DIODE LASER-BASED MEASUREMENTS OF FUELS, OXIDIZERS, AND COMBUSTION PRODUCTS DURING FIRE SUPPRESSANT TESTING

Kevin L. McNesby, R. Reed Skaggs, and Andrzej W. Miziolek
Army Research Laboratory, Aberdeen Proving Ground, MD
and
Michael Clay, Steven H. Hoke, and Craig S. Miser
Aberdeen Test Center, Aberdeen Proving Ground, MD

ABSTRACT

Near infrared tunable diode laser (NIR-TDL) spectroscopy is used to quantify HF gas produced during fire suppressant testing of halon alternatives. Results of comparisons with other techniques for measuring HF gas concentrations are discussed. Measurements of HF gas produced in laboratory and real-scale fire suppression testing are presented. The necessity for time-resolved measurements during testing of suppression systems designed to scavenge HF gas is demonstrated.

INTRODUCTION

Fire and explosion suppression is of critical importance on board land combat vehicles. Currently, Halon 1301 (CF_3Br) is employed to suppress fires and explosions in most military vehicles. However, due to its high ozone depletion potential (ODP), Halon 1301 was banned from production by international agreement [1] as of 1 January 1994. A current, service-wide program [2] is underway to identify near-term, environmentally acceptable halon alternative technologies.

Important properties for successful Halon alternatives are high suppression efficiency, low ODP, low suppressant residue after use, low electrical conductivity, stability under long term storage, and non-toxicity prior to and during dispersion. Recent work [3] has shown that hydrogen fluoride gas (HF) is the principal toxic gas produced during fire suppression by Halon 1301 and by fluorocarbon-based fire suppressants. Therefore, for fluorocarbon-based halon alternatives, minimization of HF gas production during fire suppression is an important criterion. The work presented here describes our efforts using near-infrared tunable diode lasers (NIR-TDL) to measure HF gas produced during fluorocarbon-based chemical suppression of laboratory and real scale fires.

BACKGROUND

When a projectile penetrates the hull and fuel cell of a land combat vehicle, fuel cell penetration may result in a fine mist of fuel being dispersed into the crew compartment. The ensuing "mist fireball explosion" [4] is extinguished within 250 ms of detection, using the currently deployed Halon 1301 suppression system. Diagnostic equipment designed to measure HF gas produced during testing of Halon alternative systems needs to provide data on a time scale shorter than the suppression event. The extreme reactivity of HF gas dictates the additional requirement that the measurement be made in-situ.

NIR-TDL absorption spectroscopy for HF measurement provides the mid-range sensitivity (50-5000 ppm) [2], speed of data collection, and ability to use low replacement cost optics and

detectors necessary for data sampling in hostile environments. Relatively low cost, narrow band diode lasers emitting near-infrared radiation at wavelengths absorbed by HF gas (–1.3 micrometer wavelength-overtone transition) are commercially available. Diode lasers emitting in the mid-infrared region at wavelengths where HF absorbs (2.5 micron wavelength-fundamental transition) are not yet commercially available.

EXPERIMENTAL

The experimental apparatus does not appreciably change according to the type of fire being investigated. Figure **1** shows a schematic of the experimental setup and signal processing electronics. For experiments described here, an InGaAsP distributed feedback (DFB) near-infrared tunable diode laser (Sensors Unlimited, Inc.) operating near 7665 cm-1 (corresponding to P(2) of the first vibrational overtone of HF **[5]**) is mounted in a temperature controlled laser diode mount (ILX Lightwave model LDM-4980). The temperature of the diode mount is controlled by a thermoelectric temperature controller (ILX Lightwave model LDT-5412). Laser diode current and internal TEC control are provided using a laser diode controller (ILX Lightwave model 3700). A low frequency sawtooth modulation (–100 Hz, Tektronix FG 504 Function Generator) is combined with a higher frequency modulation (–20 KHz, sine output from a SRS Model 830 DSP Lock-in Amplifier). This modulation is superimposed onto the laser drive current, allowing the laser wavelength to be scanned through the spectral region of interest (low frequency modulation) while also providing a high frequency wavelength "dither" to allow second harmonic signal detection.

