Designing of a Prototype Fiber Optic Raman Sensor

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ABSTRACT

A novel fiber optic prototype sensor based on Raman spectroscopy for qualitative and quantitative monitoring of various chemicals in the sample was developed. The sensor employs a high power 670nm laser diode as an excitation light source and a specially designed fiber optic Raman probe with launching and collecting fibers. Raman signal was collected by six optical fibers; filtered, and then fed to the spectrometer through another optical fiber bundle. The uniqueness of the sensor lies in its compact and stable design configuration, that includes carefully aligned optical components, viz. laser diode, filter holder, and miniature spectrometer. Developed sensor is immune to ambient light fluctuation and offers a cost effective solution for probing several species in harsh environment. Various issues like system fabrication, optimization, functional stability, signal/noise ratio, repeatibility etc are well addressed and presented in this paper.

Keywords: Raman spectroscopy,fiber optic.

1. INTRODUCTION

Miniaturized optical systems are gaining importance in the present era of rapid industrial growth and emerging technologies. Need for online process characterization, monitoring of sample species has led to the fabrication of several kinds of field deployable instrumentation systems [1-2]. Various spectroscopic techniques using diode lasers are being explored for measuring temperature, velocity, density of flow gases as well as developing understanding of gas-dynamics [3]. Combined with fiber optic distribution networks and ultra sensitive detection strategies, compact and portable sensors are now appearing for a variety of applications. Researchers are involved in testing and evaluating non-intrusive embedded sensors for sustained operation, especially in extremely supercritical environment where conventional measurement methods fail to provide accurate results. Engine within liquid-propellant rockets is an example of such an environment with high turbulent fluid injection and mixing under high temperature and pressure [4]. Several types of sensors like electronic, capacitance based, electrochemical etc are commercially available but loose their relevance in the supercritical environment of rocket/ aircraft, where high temperature and pressure severely inhibits their optimal performance [5-7].

Presented work is motivated by a specific need of NASA/SSC for long-term detection and monitoring of the quality of liquid oxygen (LOX) in the delivery line during rocket engine test [8]. To achieve this objective, a prototype sensor, based on Raman spectroscopy, has been designed and tested for optimal performance under the laboratory conditions. In addition to this, designed prototype sensor presents a classic example of a miniaturized optical system, that enables a real time display of Raman 'spectral signature' of various chemical species viz. Acetone, Ethanol, Benzene. Designed system not only fulfills the specific requirement for cryogenic environment but also gives an insight into the preliminary concepts related to Laser Raman Spectroscopy (LRS). LRS has been known for years as a relatively simple analytical method for identification of molecules in gases, liquids and solids [9-19]. The Raman scattered light occurs at frequencies that are shifted from the incident laser light by a change in vibrational, rotational or electronic energies of molecule. By measuring the frequency and intensity of the inelastically scattered light, the molecules in the sample can be qualitatively and quantitatively measured. It enables real-time, non-intrusive multi-component measurement. In contrast to FT-IR, visible or near IR, Raman wavelengths are efficiently transported by fiber optics and this makes LRS suitable for remote sensing using fiber optic probe in harsh and difficult environment.

Uniqueness of the prototype sensor lies in its compact design configuration that includes carefully aligned optical components viz., laser diode, filter holder, spectrometer. Non-intrusive nature and online monitoring

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capabilities of the designed sensor, along with the high degree of portability, offer real time measurements of species constituents in a sample.

2. PROTOTYPE DESIGN

2.1 Excitation source

The optical source for the fabrication of miniaturized optical system is very critical. The application of diode laser in portable sensors and in other areas of optical diagnostics is widely known. The line width, peak wavelength position and the laser power of the diode laser were the main criteria used for selecting laser for our application. We have evaluated the characteristics of two laser diodes (Thorlabs, DL 5038-021 at 635 nm and Power Technology Inc. at 670 nm) for this prototype Raman sensor. We have also estimated the Raman signal from these diode lasers based on the available laser energy, and detection system sensitivity. The results are summarized in Table1.

