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# Evaluation of Ultraviolet Spectrophotometry for Simultaneous Analysis of Alkylbenzenes, Alkyl-naphthalenes, Alkylanthracenes/ Phenanthrenes and Total Aromatics in Mid-distillate Fuels

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EVALUATION OF ULTRAVIOLET SPECTROPHOTOMETRY FOR  
SIMULTANEOUS ANALYSIS OF ALKYL BENZENES, ALKYL NAPHTHALENES,  
ALKYL ANTHRACENES/PHENANTHRENES AND TOTAL AROMATICS  
IN MID-DISTILLATE FUELS

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SUMMARY

An ultraviolet spectrophotometric method was developed for the simultaneous determination of alkylbenzenes, alkylnaphthalenes, alkylanthracenes/phenanthrenes and total aromatics in mid-distillate fuels. Matrix equations were established from ultraviolet spectra of aromatic hydrocarbons, then applied to the analysis of aromatics in jet fuels. To determine the accuracy and precision of the analytical method, fuels with known compositions were prepared by blending aromatic hydrocarbons. Analyses of these standard fuels for total aromatics resulted in an accuracy of 14 percent for a Jet A type fuel and 19 percent for a broadened-properties jet turbine fuel. With matrix equations based on known aromatic components in the standard fuels, the accuracy improved to 5 percent for the Jet A and 0.6 percent for the broadened-properties jet turbine fuels. Precision, expressed as relative standard deviations, ranged from 2.9 percent for the alkylanthracenes/phenanthrenes to 15.3 percent for the alkylbenzenes. In addition, the ASTM D-1840 method for naphthalenes by ultraviolet spectroscopy was evaluated. Results indicated that the ASTM D-1840 method may be applicable for fuels containing more than 5 percent naphthalenes and having end points above 315° C if some decrease in accuracy and precision is acceptable.

INTRODUCTION

While the availability of high quality petroleum crudes for fuel production has declined, the demand for jet fuel has increased, causing severe competition for the available mid-distillates. Changes in property specifications for future fuels could minimize potential curtailments in supplies and might also minimize costs. Of particular interests are those changes which may occur in the aromatics fraction of future fuels. A recent Department of Energy study has indicated a trend toward higher concentrations of aromatics in jet fuels (Ref. 1). In addition to a higher aromatic content, changes in the distribution of mono- and polynuclear aromatics may be found in future fuels. Both of these variations in fuel composition might become important as a result of an increase in the final boiling points of jet fuels, an increase in the amounts of cracked stock streams employed to produce jet fuels, or with the introduction of syncrudes into the refineries. Fuels with high concentrations of aromatics or higher proportions of polynuclear aromatics in the aromatic fraction produce more soot in the combustion process causing increased flame radiation and smoke in the engine exhaust (Ref. 2). These two effects decrease combustor liner life and turbine life (Ref. 3). Aromatics are also known to be detrimental to the jet

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turbine fuel system through seal destruction and reduced fuel thermal stability. Thus, while the use of highly aromatic fuel may reduce fuel processing requirements and cost, turbine engine fuel efficiency may decrease and maintenance costs may increase. It is important, then, to determine the aromatic content of jet turbine fuels, particularly in the research investigations into the effects of fuel property variations on the performance of combustion and fuel systems.

Currently there is no reliable method for simple and rapid determination of alkylbenzenes, alkyl naphthalenes, and alkylanthracenes/phenanthrenes in mid-distillate fuels. Because of the wide range of aromatics present in jet turbine fuels and the overall complexity of fuels, analytical methods for aromatics generally suffer numerous interferences.

Gas chromatography (GC) has been applied to the determination of aromatics in gasoline, but this analytical method is limited to compounds with boiling points lower than 250° C (Ref. 4). Generally, gas chromatography is limited in its capability to determine the complex variety of the components in mid-distillate fuels. Although not fully developed, fused silica capillary column gas chromatography with a modified ultraviolet detector shows promise in determining individual aromatic components (Ref. 5). Alkylbenzenes at levels down to 0.1 percent and alkyl naphthalenes down to 0.02 percent were separated and identified using a modified ultraviolet detector at 208 nm.

Other methods such as mass and nuclear magnetic resonance spectroscopy (MS and NMR) are capable of measuring the aromatic ring structures and the amount of hydrogen bound to the aromatic rings. However, the instruments are expensive and the analytical techniques require specially trained analysts to interpret the data. High performance liquid chromatography (HPLC) has been applied to group analysis of saturates, olefins and aromatics (Ref. 6). This technique accurately determines the total aromatic content of a fuel. In an HPLC method using an ultraviolet and fluorescence detector, a chemically-bonded aminosilane liquid chromatographic packing material was used to isolate polynuclear aromatic compounds according to the number of condensed rings (Ref. 7). Another HPLC method showing promise and currently in publication uses the amino column and refractive index detector to separate aromatic compounds (Ref. 8).

The most widely used method for aromatics is the fluorescent indicator adsorption (FIA) method (Ref. 9). This method is specific for fuels distilling below 315° C, and thus erroneous results may be obtained for higher distilling and dark fuels (Ref. 10). This method does not differentiate alkylbenzenes, alkyl naphthalenes, or alkylanthracenes and phenanthrenes. Another analytical technique widely used for aromatics is the ultraviolet (UV) method, but, generally, UV methods such as the ASTM Method D-1840 are not applicable to all classes of aromatics (Ref. 11). Recently a UV spectrophotometric method was developed for determining all classes of aromatics, but specific wavelengths and absorptivities were not reported in the literature and this method was applied only to lubricating oils (Ref. 12).

This report describes a UV spectrophotometric method for determining aromatics in mid-distillate fuels. The method was evaluated for use with specification jet turbine fuels, broadened-properties jet fuels, diesel fuels, and shale derived jet fuels. From the average absorption wavelengths of substituted benzenes, naphthalenes, anthracenes and phenanthrenes, sets of matrix equations were established to simultaneously determine the concentrations of alkylbenzenes, alkyl naphthalenes, alkylanthracenes/phenanthrenes, and total aromatics in middle distillate fuels. For conven-

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UTTL: Evaluation of ultraviolet spectrophotometry for simultaneous analysis of alkylbenzenes, alkyl naphthalenes, alkylanthracenes/phenanthrenes and total aromatics in mid-distillate fuels

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MAJS: /\*ANTHRACENE/\*BENZENE/\*JET ENGINE FUELS/\*NAPHTHALENE

MINS: / ABSORPTION SPECTRA/ SPECTROPHOTOMETRY/ ULTRAVIOLET SPECTROSCOPY

ABA: S.L.

ABS: A rapid ultraviolet spectrophotometric method for the simultaneous determination of aromatics in middistillate fuels was developed and evaluated. In this method, alkylbenzenes, alkyl naphthalenes, alkylanthracenes/phenanthracenes and total aromatics were determined from ultraviolet spectra of the fuels. The accuracy and precision were determined using simulated standard fuels with known compositions. The total aromatic fraction accuracy was 5% for simulated fuel and 0.6%

ience, these three classes of aromatics are referred to in this paper simply as benzenes, naphthalenes, and anthracenes. The results are compared to results obtained from MS, NMR, FIA, and HPLC methods. The procedure, results, and evaluation of the UV spectrophotometric method are discussed in this paper.

## EXPERIMENTAL

### Ultraviolet Spectroscopy of Aromatic Molecules

Saturated hydrocarbons do not absorb ordinary UV radiation in the region between 180 and 320 nm, and therefore do not interfere with aromatic hydrocarbon absorption. On the other hand, olefins may absorb near below 210 nm, but the intensities are much weaker than those of the substituted benzenes. Furthermore, the olefin content is generally very low so the interference is inconsequential. Aromatic molecules show a low-intensity band, or a fine-structure band, at about 254 nm. Thus, this wavelength is often used in qualitative analysis to detect the presence of aromatics in a sample. As functional groups are substituted on the aromatic nucleus, bathochromic or red shift occurs with greater intensity. But, unlike the dienes and unsaturated ketones in which the shift can be calculated by adding the contributions of the substituents, the effects of various substituents on the aromatic nucleus cannot be predicted. For aromatics, each compound must be scanned in the UV region to obtain the maximum absorption wavelengths. The absorbance of UV radiation is then related to the concentration of aromatics by the Beer-Lambert Law.

### Instrument

A Cary 210 ultraviolet-visible recording spectrophotometer was used. The source of the UV radiation was a deuterium discharge lamp, and the monochromator was of a grating type. The detector was a photomultiplier tube, and the absorbance was recorded on a potentiometric servo-recorder, as well as displayed on a digital readout. The instrument had the capability of blank correction by storing the solvent spectrum, and subtracting it from the sample spectrum.

### Obtaining the Spectrum

The UV spectrophotometer was used in the double beam mode with the reference cell containing a high purity solvent, either isooctane or cyclohexane. Other solvents such as pentane and hexane have lower cutoff wavelengths but were not used because of their higher volatility. The blank solvent spectrum was scanned and simultaneously stored for later retrieval to be subtracted from the sample spectrum. Sample solutions were diluted with solvent to keep the concentration in the range of 0.2 to 0.9 absorbance units. The spectrum was scanned from 300 nm to 194 nm.

### Average Maximum Absorption Wavelengths

The first step towards the development of a matrix equation for aromatics was obtaining the average maximum absorption wavelengths of benzenes, naphthalenes, and anthracenes. The primary absorption band for benzene occurs at 184 nm, naphthalene at 220 nm, and anthracene at 252 nm. These absorption wavelengths are shifted upward with each substitution. Since jet fuels contain a variety of substituted aromatics, averages of the maximum absorption wavelengths were obtained from individual UV spectra of pure com-

pounds. When available in the literature such as the API Research Project 44, maximum absorption wavelengths were obtained directly from the published data (Ref. 13). Where inadequate or no data was available, the reference spectra were obtained by scanning the pure aromatic compounds from 300 nm to 194 nm. A total of 34 spectra were obtained: 13 substituted benzenes, 11 naphthalenes, and 10 anthracenes. Each of these UV spectra are presented in the Appendix. Combining the spectra obtained in the laboratory and the spectra reported in the literature, a total of 90 spectra were obtained: 31 benzenes, 43 naphthalenes and 16 anthracenes. The list of aromatic compounds used in the calculation is presented in Table I. Based on these spectra, the average of the maximum absorption wavelengths were determined to be 198.1 nm for benzenes, 226.7 nm for naphthalenes, and 254.5 nm for anthracenes.

#### General Matrix Equation

The absorptivities at the three average maximum absorption wavelengths presented previously were calculated from the spectrum of each compound, and for each aromatics class the average absorptivities were determined. For example, at 198.1 nm, the average absorptivity was 298.22  $\mu$ /g-cm for benzenes, 90.26  $\mu$ /g-cm for naphthalenes, and 80.82  $\mu$ /g-cm for anthracenes. Thus, the absorbance reading at 198.1 nm was expressed as:

$$A_{198.1} = 298.22 [B] + 90.26 [N] + 80.82 [A]$$

where

$$\begin{aligned} A &= \text{absorbance} \\ [B] &= \text{concentration of benzenes, Wt percent} \\ [N] &= \text{concentration of naphthalenes, Wt percent} \\ [A] &= \text{concentration of anthracenes, Wt percent} \end{aligned}$$

Similarly, by calculating the average absorptivities at 226.7 nm and 254.5 nm, the absorbance reading at these wavelengths were expressed as:

$$A_{226.7} = 10.71 [B] + 420.87 [N] + 57.29 [A]$$

and

$$A_{254.5} = 2.14 [B] + 18.86 [N] + 507.31 [A]$$

In these linear equations, the path length was disregarded since the constant is 1 cm. From the above equations a matrix equation was established such that simultaneous solution of the equations would provide the concentrations of benzenes, naphthalenes, and anthracenes. Thus, the set of three linear equations was described in the matrix equation format as follows:

$$\begin{bmatrix} 298.22 & 90.26 & 80.82 \\ 10.71 & 420.87 & 57.29 \\ 2.14 & 18.86 & 507.31 \end{bmatrix} \begin{bmatrix} [B] \\ [N] \\ [A] \end{bmatrix} = \begin{bmatrix} A_{198.1} \\ A_{226.7} \\ A_{254.5} \end{bmatrix} \quad (1)$$

Sample fuels were diluted in isooctane to bring the concentration levels in the range of 0.2 to 0.9 absorbance units. Following the dilutions, the sample fuels were scanned from 300 nm to 194 nm, and the absorbances were measured at 198.1, 226.7, and 254.5 nm. These absorbance readings were substituted into equation 1, and the concentrations were determined by solving the matrix using the Gauss elimination technique.

## Fuels

The experimental fuels are generally classified into two types according to their distillation ranges. These two types are the aviation turbine fuels such as commercial Jet A or Navy JP-5, and the higher-boiling intermediate fuels which range between aviation turbine fuels and common diesel fuels. The following fuels were employed in the study (Refs, 14-16).

ERBS-3:	Experimental Referee Broadened Specification (ERBS) aviation turbine fuel, lot -3, 65% kerosene by volume and 35% hydrotreated catalytic gas oil.
ERBS-3-11.8%H:	ERBS/Blending stock (60/40 vol %) blend, 11.8% hydrogen.
ERBS-3-12.3%H:	ERBS/Blending stock (79/21 vol %) blend, 12.3% hydrogen.
ERBS-3S:	ERBS blending stock, 45% xylene bottoms by volume, and 55% hydrotreated catalytic gas oil.
ERBS-2:	ERBS, lot -2.
Jet A:	Commercial Jet A, paraffinic stock.
JP-5 Paraho Shale:	Shale oil derived fuel, distilled to the nominal range of a military aviation turbine fuel, JP-5.
IRS:	Intermediate Refinery Stream, paraffinic stock.

The Experimental Referee Broadened Specification (ERBS) fuel is a blend of kerosene and hydrotreated catalytic gas oil and is a representation of a kerojet fuel with broadened properties. The ERBS fuel is intended to serve as a reference fuel in research investigations into the effects of fuel property variations on the performance and durability of jet aircraft components, including combustors and fuel systems.

## RESULTS AND DISCUSSION

### Ultraviolet Spectra of Mid-Distillate Fuels

Typical UV spectra of Jet A and ERBS type fuels are presented in Figures 1 through 8. As shown in these figures, there is a distinct difference in the UV spectra between the Jet A and ERBS type of fuels. The difference is particularly noticeable in the 254 nm area where anthracenes have an average maximum absorption. For naphthalenes, the absorption wavelength experiences a slight bathochromic shift with the ERBS fuels which indicates a higher concentration of substituted naphthalenes.

In the analysis of jet fuels, the repeatability of spectra near 200 nm may be influenced by factors such as oxygen absorption and stability of the dilute fuels. The optical system of the UV spectrophotometer was purged with nitrogen gas to minimize the effects of oxygen absorption around the 200 nm region, but nitrogen purges did not produce any improvement in the spectra of the fuels. The effect of oxygen in the determination of the benzenes is more pronounced when oxygen is present in the fuel and solvent rather than within the overall optical path of the instrument. With sample manipulation and a series of dilutions, more oxygen is introduced into the sample solution than the blank solvent and this affects the spectra below 200 nm. This situation is particularly observed when the spectra of a freshly opened bottle of solvent is compared with the spectra of the same solvent after exposure to air. The absorbance in the region below 200 nm

sharply increases as more oxygen dissolves in the solvent. However, this effect is minimized by frequently checking and compensating for the blank solvent during a series of analyses.

