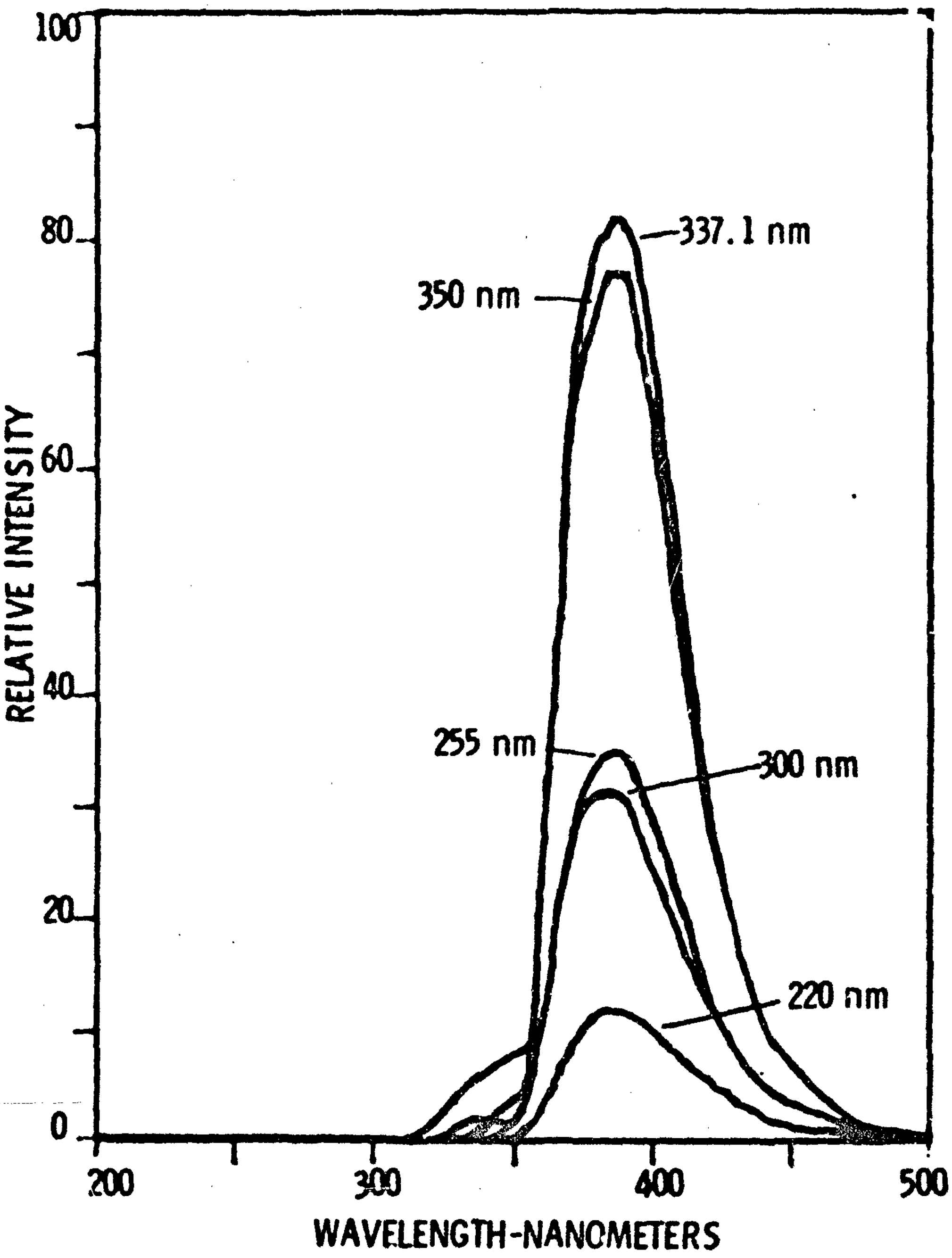

Figure 1. Fluorescence Excited at Various Wavelengths for Mobil Jet Oil II.

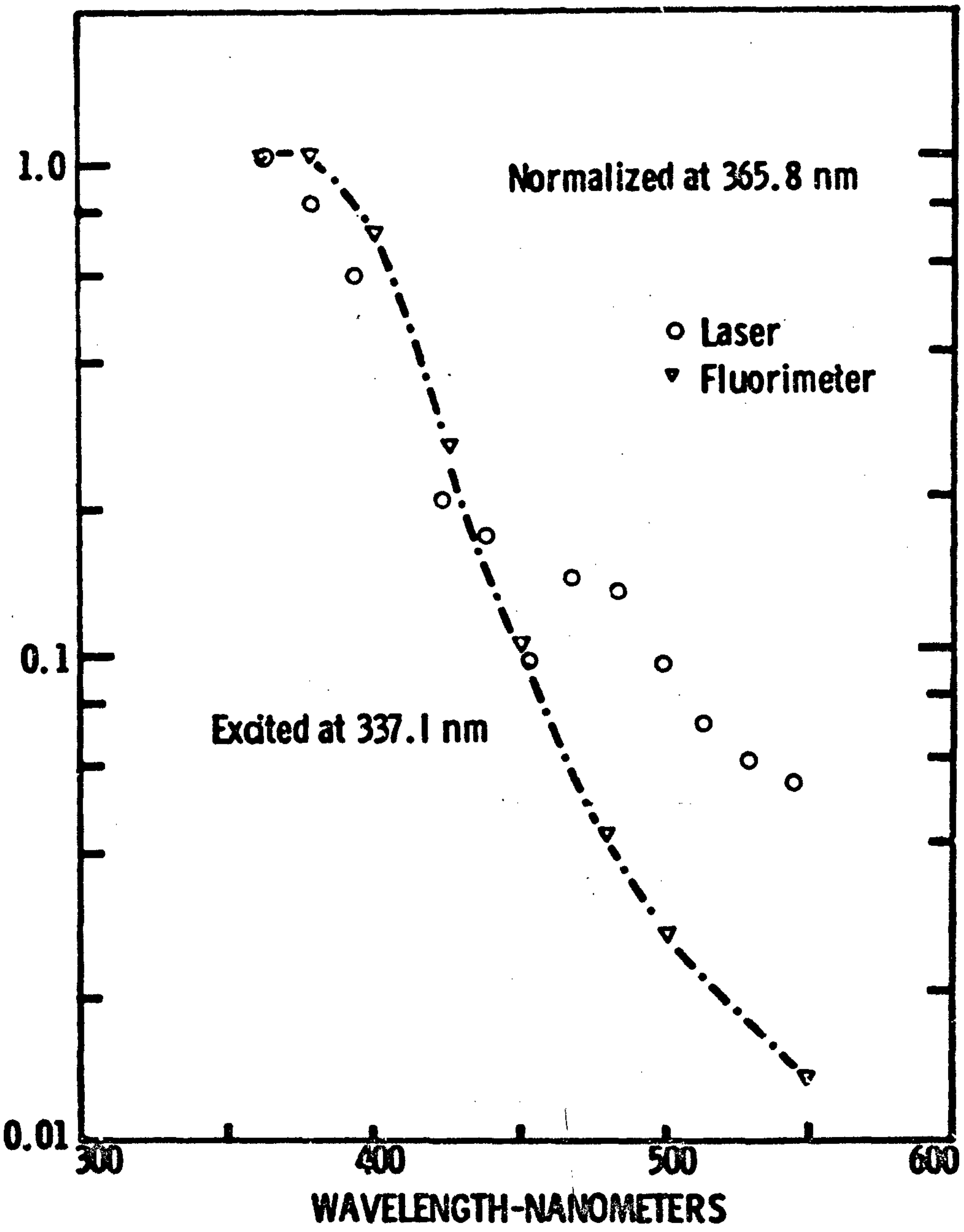

Figure 2. Comparison of Fluorescence Excited by Laser to That of a Laboratory Fluorometer for Exhaust of T-53 Combustor Using Synthetic Lubricant.

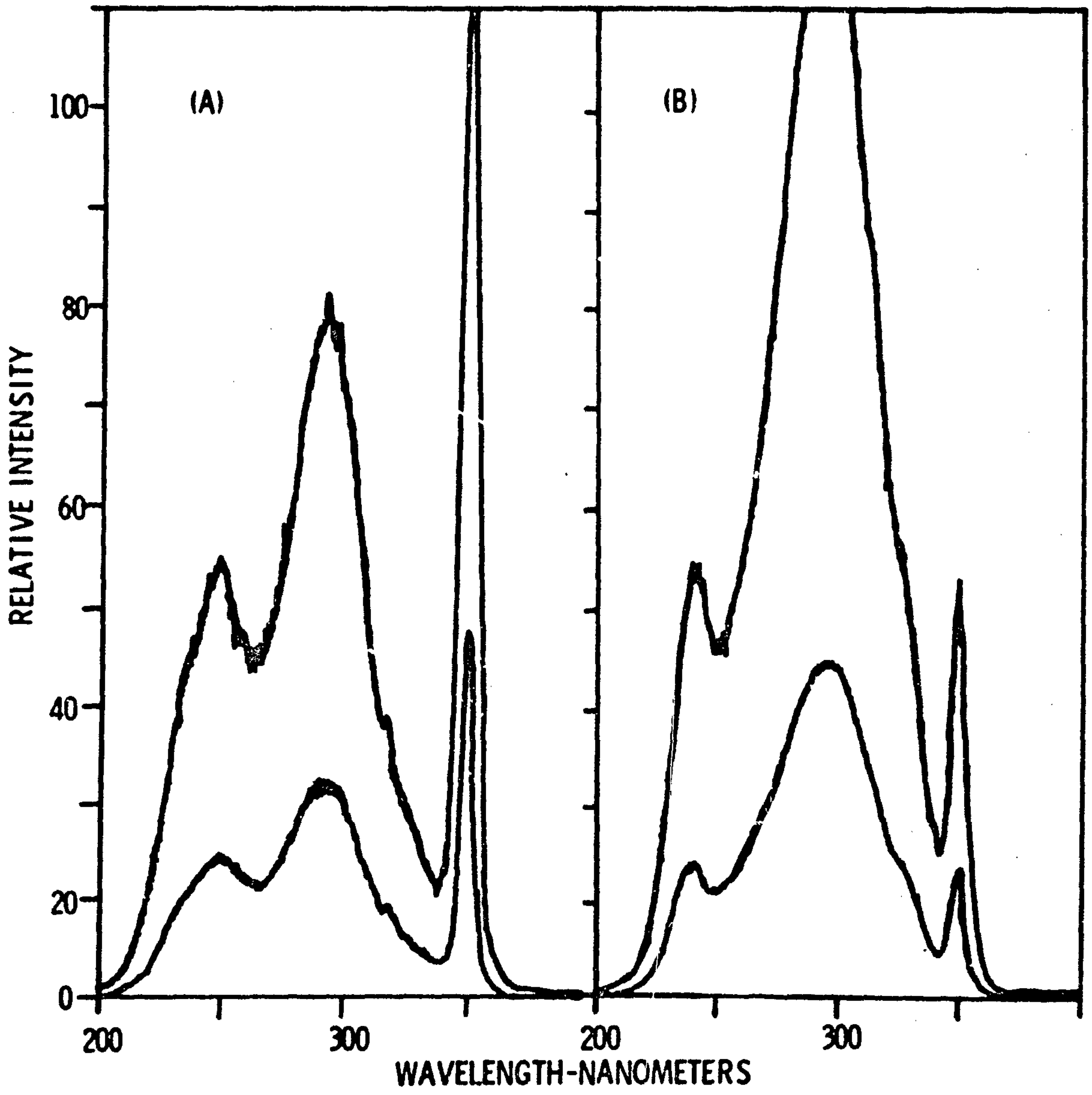

Figure 3. Excitation Spectra of: (a) Vapors Condensed from Sample Bag, (b) Materials Rinsed from Sample Bag with Hexane.

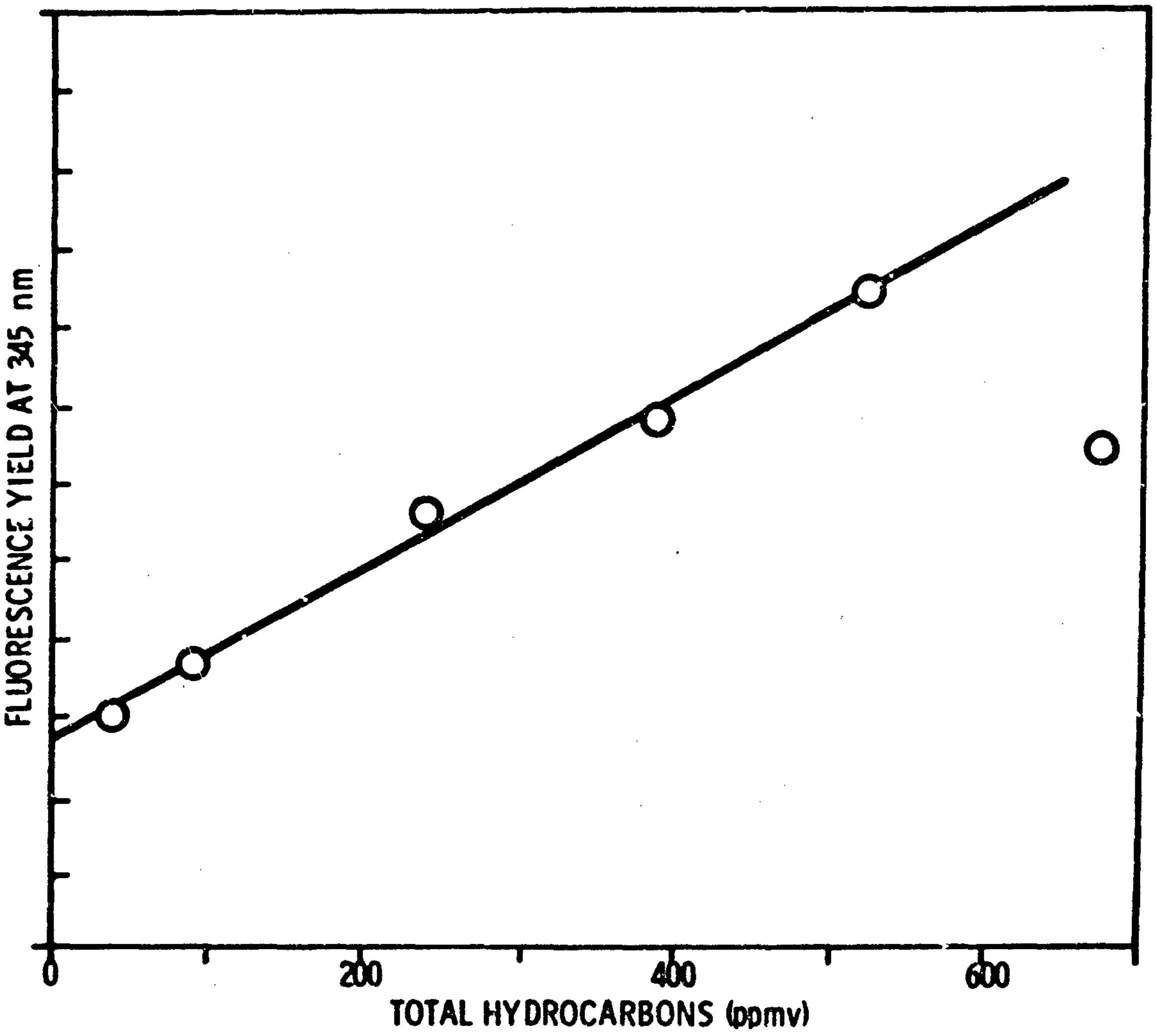

Figure 4. Correlation of Exhaust Total Hydrocarbon Content with Fluorescence for JP-4 Fuel.

fluorescence. This is believed to be because the hydrocarbon content is largely due to unburned JP-4 fuel in this particular specimen. Tests have shown that JP-4 does not fluoresce significantly under these excitation conditions.

This correlation of THC with fluorescence agrees with observations made using the laser Raman system.

Because the hexane bubbler collector was cooled with dry ice, moisture in the exhaust caused icing with an attendant stoppage of flow. Periodic deicing was required or the use of ice water cooling.

For later experiments (joint combustor experiments) the apparatus was redesigned to have three separate sections as shown in Figure 5. Either hexane, as used previously, or cyclohexane, is a satisfactory solvent. Cyclohexane was selected because it has better solvent properties for polyaromatic compounds and is a commonly used solvent in spectrofluorometry. The solvent cyclohexane required the use of only two legs of the collection system. The bubbler was cooled with an ice-water mixture while solvent vapors carried out of the bubbler were recovered in the dry ice trap which followed.

In order to obtain information on particulates, a filtering unit was incorporated into the apparatus. By this means, both filtered and unfiltered exhaust vapors were sampled. Comparison of these samples provided a means of determining if fluorescing material was present as particulate matter or as vapors. The filter system was also used to collect particulate matter for particle size distribution measurements.

3. Magnitude of Fluorescence Interference with Raman Signal

A 3371 Å laser source is employed on the experimental Raman system. Quantitative information was required on how the fluorescence interference would shift at wavelengths above and below the 3371 Å excitation wavelength. For this purpose the fluorescence data were used to calculate ratios of the relative magnitude of fluorescence measured at 2330 wave numbers from 3371 Å to that at 2330 wave numbers from other excitation wavelengths. The value 2330 cm^{-1} corresponds to the Raman shift for diatomic nitrogen. A plot of these ratios versus excitation wavelengths gives the relative magnitude of the fluorescence interference which might be expected with the N_2 Raman line. All data, of course, were corrected for instrument response.

Since the Raman signal is wavelength dependent and varies with the fourth power of the wavelength (λ), this variation should be taken into account when analyzing the fluorescence data. Thus if the fluorescent intensity excited at λex and

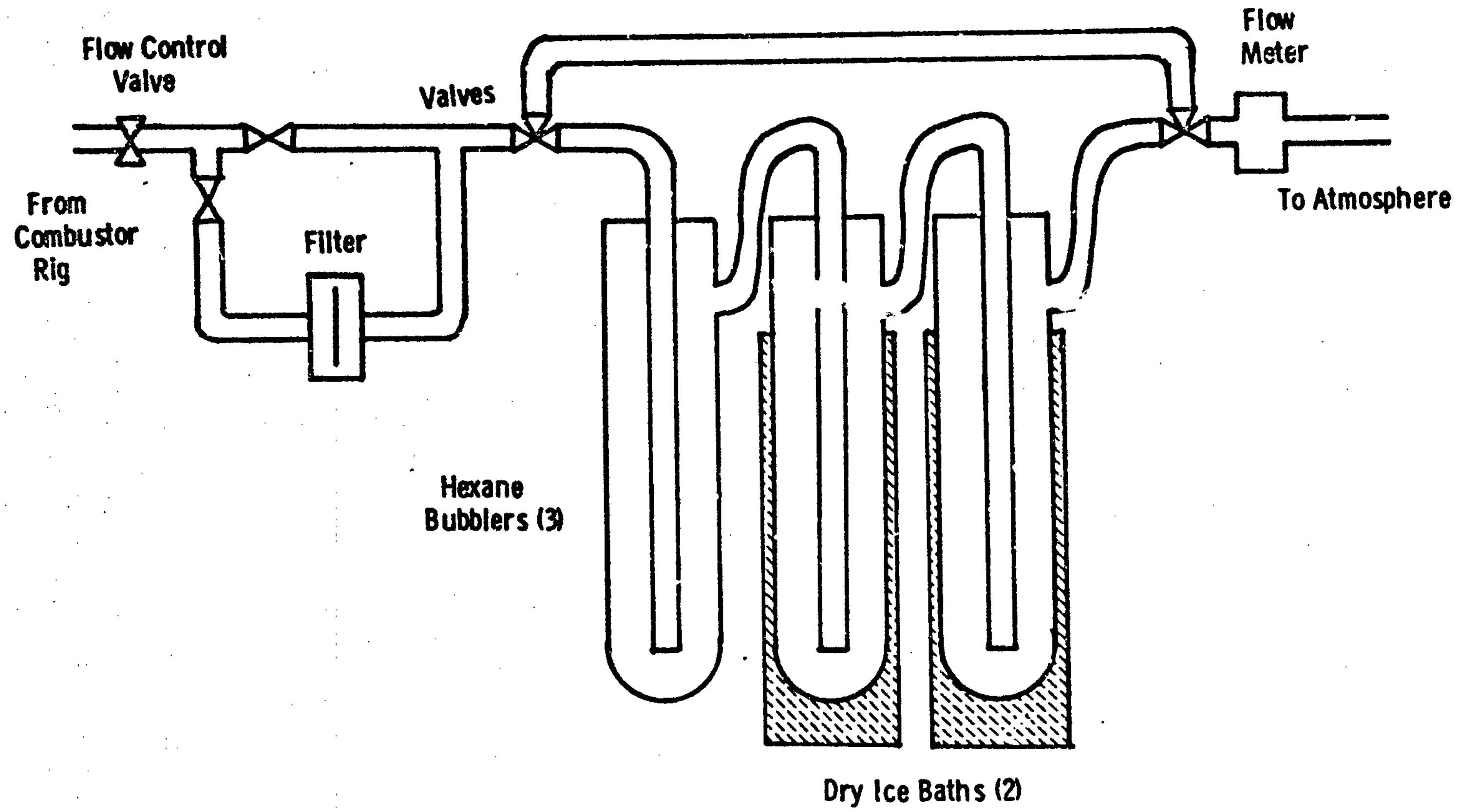

Figure 5. Modified Exhaust Gas Collection Apparatus.

measured at λ is represented by $n_F^{\lambda ex}(\lambda)$, the variation of the fluorescence interference with the Raman signal may be expressed by a plot of

$$\frac{n_F^{337.1}(365.8) \cdot (365.8)^4}{n_F^{\lambda ex}(\lambda) \cdot \lambda^4}$$

versus excitation wavelengths, λex.

To calculate a series of these ratios, fluorescence measurements were made for each specimen at five different excitation wavelengths from 300 to 400 nm. Essentially no fluorescence was observed at λex above 400. Representative data are plotted. Using a semilog presentation, data points adhere reasonably well to a straight line plot as shown in Figure 6. Plots are for samples collected both by sample bag and hexane bubbler.

4. Data from Joint Combustor Experiments

Data were collected as a part of a joint test program between the Air Force Aeropropulsion Laboratory (AFAPL) and four other organizations, one being Monsanto Research Corporation. The AFAPL T-56 combustor was used to generate exhaust emissions under different conditions and burning different hydrocarbon fuels.

Samples from a total of 13 tests were collected. Two specimens, one filtered and the other unfiltered, were collected for each test point. Uniform volumes of exhaust gas (1.055 ft^3) were collected in all cases. Each sample was collected in 40 ml of cyclohexane. Filtered samples (using glass fiber membranes, Scientific Glass Blowing, Type A PR1002-GFS) were taken during approximately the first twenty minutes of the test and unfiltered samples were taken during the second twenty minutes. During the third twenty-minute period, vapors were drawn through a filter (AAWP 293 Millipore, 0.8μ) for particle size distribution measurements. A glass membrane was used for the first filtration because this type of filter is unaffected by solvent and thus could be subjected to solvent extraction if required.

a. Evaluation of Fluorescence

An Aminco-Bowman spectrophotofluorometer which has been modified by the addition of a ratio recording photometer was used for all fluorescence measurements. The ratio recording system provides automatic correction of spectra for variations in the spectral distribution of the xenon lamp, the spectral characteristics of the optical system, and the spectral response of the photomultiplier.