Table 1. Estimation of the Raman signal from 635nm and 670 nm Diode Laser

		635 nm Laser Diode	670 nm Laser Diode
A	Laser Power (Maximum power)	250 mW	1000 mW
B	CCD Detector Efficiency	1.6	1
C	Grating Efficiency	80%	80%
Overall relative Raman signal		1	2.5

Based on these results, we decided that the 670 nm diode (Power Technology Inc.) operated at 700 mW power is a reliable optical source for the present work.

2.2 Optical fiber probe

In the sensor design, the selected diode laser need to couple to an optical fiber probe to guide the laser light to the sample and collect the Raman signal. The optical fiber probe is an Ocean Optics reflection/backscattering Y-shaped probe (R200-REF). This probe consists of seven optical fibers, each having 200 μm core diameter and 0.22 as numerical aperture, with one launching fiber and six surrounding fibers to collect the Raman signal. To focus the guided light on the sample cell (standard quartz cuvette with 5-cm path length); a suitable exciting/coupling (E/C) optics was embedded at the end of the fiber probe. The E/C optics, employed here was having two UV-grade fused silica plano-convex lenses with the same focal lengths f_1 and f_2 equal to 2 cm (matching the numerical aperture of the fiber and that of the lens). First lens was used to collimate the laser beam and the second lens was used to focus the laser beam on the sample. The separation between f_1 and f_2 was equal to 1 cm. The six optical fibers surrounding the launching fiber collect the emitted Raman signal in the backward direction.

2.3 Detection System

The collected light has not only the components of Raman signal but also the scattered laser light, which needs to be filtered out before entering the spectrometer. For this purpose, a filter holder box was constructed which holds two identical cut-off filters (~725nm). Before this, various combination of neutral density filters and notch filter were employed in the collection optic train to achieve effective signal-noise ratio of the sample. In order to avoid any leakage of ambient light through the sensor, which can interfere and affect the Raman light signal, 'filter holder box' was painted black from inside. This design offers an extra advantage for the sensor to be operated in a day light environment as well as making it immune to ambient light fluctuations. A miniaturized ocean optic spectrometer was placed within the sensor box that would receive the filtered light i.e. Raman signal from the filter holder box. For this purpose a 600 μm optical fiber was attached to the opposite face of the filter holder box through an SMA (Sub Miniaturized version A) connecter and the other end of the fiber was connected to the spectrometer. An exit point was created in the prototype box through which the spectrometer was interfaced to a computer via USB port for monitoring the spectrum. Figure 1 shows the system components inside the prototype box. Apart from these, a fan, which is built within the laser power supply (PS), is fixed in a manner to facilitate air circulation and heat dissipation across the sensor. The *air circulatory system* plays a vital role in maintaining an optimum temperature within the prototype enclosure, which is essential for the stable operation of the sensor.

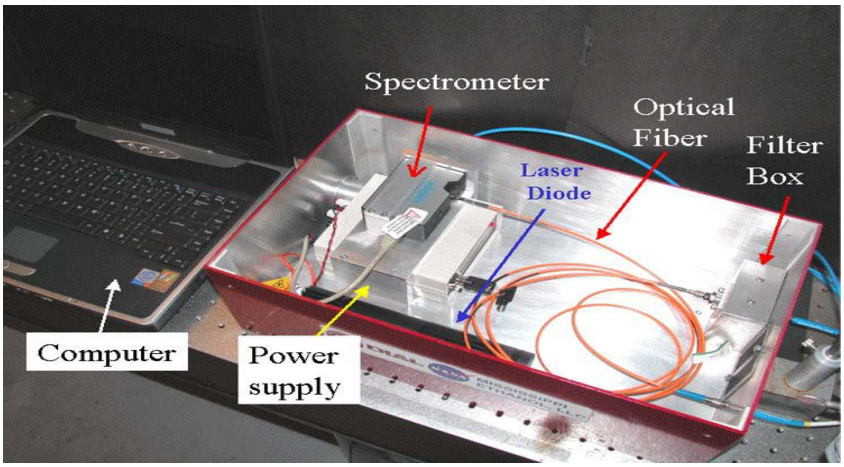

Fig. 1: Photograph of prototype sensor showing various optical components.

