

Infrared overtone spectroscopy measurements of ammonia and carbon dioxide in the effluent of a biological water processor

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ABSTRACT

NH₃ and CO₂ concentration measurements performed on a Biological Water Processor (BWP), under development at NASA-JSC for water recycling, using near infrared laser diode absorption spectroscopy are reported. The gaseous effluents from the bioreactor are a concern for potentially introducing harmful amounts of NH₃ in a spacecraft environment. Furthermore, NH₃ and CO₂ monitoring is important for understanding the nitrogen and total organic carbon (TOC) balance and conversion dynamics in the BWP, and real time continuous monitoring could reveal dynamic situations that are hard to detect otherwise. Diode lasers operating at wavelengths that access NH₃ and CO₂ absorption lines near 1.53 μm and 1.99 μm are used in a portable and automated gas sensor system. Concentration measurements were performed during a 16 day period starting in August 25, 2000, and a 5 day period starting in November 10, 2000. A sensitivity of 0.7 ppm (signal to noise ratio -SNR- ~ 3) with a precision of 0.2 ppm will be reported for ammonia, and of 1000 ppm (SNR~3) for CO₂. Ammonia levels up to 5.6 ppm were observed, with fluctuating dynamics that depended upon the operating conditions of the bioreactor. Carbon dioxide levels fluctuated from 0.05% to 3.5%.

INTRODUCTION

Laser-based spectroscopic techniques to detect trace gases sensitively and selectively in real time in the infrared spectral region have been the focus of considerable research and development activities in

recent years.¹⁻⁵ The principal optical gas sensor technologies are based on absorption spectroscopy of fundamental bands in the 3 to 25 μm spectral region and near-infrared vibrational overtone and combination bands from 1 to 3 μm. Common radiation sources include continuous wave (cw) diode lasers (AlGaAs, antimonide-based, lead salt), parametric frequency conversion devices (difference frequency generation and optical parametric oscillators), gas lasers (CO and CO₂) and quantum cascade lasers. Telecommunications-grade distributed-feedback (DFB) AlGaAs diode lasers are ideally suited for overtone spectroscopy of molecules with chemical bonds such as C-H, O-H and N-H, in the near-infrared region (0.78 - 2.5 μm). In this work, we employ such diode lasers to develop a gas sensor suitable for simultaneous NH₃ concentration measurements at the 1 ppm level with a precision of 0.2 ppm and CO₂ measurements between 1000 and 20,000 ppm.

THEORY -

A gas concentration measurement for narrow linewidth radiation sources is obtained by using the Beer-Lambert absorption law, which relates the intensity of light entering into an absorption medium, I₀, to the transmitted intensity, I, as follows:

$$\frac{I}{I_0} = \exp(-s_v \phi_v \kappa P \chi_j l) \quad (1)$$

where S_v is the absorption linestrength for a specific transition denoted by v [cm/molecule], φ_v is the line-

shape function [cm], χ_j is mole fraction of the species, j , P is pressure [atm], κ is Loschmidt's constant [2.68×10^{19} molecules/cm³atm] and l is the optical path length through the medium [cm].

The normalized line-shape function describes the effects of thermal motion (Doppler broadening) and intermolecular collisions (pressure broadening), which have Gaussian and Lorentzian profiles, respectively. Ammonia and carbon dioxide absorption transitions at room temperature and sub-atmospheric pressure will have lineshapes that are described by a convolution of the Gaussian and Lorentzian functions which is known as the Voigt function.

