Rapid identification of organic contaminants in pretreated waste water using AOTF near-IR spectrometry

Abstract:

A near-infrared analyzer utilizing state-of-the-art acousto-optic tunable filter (AOTF) spectrometry with digital wavelength control and a high D* extended-range InGaAs TE-cooled detector provides excellent wavelength repeatability (better than 0.02 nm) and very high signal-to-noise ratio. Because the AOTF dispersive element is completely solid-state (no-moving parts), as is the entire spectrometer, the instrument is small, rugged and very reliable. Using this spectrometer, methods employing chemometrics have been developed and applied to measure organic contaminants such as gasoline and a variety of jet fuels in water. Qualitative identification of contaminants was achieved with discriminant analysis software developed specifically for this task. Both the technique of grouping sample spectra into specific clusters based of Mahalanobis distances and that of matching each spectrum with the most representative member of the appropriate group of calibration spectra were used to identify contaminants. After initial classification, appropriate qualitative chemometric calibrations may be applied to more accurately assess the level of contamination. This instrument will be used to evaluate ground water supplies.

Keywords:

Introduction

Certain industrial or military installations may be susceptible to the unexpected or accidental introduction of organic contaminants in waste water streams. In some cases, these contaminants can be destructive to the water treatment facilities. At Edwards Air Force Base, dumping of fuel oils (diesel, jet fuel, etc.) has proven to be fatal to the biological organisms used in their waste water treatment system. However, chemically similar materials, such as vegetable oil, have no detrimental effects. A method for real-time analysis of waste water, ultimately capable of automatically diverting contaminated streams when appropriate, is desirable.

Near-IR spectroscopy offers an attractive solution for the rapid, routine detection and identification of organic substances in water at non-trace contaminant levels. Combinations and overtones of fundamental molecular vibrational modes are primarily responsible for the absorptions that occur in the near-IR. Because the absorptivities are substantially lower than those of the fundamental frequencies observed in the mid-IR region, the use of longer path lengths (1 to 10 mm) is possible. Near-IR spectroscopy can be successfully used for routine quantitative and qualitative analysis of bulk materials in numerous instances where conventional mid-IR spectroscopy fails due to practical sampling considerations.

The molecular absorptions observed in the near-IR spectrum involve strong bonds between relatively light atoms, as exist in water and are typical of organic materials. Relatively high absorptivities of water in selected regions of the near-IR spectrum, crude assessment of overall water purity can be achieved by simply measuring the magnitude of absorption bands in the vicinity of 1450 and 1940 nm. Organic substances (hydrocarbons, solvents, etc.) can easily be detected using near-IR spectroscopy. Detection is based upon the characteristic absorptions of these materials occurring at specific wavelengths throughout the near-IR spectrum. Computerized discriminant analysis algorithms can be employed for identification of the particular

contaminant or contaminants involved. It may also be possible to determine the contaminant concentration levels for contaminants that are miscible in water.

Experimental

Mixtures of water, hydrocarbons and organic solvents were spectroscopically analyzed to establish the feasibility of contaminant level detection and contaminant identification. Spectra were collected with the Brimrose Luminar 2000 near-IR spectrometer. This spectrometer provides excellent wavelength repeatability and very high signal-to-noise ratio. Utilizing state-of-the-art acousto-optic tunable filter (AOTF) spectrometry with digital wavelength control and a high D* extended-range InGaAs TE-cooled detectors. The AOTF dispersive element is completely solid-state (no-moving-parts), as is the entire spectrometer. Therefore, the instrument is small, rugged and very reliable. Spectra were collected over a 1200-2200 nm wavelength range at 2 nm resolution. 100 scans were averaged at a rate of approximately 10 scans per second for each sample spectrum. Sampling was performed by immersing the reflectance probe with its transreflectance attachment (effective path length of 3 mm) directly into the liquid. Spectra of pure jet fuel, contaminated jet fuel, water, and various other organic materials were collected in order to identify characteristic spectral features. A series of water and JP8 jet fuel mixtures were sampled over a wide concentration level range, as were various mixtures of water and methanol in acetone and ethanol.