3. EXPERIMENTAL DETAILS

After assembling various parts of the prototype sensor, experiments were carried out to test the performance of the assembled system. In the first part of experimental investigation, acetone and benzene were used as a test samples for system optimization. Raman spectra of theses samples were recorded under various experimental conditions for achieving maximum signal to noise of the Raman signal. In the second part of the experiment, Raman spectra were recorded for various concentration (weight) ratios of liquid nitrogen (LN_2) and

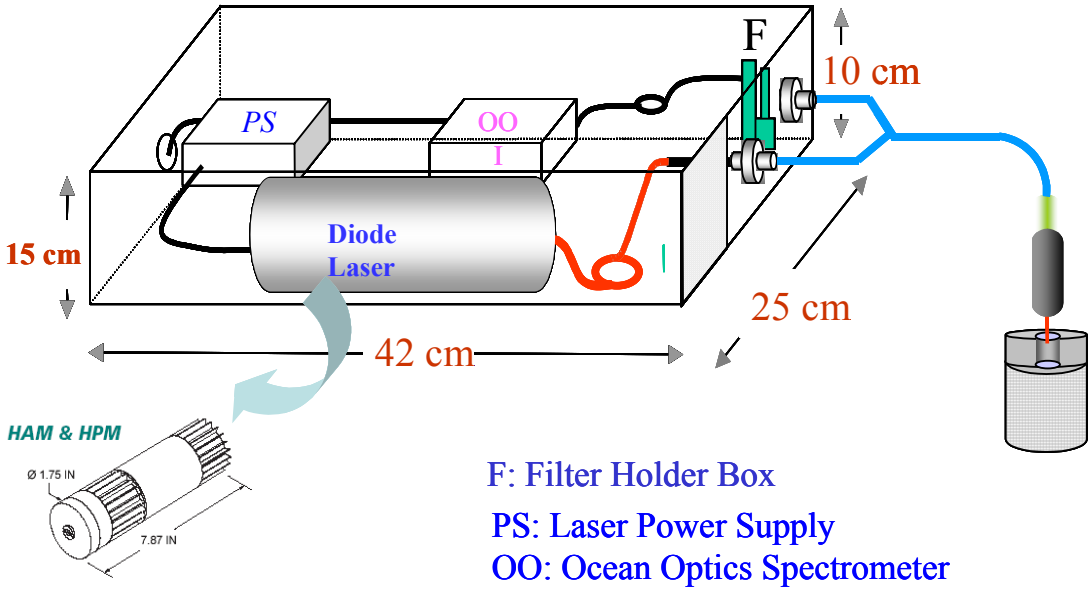

Fig.2: Schematic of prototype Raman sensor for monitoring LN_2/LOX in a dewar

liquid oxygen (LOX) as shown in Fig.2, which is also the ultimate objective of the project. Owing to the continuous vaporization of the supercritical mixture of LN_2 and LOX, greatest challenge was to minimize the vaporization loss,

and also to determine accuracy in the weight ratios of the sample constituent. In the initial phase of experiment, a cap with a hole was mounted on the dewar that contains the LN_2 and LOX mixture. Though it allowed a clear passage for the laser light to be focused onto the liquid N_2/O_2 mixture from the probe but couldn't prevent the vapors from escaping out and condensing onto the tip of the fiber probe. As a result, attenuation in the laser power was observed that severely hampered the observed liquid N_2/O_2 spectrum, thereby reducing the signal to noise ratio of the Raman signal. To overcome this problem, two identical quartz windows (1/4") were being introduced within the cap hole, with a separation of ~5 cm, to provide an optical access as well as to prevent vapors from reaching the tip of the probe. A dryer was also installed in the vicinity of fiber probe to eliminate the remote possibility of vapor deposition on to the tip of the probe and thus, to achieve long term stable operation of the Raman sensor. Recorded spectra were then processed and a calibration curve was obtained for the peak intensity ratios of LN_2 /LOX against their corresponding weight ratios.