A disadvantage of overtone spectroscopy is that absorption linestrengths are typically about 1 to 2 orders of magnitude weaker than those of the fundamental vibrations in the mid-infrared. To obtain the required sensitivity in the near IR, longer absorption pathlengths and a reduction of noise sources is required. A compact multi-pass, Herriott type cell, configured for a 36 m total optical path-length and an auto-balance detection technique were used.⁶

LINE SELECTION -

Designing a laser-based sensor for NH₃ and CO₂ in the bioreactor effluent gases requires careful selection of optimum transitions that offer adequate sensitivity over the range of expected populations and isolation from potential interfering species. The main constituents of the bioreactor vent gases include N₂, NH₃ up to a few tens of ppm, 500 ppm - 50% CO₂, and water vapor. For trace NH₃ detection, the strongest available and isolated transitions have to be selected. For CO₂ detection, an isolated transition needs to be employed that offers sufficient signal at the low concentration end (~500 ppm), yet is not optically thick for high concentrations (> 5%). The NH₃ transitions must be isolated from water vapor and CO₂, while CO₂ transitions need to be isolated from water vapor and NH₃.

Figure 1 shows a survey of absorption lines from NH₃, H₂O, and CO₂ in the near-infrared wavelength region, from 1.4 to 2.5 μ m. The Hitran96 data base does not include overtone transitions of NH₃ in the spectral range from 1450 nm to 1560 nm (~ 6400-6900 cm⁻¹). However, Lundsberg-Nielsen, *et al*⁷ have identified 1710 ammonia absorption lines in this region, and assigned 381 of them to rotational-vibrational transitions in the combination band $\nu_1 + \nu_3$ and the overtone $2\nu_3$. Webber *et al*⁸ examined these lines for interferences and pointed out the best lines for monitoring purposes. An absorption line at 1531.7 nm (6528.8 cm⁻¹) was chosen as the best suited operating wavelength for the NH₃ sensor described here. At this wavelength, low noise InGaAs detectors are available that operate with quantum efficiencies close to unity and require no cooling or temperature control. This particular line has the merit of being more than 1 cm⁻¹ away from the next

H₂O absorption line, and about 0.13 cm⁻¹ away from an adjacent NH₃ and CO₂ overtone transition,⁹ which permits simultaneous concentration measurements of NH₃ and CO₂ at 6528.9 cm⁻¹. In the 2.0 μ m region the linestrengths are approximately 3 times stronger for NH₃ as compared to the 1.53 μ m spectral region, and for CO₂ the linestrengths are approximately 100 times stronger. Thus, using DFB diode lasers at the longer wavelength offers the opportunity of more sensitive detection, and eliminates the need for the more complex auto-balancing detection technique.

Table 1 depicts the absorption lines that are used in this work. Lines A and B are the two ammonia lines used: A is an isolated line useful for measuring ammonia concentrations while line B overlaps with line C, which is the (00001) \leftarrow (30011), R(36), overtone transition of CO₂. These three lines, A, B and C, are accessed by one of the diode lasers used, at 1.53 μ m. Line D is the ¹P₃(3)_s overtone transition of ammonia, corresponding to the $\nu_3 + \nu_4$ combination band, about 3 times stronger than line A, and line E is the (00001) \leftarrow (20012), R(50) transition of CO₂. Lines D and E were accessed using a second diode laser, at 1.99 μ m.

The linestrength values reported in Table 1 correspond to a temperature of 296 K. The linestrength of C is about a factor of 5000 smaller than that of A. However, in the bioreactor exhaust CO₂ concentrations can be as high as 50% or more, with the result that line A ends up buried within line C. On the other hand, if CO₂ levels are below 30%, overlapping between lines A and C is negligible and the ammonia concentration can easily be extracted using line A. Furthermore, under these conditions, the three lines A, B and C can be used to perform simultaneous NH₃ and CO₂ concentration measurements.

