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A LASER RAMAN SYSTEM FOR OBTAINING N_2 AND CO_2 CONCENTRATIONS IN PROBE-SAMPLED COMBUSTION GASES

ENGINE TEST FACILITY
ARNOLD ENGINEERING DEVELOPMENT CENTER
AIR FORCE SYSTEMS COMMAND
ARNOLD AIR FORCE STATION, TENNESSEE 37389

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This technical report has been reviewed and is approved for publication.

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A system for obtaining N_2 and CO_2 concentrations in probe-sampled combustion gases by means of vibrational Raman scattering of an argon laser beam passed through a small cell located in the sample transfer line has been designed and tested. The detectors consisted of conventional photomultiplier tubes windowed by narrow bandpass (~1 nm) interference filters and Rayleigh rejection filters. For N_2, the center wavelength of the filter was 584.6 nm

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20. ABSTRACT (Continued)

with a half-width of 1.2 nm, and for CO_2, the wavelength was 554.1 nm with a half-width of 1.3 nm. Laboratory tests with calibration gases indicated excellent system linearity with respect to species concentration and partial pressure. The detection threshold was found to be approximately 1 percent at a sample pressure of 0.5 atm. The factors which determine this limit were photomultiplier noise levels and out-of-band leakage of the Raman interference filters.

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PREFACE

The research reported herein was conducted by the Arnold Engineering Development Center (AEDC), Air Force Systems Command (AFSC), under Program Element 65807F. The results were obtained by ARO, Inc., AEDC Division (a Sverdrup Corporation Company), operating contractor for the AEDC, AFSC, Arnold Air Force Station, Tennessee. The work was accomplished in the Engine Test Facility (ETF) under ARO Project Number R32I-01A. The authors of this report were D. B. VanDyke and W. K. McGregor, ARO, Inc., and the manuscript (ARO Control No. ARO-ETF-TR-76-107) was submitted for publication on September 21, 1976.

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ILLUSTRATIONS

1.0 INTRODUCTION

The analysis of the constituents of a gas flow is usually accomplished by extracting a sample through a probe and either capturing it in a bottle for later analysis in the laboratory, or passing it through an on-line analyzer of some description. The latter method is to be preferred, generally, but the analyzer instrumentation is usually bulky, response is slow, and the constituents that can be analyzed are limited. One important limitation is that there are no commercial analyzer instruments for homonuclear species such as nitrogen (N_2), oxygen (O_2), or hydrogen (H_2). In this report, an approach to on-line analysis is described, which utilizes Raman spectroscopy and is capable of providing concentrations of many gases, including homonuclear species.

In recent years, the advent of compact high-power lasers has led to rapid growth in the application of Raman spectroscopy to diagnostic measurements in gas flows (e.g. Refs. 1 through 6). The attractiveness of the "Laser-Raman" (L-R) scattering technique has mainly stemmed from the possibility of direct, in situ measurements in such tenuous media as exhaust flows from combustion devices. Indeed, the in situ application has been successful (Ref. 5). However, the use of L-R scattering can also be very helpful in on-line analysis of sampled gases (Ref. 7). A case in point is the analysis of gases in mixing regions between combustion gas flows and external airflow, in which the objective is to measure the mixing rate of the two gas flows. The measurement of two species, one common to each flow such as N_2 and CO_2, would provide such a mixing rate measurement. The L-R technique offers a unique solution to the mixing rate measurement problem, and this application will be used here to illustrate the utility of L-R analysis cells in sampled gases.

The purpose of this report is to describe briefly the principles upon which the L-R analysis cell technique is based, the design features of a typical device, and the performance achieved. It will be shown that the device which was built and tested was moderately successful, but suggested modifications in the design would improve performance markedly.

2.0 PRINCIPLE OF OPERATION

When a beam of monochromatic light passes through a medium, one result of the interaction of the electromagnetic field of the light beam with the molecular species in the medium is a scattering event in which the frequency of the scattered light is either increased, or decreased by the frequency of a stationary energy state of the molecule (Refs. 8 and 9). If the frequency of the incident beam of photons is ν_o, then the frequency of the scattered photons will be either $\nu - \nu_o$ (Stokes line) or $\nu + \nu_o$ (anti-Stokes line) where ν_o corresponds to the energy between stationary states as illustrated in Fig. 1. If E' and E'' correspond to the ground and first vibrational states of a molecule, then the scattering is referred to as vibrational Raman scattering. In the work reported here, only the Stokes vibrational lines will be of interest.

A second kind of scattering may also occur, in which no change in frequency of the scattered photons takes place. This type of elastic scattering results from simple interaction between the electromagnetic field of the molecule and the photon beam and has been termed Rayleigh scattering (also indicated in Fig. 1).

Consider the scattering from a beam of laser light as shown in Fig. 2. The number of photons (Q_S) scattered per second into a solid angle (Ω) from a length of the beam (ℓ) of photons passing at a rate (Q_L) per second is given by (Ref. 1):