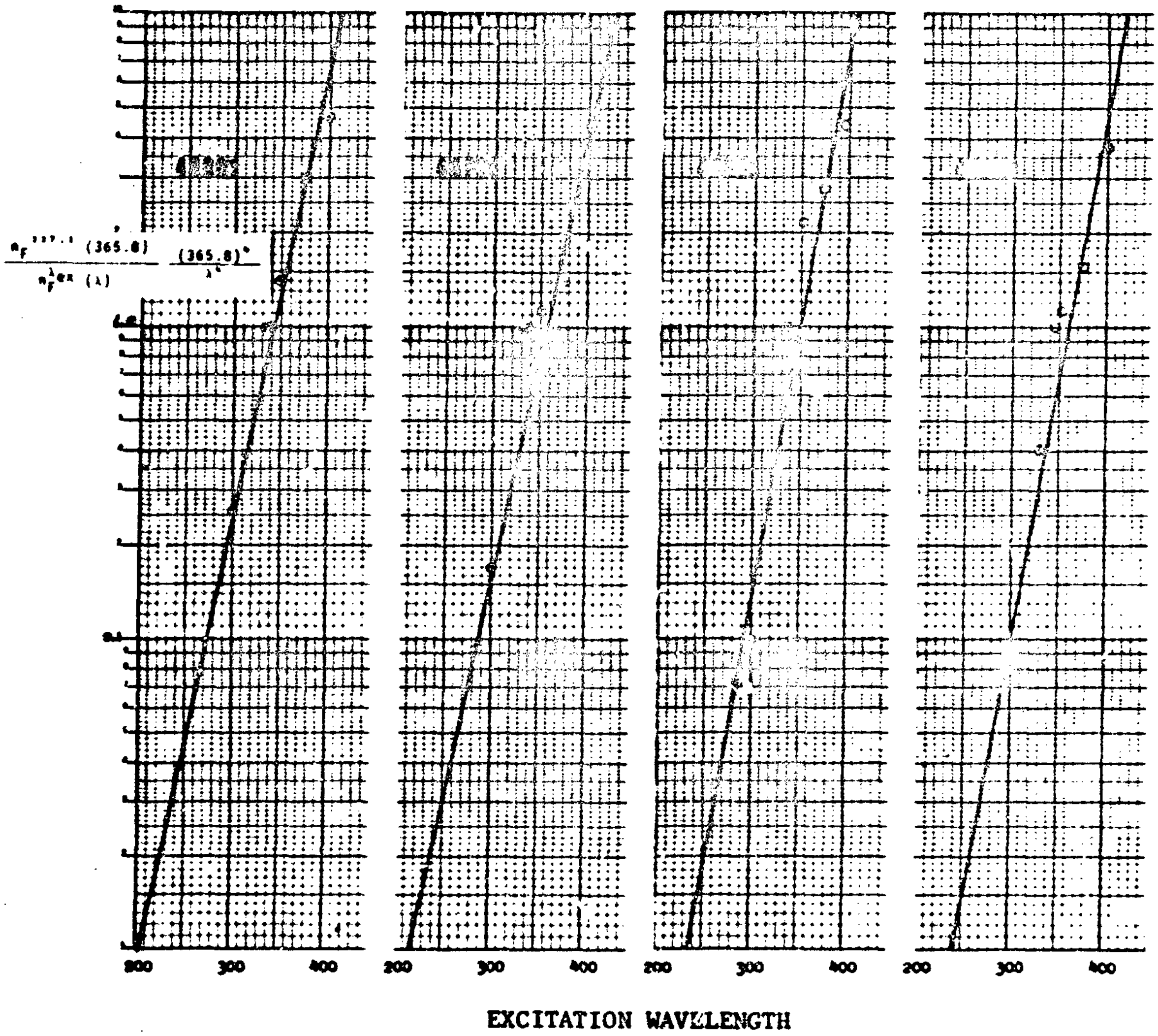

Figure 6. Variation of Fluorescence Interference with Raman Signal with Excitation Wavelength.

Preliminary spectral data for the cyclohexane solutions showed maximum fluorescence at approximately 325 nm. An excitation spectrum, with emission at 325 nm, was recorded for one of the stronger fluorescing samples (5BI02). This spectrum indicated that maximum fluorescence at 325 nm is obtained by irradiation at 255 nm. That excitation wavelength was used to record a fluorescence spectrum for each of the cyclohexane solutions. As expected, the fluorescence intensity varied considerably from sample to sample but in each case, filtered and unfiltered exhaust gases from the same test point gave fluorescence of essentially identical intensity. This indicates that the fluorescing exhaust components were not removed with the particulate matter by the filter. Cyclohexane extraction of several of the filters yielded no observable fluorescence, thus confirming this finding.

Table 1 presents a summary of the fluorescence data. Fluorescent peak intensities (325 nm) versus the total hydrocarbon content of the exhaust are plotted in Figure 7. Data for pure hydrocarbon fuels, that is, those having neither pyridine or ferrocene added, adhere to the curve. The JP-8 data point which falls above the curve is an exception. Samples containing 1.6% pyridine also contained added aromatics at the 25% level, a factor that may be more important than the presence of pyridine in causing the increase in fluorescence. Pyridine itself in cyclohexane gives no significant fluorescence. Both ferrocene-containing fuels showed only low hydrocarbon levels in their combustion products. However, one of them (5BK02) showed more intense fluorescence than the other (5BH02).

In all cases, fluorescence peaked at 325 nm and this is the point where intensities were measured. It thus does not seem likely that the correlation of fluorescence peak integrated area to total hydrocarbons would substantially change the Figure 7 plot.

Qualitatively spectra are similar to those obtained in previous combustor tests. In those tests, the major fluorescence occurred at 345 nm rather than the currently observed 325 nm.

Figures 8 and 9 illustrate excitation and emission spectra of collected exhaust specimens from the alternate fuel (5BM) and Jet A fuel (5BL), respectively. These are typical of the fluorescence spectra obtained in these experiments.

A complete account of these experiments has been prepared and are given in references 3 and 4.

b. Particle Size Distribution Measurements

Filters, on which particles for size distribution measurements were collected, were sectioned prior to preparation for microscopic examination. The procedure consisted of placing the filter section on a drop of cement which acted as both a clearing agent and a mounting medium. After the cement hardened, a X970 occular micrometer was used for the particle size classification. The range of diameters was divided into class intervals, the size of which increased by a geometrical progression. The percent of the particles for each class interval is given in microns (μm) and is presented in Table 2.

5. Possible Fluorescing Compounds

In recording fluorescence spectra of complex mixtures such as presented by combustor exhaust vapors, component interactions such as quenching, stabilization, and sensitization invariably take place. These processes together with increased temperature and pressure, tend to produce a total fluorescence spectrum somewhat different than the sum of the spectra for the individual components. Differences exist between the fluorescence of hexane bubbler specimens and that of the exhaust vapors as observed with the Raman spectrometer; these must be taken into consideration in interpreting results. Firm conclusions cannot yet be drawn concerning the identity of fluorescing exhaust species; however, a number of possibilities can be considered.

Nonaromatic hydrocarbons and alcohols can be virtually eliminated from consideration since any fluorescence, if it occurs, is in the vacuum ultraviolet region. Other groups of compounds also fall in this category, as indicated in the previous section. Similarly, inorganic gases do not seem likely to be among the fluorescing components since only NO_2 is excited in the range of interest. Fluorescence is excited at 400 nm but completely disappears at pressures above 100 torr. When subjected to radiation below 380 nm, this gas undergoes dissociation.

Three of the classes of compounds considered in the previous section contain compounds which may be partially responsible for the observed fluorescence; these are aliphatic aldehydes, aliphatic ketones and aromatic hydrocarbons. Aldehydes and ketones both yield the fluorescent compound, biacetyl, when irradiated. The fluorescence of this compound is quenched by oxygen, thus it is not likely a contributor to the fluorescence background. Both aldehydes and ketones, however, exhibit endogeneous fluorescence which can be excited by radiation of 300-330 nm wavelength. Fluorescence yields are quite low, in the range of 10^{-3}.

The fluorescence of many aromatic vapors is not quenched by nitrogen, carbon dioxide, or air. The relatively light aromatics, detected in the analysis of the exhaust gases, fluoresce more into the UV than the observed broad fluorescence band. These compounds (alkylbenzenes) are common exhaust constituents. Other aromatic materials are almost always present in exhaust gases even though at a much lower level. These consist of multiple-ring compounds such as biphenyl derivatives and polynuclear aromatic hydrocarbons.

Table 1

SUMMARY OF FLUORESCENCE DATA FROM JOINT COMBUSTOR EXPERIMENTS

Test Point	Fuel	Total Hydrocarbons[a] (ppm)	Relative Fluorescent Yield (%)[b]
5BB02	JP-4	165	45
5BC02	JP-5	337	60
5BD02	JP-5	6	10
5BF02	JP-4	57	20
5BG02	JP-5	6	5
5BH02	JP-5 + 0.04% Ferrocene	14	5
5BI02	JP-4	636	77
5BK02	JP-5 + 0.04% Ferrocene	9	30
5BL02	JP-8	203	62
5BM02	JP-4 with 25% Aromatic + 1.6% Pyridine	113	66
5BP02	" "	154	73
5BQ02	Isooctane	32	11
5BR02	"	30	10

[a] Measured by AFAPL personnel.

[b] 1.055 ft^3 exhaust; 40 ml cyclohexane.

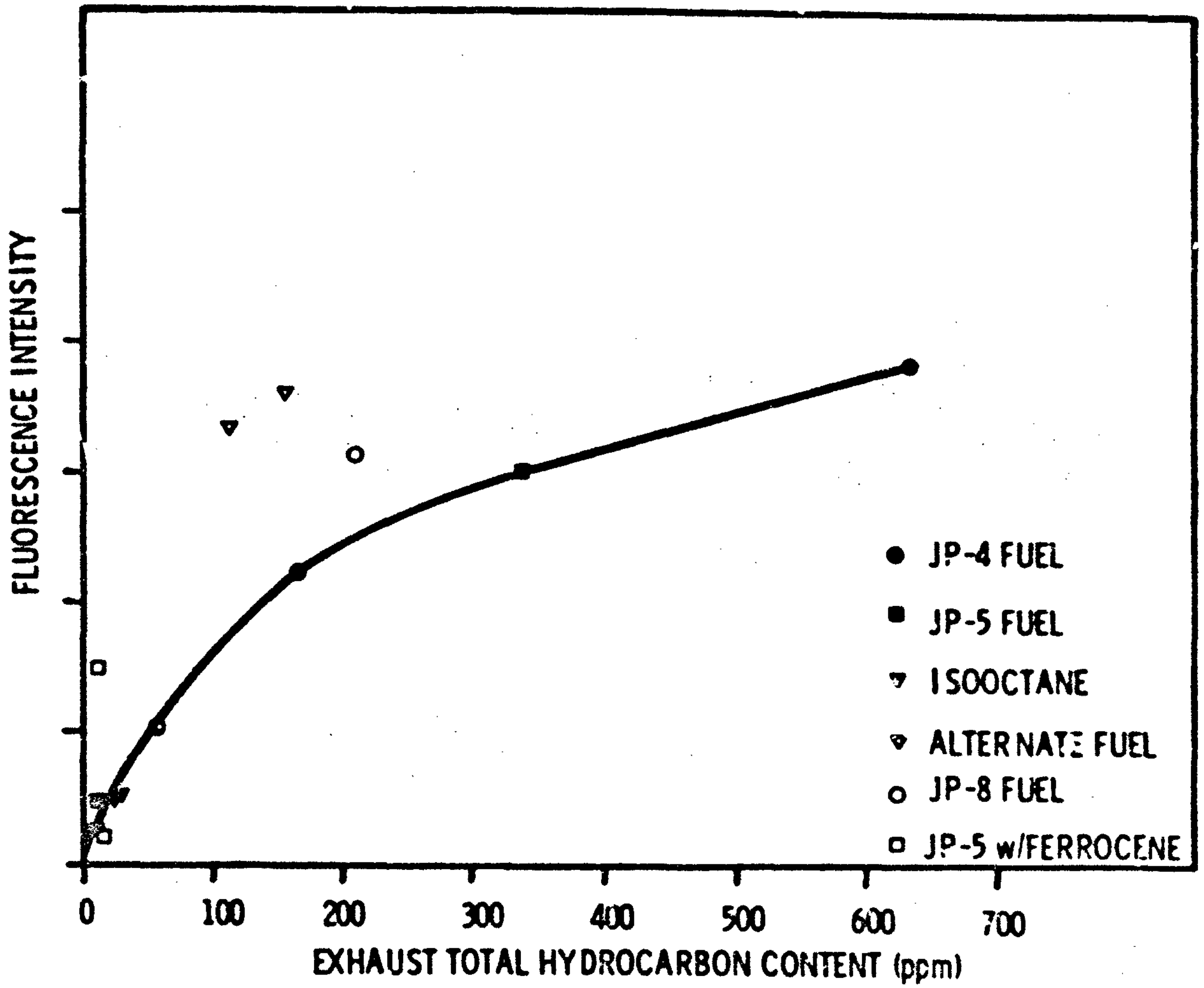

Figure 7. Correlation of Exhaust Total Hydrocarbon Content with Fluorescence for Various Fuels.

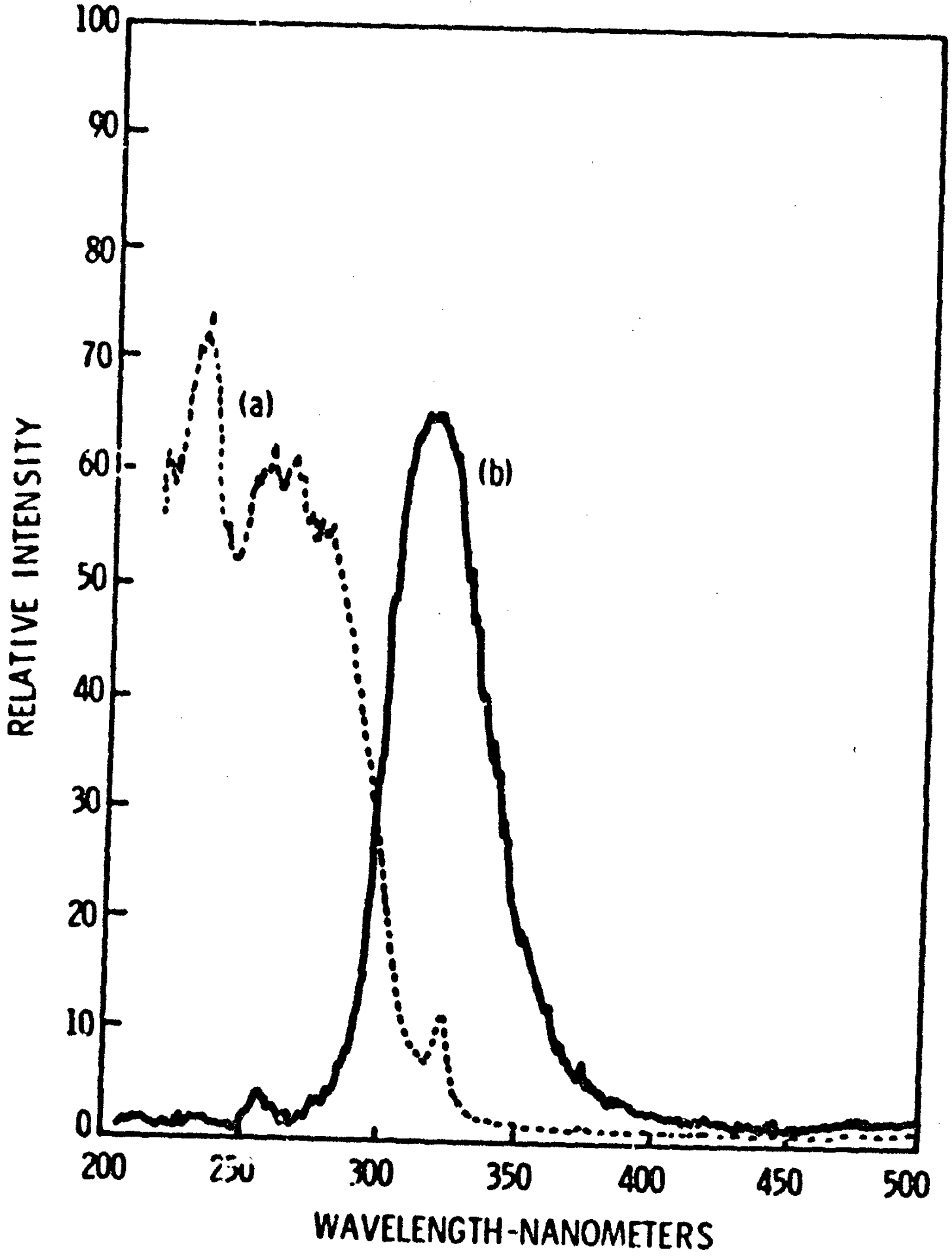

Figure 8. Excitation (a) and Emission (b) Fluorescence Spectra of Exhaust Sample 5 BM.

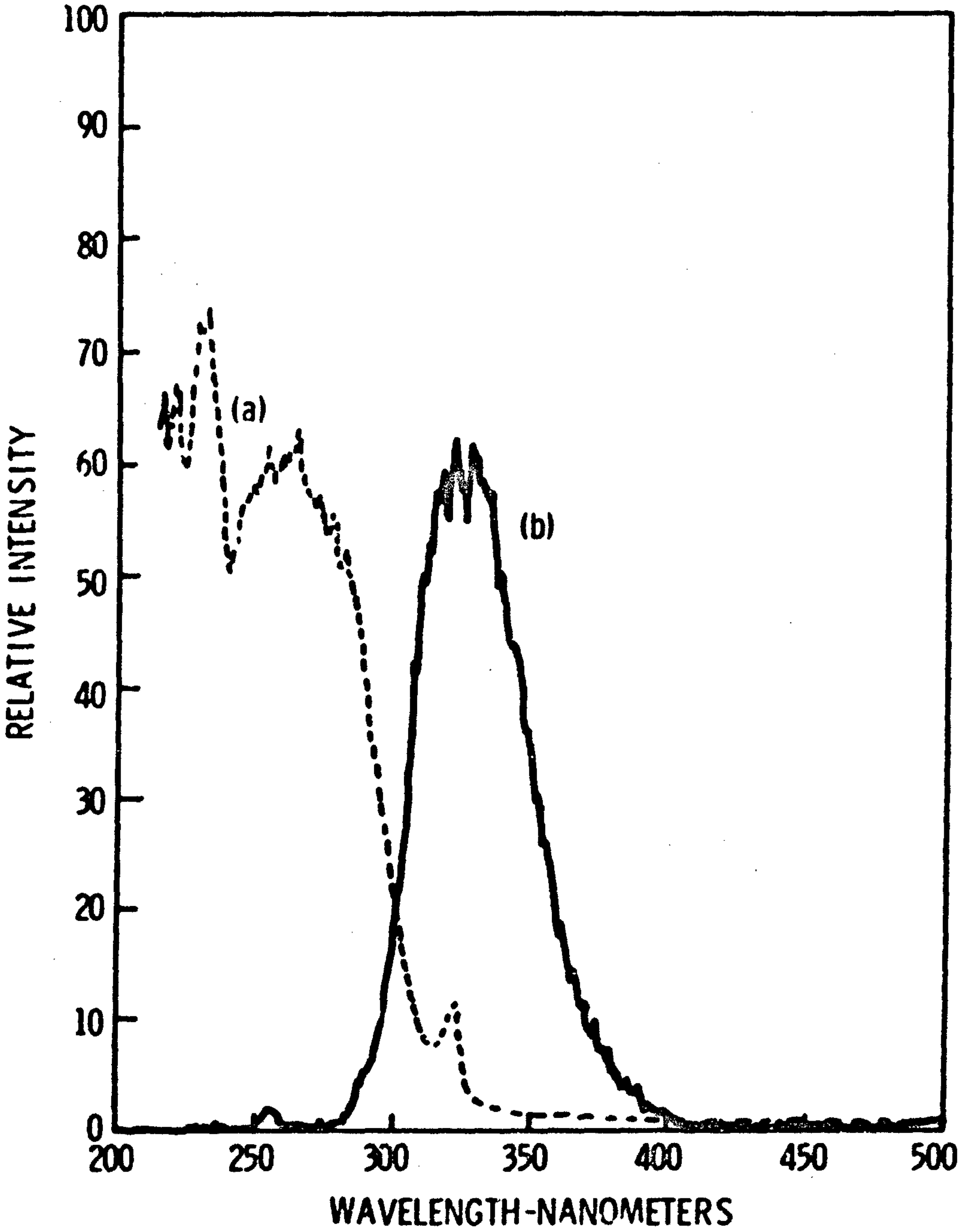

Figure 9. Excitation (a) and Emission (b) Fluorescence Spectra of Exhaust Sample 5BL.

Table 2

PARTICLE SIZE DISTRIBUTION (PERCENT)

Data Point	Class Interval (µm)						
	0-0.5	0.5-1	1.0-2.0	2.0-4.0	4.0-8.0	8.0-16.0	16.0-32.0
5BB03-04	19.9	40.6	29.5	10.0	-	-	-
5BC03-04	28.0	34.5	26.5	11.0	-	-	-
5BF03-04	26.5	26.4	32.2	13.8	0.8	-	-
5BG03-04	25.6	46.4	22.3	5.5	-	-	-
5BH03-04	49.8	33.6	12.6	3.2	0.8	-	-
5BI03-04	69.9	22.8	7.3	-	-	-	-
5BK03-04	77.2	22.1	0.7	-	-	-	-
5BL03-04	28.4	27.2	28.3	14.2	1.9	-	-
5BM03-04	40.1	30.9	18.4	10.6	-	-	-
5BP03-04	20.5	31.4	30.1	13.5	3.0	0.4	0.9

A fluorescence spectrum of exhaust vapor, collected by means of a hexane bubbler, is shown in Figure 10. This spectrum is quite similar to the ones obtained for a series of biphenyl derivatives, the spectrum of 4-methylbiphenyl being shown by the dotted trace. Biphenyl derivatives having various alkyl groups give spectra differing only by small shifts in the fluorescence peak. Figure 10 is, of course, not conclusive proof of the presence of a biphenyl compound. It is interesting to note, however, that while biphenyl in solution gives a strong spectrum, this compound in the vapor phase gives a weaker and more diffuse spectrum consisting of a broad continuum. This difference between vapor and solution spectra for biphenyl has been attributed (ref. 5) to the stabilization phenomenon, which also has the effect of allowing the fluorescence of biphenyl in solution to be excited at a shorter wavelength than the fluorescence of biphenyl vapor. Thus the vapor spectrum of biphenyl would more closely match the laser-excited fluorescence than would the liquid solution spectrum.

Polynuclear (PNA) hydrocarbons are well-known to fluoresce in the visible region of the spectrum. PNA hydrocarbons have been determined in automotive exhaust (ref. 6), aircraft exhaust (ref. 7) and even in exhaust of engines burning liquid petroleum gas (ref. 8). These compounds, though present at low levels in exhaust, have high fluorescence yields, from 0.2-0.8 compared to 10^{-3} for many of the other compounds discussed. A series of twenty-one polynuclear hydrocarbons were determined in gasoline engine exhaust after chromatographic separation. Amounts ranged from 140 mgs per 100 m^3 of exhaust gas for naphthalene to 0.4 mg per 100 m^3 for anthanthrene. Other typical amounts are presented in Table 3 along with the fluorescence wavelength range. In Figure 11, the spectrum of naphthalene is compared to that of exhaust sample 5BI.

