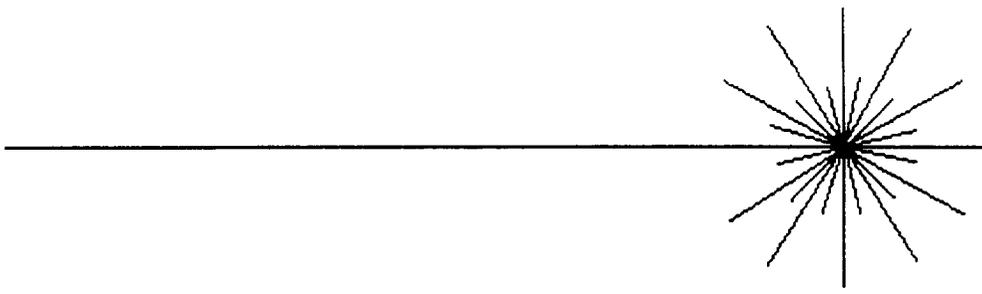


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Enhanced Raman Monitor Project



NASA - Ames Cooperative Agreement

No. NCC 2-890

"Development of On-Line Real-Time Environmental Monitor for Air and Water
Quality"

JWD
Technical Report 12/23/96

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SUMMARY

Monitoring of gaseous contaminants stems from the need to ensure a healthy and safe environment. NASA/Ames needs sensors that are able to monitor common atmospheric gas concentrations as well as trace amounts of contaminant gases. To provide an accurate assessment of air quality, a monitoring system would need to be continuous and on-line with full spectrum capabilities, allowing simultaneous detection of all gas components in a sample, including both combustible and noncombustible gases. The system demands a high degree of sensitivity to detect low gas concentrations in the low-ppm and sub-ppm regions. For clean and healthy air (“good” category), criteria established by the EPA requires that contaminant concentrations not exceed 4 ppm of carbon monoxide (CO) in an 8 hour period, 60 ppb of ozone(O₃) in a one hour period and 30 ppb of sulfur dioxide (SO₂) in a 24 hour period. One step below this is the National Ambient Air Quality Standard (“moderate” category) which requires that contaminant concentrations not exceed 9 ppm of carbon monoxide (CO), 120 ppb of ozone (O₃) and 140 ppb of sulfur dioxide (SO₂) for their respective time periods [1,2]. Ideally a monitor should be able to detect the concentrations specified in the “good” category.

To benchmark current abilities of Raman technology in gas phase analysis, laboratory experiments were performed to evaluate the RASCAL II anesthetic gas monitor manufactured by Ohmeda Medical Inc. of Madison, Wisconsin. Laboratory data

shows that for a 60 second integration period, the lowest concentration of nitrogen detectable by the RASCAL II is ~40 ppm. For other gases with known scattering cross-sections relative to nitrogen, we can project that the RASCAL II is capable of detecting 44 ppm of CO, 10 ppm of O₃ and 7 ppm of SO₂ during the same 60 second integration period. The standard RASCAL II does not have the ability to measure CO, O₃ or SO₂ for verification of projected values. The calculated projections and laboratory measurements for nitrogen show that the RASCAL II does not have the sensitivity to detect the concentrations specified in the NAAQS. A table of the projected minimum detectable concentration levels (MDL) in a 60 second period for other gases is provided as Table 1.

The prototype system design is a successful first step toward development of a highly sensitive Raman device capable of low-concentration gas analysis. Laboratory experiments show that the detection ability of the prototype is comparable to that of the RASCAL II. For a 60 second integration period the MDL of the prototype for nitrogen is ~82 ppm, which is two times the MDL of the RASCAL II. From the scattering cross-sections we can project that the prototype is capable of detecting 91 ppm of CO, 20 ppm of O₃ and 15 ppm of SO₂ during the same 60 second integration period. Please see Table 2. At this stage, the prototype is slightly less sensitive than the RASCAL II, but it has the major advantage of full-spectrum capabilities rather than selective detection of a few channels. Extensive experiments with the prototype revealed several obstacles contributing to the limitation of system sensitivity.