Figure 1 shows the NIR absorbance spectrum of pure jet fuel that was obtained. The large absorption peak occurring between 1600 and 1800 is very useful for spectroscopic identification and quantitation. Less prominent spectral features in the 1200 and 1400 nm wavelength regions might also be useful for longer path lengths. Figure 2 shows the absorbance spectra of several different concentrations of jet fuel and water. The concentrations of jet fuel in the water are relatively high. Water absorption peaks in the vicinity of 1450 and 1940 nm are clearly visible. Absorptions corresponding to the jet fuel between these peaks can be easily seen. This region provides a useful window that can be utilized for the identification and quantitative determination of jet fuel in water. Figure 3 shows spectra of water with small amounts (one or more drops) of jet fuel added. The spectral features of water predominate, although slight differences can still be readily observed. The high signal-to-noise that can be achieved enables extraction of analytically useful information from subtle spectral differences. This information can be extracted via computer upon applying appropriate statistical algorithms.

The utility of the spectrometer for performing rapid qualitative material identification was demonstrated. Figure 4 shows superimposed spectra obtained for several different liquids using the spectrometer with reflectance probe and transflectance attachment (overall path length approximately 2 mm). The water and ethanol spectra, although substantially different, both exhibit significant O-H absorptions in the 1400-1500 nm and 1850-2000 nm regions. Chemical similarities of jet fuel and vegetable oil (both hydrocarbons) are reflected in certain similar spectral features, although significant spectral differences are also readily apparent. The region between 1650 and 1800 nm yields useful chemical information about the C-H bonding for a particular substance. Organic materials and solvents (ethanol, acetone, fuel oils, etc.) can be easily distinguished from inorganic materials such as water. Figure 5 shows the large differences in the near-IR spectrum of water in comparison to hydrocarbons such as gasoline and jet fuel. Figures 6 and 7 show that, although the spectra of different hydrocarbons are somewhat similar, definite spectral differences exist enabling discrimination. These spectral differences are most apparent in the 2050-2200 nm (Figure 6), 1600-1850 nm (Figure 6), and 1350- 1450 nm (Figure 7) spectral regions. The entire near-IR spectrum can be effectively used for qualitative identification of a wide array of materials.

An automated system was required for analysis of the near-IR spectral information and identification of unknown substances although spectroscopic differences were apparent . An identification software package was tested for this purpose. This software package is capable of

utilizing spectral information to discriminate between sample types and spectrally match materials within a group. The software is Microsoft™ Windows™ based, providing high computer platform compatibility and user friendly operation. Spectra were assembled into calibration, or training sets by logically grouping them into distinct categories based on known chemical differences between corresponding samples. This information was used to train the software.

The identification software enables characterization of unknown materials on various levels. Most fundamentally, the software allows for discrimination between different groups, or types of materials. The software may be trained to distinguish between water and different alcohols, hydrocarbons (jet fuel, vegetable oil, etc.), organic solvents, or other organic materials based upon their respective spectral features, for example. This is accomplished by first performing a calibration, whereby spectra from numerous samplings of these materials are first collected. These spectra are used to train the system by creating multiple group files, each of which specify the spectra that will define the spectral characteristics for a certain substance. Once created, various parameters associated with these group files can be viewed and/or edited. Descriptions of the specific spectra that comprise a group can be viewed and individual group members may be selectively deleted. Once a system of substance groups is developed, the spectral similarities within a particular group and the spectral differences between groups are utilized for future prediction of unknown samples. Addition of new material types or deletion of irrelevant material is easily performed by the addition or deletion of group files. Discrimination between groups is achieved by measuring distances between a particular "unknown" sample spectrum and the defined groups consisting of spectra collected from "known" materials as measured in multidimensional space in Mahalanobis distance units. If the spectrum of a spectroscopically analyzed material is found to be sufficiently far away from any of the defined groups, the material is classified as a truly unknown material, the identity of which requires some other manner of determination.