$$Q_S = Q_L N \sigma \ell \Omega$$

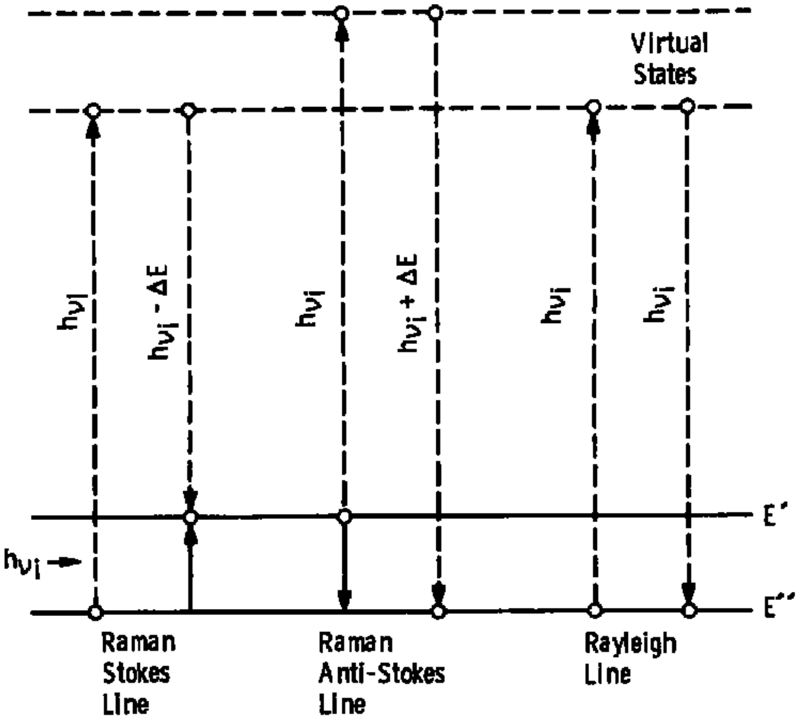


Figure 1. Energy level diagram.

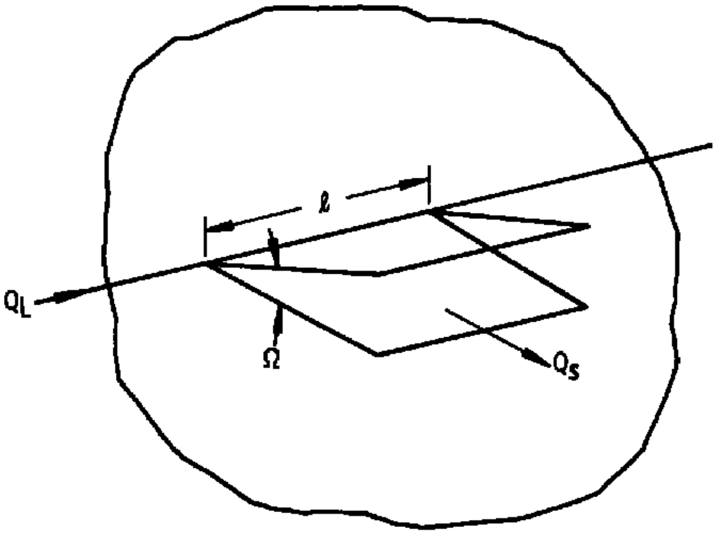


Figure 2. Scattering geometry.

where N is the density of scatterers and σ is the cross section for the scattering event and is much larger for Rayleigh scattering than for Raman scattering. For Raman scattering, σ is dependent on the particular molecule of interest, the temperature of the gas, and the frequency of the incident laser beam. As expressed in Eq. (1), σ is the total cross section for a vibrational transition, which in reality is spread over a finite frequency range because of rotational fine structure. Thus, σ must be defined for a particular bandpass ($\Delta\lambda$).

The number of photons per second registered by an instrument which views a length (ℓ) of the beam, collects all the photons scattered into a solid angle (Ω), and has a bandpass ($\Delta\lambda$) is given by

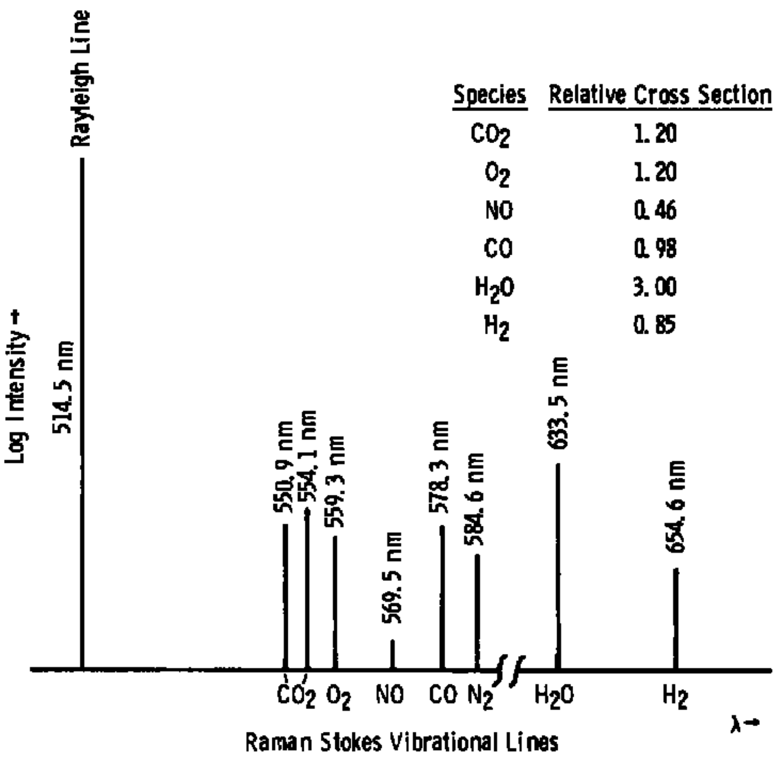
$$Q_s(\Delta\lambda,t) = \varepsilon\, Q_L\, N(t)\, \sigma\, (\Delta\lambda,t)\, \ell\Omega$$

where ε is an instrument efficiency factor. Now, in an analysis cell, the temperature may be maintained constant, the collecting optics and cell dimensions render ℓ and Ω constant, the instrument bandpass may be selected as a constant, the instrument efficiency is a constant, and the laser intensity may be held constant. Hence, for any species (i) which has a Raman transition, the rate of photon collection is just

$$Q_i = k_i N_i$$

where k_i is an instrument constant, which can be determined by calibration.

Raman vibrational spectra are made up mostly of $\Delta J = 0$ rotational transitions, so called Q-branch bands, which are closely spaced lines that are generally not resolvable. By treating them as single lines, species in an air-fuel combustion gas produced by the 514.5-nm line of an argon-ion laser are illustrated in Fig. 3. Note that the lines are sufficiently wide spaced that interference filters can be applied to each species. Also note the double line for CO_2 which is due to Fermi resonance (Ref. 8).



