

# RAMAN MONITORING OF ENVIRONMENTAL CONTAMINANTS IN A SPACE HABITAT

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## ABSTRACT

NASA needs sensors to accurately monitor the water and atmospheric quality in its space habitat. Concerns for health and safety necessitate the development of sensors to measure common atmospheric gas concentrations, as well as trace contaminants (low ppm or ppb), including both combustible and non-combustible gases. The University of Utah is developing an enhanced Raman monitoring system to detect airborne contaminants at levels of less than 5 ppm. We have collected laboratory data to benchmark current laser Raman technology for gas analysis which provides a reference for future developments. Minimum detection measurements were obtained for the RASCAL™ and RASCAL II Raman technology. The results show that the RASCAL II is capable of detecting ~40 ppm of nitrogen. Improvements are needed that will increase its sensitivity to meet the level of detection required by NASA for air quality monitoring. New CCD arrays with high sensitivity and low noise are now available for obtaining Raman spectra in parallel. Additional improvements planned for the enhanced system are better collection efficiency and a larger numerical aperture.

## 1. BACKGROUND

The Raman scattering effect relies on the interaction of light with the vibrational and rotational modes of a molecule. It was discovered in 1928 by Dr. C. V. Raman while conducting experiments on the fundamental nature of light scattering by transparent media. He found the scattered light to be strongly polarized and that the scattered intensity depended on the wavelength of the excitation source. Experiments showed the appearance of modified lines of light on either side of the excitation line when the scattered light was examined through a spectrograph. These modified lines are bands of light that have been shifted in frequency (or wavelength). The appearance of modified radiation in light scattering is now known as the Raman effect.

Even though Raman scattering has been studied for many years, its use did not

become practical until lasers were developed. When a laser is used as the excitation source, its photon energy is given by  $E = h\nu$ , where  $h$  is Planck's constant and  $\nu$  is the frequency of the light. As a photon from the laser collides with a gaseous or liquid molecule in the ground state, the photon is absorbed and the molecule is temporarily excited to a virtual energy state. As the molecule loses energy after the collision, it re-emits scattered light having a lower energy than the original photon. This is referred to as Stokes Raman. A decrease in the photon energy means the frequency of the scattered light must also decrease (and wavelength increase) to satisfy the energy equation. When the molecule re-emits light with higher energy, it is referred to as anti-Stokes Raman (see Figure 1). In terms of conversion efficiency from incident to scattered light, the overall process is a very weak effect [1,2].

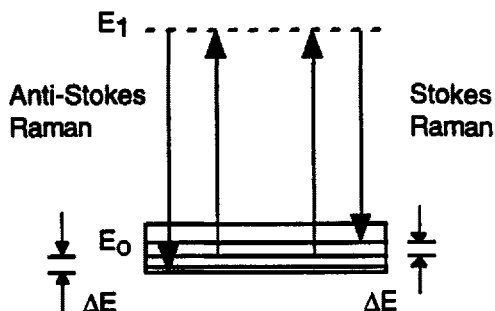


Figure 1. - Diagram of Raman energy transitions for both the Stokes and anti-Stokes lines .

The observed shifts in frequency (from that of the laser) are the frequencies of oscillation relating to characteristic vibrational and rotational energies of the chemically bonded atoms of the molecule. A unique set of Raman lines is produced for each molecule or substance [3]. Therefore, Raman scattering is a convenient way of mapping the characteristic vibrational and rotational spectra of different chemical compounds. In addition, the frequency components produced in the Raman spectra provide specific chemical identification of each molecule present in a sample. The quantities of scattered photons produced at each shifted frequency are linearly proportional to the species concentration within the sample. This is why Raman spectroscopy is one of the most versatile methods of molecular analysis.

When working in the liquid phase, it is a common practice to use the Raman spectra of common organic liquids as reference curves. Toluene works well as such a reference because it has several distinct peaks which can be easily identified at 784, 1000, 1028 and 1207 wavenumbers. As an example, a typical Raman spectrum for toluene is shown in Figure 2. Please note that when discussing Raman shifts, the conventional unit of measure is the wavenumber which has units of  $\text{cm}^{-1}$ .