In addition to dissolution of oxygen in the solvent, the stability of the diluted sample can affect the analyses. Within an hour, sample solutions showed decreases in absorbance readings by about 0.5 percent for benzenes, and 0.05 percent for naphthalenes. No changes were observed for anthracenes during this period. In two hours the absorbance loss was about 7 percent for benzenes, 1 percent for naphthalenes, and 0.5 percent for anthracenes; in 24 hours, 30 percent, 19 percent, and 8 percent, respectively.

#### Equations Based on the Jet Fuels

Based on the differences observed between the jet fuels and ERBS fuels at 254 nm, and since the calculated absorption wavelengths of pure compounds did not exactly coincide with the actual fuels, average absorption wavelengths were obtained from the spectra of actual jet fuels. Absorptivities were calculated from observed spectra of fuels to establish Jet A type and ERBS type equations in an attempt to represent the matrix equation as close to the actual fuels as possible. The matrix equation for the Jet A type fuel was determined to be:

$$\begin{aligned} A_{196.5} &= 349.60 [B] + 94.13 [N] + 149.52 [A] \\ A_{221.5} &= 36.65 [B] + 397.36 [N] + 78.13 [A] \\ A_{254.5} &= 2.14 [B] + 18.86 [N] + 507.31 [A] \end{aligned} \quad (2)$$

and similarly the equation for ERBS type was established as follows:

$$\begin{aligned} A_{196.5} &= 349.60 [B] + 94.13 [N] + 249.52 [A] \\ A_{224.6} &= 19.65 [B] + 438.73 [N] + 63.81 [A] \\ A_{253.6} &= 1.68 [B] + 18.31 [N] + 494.47 [A] \end{aligned} \quad (3)$$

With these equations available, fuel samples were reanalyzed using either the Jet A or ERBS equation depending on the fuel spectra. Results using the general matrix equation were compared against those obtained using the Jet A or ERBS equations. All UV results were compared against other results obtained using different analytical techniques such as FIA, HPLC, and MS.

#### Results for Jet Turbine Fuels

The analytical results obtained by the calculated general and fuel derived equations are presented in Table II. Results are grouped into benzenes, naphthalenes, anthracenes, and total aromatics. The units are weight percent and standard deviations are reported for six separate measurements. After determining the individual concentrations of benzenes, naphthalenes, and anthracenes, these results are combined to get the total concentrations of aromatics.

The difference in the results determined using the calculated general equation and those determined using the fuel derived equation is about 6 percent for the ERBS-3, ERBS-3-11.8% H, ERBS-3-12.3% H, ERBS-3S, and ERBS-2 fuels. But, for the Jet A, JP-5, and IRS fuels, the difference increases to about 11 percent. This is simply due to a larger variation in the absorptivities of the general and Jet A type equations.

In Table III the results obtained by the UV method are compared to those obtained using other analytical methods. In the FIA/MS technique, the

aromatics fraction is separated by the fluorescent indicator adsorption method, then analyzed by the ASTM mass spectrometric method D-2425. The UV (D-1840) denotes the ASTM D-1840 method for naphthalenes, and the HPLC method designates the group analysis of saturates, olefins, and aromatics. The HPLC results were obtained using the method described in Reference 6. For those results designated MS, separation is done by elution chromatography using the ASTM D-2549 method, then the aromatics are analyzed by mass spectrometric method ASTM D-2425. These MS results (Jet A and IRS fuels) were abstracted from a NASA publication (Ref. 17). The FIA method is the fluorescent indicator adsorption method, ASTM D-1319.

For tabulating the mass spectrometric results, alkylbenzenes, indans, tetralins, and indenenes were grouped into the benzenes. For the naphthalenes class, acenaphthenes, acenaphthylenes and fluorenes were combined with the naphthalenes. Unfortunately, with the relatively poor precision (six trials per result) obtained using the UV method, it is somewhat difficult to identify trends. For actual jet fuels, as is the case here, comparisons are further complicated by errors in the results of the baseline method (i.e., MS, FIA, etc.), or due to the fact that completely corresponding data is unavailable. For example, in the mass spectrometric data, the combined acenaphthylenes/fluorenes ( $C_n H_{2n-16}$ ) results have been categorized as naphthalenes. Nevertheless, several general comments are possible regarding the UV method results.

In comparing the results for the ERBS fuels using the UV ERBS equations to that obtained from the mass spectrometric method, one finds that the UV results for benzenes are generally high, while the naphthalenes and anthracenes are generally low. On the other hand, for the Jet A type fuels using the UV Jet A equation, the benzenes are low, and the naphthalenes and anthracenes are high. With the limited data available, it appears as if the general equation yields better results for all classes of aromatics than does the Jet A equation. Generally, for the total aromatics the difference between the UV and FIA/MS method is greater as the fuel contains more aromatics. The difference of about 5 percent in the concentration of total aromatics for ERBS-3 fuel increases to about 10 percent for ERBS-3-12.3% H, 12 percent for ERBS-3-11.8% H, and about 31 percent for ERBS-3S fuel. That is, the UV result for ERBS-3 fuel is 82.4 percent of the FIA result (note that this is a modified FIA which yields a weight percent result). With a higher aromatics content such as in the ERBS-3S fuel, the UV method results in 62.3 percent of the FIA result. For comparing the HPLC results, note that these results are in volume percent of total aromatics which is slightly higher than the corresponding value expressed as a weight percent. In any event, the HPLC results are between the UV and FIA/MS methods, and the difference between the HPLC and FIA/MS methods is less than that between the UV and FIA/MS methods.

#### Simulated Standard Fuels

Mixtures of simulated standard fuels were prepared to determine the accuracy and precision of the UV method for the analysis of a fuel with a known composition. Using a number of representative hydrocarbon compounds, simulated fuels with concentrations similar to Jet A type and ERBS type fuels were prepared to be used as standard fuels. The aromatic hydrocarbon compounds and concentrations are listed in Table IV. Of the total of 19 aromatic compounds, 7 were benzenes, 7 naphthalenes, and 5 anthracenes. These aromatic compounds were blended into the matrix of saturated hydrocarbons also presented in Table IV. These simulated fuels were analyzed by

the UV method in the same manner as the actual jet fuels. These results are shown in Table V, and their spectra are shown in Figures 9 and 10.

For the total aromatics in the simulated Jet A fuel, the result is 80.0 percent of the true value using the general equation, and 85.5 percent using the Jet A equation. As is the case with the actual jet fuels, lower results are obtained for the benzenes, but higher results are found for the naphthalenes and anthracenes. In spite of the lower total aromatics result, the general equation again appears to give slightly better results for each individual aromatics class. For the total aromatics in the simulated ERBS fuel, the result is 123.6 percent of the true value using the general equation, and 119.1 percent using the ERBS equation. For this fuel, the higher total result is due to the relatively higher concentrations of naphthalenes and anthracenes. These results indicate, as expected, that the selection of compounds used in the development of the equations have a significant influence on the analytical results. Depending on the aromatic compounds present in the fuels, the average absorption wavelengths would vary and the average absorptivities at these wavelengths would also vary.

#### Equation Based on the Known Components

To determine the inherent accuracy and precision of the UV method, new equations were developed based on the UV spectra of the simulated fuels prepared with the compounds shown in Table IV. As before, absorptivities at the maximum absorption wavelengths were calculated and new equations were established for recalculation of the results. However, in these equations, the weighted average of the absorptivity for each individual simulated fuel component was employed to determine the final values derived.

Equation based on the simulated Jet A fuel:

$$\begin{aligned} A_{197.6} &= 324.31 [B] + 84.40 [N] + 73.44 [A] \\ A_{220.0} &= 50.01 [B] + 500.67 [N] + 103.07 [A] \\ A_{255.1} &= 1.43 [B] + 18.53 [N] + 480.56 [A] \end{aligned} \quad (4)$$

Equation based on the simulated ERBS fuel:

$$\begin{aligned} A_{195.0} &= 442.02 [B] + 85.58 [N] + 141.72 [A] \\ A_{220.0} &= 50.01 [B] + 500.67 [N] + 103.07 [A] \\ A_{251.7} &= 1.11 [B] + 15.05 [N] + 485.11 [A] \end{aligned} \quad (5)$$

The results of simulated standard fuels recalculated using the above equations are presented in Table VI. As expected, far better accuracies are obtained for the benzenes, naphthalenes, and anthracenes. For the total aromatics in simulated Jet A fuel, the result is 105.0 percent of the true value, whereas the result is 100.6 percent for the simulated ERBS fuel. However, this improvement in the accuracy for the total aromatics concentration is not observed in the standard deviation of the results. As shown in Table VI, the UV results based on known components compare well with reference values and other analytical methods such as the FIA and HPLC.

#### Analysis of Naphthalenes by the ASTM D-1840 Method

While scanning the UV region for aromatics, absorbances were measured at 285 nm for naphthalenes determination by the ASTM D-1840 method. This method is intended for the analysis of naphthalenes in straight-run jet fuels containing not more than 5 percent of these components and having end

points below 315° C. The concentration of naphthalenes in the simulated fuels determined by the ASTM D-1840 method was compared to the matrix equation method using the equations based on the known components. As shown in the Table VI, the ASTM D-1840 method gave results similar to the actual amount of naphthalenes blended into the fuels: 89.1 percent for the simulated Jet A type and 97.9 percent for the simulated ERBS type fuel. This is due to the choice of wavelength employed in the method. At this wavelength the interference from benzenes and anthracenes is small, as is observed in the spectra of the pure compounds. However, when the UV spectra of jet fuels are examined near 285 nm, this wavelength, used for naphthalene measurements, is on the shoulder of a rising broad peak. It appears to be a poor choice for analytical measurements, but the results of the simulated fuels correlate well with the true values. These results indicate that the ASTM D-1840 method may be applicable for more of a variety of fuels than specified by the method, if slightly less precision and accuracy is acceptable. For example, the total naphthalenes concentration in simulated Jet A fuel was 4.11 percent, and 13.28 percent for simulated ERBS fuel, whereas the ASTM D-1840 method specified less than 5 percent. Thus, it suggests that the ASTM D-1840 method may be applicable to fuels containing 13.3 percent or possibly more naphthalenes and having end points of 328° C or higher. However, when different analytical methods for naphthalenes are compared using actual fuels, as shown in Table III, there is a considerable difference between the results. Thus, although the ASTM D-1840 method appears to be reasonably accurate based on the simulated fuel mixtures with arbitrary components and concentrations, for actual fuels the accuracy is only slightly better than that obtained using the matrix equations.

## CONCLUSIONS

A rapid ultraviolet spectrophotometric method for the simultaneous determination of aromatics in mid-distillate fuels was developed. In this method, alkylbenzenes, alkyl naphthalenes, alkylanthracenes/phenanthrenes, and total aromatics were determined from the ultraviolet spectra of the fuels. Absorbances were measured at selected wavelengths, then used in the established matrix equations to determine the aromatics concentrations.

The matrix equations were derived from a total of 90 ultraviolet spectra of aromatic hydrocarbons: 31 benzenes, 43 naphthalenes, and 16 anthracenes/phenanthrenes. From these reference spectra, the average maximum absorption wavelength was determined for each group of aromatics, then, the average absorptivities at the three absorption wavelengths were calculated and used to establish the matrix equations. From this work, 37 UV spectra of aromatic hydrocarbons are made available by scanning pure compounds between 300 and 194 nm region. These spectra can be used to complement reference spectra files such as those of API Research Project 44.

Generally, for the total aromatics, the difference in the results between the UV and FIA/MS method increases as the fuel contains more aromatics. For the ERBS-3 fuel the UV result is 82.4 percent of the modified FIA result. With more aromatics content such as in the ERBS-3S fuel, the UV method yields 63.0 percent of the FIA result. For the total aromatics in the simulated Jet A type fuel, the UV result is 85.5 percent of the true value. For the simulated ERBS type fuel, the UV result is 119.1 percent of the true value. When the UV results are recalculated with the equations derived from known compositions, the simulated Jet A type fuel yields in

105.0 percent of the true value, whereas the result is 100.6 percent for the simulated ERBS type fuel. However, definite conclusions are difficult to reach for actual jet fuels since they are based on one FIA/MS result.

In the analyses, a nitrogen purge of optical system of the instrument has no effect in the spectra, but the dissolved oxygen in the fuel and solvent causes higher absorbances in the 200 to 194 nm region. This oxygen effect is minimized by frequently checking the blank solvent between the analyses. Dilute fuel solutions show an unidentified instability with respect to time, but this problem is also avoided by analyzing the sample fuels immediately after the dilutions.

The ASTM D-1840 analysis of the simulated fuels with known naphthalenes concentrations indicates that the results for naphthalenes in the Jet A type fuel is 89.1 percent of the true value, and 97.9 percent for ERBS type fuel. These results indicate that, instead of being limited to 5 percent naphthalenes, the ASTM D-1840 method may be applicable for fuels containing 13.3 percent or more naphthalenes and having end point of 328° C or higher. However, since these results were obtained from simulated fuel mixtures with arbitrary components and concentrations, the accuracy and precision of the ASTM D-1840 method should be further investigated by using reference fuels with known compositions.

Although the UV method did not demonstrate the precision and accuracy sought, it might be further improved by rough weighting of standards based on the boiling range, or by using a UV spectrophotometer that is capable of scanning below 190 nm. Further work on wavelength selection may provide additional improvements in this UV method if improved wavelengths for the naphthalenes and anthracenes can be found where interferences are further minimized. In this analytical scheme, naphthalenes and anthracenes can be determined, and subtracted from the total aromatics obtained by another more reliable method such as HPLC, to yield concentration of benzenes. In any case, more MS, HPLC, and modified FIA analyses of actual jet fuels and simulated fuels are needed for further evaluation and comparison with the UV method. Other analytical methods besides MS that show promise in determining alkylbenzenes, alkyl naphthalenes, and alkyl anthracenes/phenanthrenes are capillary GC with a UV detector, and HPLC using an amino column and a refractive index detector.

APPENDIX. ULTRAVIOLET SPECTRA OF PURE COMPOUNDS.