The broad continuum of fluorescence observed with the Raman instrument upon laser excitation could readily originate from either or both of the foregoing groups of compounds (biphenyl derivative and PNA hydrocarbons). The effect of increased temperature on fluorescence spectra, as discussed in Appendix I, appears to have the effect of broadening fluorescence bands, so that the continuum observed by laser excitation of hot exhaust gases is readily explained.

B. SPECTRAL EVALUATION OF THERMALLY STRESSED RUELS

A study was performed to determine whether thermally stressing hydrocarbon fuels causes changes in them which can be progressively followed by means of ultraviolet absorption spectrophotometry or spectrophotofluorometry. If the spectral data reflect temperature produced compositional changes, a technique might be devised whereby measurements could be used to supplement coker thermal stability data.

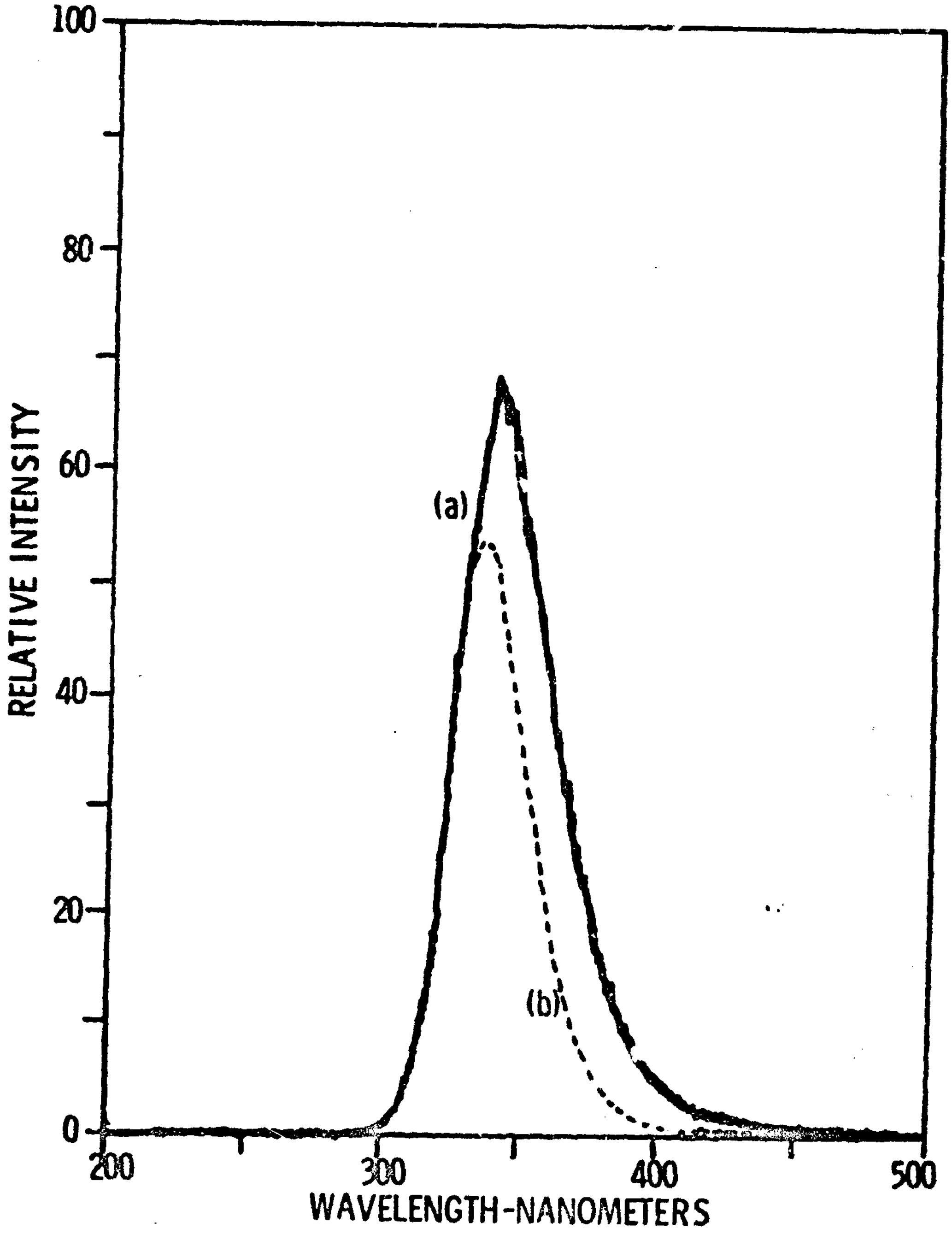

Figure 10. Comparison of Fluorescence Emission Spectra of Exhaust Sample 4ANC4 (a) and Methylbiphenyl (b).

Table 3

CONCENTRATIONS AND FLUORESCENCE EMISSION OF SOME PNA HYDROCARBONS FOUND IN AUTOMOTIVE EXHAUST

Compound	Fluorescence (ref. A-22) Wavelengths (nm) Average	Range	Concentration (ref. 8) (mgs/100 m^3)
naphthalene	334	310-380	140.4
anthracene	401	370-470	1.45
phenanthrene	367	340-420	8.50
chrysene	381	360-440	1.27
anthanthrene	447	430-550	0.45
fluoranthene	477	390-680	7.44
perylene	465	420-580	0.55

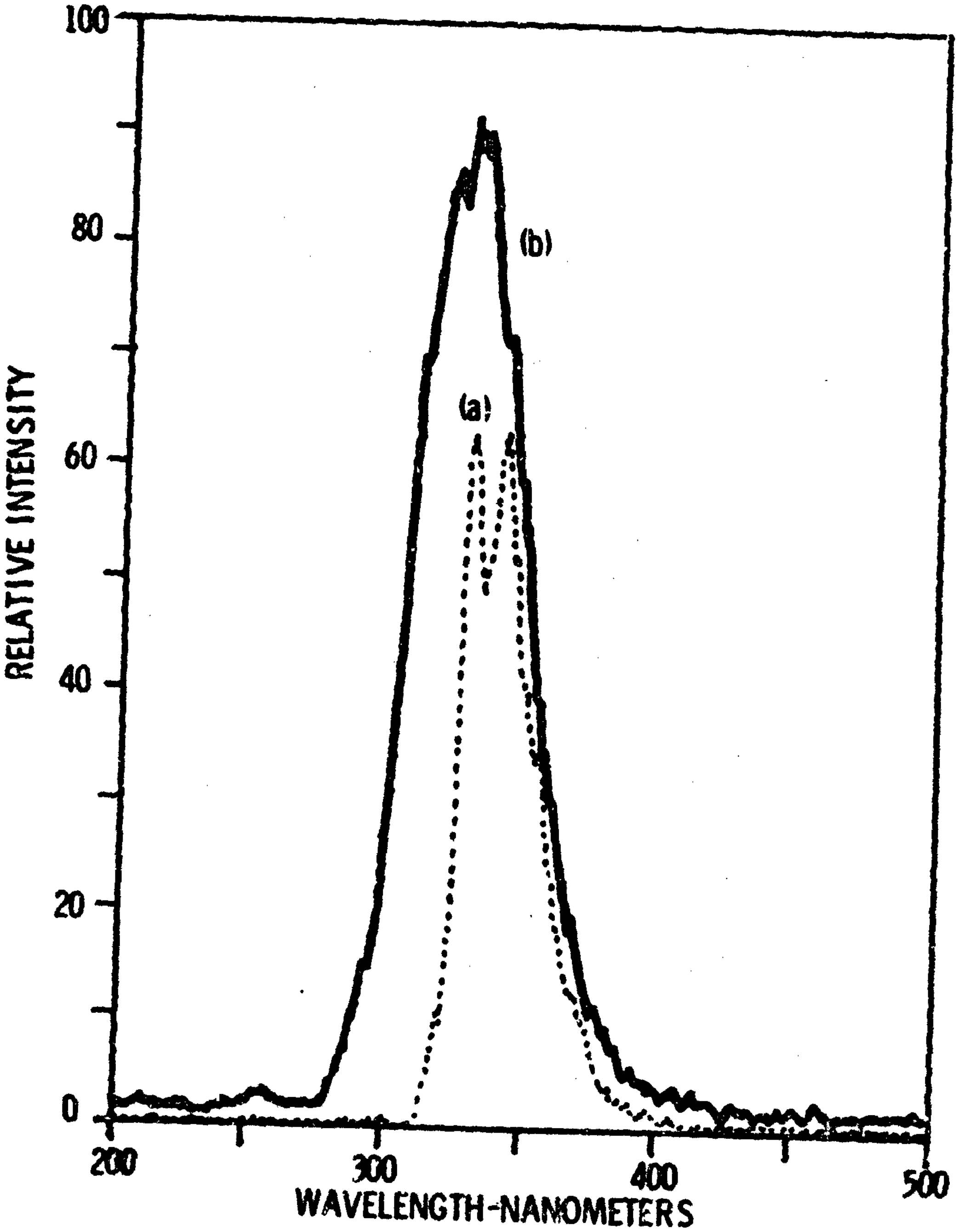

Figure 11. Comparison of Fluorescence Emission Spectra of Naphthalene (a) and Exhaust Sample 5BI (b).

1. Experimental

Samples of JP-4 fuel AFFB 16-73 which had been thermally stressed, each at a different temperature, were used for the investigation. Fluorescence spectra were recorded using the neat fuels, but for ultraviolet absorption spectra, samples were diluted with cyclohexane.

Ultraviolet absorption spectra for all fuel samples were identical, both in intensity and spectral distribution.

The baseline (unstressed) fuel showed its strongest fluorescence band at 405 nm, with minor bands at 430, 440, and 470 nm. An excitation spectrum with emission at 405 nm showed 385 nm to be the most efficient excitation wavelength. This wavelength was used to excite fluorescence spectra of the other fuel specimens. These spectra show that small changes in the fluorescence pattern occur for various stress temperatures as:

(1) Changes in intensity of the peak at 405 nm relative to the doublet at 430 and 440 nm.

(2) A tendency for the band at 470 nm to be slightly better resolved in stressed specimens.

(3) Shifts in the intensity of the doublet lines at 430 and 440 nm.

Considering these features, (1) appears to be at least in part associated with a photolytic reaction, since the change also varies with irradiation time; (2) is subtle and difficult to quantitate, but (3), the intensity rates of the doublet lines, can be measured and used in a temperature correlation.

Data from long term JFTOT tests at AFAPL were used to relate the individual stress temperatures to JFTOT time-to-failure. Table 4 presents intensity measurements for the doublet peaks (a & b) at 430 and 440 nm and time-to-failure values for each temperature. In measuring doublet peak intensities, a level base line was drawn at the base of the valley between peaks. In some cases, peaks are small and are subject to substantial errors in measurement. For some fuels, several different spectra were recorded as a check on reproducibility. The plot shown in Figure 12 includes all data points.

2. Conclusions

The absence of differences in the UV absorption spectra of thermally stressed fuels is not surprising, since UV absorption is a much less specific technique than fluorescence. Differences appearing in the fluorescence spectra are not large and are not known to be general for all JP-4 fuels. Thus, a fluorescence monitoring device for fuel stability evaluation would not readily lend itself to routine and automated recording. Additionally, judgments as to best data evaluation procedure would probably be required for each fuel unless the baseline fluorescence spectra of all fuels were identical.

Table 4

CORRELATION OF FLUORESCENCE SPECTRAL CHANGES WITH THERMAL STRESSING OF JP-4, AFFB 16-73

Temperature (°F)	JFTOT Time to Failure[a] (min)	Fluorescence Peaks (mm)		Ratio
		I_a	I_b	I_B/I_a
82	-	7.1	2.0	0.28
320	2.2×10^4	5.5	3.0	0.55
370	3.5×10^3	2.5	5.0	2.00
420	6.5×10^2	2.0	6.1	3.05
		3.3	11.5	3.48
		2.5	7.8	3.12
470	1.8×10^2	3.0	11.0	3.66
		2.3	10.5	4.56

[a] Taken from AFAPL long term JFTOT Test Results.

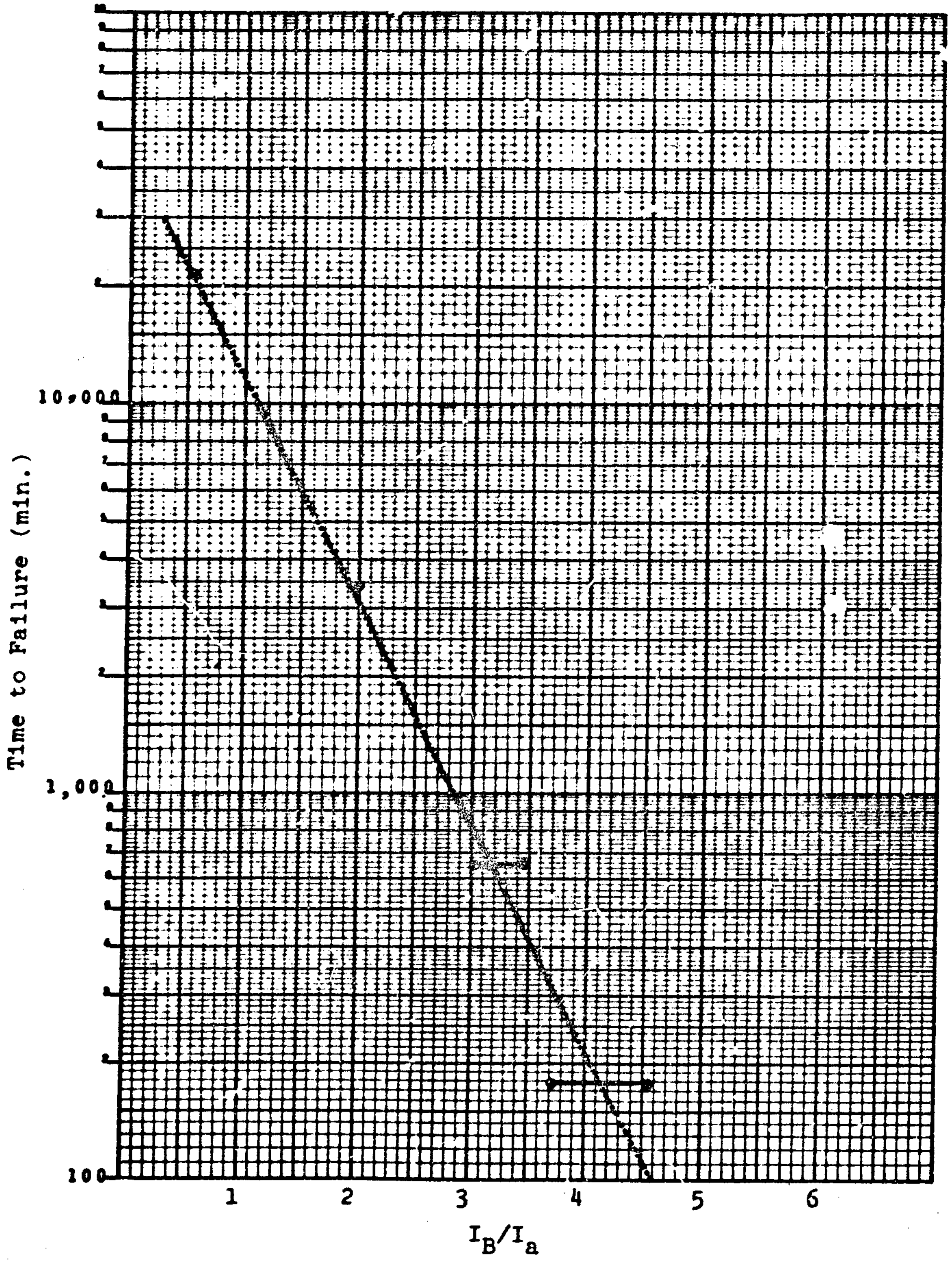

Figure 12. Correlation of JFTOT Time-to-Failure With the Fluorescence Intensity Ratio of Doublet Lines.

SECTION III

FIRE SAFETY STUDIES

A. HYDRAULIC FLUID HOT MANIFOLD IGNITION TESTS

Hot manifold ignition tests were performed on five aircraft hydraulic fluid specimens to compare the relative hot-surface fire resistance of MIL-H-5606, various lots of MIL-H-83282 and a commercial phosphate ester based hydraulic fluid. The fluids were coded as follows:

Fluid A - MIL-H-5606C
Fluid B - MIL-H-83282A
Fluid C - MIL-H-83282
Fluid D - MIL-H-83282A
Fluid E - Skydrol 500B

Ignition tests followed procedures given in AMS 3150 (ref. 9) and FS 791 Method 6053 (ref. 10). Messrs. Greg Gandee and Bill Allen, AFAPL/SFH, witnessed tests and recorded complete film documentation. For this reason, data and observations are presented in this report in exactly the same chronology as the actual tests.

1. Hot Manifold Drip Tests

Initial tests were performed by pouring each fluid from a beaker onto the hot manifold apparatus. This method of delivery, in retrospect, was considered too erratic in time and fluid volume; however, delivery at the AMS 3150 rate (10 ml in not less than 40 seconds) was felt to be too slow. A 10-ml burette was employed for delivery of the fluid to the hot manifold with first tests using the delivery rate of 10 ml in 10 seconds. The flow was later adjusted to 10 ml in 18-20 seconds, a rate which was then used for the bulk of the testing. These data are presented in Appendix II, Section A.

During the course of the manifold tests, the actual temperature of the surface was questioned. Tests were conducted at 400, 500, 600, 700 and 800°F using Tempilstik markers and a Wahl HSA-4G automatic infrared thermometer. These tests indicated that the thermocouple and recorder combination attached to the manifold was reading approximately 150° lower than the surface temperature measured by the other methods. In order to facilitate comparison of data, all reported temperatures are those indicated by the manifold thermocouple.

2. Low Pressure Spray Tests

Low pressure spray tests were conducted by directing a spray of fluid over burning cotton waste saturated with 150 SUS petroleum oil. An AMS-3150 Low Pressure Binks Spray Gun was used to spray the fluids which were at ambient temperature. Results of these tests are given in Appendix II, Section B.

3. High Pressure Spray and Drip Tests

The first tests in this series were conducted by charging 100 cc of fluid to a 150 cc Hoke "bomb" pressurized to 1,000 psi. A 1.0 gallon per hour rated atomizing nozzle and an AM-3150 high pressure stream-type nozzle (flat disc orifice 0.063-in. thick with a 0.0145-in. dia. hold) were evaluated for the tests.

Tests were conducted on Fluid A using a small spray pattern, with the spray directed at a 45° angle to the manifold at its center. The end of the nozzle was about six inches away from the center spot on the manifold. With the manifold at 1200°F, a momentary spray gave almost immediate ignition with burning on the manifold and in the pan. At 1100°F, ignition occurred 1-2 seconds after the spray had been turned off. For a manifold temperature of 1150-1200°F, the fluid was quickly ignited after spraying had stopped.

At three feet from the 1200°F manifold, using the AMS-3150 high pressure stream nozzle, Fluid A at ambient temperature ignited twice, but failed to ignite on three additional attempts. Four more repetitions gave ignition which was delayed until the spray was stopped.

The 1.0 gallon per hour atomizing nozzle was selected for the remainder of the tests. Tests using both burette and spray deliveries are presented in Appendix II, Section C. As indicated by a note in that table, a problem developed with the small atomizing nozzle and it was subsequently replaced with a slightly larger atomizing nozzle used in Factory Mutual Testing (rated 1.5 gph). During these tests, the spray nozzle was located 72 mm from the center of the manifold, the angle from a normal to the manifold being about 30°. Entering air on the days of the tests ranged from 22° to 26°C and 50 to 55% relative humidity.

Tests were performed with the fluids both heated and at room temperature. For the dripping test, the heated fluid was at 210°F and for the spray tests the fluids were 150°C in the container and 200°F in the line and spray nozzle.

This work has raised the question of actual manifold surface temperature. At this time, the question has not been completely resolved. Physical size and attachment of the thermocouple to the manifold are obviously not completely satisfactory for obtaining true surface temperatures. Unfortunately, AMS-3150 and FS 791 Method 6053 do not fix the details of thermocouple size and attachment.

After the tests were completed, thermocouple temperature values were further compared with temperatures obtained by Tempilstik markers and an infrared radiation thermometer. These values are tabulated in Appendix II, Section D.

B. EXAMINATION OF SPECIMENS RECOVERED FROM AIRCRAFT WRECKAGE

Aircraft wreckage specimens have been examined to determine factors which may have contributed to aircraft failure.

1. F-4 Aircraft Wreckage

a. Wire Bundle

The first specimen to be examined was a bundle of wires which constituted a part of the aircraft electrical system. The wires were enclosed in a plastic sheath which was darkened and totally degraded at one point. A rubber lined retainer through which the wires passed showed no evidence of deterioration. Information was required on the cause of deterioration of the plastic sheath, i.e., whether due to normal aging or to excessive heating. If heat was a factor, it was required to know whether it originated from the interior (the wires) or from an outside source.

An infrared spectrophotometric measurement of the polyvinyl chloride plasticizer ratio showed that plasticizer loss was the major compositional difference between good and deteriorated portions of the polymer. However, the fact that some of the polymer remained clear and soft tends to discount deterioration by aging. The deterioration in fact was quite readily duplicated by heating a good section of the polymer.

A cross section of the polymer was examined microscopically in order to determine whether heating originated from the interior or exterior. By selecting a portion of the polymer near the edge of the deteriorated zone, a section was obtained in which a color gradient existed across the thickness of the polymer sheet. Since the greatest discoloration was at the outer surface, it was concluded that the deterioration was caused by an exterior heat source.

b. Black Deposits Contained on Cotton Swabs

Three cotton swabs which had been used to sample unknown black deposits, were examined. X-ray emission (EDAX) measurements showed no elements in the deposit which did not also appear in the clean swab. X-ray emission, as performed, can be used to detect all elements except for the first eleven in the periodic table. The fact that no elements were detected indicates that the black deposit is composed of only light (low atomic number) elements.

The swabs were rinsed with a few drops of spectroscopic grade hexane and carefully worked to dislodge some of the black material. The hexane was evaporated and a potassium bromide disc was pressed for infrared absorption measurements. The infrared spectra indicated the presence of only very low levels of hydrocarbons. The small C-H stretch band which was observed was probably due to traces of fuel or to a contaminant extracted from the cotton swab. The bulk of the sample material, however, did not absorb infrared radiation.

The possibility that the deposit consisted of light metal oxides was eliminated by the observation that, upon heating in a crucible over a burner flame, the material slowly disappeared. All observations point to the conclusion that the residue was carbon, likely soot.

c. Deposit on Metal Fracture Surface

A black deposit which was contained on the fracture surface of an aluminum structural component was examined. The deposit contained on a metal fracture surface showed no organic functionality. X-ray emission analysis showed that the film was composed only of light elements. Auger electron spectroscopy confirmed that the surface consisted of only the elements carbon, oxygen, and aluminum.

The absence of silicates, and metals characteristic of soil ruled out swamp silt as a source of the deposit. Despite the absence of cellulosic material, swamp peat remains a possible source of the black residue. Though the composition of the residue has been firmly established, no definite conclusion has been reached on its source.

d. Left Wing to Fuselage Seal

Several sections of wing to fuselage seal were examined to determine the significance of a dark discoloration along the bead. Investigation showed that it was composed of polychloroprene containing 50% inorganic filler (calcium and zinc salts). The black discoloration on the elastomer seal was shown to contain inorganic filler and to give an infrared spectrum characteristic of that obtained from the thermally stressed elastomer. Heat induced degradation generally affects the entire elastomer mass rather than just its surface. The thin surface location of the black material led to the conclusion that aging of the elastomer was responsible for the observed degradation.