## 2. NEEDED MONITORING CAPABILITIES

The space habitat is a closed system that must recycle its life sustaining resources, namely water and air. Concerns for health and safety necessitate the development of sensors to measure common atmospheric gas concentrations, as well as trace contaminants

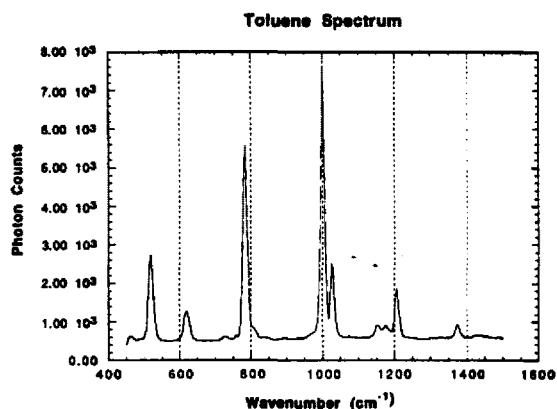


Figure 2. - A Raman spectrum for toluene.

(low ppm or ppb), including both combustible and non-combustible gases. To ensure a safe environment, the monitor would need to be on-line and operate at nearly real-time, which means having a short sampling time. The system must also be able to simultaneously detect all components within the sample. In order to know what level of sensitivity would be needed, we rely on the National Ambient Air Quality Standard and air quality ratings published by the EPA listed in Tables 1 & 2. The air quality standard contains a value for the maximum concentration of contaminant allowable for a given time period. Concentrations in excess of these limits are potentially dangerous. The air quality standards found in Table 1 (which are recorded on a daily basis for every major city in the US) are helpful in determining the quality and safety of an air sample. This provides a standard by which to determine the level of sensitivity required by a feasible monitoring device. The ideal situation for a monitor would be to have the capability of detecting below the levels which are considered to be safe concentration levels of contaminants.

Table 1 National Ambient Air Quality Standards.  
(Max concentrations allowed for a given time period)

Pollutant	1 hr	3 hr	8 hr	24 hr	Annual
Carbon Monoxide	35 ppm (40 $\mu\text{g}/\text{m}^3$ )	—	9 ppm (10 $\mu\text{g}/\text{m}^3$ )	—	—
Ozone	0.12 ppm (235 $\mu\text{g}/\text{m}^3$ )	—	—	—	—
Sulfur Dioxide	—	0.5 ppm (1300 $\mu\text{g}/\text{m}^3$ )	—	0.14 ppm (365 $\mu\text{g}/\text{m}^3$ )	0.03 ppm (80 $\mu\text{g}/\text{m}^3$ )
Nitrogen Dioxide	—	—	—	—	0.053 ppm (100 $\mu\text{g}/\text{m}^3$ )

Table 2 EPA Categories of Air Quality.  
(all values given in ppm)

	<u>Carbon Monoxide</u>	<u>Ozone</u>	<u>Sulfur Dioxide</u>
Good	0 - 4	0.00 - 0.06	0.00 - 0.03
Moderate	5 - 9	0.07 - 0.12	0.04 - 0.14
Unhealthful (alert)	10 - 14	0.13 - 0.19	0.15 - 0.29
Very Unhealthful (warning)	15 - 29	0.20 - 0.39	0.30 - 0.59
Hazardous (emergency)	30 - 39	0.40 - 0.49	0.60 - 0.79
Very Hazardous (never exceed)	40 - 50	0.50 - 0.60	0.80 - 1.00

There are several methods of gas analysis that are capable of providing sub-ppm detection sensitivity. Gas chromatography and mass spectrometry fall into this category. Even though these techniques are sensitive, there are some significant disadvantages that eliminate them as potential candidates for this application. The time required to analyze a gas sample via these methods is on the order of 20+ minutes. Clearly the length of time is too long to provide a real-time analysis. Mass spectroscopy can only be used to analyze samples in the gaseous state and the quantitative analysis is based upon the total mass/charge ratio, and not molecular structure. The equipment is also very large, heavy, and requires a lot of power, which makes it undesirable for use in a space environment.