The wavelength modulated radiation from the laser diode is fiber coupled. This fiber is terminated by a gradient index (GRIN) lens (Sentech Systems, Inc.), which collimates the laser radiation. The GRIN lens-tipped fiber is placed into a small test rig designed to maintain fiber and detector alignment. Laser radiation is detected using an InGaAs detector. The path length from grin lens to detector is typically 10 cm. The modulated detector signal is demodulated at twice the higher frequency modulation (SRS Model 830 DSP Lock-in Amplifier), the second derivative lineshape displayed on an oscilloscope (LeCroy Model 4600), and the output from the oscilloscope stored on a laptop computer.

MEASUREMENTS IN PARTICULATE MATTER LADEN ENVIRONMENTS

Normal transmission spectroscopy cannot distinguish between light attenuation (measured at the detector) resulting from gas absorption **or** light scattering such as might occur in a smoke or soot filled environment. Partly for this reason, we employ derivative spectroscopy to exclude contributions to light attenuation by scattering from particulate matter. In this method, the laser output wavelength is scanned through a wavelength range, which includes the wavelength of absorption of the gas species of interest (HF). A lock-in amplifier is used to measure the change in detector signal intensity with the change in wavelength. Attenuation of laser radiation by a ro-vibrational transition of a small gas molecule is detected because the wavelength range of the scan is several times the width of the spectral absorption feature (typically on the order of **0.1** cm⁻¹ at atmospheric pressure). Because light scattering by particulate matter is nearly constant over the very small wavelength range of the laser scan, the change in detector signal intensity with the change in Wavelength is effectively zero in the absence of any absorbing gas. In this way, the measurement discriminates against light attenuation by particles.
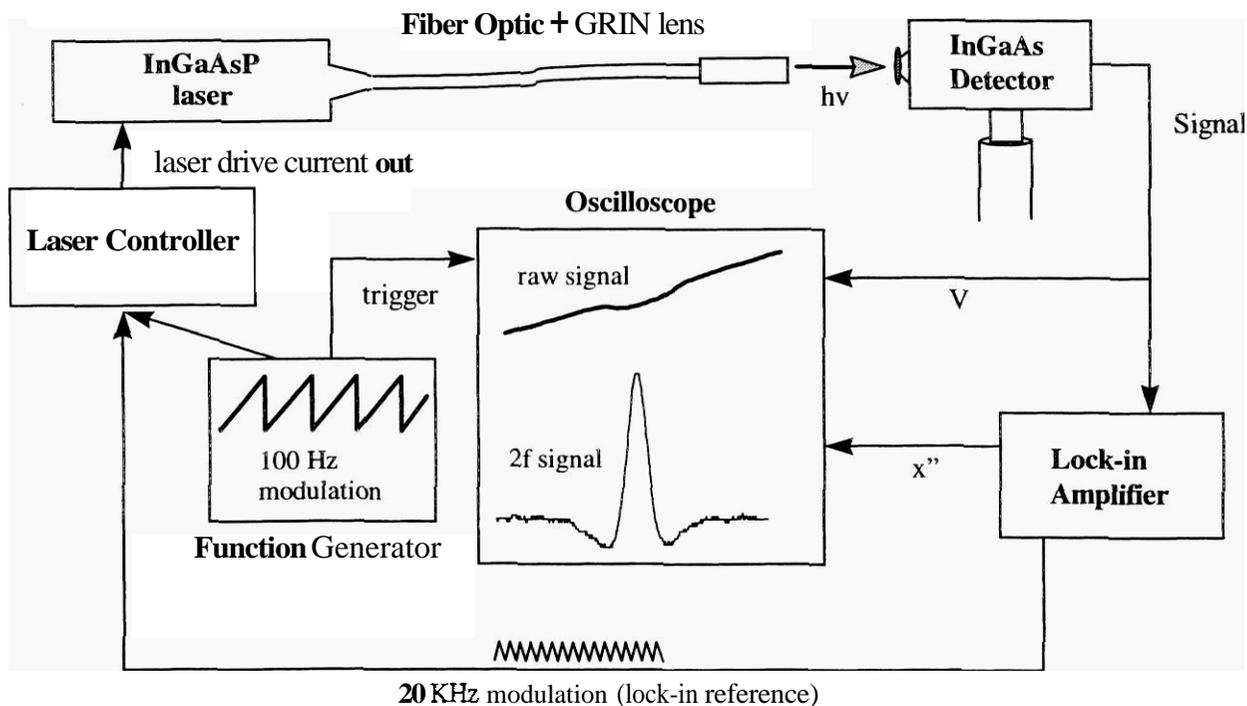
Figure 1. **A** schematic of the experimental apparatus used and signal processing electronics used in these experiments. **V** describes the signal prior to demodulation; **x''** describes the signal following demodulation at twice the reference frequency.