This appendix contains the ultraviolet spectra of the following compounds:

n - Butylbenzene	Naphthalene
sec - Butylbenzene	1 - Phenyl-naphthalene
tert - Butylbenzene	2,3,5-Trimethyl-naphthalene
Cyclohexylbenzene	2 - Vinyl-naphthalene
p - Diethylbenzene	Anthracene
Diethylbenzene, mixture	2 - tert - Butyl-anthracene
Indan	9, 10 - Dimethyl-anthracene
Tetralin	2 - Ethyl-anthracene
1,2,3,4 - Tetramethylbenzene	2 - Methyl-anthracene
1,2,3,5 - Tetramethylbenzene	9 - Methyl-anthracene
Toluene	1 - Methyl-phenanthrene
1,2,4 - Trimethylbenzene	Phenanthrene
Xylene	9 - Phenyl-anthracene
1,3 - Dimethyl-naphthalene	9 - Vinyl-anthracene
1,4 - Dimethyl-naphthalene	Decalin
2,3 - Dimethyl-naphthalene	Fluoranthene
2,6 - Dimethyl-naphthalene	Pyrene
2 - Ethyl-naphthalene	
1 - Methyl-naphthalene	
2 - Methyl-naphthalene	

## REFERENCES

1. Shelton, E. M.: Aviation Turbine Fuels, 1978. BETC/PPS-79/2, U. S. Department of Energy, May 1979.
2. Naegeli, D. W.; and Moses, C. A.: Effect of Fuel Molecular Structure on Soot Formation in Gas Turbine Combustion. Aircraft Research and Technology for Future Fuels, NASA CR-2146, Apr. 1980, pp. 147-152.
3. Longwell, J. P.; and Grobman, J.: Alternative Aircraft Fuels. ASME Paper 78-GT-59, 1978.
4. Stavinoha, L. L.; and Newman F. M.: The Isolation and Determination of Aromatics in Gasoline by Gas Chromatography. J. Chromatography Sci., Vol. 10, Sept. 1972, pp. 583-589.
5. Warner, J. S.; Danison, T. H.; and McNulty, J. S.: Analytical Techniques for Aromatic Components in Aircraft Fuels. AFWAL-TR-82-2015, Air Force Aero Propulsion Laboratory, Oct. 1979.
6. Seng, G. T.; and Otterson D. A.: High Performance Liquid Chromatographic Hydrocarbon Group-Type Analyses of Mid-Distillates Employing Fuel-Derived Standards. NASA Technical Memorandum in publication.
7. Wise, S. A.; et al: Chemically-Bonded Aminosilane Stationary Phase for the High-Performance Liquid Chromatographic Separation of Polynuclear Aromatic Compounds. Anal. Chem., Vol. 49, no. 14, Dec. 1977, pp. 2306-2310.
8. Rippen, M.: Private Communication, United Technologies Corp., Pratt & Whitney Aircraft Group, West Palm Beach, FL, April 1981.
9. Hydrocarbon Types in Liquid Petroleum Products by Fluorescent Indicator Adsorption. Am. Soc. Test. Mater. Stand. D-1319-81, Part 23, 1982, pp. 708-713.
10. Buchar, C. S.: Infrared Spectroscopy for the Determination of Hydrocarbon Types in Jet Fuels. NASA TM-82674, Aug. 1981.
11. Naphthalene Hydrocarbons in Aviation Turbine Fuels by Ultraviolet Spectrophotometry. Am. Soc. Test. Mater. Stand. D-1840-81, Part 24, 1982, pp. 105-108.
12. Newman, F. M.; and Greenberg, M. M.: Determination of Aromaticity of Fuels and Lubricant Basestocks by Ultraviolet Spectroscopy. AFLRL-103, U. S. Army Fuels and Lubricants Research Laboratory, Southwest Research Institute, Feb. 1980. (AD-A086654.)
13. Ultraviolet Spectral Data. American Petroleum Institute Research Project 44, Chemical and Petroleum Research Laboratory, Carnegie Institute of Technology, 1959.
14. Prok, G. M.; and Seng, G. T.: Initial Characterization of an Experimental Referee Broadened-Specification (ERBS) Aviation Turbine Fuel. NASA TM-81440, Jan. 1980.
15. Friedman, R.; and Stockemer, F. J.: Temperature and Flow Measurements on Near-Freezing Aviation Fuels in a Wing-Tank Model. NASA TM-79285, Mar. 1980.
16. Seng, G. T.: Characterization of an Experimental Referee Broadened Specification (ERBS) Aviation Turbine Fuel and ERBS Fuel Blends. NASA TM-82883, Aug. 1982.
17. Stockemer, F. J.: Experimental Study of Low Temperature Behavior of Aviation Turbine Fuels in a Wing Tank Model. NASA CR-159615, 1979.

TABLE I. - LIST OF AROMATIC COMPOUNDS INCLUDED IN THE MATRIX EQUATION

Benzene

n - Butylbenzene

sec - Butylbenzene

t - Butylbenzene

5-n-Butyl[1,2,3,4-tetrahydronaphthalene]

Cyclohexylbenzene

Diethylbenzene, mixture

p - Diethylbenzene

1,2-Dimethyl-4-ethylbenzene

1,4-Di-tert-butylbenzene

2-Ethyl[1,2,3,4-tetrahydronaphthalene]

5-Ethyl[1,2,3,4-tetrahydronaphthalene]

6-Ethyl[1,2,3,4-tetrahydronaphthalene]

5-Isobutyl[1,2,3,4-tetrahydronaphthalene]

1-Methyl-2-n-propylbenzene

1-Methyl-3-n-propylbenzene

1-Methyl-4-n-propylbenzene

2-Methyl[1,2,3,4-tetrahydronaphthalene]

5-Methyl[1,2,3,4-tetrahydronaphthalene]

6-Methyl[1,2,3,4-tetrahydronaphthalene]

Tetralin

1,2,3,4-Tetramethylbenzene

1,2,3,5-Tetramethylbenzene

Toluene

1,2,4-Trimethylbenzene

TABLE I. - (Continued)

1,3,5-Trimethylbenzene  
Xylene, mixture  
o - Xylene  
m - Xylene  
p - Xylene  
Acenaphthene  
2-n-Butyl-3-n-hexylnaphthalene  
7-n-Butyl-1-n-hexylnaphthalene  
1-n-Butylnaphthalene  
2-n-Butylnaphthalene  
1-(1-Cyclohexen-1-yl)naphthalene  
1-Cyclohexylnaphthalene  
1,2-Dimethylnaphthalene  
1,3-Dimethylnaphthalene  
1,4-Dimethylnaphthalene  
1,5-Dimethylnaphthalene  
1,6-Dimethylnaphthalene  
1,7-Dimethylnaphthalene  
1,8-Dimethylnaphthalene  
2,3-Dimethylnaphthalene  
2,6-Dimethylnaphthalene  
2,7-Dimethylnaphthalene  
2,6-Dimethyl-3-n-octylnaphthalene  
1,10-Di-1'-naphthyldecane  
1,1-Di-( $\alpha$ -naphthyl)-1-hendecene

TABLE I. - (Continued)

1-Ethyl naphthalene  
2-Ethyl naphthalene  
1,2,3,4,6,7-Hexamethyl naphthalene  
1-Isopropyl naphthalene  
1-Methyl naphthalene  
2-Methyl naphthalene  
1-(2-Methylphenyl) naphthalene  
2-(2-Methylphenyl) naphthalene  
Naphthalene  
1- $\alpha$ -Naphthyl hendecane  
11- $\alpha$ -Naphthyl-10-heneicosene  
1- $\alpha$ -Naphthyl pentadecane  
5-n-Pentadecyl acenaphthene  
1-n-Pentyl naphthalene  
1-Phenyl naphthalene  
2-Phenyl naphthalene  
1-n-Propyl naphthalene  
1,2,4,8-Tetramethyl naphthalene  
1,2,3-Trimethyl naphthalene  
1,3,5-Trimethyl naphthalene  
1,4,6-Trimethyl naphthalene  
2,3,5-Trimethyl naphthalene  
2,3,6-Trimethyl naphthalene  
Anthracene  
2,3-Benzofluorene

TABLE I. - (Concluded)

9-(n-Butyl)anthracene  
2-(tert-Butyl)anthracene  
9,10-Dimethylanthracene  
4,5-Dimethylphenanthrene  
9-n-Dodecylanthracene  
9-n-Dodecylphenanthrene  
2-Ethylanthracene  
2-Methylanthracene  
9-Methylanthracene  
1-Methylphenanthrene  
3-Methylphenanthrene  
Phenanthrene  
9-Phenylanthracene  
9-Vinylanthracene

TABLE II. - DETERMINATION OF ALKYL BENZENES, ALKYL NAPHTHALENES,  
ALKYL ANTHRACENES/PHENANTHRENES, AND TOTAL AROMATICS IN JET FUELS

Sample	Equation*	Benzenes		Naphthalenes		Anthracenes		Total Aromatics	
		Average Wt %	St. Dev.	Average Wt %	St. Dev.	Average Wt %	St. Dev.	Average Wt %	St. Dev.
ERBS-3	General	11.7	3.8	11.8	0.8	1.3	0.0	24.8	4.4
	ERBS	10.8	2.2	11.6	0.7	1.4	0.0	23.8	2.8
ERBS-3- 12.3%H	General	18.1	2.5	13.1	1.2	1.5	0.0	32.7	3.5
	ERBS	17.5	2.2	12.5	1.3	1.6	0.0	30.1	3.3
ERBS-3- 11.8%H	General	21.6	3.7	14.0	0.8	1.7	0.1	37.3	4.3
	ERBS	22.3	2.4	13.5	0.8	1.7	0.1	37.5	3.3
ERBS-3S	General	29.9	6.1	18.2	2.8	2.3	0.1	50.4	8.2
	ERBS	30.8	6.0	18.2	1.4	2.3	0.0	51.3	7.2
ERBS-2	General	15.8	0.9	9.5	0.5	1.7	0.0	27.0	1.2
	ERBS	12.4	0.8	9.1	0.4	1.7	0.0	23.2	1.0
Jet A	General	15.9	0.8	1.5	0.1	0.1	0.0	17.5	0.8
	Jet A	12.7	0.7	2.8	0.1	0.1	0.0	15.6	0.7
JP-5	General	22.0	0.3	1.4	0.1	0.1	0.0	23.5	0.4
	Jet A	17.3	0.3	3.0	0.1	0.1	0.0	20.4	0.4
IRS	General	7.7	0.6	5.6	0.4	0.4	0.0	13.7	0.9
	Jet A	6.9	0.5	5.6	0.3	0.4	0.0	12.9	0.7

\* General Equation - Measurements at 198.1, 226.7, and 254.5 nm.  
ERBS Equation - Measurements at 196.5, 224.6, and 253.6 nm.  
Jet A Equation - Measurements at 196.5, 221.5, and 254.5 nm.

TABLE III. - COMPARISON OF ULTRAVIOLET SPECTROPHOTOMETRIC  
METHOD RESULTS WITH RESULTS FROM OTHER METHODS

Sample	Technique	Benzenes Wt %	Naphthalenes Wt %	Anthracenes Wt %	Total Aromatics
ERBS-3	UV	10.8	11.6	1.4	23.8 Wt %
	FIA/MS	9.0	16.5	3.4	28.9 Wt %
	UV (D-1840)	--	14.0	--	--
	HPLC	--	--	--	26.3 Vol %
ERBS-3 -12.3%H	UV	17.5	12.5	1.6	30.1 Wt %
	FIA/MS	11.4	24.0	5.2	40.6 Wt %
	UV (D-1840)	--	15.7	--	--
	HPLC	--	--	--	37.7 Vol %
ERBS-3 -11.8%H	UV	22.3	13.5	1.7	37.5 Wt %
	FIA/MS	14.6	30.0	5.3	49.9 Wt %
	UV (D-1840)	--	17.1	--	--
	HPLC	--	--	--	47.8 Vol %
ERBS-3S	UV	30.8	18.2	2.3	51.3 Wt %
	FIA/MS	33.7	42.5	6.3	82.3 Wt %
	UV (D-1840)	--	22.9	--	--
	HPLC	--	--	--	78.2 Vol %
ERBS-2	UV	12.4	9.1	1.7	23.2 Wt %
	FIS/MS	17.2	10.0	2.0	29.3 Wt %
	UV (D-1840)	--	14.2	--	--
	HPLC	--	--	--	26.5 Vol %
Jet A	UV	12.7	2.8	0.1	15.6 Wt %
	MS	19.5	0.1	0.0	19.6 Wt %
	UV (D-1840)	--	0.97	--	--
	FIA	--	--	--	17.9 Vol %
	HPLC	--	--	--	17.6 Vol %
JP-5	UV	17.3	3.0	0.1	20.4 Wt %
	UV (D-1840)	--	0.83	--	--
	FIA	--	--	--	22.2 Vol %
	HPLC	--	--	--	20.2 Vol %
IRS	UV	6.9	5.6	0.4	12.9 Wt %
	MS	12.02	5.0	0.2	17.4 Wt %
	UV (D-1840)	--	5.5	--	--
	FIA	--	--	--	16.7 Vol %
	HPLC	--	--	16.9 Vol %	

TABLE IV. - COMPOSITION OF SIMULATED FUELS

## (a) Aromatic Hydrocarbon Fractions, Wt %

Compound	Jet A Type Fuel	ERBS Type Fuel
Tetralin	2.94	2.66
1,2,3,5-Tetramethylbenzene	2.68	2.43
Xylene	2.59	2.35
1,2,4-Trimethylbenzene	2.67	2.42
n-Butylbenzene	2.68	2.35
Diethylbenzene	2.62	4.74
1,2,4,5-Tetramethylbenzene	1.98	1.84
Naphthalene	0.57	2.02
2-Methylnaphthalene	0.68	2.01
Acenaphthene	0.48	1.77
2,6-Dimethylnaphthalene	0.54	2.15
2,3-Dimethylnaphthalene	0.64	2.06
2-Ethylnaphthalene	0.60	1.08
1-Methylnaphthalene	0.60	2.18
Phenanthrene	0.021	0.41
Anthracene	0.025	0.37
9-Methylanthracene	0.023	0.37
9,10-Dimethylanthracene	0.022	0.13
1-Methylphenanthrene	0.020	0.28
Total benzenes	18.16	18.79
Total naphthalenes	4.11	13.27
Total anthracenes/phenanthrenes	0.11	1.56
Total aromatics	22.38	33.62

## (b) Saturated Hydrocarbon Fraction, Wt %

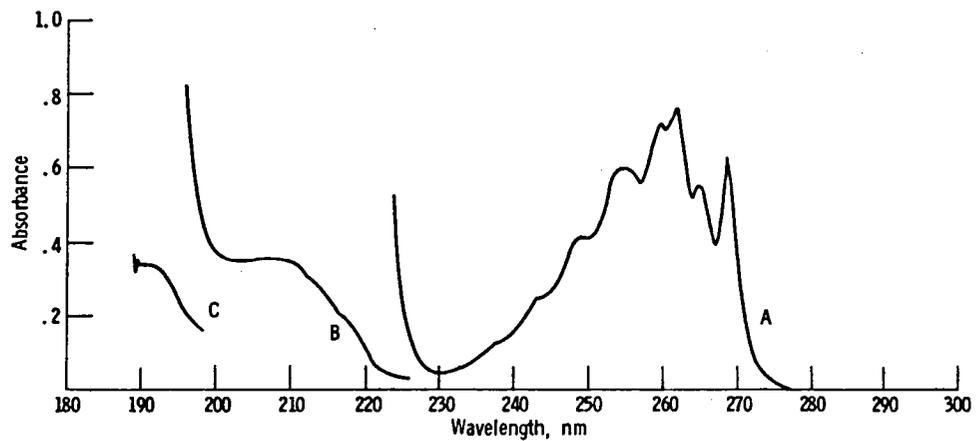
Compound	Jet A Type Fuel	ERBS Type Fuel
Isooctane	10.09	8.63
Cyclooctane	17.85	15.27
Decalin	13.20	11.28
Dodecane	36.48	31.20