Species	Relative Cross Section
CO_2	1.20
O_2	1.20
NO	0.46
CO	0.98
H_2O	3.00
H_2	0.85

Figure 3. Relative intensities of Raman stokes vibrational lines for various combustion gases.

The cross sections relative to N_2 for the Q-branch bands of the species are also shown in Fig. 3 (Ref. 1). The relative sensitivity of an instrument for detection of each specie will follow the relative values of the cross sections.

3.0 ANALYSIS CELL DESIGN AND EVALUATION

3.1 MEASUREMENT OF SPECTRA

To determine spectral characteristics and signal levels, vibrational Raman spectra of CO_2 and N_2 were obtained for various pressure and concentration conditions using the laboratory set-up shown in Fig. 4. The beam from a Spectra-Physics model 170 argon-ion laser operating at 514.5 nm with a power output of 5 w was passed through a half-wave plate to rotate the plane of polarization 90 deg and then reflected by a front surface, plane mirror into the scattering chamber. This chamber consisted of a 10-in. section of 2-in.-diam mild steel pipe internally coated with flat black paint. The laser beam was brought into the chamber through a fused-silica window positioned at the Brewster angle to minimize reflection losses and forward scatter. After traversing the scattering chamber, the beam entered an energy absorbing dump, which consisted of a bundle of black steel needles mounted inside a short length of steel tubing. The viewing port was a 1-in.-diam fused-silica window cemented to the chamber wall. Opposite this window was a viewing dump similar to the laser dump described above. Vacuum fittings were provided for gas inlet and vacuum pump connections. The scattered radiation was collected by a system of lenses and focused onto the entrance slit of a 1-m Jarrell-Ash grating spectrometer, equipped with a 1,280 groove/mm grating blazed for maximum reflection of 600 nm and bilateral straight slits. Detection was accomplished by an RCA-1P28 photomultiplier tube mounted at the exit slit of the spectrometer and operated at ambient temperature. The photomultiplier output was amplified by an AD-520K preamp and recorded on a strip-chart recorder.

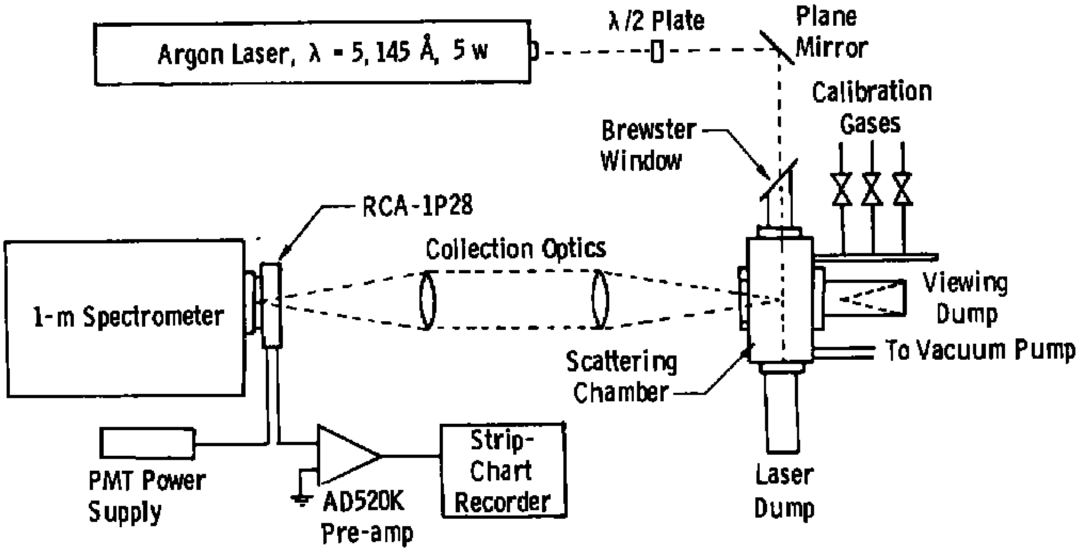


Figure 4. Laboratory set-up for obtaining Raman spectra.

Figure 5 is a Raman spectrum of room air showing the strong N_2 line at 584.6 nm and the O_2 line at 559.2 nm. Figures 6 and 7 were obtained for N_2/CO_2 gas mixtures by volume of 81.1 percent/18.9 percent and 98 percent/2 percent, respectively. The Fermi resonance effect for the CO_2 molecule is clearly shown by the two lines at 550.9 and 554.1 nm. The slit width used for obtaining these data was 100 μm, corresponding to a resolution of about 0.08 nm.

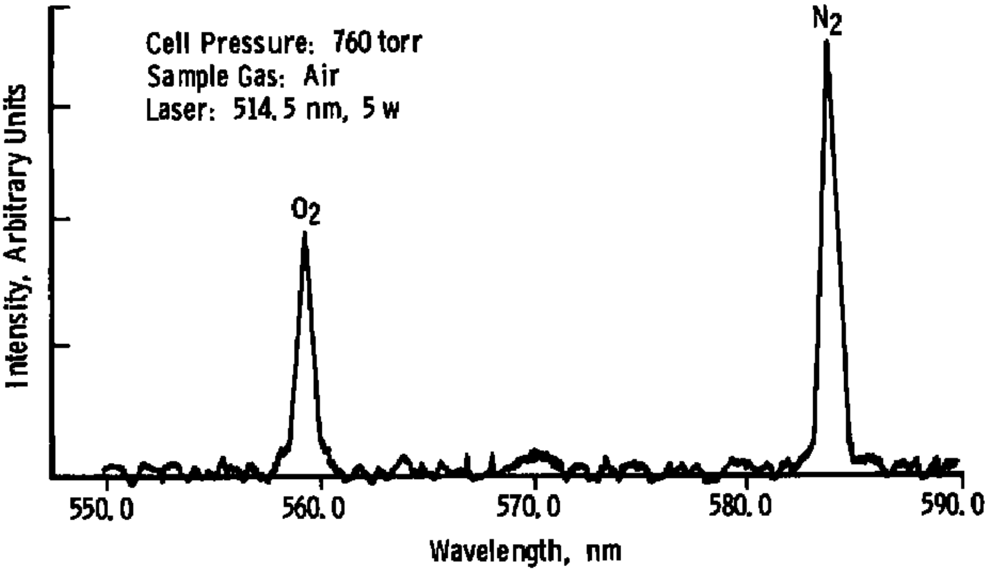


Figure 5. Vibrational Raman spectrum of air.