The identification software is capable of operating in a real-time sample I.D. monitoring mode in conjunction with the spectrometer. Identification analyses are performed at a user-defined sampling rate, averaging a user-specified number of scans per sample spectrum to make the analysis, with other scan parameters set to conform with the calibration data. Real time sample identification using this program was demonstrated upon training the identification software to distinguish between different materials, including water, fuel oils, vegetable oil, and organic solvents (as plotted in Figure 4). Utilizing the spectrometer with a reflectance probe and transflectance attachment (total path length approximately 2 mm), the system was found to be capable of reporting material identity in real time at a sampling rate of only 2 seconds. Various liquids, including jet fuel and water in a "layered" mixture, could be reliably distinguished at this sampling rate. Calibration robustness has been positively established by dismantling/reconfiguring the system and operating the system at different sites and on different days.

Furthermore, the software is capable of identification of a specific material according to the members that comprise a particular group. For example, a group may be defined for fuel oils, comprised of spectra of diesel, jet fuel, kerosene, etc. In this manner, the software can, on a primary level, identify an unknown material as belonging to the fuel oil group. On a secondary level, by matching of the unknown material spectrum with members of the fuel oil group calibration set, the particular type of fuel oil that the unknown sample represents can also be determined. This capability may be used as a semi- quantitative tool. Different concentrations of a particular component may make up the group for a certain material type. The material identification performed for spectra within that group could determine which component concentration level is most representative of a particular "unknown" sample.

Conclusions

The technique of grouping sample spectra into specific clusters based on Mahalanobis distances and that of matching each spectrum with the most representative member of the appropriate

group of calibration spectra were used to identify contaminants. Overall, the approach was found to work well for both identification of potential contaminants as well as subcharacterization within a particular substance category. Additionally, coupling of the qualitative material identification capability of the spectrometer and identification software with the excellent quantitative performance of the spectrometer should enable spectral data for a previously unknown sample to be first used for sample identification and subsequently applied to analytical calibrations appropriate for the specific material type in order to determine relevant component concentrations. It is anticipated that this instrument will be used to evaluate waste water streams in and around Edwards Air Force Base.

