

DETECTION AND MEASUREMENT OF MIDDLE DISTILLATE FUEL VAPORS USING TUNABLE DIODE LASERS

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ABSTRACT

A sensor for 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. Limits of detection are reported. Improvements to be incorporated in the next generation of the sensor are discussed.

INTRODUCTION

This paper describes initial results of quantitative measurements of vapor from the hydrocarbon-based fuels JP-8, DF-2, and gasoline using a sensor based upon near-infrared tunable diode laser absorption spectroscopy. The development of this sensor was driven by the need for rapid, quantitative measurements of middle distillate fuel vapors for detection of fire hazards on board military vehicles.

The method of detection employed here has been previously reported by us for detection of vapor from pyridine [1]. 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 the wavelength of 1.71 micrometers). 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 easily transported at low loss using inexpensive optical fibers.

BACKGROUND

Most gas phase concentration measurements using line-of-sight near-infrared tunable diode laser absorption spectroscopy use wavelength modulation spectroscopy (WMS) techniques [2-4] or balanced ratiometric detection (BRD) [5, 6]. Wavelength modulation spectroscopy (WMS) typically employs distributed feedback (DFB) tunable diode lasers. High sensitivity is achieved by phase sensitive detection at frequencies (KHz to MHz) where noise contributions to signal are minimized. Detection is made at twice the modulation frequency, and absorption features have a second derivative lineshape. Measurements are made using a single probe laser beam.

Balanced ratiometric detection (BRD) uses a balanced photoreceiver to cancel laser intensity noise. To use this technique, a signal and reference beam are generated by splitting the output beam from a single laser source. It is necessary to balance the DC photocurrent from signal and reference lasers, in the absence of any absorption, prior to making a measurement. This technique has the advantage of reporting the true absorption lineshape, and may be employed with widely tuneable lasers such as external cavity tunable diode lasers, which are not suitable for use with phase sensitive detection at high modulation frequencies.

BROAD BAND ABSORBERS

Both WMS and BRD techniques 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. [7]. However, large and/or heavy molecules may not possess well-resolved ro-vibrational absorption bands because of overlap between fundamental, combination, and/or overtone vibrations, and because of rotational constants that may be less than typical gas phase linewidths [8]. Figure 1 shows the near-infrared gas phase absorption spectrum of dry air saturated at 294 K by the hydrocarbon fuels JP-8, DF-2, and gasoline over a 0.75 m optical path. Each fuel is composed of several hundred hydrocarbons [9]. As suggested by the spectra (Figure 1), and by separate measurement in our laboratory, the vapors from each fuel fit criteria [1] to be classified as having unstructured absorption spectra ("broad band absorber") near the 1.71 micrometer wavelength spectral region.

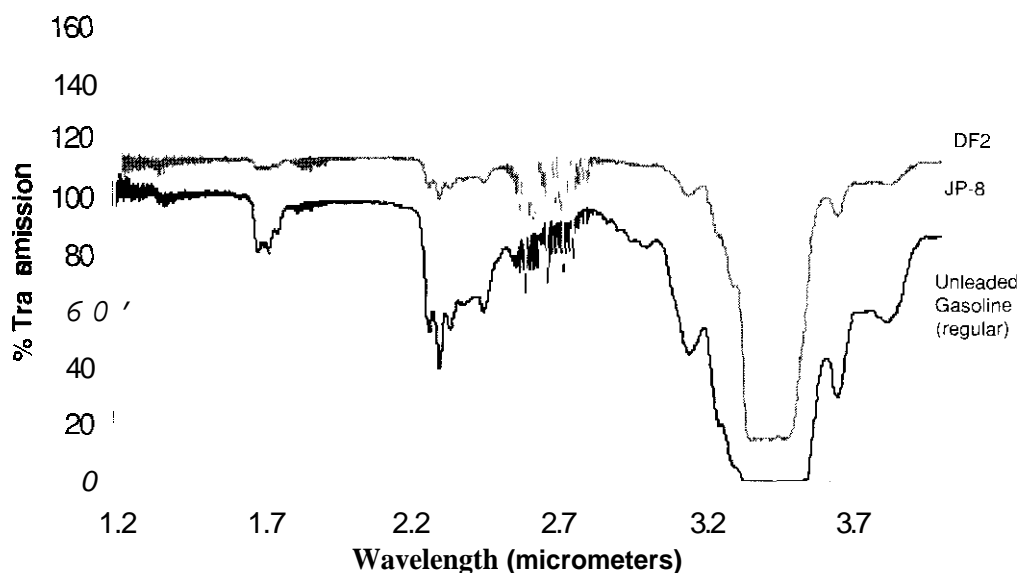


Figure 1. Spectrum of dry air saturated at 294 K with vapor from unleaded gasoline, JP-8, DF 2 (spectra offset for clarity).