TABLE V. - RESULTS FOR SIMULATED FUELS

Fuel	Equation	Benzenes		Naphthalenes		Anthracenes		Total Aromatics
		Average Wt %	St. Dev.	Average Wt %	St. Dev.	Average Wt %	St. Dev.	Average Wt %
Simulated	General	12.26	1.07	5.34	0.02	0.31	0.01	17.91
Jet A	Jet A	12.23	0.40	6.58	0.10	0.32	0.01	19.13
	True Value	18.16	--	4.11	--	0.11	--	22.38
	D-1840	--	--	3.66	0.15	--	--	--
Simulated	General	21.77	4.60	17.72	1.29	2.07	0.64	41.56
ERBS	ERBS	18.27	3.78	19.85	0.79	2.19	0.00	40.31
	True Value	18.78	--	13.28	--	1.56	--	33.62
	D-1840	--	--	13.00	0.45	--	--	--

TABLE VI. - RESULTS FOR SIMULATED FUELS  
 USING EQUATIONS BASED ON KNOWN COMPONENTS

Fuel	Technique	Benzenes		Naphthalenes		Anthracenes		Total Aromatics	
		Wt %	St. Dev.	wt %	St. Dev.	Wt %	St. Dev.	Wt %	St. Dev.
Simulated	UV	19.27	1.26	3.89	0.32	0.35	0.01	23.51	1.32
Jet A	FIA	--	--	--	--	--	--	23.80	--
	HPLC	--	--	--	--	--	--	22.17	--
	True Value	18.16	--	4.11	--	0.11	--	22.38	--
	D-1840	--	--	3.66	0.15	--	--	--	--
Simulated	UV	17.14	2.63	15.15	0.97	1.53	0.06	33.82	3.14
ERBS	FIA	--	--	--	--	--	--	33.96	--
	HPLC	--	--	--	--	--	--	33.56	--
	True Value	18.78	--	13.28	--	1.56	--	33.62	--
	D-1840	--	--	13.00	0.45	--	--	--	--

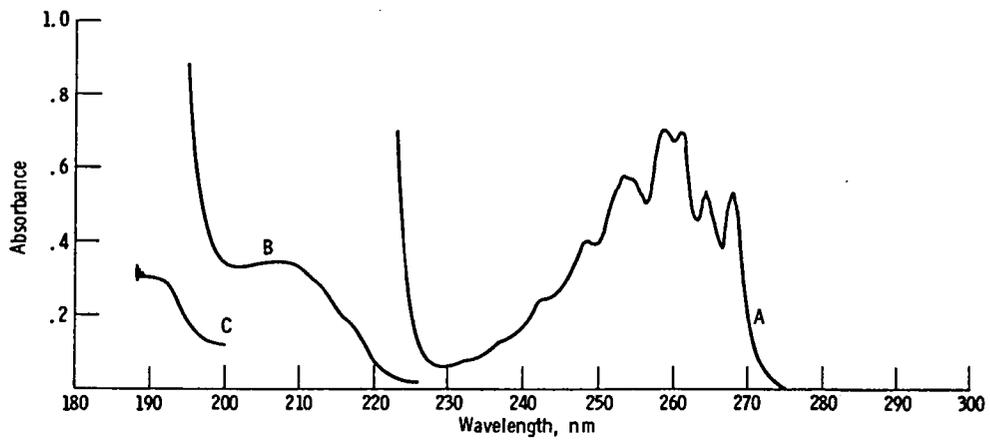


Ultraviolet spectrum

n- Butylbenzene  
 1.0 cm cell  
 10.0 nm/cm chart  
 0.2 nm/sec scan  
 0.5 sec period  
 1.0 nm band width  
 24.7 °C

A 0.43005 g/l  
 B 0.0043005 g/l  
 C 0.00043005 g/l  
 Solution in isooctane

Figure A-1.

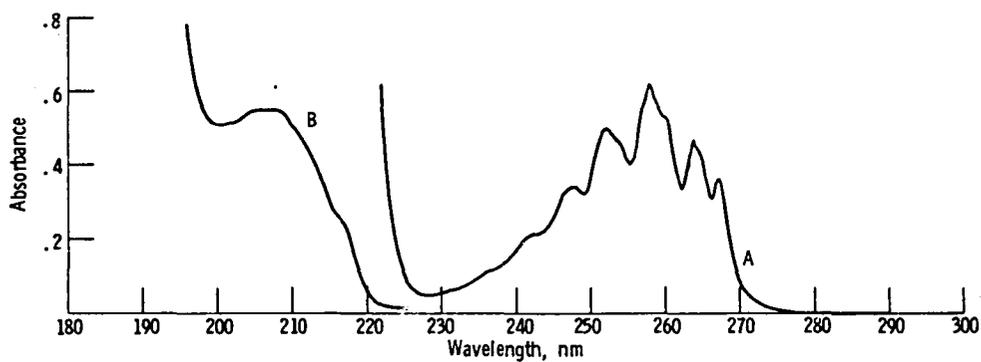


Ultraviolet spectrum

sec-Butylbenzene  
 1.0 cm cell  
 10.0 nm/cm chart  
 0.2 nm/sec scan  
 0.5 sec period  
 1.0 nm band width  
 247 °C

A 0.43105 g/l  
 B 0.0043105 g/l  
 C 0.00043105 g/l  
 Solution in isooctane

Figure A-2.

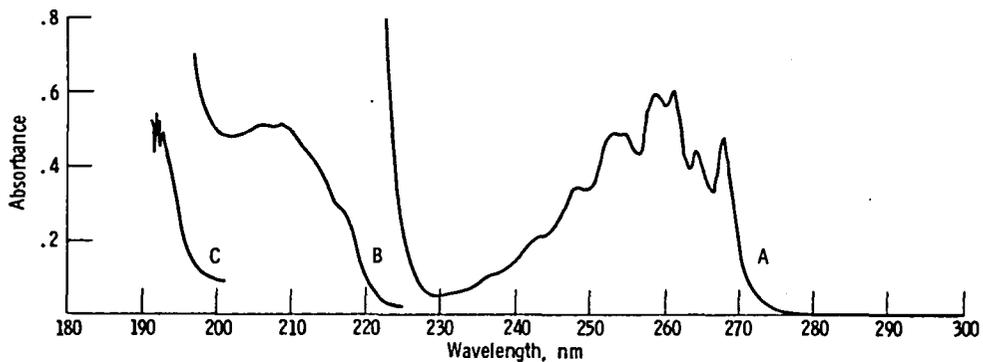


Ultraviolet spectrum

Tert-butylbenzene  
 1.0 cm cell  
 1.0 nm/cm chart  
 0.1 nm/sec scan  
 1.0 sec period  
 1.0 nm band width  
 21.4° C

A 0.4335 g/l  
 B 0.00867 g/l  
 Solution in isooctane

Figure A-3.

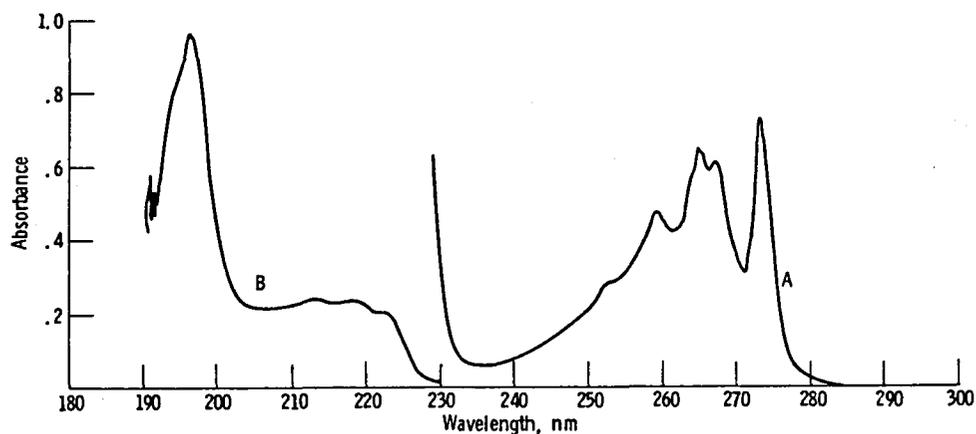


Ultraviolet spectrum

Cyclohexylbenzene  
 1.0 cm cell  
 10 nm/cm chart  
 0.1 nm/sec scan  
 1.0 sec period  
 1.0 nm band width  
 24.5° C

A 0.456 g/l  
 B 0.0456 g/l  
 C 0.00912 g/l  
 Solution in isooctane

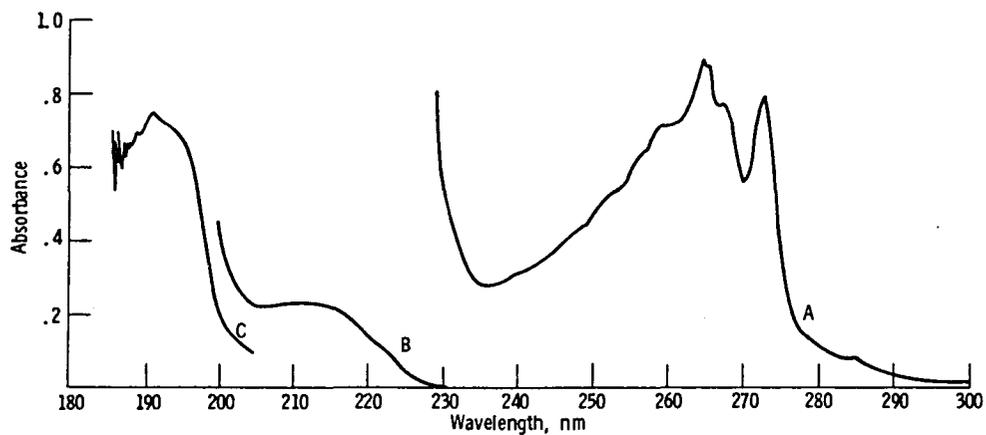
Figure A-4



Ultraviolet spectrum

p-Diethylbenzene      A 0.1724 g/l  
 1.0 cm cell            B 0.00345 g/l  
 10 nm/cm chart        Solution in Isooctane  
 0.1 nm/sec scan  
 1.0 sec period  
 1.0 nm band width  
 24.7° C

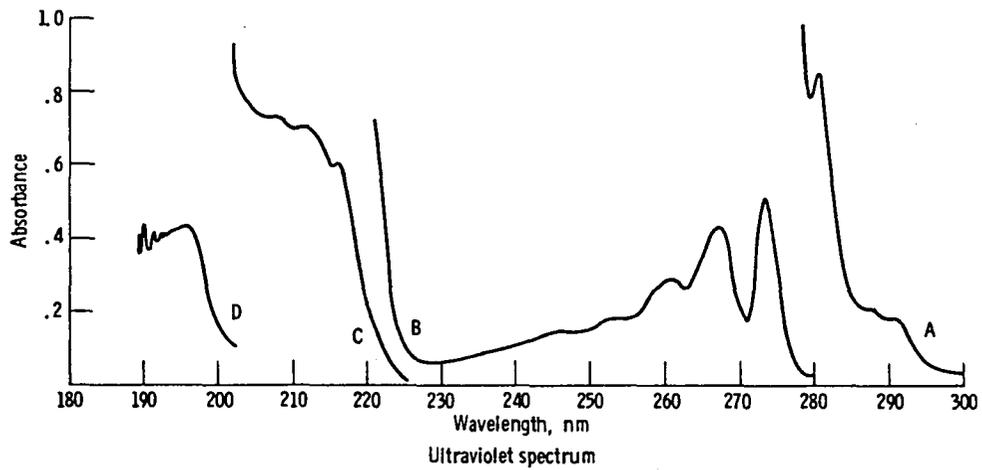
Figure A-5.



Ultraviolet spectrum

Diethylbenzene      A 3.4696 g/l  
 mixture              B 0.034696 g/l  
 0.1 cm cell            C 0.017348 g/l  
 10.0 nm/cm chart     Solution in Isooctane  
 0.2 nm/sec scan  
 0.5 sec period  
 1.0 nm band width

Figure A-6.

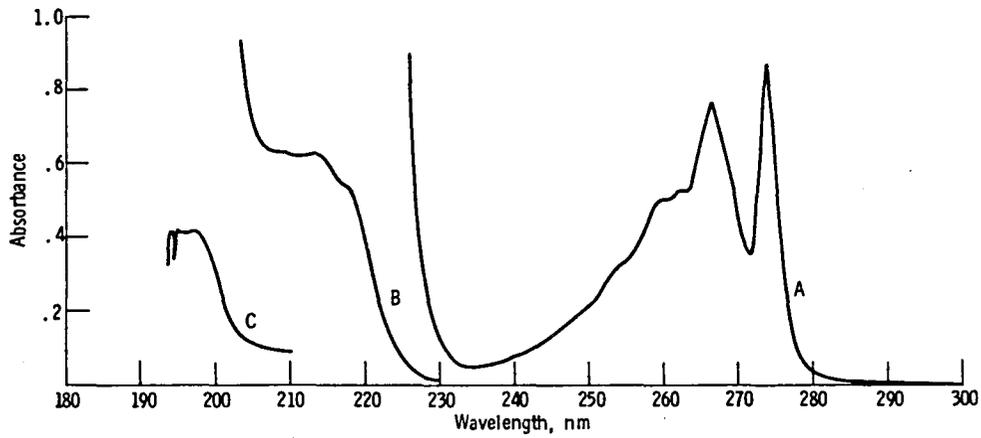


Ultraviolet spectrum

Indan  
 1.0 cm cell  
 1 nm/cm chart  
 0.1 nm/sec scan  
 1.0 sec period  
 1.0 nm band width  
 22.6° C

A 0.965 g/l  
 B 0.0386 g/l  
 C 0.00965 g/l  
 D 0.000965 g/l  
 Solution in isooctane

Figure A-7.