Acknowledgments
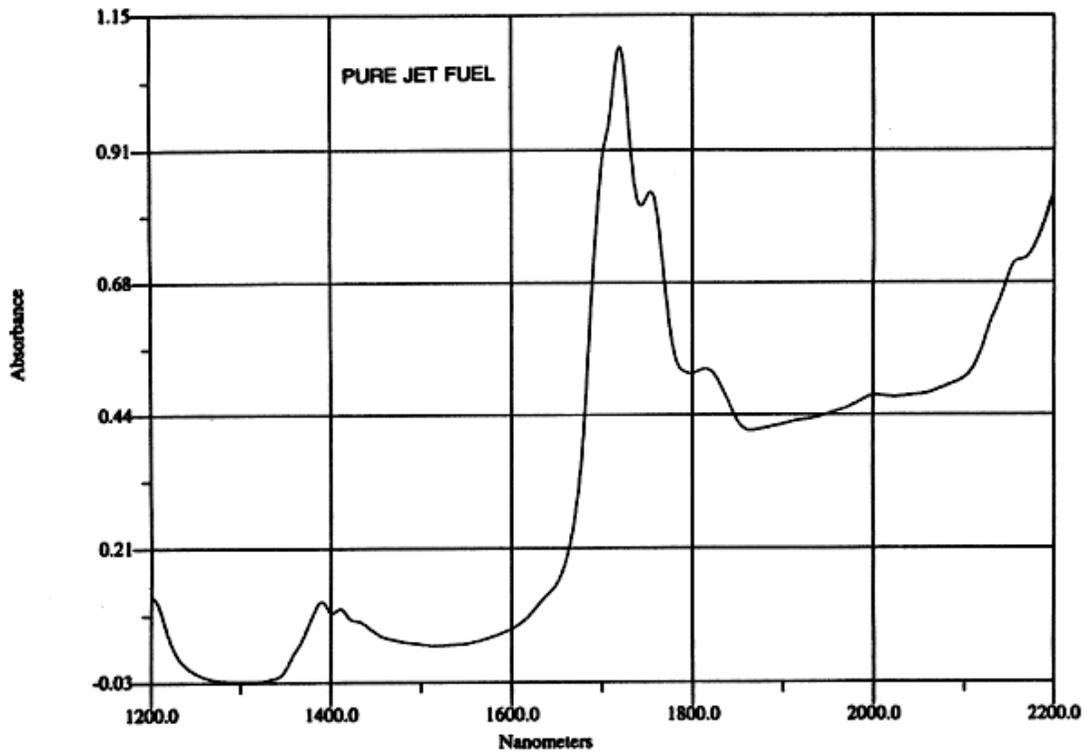
Figures

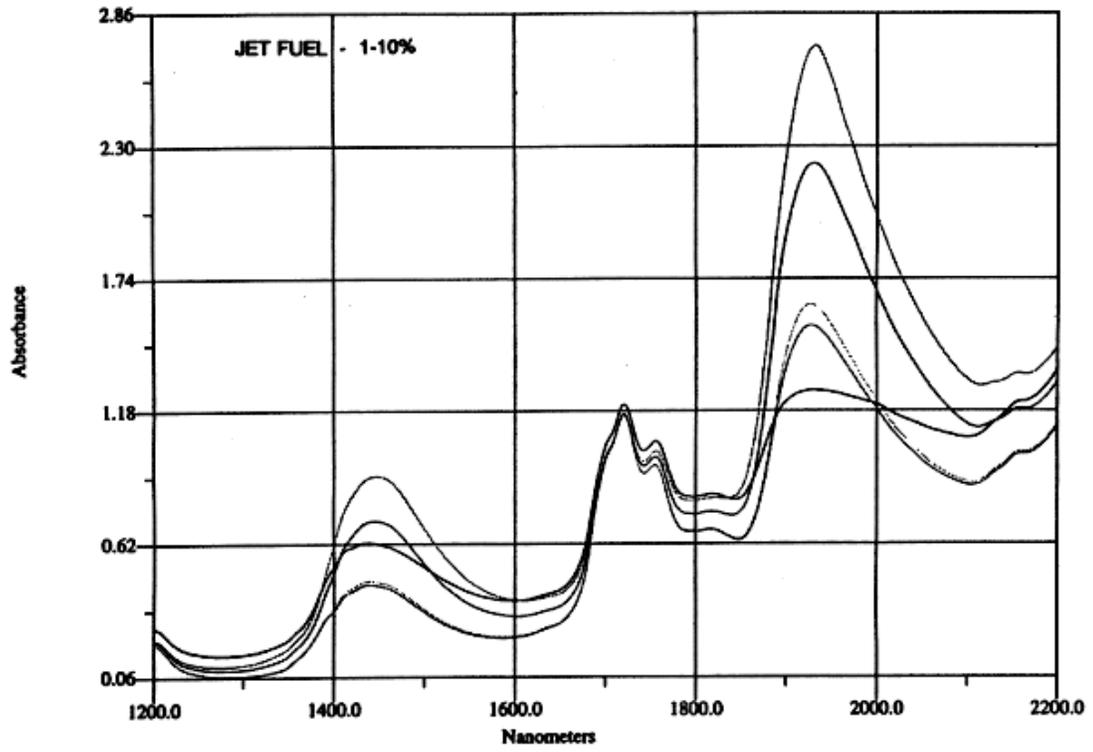
Figure 1. *Spectrum of JP8 jet fuel*

Figure 2. Jet fuel containing