The data of Figs. 5, 6, and 7 are useful in selecting wavelength intervals, Rayleigh rejection filters, and other features for a compact, instrument-oriented, laser Raman analysis cell to be described in the next section.

3.2 CELL DESIGN

A diagram of the laser Raman analysis cell is shown in Fig. 8. To ensure precise optical alignment and to minimize volume, the cell was machined from 3-in.-long sections of 3-in.-diam aluminum bar stock. After all machining was complete, the cell was sand blasted to provide a matte finish and was then black anodized.

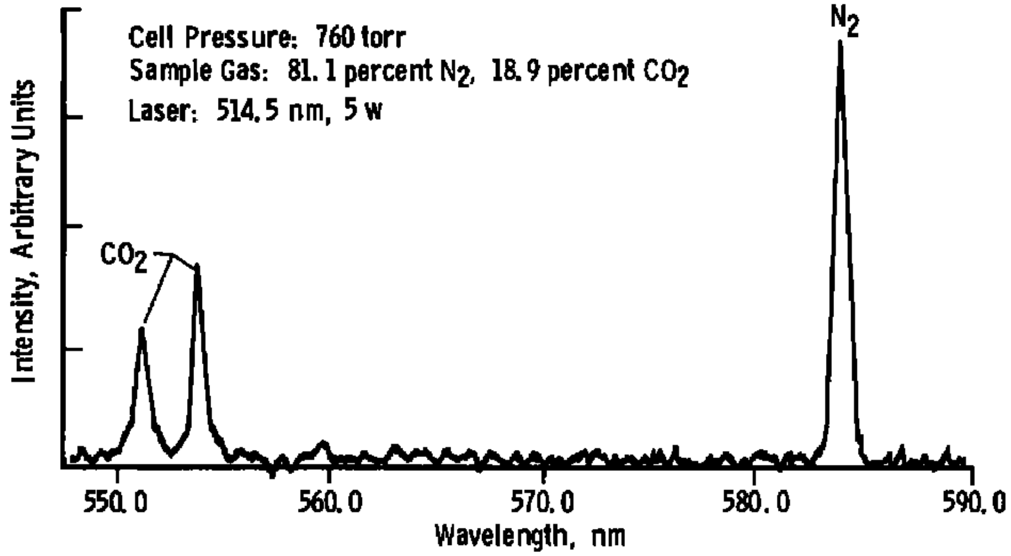


Figure 6. Vibrational Raman spectrum of 81.1/18.9 N_2/CO_2 gas mixture.

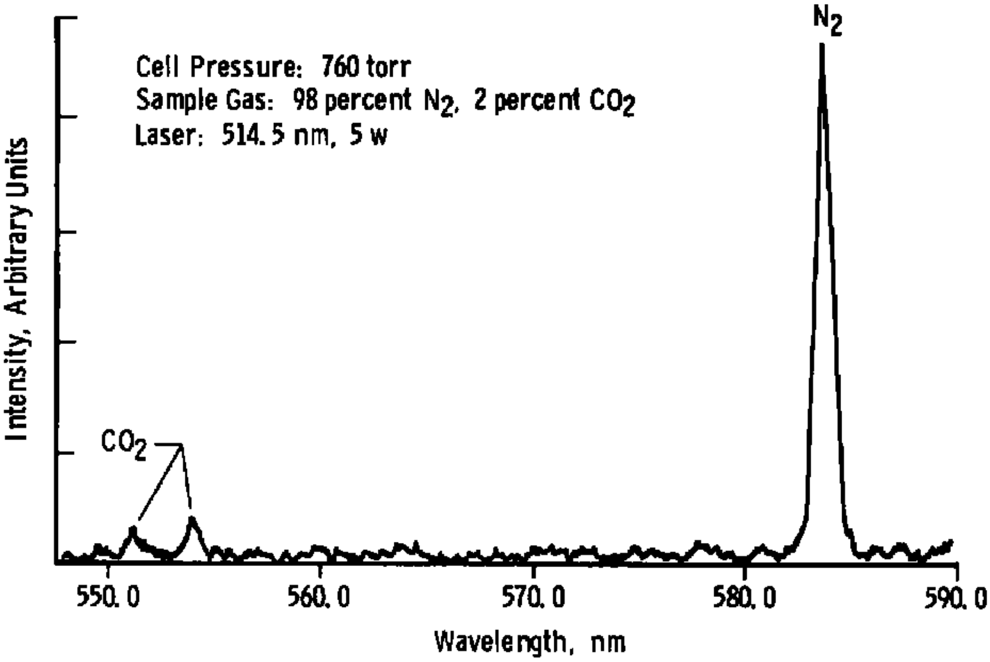


Figure 7. Vibrational Raman spectrum of 98/2 N_2/CO_2 gas mixture.