Second harmonic detection using tunable diode lasers has been extensively discussed in the literature [6]. Figure 2 shows a graphical simulation of the signal processing employed in these experiments. Briefly, the laser output wavelength **is** slowly scanned through a spectral region where HF gas absorbs (in this case, $P(2)$ of the first vibrational overtone). The absorption in the absence of any modulation may he seen in the upper trace of Figure 2. **A** small amplitude high frequency modulation is super-imposed on the laser drive current (middle trace in Figure 2). Demodulation at twice the frequency of the small amplitude, high frequency, laser drive modulation yields the second derivative signal shown in the lower trace in Figure 2. It should be noted that the upper trace in Figure 2 shows that the laser diode output power is a function of wavelength. While this is non-ideal behavior, in our experience this is a common trait of commercially available laser diodes. The power dependence on wavelength causes the sloping baseline (exaggerated here for illustration) for the second derivative signal in Figure 2. For measurements at extremely low concentrations or for gases with small absorption cross sections, laser diode output power dependence on wavelength may affect limits of detection.
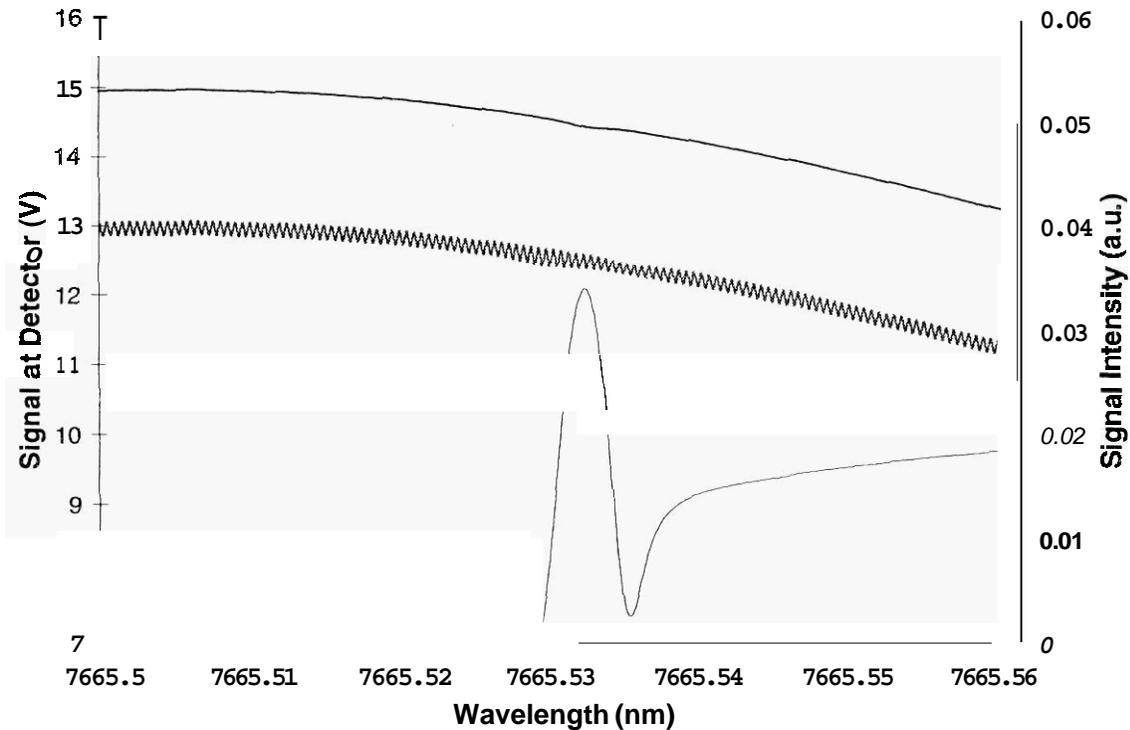
Figure 2. **A** graphical simulation of signal processing for 2f measurement of HF gas concentrations. The slope in the baseline **is** caused by the change in laser diode output power with wavelength.

