Automated Remote Monitoring of Toxic Gases with Diode-Laser-based Sensor Systems

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ABSTRACT

Spectral Sciences has developed a family of automated remote gas sensors including a long-path absorption system, and a fiber-optic-based system utilizing multiple remote sensing heads. Results are presented from initial field tests of the long-path sensor.

INTRODUCTION

There is a growing need for compact sensor systems that provide reliable and automated monitoring of toxic gases and pollutants. Near infrared (NIR) diode lasers, originally developed for the communications industry, have the necessary reliability for use in such automated sensor systems. Spectral Sciences combines NIR lasers with its patented line-locked absorption techniques to create the DiRTiGAS family of automated sensor systems for continuous remote monitoring of gas concentration.

A broad variety of small polyatomic gases can be detected using GaAs-based diode lasers. Table 1 lists some representative gases along with the corresponding laser wavelengths, and projected minimum detectable column densities, based on our laboratory benchmark absorption detection limits of one part in 10^5 .¹⁻² We report here tests on NO_2 , O_2 , NH_3 , C_2H_2 , and CO_2 with two source modules operating at 760 and 1540 nm, respectively.

Our DiRTiGAS family of remote sensors uses modular components which can be assembled in two basic configurations for process control and ambient air monitoring. As shown in Figure 1, the fiber-optic configuration uses a central control unit linked by a fiberoptic network to remote sensor heads. The long-path configuration uses a similar control unit and a distant retroreflective target to monitor the concentration in the intervening distances. Figure 2 shows a fieldable prototype long-path unit, and a fiber-optic head developed for process water vapor monitoring in exhaust stacks at temperatures up to 650°C. This work describes laboratory tests of both systems, and preliminary field tests of the prototype long-path system. Based on these results, we have made design revisions which will be incorporated in a second stage long-path prototype. This prototype will be ready for β site tests in early 1994.

METHOD OF OPERATION

DiRTiGAS sensors are based on the line-locked absorption techniques described in recent publications.¹⁻⁵ The diode-laser output frequency is modulated about the center of a specific absorption line of the gas of interest. Molecular absorption is characterized by the ratio of the returned second harmonic signal, I_{2f} , to the returned first harmonic signal, I_{1f} . The laser is automatically locked to the center of the absorption line using an error signal developed from the

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third harmonic, I_{3f} , of the transmitted intensity through a reference cell contained in the laser source module. Gas concentration is calculated from the harmonic ratio, I_{2f}/I_{1f} , using analytic expressions for the line shape, and independently determined values for the molecular line strength and line width.^{1,4}

Embedded electronic components are used to control the laser operating conditions, process the returned signal into concentration values, perform periodic self calibrations, and display and store the gas concentrations. All operational parameters, such as laser set points, modulation amplitudes, and calibration functions are under software control. This allows a single sensor platform to be configured for multiple gases by changing the source module and software.

The exact laser operating temperature and current are determined from a scan of the laser temperature at constant current. Figure 3 shows a typical result of such a scan. The lower trace shows the third harmonic spectrum observed through the ammonia reference cell. The upper spectrum shows the simultaneous spectrum of ambient air over a 700 m optical path. The atmospheric spectrum is dominated by water and contains a number of CO_2 features such as the P6 line at 28.5° . The feature selected for ammonia monitoring is indicated by a dashed line showing the laser lock position. On close examination it can be seen to be displaced from the neighboring water absorption feature, and is therefore free of water interference. The laser operating parameters associated with the line center are recorded in a parameter file along with spectroscopic parameters for this line determined as in Ref. 1.

LABORATORY TESTS

A series of laboratory studies have demonstrated system calibration, long term stability, and detection of transient gas concentration. Analytical curves were generated using a gas cell inserted in the sample path with precalibrated gas mixtures. These curves all agree with the analytical calibration function computed from first principles. Figure 4 shows a representative curve for acetylene monitoring using the $\nu = 6497.2 \text{ cm}^{-1}$ line. Long term tests were also conducted with known samples. Figure 5 shows the results of two 24-hour tests, conducted over open air paths of 1.7 and 12 m, monitoring the minor $^{18}\text{O}^{16}\text{O}$ isotope at $\nu = 13097.3 \text{ cm}^{-1}$. The lower curve demonstrates the variations in instrument background signal that limit sensitivity. The long term variation is equivalent to an rms optical depth variation of 1×10^{-5} . The short term variations are smaller than 10^{-6} . The upper curve shows additional variation due to real fluctuations in O_2 density due to temperature variations in the laboratory. Similar tests with the major O_2 isotope and water vapor have demonstrated better than 2% absolute accuracy over a four-order-of-magnitude variation in optical depth.²