The maximum intracavity laser power we obtained with the Brewster prism in place was 5 - 10 Watts, and increased to 10 - 20 Watts without the prism. However, when operating without the prism, the power level was constantly fluctuating because of

competition between laser lines. Dust particles in the room also cause fluctuations in the power. Higher power is obtainable by significantly decreasing the cavity length to where only a few centimeters of space exists between the Brewster window and the free mirror, yet this does not leave room for the gas sample cell.

Measurements of the holographic transmission gratings showed less than optimal diffraction efficiency for the desired (p) polarization. The efficiency of the High Frequency Stokes Grating is especially poor. Experiments using a laser diode at 780 nm (approximate location of the nitrogen Raman peak from 632.8 nm excitation) shows a diffraction efficiency of only 18% for the (p) polarization. Efficiency curves at 670 nm, corresponding to the approximate location of the oxygen Raman peak from 632.8 nm excitation were also measured. Plots of the diffraction efficiency for both the high range and low range gratings for both polarizations are shown in Figures 1 and 2, where the angle θ is with respect to normal incidence.

We also found that the background floor of the CCD camera was drastically changing as a result of temperature fluctuations during and between measurements. It appears that by taking successive exposures, the camera CPU briefly neglects temperature control causing the temperature to increase by nearly 1° C. After the first three or four exposures, the temperature of the camera stabilizes and follows the preset value for remaining exposures. The software controlling the camera also produced a variable offset value used to avoid having numbers below zero. In addition, we discovered that the pattern noise increased with increasing integration time.

To achieve greater sensitivity, these problems contributing to the noise of the system must be eliminated. The smallest concentration we need to measure is 30 ppb of

SO₂ . If we can achieve that goal, then we can do well at measuring the other gases of interest. At present we still need a factor of 500 times improvement to achieve the sensitivity needed to measure 30 ppb of SO₂ . We recommend several solutions:

- First enclose the laser cavity to achieve greater stability and increase the laser power. Although the gas sample cell was free of particulates, the dust floating through the air in the room significantly interfered with the laser beam causing the power to continually fluctuate and limiting the maximum amount of power obtainable. Increasing the power from 5 W to 40 W provides a factor of eight times improvement.
- Next use a heated and pressurized gas sample cell. Although difficult to implement, a pressurized cell would help to increase the signal strength. The heated system is simply a method of avoiding condensation.
- Consider using an external cavity laser diode and enhancement cell configuration in place of the intracavity design.
- The Kaiser spectrograph implemented in the prototype system has many advantages. This type of spectrograph configuration with holographic gratings optimized for the (p) polarization would provide five times improvement .
- Consider using a more advanced CCD camera. Eliminating the temperature variation (which is a major contributor to system noise) and other problems by using a better CCD could improve performance by a factor of two.
- Use longer integration times to lower the minimum detectable concentration level by improving the signal-to-noise ratio. In general, the signal intensity improves by the square root of the integration time. If we integrate for a period of 4 minutes instead of one, then we gain approximately another factor of two.
- Finally, by using some additional collection optics such as a reflector or mirror behind the sample cell we can increase the signal by two.

5x optimized grating
8x higher laser power
2x better CCD
2x longer integration
2x back mirror
= 320x improvement

With a factor of 320 times improvement in signal, we can project the prototype to be capable of measuring 0.28 ppm of CO, 63 ppb of O₃ and 47 ppb of SO₂ in a 4 minute integration period. In comparison with the “good” category concentrations, we are well below the required 4 ppm for CO, right on target with the 60 ppb of O₃, and slightly above the 30 ppb requirement for SO₂. Therefore, with proper modifications and continued development, the prototype gas phase monitor would be capable of detecting sub-ppm concentration levels.

RASCAL II Projected Sensitivity

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

Table 1 Scattering cross-section and projected sensitivity (MDL) of the RASCAL II, for a 60 second integration time.

