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Raman-based oxygen and nitrogen sensor for monitoring empty airplane fuel tanks

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INTRODUCTION

The purpose of this project was to develop a Raman-based method for detecting oxygen and nitrogen in empty fuel tanks. The need for such a method comes from the potential danger of allowing explosive oxygen-fuel mixtures to accumulate in empty airplane fuel tanks. An explosion resulting from such a mixture is believed to have caused the Flight TWA 800 disaster in 1996. Recently, (e.g., February 17, 2004 press release) the FAA announced its intentions to make fuel tank inerting mandatory. One potential solution to this problem is to use an inert gas such as nitrogen to flood the empty fuel tanks in order to reduce the concentration of oxygen.

The use of nitrogen purging would greatly benefit from a "smart" sensing device that could detect and regularly monitor the levels of nitrogen and oxygen in the fuel tank. Such a device could allow both oxygen and nitrogen to be monitored simultaneously, so that any problematic elevation in the relative level of oxygen in the fuel tank would trigger an alarm. The alarm would then be used to flood the tank with nitrogen so that the level of oxygen remained below that needed for ignition. This instrument would also be used to determine the amount of nitrogen needed in order to sufficiently displace the oxygen during the initial nitrogen filling.

During the past few years, our research group has explored several different approaches to building such a sensing device. The most promising approach is based upon conventional Raman spectroscopy. Raman spectroscopy is attractive for the following reasons.

1. Raman spectroscopy is both highly selective and quantitative. It can be used to identify molecules, to detect a specific molecule, and to determine the concentration of that molecule. The detection wavelengths for nitrogen and oxygen are sufficiently different to resolve easily.
2. Raman spectroscopy is universal; unlike fluorescence, Raman signatures can be detected from any molecule.
3. Raman spectroscopy is potentially a fast technique; the Raman process itself is almost instantaneous, although longer collection time may be required when the intensity of the scattered light is very low. If the intensity of the scattered light is sufficiently intense, Raman spectroscopy can be used for real-time monitoring.
4. A wide selection of laser wavelengths can be used when performing Raman experiments.
5. Raman spectroscopy is non-destructive
6. Recently, improvements in spectroscopic instrumentation has reduced the cost, size, and laser power needed to build Raman-based instruments.

The primary drawback for a Raman system are:

1. Potential spectral interference from laser-induced fluorescence, ambient light, or elastic scattering.
2. The possibility of the laser acting as a source of ignition if the laser beam intensity is high.
3. The sensitivity and potential damage of optical devices due to vibration, shock, abrasion, extreme temperatures/pressures, or contamination (e.g., by fuel).

One of the initial primary challenges with using conventional Raman in this application is the weakness of the Raman scattering process in gaseous samples. Using conventional instrumental designs, generating gas phase Raman spectra has required either very long collection times or the use of very intense beams of light. This particular application requires relatively short collection times and beams of light that are much weaker than the ignition threshold.

SYSTEM DESIGN
The Raman based system was designed to facilitate rapid (real-time) monitoring of oxygen and nitrogen while using minimal laser power. The resulting system described below permits high throughput through the use of non-tunable filters instead of a spectrograph. Although not tunable, simple interference filters provide significantly greater throughput than spectrometers. They are also smaller, less expensive, simpler, and more rugged.

Another important feature of this design is that the optical axis of the laser beam is slightly angled from that of the detection optical axis. Therefore, the window between the detection system and the sample are not be illuminated by the laser. This off-axis approach is shown in below.