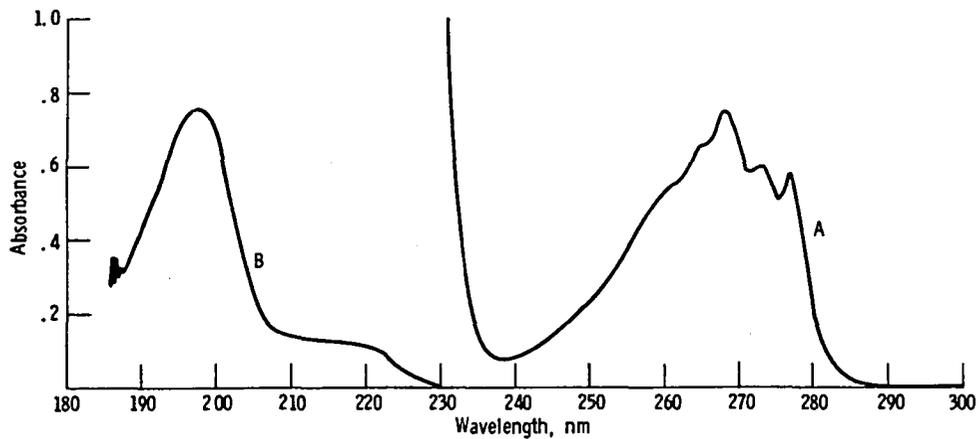


Ultraviolet spectrum

Tetralin  
 1.0 cm cell  
 1 nm/cm chart  
 0.1 nm/sec scan  
 1.0 sec period  
 1.0 nm band width  
 26.1° C

A 0.1946 g/l  
 B 0.00973 g/l  
 C 0.000973 g/l  
 Solution in isooctane

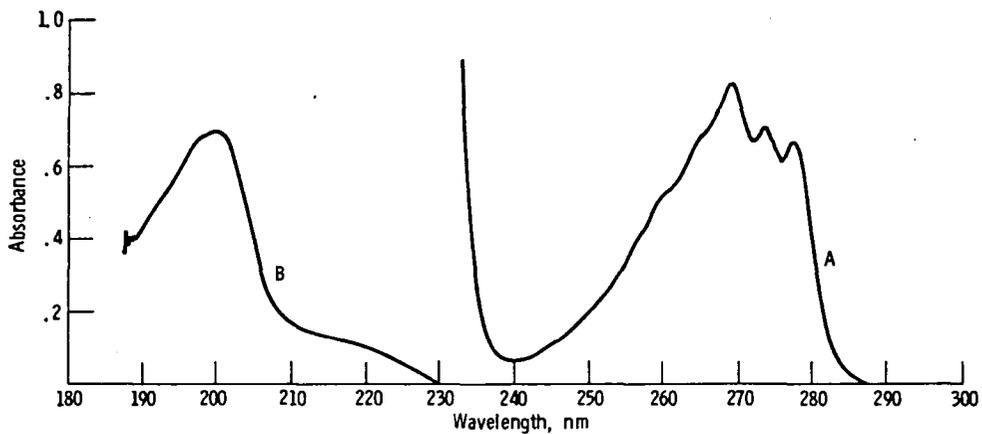
Figure A-8.



Ultraviolet spectrum

1,2,3,4 - Tetramethylbenzene      A 3.4238 g/l  
 0.1 cm cell                              B 0.01712 g/l  
 10.0 nm/cm chart                      Solution in isooctane  
 0.2 nm/sec scan  
 0.5 sec period  
 1.0 nm band width  
 24.6° C

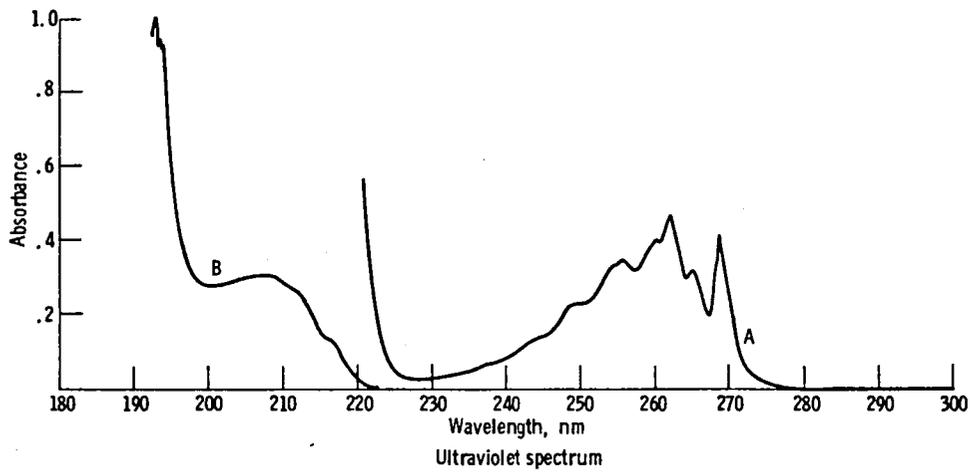
Figure A-9.



Ultraviolet spectrum

1,2,3,5 - Tetramethylbenzene      A 0.3564 g/l  
 1.0 cm cell                              B 0.0001782 g/l  
 10.0 nm/cm chart                      Solution in isooctane  
 0.2 nm/sec scan  
 1.0 sec period  
 1.0 nm band width  
 23.6° C

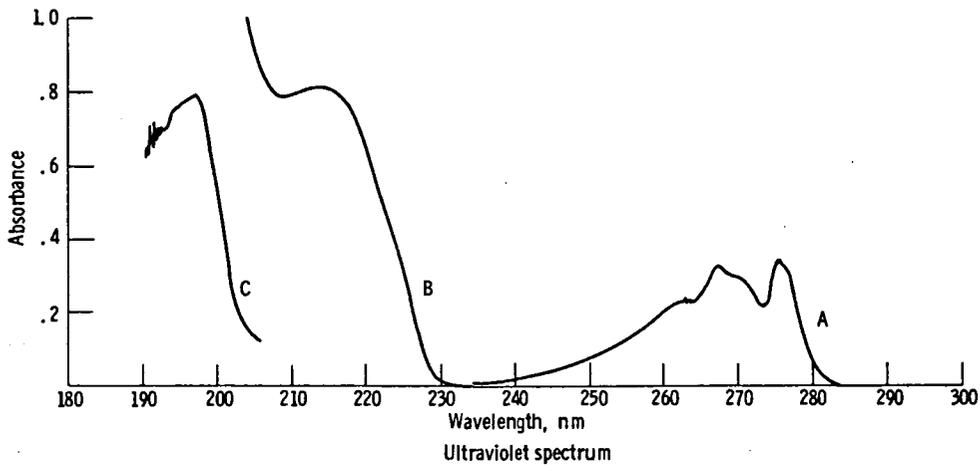
Figure A-10.



Toluene  
 1.0 cm cell  
 1 nm/cm chart  
 0.1 nm/sec scan  
 1.0 sec period  
 1.0 nm band width  
 24.9° C

A 0.1734 g/l  
 B 0.003668 g/l  
 Solution in isooctane

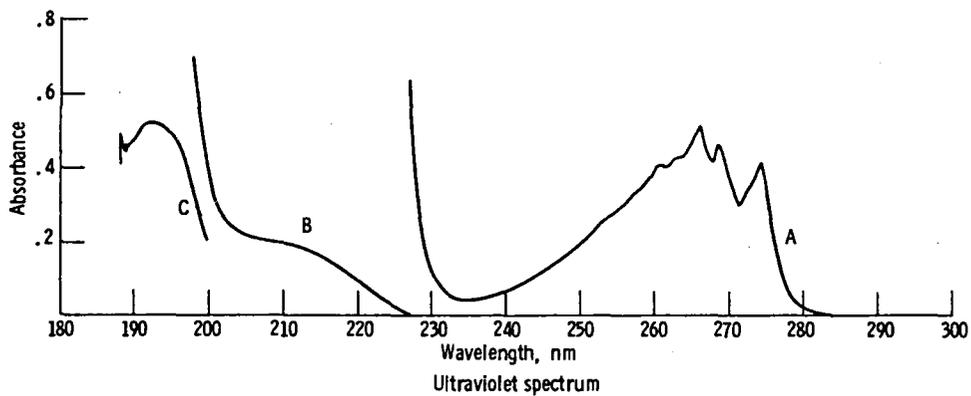
Figure A-11.



1,2,4-Trimethylbenzene  
 1.0 cm cell  
 1 nm/cm chart  
 0.1 nm/sec scan  
 1.0 sec period  
 1.0 nm band width  
 22.6° C

A 0.0889 g/l  
 B 0.00889 g/l  
 C 0.001778 g/l  
 Solution in isooctane

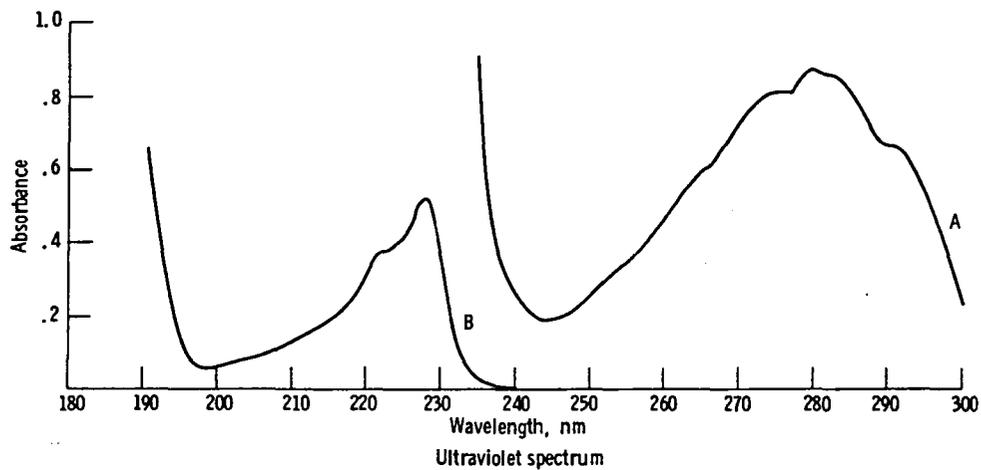
Figure A-12.



Ultraviolet spectrum

Xylene mixture	A 0.17434 g/l
1.0 cm cell	B 0.0017434 g/l
10.0 nm/cm chart	C 0.0008717 g/l
0.2 nm/sec scan	Solution in Isooctane
1.0 sec period	
1.0 nm band width	
28.9° C	

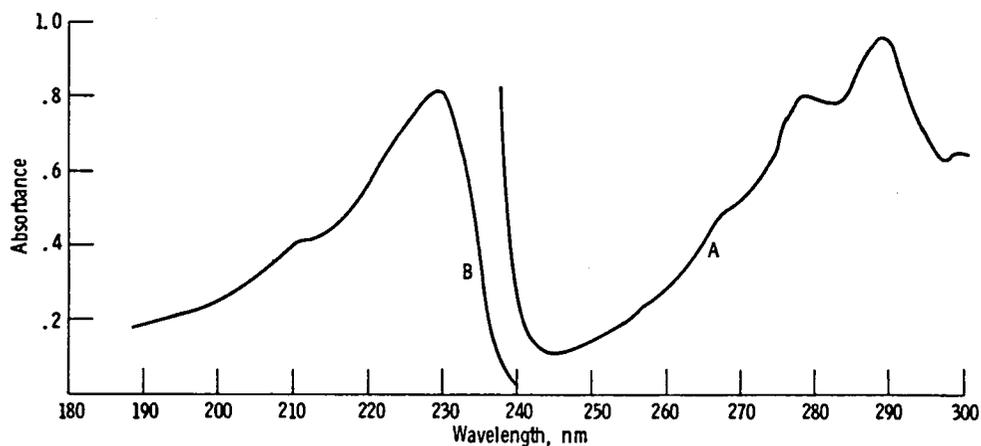
Figure A-13.



Ultraviolet spectrum

1,3 - Dimethylnaphthalene	A 0.0204 g/l
1.0 cm cell	B 0.000816 g/l
10 nm/cm chart	Solution in isooctane
0.2 nm/sec scan	
1.0 sec period	
1.0 nm band width	
21.9° C	

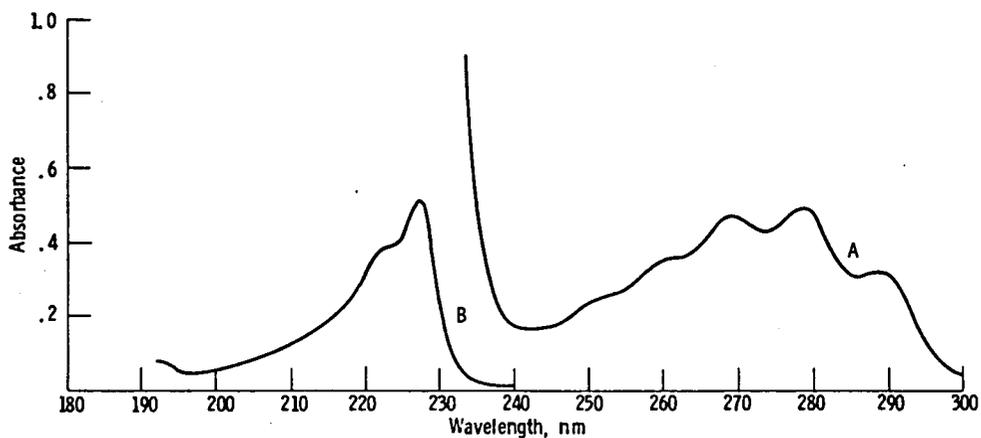
Figure A-14.



Ultraviolet spectrum

1,4 - Dimethylnaphthalene      A 0.02032 g/l  
 1.0 cm cell                      B 0.002032 g/l  
 10.0 nm/cm chart              Solution in isooctane  
 0.2 nm/sec scan  
 0.5 sec period  
 1.0 nm band width  
 25.0° C

Figure A-15.

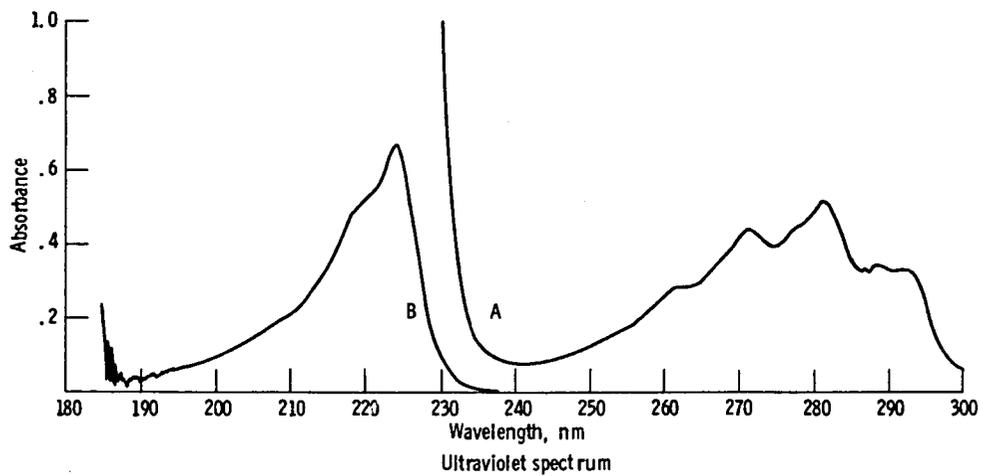


Ultraviolet spectrum

2,3 - Dimethylnaphthalene      A 0.0152 g/l  
 1.0 cm cell                      B 0.00076 g/l  
 10.0 nm/cm chart              Solution in isooctane  
 0.2 nm/sec scan  
 1.0 sec period  
 1.0 nm band width  
 25.0° C

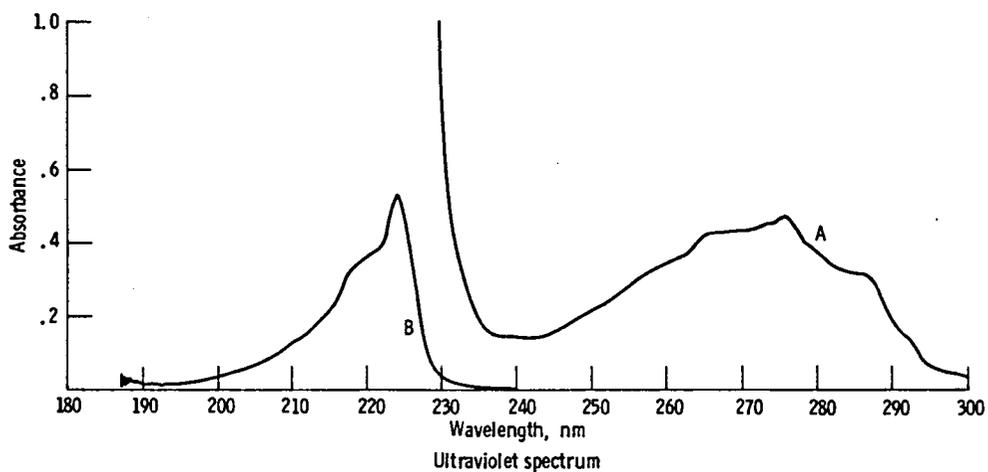
Figure A-16.





