

DEVELOPMENT OF A FULL-SPECTRUM RAMAN DEVICE FOR DETECTION OF ENVIRONMENTAL CONTAMINANTS

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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, environmental contaminants. We have collected laboratory data to benchmark current laser Raman technology for gas analysis, which provides a reference for future developments. The objective of this project was to design a prototype gas-phase monitor, incorporating new technology that would provide an accurate assessment of air quality aboard the space habitat. To accomplish this task, the monitoring system would need to be real-time, with full-spectrum capabilities for detection of all gas species contained in a sample. Finally, the instrument requires a high degree of sensitivity to detect gas concentrations in the low part-per-million range. Evaluation of the prototype instrument was performed to experimentally measure the lower detection limits for nitrogen and carbon monoxide. The experiments revealed several factors which were limiting the sensitivity of the system. These limitations can be resolved, and improvements will be implemented in a modified version of the device.

1. OBJECTIVE

NASA's plan for the Space Habitat Environmental Life Support includes sensors for environmental monitoring and control. Monitoring of gaseous environmental contaminants stems from the need to ensure a healthy and safe environment. In a closed system such as a space habitat, life sustaining resources of air and water must be regenerated and/or purified for reuse. To monitor the environment, NASA needs sensors that are able to measure common atmospheric gas concentrations as well as trace amounts of contaminant gases. The objective of this project was to design a prototype gas-phase monitor that would provide an accurate assessment of air quality. To accomplish this task, a monitoring system would need to be continuous, with a short measurement time. In addition, full spectrum capabilities are necessary for

simultaneous detection of all gas components in a sample, including both combustible and noncombustible contaminant gases. The species of main interest are oxygen, nitrogen, carbon monoxide, carbon dioxide, ozone, sulfur dioxide, NO_x, methane, pentane, ethylene, and ammonia. Finally, the system requires a high degree of sensitivity to detect gas concentrations in the low part-per-million range.

2. BACKGROUND

Raman scattering 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 the scattering 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 [1].

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 ν is the frequency of the light. As shown in Figure 1, when 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 [2].

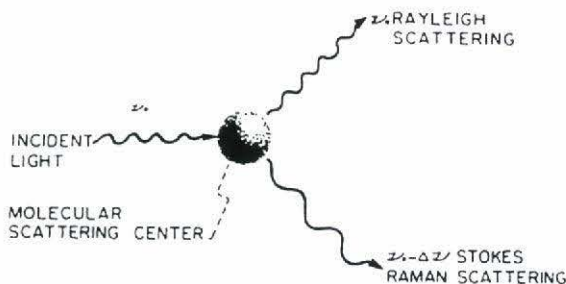


Figure 1. - Diagram of Raman energy transitions for both the Stokes and anti-Stokes lines.

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]. As an example of a typical Raman spectrum, the spectrum for liquid toluene is shown as Figure 2. This molecular "fingerprint" makes Raman scattering 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.

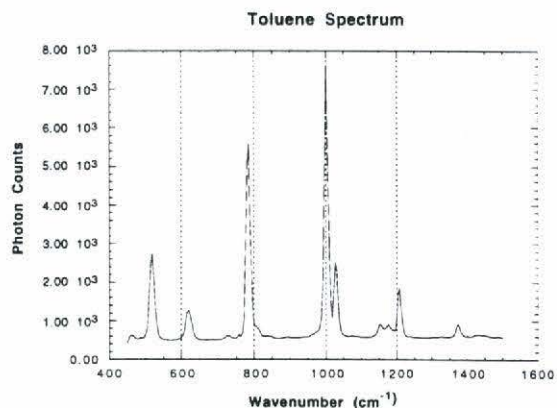


Figure 2. - A Raman spectrum for toluene.

3. AIR QUALITY STANDARDS

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 (low-ppm or sub-ppm), 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 integration period. The system must also have full-spectrum capabilities to simultaneously detect all gas components within the sample.

In order to know exactly what level of sensitivity would be needed, literature containing air pollution criteria was obtained from the Environmental Protection Agency (EPA). The EPA has spent an enormous amount of time researching the causes and effects of air pollution. As a result, federal law now requires every major city in the United States to monitor general air quality and specific pollutants on a daily basis. Several contaminant gases of primary interest are carbon monoxide (CO), sulfur dioxide (SO₂) and ozone (O₃). Each contaminant is individually monitored at least on a daily basis and rated according to the Air Pollution Index (API) shown in Table 1 [4].

