Detection and Measurement of Middle Distillate Fuel Vapors Using Tunable Diode Lasers

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Abstract

A sensor for rapid (10 msec response time) measurement of vapors from the

hydrocarbon-based fuels JP-8, DF-2, and gasoline is described. The sensor is

based upon a previously reported laser mixing technique that uses two tunable

diode lasers emitting in the near-infrared spectral region [1] to measure

concentrations of gases having unstructured absorption spectra. The fiber-mixed

laser beam consists of two wavelengths, one of which is absorbed by the fuel vapor, and one of which is not absorbed. By sinusoidally modulating the power of the two lasers at the same frequency but 180 degrees out of phase, a sinusoidal signal is generated at the detector (when the target gas is present in the line of sight). The signal amplitude, measured using standard phase sensitive detection techniques, is proportional to fuel vapor concentration. Limits of detection, at room temperature, are reported for vapors of the three fuels studied. Improvements to be incorporated in the next generation of the sensor are discussed.

Introduction

This paper describes initial results of quantitative measurements of room temperature vapor from the hydrocarbon-based fuels JP-8, DF-2, and gasoline using a sensor based upon near-infrared tunable diode laser absorption spectroscopy. These fuels typically are mixtures of several hundred hydrocarbons, with an average molecular weight near 110 grams/mole (vapor), 150 grams/mole (liquid), and boiling points near 440K [2]. The fuels are liquids near room temperature and have flash points (often depending on age, storage conditions, etc.) in the vicinity of 315K. Recent work [2] on JP-8 found that no single component was present in amounts greater than 1% by volume. This same study identified the most prevalent hydrocarbon in JP-8 as methylcyclohexane. Because these fuels change composition with age,

formulation location, and formulation time, the physical constants above should be used only as estimates.

The development of the sensor described here was driven by the U.S. Army need for rapid, in-situ, quantitative measurements of JP-8 fuel vapors for detection of fire hazards in crew compartments on board military vehicles. When it was found that DF-2 (also called diesel fuel #2) and gasoline vapors could be measured with no modification to the sensor, these fuels were included in this preliminary study. When a fire occurs on board a military vehicle (in worst case scenario a ballistically initiated fuel/air "mist-fireball explosion"), sensors detect and extinguish the fire (often using halocarbons) in as little as 250 ms [3]. In order to properly evaluate fire suppression equipment, it is necessary to make several fuel vapor concentration measurements during the suppression event. A constraint on the sensing device is that it must ultimately be disposable, since in-situ measurements of fuel/air explosions may destroy/damage the test equipment. Hence the need for a sensor capable of making rapid, in-situ fuel vapor measurements, while keeping (expensive) electronics and optics at remote locations.

The method of detection and sensor type used here has been previously reported by us for detection of vapor from pyridine [1], but is readily applicable to any gas or vapor that has unstructured absorption spectra. Briefly, we employ a two laser mixing technique that relies upon absorption of radiation of one of the

lasers by the first overtone of the C-H stretching vibration of hydrocarbon vapor (near a wavelength of 1.71 μmeters). The near-infrared spectral region is used because of the commercial availability of room temperature lasers and detectors and because laser radiation in this spectral region may be transported at low loss using inexpensive optical fibers.

Background

Fieldable detectors for hydrocarbon vapor measurements typically rely upon infrared absorption (DOAS (differential optical absorption spectrometry), FT-IR (Fourier transform infrared) emission/absorption) [4,5] or electrochemical / electrothermal techniques [6]. These methods give good results, but have found limited use for measurements of fire scenarios just described. FT-IR and DOAS spectrometers are usually bulky, expensive, measurements require placement/alignment of interferometer/source optics and detector or retro-reflector, and are generally limited to a single line of sight. Placement of the instrument within the test environment (crew compartment) is not feasible (potential damage), looking across the entire measurement space does not isolate the region of interest, and although extractive sampling has been shown to be useful [3], it does not provide necessary temporal information. Additionally, the interferometer temporal resolution is limited by the mirror scan speed (although some new designs are approaching scan rates near 1 KHz) [7]. Nevertheless, use of FTIR and DOAS for measurement of the fundamental C-H stretch in hydrocarbon fuels near 3.4 um can yield sensitivities in the ppb range,