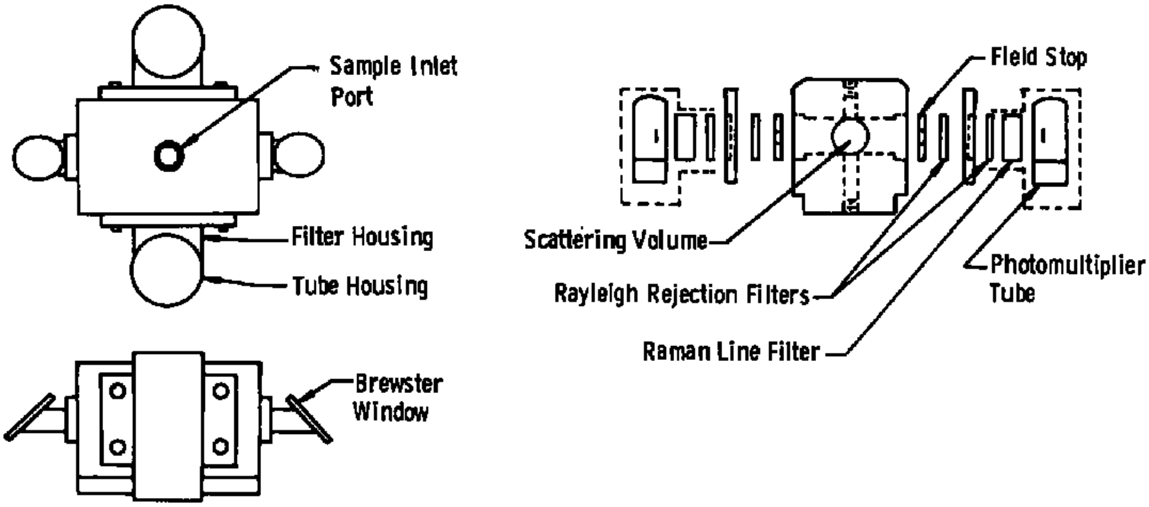


Figure 8. Laser-Raman analysis cell.

The laser beam enters the cell through a fused-silica window positioned at the Brewster angle to minimize reflection losses and forward scatter. The beam passes through the scattering volume and exits via another Brewster window. The spectroscopic element of the detection system consists of a narrow bandpass interference filter and two sharp cut-on absorption filters. The central wavelength of the interference filters correspond to the Q-branch Stokes line of CO_2 (554.1 nm) or N_2 (584.6 nm) for incident radiation at 514.5 nm. Further reduction of the Rayleigh component of the scattered radiation is provided by the two absorption filters. The spectral characteristics of the interference filters and the absorption filters are shown in Figs. 9, 10, and 11, respectively. The spectral profiles of CO_2 and N_2 as predicted in Ref. 1 are also shown in Figs. 9 and 10, respectively. At about 367°K (the temperature of the gas in the analysis cells), the Q-branch spectral widths of the CO_2 and N_2 Raman bands are about 6.0 and 4.0 nm, respectively, as indicated in Figs. 9 and 10 (Ref. 1).

The Raman scattered radiation is detected by commercial grade RCA 1P28 photomultiplier tubes specially selected for low noise and high gain. The tubes are positioned 90 deg from the laser beam optical axis. The

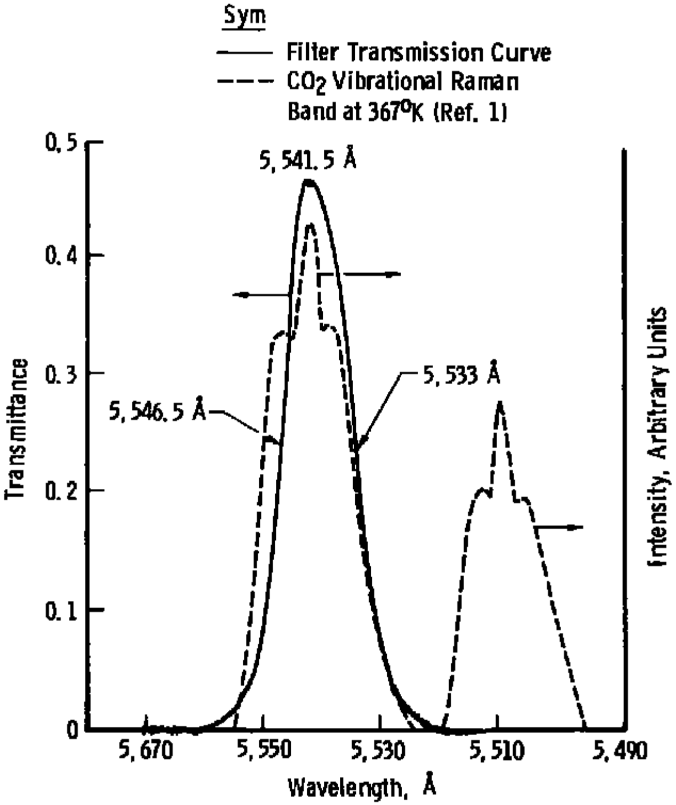


Figure 9. Spectral characteristics of CO_2 Raman line filter.