Figure 6 displays a calibration test of the DiRTiGAS fiber-optic probe with a chilled mirror dew point monitor in a controlled humidity chamber. Data are plotted along with theoretical calibration curves for two isothermal tests at 53°C and 93°C . Theory and data agree within the accuracy of the chilled mirror device and the spatial variability of temperature and humidity in the test chamber. Other work has demonstrated good agreement with theory over a water vapor temperature range of $0\text{-}400^\circ\text{C}$.⁵

Figure 7 illustrates the detection of a variable gas concentration in a Bunsen burner flame placed within the optical path. Acetylene concentration was measured using the $\nu = 6494.5 \text{ cm}^{-1}$ absorption line while varying the fuel and air supply. The trace starts out with a "HOT" well-mixed blue flame a small acetylene concentration. Turning off the air supply results in a "COLD" flame with a yellow color, and a highly variable acetylene concentration, data are recorded on a one second time scale.

PROTOTYPE FIELD TESTS

A fieldable prototype long-path sensor has been tested with a variety of source modules and gases, over an ambient temperature range of 15-40°C. Multiple-day runs were conducted for several gases over a 700 m optical path between our laboratory building and the edge of a major controlled access highway 350 m away. This is the maximum unobstructed line-of-sight available from our building. Analysis of the returned signal indicates similar operation could be achieved at path lengths in excess of 2 kilometers. Representative data for acetylene at $\nu=6495.9\text{ cm}^{-1}$ and carbon dioxide at $\nu=6493.4\text{ cm}^{-1}$ are shown in Figures 8 and 9. The measured average acetylene concentration over the path was 0.03 ± 0.01 ppm. The signal variation is consistent with long term drifts seen in all of the above preliminary field tests. As we have not yet completed the calibration process for this CO₂ line, the reported concentrations are based on literature values for the line strength and line width⁶ and may differ from the true concentration by a multiplicative constant. The measured CO₂ signal is more variable than the measured C₂H₂ signal, and may reflect in part variations in CO₂ concentrations.

Table 2 summarizes the results of the preliminary tests on four gases. Detected concentrations and standard deviations are expressed in terms of average concentrations over the 700 m optical path. As expected, CO₂ was the only gas with significant detectable concentrations. The measured concentrations of NO₂, C₂H₂, and NH₃ were well below the detection limit required for most industrial trace gas monitoring and process control applications.

CONCLUSIONS

We have demonstrated automated long term operation of diode-laser-based sensor systems with absorption detectivities as low as 10^{-5} and absolute accuracy over a five order of magnitude dynamic range. Initial tests of a fieldable prototype long-path sensor system have successfully demonstrated monitoring of several representative gases over a range of ambient conditions. Based on the results of these tests, we are completing design modifications which will be incorporated in a second stage prototype system. This system will be ready for β site tests in early 1994. These prototypes feature modular construction and software control which allow them to be configured for monitoring a variety of trace gases in a number of applications including process control, continuous emission monitoring, fence line monitoring, and fugitive emission monitoring.

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Table 1. Gas detection with GaAs-based diode lasers.

GAS	λ (nm)	Minimum Column Density (ppm-m)*
O ₂	760	100
NO ₂	760	2
HCl	1193	16
HF	1321	0.02
HCN	1540	0.1
NH ₃	1540	2
C ₂ H ₂	1540	0.4
CO ₂	1540	500
CO	1570	35
H ₂ S	1580	15
CH ₄	1650	5

*based on a fractional absorption of 10^{-5} .

Table 2. Field measurements with a target distance of 350 m.

Molecule	λ (nm)	24 hour Density Averages (ppm)	
		ρ	σ
CO ₂	1540.2	465	19
C ₂ H ₂	1539.4	0.03	0.01
NH ₃	1539.3	1.2	0.4
NO ₂	756.8	0.22	0.09

Figure 1. DiRTiGAS configurations for remote sensing.

Figure 2. Fouling resistant fiber optic head for high temperature environments and the fieldable prototype long-path sensor system.

Figure 3. Simultaneous scan of ambient air (sample) and reference cell harmonic spectra showing the lock point for ammonia.

Figure 4. Theoretical and measured calibration for C_2H_2 .

Figure 5. Laboratory measurements of $^{18}\text{O}^{16}\text{O}$ column density over 1.7 m and 12 m paths.² Predicted ranges are based on the standard composition of air and observed temperature variations.

Figure 6. Cross calibration of DiRTiGAS fiberoptic sensor vs a chilled mirror dewpoint monitor at two temperatures. Solid lines are the theoretical curves.

Figure 7. Time record of C_2H_2 concentration in a Bunsen burner flame. High and low refer to fuel flow rate.

Figure 8. Two day field measurement of average C_2H_2 concentration over a 350 m path. The time base is referenced to midnight of day 1.

Figure 9. Two day field measurement of average CO₂ concentration over a 350 m path. The time base is reference to midnight of day 1.