Raman technology is an attractive solution to these problems. A Raman analyzer can be designed to work in either the gaseous, liquid or solid phase, with the ability to nondestructively identify and quantitate a substance. In comparison to other devices, a Raman analyzer is faster, lighter, smaller, and a more economical approach to monitoring applications.

### 3. RASCAL TECHNOLOGY

In recent years, research in Raman spectroscopy has made impressive advancements. In 1986 research was initiated at the University of Utah to develop a device that

would measure the inspired and expired gas concentrations for patients under anesthesia. This work resulted in the production of the RASCAL™, which stands for Raman SCattering AnaLyzers. This first generation Raman scattering gas monitor was designed to measure anesthetic and respiratory gases to within 0.1%, with a 250 msec response time, using an air-cooled argon laser and six photomultiplier tubes (PMTs) for detection.

Laboratory measurements of the RASCAL's detection linearity and minimum detectable level (MDL) performance were obtained by Lee Smith et al. [4]. The MDL is defined as two standard deviations above the background level. It was determined that the MDL of N<sub>2</sub> for a 60-second integration time is approximately 13 ppm. This means it would take the RASCAL 60 seconds to detect a nitrogen concentration of 13 ppm and even longer time periods to detect lower concentrations. Measurements of increasing oxygen concentrations demonstrated the high degree of detection linearity obtainable with this system. The data were collected in a temperature controlled environment with the sample cell pressure at 10 atmospheres to obtain greater accuracy and better performance.

Many air contaminants such as SO<sub>2</sub>, H<sub>2</sub>S, O<sub>3</sub> and NH<sub>3</sub> have large normalized signal cross sections relative to N<sub>2</sub>, and therefore generate a Raman scattering signal greater than N<sub>2</sub> for a given concentration. This allows for greater detectability at any given sampling time. From their normalized cross sections, we are able to project the 60-second MDL for other gases of interest. These projections are listed in Table 3. In comparison with the published EPA National Ambient Air Quality Standards (Tables 1 & 2), the RASCAL does not have the ability to detect dangerous contaminant levels within 60 seconds of integration time for any of the contaminant gases.

### RASCAL II

The newer RASCAL II manufactured by Ohmeda employs a smaller and more power efficient air-cooled helium-neon (HeNe) laser with eight avalanche photodiodes (APDs) in its detection system. At one-third the size and weight of the RASCAL I, the RASCAL II is more attractive for space applications.

Table 3 Projected Sensitivity of the RASCAL I.  
(60-second integration time)

Molecule	Wave Number	Relative Cross-section	Projected MDL (ppm)
CH <sub>4</sub>	2914	[8.0]	1.6
CH <sub>4</sub>	3020	[0.79]	16.5
CO	2145	[0.9]	14.4
CO <sub>2</sub>	1286	[1.0]	13.0
CO <sub>2</sub>	1388	[1.5]	8.7
H <sub>2</sub>	4160	[2.2]	5.9
H <sub>2</sub> O	3652	[2.5]	5.2
H <sub>2</sub> S	2611	[6.6]	2.0
N <sub>2</sub> (reference)	2331	[1.0]	- 13 ppm measured
N <sub>2</sub> O	1287	[2.7]	4.8
N <sub>2</sub> O	2223	[0.53]	24.5
NH <sub>3</sub>	3334	[3.1]	4.2
NO	1877	[0.55]	23.6
O <sub>2</sub>	1556	[1.2]	10.8
O <sub>2</sub>	1103	[4.0]	3.3
SO <sub>2</sub>	519	[0.11]	118.2
SO <sub>2</sub>	1151	[5.5]	2.4

An experimental set-up consisting of a Medcor gas mixer, gas cylinders, and the RASCAL II was used to measure the RASCAL II's performance (see Figure 3). The gas mixer allows for the combination of two or three different gases according to the desired volume percent of each gas. Gas cylinders of ultra-pure argon, ultra-pure argon with nitrogen (N<sub>2</sub> at 1000 ppm), and ultra-pure argon with carbon monoxide (CO at 1000 ppm) were purchased from Scott Specialty Gases. Cylinders of oxygen were obtained from the Department of Anesthesiology at the University of Utah Medical Center. The reason why argon is used to measure dark count and to dilute the gas concentration is that it does not produce Raman scattering.