PHASE SENSITIVE DETECTION

The method used here for detection of hydrocarbon fuel vapors, and vapors of other molecules that may be classified as broad band absorbers, as well as other detection methods based upon phase sensitive detection, takes advantage of the following relations:

$$\int_0^{\pi} m(\sin at)n(\sin bt) dt = 0 \quad a \neq b \quad (1)$$

$$2C \int_0^{\pi} m(\sin at)n(\sin bt) dt = Cmn\pi \quad a=b \quad (2)$$

For the following discussion, a and b are laser amplitude modulation frequencies, t is time, m and n are amplitudes, and C represents the number of periods over which the integration is carried out.

If the signal of interest is sinusoidal at frequency a (Eq. 1), upon multiplication of this periodic signal by a reference sinusoid at frequency b , the resulting integral will be non-zero only when

$a=b$. If the measurement is made at a frequency at which the Fourier component of the broadband noise in the signal is small, the integral of the product of the signal and the reference will exclude broadband signal noise and only include the signal noise component at the reference frequency. Furthermore, the result of the integration in Eq. 2 yields a value directly proportional to the amplitude of the signal of interest.

EXPERIMENTAL DESIGN

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. For the experiments described here, two different DFB lasers are driven using a sinusoidally varying injection current. Each laser is modulated at the same frequency but out of phase by 180deg.* 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 proportional to the concentration of absorbing gas.

MODULATION DESIGN

A time (t) dependent sinusoidal wave, $S(a,n,t)$, at frequency a with amplitude n may be expressed as:

$$S(a,n,t) = n\sin(at) \quad (3)$$

The signal at the detector, in the absence of any absorption, from two combined sinusoidally amplitude modulated lasers differing in phase by 180deg is:

$$S1(a,n,t) + S2(a,m,t) = n\sin(at) + m\sin(at+\pi) \quad (4)$$

Using the relationship $-\sin(ax) = \sin(ax + \pi)$, multiplying by a reference sine wave (frequency locked to the laser modulation) and integrating gives:

$$2C \int_0^{\pi} (S1(a,n,t) + S2(a,m,t)) \sin(at) dt = C\pi(n-m) \quad (5)$$

Here, p is the amplitude of the reference sine wave and C is the number of periods over which the integration is carried out. Eq. 5 shows that for a probe beam composed of modulated lasers with equal amplitude, the signal at the detector is zero in the absence of any absorption. When the amplitudes of the modulated lasers differ, then the zero absorption signal must be corrected for offset. When the output radiation of laser two is preferentially absorbed by an analyte gas in the path of the probe beam, Eq. 5 becomes:

$$2C \int_0^{\pi} (S1(a,n,t) + S2(a,m,t)) (\exp(-\alpha l)) \sin(at) dt = C\pi(n-m(\exp(-\alpha l))) \quad (6)$$

* Mark Allen, personal communication, Physical Sciences, Inc., 1998.

Where a is the absorption coefficient of the analyte gas ($\text{cm}^2/\text{molecule}$), c is analyte gas concentration ($\text{molecules}/\text{cm}^3$), and l is the probe beam path length through the analyte gas (cm). When the product $\alpha cl \ll 1$, $\exp(-\alpha cl)$ may be rewritten as $1 - A$, (where A is absorbance $= (\alpha cl)$) so Eq. 6 may be rewritten:

$$2C_0 \pi \int (S1(a,n,t) + S2(a,m,t)) (\exp(-\alpha cl)) \sin(at) dt = C_p \pi (n-m + mA) \quad (7)$$

For component lasers of equal amplitude, Eq. 7 becomes:

$$2C_0 \pi \int (S1(a,n,t) + S2(a,m,t)) (\exp(-\alpha cl)) \sin(at) dt = C_p \pi mA \quad (8)$$

The value of the integral in Eq. 8 is directly proportional to the absorbance, A , and hence to the concentration of the analyte gas. Additionally, the value of the integral is directly proportional to the amplitude of the reference sine wave, to the base amplitude of the detector laser signal, and to the number of periods over which the integration is carried out. Figure 2 shows the value of the integral in Eq. 8 (calculated signal) for a moderately strong absorbing gas as a function of Absorbance, ($A = \alpha cl$). The measured signal using the mixed laser method described here is predicted to vary linearly with pressure.