and because the full spectrum may be measured (when using FT-IR), it is often possible to determine species of hydrocarbons present in a simple mixture. For stable, relatively safe sampling sites with an accessible line of sight, incoherent infrared absorption techniques (FT-IR, DOAS) are often the techniques of choice. Electrothermal/electrochemical detectors are generally inexpensive (2-5 K$), are often one-man portable, and have sensitivities (~100's of ppm) well below lower explosion limits for most hydrocarbon vapors [2]. Time sensitivity is typically from 1 to 15 seconds. Some units may have accuracy problems when used in the presence of methane gas, and may be less sensitive to heavier hydrocarbon vapors [6]. For measurement sites requiring full portable instrumentation with time resolution from one to tens of seconds, these instruments can also provide excellent results.

Gas detection methods using near-infrared tunable diode lasers can use optical fibers and relatively inexpensive (room temperature operation) semiconductor detectors to separate electronics and laser sources from hazardous testing locations. Using modulation techniques and phase sensitive detection methods, temporal resolution routinely exceeds 1 ms per measurement. Detection methods employed (typically wavelength modulation spectroscopy (WMS) and balanced ratiometric detection (BRD) techniques) [8,9] give good results for gas phase concentration measurements of small molecules with well resolved ro-vibrational absorption lines, such as hydrogen fluoride, methane, carbon monoxide, water, etc [10]. However, large and/or heavy molecules may not

posses well resolved ro-vibrational absorption bands because of overlap between fundamental, combination, and/or overtone vibrations, and because of rotational constants which may be less than typical gas phase linewidths [11]. For mixtures of heavy molecules, e.g., the middle distillate fuels, the spectra may be even less structured. Figure 1 shows the near-infrared gas phase absorption spectrum of dry air saturated at 294K by the hydrocarbon fuels JP-8, DF-2, and gasoline (0.75 meter optical path), measured using a Fourier transform spectrometer. As suggested by the spectra shown in Figure 1, and by separate measurement in our laboratory, the vapors from each fuel fit criteria [1] to be classified as a gas having unstructured absorption spectra (often called a "broad band absorber") near the 1.71 μmeter wavelength spectral region. Both WMS and BRD, as usually employed, are not suitable for gases that have broad, unstructured absorption spectra [8,9,10]. For both techniques, the main limitation for fuel sensing is the narrow tuning range of the diode laser. Because the tuning range is usually several orders of magnitude smaller than the width of the spectral feature in broad band absorbers (0.4 cm^{-1} vs. >100 cm^{-1}), it is not possible to tune from the region of maximum absorption to a region of zero absorption. The purpose of this work is to overcome this limitation for measurement of such molecules, while approaching the sensitivity and time response of WMS and BRD methods.

Measuring Broad Band Absorbers with Narrow Band Lasers

The method used here takes advantage of the residual amplitude modulation (RAM) which occurs when a DFB diode laser is driven by a time varying injection current. This RAM occurs when the wavelength of a semiconductor tunable diode laser is varied by modulating the laser injection current. Typically (for WMS and BRD), RAM is a nuisance, and what is important is the wavelength modulation. For the experiments described here, the RAM is what enables the technique to work, and the (relatively) small variation of wavelength during the modulation is largely ignored (but will be commented upon later). For the experiments described here, two different DFB lasers are driven using a sinusoidally varying injection current. Each laser injection current is modulated at the same frequency but out of phase by 180 degrees [12]. These two lasers are combined to produce the probe beam used for the line-of-sight measurement. When the power output amplitudes of each sinusoidally modulated laser are the same, the combined output of the two lasers will have an amplitude that is (ideally) invariant with time. The key to the method is selection of one laser wavelength coincident with a wavelength absorbed by the gas of interest, and selection of the second laser wavelength in a region where no absorption is anticipated. When the mixed, modulated probe beam is passed through a gas which preferentially absorbs the laser radiation from only one of the lasers, the signal at the detector is modulated at the injection current modulation frequency and, for small absorptions, has an amplitude whose magnitude is proportional to the concentration of absorbing gas.