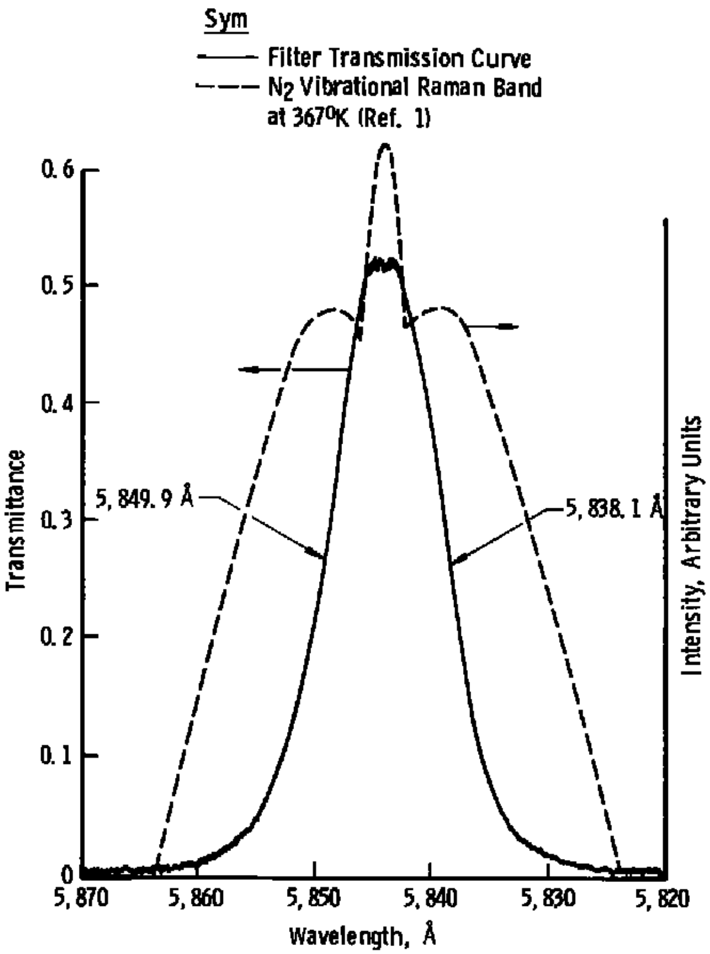


Figure 10. Spectral characteristics of N_2 Raman line filter.

output current from the photomultiplier is proportional to the rate of photon flux at the photocathode surface. The voltage produced by this current passing through a load resistor is amplified by an Analog Devices AD520K instrumentation amplifier. The AD520K is a closed-loop, high-gain operational amplifier with high-input impedance and an accurately predictable gain relationship. Single-resistor gain adjustment from 1 to 1,000 is provided as well as zero-offset trim adjustment. This variable-gain feature allows for optimum gain setting on each channel to compensate for variation in individual photomultiplier performance.

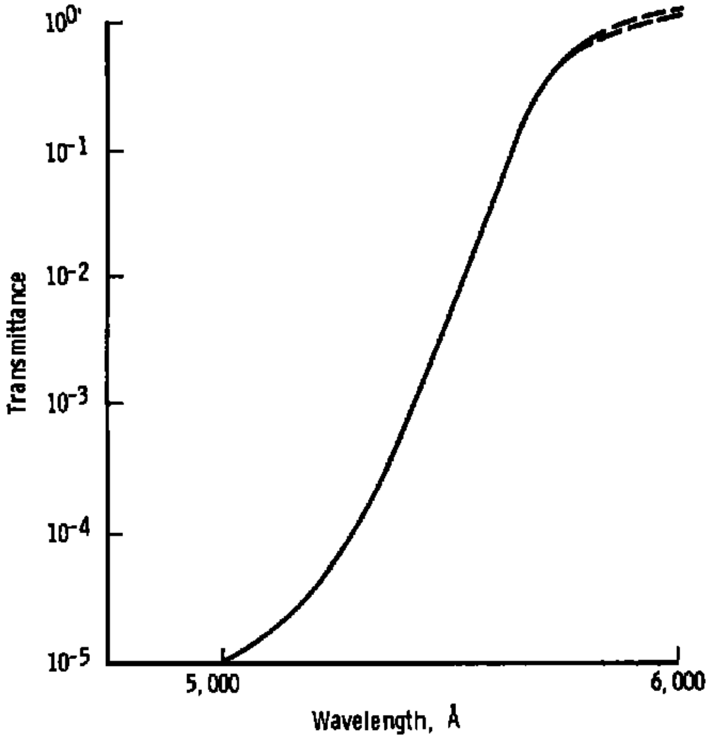


Figure 11. Spectral characteristics of absorption filter.

3.3 EVALUATION OF CELL PERFORMANCE

Laboratory measurements were made of N_2 and CO_2 concentrations in calibration gases to evaluate overall system performance and to establish criteria for calibration and data reduction procedures. The following calibration gases were used in these experiments:

1. N_2: 99.9-percent pure
2. 98-percent N_2 and 2-percent CO_2 (Scott Research Corporation)
3. 81.1-percent N_2 and 18.9-percent CO_2 (Scott Research Corporation)
4. Argon: 99.99-percent pure
5. CO_2: 99.9-percent pure

The pure argon, N_2, and CO_2 were used to establish 0- and 100-percent levels. The CO_2/N_2 gas mixes were then introduced into the analysis system, and signal output levels were recorded on strip-chart recorders. Data were obtained by averaging 15-sec records for the various gas mixtures. A typical strip-chart record for N_2/CO_2 gas mixtures of 81.1 percent/18.9 percent and 98 percent/2 percent is shown in Fig. 12.

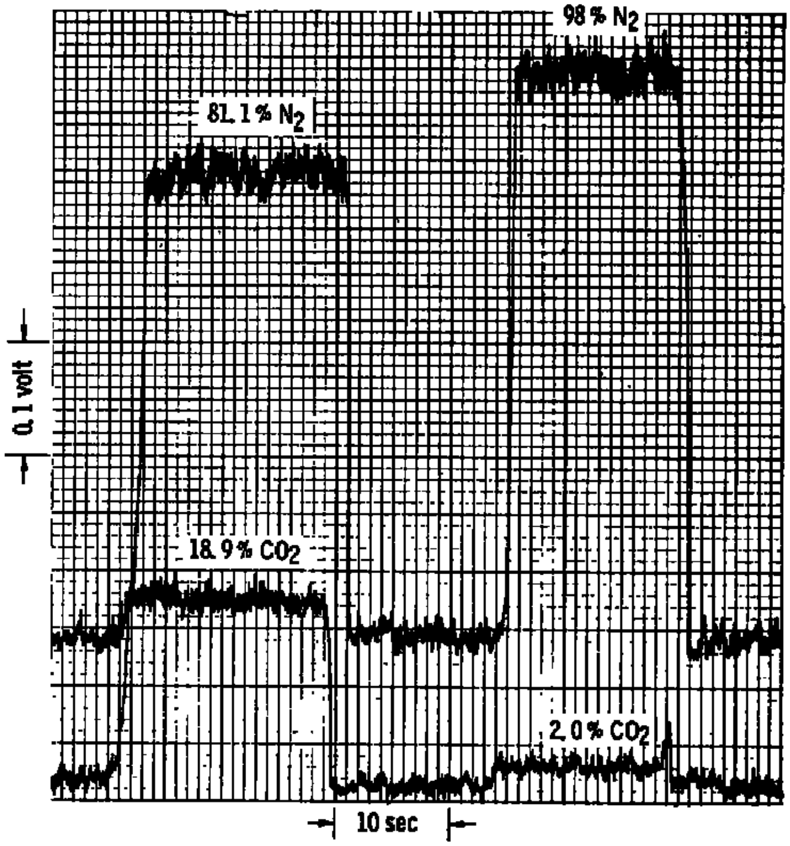


Figure 12. Laser-Raman cell calibration data.