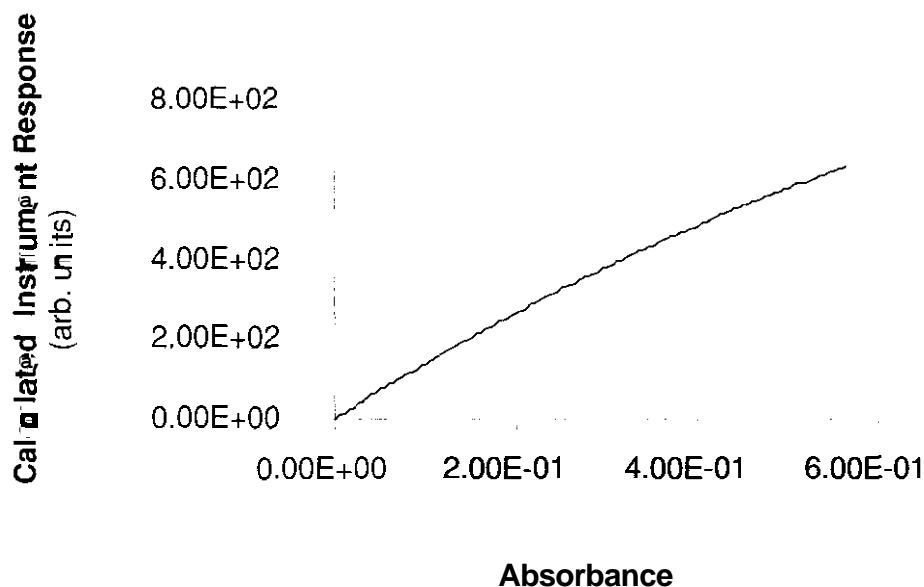


Figure 2. The value of the integral in Eq. 8 (calculated signal) for a moderately strong absorbing gas as a function of Absorbance ($A = \alpha cl$) (see text).

EXPERIMENTAL APPARATUS

A diagram of the experimental apparatus is shown in Figure 3. The two DFB laser diodes (Sensors Unlimited) used to produce the mixed wavelength probe beam have nominal wavelengths of 1.307 micrometers and 1.71 micrometers. 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 amplitude modulated (30KHz) 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

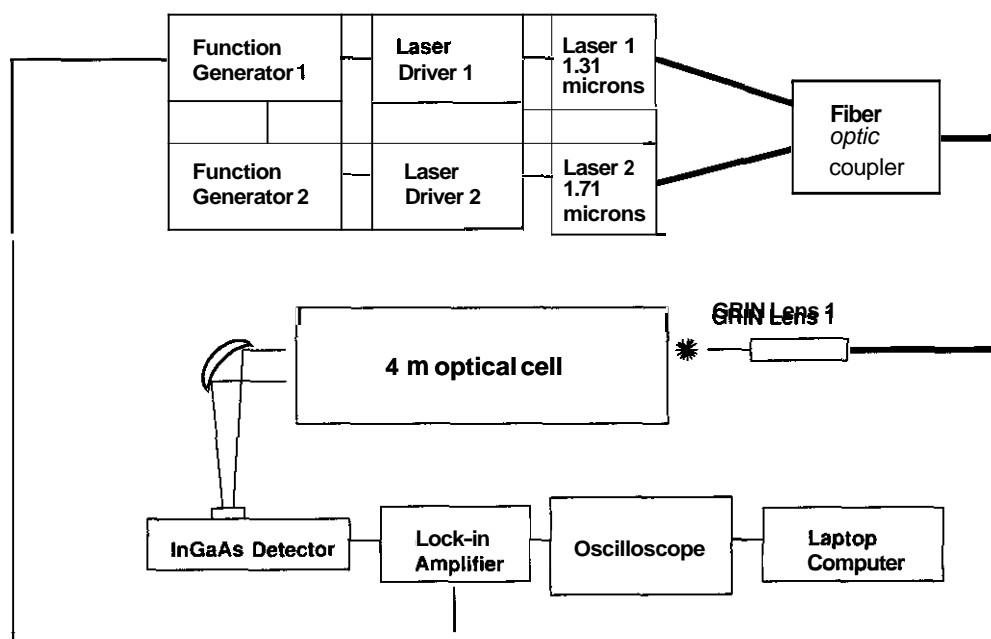


Figure 3. The experimental apparatus used to measure vapors from middle distillate fuels.