CALIBRATION

Calculation of HF gas concentration relies upon the Bouguer-Lambert Law [7], which states that for optically thin media at the absorption line center, the negative logarithm of the fraction of transmitted light intensity (referred to as absorbance, **A)** is equal to the absorption coefficient of the molecule of interest (a) times path length (L) times pressure (P): $A = a\,L\,P$. Since the absorption coefficient, α, is constant, and L is known, a measurement of absorbance, **A,** is sufficient to determine pressure, **P.** The second derivative signal peak height may be shown [8] to be proportional to absorbance, **A:**

$$X''/V = kA \qquad\qquad \text{Equation 1}$$

Were, X is the peak height of the second derivative signal (volts), V is the DC voltage measured by the detector in the absence of any absorbance, and **k** is a constant which includes the measuring instrument and optics function. Letting S, denoted as 2f Signal peak height (peak to trough), equal X"/V, yields:

$$S = (k\alpha)\,L\,P \qquad\qquad \text{Equation 2}$$

The slope of a plot of LP versus S provides the value of $k\alpha$. A calibration of the system using known concentrations of the absorbing gas must be performed to determine the value of ka. Once this value is known, the HF gas pressure (P) may be obtained directly from Equation 2. Care must be exercised so that HF degradation of optical surfaces during measurement does not affect the value of $k\alpha$, since this value is instrument function dependent. For this reason, calibration should be performed at the beginning and end of each measurement set. Additionally, for HF concentrations that attenuate more than 5% of the incident light, the linear relationship between HF gas pressure and 2f Signal peak height may no longer hold [8].

COMPARISON WITH OTHER TECHNIQUES

A flow cell was constructed to allow simultaneous measurement of HF gas mixtures (HF in N_2) using NIR-TDL absorption spectroscopy, Fourier transform infrared (FT-IR) spectroscopy, and using a fluoride-ion selective electrode (ISE). The flow cell is designed with five radial sampling ports at four longitudinal distances from the **gas** inlet port. All measurements were made at atmospheric pressure. A schematic of the flow cell is shown in Figure 3. Results from measurements of HF gas using the three techniques are shown in Figure 4. The limit of detection (LOD) of HF gas using the NIR-TDL absorption spectroscopy apparatus described here is approximately 40 ppm. Calibration of the FT-IR data used the peak absorbance of the R(3) line of the fundamental ($v = 0$-1) vibrational transition. The limit of detection of HF gas using ET-IR absorption spectroscopy was approximately 10 ppm. The absorption techniques give similar limits of detection because the increased signal-to-noise ratio achieved using phase-sensitive detection with the NIR-TDL ($v = 0$-2) is offset by the higher absorption coefficient for the fundamental transition measured using FT-IR absorption spectroscopy. The non-linearity of the ET-IR absorbance versus concentration data is caused by an interpolation error, which occurs because the instrument resolution (4 cm^{-1}) is large compared to the linewidth being measured. Fitting the entire ro-vibrational envelope of the ET-IR spectrum results in improved linearity. The limit of detection for HF gas using the **ISE** was approximately 1 ppm. It should be pointed out that the **ISE** measures total fluoride ion concentration, so the technique is unable to distinguish between HF and CF_2O, which is produced in appreciable quantities during chemical suppression of large-scale fires [3].