The simple mathematical description begins by considering Beer's law [13] for narrow band laser radiation exiting an absorbing sample gas of concentration c molecules per cm^3, for a path length of l cm. The absorption coefficient (cm^2/molecule) at the most intense region of absorption (the resonant wavelength, λ_R) , is $\alpha(\lambda_R)$. $I_0(\lambda_R)$ is the intensity of the incident radiation at the resonant wavelength. $I(\lambda_R)$ is the intensity of radiation at the resonant wavelength after exiting the sample gas:

$$I(\lambda_R)=I_0(\lambda_R) \exp(-\alpha(\lambda_R)cl) \qquad (1)$$

If the incident radiation at the resonant wavelength is now power modulated sinusoidally at frequency a, and time t, with depth of modulation D_R , the intensity of the radiation at the resonant wavelength after exiting the gas becomes:

$$I(\lambda_R)=I_0(\lambda_R)(1+D_R \sin(at)) \exp(-\alpha(\lambda_R)cl) \qquad (2)$$

To get a measurement of transmission off resonance (important to generate a differential signal and to discriminate against scattering by particles such as smoke), we add a second laser source at a wavelength not absorbed by the gas, λ_{NR} . This non-resonant wavelength is mixed with the resonant wavelength, power modulated at the same frequency but 180 degrees out of phase with the resonant wavelength modulation, and has a depth of modulation D_{NR} . If the radiation exiting the gas is now focussed on an (ideally) wavelength-insensitive

detector (see Discussion), the power at this detector, $I(\lambda_R + \lambda_{NR})$, may be given by:

$$I(\lambda_R + \lambda_{NR}) = [I_0(\lambda_R)(1+D_R \sin(at)) \exp(-\alpha(\lambda_R)cl) + I_0(\lambda_{NR})(1+D_{NR}) \sin(at+\pi)] \qquad (3)$$

To process this signal, we multiply by a reference sine wave of amplitude p in phase with and at the same frequency, a, as the power modulation of the two lasers. We then integrate over C periods of power modulation:

$$C \int_0^\pi \{[I_0(\lambda_R) (1+D_R) \exp(-\alpha(\lambda_R)cl) - I_0(\lambda_{NR}) (1+D_{NR})] \sin(at) \, p\sin(at)\}dt$$

$$= (C/2)p\pi [I_0(\lambda_R) (1+D_R) \exp(-\alpha(\lambda_R)cl) - I_0(\lambda_{NR}) (1+D_{NR})] \qquad (4)$$

Rearranging, assuming $\exp(-\alpha(\lambda_R)cl) \ll 1$ and using A (Absorbance) is equal to $\alpha(\lambda_R)cl$:

$$2C \int_0^\pi \{[I_0(\lambda_R) (1+D_R) \exp(-\alpha(\lambda_R)cl) - I_0(\lambda_{NR}) (1+D_{NR})] \sin(at) \, p\sin(at)\}dt$$

$$= Cp\pi [I_0(\lambda_R) (1+D_R) - I_0(\lambda_{NR}) (1+D_{NR}) - I_0(\lambda_R) (1+D_R)A] \qquad (5)$$

For the special case where the power and depth of modulation of the two lasers are equal, Equation 5 becomes:

$$2C \int_0^\pi \{[I_0(\lambda_R) (1+D_R) \exp(-\alpha(\lambda_R)cl) - I_0(\lambda_{NR}) (1+D_{NR})] \sin(at) \, p\sin(at)\}dt$$

$$= -Cp\pi [I_0(\lambda_R) (1+D_R)A] \qquad (6)$$

Equation 6 is just the output of a lock-in amplifier operating on the first harmonic for measurement of the amplitude of the sine wave created by the differential absorption (for small absorptions) of the mixed laser beam by the gas at concentration c and path length l. This output is proportional to the number of periods, C, over which the integration is carried, the amplitude, p, of the reference sine wave, the incident power, $I_0(\lambda_R)$, of the laser at the resonant wavelength, and the Absorbance, A (and hence gas concentration when pressure broadening of the spectral feature is not important). It is worth noting that Equation 6 also indicates that lock-in output is increased by increasing depth of modulation (D_R). As will also be discussed later, Equation 5 shows that it is important that the two laser power amplitudes and depths of modulation are as equal as possible, especially for small values of Absorbance.