488 nm beam   mirror

Detection Axis

Fast lens   Filter(s)   PMT
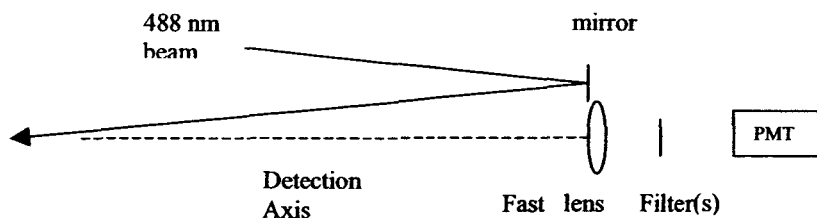
A third feature is the use of a telescope to expand the beam diameter. This feature reduces the intensity to less than 0.04W/cm^2 (to possibly reduce the risk of ignition) without reducing the power of the laser beam.

Initial results using this design were promising; we were able to detect Raman scattering from nitrogen in ambient air in real time using 30-40 mW of CW laser power. The use of

low laser power was encouraging because this specific application could benefit greatly from the commercial availability of simple, small, low-powered diode lasers.

However, several questions needed to be answered in order to determine the suitability of this Raman-based probe for actual use in the field. These questions included the following.

- Does the system work for oxygen as well as nitrogen? (Note: oxygen will be present at a much lower concentration than nitrogen)
- How well does the method work in a cell where the concentration of nitrogen and oxygen varies over time?
- What are the potential problems/interferences (temperature fluctuations, effects of fuel on the windows of the cell, etc.), and how can they be addressed?
- What design elements are required for optimum performance?

In order to answer these questions, a simulated tank was constructed and a series of experiments were conducted (see Figure 1). The tank was built of clear plexiglass to permit easy observation during troubleshooting. The plexiglass was covered with black cloth in order to block ambient light. All faces were covered by this black cloth except for the front face (side where the laser beam entered). Three holes were cut into the tank; one on the front fact to pass the laser beam, and two on the removable top to allow gases to enter and exit.

Two lasers were used during these studies: a 35 mW HeNe laser producing light at 633nm, and a multiline variable power Argon ion laser that produced up to 31 mW of light at 488 nm at the tank. A diffraction grating and/or prism was used to ensure spectral purity of the light beam. A chopper was added to chop the light at a frequency of ~100 Hz. The use of a chopper helped to remove low frequency drift associated with the detection electronics.

A beam dump was placed inside the inside of the tank in order to terminate the beam. We found that the amount of light that escaped from the beam dump had a significant dependence on the tilt of this beam dump. The beam dump performed optimally when it was tilted with respect to the beam.