4. RESULTS AND DISCUSSIONS

The present study mainly focuses on designing a rugged, reliable prototype sensor for real time monitoring of LN_2 /LOX under the harsh environment of rocket engine. System optimization was performed using acetone and benzene as test samples. Although, the Raman signals corresponding to acetone and benzene were successfully retrieved, broad background appeared on the spectrum as shown in Fig.3 (a) and Fig.3 (b). These spectra have been recorded with integration time of 100 ms and 5 average. The main concern at this stage was to find the origin, as well as to explore various ways to filter the broad background, and to improve the signal response of the Raman

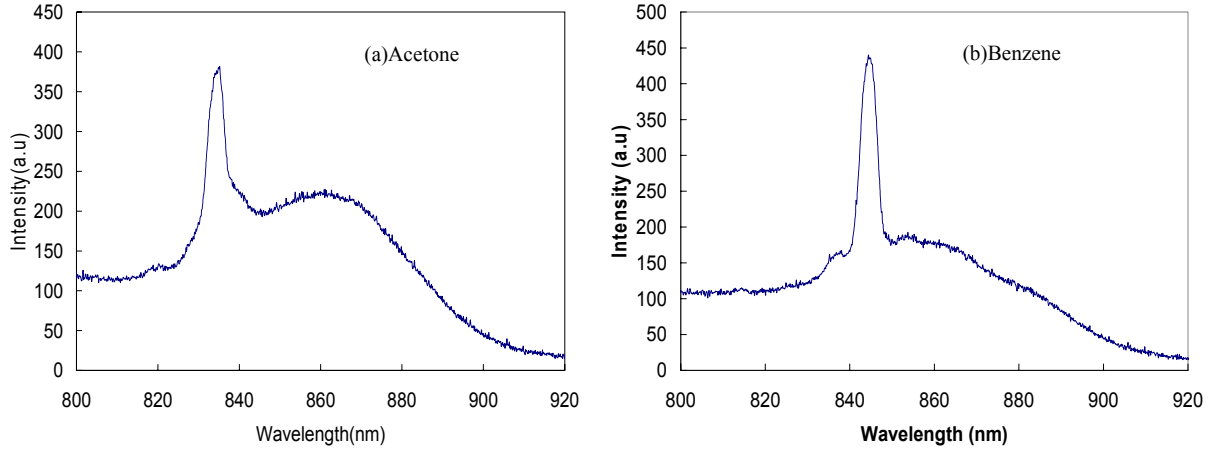

Fig.3: Raman spectrum of (a) Acetone (b) Benzene measured with built-in prototype sensor

Sensor. Various combination of cut-off filters ~ 725nm, 745nm and notch filter~670.5nm were then tried to filter the background as a step towards improving the Raman signal response of acetone and benzene under the same sample experimental condition (i.e. laser energy, probe alignment, etc.). After carefully examining the Raman spectra of acetone and comparing it with the spectra recorded with other excitation light sources, it is concluded that the Raman signal response is influenced by various parameters such as laser power, spectral line width, CCD (charge-coupled device) detector efficiency, etc. Due to the broadband spectral line width of the 670nm laser diode, a notch filter is unable to suppress the scattered incident laser light. This light is further scattered within the spectrometer and falls on the CCD detector that gives rise to broad background which appears on the spectrum. Since the Raman cross-section depends inversely to the fourth power of the laser wavelength (λ), the Raman signal of acetone from the 670nm Laser diode is less as compared to other excitation wavelengths lying in near UV or visible range.