various amounts of water
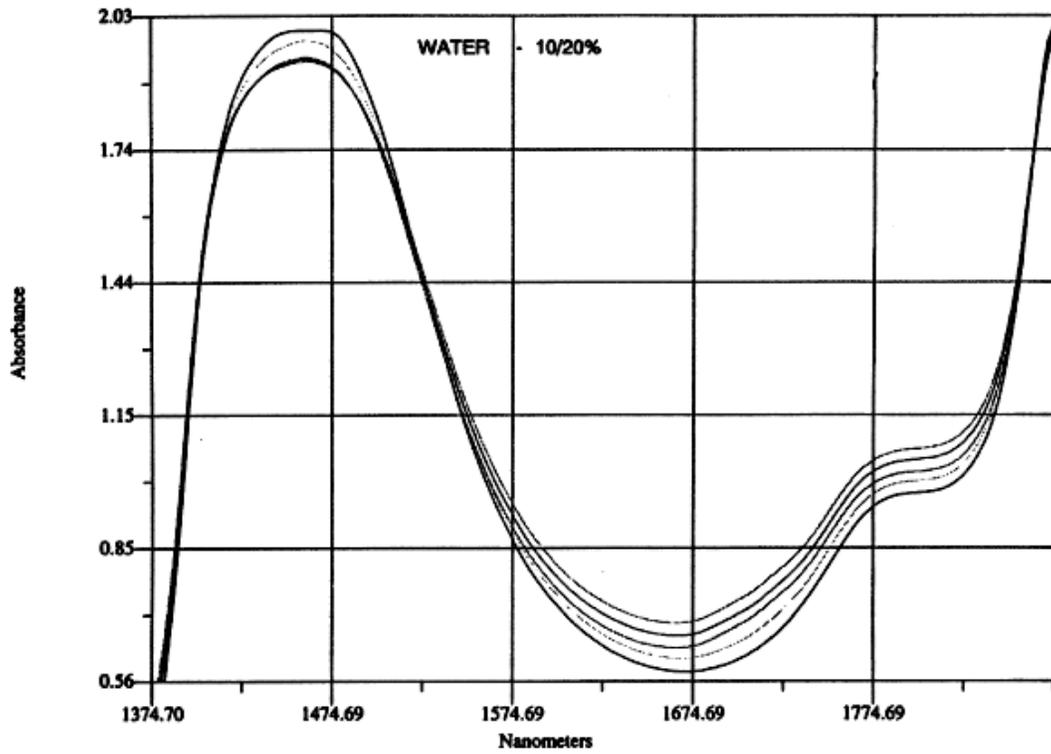
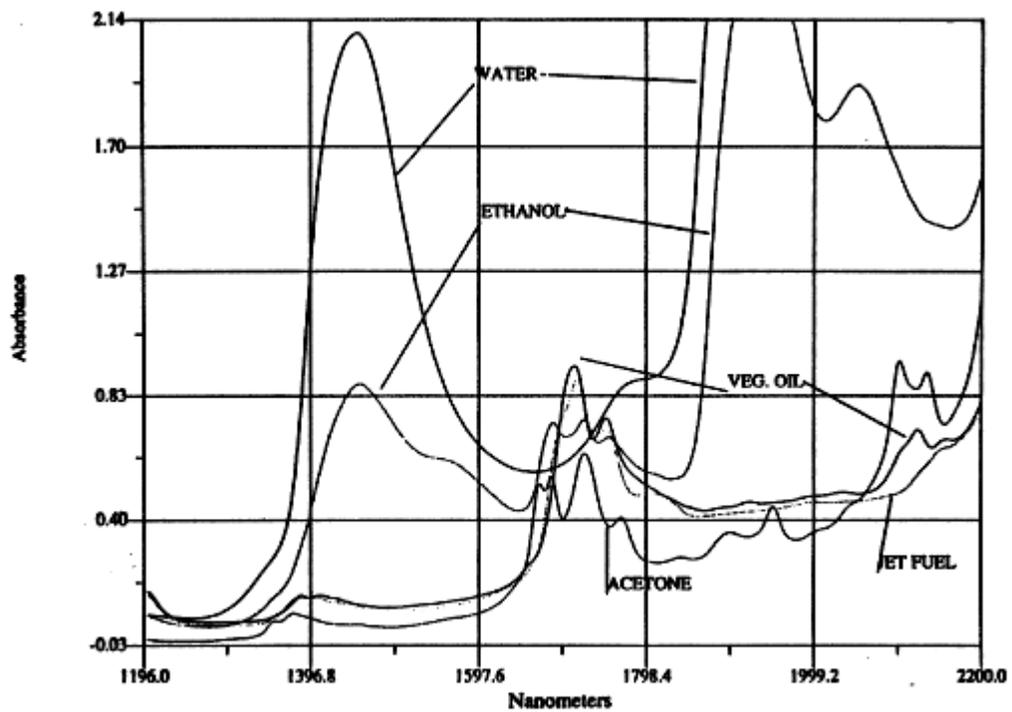***Figure 3***. *Water containing various amounts of jet fuel*