Raman and Rayleigh light scattered from inside of the tank passed through the front face of the tank and was collected by a f/2.5 lens. A stack of absorptive glass filters was used to remove elastically scattered light. One concern was that the amount of elastically scattered light could vary considerably. For example, if the beam dump were removed or blocked, the amount of elastically scattered light could change by several orders of magnitude. A very large increase in the level of elastically scattered light could not only cause erroneous readings, but it could also destroy the PMT. Therefore, a a filter stack containing five 2mm thick absorptive glass filters was used to minimize the amount of elastically scattered light (please see the appendix for a list of filters).
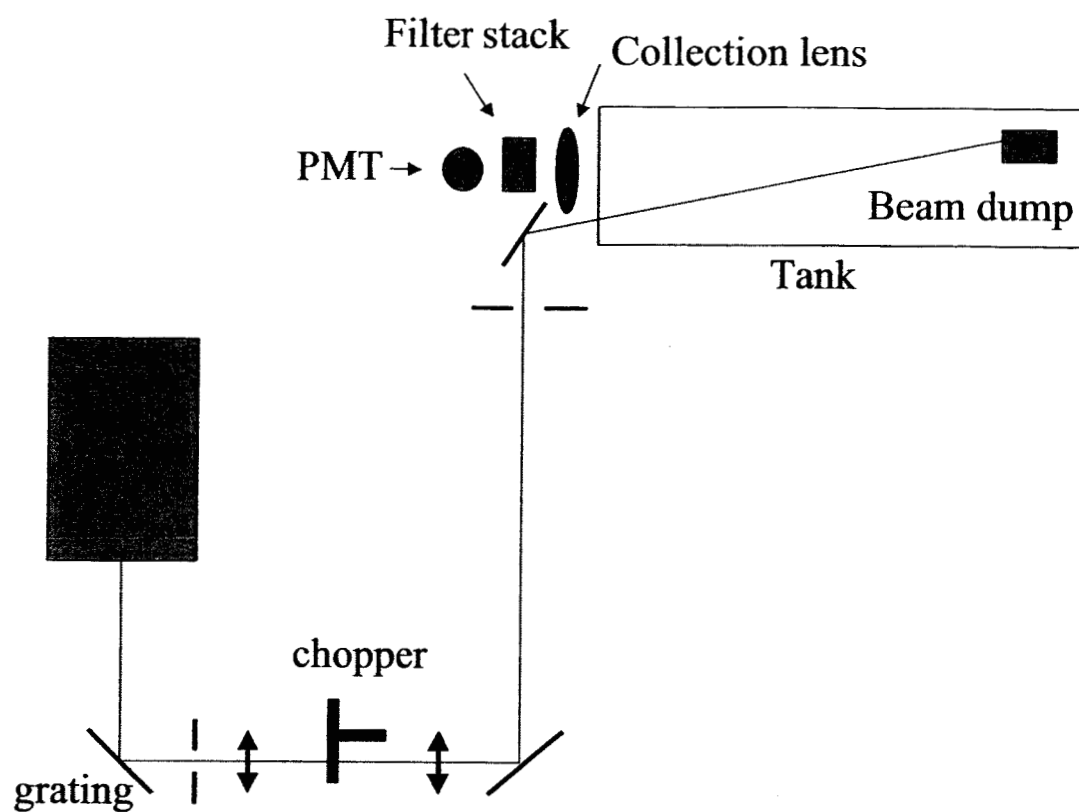
Figure 1 – Experimental design using a simulated fuel tank.

The detection system consisted of a R955 PMT (633 nm laser) or 931A PMT (488 nm laser) attached to a high voltage power supply, a preamplifier, and a digital oscilloscope. The oscilloscope was used in averaging mode in order to permit sensitive detection of small changes in the chopped waveforms. In a typical experiment, the equipment was permitted to warm up for half an hour, and then measurements (difference between light blocked and unblocked by the chopper observed as a square wave signal) were recorded while changing a key parameter (e.g., the relative concentrations of nitrogen and oxygen).

The use of this detection system permitted rapid (almost real-time) monitoring of the gas in the cell. The averaging level was typically set to 128 and the chopping speed was approximately 100 Hz. Therefore, the response time of the system was slightly more than 1 second.

EXPERIMENTAL TESTS AND RESULTS

Detection of oxygen:

The size of the oxygen signal using the 488 nm laser was larger than that for the 633 nm laser. This observation agrees with predictions, since $(633/488)^4 = 2.8$. Another possible factor is that red-sensitive PMTs tend to be more susceptible to dark noise than blue-sensitive PMTs. Consequently, the 488 nm system could clearly detect an increase in the detected Raman signal when the air in the cell was replaced with oxygen (20% $\rightarrow$ 100%) and a decrease when the air in the cell was replaced with nitrogen (20% $\rightarrow$ 0%). However, the 633 nm could only detect a change when the air in the cell was replaced with oxygen (20% $\rightarrow$ 100%), but the decrease when the air in the cell was replaced with nitrogen (20% $\rightarrow$ 0%) was less clear and too small to be considered reproducible under the conditions tested.

Potential interference from gas phase kerosene at room temperature

A beaker of kerosene was placed inside the tank and kerosene vapors were allowed to evaporate for 15 minutes. Introduction of gas phase kerosene into the tank did not cause a detectable change in the measured Raman signal for either of the two systems (633 nm laser and 488 nm laser). In order to ensure that the air had an equilibrium partial pressure of kerosene, the beaker of kerosene was then heated to 70°C and then allowed to cool to 35°C. After this cooling, the size of the Raman signal was approximately the same as it was before kerosene was introduced into the tank.