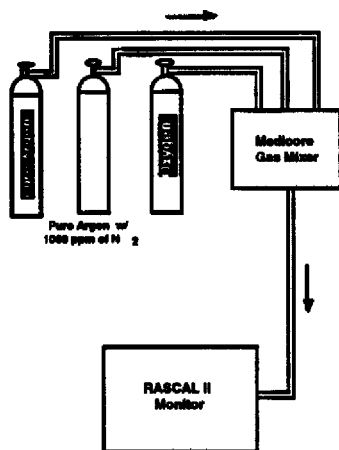


Figure 3. - Apparatus for measuring the sensitivity of the RASCAL II.

Nitrogen was diluted with argon to a known ppm concentration, and analyzed with the RASCAL II to determine the 60-second MDL. The linearity of the RASCAL II detection system was also measured. The linearity observed for the oxygen channel is shown in Figure 4. The same linearity is expected for all gases. Measurements were performed with the RASCAL II under normal operating conditions.

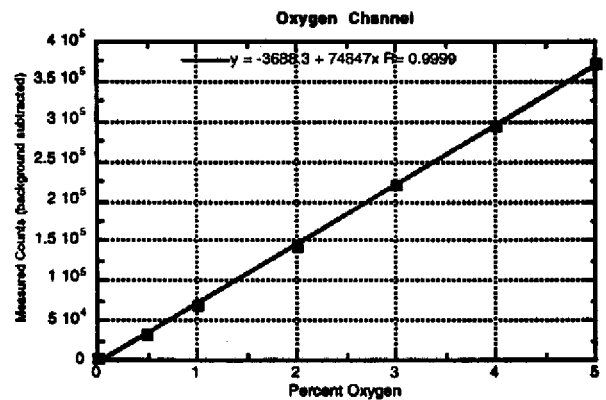


Figure 4. - Detection linearity of the oxygen channel (RASCAL II).

At room temperature, the APDs have a very high dark count. Those channels which detect low concentrations of the inhalation anesthetics employ a lower dark current detector to decrease the dark count and increase the signal-to-noise ratio. Hence, for channels detecting N<sub>2</sub> and O<sub>2</sub>, which are in high concentration, APDs having a slightly higher dark count were used. This high background level makes it very difficult to detect low concentrations of N<sub>2</sub> or O<sub>2</sub>. Therefore, when integrating longer to achieve greater sensitivity at low concentrations, the high background count became a limitation.

The background count was measured twice for each channel. With the laser turned off, the 60-second dark count was measured for the APD of each channel. With the laser on and a gas sample of pure argon in the sample cell, we again measured the background count for each channel. The counts increased significantly in some channels when the laser was on. Therefore, we can conclude that there is also Rayleigh and plasma line scattering

(spontaneous emission) that contributes to the background count. It should also be noted that there may be some signal crosstalk between the N<sub>2</sub> and N<sub>2</sub>O channels when light scattering occurs. The more accurate background count would then be the average count from multiple measurements of each channel, for a 60-second integration time, with pure argon as the sample gas. These values for each channel are then used as the zero levels for comparison with other measurements of known concentration gases. We define this procedure as argon zeroing.