2. Evidence of Pre-crash Fire Extinguisher Deployment

Aircraft components recovered from a crash site were examined too find evidence which would indicate whether the starboard fire extinguishing unit had been activated. The fire extinguishing agent used in the aircraft was Halon 1202, dibromodifluoromethane. Traces of reaction products of this material with the right heat shield were sought. The major nonvolatile products which might be formed by the reaction of the extinguishing agent with a hot metal surface would be metallic fluorides and bromides. Consequently, the investigation centered on the detection of these metal halides.

Three specimens which are part of the right heat shield were examined. Specimen A consisted of thin stainless steel sheets separated by fiberglass insulation. Specimens B and C were constructed of heavier gauge stainless steel. Only specimen A showed evidence of having been subjected to high temperatures. Several sections of one to two square inches were cut from each of the specimens. Since the metal halides in question are quite water soluble, each of the metal sections was extracted with 5 ml of triple distilled water. Water extracts were then tested for the presence of bromides and fluorides. For the former, a chemical test was employed which can be used to detect as little as approximately 2 micrograms of bromine in 5 ml of extract. A fluoride specific ion electrode (Model 96-09, Orion Research Inc.) was used for the detection of fluorides. A baseline value of less than 0.5 microgram of fluorine in 5 ml of extract was established as typical for extraction of nonfluorine-containing materials.

Bromides were not detected in any of the triple distilled water extracts. However, fluorides were detected in all samples taken from specimen A. In all cases, fluoride-containing samples came from areas of the specimen where excessive heating had obviously taken place. No fluoride was detected in any sample taken from specimen B or C.

The three aircraft components were dusty as a result of their impact in desert terrain. In order to verify that the fluorides were not constituents of the dust, soil and rock, samples from the impact site were evaluated for fluoride content. Since no more than one to two milligrams of dust could have been present on any sample, a 10-mg specimen of each soil was extracted with distilled water following the same procedure used for the metal specimens.

Extractions were performed on a heat shield similar to the one recovered from the aircraft wreckage. All surfaces as well as the interior insulation gave a negative test for fluoride.

Left heat shield fragments recovered from the wreckage also gave a negative test for fluoride.

Results of tests are summarized in Table 5.

Bromine was not detected; however, it is by nature less reactive than fluorine and the contact time was very short. Further, the test for bromine which was employed is slightly less sensitive than the fluoride test.

This study has shown that fluorides were present in significant amounts on the right heat shield. Fluoride content is not characteristic of the heat shield materials nor is the fluoride due to likely exterior contamination. These facts together with the occurrence of fluorides only in heated areas (where hot corrosive attack could take place) strongly suggest that the right heat shield was subjected to Halon 1202 fire extinguishing agent.

Table 5

DETECTION OF FLUORIDE EXTRACTED FROM AIRCRAFT COMPONENTS AND CRASH SITE SOIL SAMPLES

	Sample	Estimated[a] Level of Fluoride (microgram/sq.in.)
1.	Right heat shield (A) discolored area[b]	4
2.	" " " " " "	10
3.	" " " " " "	5
4.	" " " " " "	4
5.	" " " " " "	4
6.	Metal component (B) clear area	<0.5[c]
7.	" " " " "	"
8.	" " " " "	"
9.	Metal component (C) clear area	"
10.	" " " " "	"
11.	" " " " "	"
12.	Soil, valley floor	<0.5/10 mgs
13.	Soil, above impact area	"
14.	Impact area, left side	"
15.	Impact area, center	"
16.	Impact area, right side	"
17.	Impact area, rocks	"
18.	Reference heat shield, ridged side	<0.5
19.	Reference heat shield, smooth side	"
20.	Right heat shield, fiber insulation	0.9/20 mgs
21.	Left heat shield, fiber insulation	<0.5/20 mgs
22.	Reference heat shield, fiber insulation	"
23.	Left heat shield metal, discolored area[b]	<0.5
24.	" " " " " "	"
25.	" " " " " "	"

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[a] Does not imply that, in areas where fluoride is detected, the deposit is uniform.

[b] Discoloration due to excessive heating.

[c] Blank determinations give values less than 0.5 micrograms.

SECTION IV

FUEL CONTAMINANT INVESTIGATION

Occasionally aircraft fuels become contaminated as evidenced by their failure to pass routine quality control tests. Factors such as the exploratory nature of a fuel, or the quantity involved, may warrant investigation and characterization of the contaminant. Contaminant investigations have been conducted employing a variety fo spectroscopic techniques including infrared absorption, nuclear magnetic resonance, atomic absorption, optical and x-ray emission.

A. IDENTIFICATION OF RESIDUE FROM SHELLDYNE-H

Solid material amounting to approximately 6 mgs was isolated from a new batch of Shelldyne-H by means of a Millipore® membrane filter. X-ray fluorescence analysis indicated that the major detectable elements of the residue were iron, calcium, sodium, and chlorine; no information on carbon, hydrogen, and oxygen can be readily obtained by this technique. X-ray diffraction analysis of the residue unequivocally established sodium chloride as one of the components.

Solubility tests indicated that the deposit was completely water soluble. An infrared absorption spectrum, which was recorded of the material remaining after a water extract was taken to dryness, showed bands characteristic of an aliphatic carboxylic acid salt. The infrared spectrum closely matched that of an acetate. Additionally, a broad infrared band at approximately 9 microns, which is characteristic of a metal-oxygen bond, suggested the presence of a small amount of a metal oxide. Oxides may be present in the residue or may be a hydrolysis product formed during the water extraction step.

1. Conclusions

The residue was shown to contain iron and, likely, calcium salts of a carboxylic acid, perhaps ferric and calcium acetates. Sodium chloride was also present at a low but significant level, i.e., greater than would be due to finger-print contamination of the filter. The presence of a low level of metal oxide(s) was also indicated. The metals analysis is presented in Table 6.

Table 6

METALS CONTENT OF MILLIPORE FILTER RESIDUE

Metal	Milligrams in Total Residue[a]
Iron	1.4
Calcium	0.4
Sodium[b]	0.1
Aluminum	<0.05
Tin	<0.05

[a] Total residue - approximately 6 mg.

[b] Equivalent to 0.25 mg NaCl which was shown to be present by x-ray diffraction.

B. CHARACTERIZATION OF RESIDUE FROM SYNTHETIC JP-4

A residue which formed in synthetic JP-4 was subjected to a qualitative analysis. The fuel, which had been prepared from shale oil crude, was not known to have been contaminated; however, a precipitate gradually formed upon standing. The residue, as received, was contained on a disc of filter paper. Infrared (IR), nuclear magnetic resonance (NMR), emission (E), and x-ray fluorescence (XRF) spectroscopy were employed in characterization of the residue material.

Emission spectroscopic analysis of the residue indicated the presence of only low levels of iron, silicon, magnesium, and aluminum, totalling less than 1.5%. XRF analysis showed that no significant amounts of other elements were present except for light elements such as C, H, N, O, etc. (All elements can be detected by XRF except for the first twelve in the periodic table.)

The residue was readily soluble in chloroform. The material was deposited on a rock salt plate and an infrared spectrum (quite weak) was obtained.

Spectral assignments are:

Wavelength of Absorption Band (microns)	Structure Assignment
3.1	-OH and/or H_2O
3.4	aliphatic CH
6.0	hydrogen bonded $-\underset{\vert}{C}{=}O$ (carboxylic acid or amide) or -C=N-
6.9-7.5	aliphatic CH
9.0 (broad)	ether C-O-C
13.3	probably a trace of chloroform occluded in film

The C-O-C absorption suggests a polyether type material. Unfortunately, many different materials, ranging from polyols (polyethylene or polypropylene glycols) to cellulose, can give similar spectra.

NMR confirmed the characterization made by IR spectroscopy but did not enable a more specific identification.

X-ray diffraction examination of the residue showed it to be noncrystalline.

1. Summary of Finding

A positive identification cannot be made from the available spectral data (IR, E, NMR, XRF, XRD). The material has the following characteristics:

(1) Mostly organic (dissolves in chloroform)

(2) Noncrystalline (no x-ray diffraction pattern)

(3) Contains less than 1.5% metals (E and XRF)

(4) Appears to contain no other elements than C, H, O, and/or N

(5) Contains aliphatic hydrocarbon functionality (could be a trace of residual fuel)

(6) Contains OH functionality or water (moisture)

(7) It has principally a polyether type structure with some -C=N or carbonyl functionality. The carbonyl would not be that of an ester or ketone but, rather, a hydrogen bonded carbonyl possibly due to a primary amide or carboxylic acid.

2. Conclusions

A polyester structure having the characterized functionality is one which would not normally be expected to appear in shale oil. It is likely that the residue is not a part of the original fuel, but is probably a contaminant. Its source may be a bottle cap seal (or its adhesive) or extractable material from a vessel liner, hose, gasket, filter bonnet or another fuel handling accessory.

C. ANALYSIS OF FILTER DEPOSIT FROM NASA T-56 COMBUSTOR STUDIES

Analyses were conducted to identify a brown filter residue obtained from the exhaust stream during T-56 combustor experiments. The filter was upstream of the point where NASA emission data were collected.

The specimen was examined by infrared absorption spectrophotometry, x-ray fluorescence and Fourier transform proton resonance spectroscopy. X-ray fluorescence analysis showed no more than trace quantities of any metals or halides and no sulfur or phosphorus. Even the low levels of elements which were detected appeared to be present in the filter rather than the deposit, i.e., they were found in equal amounts on both the forward and reverse side of the filter.

The deposit was readily soluble in acetone but not in hydrocarbon solvents, chloroform, or water. An infrared absorption spectrum of the acetone extract, after evaporation of the solvent, is shown in Figure 13.

A literature spectrum (ref. 11) of bis-phenol A (4,4'-dihydroxy-2,2'-diphenyl propane) recorded under similar conditions, is shown in Figure 14. Sample and reference spectra match well except for the presence of water bands at approximately 3 and 6 microns for the sample.

A Fourier transform proton resonance spectrum was recorded for the deposit in deuterated acetone. Peaks at 2.05 and 4.02 are associated with the d-acetone. Other peaks, however, are characteristic of bis-phenol A as shown by a reference NMR spectrum for that material. The major component in the deposit is thus unequivocally identified as bis-phenol A.

The compound is commonly used in the preparation of polycarbonate and epoxy resins. It is not a natural material and would not normally be found in hydrocarbon fuels. Though antioxidants of the hindered phenol type are added to many aircraft fuels, bis-phenol A is not directly related to these compounds. More likely, it originates from the use of polycarbonate tubing (as for example, to conduct the exhaust gases), from an epoxy-lined vessel, or from a similar source of contamination.

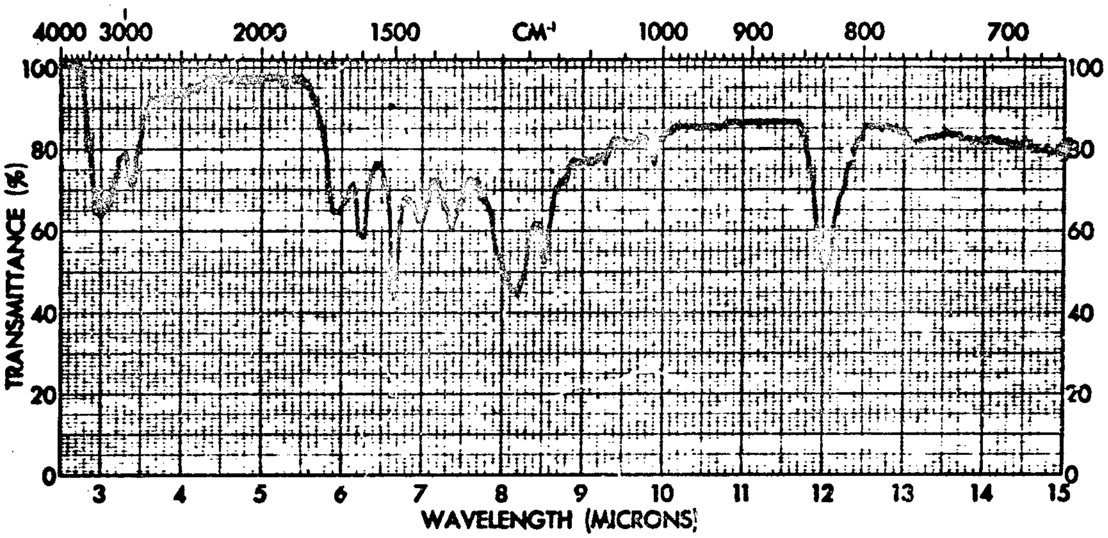

Figure 13. Infrared Absorption Spectrum of Deposit Material.

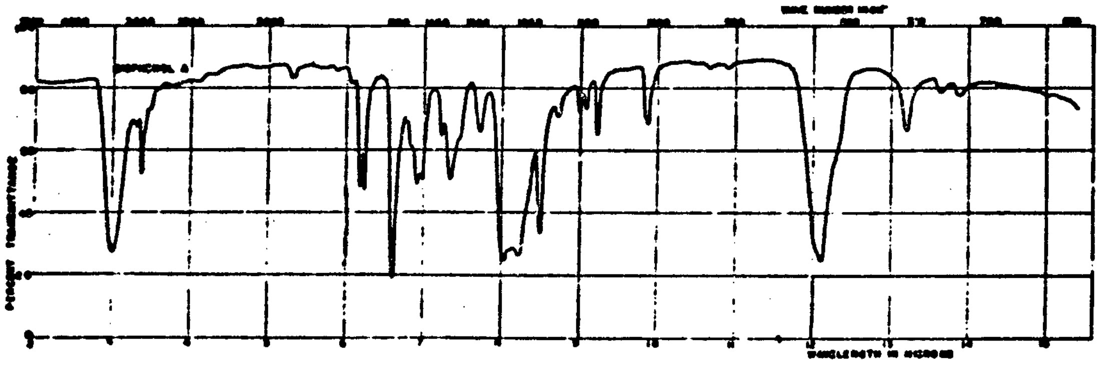

Figure 14. Infrared Spectrum of Acetone-Soluble Bis-phenol A Deposited on a Heated Sodium Chloride Plate.

D. CHARACTERIZATION OF CORROSIVE COMPONENT IN JP-4

An investigation was conducted on a JP-4 fuel which originated from a fuel depot in Denmark. The fuel reportedly passed specification tests for mercaptan and total sulfur content, but failed the copper strip corrosion quality control test (ASTM D 130-7). These tests were repeated and failure of the fuel to pass the copper strip corrosion test was confirmed. Test results are presented in Table 7.

A metals analysis was performed and the fuel's metal content was found to not be a factor.

A 50-cm column of silica gel was employed to aid in isolating the corrosive material. A nuclear magnetic proton resonance spectrum of the isolated material suggested it to be an alkylbenzenesulfonamide. This characterization was supported by an infrared absorption spectrum of the material, shown in Figure 15. The infrared spectrum very closely matches that of N-(n-butyl)-benzenesulfonamide, $C_6H_5SO_2NH(CH_2)_3CH_3$ (ref. 12) shown in Figure 16. The size of the alkyl group cannot be determined from the infrared absorption data.

In order to further assess the corrosiveness of the fuel specimen, a distillation was performed on a 100-ml specimen, with 10 fractions of approximately 10 ml each being collected. Vapor temperatures corresponding to each fraction are given in Table 8. A residue of several milliliters was allowed to remain in the flask at the end of the distillation. A copper strip test was performed on each fraction and on the residue. No corrosion was observed for any of the collected fractions; however, the residue was found to be highly corrosive to copper. An infrared spectrum of the residue showed absorption bands characteristic of the alkylbenzenesulfonamide.

As an additional test, a strip of copper which had been used to test the fuel was analyzed by x-ray emission (EDAX), with the bright part of the copper being compared to the tarnished part. The major difference between the two sections was in their sulfur content. Some sulfur was detected even on the polished surface, but sulfur was higher by at least a factor of three on the tarnished surface.

1. Conclusions

While an alkylbenzene sulfonamide has been clearly shown to be present in the fuel, its source is unknown. The presence of a strong acid such as a sulfonic acid can be discounted since a test of the fuel with moistened pH test paper shows no strong acidity. Singly alkylsubstituted benzene sulfonamides, however, have an acid character which would potentially cause the observed corrosion. Factors which substantiate the characterized compound as being the corrosive agent are: (1) its occurrence in the distillation residue of the fuel, this being the only fraction of the fuel found to be corrosive, and (b) the substantially higher level of sulfur on a copper surface after it has been tarnished by the fuel.

Table 7

SPECIFICATION TESTS ON DENMARK JP-4

Test	Observed Value	Specification Value
Mercaptan Sulfur, wt %	0.0001	0.001 max.
Total Sulfur, wt %	0.080	0.4 max.
Copper Strip Corrosion	Moderate tarnish 2b-2c	Slight tarnish 1b max.

Table 8

SEPARATION OF DENMARK JP-4 INTO FRACTIONS BY DISTILLATION

Fraction No.	Vapor Temperature Range (°C)	Copper Corrosivity
1	85-115	None
2	115-119	"
3	119-122	"
4	122-127	"
5	127-134	"
6	134-141	"
7	141-149	"
8	149-160	"
9	160-175	"
10	175-195	"
Residue	195 and above	Strong

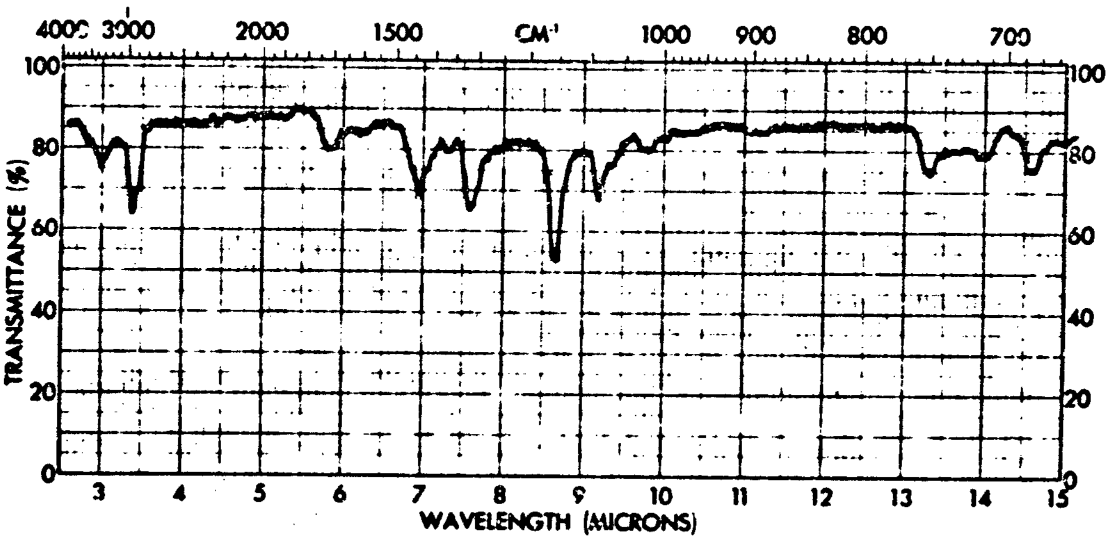

Figure 15. Infrared Absorption Spectrum of Component Isolated from Denmark JP-4.

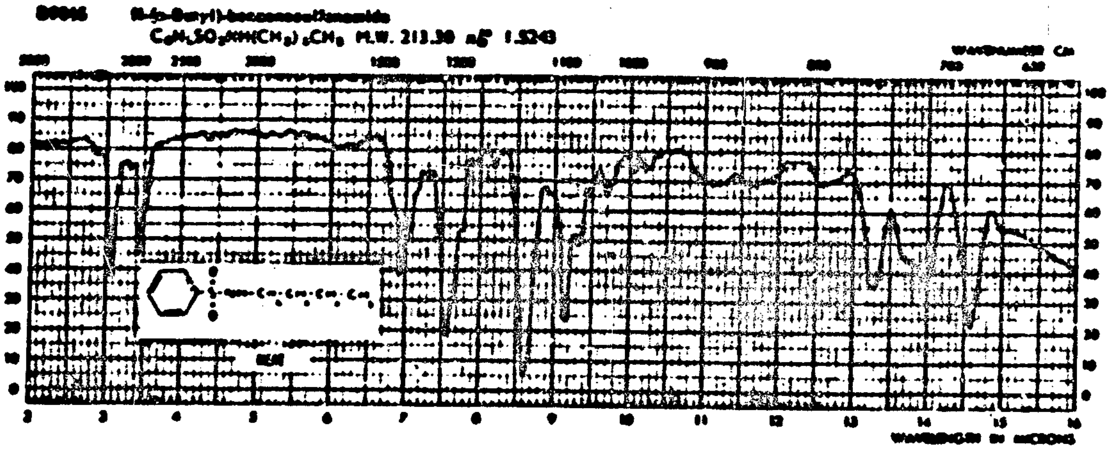

Figure 16. Infrared Reference Spectrum of of N-(n-butyl)benzenesulfonamide.

SECTION V

HIGH DENSITY FUEL STUDIES

The cruise range of volume limited missiles currently under development by the Air Force can be significantly extended by the use of high density hydrocarbon fuels. The present JP-9 high density fuel consists of a blend of tetrahydromethylcyclopentadiene dimer (RJ-4) and tetrahydronorbornadiene dimer (RJ-5) in methylcyclohexane (MCH). Studies were performed in this laboratory in support of Air Force in-house programs for the formulation and specification development of JP-9 fuel. This work involved the measurement of such properties as heat of combustion, density, low temperature viscosity and elemental and blend compositions of JP-9 fuel and its constituents. Air/fuel solubilities were measured as a function of temperature and fuel contaminants and impurities were characterized. This latter work is included in Section VI.A.

As a final phase of this task, 22 drums of JP-9 fuel were distilled to recover the three original components of the blend.

A. PROPERTIES OF JP-9 AND JP-9 CONSTITUENTS

Heat of combustion, blend composition and density and viscosity at -65°F for some JP-9 specimens are presented in Table 9. Heat of combustion values were determined using the bomb calorimeter according to ASTM Method D 240. Net heat of combustion values (Hn) were calculated from gross values (Hg) using the equation:

$$Hn = 4310 + 0.7195\ Hg \qquad (1)$$

While equation (1) is primarily intended for aviation gasoline and turbine fuels (ref. 13), it is of interest to note that it is valid for JP-9 fuels and gives values in close agreement with those obtained by the more generally applicable expression:

$$Hn = Hg - 91.23 \times H \qquad (2)$$

Where H is the weight percent hydrogen in the sample.

Tabulated below are values calculated using both equations (1) and (2).

Table 9

PROPERTIES OF SOME JP-9 FUELS

Sample	Determined Composition (Wt %)[a]			Heat of Combustion (BTU/lb)		Viscosity (-65°F)		Density (-65°F)
	MCH	RJ-4	RJ-5			Centistokes	Centipoise	g/cc
JP-9E	21.6	15.1	63.3	19,049	18,016	-[b]	-	-
-9F	26.9	13.7	59.4	19,117	18,065	-	-	-
-9H	27.0	13.1	59.9	19,177	18,108	79.3	80.3	1.0130
-9I	47.4	12.0	40.6	19,387	18,259	24.3	23.3	0.9566
ALCM JP-9 No. R 411-02A	25.8	13.6	60.6	19,220	18,139	86.5	87.5	1.0121
JP-9 F047-9	-	-	-	18,936	17,935	-	-	-

[a] Values determined directly by normalizing GC peak areas; no response factor applied.