Potential interference from gas phase kerosene at elevated temperatures

At a liquid temperatures below 45°C, kerosene vapors did not cause a detectable change in the measured Raman signal for either of the two systems (633 nm laser and 488 nm laser). However, above 45°C, a significant change was observed. We visually observed small points of light scattering in the laser beam, which corresponded to the formation of droplets that were suspended in air at this critical temperature (the kerosene liquid was 20° degrees above the temperature of the surrounding air). Therefore, this technique is susceptible to spectral interference if conditions create suspended droplets of fuel.

<u>Potential interference from liquid phase kerosene</u>
Strong fluorescence was observed after allowing either of the laser beams (488 nm or 633 nm) to strike a beaker containing liquid phase kerosene. Therefore, this technique is highly susceptible to strong spectral interference if the laser beam is allowed to contact liquid fuel. The level of fluorescence may be sufficient to cause damage to the PMT.

<u>Potential effect of allowing the laser beam to hit a black metal surface</u>
The beam dump was replaced by a painted black metal surface in order to emulate a problematic event (dark solid foreign object inside fuel tank). The level of detected light roughly doubled when the 633 nm laser was terminated by a painted black metal surface instead of the beam dump. This problem is not sufficiently serious to damage the PMT, but it might result in a slight decrease in sensitivity due to the accompanying increase in noise. If this object were to move in and out of the beam, then it could give the false impression that the levels of oxygen and/or nitrogen were fluctuating.

<u>Potential effect of entrance window being coated with kerosene</u>
A kerosene-coated glass slide was placed in the path of the laser beam at the front face of the tank. The size of the detected signal increased significantly. This problem was not sufficiently serious to damage the PMT, but it might result in a slight decrease in sensitivity due to the accompanying increase in noise. If the amount of kerosene were to change, then it could give the false impression that the levels of oxygen and/or nitrogen were fluctuating.

<u>Potential effect of kerosene-coated window placed in front of the beam dump</u>
A kerosene-coated glass slide was placed in the path of the laser beam in front of the beam dump. The size of the detected signal increased significantly. This problem was not sufficiently serious to damage the PMT, but it might result in a slight decrease in sensitivity due to the accompanying increase in noise. If the amount of kerosene were to change, then it could give the false impression that the levels of oxygen and/or nitrogen were fluctuating.

CONCLUSIONS AND RECOMMENDATIONS
A Raman-based detection system for monitoring oxygen/nitrogen in empty fuel tanks appears to have several attractive features.
- High speed (real-time) monitoring
- Relatively compact (small, lightweight, requires moderate power)
- Species-selective
- Relatively low cost
- Low risk of ignition
- Does not require replacement of consumables

However, the Raman-based system also has potential problems. These include the following.
- Interference from Laser-induced fluorescence from liquid fuel. Small amounts (e.g., laser beam hits a solid with a think layer of liquid fuel) can cause erroneously high

readings of the Raman intensity. Large amounts (e.g., laser beam hits a pool of fuel) could cause sufficient LIF intensity to damage the detector (PMT).

- The sensitivity of the 488 nm laser was better than that of the 633 nm laser, possibly due to the combination of greater scattering efficiency and better detector (PMT) performance at shorter wavelengths. Possible drawbacks of using a shorter wavelength laser include greater susceptibility to LIF and higher cost of the laser.

- Droplet formation appeared to occur when the temperature of the fuel was 45°C and the temperature of the ambient air was 25°C. Droplets caused the erroneously high readings of the Raman intensity. It is possible that droplet formation may be discouraged if the temperature inside the tank is uniform.

Three final recommendations are made for future studies or applications of this technique.

- Modify the design of the tank to avoid LIF from kerosene on the window. The following cell design should help to reduce the amount of spectral interference from kerosene LIF.