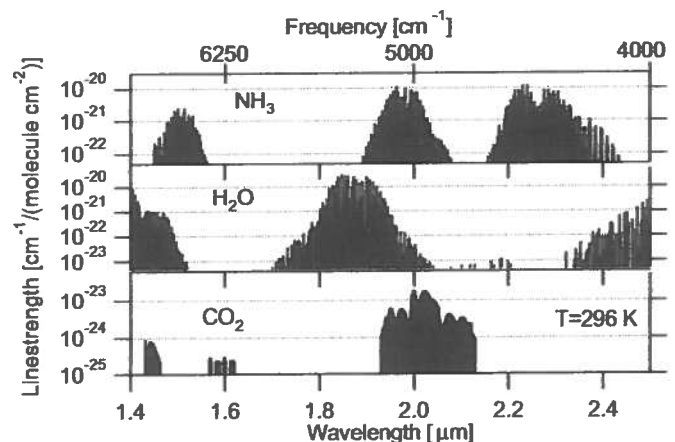


Figure 1. Calculated H₂O, NH₃, and CO₂ linestrengths in the near infrared at 296 K [7-9].

Table 1

	Linestrength cm/molecule	Frequency cm ⁻¹	Wavelength nm	Ref.
A(NH ₃)	2.33 x 10 ⁻²¹	6528.76	1531.68	[8]
B(NH ₃)	1.24 x 10 ⁻²¹	6528.89	1531.65	[8]
C(CO ₂)	5.19 x 10 ⁻²⁵	6528.895	1532.65	[9]
D(NH ₃)	8.07 x 10 ⁻²¹	5016.977	1993.23	[5]
E(CO ₂)	5.06 x 10 ⁻²³	5007.787	1996.89	[10,11]

Table 1. NH₃ and CO₂ absorption lines at 1.53 and 1.99 μm, used in this work.

Experimental

AMMONIA SENSOR -

The diode laser based gas sensor developed for on-line NH₃ monitoring in a bioreactor system is shown in Fig. 2. Its main components are two fiber-coupled DFB diode lasers (1.53 μm, and 1.99 μm), a compact 36m multi-pass, Herriott cell and an auto-balanced InGaAs detector (Nirvana 2017 from New Focus), which can also operate as a single photodetector. A two-stage, diaphragm pump was used to flow the sample gas through the multi-pass cell at a pressure of 100 Torr. The multi-pass cell was heated to a temperature of 40 °C to minimize ammonia adsorption on its glass walls, and to prevent potential water condensation on the cell mirrors.

The diode lasers were driven by a compact current supply (MPL-250, Wavelength Electronics) with ripple noise < 1 μA, so that the frequency fluctuations of the laser line due to current noise are negligible (<1 MHz). The current supply was scanned about an average current of 67 mA with a saw-tooth ramp function, for the 1.53 μm diode laser, the scan rate was 20 Hz, and for the 2.0 μm diode laser it was 125 Hz. The reason for the low scan rate at 1.53 μm was that, for that laser, an auto-balance technique was used for data collection, which involves a feedback loop that operates at lower speed. The laser temperature was controlled to within 0.003 °C near 32 °C by a current module (HTC-1500, Wavelength Electronics). The scan range of the laser under these conditions was 0.3 cm⁻¹, which allowed all three spectral lines A, B and C to be accessed on every scan, at 1.53 μm.

The fiber-pigttailed DFB laser diode delivers 15 mW at 1.53 μm, with a specified linewidth of < 10 MHz. The fiber was fusion-spliced to a 70/30(%) wavelength division multiplexer (WDM) with an insertion loss of less than 2%. The 70% power arm of the WDM was directed to the multi-pass cell, using a lens (f=7 mm, 0.5 NA)