Table 1 EPA Categories of Air Quality.
(all values given in ppm)

	Carbon Monoxide	Ozone	Sulfur Dioxide	API
				0
Good	0 - 4	0.00 - 0.06	0.00 - 0.03	
				50
Moderate	5 - 9	0.07 - 0.12	0.04 - 0.14	
				100
Unhealthful (alert)	10 - 14	0.13 - 0.19	0.15 - 0.29	
				200
Very Unhealthful (warning)	15 - 29	0.20 - 0.39	0.30 - 0.59	
				300
Hazardous (emergency)	30 - 39	0.40 - 0.49	0.60 - 0.79	
				400
Very Hazardous (never exceed)	40 - 50	0.50 - 0.60	0.80 - 1.00	
				500

For air to be clean and healthy ("good" category), contaminant concentrations cannot exceed 4 parts-per-million (ppm) of carbon monoxide (CO) in an 8-hour period, 60 parts-per-billion (ppb) of ozone (O₃) in a one-hour period and 30 ppb of sulfur dioxide (SO₂) in a 24-hour period. Each of these individual levels constitutes a rating of 50 on the API. The maximum individual concentration levels of the "moderate" category are given an index value of 100. This particular level is important because it is known as the National Ambient Air Quality Standard. The standard contains a value for the maximum concentration of contaminant allowable in a given time period. Concentrations in excess of these limits are potentially dangerous. This means that in order to maintain acceptable air quality, contaminant concentrations cannot exceed 9 ppm of carbon monoxide (CO), 120 ppb of ozone (O₃) and 140 ppb of sulfur dioxide (SO₂) for their respective time periods [4,5]. (Please see Table 2)

Any API rating below 100 below is considered to be acceptable and anything above this is considered to be unhealthy or hazardous. For any concentration falling between the maximum and minimum values of a particular category, the index rating is scaled within that specific range. This provides a standard by which to determine the level of sensitivity required by a monitoring system. The ideal situation would be to have the capability of detecting contaminant concentration levels which fall into the "good" category.

Table 2 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 mg/m ³)	—	9 ppm (10 mg/m ³)	—	—
Ozone	0.12 ppm (235 µg/m ³)	—	—	—	—
Sulfur Dioxide	—	0.5 ppm (1300 µg/m ³)	—	0.14 ppm (365 µg/m ³)	0.03 ppm (80 µg/m ³)
Nitrogen Dioxide	—	—	—	—	0.053 ppm (100 µg/m ³)

There are several methods of gas analysis that are capable of providing low-ppm detection sensitivity. NASA is currently using mass spectrometry for gas phase analysis. A mass spectrometer (MS) works by drawing in a gas sample, creating charged particles from the sample (e.g. molecular ions), sorting them based on mass-to-charge ratio, and then detecting the amount of a particular species. Molecules or fragments must be charged with an electric field, otherwise there is no method of distinguishing between different species. This must all be done under high vacuum conditions to increase the efficiency of ion transfers and detection. A mass spectrometer is capable of accurate, low-ppm measurements, with a response time of a few hundred milliseconds [6].

Despite the quick response time and sensitivity, there are several disadvantages which make this system undesirable for use in a space environment. The instrument is larger, heavier, consumes more power and costs five times more than a Raman instrument. An extensive filtering system may be needed to condition the gas sample, removing any particulates and water vapor that may be present. In addition, calibration of the MS is usually performed on a daily basis and requires several large, external calibration gas tanks. There is also a limit on the number of detection channels available.

In principle, Raman scattering has important practical advantages as a method of chemical analysis. The new technology available makes it possible to design a Raman instrument that has full spectrum capabilities. Nearly all Raman lines fall between 0 - 3500 cm⁻¹ (which is the visible region of the spectrum), for any excitation source in the range of 400-600 nm [7]. Therefore, it would have the ability to

simultaneously detect the Raman signal from all species in a sample. This is a major improvement over other instruments that are specifically designed to identify only one or two species.