RESULTS AND DISCUSSION

Measurements of HF **gas** concentrations in well controlled, optically thin environments such as described in the previous section are necessary to check on instrument performance and calibration, but may not reveal difficulties encountered in many laboratory and real-scale tests. In this section we describe measurements of HF gas using NIR-TDL absorption spectroscopy in an atmospheric pressure opposed flow propane/air flame suppressed by C_3F_7H (trade name FM-200) and in a **30 KW** heptane/air pan **fire** during extinguishment by a hybrid suppression system ($C_3F_6H_2$ (trade name **FE-36**) plus particulate) designed to scavenge HF gas.

end cap with gas tight fitting

ISE/impinger port

baffle

flowmeter

flowmeter

valve

to vacuum

gas in

to vacuum

optical port

capacitance manometer

Plexiglass tube
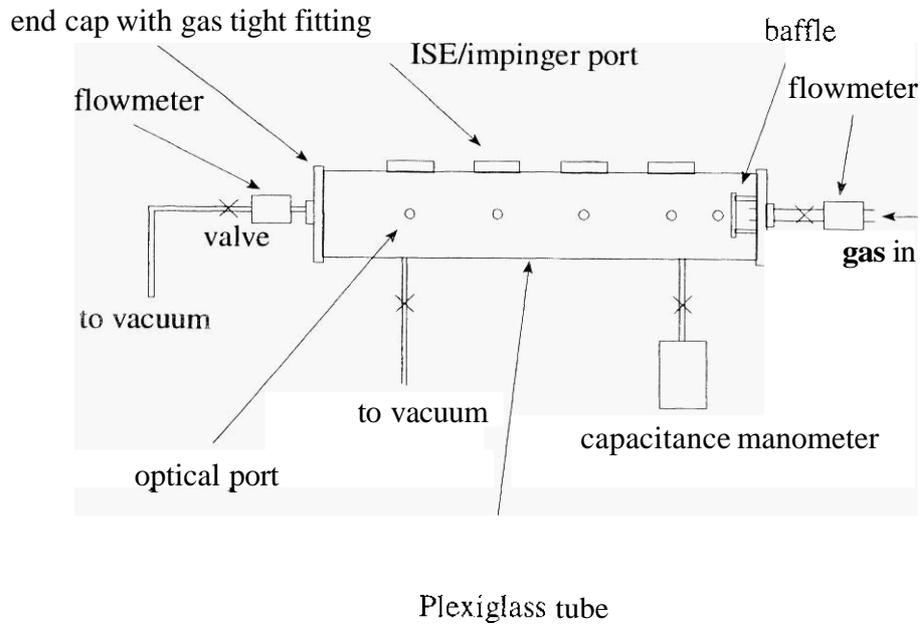
Figure **3.**   The flow tube designed to allow simultaneous measurement of HF gas using NIR-TDL absorption spectroscopy, FT-IR spectroscopy, and fluoride-ion selective electrode (ISE). There are five feedthrough ports (one for the ISE, plus four optical ports) per longitudinal position.