In order to determine the 60-second MDLs for the RASCAL II, we first took a background measurement to use as a noise reference. This was done by supplying the RASCAL II with pure argon, and integrating for 60 seconds. Continuous measurements were made over a one-hour time period to collect 60 sets of background data. These sets were used to find the average background count and the standard deviation ( $\sigma$ ) of the signal for the nitrogen channel. The minimum detectable level (as defined by previous experiments with the RASCAL I) is the number of counts needed in order to have a signal level that is two standard deviations above the average signal level. In other words, the minimum signal that we can clearly detect will have a signal level that is  $2\sigma$  above the background noise. Having calculated the MDL count for the nitrogen channel, we steadily increased the concentration of nitrogen in argon (1000 ppm of nitrogen in argon) until the nitrogen channel signal level reached the MDL value. The smallest detectable concentration of nitrogen that would produce a signal equal to the MDL value was approximately 40 ppm. Knowing the MDL for nitrogen, we calculated the minimum detectable limit signal of other gases from their known scattering cross-sections. A table comprising the MDL levels of the RASCAL II is given as Table 4. It should also be noted that under normal operation the RASCAL II uses chemometrics in determining the concentration of each species detected.

The results show that for a 60-second integration the RASCAL II is capable of detecting approximately 40 ppm of nitrogen. Improvements on the commercially available version are needed to increase its sensitivity to meet the level of detection required by NASA for air quality monitoring. RASCAL II technology is sufficient when used to monitor ambient levels of O<sub>2</sub>, N<sub>2</sub>, and CO<sub>2</sub>, but not

capable of monitoring concentrations of nitrogen lower than ~40 ppm. Therefore, according to the projected MDLs of other gases, the RASCAL II would not be able to detect the low levels of contaminants specified under the "good" category in Table 2 without some modifications.

Table 4 Projected Sensitivity of the RASCAL II. (60-second integration time)

Molecule	Wave Number	Relative Cross-section	Projected MDL (ppm)
CH <sub>4</sub>	2914	[8.0]	5.0
CH <sub>4</sub>	3020	[0.79]	50.6
CO	2145	[0.9]	44.4
CO <sub>2</sub>	1286	[1.0]	40.0
CO <sub>2</sub>	1388	[1.5]	26.7
H <sub>2</sub>	4160	[2.2]	18.2
H <sub>2</sub> O	3652	[2.5]	16.0
H <sub>2</sub> S	2611	[6.6]	6.1
N <sub>2</sub> (reference)	2331	[1.0]	~ 40 ppm measured
N <sub>2</sub> O	1287	[2.7]	14.8
N <sub>2</sub> O	2223	[0.53]	75.5
NH <sub>3</sub>	3334	[3.1]	12.9
NO	1877	[0.55]	72.7
O <sub>2</sub>	1556	[1.2]	33.3
O <sub>3</sub>	1103	[4.0]	10.0
SO <sub>2</sub>	519	[0.11]	363.6
SO <sub>2</sub>	1151	[5.5]	7.3

The RASCAL II was designed to monitor anesthetic gases within a 250 msec integration time. For short integration times, the dark count of the APDs was not a limitation. Since the detected signal improves by the square root of integration time, it would be possible to integrate for a longer time period. However, when integrating for 30 seconds and longer, the background noise becomes the limiting factor. Further cooling the APDs to -30 °C would enhance the sensitivity of the detectors, but not enough to achieve low-ppm or sub-ppm detection levels. Fortunately, new technology in the area of Raman scattering and detection will allow for improvements to be made to enhance the RASCAL II design.

#### 4. NEXT GENERATION PROTOTYPE

During the past decade, several key instrumentation developments have come together to greatly improve the prospects for Raman scattering to become a more general purpose analytical technique [5]. These developments include: (1) the use of thermo-

electrically cooled CCD array detectors with high quantum efficiency and low noise for parallel detection of Raman spectra, (2) the use of laser excitation sources in the red to reduce fluorescence and (3) the availability of holographic filters to provide elastic-light rejection and improved overall throughput for Raman spectrographs.

The University of Utah is developing an enhanced Raman monitoring system which will meet NASA's specifications for detection of airborne contaminants at levels of less than 5 ppm. Two different HeNe intracavity lasers operating at 632.8 nm were designed to be used as the sources of scattering. The intracavity design is used because of the high intracavity powers obtainable. The laser manufacturer specifies that 40 watts intracavity is possible. However, we have not been able to attain more than 20 W.