Experimental Apparatus

A diagram of the experimental apparatus is shown in Figure 2. The two DFB laser diodes (Sensors Unlimited) used to produce the mixed wavelength probe beam have nominal wavelengths of 1.307 μmeters and 1.71 μmeters. The laser diodes are driven using an ILX LDC-3900 modular laser diode controller. The variable phase sinusoidal injection currents are supplied by two SRS Model DS345 function generators operating on a common timebase, Sinusoidally modulated (100 KHz, modulation depth adjusted to near 100%) laser diode radiation from each diode laser is mixed onto a common fiber using a fiber optic coupler (Gould Fiberoptics) and launched into free space using a GRIN-lens

tipped single mode fiber (Sentech Corp.). The output beam is directed into a

variable pathlength gas cell (Laser Photonics L5210) set at the minimum setting

of 4 meters. Radiation exiting the 4 meter path length cell is detected using a

New Focus Model 2034 InGaAs large element photodetector (maximum

responsivity near 1600 nm). The detector signal is demodulated at the laser

injection current modulation frequency using a lock-in amplifier (SRS 830),

displayed on an oscilloscope (LeCroy 7200), and recorded on a laptop computer

(Dell Latitude) running LabView software (National Instruments). JP-8 and DF-2

were milspec grade and obtained from the fuel depot at the Aberdeen Proving

Ground. The gasoline was regular grade obtained during the summer months at

a commercial vendor in Aberdeen, MD. All were used as supplied. Air was

saturated with fuel vapor using a bubbler apparatus based upon a nitrogen

sparger. Air flow through the stainless steel frit immersed in the fuel was typically

100-250 cm^3/minute. Near infrared spectra shown in Figures 1 and 3 were

recorded using a Bomem DA-8 (using a liquid nitrogen-cooled InSb detector)

interfaced to a Wilks 0.75 meter path length cell.

Results

Figure 3 shows the vapor phase absorption spectrum of air saturated by vapor at

294K from JP-8, DF-2, and gasoline between wavelengths of 1.3 and 1.75

micrometers superimposed upon the emission from the optical fiber carrying the

mixed wavelength laser beam. Both sets of spectra were measured using a FT-

IR spectrometer (Bomem DA-8). The near infrared tunable diode laser radiation

was transported using optical fibers to the external source port on the FT-IR

spectrometer. This figure shows that the emission of the laser at 1.71 um falls

near the most intense region of the C-H stretch (first overtone) absorption for the

three fuels studied, and that the 1.3 um laser falls in a region where there is no

measurable absorption of the laser radiation by the fuels studied. Because of the

narrow emission linewidth of the lasers, the reported lineshape in this figure is

just the instrument lineshape (in this case, sinc) of the FT-IR spectrometer [14].

Figure 4 shows the gasoline vapor concentration (measured using the mixed

laser sensor) as dry air saturated by gasoline vapor slowly displaces (several

hundred cm^3/minute) the dry air in a 13.7 liter volume optical cell (4 meter path

length). Also shown in this figure is the change in oxygen concentration that

occurs during the displacement (oxygen sensor courtesy of Oxigraf, Inc.,

Mountain View, CA). This figure shows the sensor response as the vapor

concentration approaches and exceeds the lower explosive limit (LEL) for most

hydrocarbon vapors (e.g., for JP-8 the LEL is approximately 9500 ppm [2]). Each

data point is the average of the lock-in amplifier output measured over 10

milliseconds. All measurements were made at atmospheric pressure.

 Figure 5 shows the measured fuel vapor concentration as the dry air in the13.7

liter volume optical cell is displaced by air saturated (at 294K) by JP-8 vapor.

Run 1 is for air saturated by vapor using a fresh fuel sample in the bubbler. Run

5 is the fifth re-run of the test without changing the fuel sample in the bubbler.