Prototype Projected Sensitivity

<u>Molecule</u>	<u>Wavenumber</u>	<u>Relative cross section</u>	<u>Projected MDL (ppm)</u>
CH ₄	2914	[8.0]	10.2
CH ₄	3020	[0.79]	103.8
CO	2145	[0.9]	91.1 *
CO ₂	1286	[1.0]	82.0
CO ₂	1388	[1.5]	54.7
H ₂	4160	[2.2]	37.3
H ₂ O	3652	[2.5]	32.8
H ₂ S	2611	[6.6]	12.4
N ₂ (reference)	2331	[1.0]	~ 82 ppm measured
N ₂ O	1287	[2.7]	30.4
N ₂ O	2223	[0.53]	154.7
NH ₃	3334	[3.1]	26.4
NO	1877	[0.55]	149.1
O ₂	1556	[1.2]	68.3
O ₃	1103	[4.0]	20.5 *
SO ₂	519	[0.11]	745.4
SO ₂	1151	[5.5]	14.9 *

Table 2 Scattering cross-section and projected sensitivity (MDL) of the prototype, for a 60 second integration time.

**Comparison of
Horizontal (p) Polarization
Kaiser Grating Efficiencies**

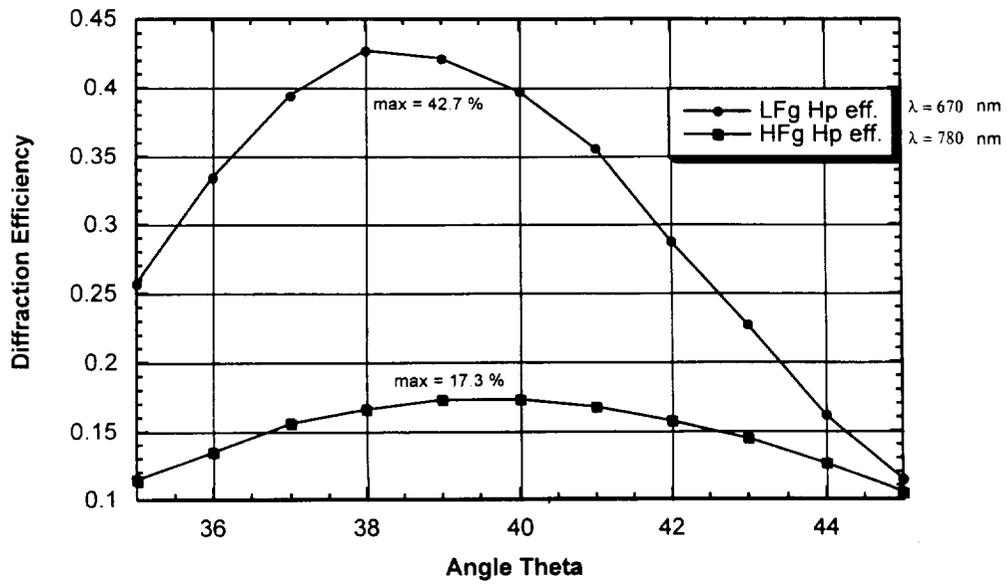


Figure 1 Diffraction efficiencies using the (p) polarization.