This part of our experimental investigation demonstrated the capability of the designed prototype sensor in displaying real time Raman 'spectral signature' of organic molecule compound like acetone and benzene. In the next phase, test samples were replaced by mixtures of LN_2 /LOX. The mixture sample was prepared by adding LOX in LN_2. Owing to the fact that the molecular weight of oxygen is higher than that of nitrogen, the rate of vaporization of liquid nitrogen is suppressed. The concentration of LN_2 was gradually increased from 10% to 66 % against LOX at normal atmospheric pressure and temperature, while maintaining a total weight around 100 gms. Raman bands corresponding to LOX (~748nm) and LN_2 (~795nm) were observed on the spectrum and critically analyzed in

terms of spectral band shape, S/N ratio, peak intensity. Peak intensity corresponding to LN_2 /LOX, at various concentration of their weight ratio was estimated for obtaining a calibration curve as shown in Fig.4. To reduce the fluctuations in the peak intensity and to improve the calibration curve, data points corresponding to multiple spectra were statistically averaged and corresponding standard deviation was obtained. Sensor response exhibits a linear

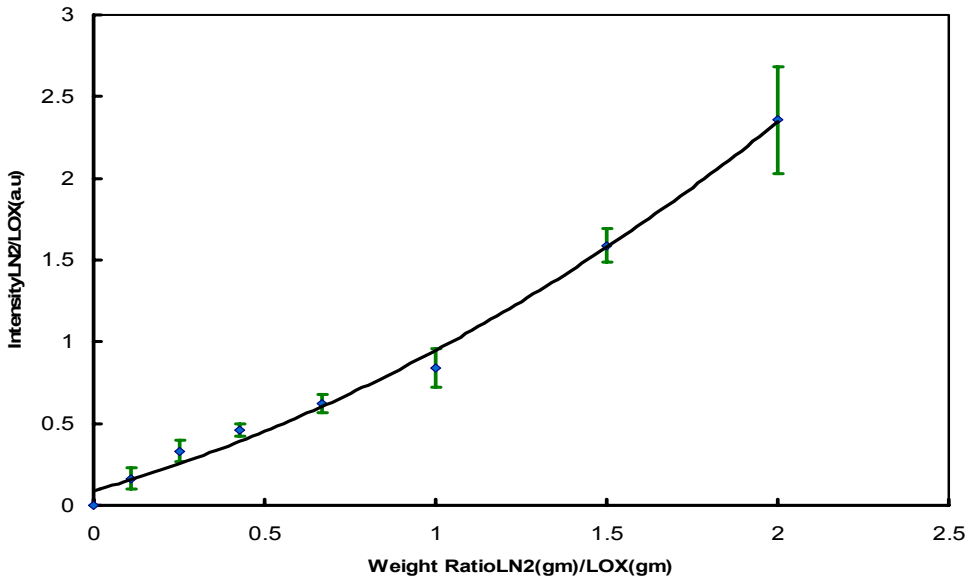

Fig.4: Raman peak intensity ratio of LN_2 and LOX against their weight ratios

trend within the limit of 10% to 66%. The following conclusions can be drawn from these results. First, the prototype sensor system is capable of monitoring successfully LN_2 /LOX level in LN_2 /LOX liquid mixture. Second, data points tend to fluctuate more towards the higher concentration region of LN_2 /LOX as indicated by the error bars. This is attributed to the fact that the vaporization rate of liquid nitrogen increases many folds resulting in the formation of cloud of semi-liquid gaseous phase mixture; and thereby affecting the Raman signal in the case of higher liquid nitrogen/liquid oxygen concentration sample mixture.

5. CONCLUSIONS

This paper presents a novel prototype Raman sensor based on the principle of Raman spectroscopy and exploits the scheme of fiber optics. Efficient light collection optics and miniaturized design of the assembled sensor system facilitates it to be operated in the harsh environments of rocket engines and successfully monitoring the quality of cryogenic fuels. Although, the designed sensor system has a unique architecture and flexible design configuration, the low signal to noise ratios of Raman signal of LN_2 /LOX raises question on its wider applicability. But inspite of this, uniqness lies in the compact design configuration, which sets up a new milestone for the growing instrumentation technology of present time.

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