The difference in peak hydrocarbon levels between runs shown in Figure 5 is caused by the gradual removal of lighter hydrocarbons from the JP-8. For brevity, results on DF2 are not presented, since the results for DF-2 were similar to those for JP-8. The partial pressures at atmospheric pressure (measured using a capacitance manometer) for gasoline, JP-8, and DF-2 fuels were found to be approximately 13, 3.5, and 1.75 torr ($\pm$20%), respectively. We measured the C-H stretch first overtone absorption coefficient for the fuel vapors to be approximately 2.7 ($\pm$.4) X 10 $^{-21}$ cm^2/molecule, which is in reasonable agreement to that for the first overtone of the C-H stretch for methane (8.7 X 10^{-22} cm^2/molecule) [15]. We estimate the current limit of detection for each of these fuel vapors to be approximately 100 ppm-meter.

Discussion

An implication of the results presented here is that the device may be used to measure hydrocarbon vapor concentration for any middle distillate fuel. However, careful examination of the C-H overtone bands for each of the fuels shows that the contours of the absorption features, when normalised to each other, are not truly superimposable. So, for best accuracy the sensor should be calibrated for each fuel vapor to be measured.

 The main purpose of these experiments was to demonstrate the feasibility of the mixed laser technique for concentration measurements of vapors from the middle

distillate fuels. However, the technique is applicable to measurement of any

vapor that exhibits unstructured absorption spectra. All that is required is

knowledge of the absorption spectrum of the target gas and proper selection of

on and off resonance lasers. It should be mentioned that we have made no

attempt to characterize the sensor for vapors at different temperatures. This is

important since the shape of the C-H overtone absorption band may vary with

temperature. Additionally, we have made no attempt to account for absorption

by finely dispersed fuel droplets. We are currently setting up the experimental

apparatus to address these shortcomings.

As mentioned previously, predicted by Equation 5, and verified experimentally,

the most important element for maximizing sensitivity is the matching of the

modulation amplitudes of the two lasers. The sensitivity reported by us for

hydrocarbon vapor (100 ppm) in the near IR is similar to that achievable with FT

spectrometers but approximately two orders of magnitude worse than that for

methane vapor measured using WMS or BRD (approx. 1 ppm for field

measurements). Differences in detector response at different wavelengths may

be compensated for by changing the power of each laser, and is not an important

factor affecting sensitivity. The underlying cause of our poor sensitivity (relative

to methane detection using WMS or BRD) is the mismatch in light - injection

current (L-I) curves for the two lasers, and that the L-I curve (as implied by the

use of *curve*) for each laser is not linear. A Fourier transform of the power output

of each laser, when driven by the sinusoidal injection current, showed significant

contributions to the RAM at frequencies other than those used for the laser modulation (typically 100 KHz, depth of modulation close to 100%). So, when the two laser outputs were mixed onto a common fiber, the measured output of the mixed laser beam, in the absence of any absorbing gas, always showed an AC component. This AC component shows up in the demodulated signal. We are currently investigating the use of dynamic modulation control, which will custom tailor one of the injection current drive waveforms, to actively null the raw signal every few milliseconds. An alternative approach, also being investigated, is to switch to square wave modulation and to sample discretely twice during each modulation period. Finally, perhaps the best choice (our original choice, but precluded by cost considerations) to minimize unwanted AC components in the mixed signal is to use downstream electro-optic modulation, eliminating the effect of non-linearity in the laser L-I characteristic. Rapid changes in technology for the telecommunications industry have made this approach near cost-effective.