**Comparison of
Vertical (s) Polarization
Kaiser Grating Efficiencies**

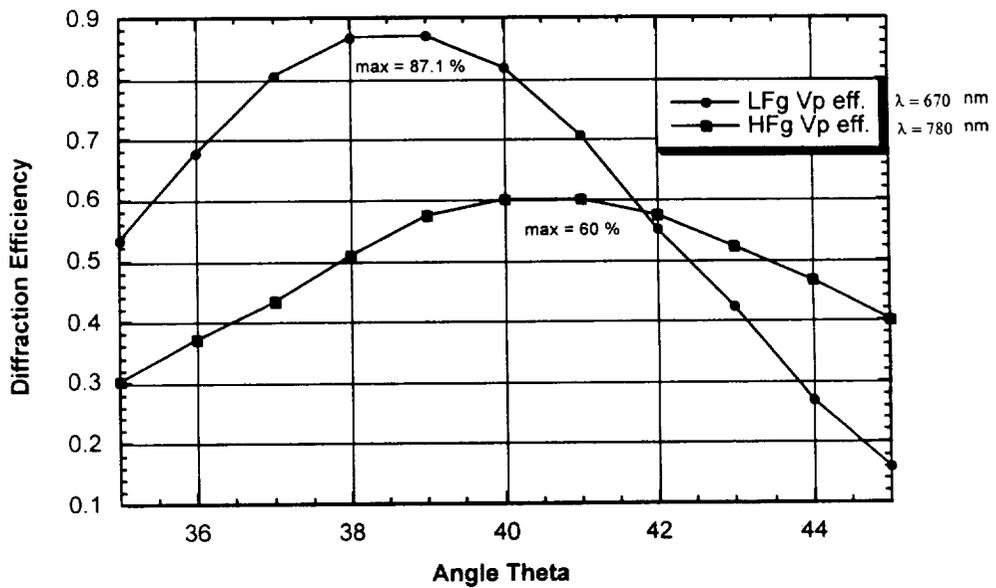


Figure 2 Diffraction efficiencies using the (s) polarization.

SYSTEM SPECIFICATIONS

Prototype Gas Monitor

Dimensions: length: 28.0 inches (70 cm)
 width: 23.0 inches (58 cm)
 height: 16.0 inches (40 cm)

(excluding the microprocessor)

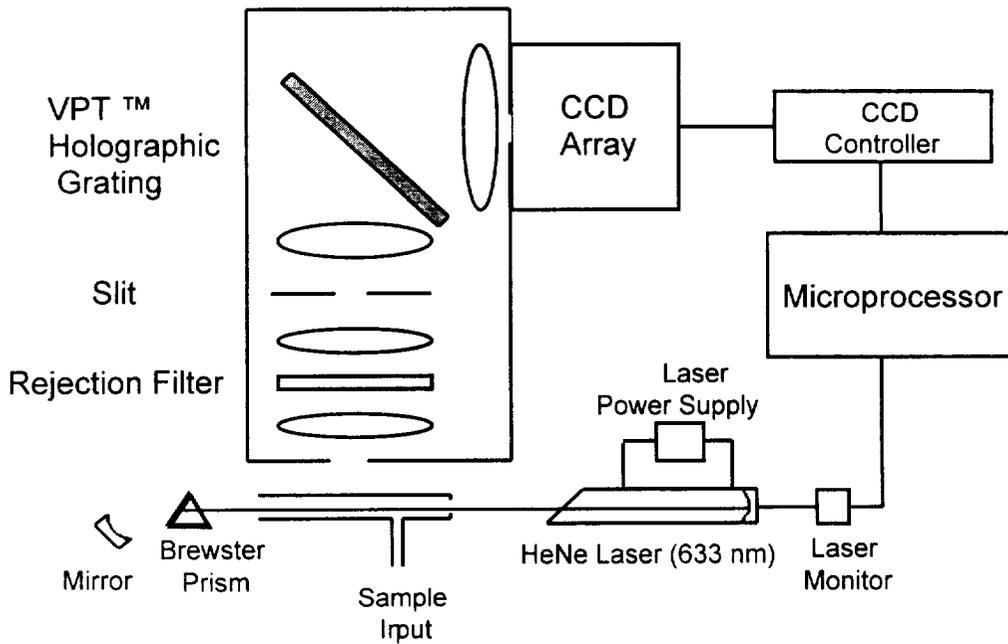


Figure 3 Prototype Configuration of the Gas Phase Raman Monitor

Laser Cavity

Two different HeNe intracavity lasers operating at 632.8 nm were designed for excitation sources. The intracavity design is desirable because of the ability to obtain high intracavity power averaging 40 - 50 Watts. Each design was based on the need to adjust the length of the cavity to include the gas sample cell and the brewster prism, using appropriate mirrors to position the beam waist at the center of the sample cell. The laser tubes and mirrors were manufactured and supplied by Research Electro-Optics Inc. of Boulder, Colorado. To test the lasers before shipping, they use a single line test bench and a cavity length of 290 mm. This means that only 20 mm of space available between the brewster window and the free mirror, and the prism occupies most of it. Therefore, the maximum power obtainable decreases as the cavity length increases to allow room for a sample cell.