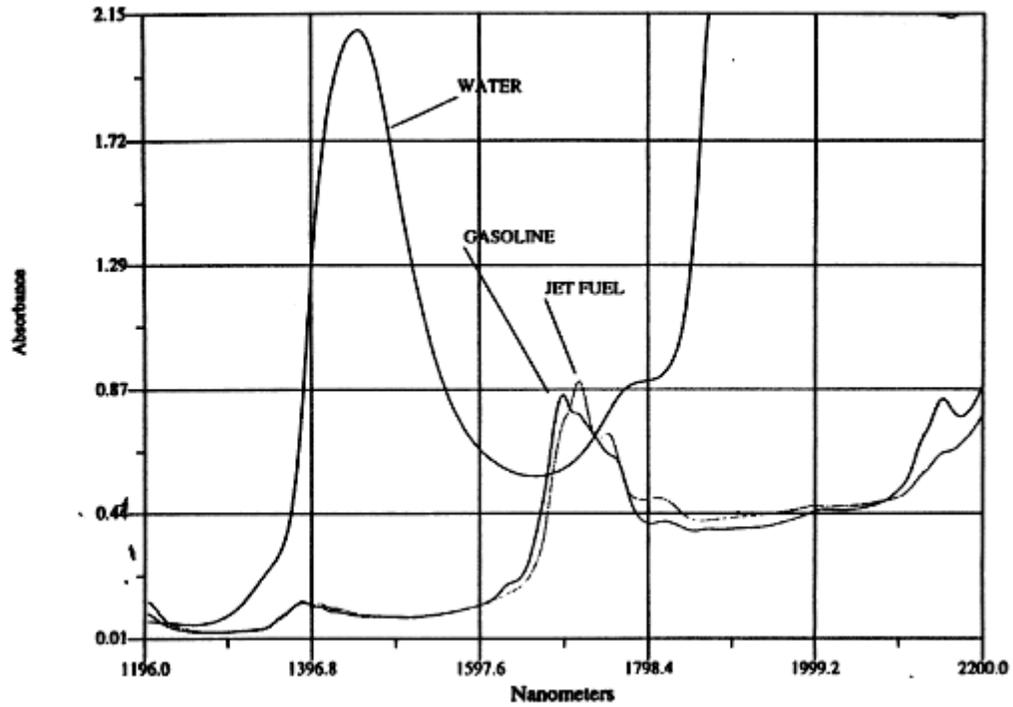***Figure 4***. *Water spectrum displayed with various organics*