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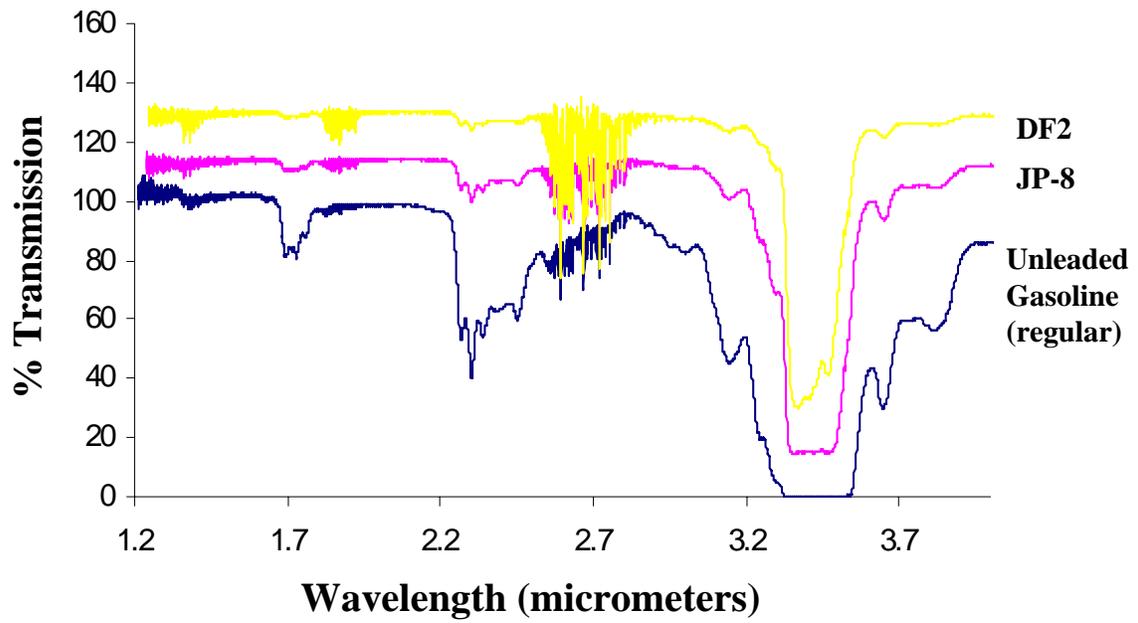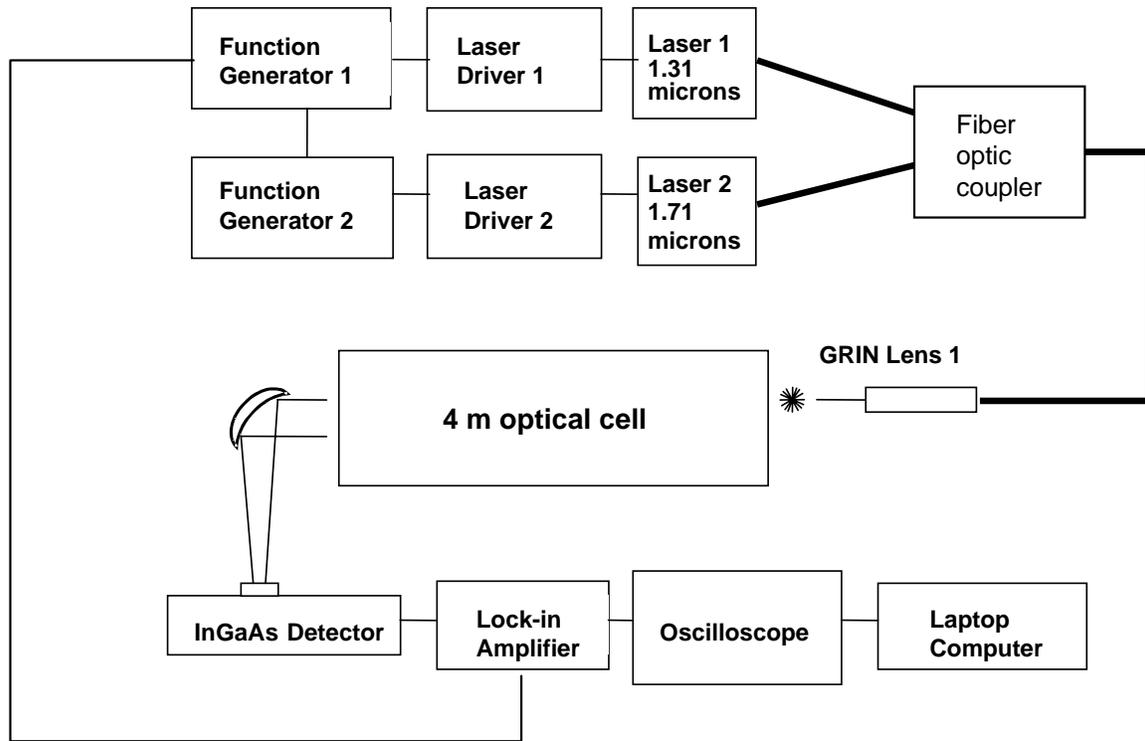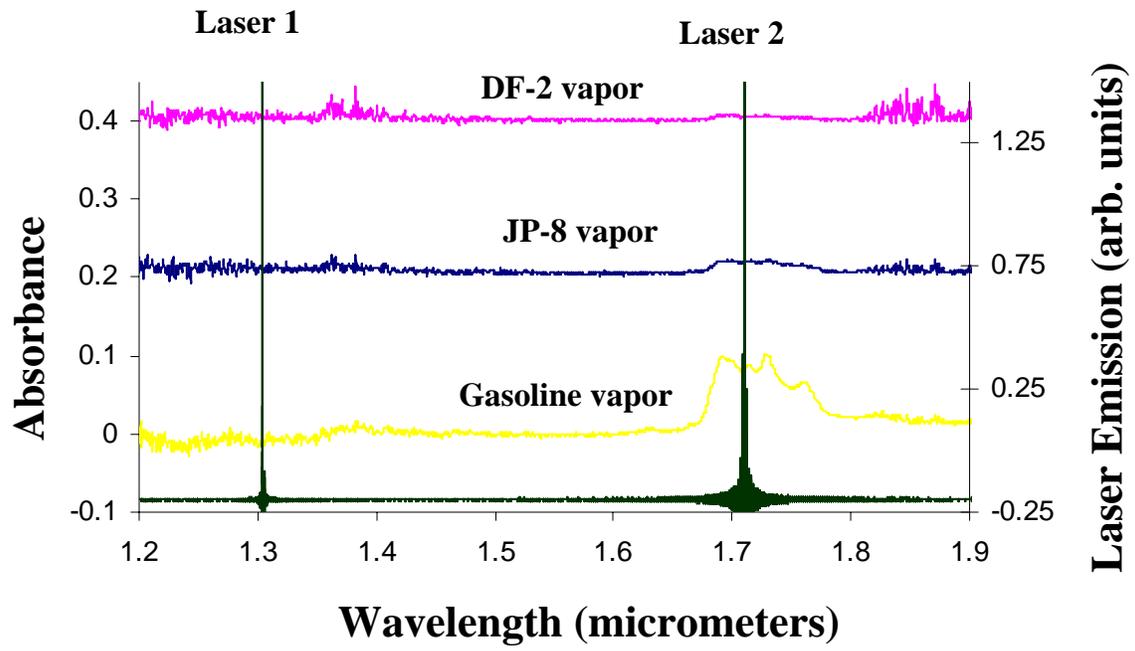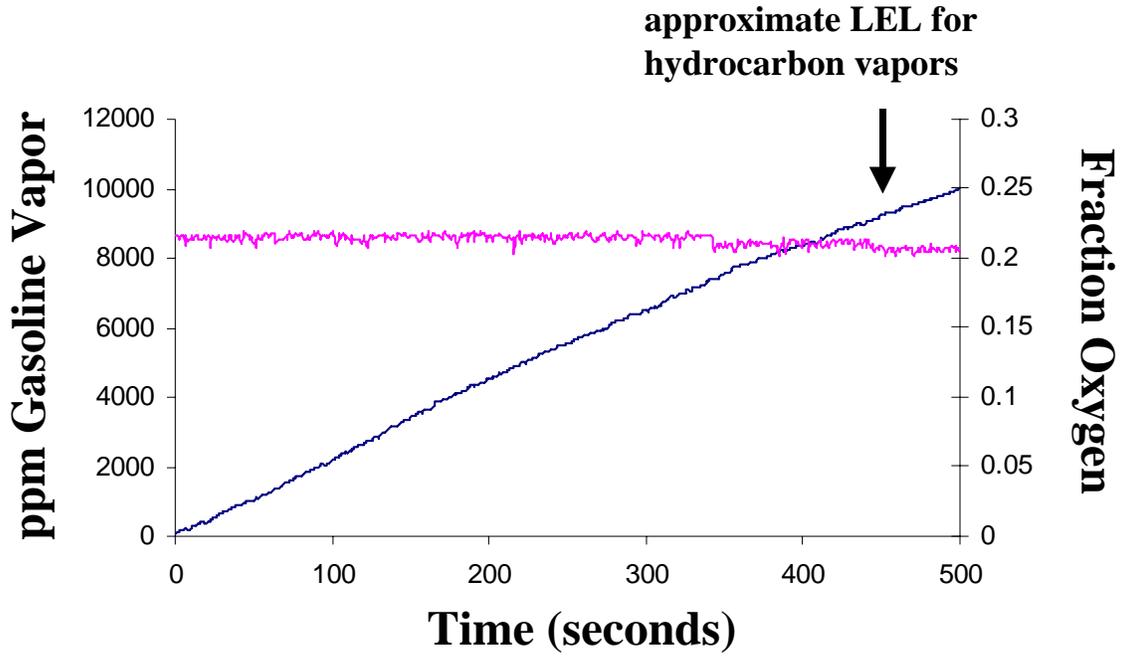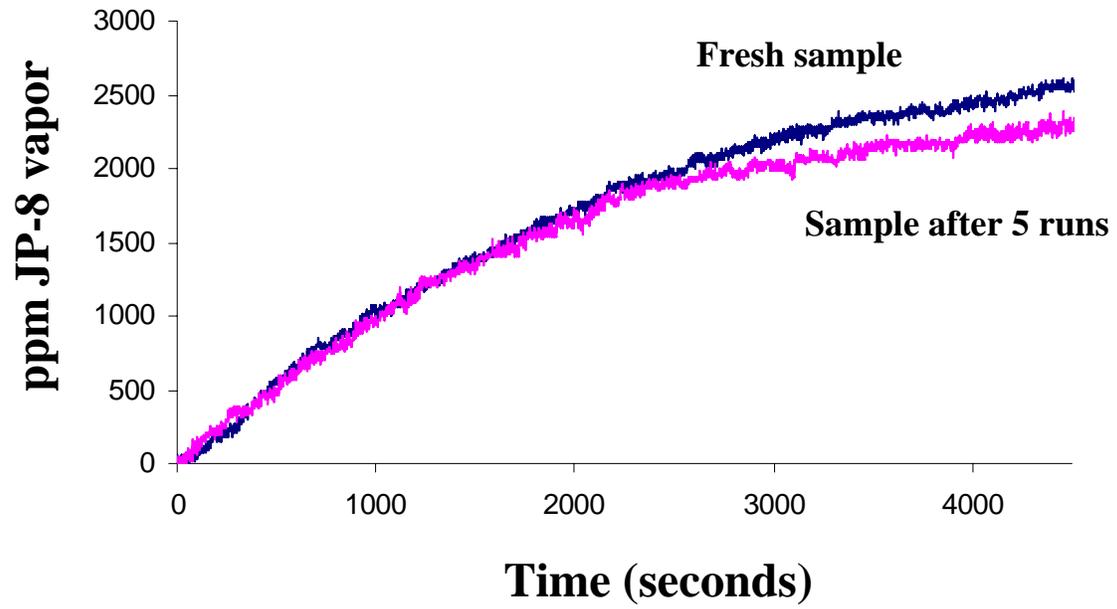
Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure Captions

Figure 1: The infrared transmission spectrum of room temperature vapor from JP-8, DF2, and gasoline. The fundamental C-H absorption in each of these fuels is near a wavelength of 3.3 μmeters. The first overtone of the C-H stretch is near a wavelength of 1.71 μmeters. Spectra are offset for clarity

Figure 2: The experimental apparatus used in these experiments.

Figure 3: The C-H first overtone region for the fuels used in these experiements. Also shown is the spectrum of the mixed laser beam (lineshapes of the mixed laser beam at 1.3μm and 1.7μm are due to the instrument lineshape of the interferometer (sinc)).

Figure 4: The approach to the lower explosion limit for hydrocarbon vapor, measured with the mixed laser sensor, as the dry air in a 13 liter optical cell is slowly displaced by air saturated with gasoline vapor at 1 atmosphere and 294K. Also shown is the change in oxygen concentration during the displacement (oxygen sensor courtesy of Oxigraf, Inc.).

Figure 5: The increase in JP-8 vapor within the 13 liter optical cell as the dry air in the cell is displaced with air saturated by JP-8 vapor at 1 atmosphere and

294K. The difference between Run1 and 5 is the loss of volatile hydrocarbons

from the fuel sample.