Quantitative analysis is also important. Measurements with Raman are just as accurate and repeatable as those obtained using other methods. The sensitivity of Raman systems are continually improving and provide reliable, low-ppm concentration measurements. The response time for such measurements are on the order of 60 seconds.

A Raman monitor may be an on-line system with remote sampling capabilities, and only one spectrometer and one detector are needed to measure samples of gases, liquids or solids. In our case for gas phase analysis, only moderate filtering is needed to remove any particulates, and unlike MS, it can easily handle water vapor. The monitor is also self-calibrating, needing only a small amount of argon gas, as opposed to several large tanks required for calibration of the MS.

4. 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 AnaLyzEr. This first generation Raman scattering gas monitor was designed to measure anesthetic and respiratory gases to within 0.1%, with a 350 msec response time, using an air-cooled argon laser and six photomultiplier tubes (PMTs) for detection.

RASCAL II

To benchmark current abilities of Raman technology for gas phase analysis, laboratory experiments were performed to evaluate the Rascal® II anesthetic gas monitor manufactured by Ohmeda Medical, Inc. of Madison, Wisconsin. The Rascal II employs a smaller, more efficient air-cooled helium-neon (He-Ne) laser with avalanche photodiodes (APDs) in its detection system. It is designed to monitor for O₂, N₂, CO₂, N₂O and three anesthetic agents, with a

response time of 350 msec [8]. Consuming much less power and physically about one-third the size and weight of the Rascal, the Rascal II is more attractive for possible space applications.

An experimental set-up consisting of a Medigor gas mixer (Utah Medical SLC) and premixed gas cylinders were used to measure the sensitivity of the Rascal II (please 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. Premixed calibration gas cylinders of ultra-pure argon, ultra-pure argon with nitrogen (N₂ at 1000 ppm), and pure oxygen were obtained for making measurements. Since argon is monatomic, it produces no Raman scattering and is therefore ideal to use for dilution of other gases and for measuring the background count, or noise level of the system.

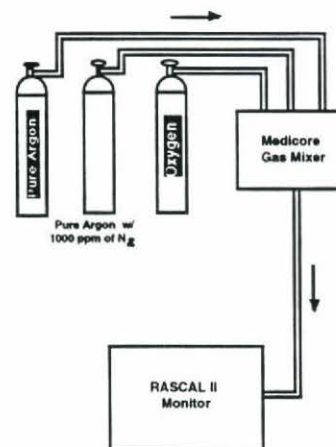


Figure 3. - Apparatus for measuring the sensitivity of the RASCAL II.

The objective of this evaluation was to determine the smallest concentration of nitrogen that could be detected by the Rascal II. Statistically, for any signal to be distinguishable from the noise of the system, the signal must have a value that is greater than or equal to the mean noise value plus the standard deviation (σ) of the noise. Therefore, to be sure we are measuring a Raman signal and not just noise, a minimum detectable level (MDL) was defined as the mean noise value plus two standard deviations of the noise. In other words, the minimum signal that we can clearly distinguish from the noise will have a value that is two

standard deviations above the average background count.

To determine the 60-second MDL for the Rascal II, we first took multiple background measurements to use as the noise reference. Once the average and standard deviation were calculated for the nitrogen channel, the MDL is set using those values. Having determined the MDL count for the nitrogen channel, we steadily increased the concentration of nitrogen in the gas mixture until the average count from the nitrogen channel approximately reached the MDL value. This procedure was repeated several times and an average nitrogen concentration was calculated. The smallest detectable concentration of nitrogen that would produce a signal approximately equal to the MDL value was 40 ppm. A graph for one group of measurements from this experiment is shown as Figure 4. It illustrates the method of determining the 60-second MDL concentration by finding the intersection of the calculated MDL line and the measured values.

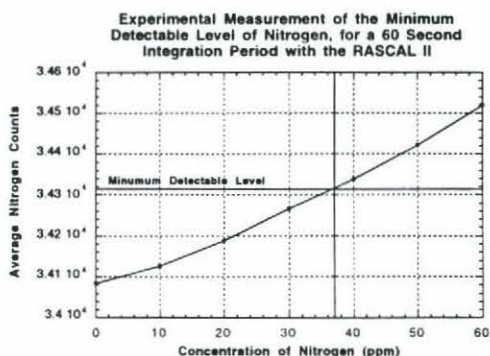


Figure 4 Experimental measurement of the 60-second MDL of the Rascal II.