mounted in a precision holder with 5 degrees of freedom (OFR) to set the beam waist at the midpoint of the multi-pass cell. The 30% power arm was used as the reference beam for the balancing detector. This integrated laser-optical fiber configuration delivers a total of 10 mW of laser light at the input of the multi-pass cell. The output power of the beam obtained from the cell after 182 passes is 17 μW, for a throughput efficiency of 0.17%. This corresponds to a 96.5% reflectivity for the cell mirrors, indicating degradation from the original reflectivity of 98% after 3 years of frequent use. The output beam from the cell is focused on the signal and reference photodiodes of the dual beam detector by a gold coated parabolic mirror of 1" diameter (f# =2) and a lens (f= 7 mm, 0.5 NA) mounted on a precision holder, respectively. The detectors used at this wavelength (1.53 μm) are 1mm in diameter InGaAs based photodiodes, with a quantum efficiency of ~ 1 at that wavelength. Since the reference beam power (P_{ref}) was much greater than the power of the signal beam coming from the cell (P_{signal}), it was attenuated using a variable fiber attenuator. For optimum performance of the auto-balanced detector, the reference power was set as P_{ref}= 2.2 x P_{signal}, at the center frequency of the laser scan. In order to perform concentration measurements using the absorption lines D and E, in Table 1, a 1.99 μm DFB diode laser was connected to the collimating lens mount located in front of the multipass cell. An InGaAs detector, enhanced for 2.0 μm, 1 mm in diameter, was placed after the focusing mirror, at the output of the multipass cell. This process required no further re-alignment procedure.

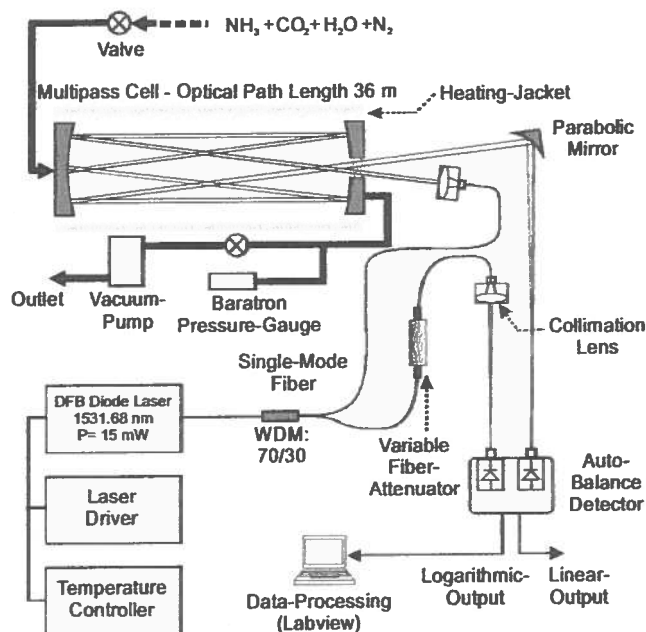


Figure 2. Schematic of the DFB diode laser based ammonia sensor.

The data acquisition and processing software used, was LabView 5.0, run on a 500 MHz laptop PC. In the autobalance mode, five hundred scans were averaged for each single concentration measurement. For the

concentration measurements made with the detector in the linear mode, 1000 scans were used for a single measurement due to the lower signal-to-noise ratio of this mode. The total data collection time, averaging, and processing to obtain a single concentration measurement is less than 30 seconds. For convenience, the sensor was configured to take measurements every minute in order to correlate the ammonia measurements to external daily events and specific chemical actions performed on the bioreactor. It was found convenient to monitor remotely the sensor performance and concentration data using "PC Anywhere" software.

BIOLOGICAL WATER PROCESSOR AND MEASUREMENT SETUP -

The Biological Water Processor (BWP) referred to above is part of a Water Recovery System (WRS) being developed at the Johnson Space Center in Houston, TX. The BWP is illustrated in Fig. 3. This system produces potable water from a wastewater stream using aerobic and anaerobic microbial processes. An equilibrium amount of ammonia-ammonium ions dissolved in water is produced through the hydrolysis of urea, and must be removed in order to preserve the bacterial population. This is done at the nitrification stage of the system, where ammonium is oxidized into NO_2^- and NO_3^- . The gases resulting from the process are separated from the fluid at a gas-liquid separator (GLS) and vented into the atmosphere, while the liquid is returned to the BWP for a new cycle. The concern is that effluent from the GLS might transfer potentially harmful amounts of NH_3 in an enclosed environment. This is the principal factor motivating the monitoring of NH_3 concentration levels in the WRS gas exhaust. The packed bed reactor contains anaerobic bacteria that decompose organic molecules found in wastewater. The nitrifier consists of a 4,000 feet long coil of 1/4" polypropylene tubing, coated on the inner surface with a bio-film of aerobic, "nitrifying" bacteria, which in the presence of oxygen produce the reaction:



The $\text{NH}_3/\text{NH}_4^+$ concentration level indicates the efficiency of the nitrifying process in the BWP, once the nitrifier loop is set in operation. If the pH is known, the total $\text{NH}_3/\text{NH}_4^+$ concentration can be calculated from measurements of the NH_3 concentration in the gas stream. The CO_2 concentration measurement also gives a quantitative indication of the conversion of TOC in the system, which is an important parameter to determine the quality of the water that is being recycled. At the end of the loop, a fraction [1/19th] of the recycled water is extracted from the BWP for post-processing, while the rest is sent back into the packed bed reactor. The gaseous residual is vented through the exhaust line into the atmosphere. Water vapor is removed from the gas exhaust by the water condenser.

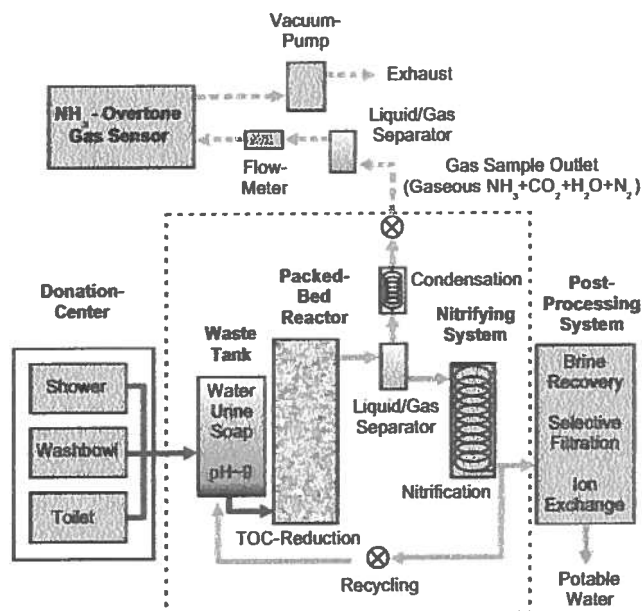


Figure 3. Diagram depicting the main subsystems of the NASA-JSC Biological Water Processing system (BWP) and attached NH_3 diode laser based gas sensor. The actual size of the BWP is 2x2x3 m.

The diode laser based sensor was connected to the exhaust line after the water condenser, as shown in Fig.3, and placed ~ 2 meters away from the BWP unit, using about 6m of teflon tubing to satisfy NASA-JSC safety protocols. A glass flask (~150 ml) was inserted along the teflon line, to collect any remaining water droplets in the gas. The flow rate to the multipass cell was adjusted to be less than the exhaust line rate, to ensure sampling of the BWP and not outside air. For this purpose, a flow meter/controller was installed immediately upstream from the sensor to ensure a constant flow rate of 10 sccm, well below the bioreactor exhaust rates of several 100's of sccm.

RESULTS AND DISCUSSION

CALIBRATION AND FITTING ROUTINES -

A convenient method for determining the accuracy of the concentration measurements from the sensor system was to measure the absorption of a 100 Torr sample of CO_2 . Using the absorption line C, and the 1.53 μm diode laser, a concentration of 97.6% was obtained, assuming an optical path length of 36 m. When the same sample was measured using a different 36 m long multi-pass cell, and the 1.99 μm diode laser, accessing absorption line E (see table 1), the CO_2 concentration was found to be $100 \pm 5 \%$. Thus, the

accuracy of the laser based gas sensor reported in this work is better than 5%.