Instrument Calibration
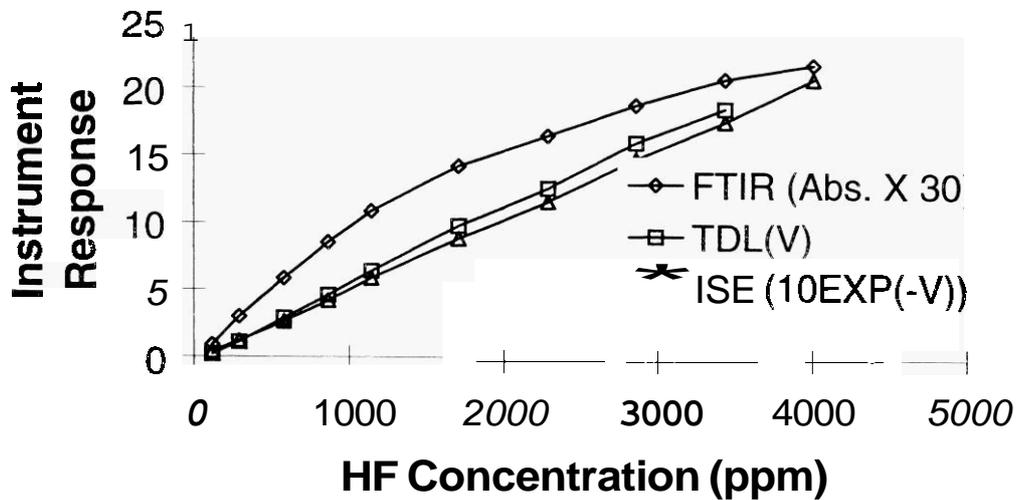
Figure **4.**   Results of comparative calibration of FT-IR, NIR-TDL, and fluoride ion selective electrode for HF gas detection.

A. Laboratory Flame Suppression Studies

Figure **5** shows a schematic of an opposed flow burner apparatus and the positioning of the fiber optic GRIN lens assembly and detector used to measure HF gas produced in a propane/air/ fluorocarbon flame. By varying the mass flow rate of fuel and oxidizer for a given flame in the opposed flow burner, the mole fraction of a given suppressant needed for extinguishment may be varied. The ability to vary the "strength" of a flame in the opposed flow burner ("strength" being inversely proportional to the ratio of diffusion to chemical times, referred to as the Damkohler number) **[9]** allows flames of different strengths to be investigated, and allows for a ranking of halon alternatives according to their flame suppression efficiency.