Spectrograph

Kaiser Optical Systems Inc.'s HoloSpec f/1.8i is the first in a new line of Holographic Imaging Spectrographs featuring significant advances in high performance laser spectroscopy. The HoloSpec 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 higher throughput. VPT™ gratings are tuned to satisfy the conditions for Bragg diffraction for any wavelength between 400 nm and 1000 nm and therefore provide maximum diffraction efficiency at the wavelength of interest, generally for the (s) polarization. The grating produces a 90° fold, allowing the optics to be placed very close to the grating

without causing vignetting. The low f-number of this system also helps to achieve excellent imaging and spectral resolution.

The HoloSpec f/1.8i incorporates a pre-filter stage comprising a pre-aligned holographic notch filter tuned to the selected excitation wavelength. The available holographic SuperNotch™ filters can provide better than 10^6 attenuation of unwanted Rayleigh scatter. Holographic optical elements are advantageous because they are easily manufactured, more economical and significantly reduce the number of optical components needed in the spectrograph.

This spectrograph may be attached to all major CCD cameras and photodiode arrays with available adapter plates. However, if the array is not 24.6 mm wide, then you can only detect a portion of the light coming from the grating. The SBIG ST-6i CCD camera used in the prototype system has an array width of only 8.63 mm. We found it necessary to create a specialized plate in combination with a translation stage to be able to move the array across the entire grating. Therefore, we saw only one third of the spectral range of the grating at any one time.

Spectral Coverage: The standard gratings available with the HoloSpec f/1.8i are Stokes gratings with the wavenumber shift relative to an excitation wavelength of 632.8 nm. Assuming a 24.6 mm wide array detector, the gratings cover the following regions:

Low Frequency Stokes Grating: 100 to 2200 cm^{-1}

High Frequency Stokes Grating: 2200 to 4000 cm^{-1}

Linear Dispersion: Low Frequency Stokes Grating: 4.1 nm/mm
High Frequency Stokes Grating: 4.7 nm/mm

Resolution: Resolution is typically limited by either the slit width or the pixel size of the detector. Resolution can be determined by multiplying the limiting width (slit or pixel) with the linear dispersion.

High Frequency Grating

linear dispersion: 4.7 nm/mm ($104 \text{ cm}^{-1}/\text{mm}$ relative to 632.8 nm)

limiting width: 0.167 mm (slit) Resolution: 0.785 nm (17 cm^{-1})

limiting width: 0.023 mm (pixel) Resolution: 0.108 nm (2 cm^{-1})

Slit Height:	8 mm
Slit Widths:	50 μm , 100 μm , 167 μm
Aperture:	f/1.8
Focal Length:	85 mm
Weight:	18 lb.
Dimensions:	length: 17.5 inches (44 cm) width: 7.5 inches (19 cm) height: 6.5 inches (17 cm)

CCD Camera

The Santa Barbara Instruments Group manufactures CCD cameras that are mainly designed for use in amateur astronomy. They offer state of the art cameras at an affordable price, with low readout noise and high sensitivity capabilities. The CCD camera used in the prototype is the Santa Barbara Instruments Group (SBIG) ST-6i which utilizes a Texas Instruments TC-241 chip array.

Array Dimensions:	8.63 x 6.53 mm
Number of Pixels:	375 x 242
Pixel Size:	23 x 27 μm
A/D Resolution:	16 bit
Temp. Regulation:	closed loop
Readout Noise:	30e ⁻ rms

Full Well Capacity: 400Ke-
Weight: ~ 1.0 lb.
Dimensions: 6" diameter
3.25" height

Literature Cited

1. Code of Federal Regulations (CFR), Title 40 - Protection of Environment, Part 50
2. Code of Federal Regulations (CFR), Title 40 - Protection of Environment, Part 58

Relative Cross Section (RCS) References

- a. Fouche DG, and Chang RK. Appl Phys Lett, 20:256, 1972.
- b. Murphy WF, Holzer W, and Bernstein HJ. Appl Spectry, 23:211, 1969.
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- e. Penny CM, Goldman LM, and Lapp M. Nature, 235:110, 1972

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