Collection lens   Exit window for Raman signal

Input window for laser beam
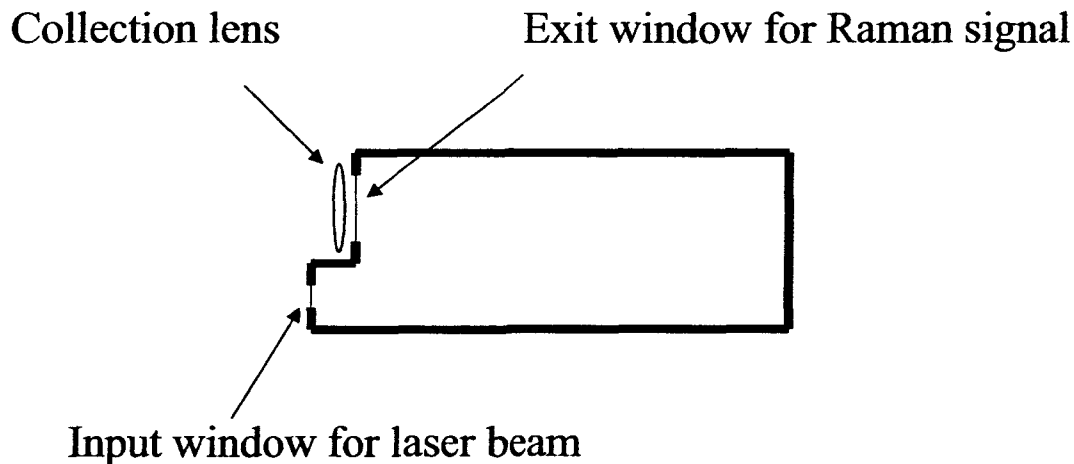
- Monitor oxygen and nitrogen simultaneously so that increases in elastic scatter, ambient light, or fluorescence can be detected and recognized. Such sources of spectral interference should simultaneous increase both the apparent nitrogen and oxygen signal. Dual monitoring could be carried out by using a dual detector that included two separate PMTs , each with a different set of filters. This approach would be most useful when the level of interference is relatively low. At higher levels of interference, the PMT may saturate or even become damaged.

- In the future, further testing in the field will be needed. The testing should involve the use of a metal fuel tank that can be heated to realistic temperatures elevated temperatures and filled with actual jet fuel. A monochromatic laser that does not

require spectral filtering (due to plasma lines) should also be mounted onto the tank in order to make the unit compact. One option would be to use an inexpensive diode laser generating a beam that can be expanded and chopped or pulsed. Improvement of the detection system (e.g., cooling of the PMT) might facilitate the use of longer wavelength diode lasers, reducing the risk of interference from laser-induced fluorescence.

APPENDIX

I. Parts list

- Lasers (Spectraphysics model 127-35 HeNe laser) (LaserPhysics Reliant 250d Ar ion laser)
- Diffraction grating and/or prism for dispersing light
- Iris Diaphragms
- Lenses for telescope
- Chopper
- Mirrors
- Beam dump (Blue Sky Research, Blackhole model 510)
- Collection lens: 185mm FL, 75mm diameter lens
- Filter stack consisting of five 2mm thick absorptive glass filters (RG 665 for the HeNe laser at 633 nm) (OG 515 for the Ar ion laser at 488 nm)
- Dichroic filters (633 nm laser: 700 nm bandpass filter for detecting oxygen and 740 nm bandpass filter for detecting nitrogen) (488 nm laser: 530 nm bandpass filter for detecting oxygen and 550 nm bandpass filter for detecting nitrogen)
- PMT (R955 for 633 nm laser; 931A for 488 nm laser)
- High voltage PMT power supply
- BNC cables
- Preamplifier
- Digital oscilloscope
- Waveform generator
- Gases (tank w/ regulator and tubing)
- Kerosene
- Other: black cloth, optical breadboard, etc.
- Cell with the following dimensions:
  Height: 6 inches
  Width: 6 inches
  Length: 40 inches
  Material: clear plexiglass, 3/8" thick, with removable top, black cloth shroud to block light. 3 holes were cut: 1 to pass laser beam, 1 for gas entry, and 1 for gas exit.