Figure *6* shows the results **of** NIR-TDL measurement of HF gas produced in a propane/air opposed flow flame (strain rate = $50 \, cm^{-1}$) to which 1% C_3F_7H (trade name FM-200) has been added to the air stream. To generate these data, the fiber optic-GRIN lens assembly and detector were kept fixed in position, and the burner assembly was translated vertically. In this figure, raw data (peak **to** trough distance of the 2f waveform) **are** represented by symbols; data corrected for changes in baseline DC level are shown by a line. The change in DC baseline level as different heights in the flame are probed is caused by density gradients that cause beam steering when the line-of-sight is in the vicinity of the luminous zone of the flame. Using 2f detection, these beam steering-induced errors may be compensated for as long as some laser radiation reaches the detector. The case where no correction is possible may be **seen** in the region from 7 to 8 *mm* from the oxidizer duct. In this region, no laser radiation was incident on the detector.
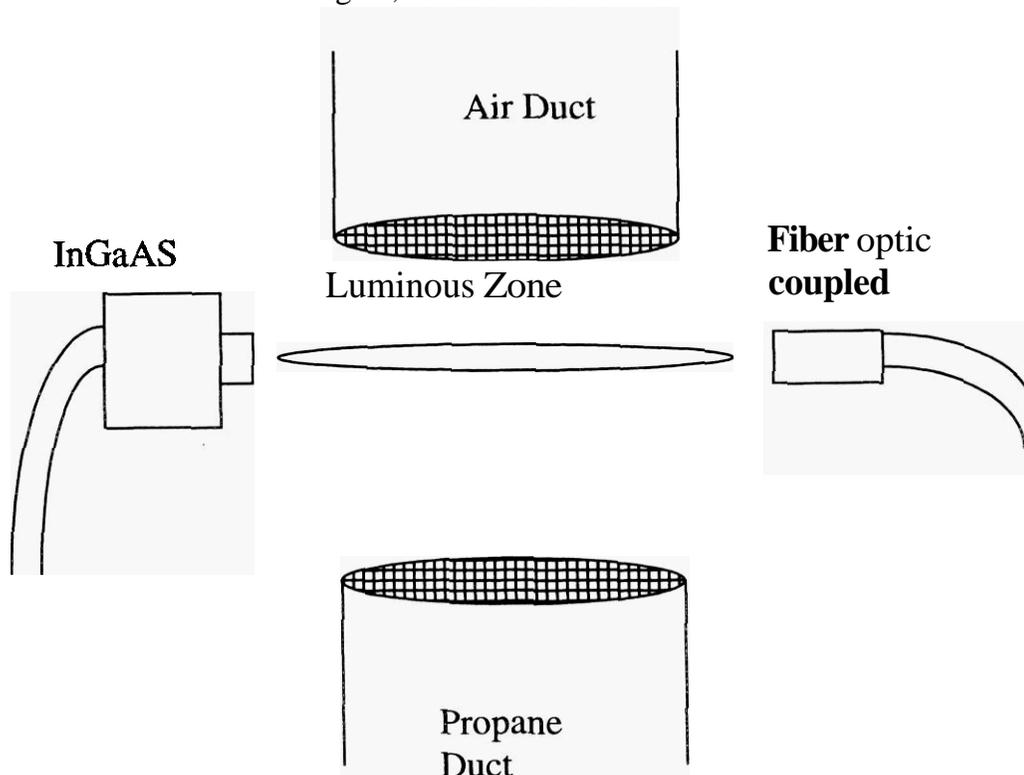
Figure **5.** Schematic of the atmospheric pressure opposed flow burner, fiber optic coupled to GRIN lens **for** delivery of laser radiation, and InGaAs detector element.
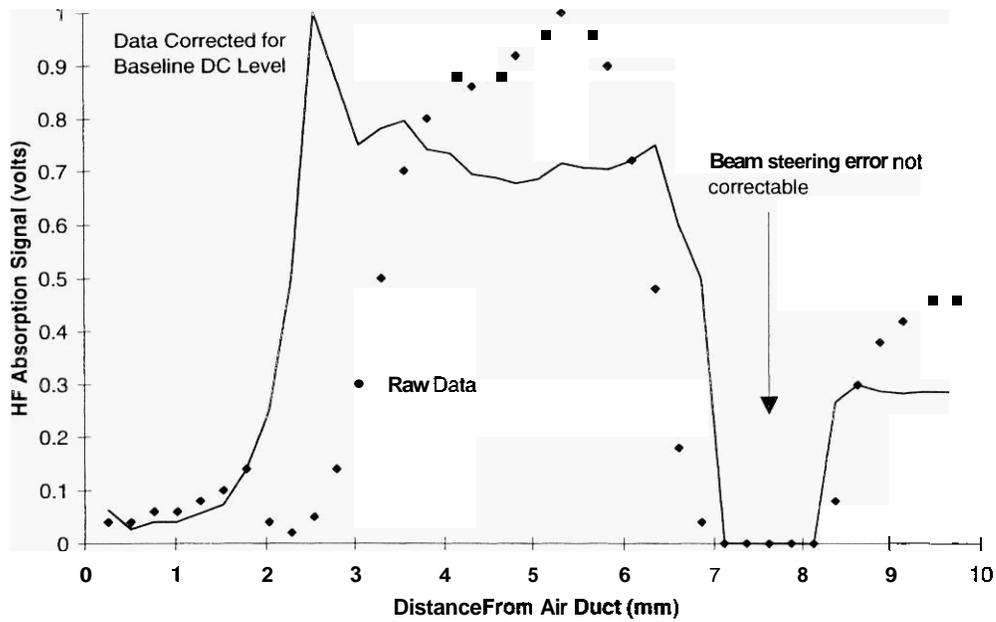
Figure *6.* HF gas absorption versus distance from the oxidizer duct for an atmospheric pressure opposed flow propane/air flame to which 1% C_3F_7H has been added to the air stream. The symbols are raw data, the line represents the data corrected for fluctuations in DC baseline signal 1.
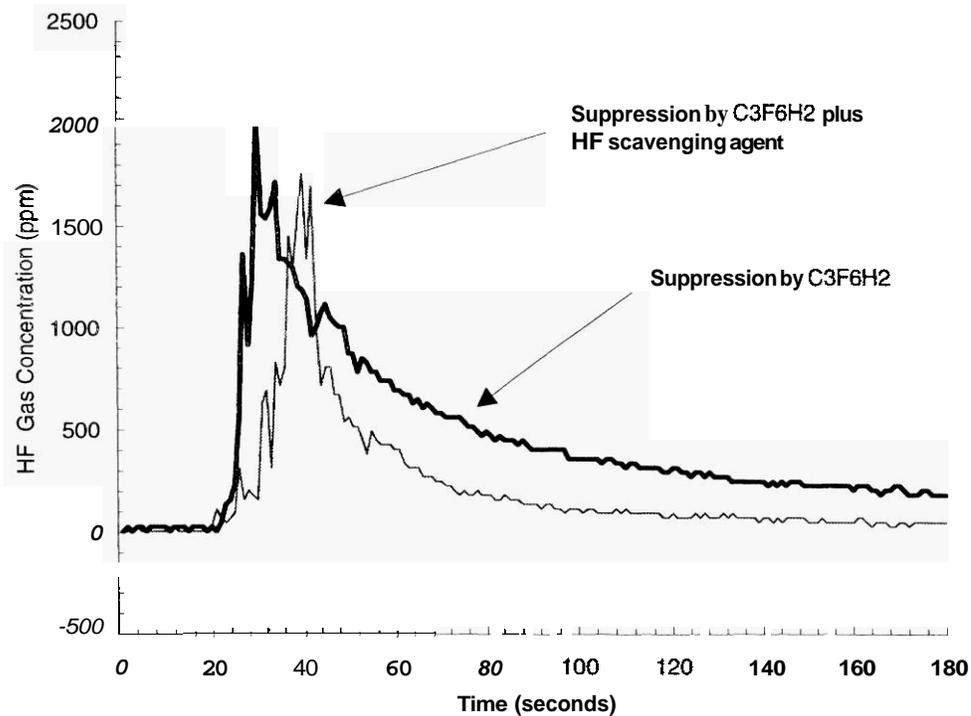
Figure 7. HF gas concentration versus time for heptane pan fires suppressed **by** C_3F_8 with and without addition of HF scavenging agent. Note the difference in the rate at which HF gas concentration decreases with and without scavenging agent.