[b] Dash (-) indicates no measurement was taken.

Sample	Wt % Hydrogen	Hn Eq (1)	Hn Eq (2)
JP-9E	11.21	18,016	18,027
JP-9F	11.13	18,065	18,102
JP-9H	11.21	18,108	18,154
JP-9I	12.18	18,259	18,277
MCH	14.38	18,692	18,677

In cases where information on the fuels hydrogen content is available, equation (2) is preferred. However, values obtained by equation (1) differ from those of equation (2) by substantially less than the 55 BTU/lb repeatability between measurements specified by ASTM D 240.

Heat of combustion values for several individual high density fuel components are presented in Table 10. Density and viscosity data as a function of temperature are presented in Table 11. Similar data for RJ-5 and monoisomeric RJ-4 (Sun Oil Company) blends are presented in Table 12.

B. DETERMINATION OF AIR/FUEL SOLUBILITIES

Data on the solubility of air in high density fuels were required to test the feasibility of eliminating fuel tank air exclusion bladders. Fuels may be subjected to temperatures as high as 130°F. If air is sealed into the tank at the time of filling and does not dissolve in the fuel, excessive pressures may result, possibly causing rupture of the tank.

To obtain solubility measurements, a simple apparatus, consisting of a degassing chamber followed by a cold trap, was assembled. Actual gas measurements were made with a CEC 21-103C mass spectrometer. The vacuum of the mass spectrometer inlet was used to aid in degassing the specimens. The degassing vessel was arranged so that constant agitation of the sample was possible. For Shelldyne-H and JP-9B, heating was also used in the degassing process. Samples were measured by weight rather than volume because of the inaccuracy inherent in delivering fixed volumes of fuel at a variety of temperatures. Sample weights of nominally five grams each were employed. Air and hydrocarbon vapors removed from the sample were passed through a cold trap where most of the hydrocarbons remained. The amount of air was determined in the desorbed gases as the total of the nitrogen, oxygen, argon, and carbon dioxide. Instrument calibration was achieved by introducing known volumes of air into the system. The determined value for air was independent of the amount of hydrocarbons in the vapor.

Fuel specimens were saturated with air at atmospheric pressure and at temperatures ranging from -60°F to 150°F. For this

Table 10

HEAT OF COMBUSTION OF JP-9 CONSTITUENTS

Sample	Gross		Net	
	BTU/lb	Cal/g	BTU/lb	Cal/g
MCH	19,968	11,093		
	20,008	11,116		
	19,989	11,116	18,692	10,384
RJ-4	19,430	10,794		
	19,419	10,788		
	19,425	10,792	18,286	10,159
RJ-5	18,826	10,459		
Batch 1065-173 1	18,846	10,470		
	18,836	10,464	17,863	9,924
RJ-5	18,698	10,388		
1 Aug 74	18,724	10,402		
	18,711	10,395	17,773	9,874
RJ-5	18,741	10,411		
Batch 2	18,790	10,439		
	18,766	10,425	17,818	9,895

Table 11

DENSITY AND VISCOSITY OF RJ-5 SPECIMENS AS A FUNCTION OF TEMPERATURE

RJ-5 Batch	Temp. (°F)	Density (g/cc)	Viscosity (Centistokes)	Viscosity (Centipoise)
2	100	1.0676	14.14	15.10
	0	1.1088	210.5	233.4
	-40	1.1265	1,727	1,910
	-65	1.1368	12,080	13,730
11410-103	100	1.0641	13.59	14.46
	0	1.1066	204.0	225.7
	-40	1.1243	1,685	1,894
	-65	1.1337	11,880	13,470

Table 12

PHYSICAL PROPERTIES FOR BLENDS OF RJ-5 AND MONOISOMERIC RJ-4[a]

Blend Ratio RJ-5/RJ-4	Heat of Combustion				Density (Gm/cc)		Viscosity (-65°F)	
	Gross		Net					
	BTU/lb	Cal/g	BTU/lb	Cal/g	-65°F	60°F	Centistokes	Centipoise
70/30	18,883 18,913							
Average	18,898	10,499	17,907	9,948	1.0903	1.0371	808.0	880.9
80/20	18,806 18,857							
Average	18,832	10,462	17,860	9,922	1.1065	1.0529	1784	1974
90/10	18,892 18,839							
Average	18,866	10,481	17,884	9,935	1.1231	1.0677	4677	5252.7

[a] Exotetrahydrodicyclopentadiene (Sun Oil Company).

purpose, a bubbler incorporating a fritted gas dispersion tube was used to pass finely divided air bubbles through the fuel. Continuous agitation of the fuel was maintained throughout the saturation period. The saturation process was arranged so that volatiles in the air stream were condensed and retained by the sample.

Saturation times ranged from 15 minutes to several hours. Fuels at 75°F and above could be readily saturated in the shorter period of time. Due to the increased viscosity at the lower temperature, longer saturation times were allowed. For Shelldyne-H, a two-hour saturation period gave the same results as a 24-hour period. Data were not obtained for this fuel below -15°F due to its high viscosity at lower temperatures. Attempts to saturate the fuel left suspended air bubbles, some of minute size, which remained even on standing for long periods of time. Less vigorous air saturation methods did not produce complete saturation. A similar problem was encountered with JP-9B at temperatures below -35°F.

Data generated in these experiements are expressed in terms of the volume of gas (mls) at the temperature and pressure at which the gas dissolves, taken up in one gram of fuel. This value may be used for direct comparison of solubilities or Ostwald Coefficients (ref. 14) can be obtained by multiplying the values by the density of the fuel (in grams per ml) at the temperature of saturation.

In order to compare air solubility values with data obtained by previous workers (ref. 15), Ostwald Coefficients were calculated for JP-4 using the foregoing procedure.

Air solubility values for the three fuels are given in Table 13. Comparative values for JP-4 are given in Table 14. Values given in the last column of Table 14 were calculated using the equation of the line representing the solubility coefficient versus temperature for JP-4 as given in reference 14.

C. DISTILLATION OF JP-9 FUEL

Approximately 1100 gallons of JP-9 fuel were distilled in order to recover the three components used in its formulation. The amounts and boiling ranges of these components were:

Material	Percent	Boiling Range
Methylcyclohexane (MCH)	33.3	212-215°F (100-102°C)
RJ-4	16.6	400-439°F (204-221°C)
RJ-5	50.0	500-550°F (260-288°C)

Table 13

SOLUBILITY OF AIR IN HIGH DENSITY FUELS

Sample	Temperature T (°F)	ml of Air at T per Gram of Fuel
Shelldyne-H	-15	.064
	0	.066
	75	.079
	150	.093
JP-9B	-35	.076
	-3	.081
	75	.098
	150	.112
JP-9A	-60	.090
	-5	.105
	75	.127
	130	.143

Table 14

SOLUBILITY OF AIR IN REFERENCE JP-4 SPECIMEN

Temperature T (°F)	ml of Air @ T/gram	Density @ T (gms/ml)	Ostwald Coefficients (ml Air @ T/ml Fuel @ T) This Work	Ref. 3
0	.212	.7854	.167	.161
75	.257	.7492	.192	.187
130	.280	.7224	.202	.207

The volume, temperature, and reflux relationships for the distillation are presented in Figure 17. Work was performed at the MRC pilot plant located at the Dayton Laboratory.

The distillation apparatus was initially charged with 700 gallons (14 drums) of JP-9 fuel. The first fraction, consisting of MCH, was distilled at atmospheric pressure and vapor temperature of 98-102°C using steam for heating. Distillation was continued until refluxing stopped.

The second fraction, consisting of RJ-4, was distilled by reducing the pressure to approximately 28 torr with a corresponding vapor temperature of 70-123°C.

Before proceeding to the third fraction, the remainder of the fuel was charged to the still and the first two fractions were recovered as before. For the third fraction, the still pressure was reduced again to 28 torr and distillation proceeded with a resulting vapor temperature of about 144°C.

The reboiler temperature never exceeded 175°C. Distillation was continued to a residue volume of about 150 gallons. The undistilled material, which was essentially RJ-5, was cooled and drained into drums.

The following amounts of materials were recovered:

Fraction 1	Methylcyclohexane	2109 lbs
Fraction 2	RJ-4	1378 lbs
Fraction 3	RJ-5	3246 lbs
Undistilled residue		1534 lbs

1. Evaluation of Fractions

Fractions 1, 2 and 3 were clear and colorless; however, the undistilled RJ-5 residue which remained in the pot had a distinct yellow color. Initial chromatographic analysis of fraction 1 showed it to be quite pure. Fraction 2, however, was found to contain an estimated 6-7% MCH. This impurity was reflected in the initial boiling point which was 240°F compared to the specification value of 400°F minimum. Some RJ-5 was also present in this fraction. The third fraction was found to contain a small amount of RJ-4, however boiling point distribution data were well within specification limits.

The undistilled RJ-5 residue showed no impurities by gas chromatography despite its decided yellow color. The color was readily removed from a specimen of the RJ-5 residue by use of a silica gel column, giving a dark brown material which could be eluted from the gel column with methanol. Gas chromatographic analysis showed a single peak* with approximately the same retention time as RJ-5. The material may be a dimer or higher oligomer of an RJ-5 component which readily reverts to the monomeric form upon vaporization. Further characterization by proton or Carbon-13 NMR would be required to test this possibility.

The RJ-5 residue was found to be also completely decolorized upon passage through Attapulgus clay. Treatment of the total residue with clay would be completely feasible, though this has not yet been done.

2. Redistillation of Fraction 2

Since fraction 2 contained a rather large amount of MCH, it was decided to make a closer cut between the MCH and RJ-4. This fraction was added to the still pot and as its initial boiling point was approached, a small cut was taken. The RJ-4 was then drained from the pot. Gas chromatographic analysis of the fraction showed that the MCH had been almost completely removed.

Distillation data (ASTM D 86) for all fractions and the RJ-5 residue are presented in Table 15.

3. Additional Analyses of Fractions

Dr. R. D. Butler (AFAPL/SFF) has performed gas chromatographic analyses (ref. 15) of all three fractions and the RJ-5 residue using a column and instrument conditions which allowed measurement of the various isomeric forms for each component. Summarized, his findings are that fraction 1 is 99.77% pure MCH, fraction 2 is 94.15% RJ-4 with the two lowest boiling isomers of RJ-5 making up the rest of the sample. Fraction 3 has a 99% purity with the major isomer of RJ-4 being the only impurity. The RJ-5 residue showed no chromatographic impurities despite its yellow color. Its isomeric composition was considerably different than that of the starting RJ-5. It appeared to be enriched in the higher boiling isomers but it cannot be conclusively stated that the composition change is due to selective fractionation rather than isomerization.

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*GC analyses were performed principally to evaluate the separation of MCH, RJ-4, and RJ-5. Resolution of the various isomers of RJ-5 was incomplete.

Table 15

DISTILLATION DATA FOR JP-9 FRACTIONS (ASTM D-86)

	Observed	Spec. Limit
Fraction 1 - Methylcyclohexane		
Initial Boiling Point, min. °F	212	212
End Point, max. °F	213	215
Fraction 2 - RJ-4 (After Redistillation)		
Initial Boiling Point, min. °F	413	400
Fuel Evaporated, 5% at max. °F	417	415
Fuel Evaporated, 50% at max. °F	426	*
Fuel Evaporated, 90% at max. °F	440	*
End Point, max. °F	454	430
Residue	1.5	1.5
Distillation Loss	1.0	1.0
Fraction 3 - RJ-5		
Initial Boiling Point, min. °F	508	470
10% Recovered, max. temp., °F	512	*
20% Recovered, max. temp., °F	514	*
50% Recovered, max. temp., °F	518	*
90% Recovered, max. temp., °F	520	*
End Point, °F	522	539
Residue, vol %, max.	1.0	1.5
Loss, vol %, max.	1.5	1.5
Undistilled RJ-5 Residue (Clay-Treated Specimen)		
Initial Boiling Point, min. °F	513	470
10% Recovered, max. temp. °F	518	*
20% Recovered, max. temp. °F	518	*
50% Recovered, max. temp. °F	519	*
90% Recovered, max. temp. °F	522	*
End Point, °F	536	539
Residue, vol %, max.	1.5	1.5
Loss, vol %, max.	1.0	1.5

*To be reported, not limited.

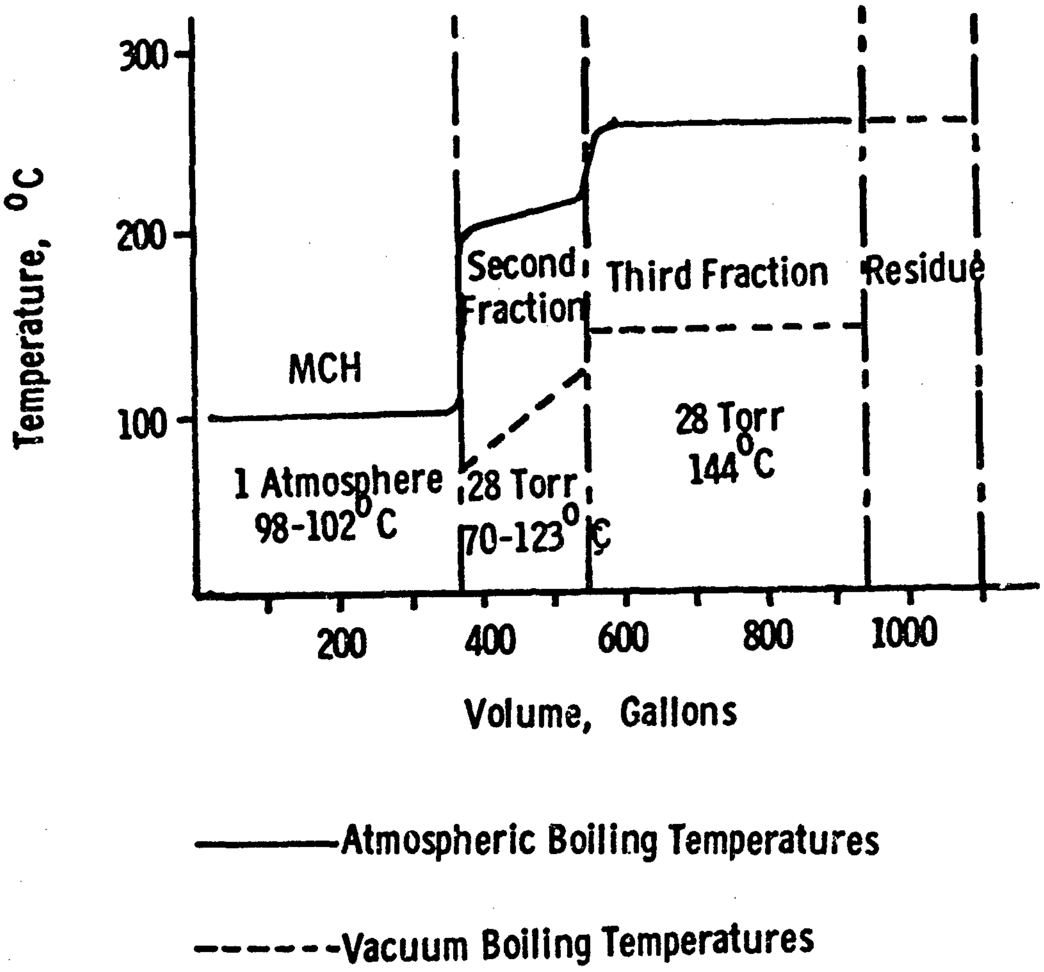

Figure 17. Volume, Temperature, and Pressure Used in Distilling JP-9 Fuel.

SECTION VI

FUEL COMPOSITION AND PROPERTIES

A. ANALYSIS OF METALS IN FUELS

1. Determination of Iron in JP-5 Fuel Sample

A sample of JP-5 fuel, to which ferrocene had been added, was submitted to this laboratory for determination of its iron content.

Ferrocene is chemically similar to Ethyl Corporation's CI-2 additive (methylcyclopentadienyl manganese, tricarbonyl), thus an established analytical procedure (ref. 16) for this latter material was modified to make it applicable to ferrocene. The major change in the procedure was in the final measuring step, with atomic absorption spectroscopy being used instead of colorimetry.

The procedure which was followed consisted of the decomposition of ferrocene which was contained in the fuel using a solution of bromine in carbon tetrachloride. Iron was then extracted with phosphoric acid solution and water. Organic matter in this extract was destroyed by a nitric acid - phosphoric acid oxidation.

The iron concentration in the extract was determined by comparing it to aqueous iron standards using atomic absorption spectrophotometry. Results for duplicate determinations are given below.

	Concentration (ppm, wt.)	
	Iron	Ferrocene
Determination 1	126	419
Determination 2	124	413

2. Trace Metals Content in Shelldyne-H Samples

Trace metals were determined in various Shelldyne specimens by emission spectrographic analysis. Included in this study were five specimens of Shelldyne-H, a specimen of Shelldyne and two other hydrocarbon fuels for comparison.

Trace metals were separated by slowly evaporating a portion of each fuel in a heated spectrographic cup-electrode. Five-gram specimens of each fuel were evaporated by drop-wise addition to heated electrodes. Results are given in Table 16.

Table 16

TRACE METALS CONTENT OF HIGH DENSITY FUEL COMPONENTS

Concentration ppm (wt/wt)

Element	Shelldyne-H 11410-103	Shelldyne-H 10659-1732	Shelldyne-H LR-103-18-174	Shelldyne 56612	Shelldyne-H Honeywell	RJ-J Hydrocarbon Fuel	Sample TMC-J
Silicon	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Manganese	0.006	0.006	0.006	0.002	0.006	0.006	0.006
Magnesium	0.04	0.04	0.04	0.04	0.04	0.04	0.04
Tin	0.4	0.2	<0.02	<0.02	<0.02	<0.02	0.02
Iron	0.16	0.16	0.16	0.16	0.16	0.12	0.12
Aluminum	0.08	0.10	0.08	0.10	0.08	0.08	0.08
Copper	0.02	0.02	0.02	0.02	0.01	0.02	0.01
Lead	0.04	<0.02	<0.02	<0.02	0.02	<0.02	0.02

3. Copper, Zinc, Lead and Iron Content of AFFB-16-73 Fuel Samples

Two samples of AFFB-16-73 were submitted for measurement of trace lead, copper, zinc and iron. These metals were determined by atomic absorption spectrophotometry, giving the following results:

Sample	Metal Content (ppb w/w)			
	Copper	Zinc	Lead	Iron
Incoming Fuel	8.5	12.4	123	22
Engine Pump Outlet	9.0	12.4	117	22

4. Determination of Trace Copper in JP-4 and JP-5 Samples

The copper content of these two fuel specimens was determined using an atomic absorption spectrophotometric procedure developed previously for that purpose (ref. 17).

Sample	Copper Content (ppb-wt)
JP-4, from cell #203 Bldg. 29E 6-13-75	28.6
JP-5, from cell #203 Bldg. 29E 6-13-75	318.8

5. Determination of Trace Metals in JP-4 Fuel Sample

A sample of JP-4 #1660 was analyzed for content of trace copper, zinc, lead, and iron. These determinations were performed by an atomic absorption procedure (ref. 17). Results are given below.

Metal	ppb (wt)
Copper	26.7, 23.1; Av. 24.9
Zinc	4.0
Lead	None detected[a]
Iron	<5[b]

[a] Lower detection limit for lead is 25 ppb (wt).

[b] Lower detection limit for iron is approximately 5 ppb (wt); iron was estimated to be at the 1 ppb level.

B. ELEMENTAL ANALYSES OF FUELS

1. Elemental Analysis of Hydrocarbon Fuels

Several samples of hydrocarbon fuels were submitted to this laboratory for the determination of carbon, hydrogen, oxygen, nitrogen, and sulfur. Duplicate analyses for each of these elements are presented in Table 17.

2. Elemental Analysis of JP-4 Blends and Additive

JP-4 fuel and an additive were blended to investigate the effect of aromatic content on fuel performance. Percent carbon and hydrogen data were sought for subsequent correlation to behavior such as heat of combustion. Further data on sulfur-containing species present were desired. Results are given below:

	Weight Percent		
Sample	Carbon	Hydrogen	Sulfur
JP-4 Additive	90.11	9.85	0.016
	90.16	9.84	0.012
Avg	90.13	9.84	0.014
Modified JP-4 Fuel	86.49	13.34	0.032
	86.54	13.46	0.038
Avg	86.51	13.40	0.035
JP-4 Baseline Fuel	85.63	14.03	0.030
	85.51	14.15	0.035
Avg	85.57	14.09	0.033

Sulfur was so low as to make it impossible to determine mercaptan sulfur by microanalysis.

C. DETERMINATION OF DISULFIDE SULFUR IN FUELS

1. Determination of Disulfide Sulfur in JP-4 Samples

Three samples were submitted to this laboratory for the determination of disulfide sulfur content. An ASTM method has not been established for this determination, however a Universal Oil Products (UOP) procedure (ref. 18) is available and was employed for this purpose.

A preliminary determination of mercaptan sulfur in the sample was performed by a potentiometric titration with silver nitrate

Table 17

ELEMENTAL ANALYSES OF HYDROCARBON FUELS

Sample		Weight Percent				
		Carbon	Hydrogen	Nitrogen	Oxygen	Sulfur
AFFB 16-73		85.09	14.61	0.011	0.10	0.016
		85.20	14.57	0.010_5	0.08	0.014
	Av.	85.15	14.59	0.010^2	0.09	0.015
Del 1		89.80	10.04	0.005	0.10	0.012
		89.78	9.91	0.006_5	0.07_5	0.010
	Av.	89.79	9.98	0.005^2	0.08^2	0.011
Del P-1		85.88	13.82	0.005	0.08	0.01;
		85.82	13.79	0.007	0.06	
	Av.	85.85	13.81	0.006	0.07	
Del P-2		86.49	13.36	0.004	0.02	0.016
		86.42	13.29	0.006	0.01_5	0.014
	Av.	86.46	13.33	0.005	0.01^2	0.015
Del P-3		86.86	12.63	0.004	0.03	0.012
		87.00	12.80	0.005_5	0.02_5	0.014
	Av.	86.94	12.72	0.004^2	0.02^2	0.013
Del P-4		84.70	13.42	0.72	0.08	0.014
		84.89	13.30	0.74	0.10	0.017
	Av.	84.79	13.36	0.73	0.09	0.016
Del P-5		85.48	13.66	0.21	0.20	0.015
		85.60	13.75	0.19	0.22	0.012
	Av.	85.54	13.71	0.20	0.21	0.014
Del P-6		86.01	13.73	0.057	0.05	0.013
		85.87	13.85	0.048_5	0.04_5	0.016
	Av.	85.94	13.79	0.052^2	0.04^2	0.015
HiSol-3		89.35	10.55	0.002	none or trace	0.021
		89.45	10.48	0.002	" "	.026
	Av.	89.40	10.32	0.002		0.024
NASA 60T/40JA		88.73	10.94	0.002	0.06	0.010
		88.76	11.10	0.002	0.07	0.013
	Av.	88.75	11.02	0.002	0.07	0.012
JP-5, 4-18-75		86.13	13.77	0.046	-	0.005
		86.18	13.80	0.049	-	0.006
	Av.	86.15	13.78	0.048	-	0.006
Syn Crude Tanker Sample 4-7-75		85.18	13.89	0.025	0.47	0.010
		85.24	14.00	0.030	0.40	0.011
	Av.	85.21	13.95	0.027	0.43	0.011
Syn Crude Tank 17 4-6-75		84.23	14.18	0.022	0.65	0.002
		84.40	14.30	0.025	0.60	0.002
	Av.	84.32	14.24	0.023	0.62	0.002
NASA CE-B5		88.31	11.59	0.007	0.09	0.004
		88.31	11.58	0.007	0.08	0.004
	Av.	88.31	11.59	0.007	0.09	0.004

solution, according to UOP Method 163. Disulfides were then reduced to mercaptans and the mercaptide ions were titrated with silver nitrate solution. The mercaptan sulfur measured by the second titration was equivalent to the amount of mercaptan originally present in sample plus that which resultd from reduction of disulfides. The disulfide sulfur in the sample is the difference between the mercaptan sulfur content before and after reduction.