Note that the equivalent noise level in each channel amounts to about 10 percent. From such measurements, the calibration constants were found for each cell. For the cell used to obtain Fig. 12,

$$N_{N_2} = 1.96\ V_{N_2}$$

$$N_{CO_2} = 1.18\ V_{CO_2}$$

where V is the signal expressed in volts, and N is the percent concentration of N_2 or CO_2.

Shown plotted in Fig. 13 are the normalized values for V_{N_2} and V_{CO_2} as a function of percent N_2 or CO_2. The linearity of the system is evident. Another demonstration of the linearity of the detection system is shown by the dependence of the output signal on the pressure of either

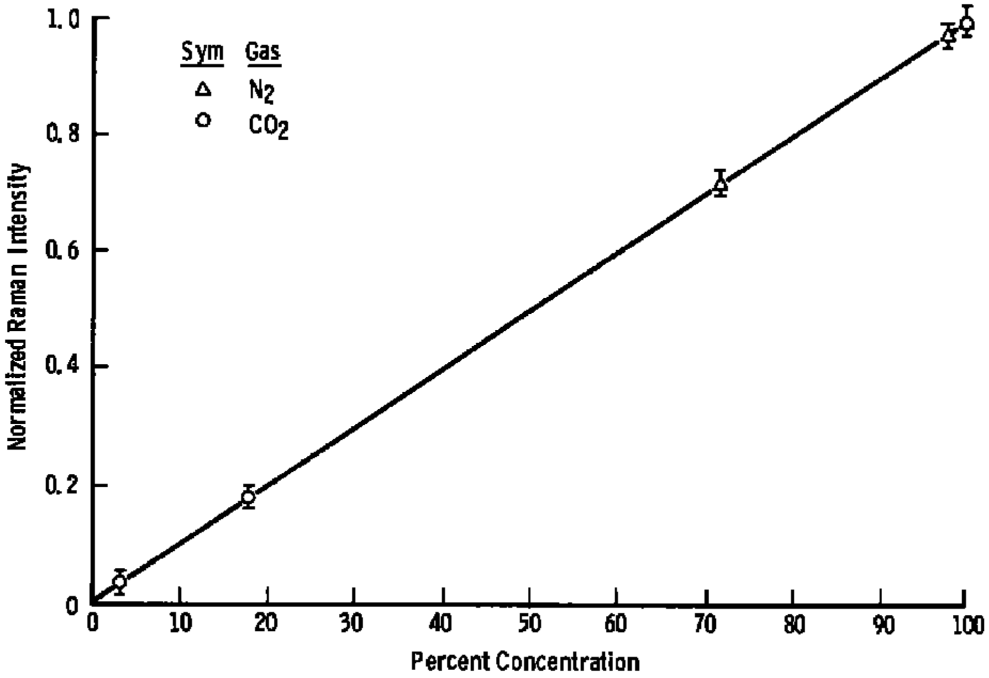


Figure 13. Raman intensity versus concentration.

pure N_2 or CO_2 in the cells, as shown in Fig. 14. Here, the normalized signal values are plotted versus pressure, and again the linearity is evident.

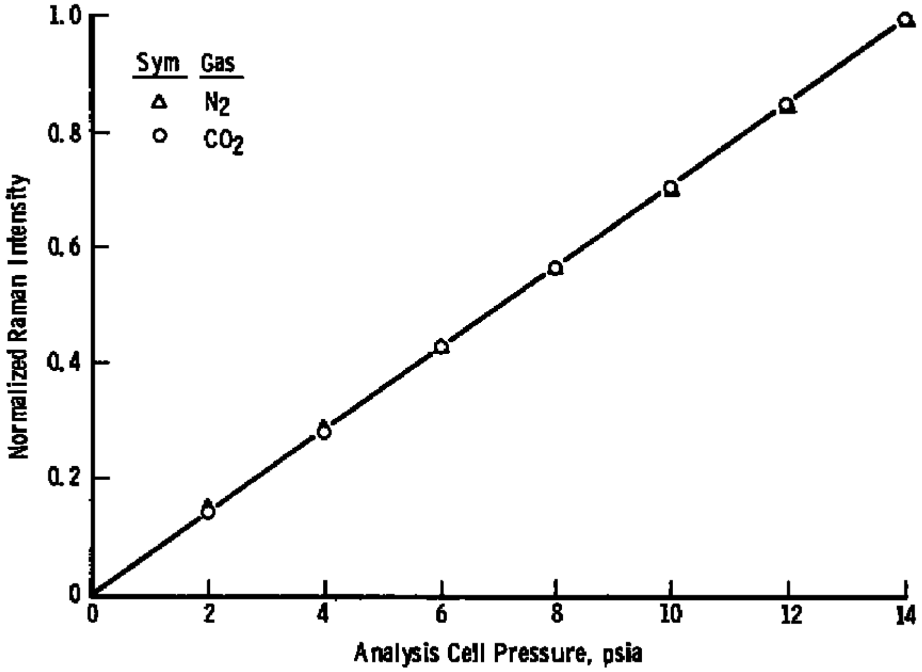


Figure 14. Raman intensity versus cell pressure.

3.4 DETECTION LIMITS

The lower limit for detection for both N_2 and CO_2 is approximately 1-percent concentration (signal-to-noise ratio equal to unity) at a sample pressure of 0.5 atm. This limit is determined by the internal noise levels and quantum efficiency of the 1P28 photomultipliers and to out-of-band rejection limitations of the optical system.