Measurements of nitrogen were chosen because it is the reference gas for determining the scattering cross sections of other gases. Nitrogen is given a relative scattering cross section equal to one [9]. For a given concentration, many gases such as SO₂, H₂S, O₃ and CH₄ generate a Raman signal greater than N₂, and therefore have larger scattering cross sections. This is useful, in that rather than independently measuring the MDL concentration for each gas, we can project what they will be from their known scattering cross sections. In other words, once we have

determined the MDL concentration for nitrogen, we can calculate the MDL concentrations for other gases of interest. However, it would be appropriate to obtain measurements for more than just nitrogen to validate the projected values. Based on a 60-second integration period and our measured value for nitrogen, a table comprising the projected MDL concentrations for other gases we wish to monitor is provided as Table 3.

In comparison with the published EPA National Ambient Air Quality Standards [1,2], the Rascal II does not have the ability, within a 60-second integration period, to detect concentration levels specified in the "good" category of Table 1. The projected MDL concentration of CO is 44 ppm, which is a factor of 11x greater than the EPA value of 4 ppm. The biggest difference occurs with the values for SO₂. The projected MDL value of SO₂ is 7.3 ppm, which is 243x greater than the EPA value of 30 ppb. Since the detected signal improves by the square root of integration time, it would be desirable to integrate for a longer time period. However, when integrating longer to achieve greater sensitivity with low concentrations, the high background count becomes a limiting factor.

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

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

5. PROTOTYPE DESIGN

The objective of this project was to design a prototype gas-phase analytic monitor to be the next generation in Raman technology.

Advancements in collection systems, spectrographs and detectors have made it possible to provide full spectrum capabilities with the sensitivity to detect low concentrations. Our design incorporates a helium-neon, intracavity laser configuration to produce more intense Raman scattering, taking full advantage of the high intracavity power available. Compact spectrographs utilizing holographic technology are now commercially available, and essential for providing access to the entire Raman spectrum. Finally, charge-coupled device (CCD) technology offers low noise detection with the advantage of simultaneous measurement of all Raman spectra.

Similar to the Rascal II, the prototype monitor utilizes a He-Ne laser as the excitation source. The laser system was designed using an intracavity configuration, meaning that we are using the light that is confined within the laser cavity. As shown in Figure 5, the cavity is comprised of a He-Ne laser tube, a gas sample cell, and an external mirror mounted together with a Brewster prism. The sample cell is simply an open-ended, glass tube that surrounds a portion of the laser beam. The sample gas is pumped into the cell, where it interacts with the laser beam to produce Raman scattering. The Brewster prism is used to provide wavelength selection of the 632.8 nm laser line.

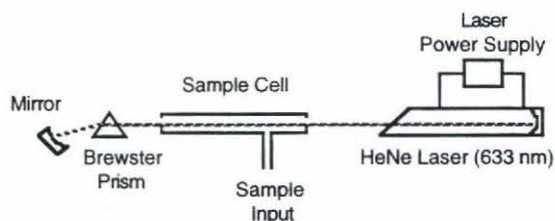


Figure 5 Intracavity laser configuration used for Raman scattering.

Typically, He-Ne lasers generate only 10 - 75 mW external cavity power at 632.8 nm [10], which is unfeasible for Raman scattering. However, power levels ranging from 5 - 50 watts can be generated inside the cavity. Research Electro-Optics, Inc. of Boulder, Colorado manufactures He-Ne laser tubes capable of generating high intracavity power for Raman work. Tube lengths of 10" or 11" were available, with and a choice of 0.061" or 0.079" as a core

diameter. The smaller diameter is for the TEM₀₀ mode only, while the other is capable of higher order modes.

The main criteria for the laser was to have a short cavity length and a small beam waist positioned at, or near the center of the sample cell. We wanted the beam waist to be less than 200 μm because the largest slit size of the spectrograph is only 167 μm. The size and position of the beam waist are primarily determined by the curvature of the two mirrors, and the overall length of the cavity.