To illustrate why the intracavity configuration works so well, we made a comparison of the Raman signal produced by the external beam of an air-cooled argon laser at 488 nm to that of the intracavity HeNe design. A Spex scanning spectrograph (model 1403) and a GaAs PMT (model C31034) were used to make the measurements. Using the argon 488 nm line at 72 mW, we measured the Raman signal of nitrogen (from room air) and obtained approximately 2100 counts/sec on the PMT. The Raman signal of oxygen was also measured to be ~660 counts/sec. As a check, we know that N<sub>2</sub> comprises 78% and O<sub>2</sub> 21% of ambient air, so the ratio of O<sub>2</sub> / N<sub>2</sub> is 0.2692. If we multiply this ratio by the number of counts/sec for nitrogen, and taking into account that oxygen has a scattering cross-section of 1.2 relative to nitrogen, we would expect the Raman signal of oxygen to be approximately 678 counts/sec, which is close to what we measured.

For the intracavity HeNe design, we must consider the difference in excitation wavelength from the argon 488 nm line because longer wavelengths produce less intense scattering by a factor of the fourth power of frequency. Taking the ratio of the two wavelengths to the fourth power, we obtain an  $\omega^4$  factor of 2.827. With seven laser lines present in the HeNe, it was estimated that the intracavity power was about 9.2 W. Since we are looking only at the scattering from the strongest line, which is the 632.8 nm line, we estimated the power of that line to be about 4 W. The ratio

of HeNe power to argon ion power is then 56. If we take that ratio, divide by the  $\omega^4$  factor, and then multiply by the 2100 counts/sec measured for nitrogen with the argon laser, we obtain an estimated value of 41,000 for the number of counts/sec we should see for ambient nitrogen from the HeNe laser. In our measurements we obtained approximately 20,000 counts/sec for nitrogen. However, the factor of two difference can be explained. When making the measurements with the argon laser, the beam was tightly focused so the power was more concentrated over the beam diameter. When using the intracavity HeNe, the beam diameter was approximately twice the size of the argon beam, so the power was spread over twice as much area parallel to the slit width. Therefore, we were effectively using only half of the beam when making the measurement. If we would have been able to collect the light scattered from the entire beam waist, we would have measured about twice as many counts, which would be in agreement with our expected value from calculation. In addition, we must keep in mind that the GaAs PMT has a lower response in the red region of the light spectrum and that the efficiency of the gratings in the spectrograph are optimized for use with the argon 488 nm line. Dispersion of the light increases as we move to the red, so for a fixed slit width, the light is spread out more. However, for the smaller, lighter, and less expensive intracavity HeNe laser, we are able to obtain a stronger Raman signal than with the external-cavity argon laser.

To further enhance the Raman signal, a holographic imaging spectrograph can be used. The Kaiser HoloSpec f/1.8i spectrograph utilizes Volume Phase Technology (VPT™) to provide a compact spectrograph with high efficiency. Employing a single holographic transmission grating, the spectrograph inherently scatters less light meaning it has a higher throughput. Holographic optical elements (HOEs) are easily manufactured and more economical. The available holographic notch filters can provide better than 10<sup>6</sup> attenuation of unwanted Rayleigh scattering. The low system f-number also helps to achieve excellent imaging and spectral resolution.

Signal detection using CCD technology offers advantages in comparison to PMT detection. A major advantage of CCD detection is that all species can be detected simultaneously. There is no need for selective

channels and filters to look at a specified peak in the spectrum of a particular species, as is the case with the RASCAL II. New silicon CCDs with extremely low background noise are now available to help increase the signal-to-noise ratio with a larger detection area. This can play a big part in the sensitivity of the monitor when trying to detect small Raman signals from samples with low concentrations of contaminants. A CCD will also provide better spatial resolution. Another advantage is the convenience of good software packages for signal acquisition and processing.

A new collection system has been designed to collect more of the scattered light. Normally only the light scattered towards the entrance slit of the spectrograph is collected and focused onto the entrance slit. The new system will implement additional collection optics so that more of the scattered light is directed towards the entrance slit of the spectrograph. In theory, by simply placing a spherical mirror directly behind the laser beam, we would expect to see approximately twice the amount of scattered light at the entrance slit of the spectrograph.