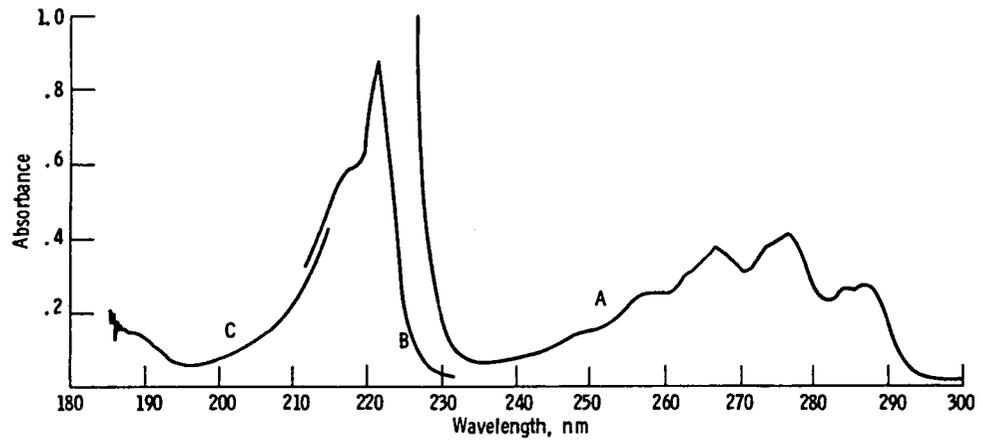
1 - Methylnaphthalene      A 0.10070 g/l  
 0.1 cm cell                    B 0.01007 g/l  
 10.0 nm/cm chart            Solution in isooctane  
 0.2 nm/sec scan  
 0.5 sec period  
 1.0 nm band width  
 27.0° C

Figure A-19.



2 - Methylnaphthalene      A 0.146 g/l  
 0.1 cm cell                    B 0.0073 g/l  
 10.0 nm/cm chart            Solution in isooctane  
 0.2 nm/sec scan  
 0.5 sec period  
 1.0 nm band width  
 26.1° C

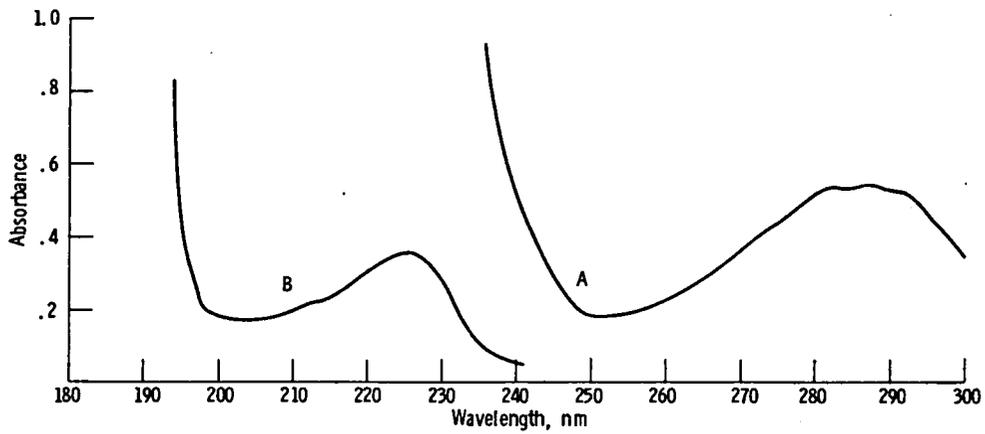
Figure A-20.



Ultraviolet spectrum

Naphthalene	A 0.091 g/l
0.1 cm cell	B 0.0091 g/l
10.0 nm/cm chart	C 0.008 g/l
0.2 nm/sec scan	Solution in isooctane
0.5 sec period	
1.0 nm band width	
25.0° C	

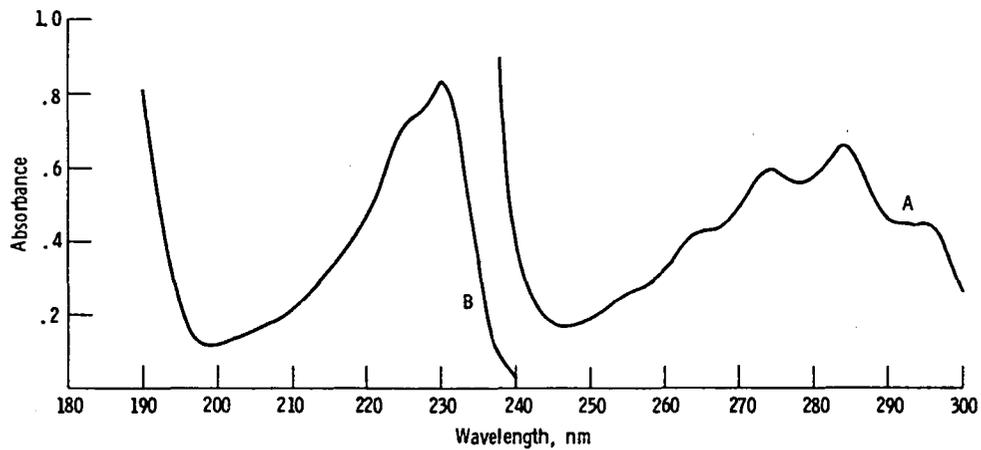
Figure A-21.



Ultraviolet spectrum

1 - Phenylnaphthalene	A 0.01096 g/l
1.0 cm cell	B 0.001096 g/l
10.0 nm/cm chart	Solution in isooctane
0.2 nm/sec scan	
1.0 sec period	
1.0 nm band width	
25.8° C	

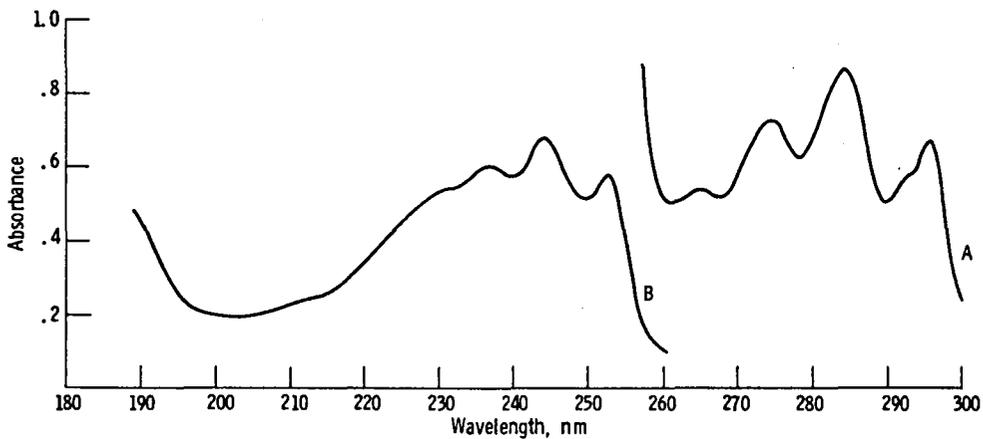
Figure A-22.



Ultraviolet spectrum

2,3,5 - Trimethylnaphthalene    A 0.0192 g/l  
 1.0 cm cell                            B 0.00096 g/l  
 10.0 nm/cm chart                    Solution in isooctane  
 0.1 nm/sec scan  
 0.5 sec period  
 1.0 nm band width  
 25.1<sup>0</sup> C

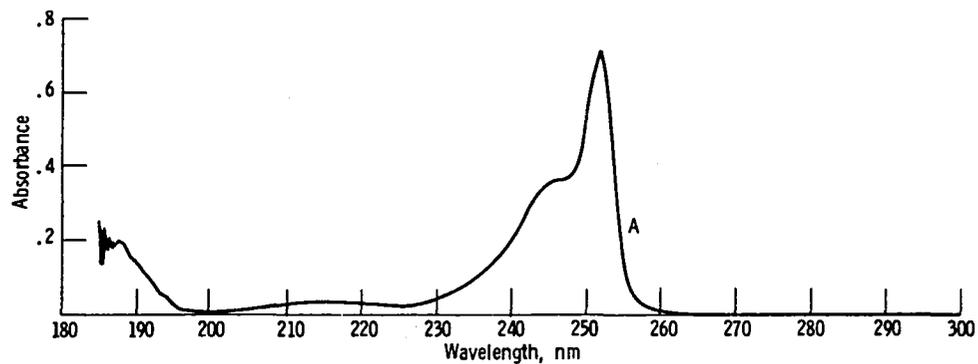
Figure A-23.



Ultraviolet spectrum

2 - Vinylnaphthalene                A 0.0111 g/l  
 1.0 cm cell                            B 0.00222 g/l  
 10.0 nm/cm chart                    Solution in isooctane  
 0.2 nm/sec scan  
 0.5 sec period  
 1.0 nm band width  
 24.8<sup>0</sup> C

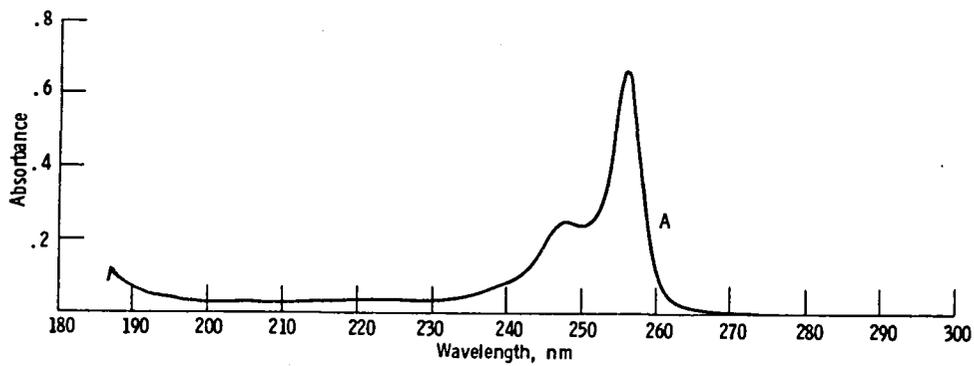
Figure A-24



Anthracene  
 0.1 cm cell  
 1 nm/cm chart  
 .05 nm/sec scan  
 1.0 sec period  
 1.0 nm band width  
 24.7° C

A 0.0030 g/l  
 Solution in isooctane

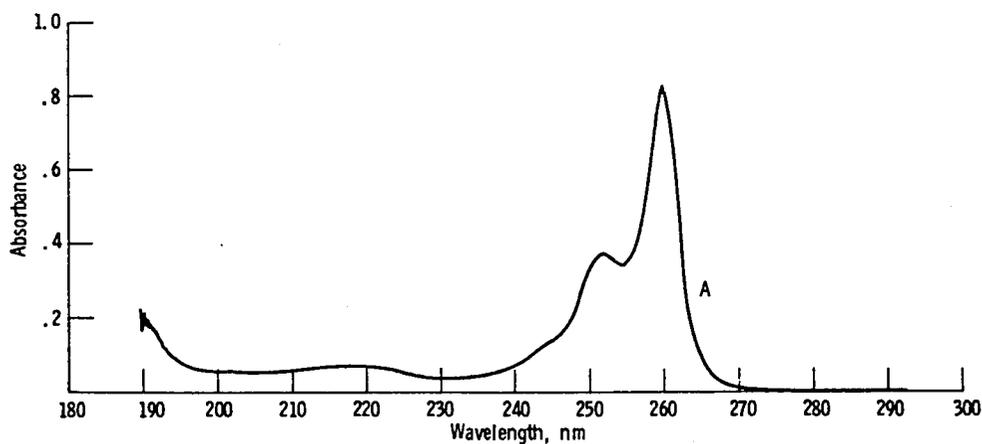
Figure A-25.



2 - Tert-butyl anthracene  
 1.0 cm cell  
 10.0 nm/cm chart  
 0.2 nm/sec scan  
 0.5 sec period  
 1.0 nm band width  
 26.1° C

A 0.00122 g/l  
 Solution in isooctane

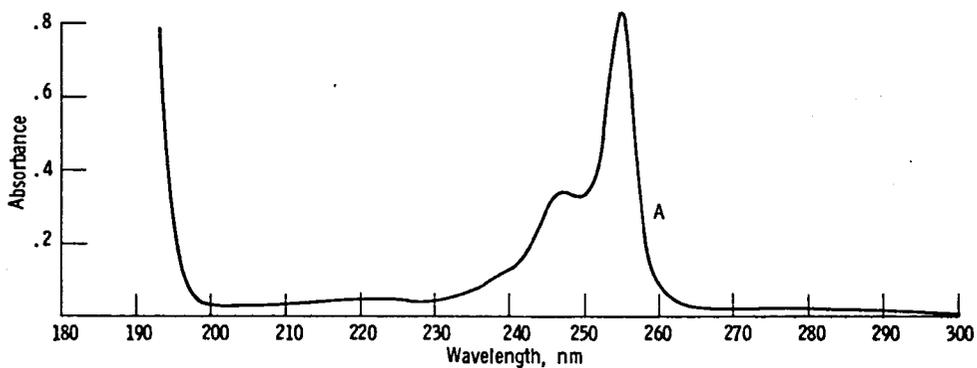
Figure A-26.