The advantage to be gained by using an intracavity He-Ne laser is high power and small size. If we consider the typical argon laser used as part of the conventional research system, the laser itself is 4-5 feet long and requires a substantial amount of water for cooling. In addition, the output power available is generally only one or two watts. The He-Ne on the other hand is very small, air-cooled, and capable of high power. Assuming we can produce 40 watts of intracavity power with the He-Ne laser, versus one watt from the argon laser, we would gain a factor of 40 times enhancement of the Raman signal.

The spectrograph we chose for the prototype monitor was the HoloSpec f/1.8i manufactured by Kaiser Optical Systems, Inc. of Ann Arbor, Michigan. It is the first in a new line of holographic imaging spectrographs featuring significant advances in high performance laser spectroscopy [11]. The HoloSpec incorporates an f/1.8 collection system to collect a greater portion of the scattered light, which helps to achieve better imaging and spectral resolution. A holographic notch filter tuned to 632.8 nm serves as a pre-filtering stage to block unwanted Rayleigh scattering of the laser beam from entering the spectrograph.

Holographic optical elements are very advantageous because they are easily manufactured, more economical and significantly reduce the number of optical components needed in the spectrograph. As shown in Figure 6, the compact size of this system is the result of a single, volume holographic transmission grating that replaces several reflection gratings found in a conventional spectrograph. Holographic transmission gratings inherently scatter less light because the light is diffracted rather than reflected, which results in higher throughput.

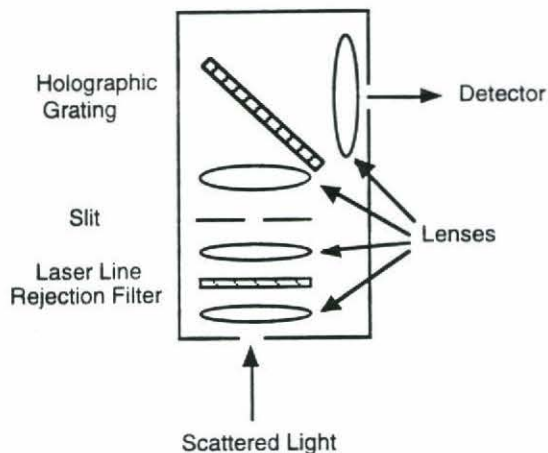


Figure 6 Basic layout of the f/1.8 holographic spectrograph.

In addition to higher throughput, the Kaiser instrument also covers a large spectral range. Relative to the 632.8 nm line of the He-Ne laser, the entire Raman spectrum can be covered by this spectrograph with two different gratings. The low-frequency grating covers all Raman shifts from 100 cm^{-1} to 2200 cm^{-1} , and the high-frequency grating covers shifts from 2200 cm^{-1} to 4000 cm^{-1} .

Simultaneous detection of many Raman spectra would be a difficult task using avalanche photodiodes. A separate detector and notch filter would be needed for each gas species being monitored. Charge-coupled device (CCD) technology eliminates the need for multiple filters and detectors, by offering the ability to measure many Raman spectra simultaneously, and without difficulty. CCDs also have a large dynamic range, which means they are capable of recording a wide variety of light intensities within a single measurement [33]. The basic function of a CCD camera is to convert incoming photons of light into electrons. The number of electrons stored by each pixel in the detector are then read out to a computer.

In contrast with a photomultiplier tube that is often used with the conventional spectrograph, CCD arrays generally have much higher quantum efficiency. A typical gallium-arsenide PMT used for photon counting has only 14% quantum efficiency at 680 nm, and decreases to 10% at 850 nm [12]. The quantum efficiency curve for the TC-241 array shows a peak efficiency of 70% at 680 nm, and then decreasing to about 29% at 850 nm [13]. Higher quantum efficiency available from CCD cameras

can be a major advantage when trying to detect weak Raman signals. Given the differences in quantum efficiency, and the ability to integrate for longer time periods, a CCD can provide about a factor of 10 times improvement over detection with a PMT.

The full-spectrum Raman monitor that we are proposing consists of the major components which have just been discussed. In theory, a substantial improvement in low-intensity Raman signal detection can be achieved through the implementation of these components to produce a highly-sensitive Raman monitoring device. If we combine the enhancement factors available from each piece of the system, we stand to gain an improvement of 2×10^5 over the conventional research apparatus. Therefore, based on the known capabilities of the research equipment, it is conceivable that the prototype system would have the sensitivity required to achieve detection of low-ppm and possibly sub-ppm concentrations of gases.