3.5 RECOMMENDED DESIGN MODIFICATIONS

The initial applications of the laser-Raman system described in this report have indicated several design modifications that could be made to improve the overall system performance. The major changes are outlined below:

1. Incorporate a focused collection system which will allow physical separation of the photomultiplier tubes and filters from the analysis cells. This will increase the collection efficiency and allow heating of the cell bodies to prevent condensation without adversely affecting detector performance.

2. Provide optical viewing dumps for all detectors to reduce observed background levels.

3. Provide a laser power monitor for the analysis cell. This would allow correction of cell calibration data in the event that variations occur in laser power or absorption or scattering occurs.

4. Incorporate low-noise, high-quantum efficiency photomultipliers rather than the conventional 1P28 tubes, thus increasing signal-to-noise ratios and lowering detection limits for the system.

4.0 SYSTEM APPLICATIONS

4.1 MULTIPLE CELL ANALYSIS SYSTEM

The first application of the laser Raman cell approach at AEDC was to the measurement of CO_2 and N_2 in samples extracted from the mixing region between a rocket engine exhaust plume and external, supersonic airflow in a wind tunnel. The requirement was mainly for the measurement of the ratio of CO_2 to N_2, but the system was structured such that the concentration of each species could be measured, provided the sampling system pressure was stabilized and good samples were introduced into the cells. The purpose of this section is to discuss the design of the laser Raman analysis system, without consideration of the specific nature of the test results.

The system consists of five identical analysis cells, in which N_2 and CO_2 concentrations in samples from a five-probe rake are to be measured. Primary radiation for all five cells is provided by an argon-ion laser operating at 514.5 nm with output power of 5-w continuous wave. The analysis cells and the argon laser are mounted on a 10-ft section of 6-in.-wide steel channel as shown in Fig. 15. This channel is bolted to a "unistrut" bench which provides mounting space for the detection electronics and allows the entire instrument to be moved as a unit. The analysis cells and a portion of the laser head are enclosed in an aluminum box hinged on one side for access to the cells. This box provides personnel protection from laser light scattered by the cell windows and reduces possible interference from ambient light sources. After passing through all five cells, the laser beam is absorbed in a light trap consisting of a bundle of black steel needles enclosed in a length of steel pipe and mounted on the aluminum cover as shown. Holes are also provided in the enclosure wall for sample inlet and outlet lines.

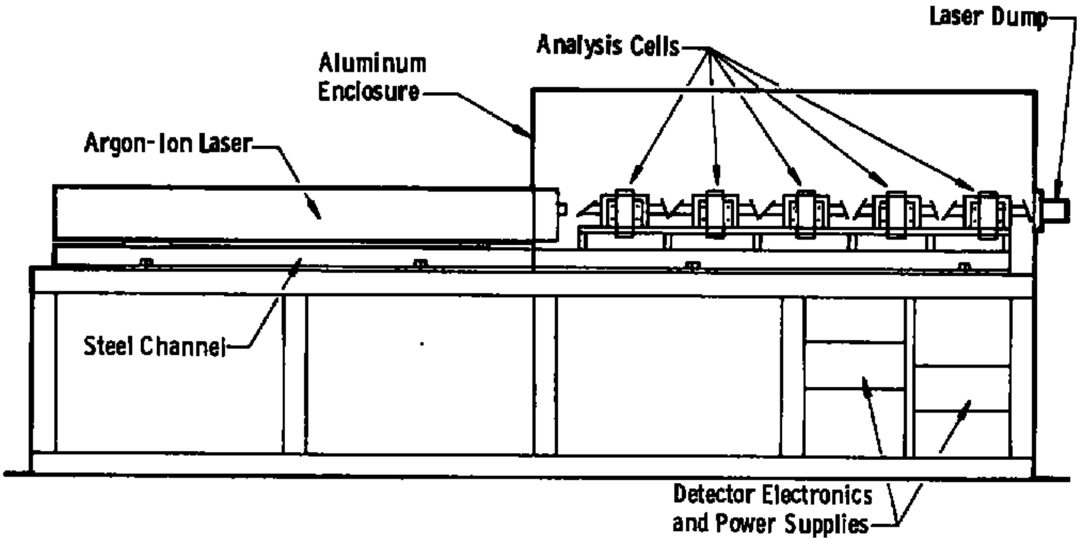


Figure 15. Laser-Raman system arrangement.

4.2 SAMPLE TRANSFER SYSTEM DESIGN CRITERIA

The design of the probe and sample transfer system by which combustion gases are delivered to the laser Raman analysis instrument will be determined, to a large extent, by mechanical considerations of the particular test configuration involved. There are, however, certain criteria which must be met in order to obtain useful data from the instrument. Of primary importance is that the system be vacuum tight. This allows the vacuum pump to thoroughly clean the system prior to the introduction of a new sample and prevents contamination of the sample by atmospheric nitrogen.

The sample must be free of particulate material in order to prevent large Mie scattering levels in the analysis cells. If solid particles or droplets of liquids from the exhaust are allowed to enter the cells, the intense scattering of laser energy will interfere with measurement of the relatively weak Raman signals. Adequate filtering of the sample as well as properly heated transfer lines must, therefore, be provided.

The sample must also be free of fluorescing species such as NO_2 and certain hydrocarbons (Ref. 7). The existence of these species in combustion gas samples will largely be determined by the particular fuel-oxidizer combination. Methods such as photo-dissociation or catalytic conversion may be used to remove the pertubing species from the sample.

5.0 SUMMARY

A system for obtaining CO_2 and N_2 concentrations in probe-sampled combustion gases utilizing laser Raman scattering was designed and tested. This system showed excellent linearity with respect to species concentration and sample total pressure. The principal limitations on detection threshold were found to be internal noise levels in the photomultiplier tubes and out-of-band rejection limitations of the interference filters used.

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