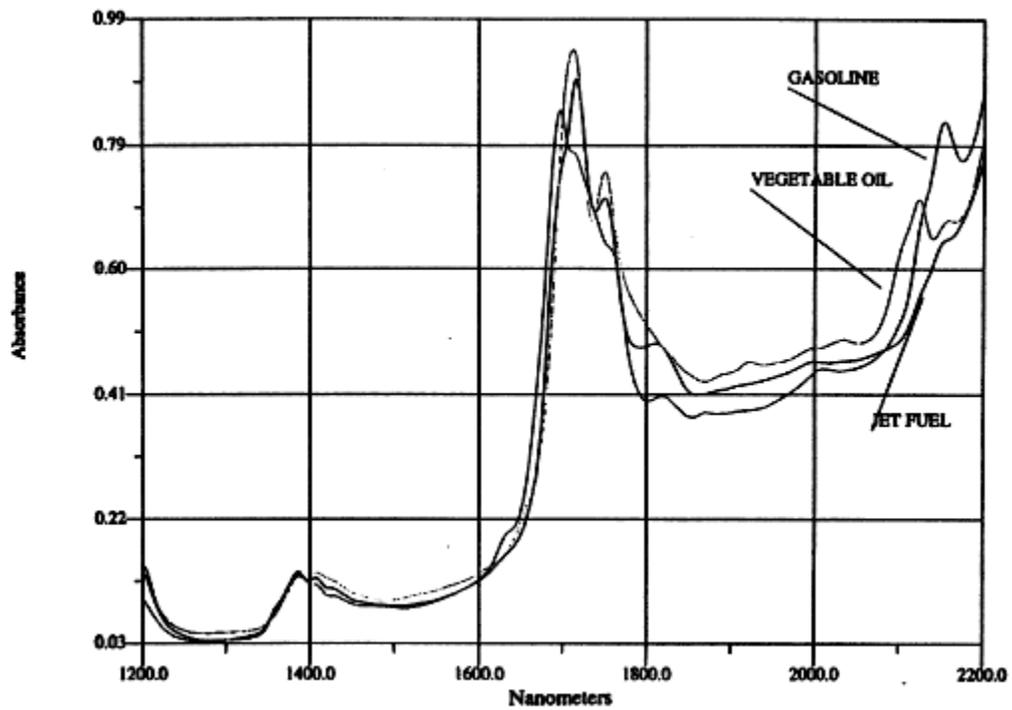*Figure 5*. Water spectrum displayed with hydrocarbons of interest

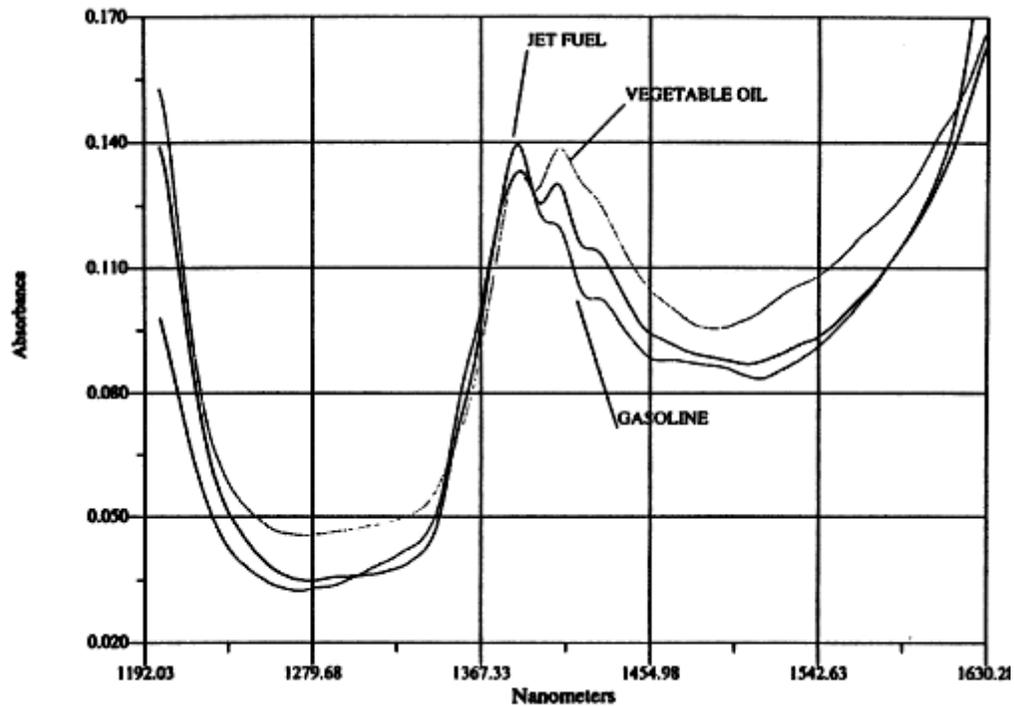*Figure 6*. Full spectral range display of hydrocarbons of interest

Figure 7. *1200-1600 nm region of hydrocarbon spectra displayed in Figure 6*

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