To collect the light that is scattered off in other directions, two parabolic reflectors are used in the configuration shown at the bottom of Figure 5. The idea is similar to that of an integrating sphere. The first reflector positioned around the sample cell will collect a portion of the light and focus it to the focal point of the second reflector which is also the focal point of the spectrograph. The second reflector may then be used to collect even more of the light, and through multiple passes between the reflectors, eventually focus the light onto the spectrograph.

The improved collection system in conjunction with a larger numerical aperture for the spectrograph will allow us to obtain a stronger Raman signal and achieve greater sensitivity. Implementing the new technology, we project that the new enhanced Raman monitor will have :

- A response time of 1 - 5 minutes
- Greater sensitivity; detection of 165 ppb for N<sub>2</sub> (which corresponds to an MDL of 30 ppb for SO<sub>2</sub>, the lowest concentration needing detection)
- Approximate size 10" x 14" x 20"
- Approximate weight 50 lbs.
- Power requirement ≤ 500 W total power.

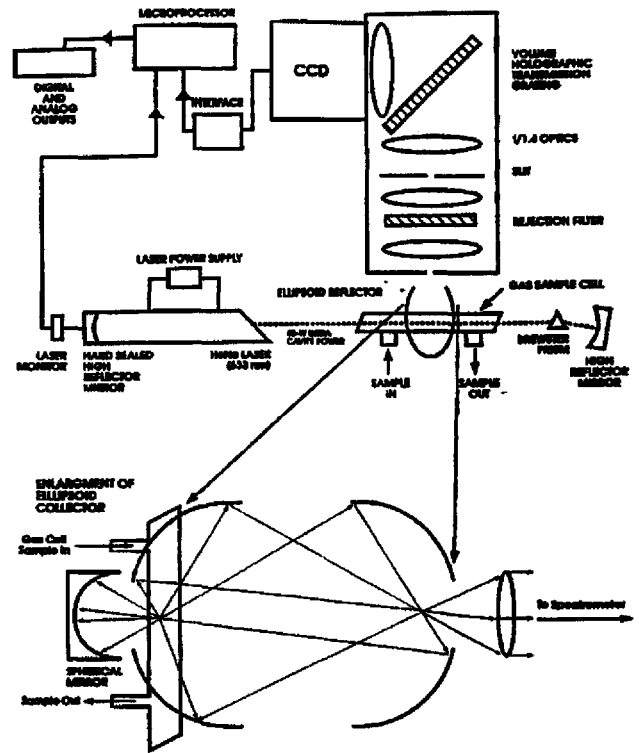


Figure 5. - Proposed full spectrum Raman analyzer.

## 5. FUTURE WORK

Characterization of several system components is still on going. This will help us understand exactly what type of enhancement factor is obtainable from each of the separate pieces of equipment. It will also aid in determining where signal is being lost and where improvements can be made to increase the signal-to-noise ratio. One important experiment will be to make a comparison of the detection and sensitivity of the CCD versus a PMT.

Since this project began, there has been a lot of interest in using Raman technology for other types of monitoring. Work has now begun on the design of a ventilation monitor for liquid breathing, similar to anesthetic monitoring with the RASCAL II. When a patient has lung lavage or respiratory distress, the lung can be filled with a liquid perfluorocarbon which allows for oxygen delivery through gaseous exchange. This liquid has a low boiling point, so it will boil off and be exhaled by the patient. It will be necessary therefore to monitor the amount of perfluorocarbon vapor being exhaled by the

patient in order to determine the amount of liquid needing replacement [6].

Work is also underway for development of a monitor that will work in the liquid phase. This will enable NASA to monitor water purity within the Space Habitat. Raman analysis in the liquid phase holds the possibility of using surface-enhanced Raman scattering (SERS)

which can provide a factor of  $10^3$  to  $10^6$  times signal enhancement. There is also interest in using this technology for drug monitoring in hospital patients. It is clear that Raman technology has matured to the point where it can be of use in many analytical applications.

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