Ultraviolet spectrum

9,10 - Dimethylantracene      A 0.00088 g/l  
 1.0 cm cell                      Solution in isooctane  
 10.0 nm/cm chart  
 0.2 nm/sec scan  
 1.0 sec period  
 1.0 nm band width  
 24.8° C

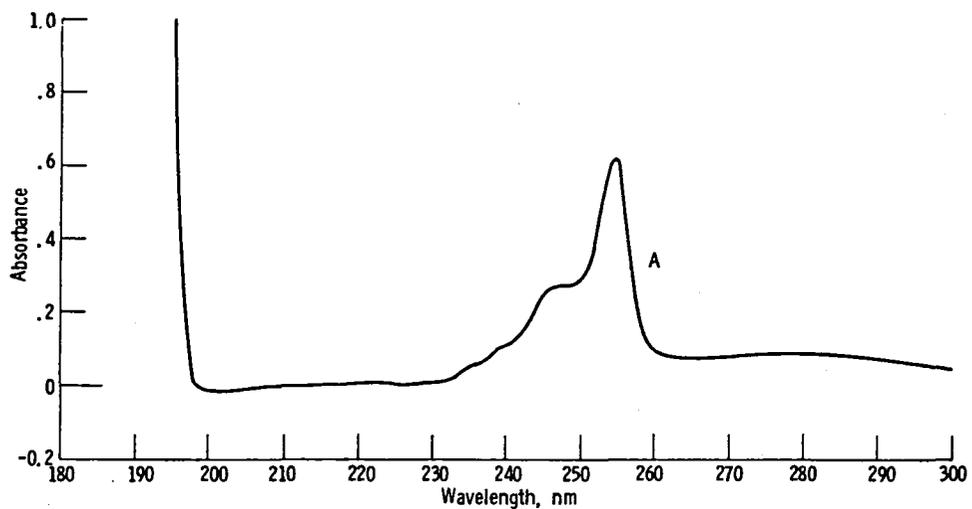
Figure A-27.



Ultraviolet spectrum

2 - Ethylantracene              A 0.00068 g/l  
 1.0 cm cell                      Solution in isooctane  
 10.0 nm/cm chart  
 0.2 nm/sec scan  
 1.0 sec period  
 1.0 nm band width  
 24.3° C

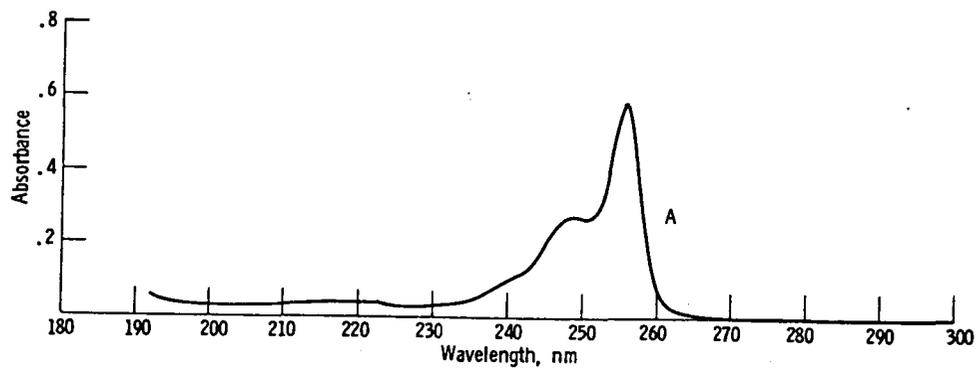
Figure A-28.



Ultraviolet spectrum

2 - Methylantracene      A 0.00050 g/l  
 1.0 cm cell                      Solution in Isooctane  
 10.0 nm/cm chart  
 0.1 nm/sec scan  
 1.0 sec period  
 1.0 nm band width  
 25.8° C

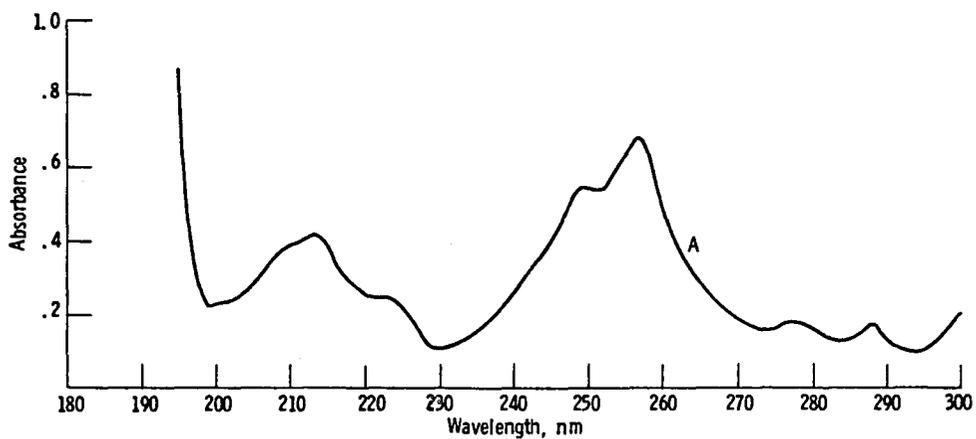
Figure A-29.



Ultraviolet spectrum

9 - Methylantracene      A 0.00055 g/l  
 1.0 cm cell                      Solution in isooctane  
 10.0 nm/cm chart  
 0.1 nm/sec scan  
 1.0 sec period  
 1.0 nm band width  
 23.7° C

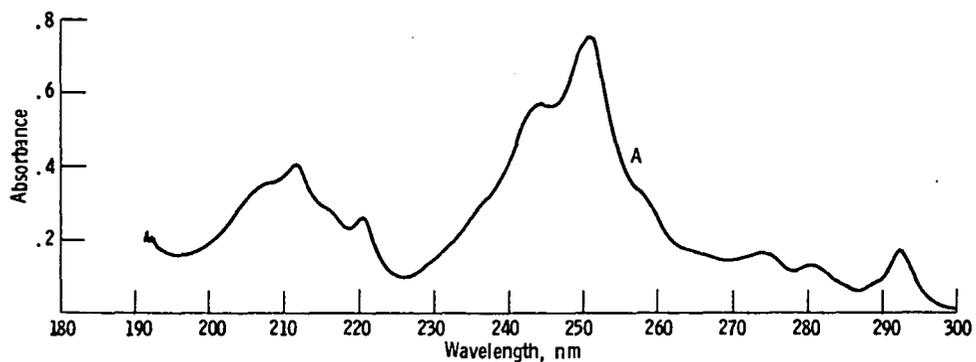
Figure A-30.



Ultraviolet spectrum

1 - Methylphenanthrene      A 0.00212 g/l  
 1.0 cm cell                      Solution in isooctane  
 10.0 nm/cm chart  
 0.2 nm/sec scan  
 1.0 sec period  
 1.0 nm band width  
 25.0° C

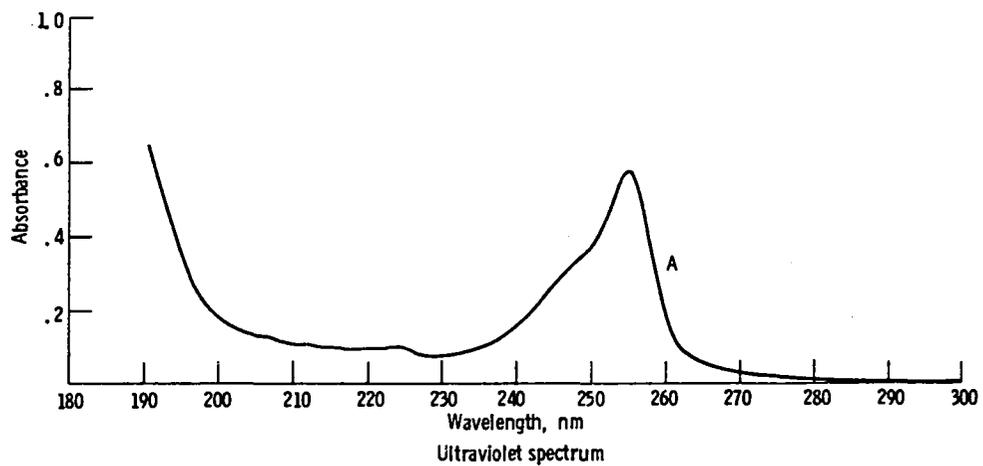
Figure A-31.



Ultraviolet spectrum

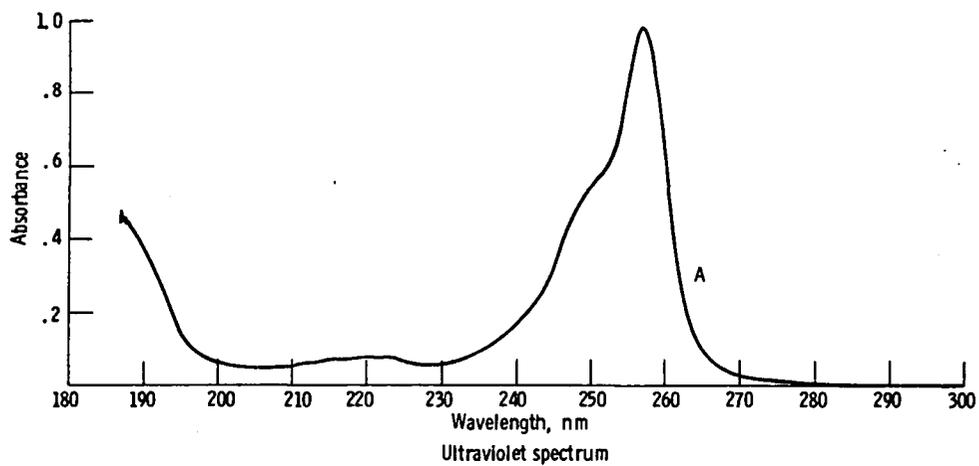
Phenanthrene                      A 0.00202 g/l  
 1.0 cm cell                      Solution in isooctane  
 10.0 nm/cm chart  
 0.1 nm/sec scan  
 1.0 sec period  
 1.0 nm band width  
 24.0° C

Figure A-32.



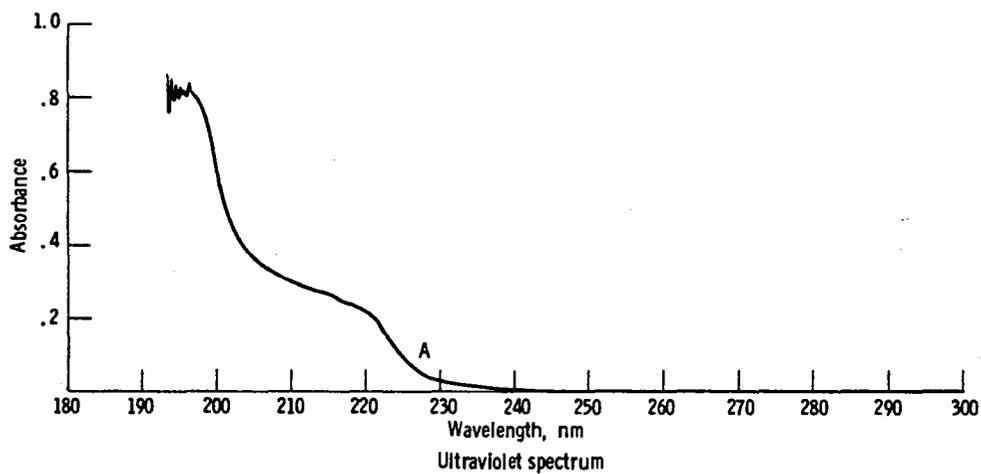
9 - Phenylanthracene                      A 0.00096 g/l  
 1.0 cm cell                                      Solution in isooctane  
 10.0 nm/cm chart  
 0.2 nm/sec scan  
 1.0 sec period  
 1.0 nm band width  
 25.8° C

Figure A-33.



9 - Vinylanthracene                      A 0.00130 g/l  
 1.0 cm cell                                      Solution in isooctane  
 10.0 nm/cm chart  
 0.2 nm/sec scan  
 0.5 sec period  
 1.0 nm band width  
 25.2° C

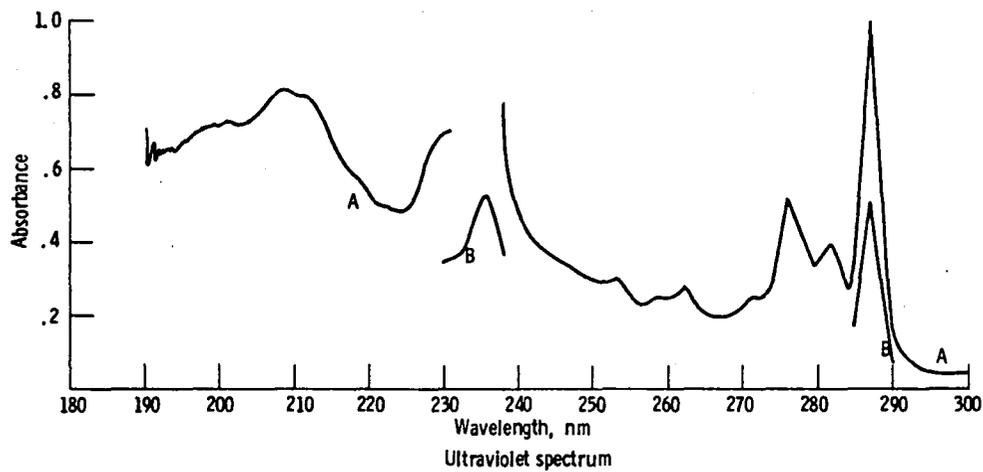
Figure A-34.



Decalin  
 1.0 cm cell  
 1 nm/cm chart  
 0.1 nm/sec scan  
 1.0 nm band width  
 22.6° C

A 89.6 g/l  
 Solution in isooctane

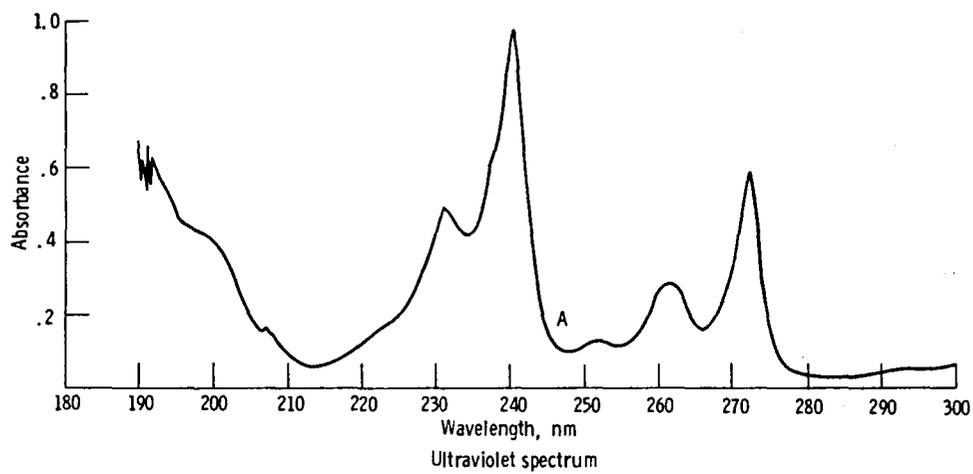
Figure A-35.



Fluoranthene  
 1.0 cm cell  
 1 nm/cm chart  
 0.1 nm/sec scan  
 1.0 sec period  
 1.0 nm band width  
 22.6° C

A 0.00408 g/l  
 B 0.00204 g/l  
 Solution in isooctane

Figure A-36.



Pyrene  
1.0 cm cell  
1 nm/cm chart  
0.1 nm/sec scan  
1.0 sec period  
1.0 nm band width  
22.6° C

A 0.00208 g/l  
Solution in isooctane

Figure A-37.