In summary, the complete prototype system as shown in Figure 7, would have the following characteristic features:

- An intracavity He-Ne laser design to obtain high power for increased signal intensity
- A small portable spectrograph such as the Kaiser Holospec, or something similar, utilizing volume holographic diffraction gratings, to maximize the overall throughput
- A low-noise CCD camera for simultaneous detection of multiple Raman spectra
- A set of ellipsoidal reflectors for collecting a greater portion of the scattered light

6. EXPERIMENTAL RESULTS

The objective of this evaluation was to determine the smallest concentration of nitrogen that could be detected by the prototype system, for an integration period of 60 seconds. The same premixed gas cylinders and gas mixer from the Rascal II experiments were also utilized in the experiments with the prototype. The Rascal II was replaced by our device, and the gas mixer was connected to the sample cell of the intracavity laser. The information we obtained was used to determine if the sensitivity of the

prototype was comparable to the sensitivity of the Rascal II.

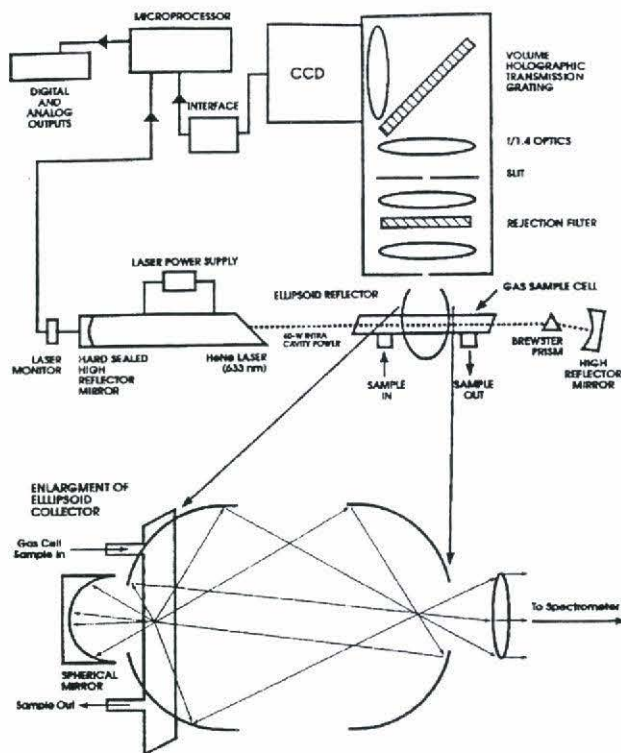


Figure 7 Proposed full-spectrum Raman analyzer.

To make a valid comparison between the prototype device and the Rascal II, it was important to consider the differences in detection methods of the two instruments. In the Rascal II, the Raman signal from nitrogen passes through a wavelength selective notch filter, and then is measured by an APD. In the prototype, there is no wavelength selective filtering, and the CCD camera is used to measure light for many different wavelengths. Therefore, we must find the location of the nitrogen signal, and consider only the portion of the CCD array which measures that signal.

To find the MDL concentration of nitrogen, it was necessary to use extrapolation of a line between the background average and measurements taken at higher concentrations. We had one gas tank containing 1000 ppm of nitrogen, and a tank of pure nitrogen that could be diluted down to 4000 ppm. The MDL concentration fell somewhere between those

two values, so measurements were taken at 0, 1000, 4000, 5000, 6000 and 7000 ppm of nitrogen, to generate points that could be used to extrapolate a line. An equation for the line was determined, and the calculated area under the curve required for the MDL was used to solve the equation for the corresponding nitrogen concentration. This procedure was repeated several times, and an average MDL concentration of approximately 1800 ppm was calculated for nitrogen. It must be mentioned that these experiments were performed without using a prism in the laser cavity, and without the ellipsoidal reflectors or spherical mirror. The reasons for this are to be explained in the conclusion section.