An error was uncovered in the equation presented in the UOP Method. Communications with Universal Oil Products have confirmed the error. The corrected equation for the calculation is:

$$\text{Disulfide sulfur as S, Wt \%} = \frac{3.2N}{G}\left(\frac{A}{25} + \frac{B}{150} - \frac{C}{V_1}\right)$$

A = volume of silver nitrate used to titrate the mercaptans in a 50-ml aliquot of reaction mixture, ml.

B = volume of silver nitrate used to titrate contents of gas washing bottle, ml.

C = volume of silver nitrate used to titrate mercaptans before reduction in a volume, V_1, of sample, ml.

N = normality of silver nitrate solution

G = specific gravity of sample.

2. Results

Fuel	Mercaptan Sulfur (ppm, wt.)	Disulfide Sulfur (%, wt.)
Amoco JP-4	5.4 6.3[a]	0.037 0.037[a]
AFFB-16-73	2.3	0.004
ARCO JP-4	0.5	0.002
JP-4 1660	<1	0.02

[a] Duplicate determinations.

D. PHYSICAL PROPERTIES OF FUELS

1. Heat of Combustion of JP-4 Samples

Heat of combustion values for ten samples of JP-4 fuel from different batches and suppliers were determined by the bomb calorimeter exactly as described in ASTM D 240. A net value for each sample was calculated from the corresponding gross heat of combustion using the equation:

$$H_n = 4310 + 0.7195\ H_g$$

where H_n = net heat of combustion, Btu/lb

H_g = gross heat of combustion, Btu/lb

A benzoic acid specimen, for which the heat of combustion has been compared to the National Bureau of Standard sample, was measured as a reference standard. Excellent agreement with the established value was obtained as shown in Table 18.

Table 18

HEAT OF COMBUSTION OF BENZOIC ACID

	Btu/lb	Cal/g
Literature Value	11,373	6318
Determined Value	11,366	6314

Heat of combustion values for the fuel specimens are presented in Table 19.

2. Determination of Luminometer Number and Smoke Point for Three Fuel Blends

Luminometer numbers for three fuel blends were obtained according to ASTM D 1740. The luminometer number of an aviation fuel, a measure of its flame temperature at a fixed flame radiation in the green-yellow band of the visible spectrum, can be correlated with the combustion characteristics of the fuel.

Smoke point (ASTM D 1322) is related to luminometer number and the 1975 ASTM Annual Book of Standards, part 22 presents a means of converting smoke point to luminometer number. Smoke points have been obtained and converted to luminometer number for the three fuels.

		Luminometer Number	
Sample	Smoke Point	Direct	By Conversion
Del-F-1	23.0	42.4	51 ± 10
Del-F-2	20.8	41.4	45 ± 10
Del-F-3	17.0	32.0	33 ± 10

Table 19

HEATS OF COMBUSTION FOR TEN JP-4 SPECIMENS

Sample		Gross Heat of Combustion		Net Heat of Combustion	
		Btu/lb	Cal/g	Btu/lb	Cal/g
992		19,784	10,991		
		19,785	10,992		
	Avg	19,785	10,992	18,545	10,303
1019		19,867	11,037		
		19,887	11,048		
	Avg	19,877	11,043	18,612	10,340
1044		19,955	11,086		
		19,973	11,096		
	Avg	19,964	11,091	18,674	10,374
1054		20,031	11,128		
		19,978	11,099		
	Avg	20,005	11,114	18,704	10,391
1055		19,974	11,097		
		19,974	11,097		
	Avg	19,974	11,097	18,681	10,378
1057		19,938	11,077		
		19,972	11,096		
	Avg	19,955	11,086	18,668	10,371
1058		20,013	11,118		
		20,006	11,114		
	Avg	20,010	11,117	18,707	10,393
1061		20,082	11,157		
		20,110	11,172		
	Avg	20,096	11,164	18,769	10,427
1063		19,925	11,069		
		19,917	11,065		
	Avg	19,921	11,067	18,643	10,357
[illegible]		20,094	11,163		
		20,114	11,174		
	Avg	20,104	11,169	18,775	10,430

3. Distillation Range and Vapor Pressure Measurements on JP-7 Samples

Samples of JP-7 fuel #209 and Exxon Refinery Tank 16, Batch 85 were examined to determine compliance with MIL-T-38219. A distillation was performed on each according to ASTM Method D 86 and vapor pressures were determined at 300°F and 500°F using the vapor reflux method (ref. 19).

a. ASTM D 86 Distillation

Results for duplicate distillations are given below.

Distillation Points	Temperature (°F) #209	Temperature (°F) Exxon	Specification Requirement (°F)
Initial Boiling Point		373	350 minimum
	356.9	372	
	358.7	372	
10% Fuel Evaporated	389.3	399	385 minimum
	394.7	400	
20% " "	407.3	413	403 minimum
	409.1	415	
50% " "	430.8	440	--
	432.6	442	
90% " "	463.2	480	500 maximum
	466.8	483	
End Point	479.4	493	550 maximum
	483.0	492	

b. Vapor Pressures by the Vapor Reflux Method

Vapor pressure values at 300°F and 500°F were determined for these two fuels by recording temperature/pressure data for various stable reflux conditions. These data are presented in Tables 20 and 21.

The vapor pressures at the indicated temperatures were determined to be:

Sample	Vapor Pressure (psi) 300°F	Vapor Pressure (psi) 500°F
#209 JP-7	2.99^{6}	42.5
Exxon JP-7	2.61	39.2

Table 20

VAPOR REFLUX DATA FOR JP-7, #209

Corrected Pressure (mm Hg)	Temperature (°C)	1000/°K
109.0	136.5	2.442
215.2	159.5	2.312
391.3	182.0	2.197
639.1	203.0	2.101
740.7 (atmospheric)	208.8	2.076

Table 21

VAPOR REFLUX DATA FOR JP-7
(Exxon, Refining Tank 16, Batch 85)

Corrected Pressure (Torrs)	Temperature (°C)	1000/°K
166.8	155.5	2.334
268.2	171.8	2.248
494.8	197.0	2.128
659.0	209	2.075
747.0	214	2.053

E. HYDROCARBON TYPE ANALYSES OF FUELS

A preliminary elution chromatographic separation was performed on the samples using a 50-cm column of activated bauxite and silica gel and following a procedure exactly as described in ASTM Method D 2549. By this operation each specimen was separated into two fractions, one containing paraffinic and naphthenic hydrocarbons and the other containing aromatics and condensed naphthenic aromatics.

This type analysis was performed on each of the collected fractions by mass spectrometry according to ASTM Method D 2425. Eleven hydrocarbon types and their average carbon numbers were determined. The analyses involved summation of mass spectral peaks characteristic of each hydrocarbon type. These data were used to construct matrices consisting of sets of ten linear simultaneous equations for the saturate fractions and five equations for the aromatic fractions. Computer solution of these equations yielded the weight percent of each compound type. Data are presented in Table 22.

Table 22

HYDROCARBON TYPE ANALYSES FOR VARIOUS FUELS (Wt. %)

Compound Type	JP-5, 4-18-75	Aviation Kerosene ASTM D 1655-74	High Aromatic Kerosene ASTM E82-74	Syn Crude Tanker[a] 4-7-75	Syn Crude Tank 17[a] 4-6-75	AFFB-16-73[a]	Del 1[a]	Del F-1[a]
Paraffins	50.7 (12)[b]	49.4 (12)[b]	46.4 (12)[b]	66.7 (8.9)[b]	66.2 (8.9)[b]	63.8 (9.1)[b]	0.6 (8.5)[b]	52.7 (9.1)[b]
Monocycloparaffins	17.6 (12)	24.1 (12)	25.1 (12)	17.8	18.4	21.8	-	17.6
Dicycloparaffins	3.0 (13)	7.3 (13)	5.5 (13)	2.4	2.4	5.5	-	4.5
Tricycloparaffins	0.3 (13)	2.8 (13)	1.7 (13)	-	-	-	-	-
Alkylbenzenes	17.7 (11)	12.7 (10.7)	17.7 (11.2)	11.6 (8.6)	11.5 (8.6)	7.7 (8.8)	99.4 (8.5)	24.5 (8.5)
Indans & Tetralins	9.3 (12)	2.1 (11)	2.0 (11)	1.5	1.5	1.2	-	0.7
Indenes	0	0.5 (10)	0.2 (10)	-	-	-	-	-
Naphthalene	0.1 (10)	0.1 (10)	0.1 (10)	-	-	-	-	-
Naphthalenes	1.1 (12)	0.7 (11.5)	0.8 (11.5)	none or trace	none or trace	none or trace	none or trace	none or trace
Acenaphthenes	0.02 (12)	0.3 (12)	0.5 (12)	-	-	-	-	-
Acenaphthylenes	0	0	0	-	-	-	-	-
Tricycloaromatics	0.02 (14)	0	0	-	-	-	-	-

[a] Data given were obtained by ASTM Method D 2789. Values given are in volume percent.

[b] Average carbon number is given in parentheses.

SECTION VII

SUPPORTING ANALYSES AND STUDIES

Certain analyses, investigations, and studies have been performed in response to AFAPL needs arising from Air Force in-house programs and from a variety of operational problems involving fuels and fuel system materials.

As an example of support of an in-house Air Force Program, in this case the T-56 combustion exhaust monitoring program, over one hundred analyses of calibrating gas mixtures were performed. An example of work performed to solve an operational problem is the measurement of carbonaceous deposits in, and subsequent thorough cleaning of, B-1 fuel/oil heat exchangers. Details of these and other investigations are presented in this section.

A. B-1 FUEL/OIL HEAT EXCHANGER

Previous work in this laboratory has resulted in the development of a method for measuring the amount of carbonaceous deposit in B-1 fuel/oil heat exchangers (ref. 20). The determination consists of measuring the amount of carbon dioxide generated by heating the tube in a flow of oxygen. This analysis has been performed periodically; results are summarized in Table 23. As a final step of this treatment, the tube is rinsed with hot (200°F) 5% oxalic acid solution to remove metal oxides and complex salts.

This final rinse, however, did not prove to be totally satisfactory for removing all of the unoxidizable material. An investigation was performed to determine the effectiveness of using commercial alkaline descaling compounds to remove both fuel deposits and non-oxidizable residues.

1. Commercial Formulations

The descaling compounds used in this evaluation are manufactured by Turco Corporation and are identified as:

Torco 4008 - A highly alkaline liquid which is used in undiluted form.

Turco 4338 - A solid material (alkaline/permanganate mixture) which is used in aqueous solution.

2. Experimental

The cleaning solutions and procedure are, in general, similar to those contained in Military Specification MIL-D-26549A

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(ref. 21). However, since that procedure deals with components which can be immersed in a bath, obvious modifications in procedure were required.

The heat exchanger tube was plumbed with stainless steel tubing so that the solutions could be circulated through its interior. The device was immersed vertically in a water bath which was heated to 200°F or greater by means of live steam. Additionally, the solutions were heated prior to entering the heat exchanger.

A solution of Turco 4338 was prepared which matched as nearly as possible the composition described in the referenced specification, i.e., 20 oz. sodium hydroxide, 20 oz. sodium carbonate, and 10 oz. potassium permanganate per gallon of solution. Accordingly, 50 oz. of the prepared formulation was used per gallon of water. Even with prolonged agitation, however, some of the material remained undissolved. These solids were removed by filtration before using the solution.

The solutions were circulated through the heat exchanger by means of a peristaltic pump. Undiluted Turco 4008, the first solution to be used, was recirculated through the tube for one hour. This operation was followed by a pressure rinse with clear water. The solution of Turco 4338, also at 200°F, was then circulated through the tube, in the same manner as the previous solution, for one hour. A pressure rinse with clear water was, again, used to remove the cleaning solution.

A third and final solution consisting of 25% by volume of 70% nitric acid (actual concentration approximately 17.5% nitric acid) was circulated through the tube at room temperature for a period of 30 minutes.

An extended high pressure rinse with water and finally with distilled water was used to remove all loose material.

This cleaning procedure appeared to be quite effective in removing both fuel deposits and non-oxidizable residues.

B. CALIBRATING GAS MIXTURE ANALYSES

Over one hundred different calibrating gas mixtures were sampled and analyzed during the course of this program. These calibrating gases included nitrogen mixtures of CO, CO_2, NO_2, NO, propane, and methane and were used in conjunction with T-56 combustor exhaust monitoring. Data are presented in Table 24 for gas mixtures whose cylinder identification numbers were provided.

Table 24

ANALYSIS OF CALIBRATING GAS MIXTURES

Gas	Nominal Conc	Cylinder Serial No.	Determined Concentration
CO	318 ppm	LK 72938	292, 292 (Av. 292 ppm)
CO	792 ppm	257737	751, 762 (Av. 757 ppm)
CO	0.146%	144564	0.144%
CO	274 ppm	LK 81256	268 ppm
CO	822 ppm	SG 20083B	791, 797 (Av. 794 ppm)
CO	0.149%	SG 12253B	0.147^{5}%
CO	0.305%	SG 22909B	0.332%, 0.332% (Av. 0.332%)
CO	0.198%	SG 6199B	0.218%, 0.218% (Av. 0.218%)
CO	1.49%	SG 5134B	1.41%, 1.40% (Av. 1.41%)
CO	0.371%	SG 5174B	0.386%, 0.394% (Av. 0.391%)
CO	1547 ppm	LK 124937	1530, 1530 (Av. 1530 ppm)
CO	303 ppm	7621	318, 317 (Av. 317 ppm)
CO_2	2.04%	SG 17192B	1.93%$^{(a)}$
CO_2	2.97%	7151	3.03%
CO_2	3.01%	SG 11757B	3.45%
CO_2	2.04%	SG 9340B	1.93%
CO_2	7.95%	SG 10506B	7.63%
CO_2	8.0%	LK 124522	7.67%
CO_2	2.19%	K 227301	2.09%
CO_2	7.8%	LK 124515	7.36%
CO_2	2.24%	SG 3800B	2.33%
CO_2	2.0%	LK 124802	2.02%
CO_2	8.64%	39009	8.56%
Propane	291 ppm	LK 124905	317, 316 (Av. 316 ppm)
NO	177 ppm	SG 17583B	169, 167, 167 (Av. 168 ppm)
NO	187 ppm	7453	142, 146, 144, 141, 153, 148, 151 (Av. 146 ppm)
NO	405 ppm	GG 20082B	317, 313, 320, 322 (Av. 318 ppm)
NO	100 ppm	G 5735	100, 95, 102, 98 (Av. 99 ppm)
NO	398 ppm	G 5694	391, 379, 389 (Av. 386 ppm)
NO	801 ppm	G 5670	780, 770, 793 (Av. 781 ppm)
NO	80 ppm	9016	71, 77, 72 (Av. 73 ppm)
NO	186 ppm	N 496391	152, 148, 154 (Av. 151 ppm)
NO	185 ppm	LK 70167	178, 183 (Av. 181 ppm)
NO	79 ppm	LK 70542	104, 106 (Av. 105 ppm)
NO_2	84 ppm	SG 2186B	80, 77, 76 (Av. 78 ppm)
NO_2	78 ppm	NM 4776	67, 61, 65 (Av. 64 ppm)
NO_2	78 ppm	6-981	<10, <10 (Av. <10 ppm)

(a) CO_2 was determined by mass spectrometry. Indicated values represent average of three analyses on each cylinder.

Mixtures containing oxides of nitrogen were sampled by using a sampling train according to a procedure presented in the Federal Register (ref. 22). The major components of the sampling train are a small pump, a rotameter and a manometer. Using this apparatus, pre-evacuated two-liter flasks containing measured amounts of oxidizing media were filled with the gas mixtures.

Gases containing carbon monoxide or propane were analyzed by gas chromatography. Carbon dioxide was determined by mass spectrometry. The phenoldisulfonic acid method (ref. 23) was used for NO and NO_2.

C. EVALUATION OF DUPONT METHOD FOR DETERMINATION OF DCI-4A CORROSION INHIBITOR

The purpose of this investigation was to evaluate DuPont Petroleum Laboratory Method M-14 for the determination of DuPont Corrosion Inhibitor No. 4A (DCI-4A) in jet fuel.

By this method, DCI-4A is removed from the fuel by ion exchange chromatography using the nonaqueous anion exchange resin, Rohm and Haas' Amberlyst® A-29, in its chloride form. The resin is rinsed with heptane and the DCI-4A is eluted with CO_2-saturated methanol. The methanol effluent is then evaporated to dryness and the resulting residue is dissolved in carbon tetrachloride and analyzed by infrared spectrophotometry. Since DCI-4A contains carbonyl functionality, the absorbance of the carbonyl band in the infrared spectrum is measured and compared to a previously prepared calibration curve.

Several problems were found to exist which lessen the usefulness of the method. The basic problem was the inability of the recommended ion exchange resin to remove all of the DCI-4A under the conditions specified in the method. A second problem of carbonyl containing impurities in the fuel was anticipated in the method and the author of the method has recommended that it not be used when such impurities occur.

The findings of this investigation may be summarized as:

a. Some JP-4 fuels contain extractable materials giving rise to interfering IR adsorption. As stated in the method, the procedure cannot be applied to such fuels.

b. Great care must be exercised in the evaporation of the methanol extract containing the DCI-4A. The evaporative bath technique is not recommended. Evaporation in a flow of air at room temperature insures that none of the additive will be lost by volatilization.

c. For complete retention of the additive, a resin column longer than the one specified by the method is required.

d. It is well to run a blank on the resin so that correction for extracted interfering materials may be obtained.

D. DETERMINATION OF TOTAL ACID NUMBER FOR CORROSION INHIBITOR NO. 4269-28

The applicability of ASTM Method D 664 to the subject corrosion inhibitor was evaluated. The procedure consists of a potentiometric titration of acidic constituents using a standard alcoholic potassium hydroxide solution. A titrating solvent, composed of toluene, isopropanol and 0.5% water was used. A solvent blank was determined prior to titration of weighed amounts of the sample. Several replicates were performed for each operation in order to establish the precision to be expected with this type of specimen.

Resulting values for Total Acid Number from four determinations are:

Total Acid No. (mg KOH/gm)	Deviation from Mean
120.3	0.5
119.5	0.3
121.0	1.2
118.4	1.4
119.8 mean	0.85 average deviation

The standard deviation for the four determinations is 1.9.

These measurements are well within the repeatability of 5 mg/g as specified by D 664.

E. T-56 COMBUSTOR EXHAUST PARTICULATE AND PROBE TIP DEPOSIT MASS INVESTIGATION

1. Particulate Mass

The mass of particulate matter obtained from the combustor exhaust stream was measured after its collection on preweighed filters. The 142-mm disc filters were principally Gelman Type A Glass Fiber; however, limited studies were conducted using Teflon® and DM Metricel® 450 filters.

Filters were allowed to equilibrate in a controlled environment of 50% R.H. and 75°F before weighing. Weighings were performed to the nearest microgram using a Mettler Instrument

Corp. Micro balance, Type M5. Sealed and labelled petri dishes were used to transport the filters to and from AFAPL. After completion of the collection, filters were allowed a 24-hour residence time in the controlled environment before reweighing.

Several control tests (9AK31, 9AL31, and 9AM31) indicated that the glass fiber filters lose a small amount of weight after the passage of 1000-2000 liters of room air. This is presumably due to the loss of fine glass fibers. Similarly, the D.M. Metricel 450 filters lost a small amount of weight during a blank run with air.

The Teflon filters lost considerable weight during their actual use at elevated temperatures. This was evident by the fact that even though a heavy dark deposit could be observed on the filter, a net weight loss was recorded. In order to estimate the amount of deposit in these cases, an attempt was made to remove the material adhering to the filter by the force of a stream of acetone. The residue was weighed after evaporation of the acetone. This operation did not completely remove the deposit, so the filter was reweighed and then treated with red fuming nitric acid. This treatment also proved to be ineffective in removing the remaining particulate. The particulate masses for the Teflon filters thus represented minimum values.

2. Probe Tip Deposits

The purpose of this study was to determine the effect of gas dilution techniques on the amount of probe tip deposit obtained. Deposits were measured after their removal by AFAPL/SFF personnel using solvent and water rinses. The water rinse, in particular, contained solids which were dislodged by the rinsing stream. It was the original intent to distinguish between dissolved material and suspended materials. However the solids formed a ring at the point where the surface of the liquid met the container inner wall. Wiping was the only effective means of removing the ring. Consequently, values reported are for the total nonvolatile residue obtained by evaporation of the solvent. The organic solvents used were methylene chloride and chloroform.

In some instances, the residues obtained had an unusual appearance. A water rinse, 5AC32, gave a large residue consisting of a white powdery material. Characterization of this material was not performed as it was believed to be airborne dust. Samples 9BA34 through 9BE34, methylene chloride rinses, gave small amounts of yellow-white residue. The material proved to be a silicone grease. Discussion indicated that it could have originated from the rubber tubing (possibly a silicone rubber) used in the collection system at AFAPL.

F. TRANSFORMER FLUID EVALUTION

Two transformer fluid specimens were analyzed for total dissolved gases and certain electrical properties.

1. Analysis of Dissolved Gases

Analyses were performed on separate portions of fluid which had been removed from the original containers with a minimum of exposure to the atmosphere.

A DuPont Instruments 21-103C mass spectrometer was used to measure and analyze dissolved gases after their removal from the fluids by vacuum desorption. Results given in ml of gas/ml of liquid at 25°C are presented in Table 25.

Table 25

ANALYSIS OF DISSOLVED GASES IN TRANSFORMER FLUIDS
(ml gas/ml fluid @ 25°C)

Components	Fluid OP-35-1	Fluid OP-35-2
Nitrogen	0.034	0.037
Oxygen	0.016	0.016
Carbon Dioxide	1.9×10^{-4}	2.0×10^{-4}
Hydrogen	5×10^{-6}	5×10^{-6}
Ethane	1.5×10^{-5}	1.9×10^{-5}
Ethylene	3.0×10^{-5}	3.4×10^{-5}
Acetylene	3.0×10^{-5}	2.8×10^{-5}
Methane	2.0×10^{-5}	2.2×10^{-5}
Carbon Monoxide	3.5×10^{-5}	5.5×10^{-5}

2. Electrical Properties

Dielectric breakdown voltage (ASTM D 877-67) was determined for each fluid. Additionally, power factors (5) at 25° and 100°C were measured and are presented in Table 26.