II. Procedure for setting up the system

Overall strategy – The following were found to be useful to include during experimental design and testing.
- Maximize throughput by using a PMT and filters rather than a PMT and monochromator.
- Reject (all) elastically scattered light by using a large stack (≥ 5 colored absorptive glass filters) in front of the PMT to effectively absorb this unwanted light.
- Minimize the distance between the collection lens and the Raman scattered light by using a large diameter lens with a small f#. Locate this lens close to the entrance port of the cell. Adjust its side position by prioritizing Raman scatter

from air close to the front of the cell over that from the back of the cell. Light from the back of the cell will be much weaker (due to spreading out over a longer distance), and will also contain more elastically scattered light from the beam block.

- Maximize the range over which Raman light is collected by using a PMT with large filters and turning the (side-on) PMT sideways so that the long part is horizontal, and by reducing the angle between the laser beam axis and the detection axis. The range can be determined by using a card or fluorescing cell and watching the range over which the generated blob of light (after lens) travels and continues to hit the PMT.

The following is the step-by-step procedure used to set up the system.

1. Set up the laser sufficiently far from the cell so that unwanted wavelengths of light from the laser can be removed. A grating or prism will probably be needed to disperse the light, and mirrors and diaphragms will probably be needed to better isolate the desired beam. Adding a Galilean telescope so that the beam is the appropriate size at the entrance of the cell (i.e., does not overfill the cell's entrance hole) helps to reduce diffraction at the entrance of the cell. The laser beam should be at the appropriate height (entrance hole in cell is 8 cm high) when it approaches the cell, preferably without sloping either up or down.
2. Set up the final mirror that reflects (roughly 45 degrees incident angle) the beam and maintains the constant height of 8 cm. Set up the beam dump so that it terminates the beam at the distance roughly 3 feet from the final mirror. Set up the collection lens behind the mirror, so that its center is exactly 34.125 inches from the beam dump and 3.125 inches from the center of the mirror (on the side that does not block the laser beam). The resulting triangle should have produce a small angle between the laser axis and the collection axis.
3. Set up the cell so that its front face is 2 cm from the final mirror and it also contains the beam dump (remove and replace). The collection lens should be situated 5-6 cm from the entrance face of the cell.
4. Tilt the lens so that it will collect light from 7 to 22 cm from the mirror (or 5 to 20 cm from the entrance hole of the cell). This should be confirmed by placing a target (card) where the horizontally mounted PMT will be. This target should be 3.875 inches from the face of the cell (which should also be about 2 inches from the center of the collection lens). Both the PMT and the lens should have their faces tilted to permit maximum collection efficiency (i.e., perpendicular to the collection axis). If needed, a cuvet of fluorescing dye can be used to help confirm the path of the Raman light. The PMT-like target will probably need to be moved perpendicular to the collection axis in order to obtain the desired range of detection.
5. Adjust the beam dump tilt for minimum back reflection.
6. Once the PMT position has been determined, insert the holder for the bandpass filter at the appropriate position between the lens and the PMT. (The distance from the PMT target should be measured, based upon the PMT housing unit).

Make sure that the light that originates over the desired range does not get attenuated by this holder. Then, insert the bandpass filter. Then insert the actual PMT at the location of the PMT target (mark spot using tape on table, also can use tape on PMT housing unit) and all absorptive glass filters.

7. Cover detection area with cloth. Securely cover all filters with cloth, and make sure that they are pressed against the PMT as light-tight as possible. Cover with a box, and then get rid of as much stray light as possible.