RESULTS

Figure 4 shows vapor phase absorption spectra of air saturated by vapor at 294 K from JP-8, DF-2, and gasoline between wavelength values of 1.3 and 1.75 micrometers superimposed upon the emission from the optical fiber which carries the mixed wavelength probe beam. The 1.3 micron laser is the laser we use to measure HF gas using WMS. It was selected to emit in a region where water vapor does not absorb. Figure 5 shows the demodulated mixed laser signal

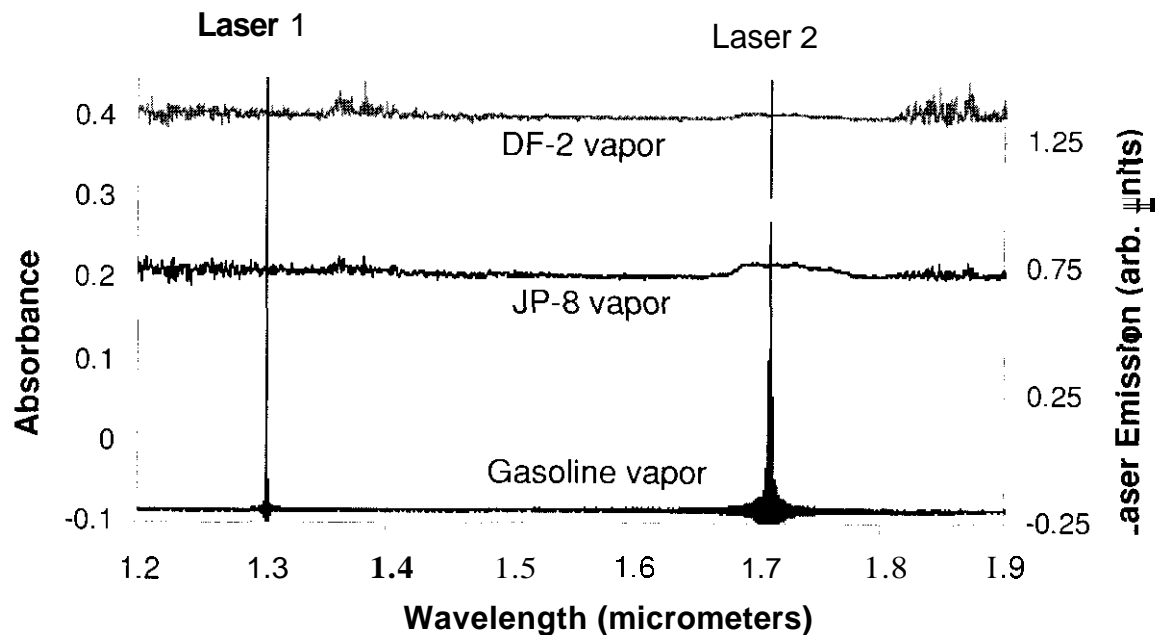


Figure 4. The vapor phase absorption spectrum of air saturated by vapor at 294 K from JP-8, DF-2, and gasoline between wavelength values of 1.3 and 1.75 micrometers superimposed upon the emission from the optical fiber which carries the mixed wavelength probe beam.