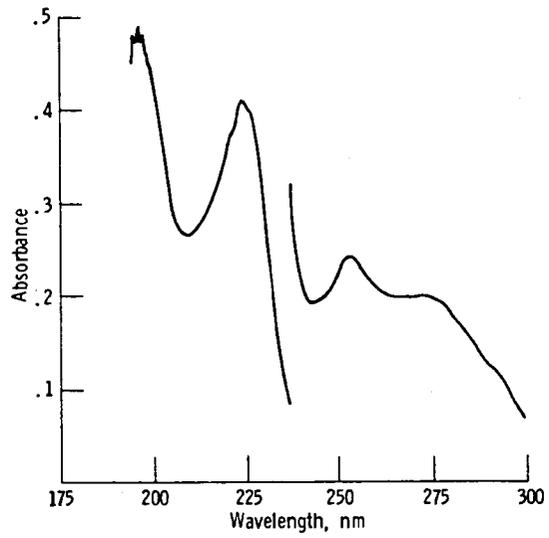


Figure 1. - Ultraviolet spectrum of ERBS-3 fuel.

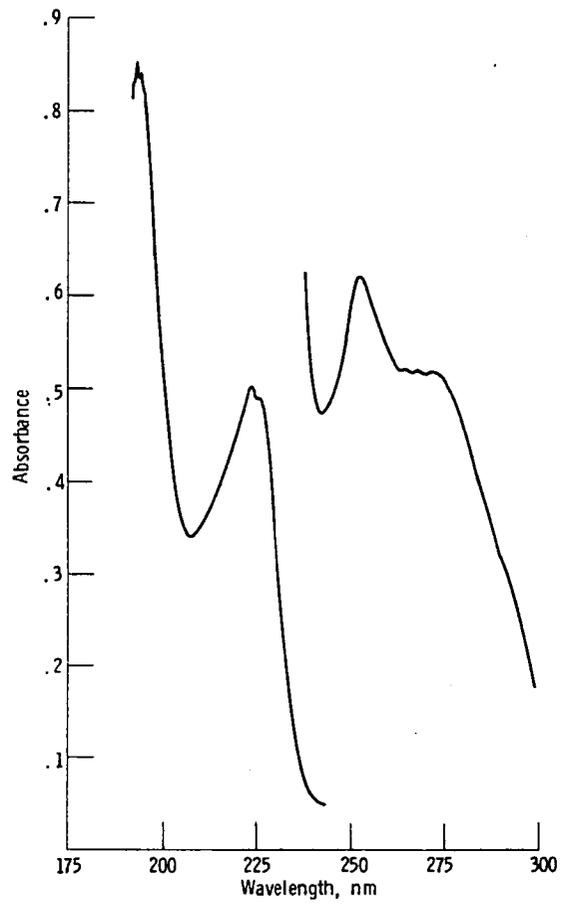


Figure 2. - Ultraviolet spectrum of ERBS-3-11.8% H fuel.

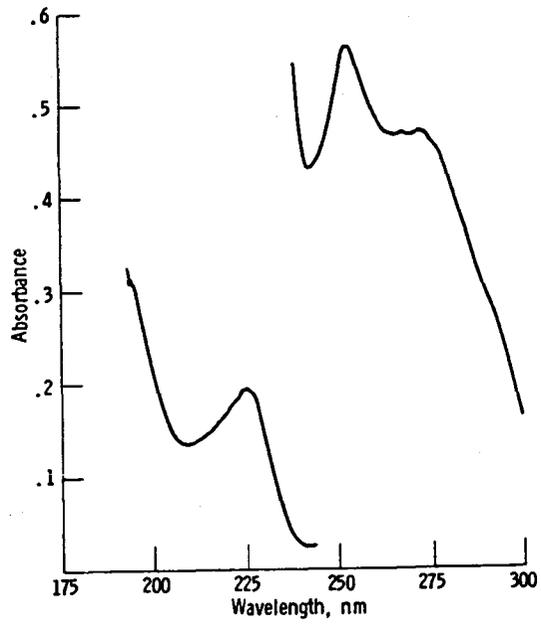


Figure 3. - Ultraviolet spectrum of ERBS-3-12, 3% H fuel.

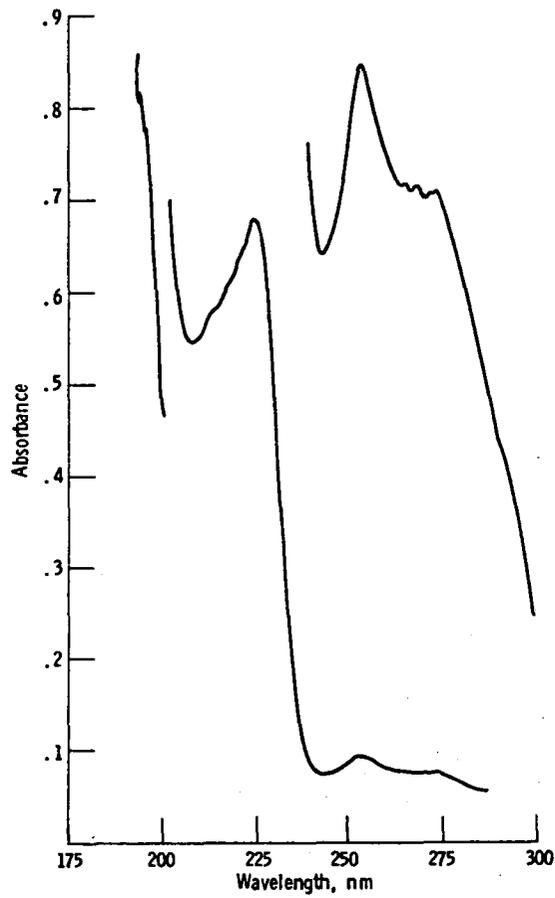


Figure 4. - Ultraviolet spectrum of ERBS-3S fuel.

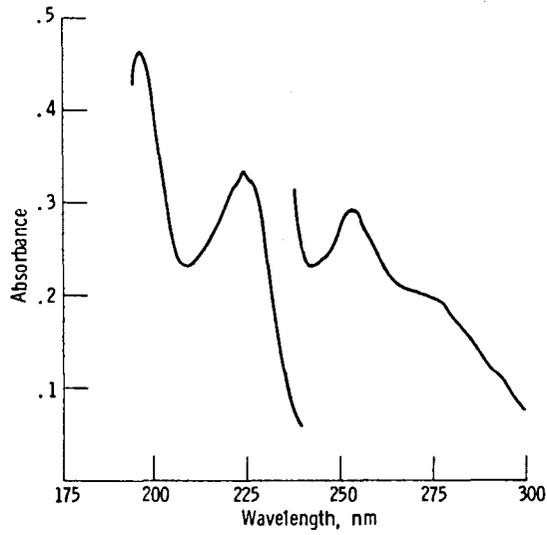


Figure 5. - Ultraviolet spectrum of ERBS-2 fuel.

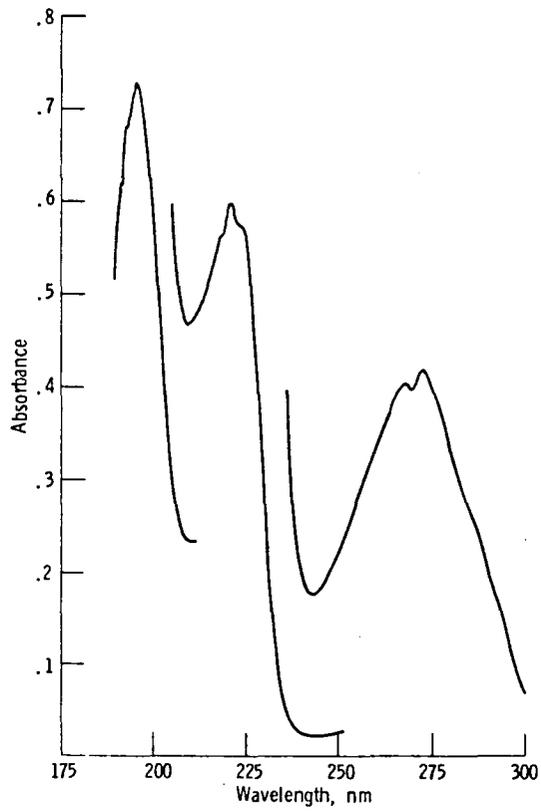


Figure 6. - Ultraviolet spectrum of Jet A fuel.

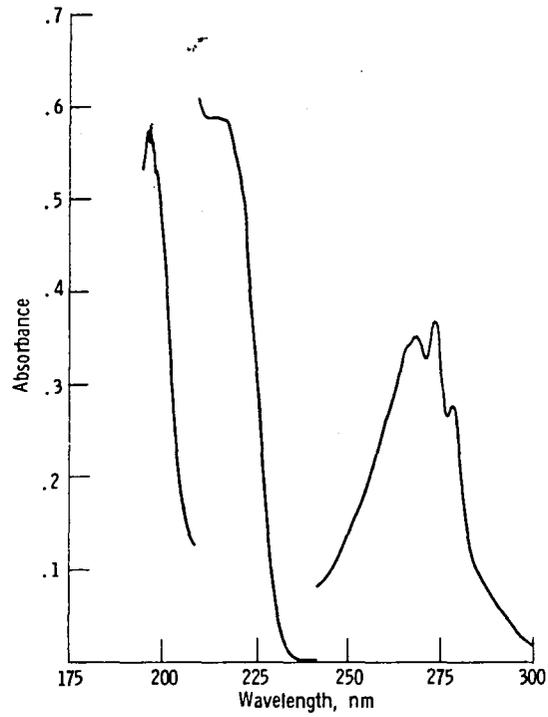


Figure 7. - Ultraviolet spectrum of JP-5 paraho shale fuel.

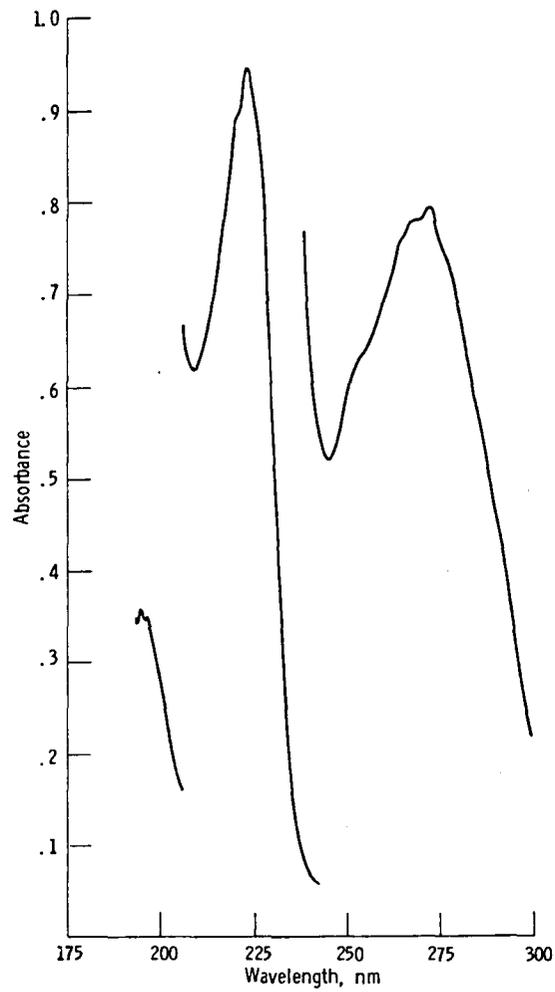


Figure 8. - Ultraviolet spectrum of the intermediate refinery stream fuel.

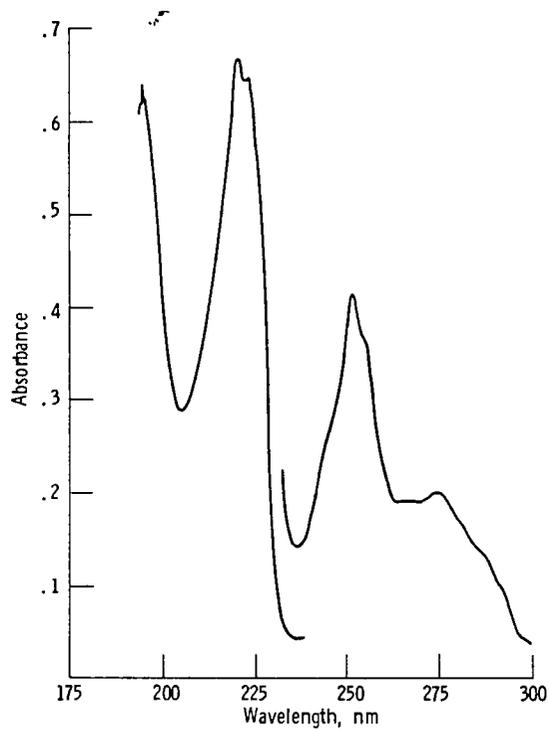


Figure 9. - Ultraviolet spectrum of simulated ERBS type fuel.

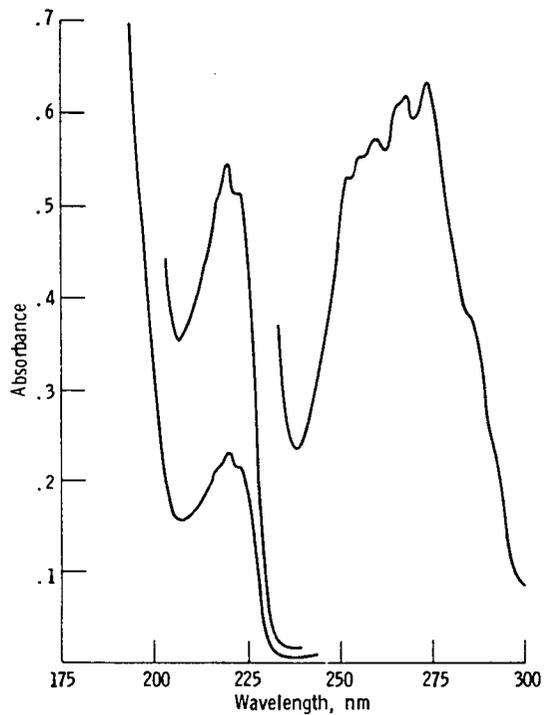


Figure 10. - Ultraviolet spectrum of simulated Jet A type fuel.

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16. Abstract <p>A rapid ultraviolet spectrophotometric method for the simultaneous determination of aromatics in mid-distillate fuels was developed and evaluated. In this method, alkylbenzenes, alkylnaphthalenes, alkylanthracenes/phenanthrenes and total aromatics were determined from ultraviolet spectra of the fuels. The accuracy and precision were determined using simulated standard fuels with known compositions. The total aromatics fraction accuracy was 5% for a Jet A type fuel and 0.6% for a broadened-properties jet turbine type fuel. Precision, expressed as relative standard deviations, ranged from 2.9% for the alkylanthracenes/phenanthrenes to 15.3% for the alkylbenzenes. The accuracy, however, was less for actual fuel samples when compared to the results obtained by a mass spectrometric method. In addition, the ASTM D-1840 method for naphthalenes by ultraviolet spectroscopy was evaluated.</p>			
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