B. Field Flame Suppression Studies

Figure **7** shows results of NIR-TDL measurement of HF gas in a test designed to measure the effect of particulates designed to scavenge HF. For these tests, a fiber optic-GRIN lens and detector assembly (pathlength = 10cm) was placed in a 1.5-m^3 cubic enclosure near an air-fed liquid heptane pan fire (fire size approximately **30** kW). After allowing the fire to burn uninhibited for 15 sec, the enclosure was flooded with 10% by volume $C_3F_6H_2$ (trade name FE-36), with and without the particulate matter additive. A new data point was measured every **10** ms. Figure 7 shows that the rate at which HF gas concentration decreases after peak concentration is reached is fastest for the fire extinguished using **FE-36** to which particles have been added. For this test, the measurement indicates that the particulate matter added to the fluorocarbon-based suppressant **(FE-36)** successfully reduced the time-weighted average HF concentration.

CONCLUSION

NIR-TDL laser absorption spectroscopy is an extremely useful tool for measuring HF gas concentrations produced during fire suppression by fluorocarbon based suppressants. The low cost of fiber optics and detectors allows for real-time in-situ measurement of HF gas in hostile environments. Care must be taken to ensure calibration is maintained during testing because most optic surfaces are damaged during measurement.

Future experiments will involve multiplexing of several lasers to enable multiple species to be measured using one fiber and one detector. Additionally, recent advances in laser fabrication have made diode lasers at wavelengths near 2 micrometers commercially available. This advance improves limits of detection for many species by decreasing the quantum number change in absorption, as well as enabling the measurement of species whose highest lying fundamental has up to now been out of reach of commercially available near infrared laser diodes.

ACKNOWLEDGMENTS

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