Table 26

ELECTRICAL PROPERTIES OF TRANSFORMER FLUIDS

Percent Power Factor	Fluid OP-35-1	Fluid OP-35-2
at 60 Hz, 25°C	0.090	0.090
at 1000 Hz, 25°C	0.017	0.004
at 60 Hz, 100°C	1.20	1.12
at 1000 Hz, 100°C	0.07	0.06
Dielectric Breakdown Voltage (KV)	34	46

G. FEASIBILITY EVALUATION OF ULTRAVIOLET PHOTOMETRIC DETECTOR FOR GAS CHROMATOGRAPHY

A rapid means of screening fuels for their aromatic constituents would be extremely useful. Gas chromatographic techniques provide the capability for rapid fuel compositional analysis but aromatic and paraffinic components cannot be readily differentiated by this means. Dr. R. D. Butler (SFF/AFAPL) has suggested the possibility of employing an ultraviolet absorption cell to detect aromatic constituents in the vapor phase as they elute from the chromatograph.

An investigation was conducted to experimentally test the feasibility of a UV photometric detector for gas chromatography. The proposed detector would employ quartz fiber optics to isolate the heated absorption cell from the delicate electronic and optical components. In this preliminary evaluation of feasibility, attention was given to the questions of specificity for aromatics, effect of increased "dead volume" and radiation loss in the fiber optics bundle.

All quartz fiber optic materials available are enclosed in a plastic of lower refraction index for optical insulation. A quartz bundle was obtained (International Light, Inc.) which was able to withstand temperatures up to 120°C. This is less than the ultimate temperature to be required of a G.C. detector cell but by having the fiber bundle tip offset and not in direct contact with the cell, no temperature problem was anticipated.

The absorption cell, in its final form, should have a 10-cm path and a volume of about 100 μl. Preliminary experiments were conducted using a quartz cell having a 1-cm path and a volume of 150 μl. As this volume approximates the volume of the proposed 10-cm cell, experiments showed the effect of cell volume. Cell, fiber optics and accessories were mounted in Aminco DW-2 spectrophotometer for these tests.

Conclusions from tests:

1. The fiber optics bundle which measured 500 x 2 mm was tested for UV transmission. At 250 nm, the shortest wavelength of likely interest, 31% transmission was measured. With a good UV source and detector, this is believed to be adequate.

2. The cell was connected to a chromatograph having a thermal conductivity (TC) detector. Vapors leaving the chromatograph and detector passed into the UV absorption cell. The volume of the interconnecting tubing was minimized but was by no means reduced to the smallest possible volume. The spectrophotometer was set for a full scale response of 10% transmission and measurements were recorded at 260 nm. An excellent response was obtained for benzene and toluene,

but no response was observed for hexane or heptane, even for a 10-fold increase in sample size. A mixture containing these four compounds was prepared with each of the aromatics being at 5% levels. The T.C. detector showed all peaks in their proper proportions but the absorption cell gave a response only to the aromatic constituents. No attempt was made to establish a detection limit. Use of a 10-cm cell will, of course, afford a 10-fold increase in sensitivity.

3. The effect of increased "dead volume" was examined. The volume of the interconnecting tubing was greater than that of the cell and may have allowed some mixing of sample after elution from the column. Nonetheless, reasonably sharp peaks, relative to those obtained with the TC detector, were obtained. Broadening as measured by half-widths was approximately 10%. There is good reason to believe that this figure can be appreciably reduced by optimizing hardware and physical layout of the apparatus.

The concept of the photometric G.C. detector is believed to be sound and to merit further work.

SECTION VIII

NONHAZARDOUS CALIBRATING FLUID DEVELOPMENT

A high flash-point calibrating fluid similar to, and suitable as a replacement for, test fluid MIL-F-7024B, Type II has been required to improve safety of operation and reduce the cost of construction of hazardous test facilities. Rigid physical property, chemical compatibility, toxicity, stability, and cost requirements greatly limited potential candidate materials for this application.

Certain of the requirements for the new calibrating test fluid were absolute with no allowable variance, while other requirements were not as stringent and some variance could be tolerated. Those requirements that are absolute are a minimum flash point of 250°F (121°C), with nonflammability being preferred, a viscosity of 1.1-1.2 cs at 25°C (77°F), compatibility with the O-ring seals and elastomers in the system, a very low order of toxicity, and noncorrosivity to the test system.

The requirements in which some variance can be tolerated are specific gravity of 0.751-0.802 (60°F/60°F; $D^{15.5°C}_{15.5°C}$), the cost of $2.80/gallon, and a thermal stability of at least 300°F (148.9°C). Although a specific gravity of 1.5 could possibly be tolerated, a value of 1.0 or less is preferable. Variable costs were considered a certainty in today's economic situation, and a set, low price is a luxury of the past. The thermal stability was required to exceed the overall test temperatures employed as well as those generated in various critical parts of the system.

The initial objective of this program was to find a test fluid that could be used in an experimental test stand to be designated by Air Force personnel. This fluid was not to be considered as the final calibrating test fluid unless its properties exactly matched those of the specifications, but rather was to serve as a guideline for future candidates. The cost of the fluid and amounts required immediately suggested that it would have to be an item of commerce. If the properties approached the desired specifications, especially in flash point and viscosity, it certainly could be considered as a future base stock for blending.

The extensive fluid data files at MRC which contain fluid-related data on over 2000 compounds representing almost all known classes of organic compounds, were searched. The files contain pertinent fluid data on the following classes of compounds:

1. Aromatic ethers
2. Alkylated aromatic ethers
3. Aliphatic aromatic ethers
4. Aromatic thioethers, alkylated aromatic thioethers, xanthates
5. Aliphatic ethers and aliphatic thioethers
6. Aromatic hydrocarbons and aliphatic-aromatic hydrocarbons
7. Aliphatic hydrocarbons
8. Esters
9. Ketones, anhydrides and hydroxyl compounds
10. Aliphatic amides, amines and nitriles
11. Heterocyclics, aromatic amines and nitriles
12. Organometallics--Al, As, B, Be, Bi, Cu, Fe, Ge, Sb, and Sn compounds
13. Silicates, silanes, and siloxanes
14. Phosphates, phosphonates, phosphines and phosphine oxides
15. Halogenated compounds--[illegible], and I--aromatic
16. Blends and commercial mixtures
17. Perfluorocarbons and partially fluorinated hydrocarbons

Classes 1-7, 9-12, and 16-17 could be eliminated immediately on the basis of one or more of the parameters. Classes 1-6 were eliminated on viscosity because they are viscous, high boiling liquids, and on compatibility with seals and elastomers. Many of these materials are good plasticizers and would attack elastomeric components of the system. The seventh class, aliphatic hydrocarbons, was eliminated because the lower members would fail on flash point and as one approached a molecular weight that would pass the flash point requirement, the compound would fail on viscosity. Classes 9-12 were failed on several parameters including viscosity, flash point, oxidative stability, cost, specific gravity, corrosivity. Class 16 was eliminated on viscosity, cost, and specific gravity because most were proprietary synthetic blends for a specific purpose that required very special properties. Class 17 was eliminated primarily on cost and on specific gravity (1.6-1.9).

Esters, silicon compounds, phosphorus compounds, and halogen compounds survived the preliminary screening as classes of compounds containing potential candidates. Esters suffer from the same deficiencies as the aliphatic hydrocarbons, i.e., the lower members have low flash points and low thermal stabilities. The compounds with molecular weights that would pass the flash point requirements would fail on viscosity. Additionally, the higher molecular weight esters are also good plasticizers and undoubtedly would attack the elastomeric components in the test system. The same is true of the phosphorus compounds except that phosphorus compounds are excellent plasticizers and paint removers. They are powerful enough solvents that aromatic phosphorus compounds are used as plasticizers for polyvinyl chloride.

Thus silicon compounds and halogen compounds were the only classes to survive a secondary screening. The silicones appeared to be excellent prospects except that they failed on viscosity. One of the lowest molecular weight silicones of commerce has a viscosity of 50 cs at 25°C (77°F). Otherwise, the silicones meet the requirements almost exactly. The silicates have a lower viscosity than and have properties similar to the silicones except that they have only a fair hydrolytic stability. If water were accidently permitted to enter the system at higher temperatures they would hydrolyze and could form abrasive siliceous materials. Silicates remain as potential candidates if the absence of water or moisture could be assured.

The required degree of fire resistance essentially dictated the use of a halogenated compound. Previous experience has taught that in order to obtain a minimum flash point of 250°F (12[illegible]) with self-extinguishing properties, an aromatic compound containing at least two bromines or three chlorines per benzene ring is required. For instance, the flash points of monochlorobenzene, dichlorobenzene, and monobromobenzene are 90°F (32°C), 150°F (65.5°C), and 149°F (65.0°C), respectively. A combination of MRC knowledge and consultation with Monsanto Company fluids experts (St. Louis, Mo.) finally led to the choice of technical 1,2,4-trichlorobenzene (1,2,4-TCB) as the best commercially available candidate calibrating test fluid.

However, it was pointed out that chlorinated materials have high densities and they could not possibly meet the specifications on specific gravity. There was a question as to whether or not the specific gravity of the fluid could be increased considerably over specifications without affecting the test stand data. It was decided that an increase in specific gravity from 0.80 to 1.45 (specific gravity of 1,2,4-trichlorobenzene) could be tolerated providing that it could be tested in an experimental test stand to determine the effect on the data. In this manner the data on the candidate fluid could be reconciled to the present data.

Chlorinated hydrocarbons are powerful solvents and are known to badly swell or even destroy rubber and certain types of elastomer seals. Normally Viton® O-rings are used to resist the action of these materials. Before using 1,2,4-TCB in a test stand, tests for its compatibility with test stand elastomers and seals was necessary.

A. COMPATIBILITY TESTS ON 1,2,4-TRICHLOROBENZENE (TCB)

1. Experimental

The dimensions and weights of the test stand and fuel system components were obtained prior to immersion in the test fluid. The components were then immersed in 1,2,4-TCB in a Petri dish, beaker, or other suitable container for the prescribed number of hours or days. The components were removed one at a time and immediately gently wiped until all visible signs of liquid had disappeared. The dimensions and weight of each were obtained and recorded.

2. Results and Conclusions

Solubility parameter calculations indicated that 1,2,4-TCB would swell rubber components in the test stand system and in fuel systems. These preliminary calculations were confirmed by the data in Table 27. All components that contained or were made of rubber swelled by about one-third and the weight gains were on the order of 175-200%.

It was concluded that 1,2,4-TCB cannot be used in the present experimental test stand because it will severely swell the rubber components. If the components have to be changed after each test, the calibration is lost.

The flash point and fire point specifications almost demand the use of a halogenated material. Silicones that meet the viscosity specifications are highly flammable and are not oxidatively stable. Phosphate esters that possess low viscosities attack rubbers and plastics nearly as badly as the halogenated materials and some of them are quite toxic. Other classes of organics can be eliminated for reasons given in report 74-23. This leaves fluorocarbons and halogenated aromatics. The fluorocarbon fluids are exceedingly expensive and are not readily available in commercial quantities.

If a halogenated aromatic such as 1,2,4-TCB is to be used as an experimental test fluid, it almost dictates that the O-rings, elastomeric seals and hoses will have to be changed. This is not always practical or desirable. However, the halogenated hydrocarbons are such powerful solvents that they will attack or swell almost any synthetic composition. Viton® [poly(vinylidene fluoride)] is one of the few known materials that will withstand the action of warm or hot halogenated hydrocarbons.

Another possibility which was considered was the use of water-based fluids. There are fluids such as the Ucons®, which could possibly be used because they contain corrosion inhibitors and other additives to stabilize the compositions. Most sealants and plastics are easily resistant to water based fluids.

Table 27

COMPATIBILITY TESTS WITH 1,2,4-TCB

Component	Before Treatment With 1,2,4-TCB Dimensions		Before Treatment With 1,2,4-TCB Weight, g	After Treatment With 1,2,4-TCB Dimensions	After Treatment With 1,2,4-TCB Weight, g	Comments
Test Stand Components*						
O-rings	34.8 mm ID 41.5 mm OD 3.6 mm thick	1	1.4929	46.3 mm ID 55.3 mm OD 4.6 mm thick	3.0942	33% swelling (OD); 161% weight gain
		2	1.4770	46.7 mm ID 56.2 mm OD 4.7 mm thick	4.2071	35% swelling (OD); 184% weight gain
		3	1.5091	49.3 mm ID 57.8 mm OD 4.6 mm thick	4.4847	39% swelling (OD); 197% weight gain
O-rings with Teflon (?) nylon(?) washer in center						
O-ring	37.4 mm ID 48.2 mm OD 5.4 mm thick		3.9186	49.6 mm ID 63.6 mm OD 7.2 mm thick	10.7267	32% swelling (OD); 174% weight gain
Teflon(?) nylon(?) washer	15.8 mm ID 38.7 mm OD 3.8 mm thick		3.8571	15.9 mm ID 38.2 mm OD 3.8 mm thick	3.8567	No swelling; no weight gain
Large O-ring	36.8 mm ID 47.8 mm OD 5.4 mm thick		3.7880	50.9 mm ID 65.4 mm OD 6.3 mm thick	11.0731	37% swelling (OD); 192% weight gain
Metal ring with rubber washer	20.6 mm ID 30.8 mm OD 4.6 mm thick		15.8739	36.9 cm ID 23.3 mm OD 6.1 mm thick	18.6865	20% swelling (OD); 17% weight gain; washer swelled away from ring
Black plastic and metal fitting with rubber lip and bushing	15.8 mm ID 20.2 mm OD 13.7 mm thick		3.9106	-	-	Rubber bushing swelled completely out of fitting
Large gasket	75.9 mm OD 0.4 mm thick		2.3397	79.1 mm OD 0.8 mm thick	4.3345	4% swelling (OD); 85% weight gain; gasket warped
Large gasket	85.7 mm OD 1.3 mm thick		9.1259	85.8 mm OD 2.0 mm thick	16.4940	Slight swelling; 81% weight gain; gasket warped
Moore gasket	85.8 mm OD 2.7 mm thick (outside edge)		61.0691	-	-	Could not be measured; adhesive removed; gasket fell apart
White circular plastic strip	0.8 mm thick 3.1 mm band width		1.0887	0.8 mm thick 3.2 mm band width	1.0887	No swelling; no weight gain
MIL-H-8794 hose	9.9 mm ID 19.1 mm thick 29.4 mm long		10.9203	-	-	Rubber or inside metal reinforcing ring swelled and extruded forcing fibrous casing out of shape
MIL-H-8788 hose	4.8 mm ID 16.8 mm thick 29.9 mm long		12.5192	-	-	Rubber inside metal reinforcing ring badly extruded; rubber casing swelled away from reinforcing ring
Fuel System O-rings**						
Precision No. 7177; AMS 7270E; O-ring	24.5 mm ID 31.9 mm OD 3.6 mm thick		1.1658	34.1 mm ID 43.2 mm OD 4.7 mm thick	3.0958	35% swelling (OD); 165% weight gain
Precision No. 7864; MIL-P-5315; O-ring	24.6 mm ID 31.9 mm OD 3.6 mm thick		1.0963	35.2 mm ID 45.1 mm OD 4.8 mm thick	3.6061	41% swelling (OD); 229% weight gain

*Immersed in 1,2,4-TCB for 64 hours at ambient temperature.

**Immersed in 1,2,4-TCB for 20 days at ambient temperature.

Water-based fluids were recommended for evaluation as the calibrating test fluid to replace MIL-F-7024B. They comprise the one remaining large class of fluids which have a potential of meeting the specifications for the calibrating test fluids, since organic fluids have been essentially eliminated.

There is some concern over the corrosivity of the water-based fluids, but they contain corrosion inhibitors and other additives to stabilize the composition. They are cheap in comparison to organic fluids, nonflammable, and their properties match the specifications more closely than do a majority of the organics. Additionally, they can be blended to almost any composition to meet property specifications within reasonable limits.

Several factors have recently developed which indicate that Freon materials, specifically Freon TF, mixed with fluid MIL-F-7024B Type II, should be reevaluated for use as a candidate fluid. The behavior of this material under test conditions has not fully been defined and should be the subject of an investigation.

SECTION IX

CONCLUSIONS

1. Studies of combustor exhaust products have shown that exhaust constituents can be collected in solvent-filled impingers to obtain reproducible fluorescence data using a laboratory spectrophotofluorometer. The fluorescence intensity is dependent upon the type of fuel being burned and can be correlated with the total hydrocarbon content of the exhaust. Multiple ring compounds such as biphenyl and polynuclear aromatics were believed to be responsible for the fluorescence. Broad band fluorescence, which interfered with in-situ Laser Raman measurements of exhaust gases, was shown to sharply decrease by increasing the wavelength of the exciting radiation.

2. Thermal stressing of hydrocarbon fuels causes compositional changes which can be monitored by spectrophotofluorometry. Fluorescence spectral changes were shown to correlate with JFTOT time-to-failure values for each temperature. This approach may have merit as a means of providing data to supplement thermal stability measurements.

3. Analyses of aircraft component fragments recovered from crash sites have shown that hot metal surfaces exposed to dibromodifluoromethane fire extinguishing agent may contain traces of metal fluorides. The presence of fluorides can be used as evidence of the deployment of the extinguisher unit. Hydrolyzable fluoride was not detected on control metal surfaces (those far removed from the extinguisher unit) which were recovered from the crash site or on similar components of aircraft unrelated to the crash.

4. Hot manifold ignition tests on various hydraulic fluids have shown the importance of the method used for applying the fluid to the heated surface and of the technique for measuring the manifold surfach temperature, i.e., thermocouple size, method of attachment, etc. Data were collected for five fluids under a number of different conditions and using a variety of application methods.

5. Over 2000 fluids were considered in a search for a suitable nonhazardous replacement for test fluid MIL-F-7024B, Type II. No suitable organic fluid was found which would meet all criteria. Water containing a suitable corrosion inhibitor formulation was believed a workable alternative to an organic fluid.

6. The feasibility of a vapor-phase UV absorption detector for use in gas chromatography has been established. The detector has been shown to be specific for aromatic molecules with paraffins not being detected.

Work under this contract has been, by nature, diverse and of a problem solving character. Many separate and unrelated investigations were conducted. For better clarity and continuity, conclusions for these tasks are presented along with discussion of the work in the various Sections.

Investigations in support of Air Force in-house research have been conducted for the purpose of providing data for which conclusions will later be obtained at the completion of those investigations.

APPENDIX I

LITERATURE & LABORATORY SURVEY RELATED TO FLUORESCENCE OF EXHAUST COMPONENTS

This Appendix summarizes both literature and laboratory investigations concerning the luminescent properties of compounds known to be present in the exhaust gases. A gas chromatograph mass spectrometric analysis performed at the School of Aerospace Medicine (ref. A1) provided a tabulation of the exhaust constituents.

References reported herein do not represent an exhaustive search of the literature, just as the laboratory screening of compounds does not characterize the luminescence of the constituents at all excitation wavelengths.

I. TYPES OF COMPOUNDS

A complete examination of potential fluorescing species in an exhaust specimen requires that both organic and inorganic compounds be considered. In contrast to the large number of organic compounds which are known to fluoresce in the vapor state, instances of fluorescing inorganic polyatomic vapors are few. Inorganic compounds which might be found in combustion exhaust gases include the oxides of nitrogen, carbon monoxide, carbon dioxide and water.

The fluorescence of nitrogen dioxide has been thoroughly investigated (ref. A2-A4). These studies have shown that NO_2 is excited to strong visible fluorescence, extending beyond 700-800 nm, by irradiation with light of wavelength above 400 nm. Fluorescence, however, is visible only up to pressures of approximately 100 torr. Radiation below 380 nm produces no fluorescence but causes dissociation of the molecule.

Fluorescence in nitric oxide, NO, can be effectively excited only by irradiation at a wavelength of about 180 nm (ref. A5). By this means, fluorescence β-bands extending from 218 to 527 nm are observed.

Nitrous oxide, N_2O, does not fluoresce, though when irradiated at very short wavelengths (120-130 nm), it undergoes a photolytic reaction involving dissociation to form a nitric oxide molecule, the β-bands of which can then be observed (ref. A6).

It has been noted by one investigator (ref. A7) that a fluorescence band between 240-580 nm is excited in carbon monoxide by radiation of wavelengths below 160 nm. No fluorescence has been observed for carbon dioxide gas, however.

In an investigation of the Raman effect, Rassetti (ref. A8,A9) found that water and ammonia vapors are excited to fluorescence by the mercury 253.7 nm line. The emission band for ammonia reaches from 270 nm far into the visible. The intensity of the water-vapor band has its maximum close to the excitation line and drops rapidly in the direction of greater wavelength.

The compounds which fluoresce only when excited in the vacuum ultraviolet spectral region (wavelengths <200 nm) can be virtually eliminated from consideration in this investigation. Additionally, such factors as pressure, temperature, quenching and stabilization effects must be considered before conclusions can be drawn concerning their potential fluorescence interference with Raman measurements.

Among organic compounds, aromatic hydrocarbons and their derivatives are the principal fluorescers. Organic compounds which are known to fluoresce in the vapor state, without exception, also fluoresce in liquid solutions (ref. A10). Such factors as concentration and solvent effects can alter spectra of solutions just as perturbation effects may modify vapor phase spectra. Fluorescence spectra for a number of individual organic compounds have been recorded in this laboratory in a compound screening process which will be discussed later in this Appendix.

II. COMPARISON OF FLUORESCENCE SPECTRA OF VAPORS AND LIQUID SOLUTIONS

In order for fluorescence spectra of exhaust condensates in solution to be validly compared to spectra of exhaust vapors, spectral differences associated with the physical state must be recognized. Most of the early fluorescence work on organic compounds found in the literature was performed on solutions. The fluorescence of most pure liquids is very low due to self quenching. Fluorescence spectra of compounds which are not ionized in solution are, in general, the same for vapors, solutions, and solid crystals (ref. A11); the bands being only slightly displaced in the direction of greater wavelengths by passing from the vapor to the solution and to the crystal. Recent studies (ref. A12) performed on the photoluminescence of acetaldehyde show essentially the same fluorescence spectrum for the material, whether in solution or the vapor state.

In the development of a vapor phase fluorescence detector for gas chromatography, Burchfield et al. (ref. 13) compared gas and liquid phase fluorescence spectra of polynuclear arenes. These investigators found the fluorescence intensity to vary with the matrix gas, decreasing in the order N_2 > He > CO_2 > H_2, at a temperature of 150°C. Their observation that the emission maximum undergoes a hypsochromic shift going from the liquid to the gas phase is in accord with the general rule stated above.

III. EFFECTS OF TEMPERATURE AND PRESSURE ON THE FLUORESCENCE OF VAPORS

Unperturbed fluorescence of gases and vapors occurs only as zero pressure is approached. Under these conditions, excitation with monochromatic radiation may yield a resonance fluorescence spectrum, most of the bands of which arise from the higher vibrational levels directly as excited.

In many weakly fluorescing vapors, fluorescence cannot, in practice, be observed below 50-100 torrs pressure. Collisional redistribution of vibrational energy between the excited molecule and molecules of the surrounding gas occurs long before these pressures are reached. Fluorescence, thus, does not originate from the vibrational level that was initially attained during the absorption process but from a vibrationless level or one of the lowest vibrational levels (ref. A14). Consequently, at higher pressures, the wavelength of emitted radiation is changed or its intensity is diminished or completely quenched. Schartz and Johnston (ref. A4), for example, observed a considerable shift of fluorescence toward lower energy (higher wavelength) for NO_2 as pressure was increased. The fluorescence of NO_2 drops with further increase of pressure and is visible only up to pressures of approximately 100 torr (ref. A2). Similar quenching is produced by the addition of CO_2 and to a lesser extent by N_2, O_2, and H_2 (ref. A15).