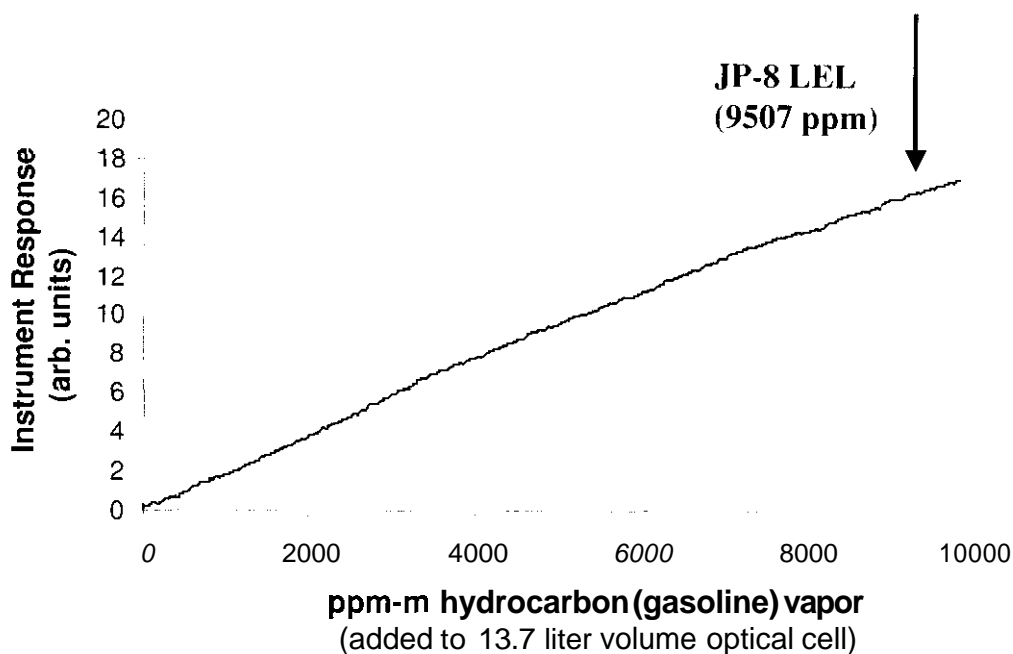


Figure 5. The demodulated mixed laser signal from dry air saturated by gasoline vapor as this saturated air displaces the air at atmospheric pressure in a 13.7-L optical cell (4-m path length). This region is shown because it includes the vapor concentration that corresponds to the lower explosive limit (LEL) for most hydrocarbon vapors (e.g., for JP-8 the LEL is approximately 9500 ppm).

from dry air saturated by gasoline vapor as this saturated air displaces the air at atmospheric pressure in a 13.7-L optical cell (4-m path length). This region is shown because it includes the vapor concentration that corresponds to the lower explosive limit (LEL) for most hydrocarbon vapors (e.g., for JP-8 the LEL is approximately 9500 ppm). Each data point is the average of the lock-in amplifier output measured over 10 ms. Figure 6 shows the measured fuel vapor concentration as the dry air in the 13.7-L volume optical cell is displaced by air saturated (at 294 K) by JP-8 vapor. The two measurements shown in Figure 6 are for a fresh sample of JP-8 fuel and the same sample after 25000 seconds of use in the bubbling apparatus used to saturate air with the fuel vapor. We believe that the reason the older fuel sample shows less of a peak concentration of fuel vapor is because the bubbling apparatus preferentially removes higher vapor pressure components of the liquid fuel. We estimate the current limit of detection for each of these fuel vapors to be approximately 100ppm-meter.

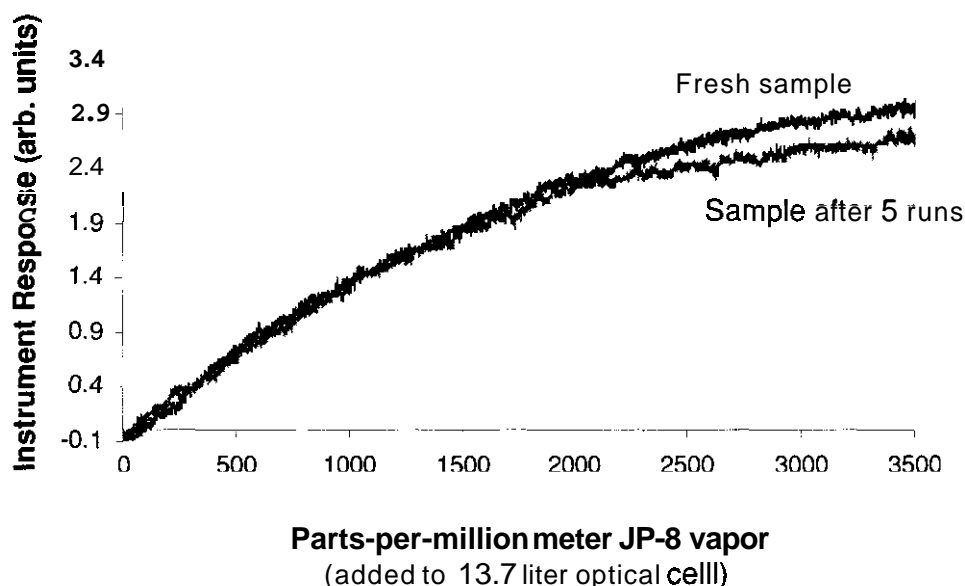


Figure 6. The measured fuel vapor concentration as the dry air in the 13.7-L volume optical cell is displaced by air saturated (at 294 K) by JP-8 vapor.

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. We believe this to be true, but note that the device must 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 rapid concentration measurements of vapors from the middle distillate fuels. During the course of the design and implementation of the method, criteria were developed to maximize sensitivity, and several improvements were considered for future experiments using the technique.

For the mixed laser technique using sinusoidal modulation, the most important element for high sensitivity is the minimization of the amplitude of the unattenuated mixed laser probe beam. The most efficient way to accomplish this is to have a dynamic modulation control to null the raw signal (split from the main fiber prior to introduction to the measurement region) every few milliseconds. An alternative approach is to switch to square wave modulation and to sample

discretely twice during each modulation period. Both of these approaches are currently being evaluated in our laboratory.

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