Based on the extrapolated MDL concentration for nitrogen, Table 5.1 shows the projected MDL concentrations for the other gases, calculated from their relative cross sections. In particular, NASA was interested in the ability of this system to measure low concentrations of CO. Therefore, to validate the projections calculated in Table 4, additional experiments were performed to determine the measured MDL concentration of CO, for a 60-second integration period. The experimental value for the minimum detectable limit of CO was approximately 2000 ppm, which agrees with the projected value.

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

Molecule	Wave Number	Relative Cross-section	Projected MDL (ppm)
CH ₄	2914	[8.0]	225
CH ₄	3020	[0.79]	2278
CO	2145	[0.9]	2000 * measured
CO ₂	1286	[1.0]	1800
CO ₂	1388	[1.5]	1200
H ₂	4160	[2.2]	818
H ₂ O	3652	[2.5]	720
H ₂ S	2611	[6.6]	273
N ₂ (reference)	2331	[1.0]	- 1800 ppm measured
N ₂ O	1287	[2.7]	667
N ₂ O	2223	[0.53]	3396
NH ₃	3334	[3.1]	581
NO	1877	[0.55]	3273
O ₂	1556	[1.2]	1500
O ₃	1103	[4.0]	450 *
SO ₂	519	[0.11]	16,364
SO ₂	1151	[5.5]	327 *

At this stage, the prototype is less sensitive than the RASCAL II, and also not yet capable of measuring the safe concentration levels established by the EPA. According to the

projected MDL concentrations in Table 5.1, the prototype is still a factor of 500 times short of having the sensitivity required to detect 4 ppm of CO. Although we did not achieve the level of sensitivity that was hoped for with this prototype, the possibility of getting there still exists. A great deal was learned about where the signal was being lost and what could be done differently to improve the performance. Extensive experiments with the prototype revealed several factors which were limiting the sensitivity of the system. Fortunately, these are limitations which can be resolved, and the necessary improvements will be implemented in a modified version of the device.

7. CONCLUSIONS

The objective of this project was to design a full-spectrum Raman device to provide an accurate assessment of air quality within the space habitat environment. We obtained information from the EPA concerning air quality standards, including limits on concentration levels of contaminant gases required to maintain a healthy environment. The category of air quality rated as the healthiest, contains ≤ 4 ppm of CO, ≤ 60 ppb of O₃ and ≤ 30 ppb of SO₂. Our primary goal was to achieve the capability to detect ≤ 4 ppm of CO and then work toward the greater sensitivity needed to achieve sub-ppm detection.

Experiments were conducted to evaluate our Raman device, and determine the gas concentration levels which represented the lower detection limits. At present, the prototype is capable of detecting 1800 ppm of N₂, 2000 ppm of CO, 450 ppm of O₃ and 327 ppm of SO₂, when integrating the Raman signal for a period of 60 seconds. The results indicate that we still need a factor of 500 times improvement to achieve the sensitivity required to detect 4 ppm of CO.

To achieve greater sensitivity, problems which contribute to the noise of the system must be addressed. Several solutions to these problems have been included with the evaluation sections above. Implementation of these solutions will effectively increase the sensitivity and bring down the lower detection limits, making it possible to detect ≤ 4 ppm of

CO. The areas where additional enhancement may be obtained are as follows:

- 8x higher intracavity laser power (from 5W to 40W)
- 5x optimized diffraction gratings
- 9x replacing the SBIG CCD with the Princeton Instr.
- 1.5x using a spherical mirror behind the laser beam
- 2x increasing the period of integration
-
- 1080x

With a factor of 1080 times improvement in sensitivity, we can project the prototype to be capable of detecting 2 ppm of N₂, 2 ppm of CO, 0.4 ppm of O₃ and 0.3 ppm of SO₂. Although we would meet the requirement of detecting ≤ 4 ppm of CO, the device still remains a factor of 10 away from reaching the ultimate goal of detecting ≤ 30 ppb of SO₂.

In conclusion, this project was very successful in demonstrating the feasibility of developing a full-spectrum Raman Instrument. The experiments which were conducted to evaluate the system have provided great insight into the areas where problems can occur, and have lead us to develop new strategies to overcome those problems. The prototype has proven itself to be a good design, and with continued development and proper modifications, the instrument will eventually achieve the sensitivity required for detection of sub-ppm gas concentrations.

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