Increase in pressure can, in some cases, have the opposite effect, that of stabilizing fluorescence. If the fluorescence of a vapor at low pressure is only poorly excited by the absorption of a radiation which produced predissociation and internal conversion almost exclusively, the total fluorescence yield can be increased many-fold by the addition of a foreign gas at atmospheric pressure. This process of fluorescence stabilization (ref. A16) results from the collisional removal of vibrational energy by molecules of the added gas which reduces the probability of nonradiative processes and, thus, increases the fluorescence yield. Stabilization effects are important in liquids as well as vapor specimens.

Increase in temperature of vapor specimens has been shown to have the effect of decreasing fluorescence and causing fluorescence bands to become more diffuse. For example, fluorescence has been excited (ref. A17) in acetaldehyde vapor at room temperature by excitation with the 313.2 nm mercury line. The fluorescence yield was observed to decrease with increasing temperature and to disappear when the temperature exceeds 150°C. The decrease in fluorescence intensity was related to an increase in photodissociation which competes with the fluorescence at all temperatures.

The fluorescence of benzene vapor is affected very little by self-quenching and the quenching efficiency of foreign gases such as N_2, CO_2, or atmospheric air is relatively small. If the temperature, however, is raised to 200°C at constant vapor pressure (ref. A18), the fluorescence becomes much weaker and its structure more diffuse. At 400°C, the fluorescence spectrum consists only of a faint continuous band. Benzene derivatives exhibit much the same fluorescence character as benzene itself.

IV. EVALUATION OF THE FLUORESCENCE OF KNOWN EXHAUST CONSTITUENTS

Recent analyses (ref. A1) at the School of Aerospace Medicine (SAM) have determined the composition of combustor exhaust gases for various fuels and combustor inlet pressures. Thirteen classes of organic compounds were established. These lists of compounds have been examined to determine potential fluorescing constituents.

Relatively few nonaromatic organic compounds in which fluorescence can be excited are to be found in the literature. The reasons are that (ref. A15):

(1) the first absorption bands of many aliphatic compounds (methane, ethane, methanol, ethanol, and other alcohols, etc.) lie in the far UV;

(2) many others have only continuous absorption bands;

(3) even if absorption bands show structure, the absorption process leads only to predissociation or, perhaps, to internal conversion.

Even in vapors of compounds in which fluorescence can be obtained, the yield is generally small and dissociation or internal conversion competes with the emission process. In cases where no clear evidence is available in the literature concerning the fluorescent nature of certain compounds or compound types, their fluorescence was evaluated in the laboratory. Fluorescence which could be excited by irradiation at wavelengths of 300, 337.1, and 350 nm was of principal interest. In each case, measurements were performed on solutions at concentrations of 100, 500, and 1000 ppmV in spectral quality hexane.

The classes of compounds presented in the SAM report are:

Paraffins and Naphthenes

These classes of compounds are, of course, representative of a large number of the constituents of the original fuel and the fuel itself did not fluoresce when excited at the wavelengths given above. Ample evidence is available in the literature to indicate the nonluminescent nature of compounds in these classes. Hexane and cyclohexane are used as fluorescence-free solvents for spectrofluorometry.

Though not relevant to this investigation, recent studies (ref. A19) in the vacuum ultraviolet have shown that paraffins and naphthenes can be excited at 147 nm to yield emission in the 200-230 nm wavelength range. Fluorescent quantum efficiencies for a series of hydrocarbons ranged from 0.00006 to 0.02 at 25°C.

Olefins

Olefins similar to those reported in the combustor exhaust components have been studied by Hirayama and Lipsky (ref. A19) and they found no fluorescence to be excited even in the vacuum UV. While not all of the olefins given in the SAM report were included in that study, mono-olefins as a class were rather well established as being nonfluorescing. This conclusion was supported by spectrofluorometric examination of olefins in this laboratory.

Aromatics

Aromatic compounds comprise the largest category of compounds in which fluorescence can be readily excited. Aromatic compounds determined to be present in the exhaust gases are benzene and alkyl substituted benzenes with variously branched alkyl groups from C_1-C_4.

The luminescence properties of these compounds have been thoroughly studied by various investigators (ref. A20,A21) and many of the compounds are included in Berlman's compendia (ref. A22).

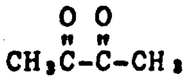
The fluorescent spectra of benzene derivatives, which are mono- or di-substituted by other hydrocarbon radicals are very similar to those of benzene itself. The fluorescence bands, however, are always shifted in the direction of greater wavelength. Thus toluene fluoresces further to the red than does benzene. An ethyl group has a slightly smaller effect on the shape of the spectrum than does a methyl group. Alkyl groups larger than the ethyl group appear to effect the fluorescence to the same extent as does the ethyl group.

The aromatic components reported from the exhaust analysis all exhibit a fluorescence band extending from approximately 275 to 320 nm with a maximum at approximately 282. Maximum fluorescence is excited at 265 for the compounds.

Examination in the laboratory of selected compounds from this group yielded no fluorescence when irradiated at excitation wavelengths of 300, 337.1, and 350 nm.

Aldehydes

Most of the aldehydes detected as exhaust components either have been observed to fluoresce or to undergo a photo-oxidation reaction in which the fluorescent compound biacetyl,



$$CH_3\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-CH_3$$

is formed. Acetaldehyde was studied extensively by Archer et al. (ref. A12) in the vapor state and as cyclohexane solutions. This compound was shown to yield a broad fluorescence band from 345-610 nm with a maximum at 415 nm by excitation at 303 nm. The shape and the position of the spectral band was unchanged by variation of temperature and the pressure of an added gas. Absorbance and emission by acetaldehyde was, however, very weak. Quantum yields were in the order of 0.001. Archer and his coworkers took particular attention to change samples sufficiently often to prevent buildup of biacetyl, thus assuring that the fluorescence was due to acetaldehyde not biacetyl. This latter compound, which has a comparatively strong green fluorescence, has three broad fluorescence bands with maxima at 511.7, 557.2, and 609.5 nm. It is only slightly self-quenching, but is extremely sensitive to quenching by oxygen. Early discussions centered on the question of whether this observed emission actually originated from the aldehydes and ketones or from the photolysis product.

Acrolein, another exhaust component, was shown (ref. A23) to fluoresce weakly with a maximum at approximately 397 nm. The fluorescence yield at room temperature was 0.004.

Two other exhaust constituents, propionaldehyde and butyraldehyde, upon radiation of their vapors (ref. A24) give spectra differing only slightly from the spectrum of biacetyl. In the case of propionaldehyde, according to a proposed mechanisn (ref. A25) bipropionyl diketone, a compound analogous to biacetyl, is generated.

The weak fluorescence of n-butyraldehyde, too, is assumed to originate from a compound produced by a primary photochemical reaction.

Benzaldehyde, which appears as an exhaust constituent only infrequently, exhibits fluorescence from 394-500 nm as a vapor (ref. A26).

Ketones

The most prominent ketones on the list of exhaust constituents are acetone and 2-butanone. Acetone (ref. A27), in a mechanism similar to that of aldehyde, forms biacetyl under the action of irradiation. If the fluorescence of the biacetyl is quenched with oxygen, a blue fluorescence due to acetone alone can be excited by radiation of 310-330 nm in wavelength.

In an investigation of the fluorescence of aliphatic ketones (ref. A28), it was demonstrated that open chain and cyclic ketones ranging from C_3 to C_8, when excited in hexane solution by radiation of 313 nm wavelength, gave fluorescent peaks at 405 nm. The quantum yields increased with alkyl substitution at the alpha-carbon and ranged from 1×10^{-3} to 4×10^{-3}.

Diolefins

Diolefins having conjugated double bonds are well known to have strong absorption bands at 220-250 nm. Isoprene (2-methyl-1,3-butadiene) is the only conjugated diolefin listed among the exhaust constituents. Laboratory tests of several substituted 1,3-butadiene derivatives, however, showed no fluorescence in the range of interest. Similar tests on substituted 1,2 and 2,3 diolefins gave the same result.

No evidence has been found in the literature to indicate that diolefins can be excited to fluorescence. The fact that a molecule absorbs radiation is, of course, not an indication that it will fluoresce; various other processes may provide a means for the radiationless relaxation of excited molecules.

Alcohols

All of the alcohols which were reported to be combustor exhaust products are aliphatic. No fluorescence has been reported for aliphatic alcohols; in fact, they are commonly used as solvents in which fluorescence measurements are performed.

For a series of aliphatic alcohols tested in this laboratory, the only fluorescence detected was eliminated by obtaining a purer specimen.

Esters and Ethers

Essentially the only ester among the exhaust products is n-amyl acetate. Tests in the laboratory produced no fluorescence in this material. Similar results were obtained for furan, methyl furan and 2,3-epoxybutane.

Other Compounds

Nitrogen and halogen containing compounds were tested for fluorescence. Nitromethane and several aliphatic nitriles were shown not to fluoresce under the test conditions. Trichloroethylene and several fluoroparaffins gave similar results.

APPENDIX II

SECTION A - Ignition Tests; Fluid Dripped from 10-ml Burette onto Heated Manifold

SECTION B - Ignition Tests; Fluid Sprayed from AMS-3150 Low Pressure Binks Spray Gun Over Burning Cotton Waste Saturated with 150 SUS Petroleum Oil

SECTION C - Ignition Tests; Fluids Dripped and Sprayed on Heated Manifold

SECTION D - Comparison of Temperatures Measured by Various Methods

SECTION A

IGNITION TESTS

FLUID DRIPPED FROM 10 ML BURETTE ONTO HEATED MANIFOLD

TEMPERATURE (°F)	FLUID	SPECIAL CONDITIONS	OBSERVED IGNITION
900°	A	10 sec. delivery	no ignition or burning on manifold
	B		delayed ignition w/burning on tube; flames carried to pan but no burning in pan.
	C		7-8 seconds delayed ignition w/burning on tube; flames carried on droplets to pan but no burning in pan
	D		~3 seconds delayed ignition w/burning on tube, flames carried to pan but no burning in pan.
	E		no ignition
1000°	A	18-20 sec. delivery	no ignition
	B		no ignition
1100°	A		ignition at ~3 sec. and 5 sec., self-extinguishing, not carried to pan
	A (repeat)		ignition at 8 sec., self-extinguishing, reignition at 10-15 sec., not carried to pan
	E		no ignition
1200°	A		ignition delay ~2 sec., flames carried to pan where burning continues
	B		slight sparks at 2-3 sec.

IGNITION TESTS

TEMPERATURE (°F)	FLUID	SPECIAL CONDITIONS	OBSERVED IGNITION
1200°	B (repeat)	18-20 sec. delivery	sparks and flames, flames on burning droplets but no burning in pan
	C		some burning on manifold and on droplets but no burning in pan
	D		burning on manifold, flames not carried to pan
	E		occasional flash on manifold along head
1300°	A		burning on manifold; droplets spread flames to pan where burning continues
	B		ignition at ~3 sec. sporadic burning on bead and on manifold; burning droplets but flame not carried to pan
	C		flashing at ~3 sec., ignition the same as fluid B above
	D		flashing at 2-3 sec., small flames, burning drops but burning does not continue in pan
	E		small flames, sporadic burning along bead, falling drops do not have flames
1300°	A	Burette at one spot ~1" above bead on manifold, 18-20 sec. delivery	burning at 5 sec., burning droplets spread flame to pan where burning continues

Section A - cont'd

IGNITION TESTS

TEMPERATURE (°F)	FLUID	SPECIAL CONDITIONS	OBSERVED IGNITION
1300°	B	Burette at one spot ∼1" above bead on manifold, 18-20 sec. delivery	small flame at 3 sec., 5 sec. and at 10-12 sec., no flames carried to pan
	C		small flames at 5 sec., 7-8 sec. and at end
	D		slight flash at ∼3 sec. and 5 sec., intermittent flashing, flame on droplets carry past-way to pan
	E		small flash at 3-5 sec., no burning of droplets past bead
1100°	B	Dripped on wider area of manifold surface and head, 18-20 sec. delivery	ignition at ∼2 sec. with continued burning flames on droplets almost to pan but no burning in pan
	C		burning at 1-2 sec. on manifold and bead, flames on droplet to pan but no burning in pan
	D		burning at 1-2 sec. on manifold, burning droplets to pan but no burning in pan
1000°	B		ignited at 3-4 sec., burning droplets to pan but no burning in pan
	C		flashing and burning at about 3-4 sec., burning droplets fall to pan, no burning in pan

Section A - cont'd

IGNITION TESTS

TEMPERATURE (°F)	FLUID	SPECIAL CONDITIONS	OBSERVED IGNITION
1000°	D	Dripped on wider area of manifold surface and head, 18-20 sec. delivery	ignited at 2-3 sec. burning droplets fall to pan but no burning in pan
	B* (repeat)		ignited on manifold, droplets fall to pan, burn not continued in pan
	A		ignition at 1-2 sec., burning droplets fall to pan, burning continues in pan
900°	A		ignition at 9 sec., burning droplets fall and continue burning in pan
	B		ignition at 6 sec., fluid burns down from manifold to pan but does not continue burning in pan
	C		ignition at 3-5 sec., burning droplets carried to pan but does not continue burning in pan
	D		ignition at 3-4 sec., burning on manifold, burning drops carried to pan but does not continue burning in pan
800°	A		no ignition
	B		ignition in ∼2 sec. continues to burn on manifold, droplets falling to pan, no burning in pan
	C		ignition in 1-2 sec., burning on manifold, droplets carried to pan but no burning in pan

Section A - cont'd

IGNITION TESTS

TEMPERATURE (°F)	FLUID	SPECIAL CONDITIONS	OBSERVED IGNITION
800°	D	Dripped on wider area of manifold surface and head, 18-20 sec. delivery	same as C
	E		no ignition
700°	A		ignition at ∼5 sec. flame carried to pan and continues to burn in the pan
	B		ignition in ∼2 sec., burning droplets carried to pan but does not continue to burn in the pan
	C		ignition at 1-2 sec., burning on manifold, burning drops fall to pan but no burning in pan
	D		ignition at 1-2 sec., same as C
	E		no ignition
600°	A		no ignition
	A (repeat)		no ignition
	B		ignition at 3 sec., burning on manifold, burning doplets fall to pan, no burning in pan
	C		ignition at 2-3 sec., same as B
	D		ignition at ∼4 sec., same as B

Section A - cont'd

IGNITION TESTS

TEMPERATURE (°F)	FLUID	SPECIAL CONDITIONS	OBSERVED IGNITION
510 - 520°	A	Dripped on wider area of manifold surface and head, 18-20 sec. delivery	no ignition
	B		no ignition
	C		[illegible] ignition
	D		no ignition
	E		no ignition

*Test on Fluid B repeated without replacing pan, consequently, there was a slight excess of fluid in the pan.

SECTION B

IGNITION TESTS

FLUID SPRAYED FROM AMS-3150 LOW PRESSURE BINKS SPRAY GUN OVER BURNING COTTON WASTE SATURATED WITH 150 SUS PETROLEUM OIL

Fluid	Observed Ignition
A	Flame increases during bursts, flame carried downstream ∿1 meter
B	Slight increase of flames with flames carried downstream ∿1 meter
C	Slight increase in flame, intermittent flashes, carried down ∿1 meter
D	Moderate increase in flames, slightly greater than B and C above, carried downstream ∿1 meter
D	Essentially no change in flame, possibly some flame carried downstream ∿0.25 meter

SECTION C

IGNITION TESTS

FLUIDS DRIPPED AND SPRAYED ON HEATED MANIFOLD

Manifold Temperature	Method of Delivery	Fluid(a)	Results
600°F	Burette(b)	A	No ignition
	Spray(c)	A	
700°F	Burette	A	
	Spray	A	
800°F	Burette	A	
	Spray	A	
900°F	Burette	A	
	Spray	A	
1000°F	Burette	A	
	Spray (3 bursts)	A	1. 1 sec. burst, 20 sec. clear 2. 1 sec. burst, ignition/after (d) 3. 1 sec. burst, (temperature dropped to 980°F), no ignition
1100°F	Burette	A	slight flash
	Spray (3 bursts)	A	1. ignition/after 2. ignition/after 3. ignition/after
1200°F	Burette	A	slight burning on channel
	Spray (2 bursts)	A	1. ignition/after 45 second clearing 2. instant ignition
1000°F	Spray (d) (3 bursts)	A	1 sec. bursts, 15 sec. clearing, no ignition
1100°F	Spray (2 bursts)	A	1. burst of flame/after 2. burst of flame/after
	Burette	A	flashes self-extinguishing, burning drops but no flame in pan

Section C - cont'd

Manifold Temperature	Method of Delivery	Fluid[a]	Results
1200°F	Spray (2 bursts)	A	1. burst of flame/after 2. burst of flame/after
	Burette	A	flashes self-extinguishing, burning drops, but no flame in pan
1300°F	Burette	A	ignition w/flames going to pan where burning continues
1315°F	Burette	A	immediate ignition w/burning in pan
600°F[e]	Burette	B	flashes and burns after delay 5-6 sec., no flames in pan
600°F	Burette	C	ignited after delay, no flames in pan
	Burette	E	no ignition
	Burette	B	ignition after 2-3 sec. delay, burning droplets but no flame in pan
	Spray (2 bursts)	B	1. 1 sec. burst-ignition/after 2. 1 sec. burst-ignition/after
700°F	Burette	A	no ignition
	Burette	B	1-2 sec. delayed ignition, burning droplets but no flame in pan
	Burette	C	same as B above
	Burette	E	no ignition
	Spray (3 bursts)	B	no ignition at any time

Section C - cont'd

Manifold Temperature	Method of Delivery	Fluids[a]	Results
800°F	Burette	A	no ignition
	Burette	B	4 sec. delayed ignition, burning droplets, no flame in pan
	Burette	E	no ignition
	Spray (3 bursts)	B	no ignition at any time
	Burette	A	no ignition
900°F	Burette	B	ignition delay $\sim$7 sec., burning droplets but no flame in pan
	Burette	E	no ignition
	Spray (3 bursts)	B	no ignition at any time
1000°F	Burette	A	no ignition
		B	sporadic ignition, self-extinguishing
		E	no ignition
	Spray (3 bursts)	B	no ignition at any time
1100°F	Burette	A	no ignition
		B	intermittent flashing and burning by couple, self-extinguishing
		E	no ignition
	Spray (3 bursts)	B	1. ignition 2. ignition/after 3. no ignition
1300°F	Burette	A	flashing & ignition burning on manifold and in pan
	Burette	B	ignition and sporadic burning, falling droplets, do not continue burning in pan

Section C - cont'd

Manifold Temperature	Method of Delivery	Fluids(a)	Results
1300°F	Burette	E	one or two intermittent flashes, no burning droplets to pan
	Spray (3 bursts)	B	1. ignition/after 2. ignition 3. ignition
1400°F	Burette	A	burning on tube, burning droplets to pan, burning in pan
	Burette	B	intermittent flashing along bead, burning droplets to pan, no flames in pan
	Burette	E	intermittent flashing along bead, no burning droplets
500°F	Burette	A	no ignition
	Burette	B	no ignition
	Spray	A (150°F) (g)	no ignition
600°F	Burette	A	no ignition
		B	15-16 sec. delayed ignition, no burning in pan
	Spray (3 bursts)	A	no ignition at any time
	Burette	A (210°F)	no ignition
		B (210°F)	no ignition
		B (210°F)	no ignition
		(repeat)	ignition with burning droplets to pan, no flames in pan
700°F	Burette	A (210°F)	no ignition
		B (room temp.)	2-3 sec. delayed ignition, burning droplets to pan, but no flames in pan

Section C - cont'd

Manifold Temperature	Method of Delivery	Fluids(a)	Results
700°F	Burette	A (room temp.)	no ignition
	Spray (3 bursts)	A (150°F)	no ignition at any time
800°F	Burette	B (hot)	~3 sec. delayed ignition, burning fluid goes to pan, some burning in pan, self-extinguishing
	Burette	A (hot)	no ignition
	Spray (3 bursts)	A (hot)	no ignition at any time
900°F	Burette	B (hot)	ignition after ~4 sec. burning in pan but self-extinguishing
	Burette	A (hot)	no ignition
	Spray (3 bursts)	A (hot)	no ignition at any time
1000°F	Burette	B (hot)	no ignition
	Burette	A (hot)	no ignition
	Spray	A (hot)	no ignition
1100°F	Burette	B (hot)	flash at 3 and 5 sec. no continued burning
	Burette	B (hot)	no ignition
1200°F	Burette	B (hot)	sporadic flashes not carried to pan
	Burette	A (hot)	flashes at 3-5 sec., some burning
1000°F	Spray (3 bursts)	A	no ignition at any time

Section C - cont'd

Manifold Temperature	Method of Delivery	Fluids[(a)]	Results
1100°F	Spray (3 bursts)	A	no ignition at any time
1200°F	Spray (3 bursts)	A	ignition/after for each burst
1300°F	Spray	A	immediate ignition
	Burette	B (hot)	small flash on tube, burning on head, burning droplets almost to pan, no burning in pan
	Burette	A (hot)	burning along bead enters pan, burning in pan
500°F	Spray (2 bursts)	B (hot)[(g)]	no ignition
600°F	Spray (3 bursts)	B (hot)	no ignition at any time
700°F	Spray (3 bursts)	B (hot)	no ignition at any time
800°F	Spray (3 bursts)	B (hot)	no ignition at any time
900°F	Spray (3 bursts)	B (hot)	no ignition at any time
1000°F	Spray ([illegible] bursts)	B (hot)	no ignition on first three bursts, fourth burst, ignition
1100°F	Spray (3 bursts)	B (hot)	1. ignition 2. ignition/after 3. ignition/after
1200°F	Spray	B (hot)	ignition/after
1215°F	Spray	B (hot)	ignition

Section C - cont'd

Manifold Temperature	Method of Delivery	Fluids[a]	Results
1200°F	Spray (3 bursts)[h]	E (hot)	1. slight ignition, not sustained 2. slight ignition/after 3. small flash/after
1300°F	Spray[h] (3 bursts)	E	1. slight ignition/after 2. slight ignition with a puff 3. slight ignition/after

(a) at ambient temperature unless otherwise indicated
(b) ten ml burette, emptying in 18-20 seconds
(c) spray, 1000 psi, using 1 gph atomizing nozzle, later changed to the Factory Mutual spray nozzle, see note (e).
(d) "ignition/after" indicates that ignition took place just after the spray was turned off.
(e) changed to Factory Mutual spray nozzle for this and succeeding tests
(f) tests resumed the next day
(g) bomb line temperature to spray nozzle, 225°F; thermocouple temperature, 150°F
(h) the three bursts were followed by several sprays in rapid succession with no ignition resulting; the manifold temperature had dropped 10-20°F

SECTION D

COMPARISON OF TEMPERATURES MEASURED BY VARIOUS METHODS

Tempilstik*	Wahl HSA-4G* Infrared Thermometer (0.75 emissivity setting)	Manifold Thermocouple Recorder-Potentiometer
400°F	405°F	--
500°F	510°F	--
--	520°F	380°F
--	535°F	385°F
600°F	615°F	435°F
--	640°F	465°F
--	700°F	515°F
700°F	740°F	545°F
--	835°F	610°F
800°F	810°F	595°F
--	900°F	655°F
--	1015°F	735°F
--	1040°F	750°F
--	1060°F	770°F
--	1100°F	790°F

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*Temperature indicated approx. 30° above bead at mid-length of manifold tube (Point A on profile diagram, Figure 1).

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