A second calibration procedure was performed with a calibrated ammonia sample (100 ± 2 ppm in N_2), that was diluted with N_2 to a nominal 5ppm mixture using a gas mixer capable of controlled temperature, pressure and flow rate operating conditions. NH_3 concentration measurements were performed simultaneously with the overtone-based sensor operating at $1.53 \mu m$ and with a quantum cascade laser based sensor that uses the fundamental NH_3 absorption band, ν_2 , at $10.07 \mu m$.¹² The results for the two procedures are shown in Fig. 4, and demonstrate an agreement of better than 5% between the two independent measurements. These are within the standard deviation of the overtone measurements of 0.2 ppm, or 7%. The fundamental absorption measurement was obtained using a linestrength available from the HITRAN96 database, whereas the overtone measurement uses a value reported in Ref. 10. Both measurements yield values below the expected NH_3 concentration, most likely due to the fact that ammonia adsorbs to the stainless steel surface of the gas mixer, and insufficient time elapsed to reach a steady state in adsorption-desorption.

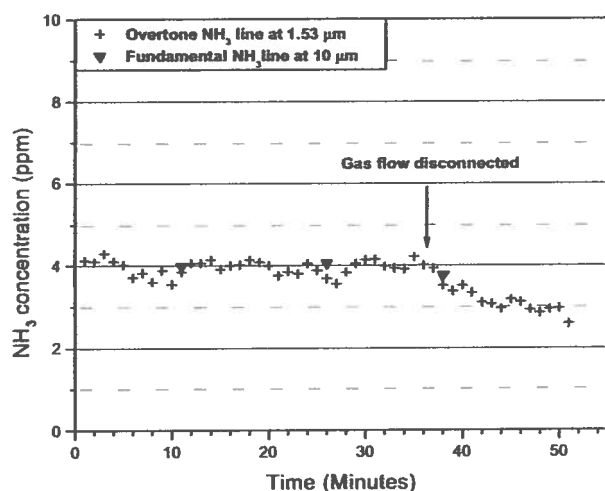


Figure 4. Inter-comparison of concentration measurements of a 4 ppm NH_3 in N_2 mixture with a $1.53 \mu m$ DFB diode laser and a single frequency quantum cascade (QC) laser based sensor operating at $10.07 \mu m$.

The real-time fitting routine implemented in LabView has been reported elsewhere,¹³ and only minor software modifications were required for this work in order to process the logarithmic signal from the detector operating in the auto-balance mode. The fit employs a non-linear, least squares Levenberg-Marquardt algorithm and uses a given absorption profile to fit the data. Since the pressure regime of operation (100 Torr) lies between the predominantly Doppler and pressure broadened regimes, a Voigt profile with fixed pressure broadening and Doppler width was used. A Lorentz function overestimates the area under the curve by $\sim 6\%$. Figure

5 shows a typical absorption spectrum obtained using the $1.53 \mu m$ diode laser. The baseline has been removed using a third order polynomial, and a Voigt profile has been fitted to the resulting data,^{14,15} with a linewidth of 0.027 cm^{-1} and a pressure broadening contribution of 0.020 cm^{-1} . Due to pressure fluctuations in the system of ± 2 Torr, not accounted for by the fitting routine, and the fluctuations observed in the CO_2 concentration from the exhaust gases, of $\pm 2\%$, the linewidth of the ammonia absorption peaks is expected to fluctuate by $\sim \pm 0.002 \text{ cm}^{-1}$.¹⁶ This introduces an error for the ammonia concentration measurement in the fitting routine of 4%. The residual of the Voigt fit yields a minimum detectable absorption for a single measurement (with 500 averages) of $\pm 0.01\%$ (note that $100 \times \ln(I/I_0)$ is equivalent to % absorption for small absorptions). From Figure 5, it is seen that detection with a SNR of 3 corresponds to a concentration of 0.7 ppm. This is the minimum concentration that can be measured reliably with the reported gas sensor design. Optical fringes from interference effects introduced by the multi-pass cell limit the sensitivity and are the primary source of uncertainty in the ammonia concentration values reported. Other groups implementing a dual-beam auto-balancing technique like the one used in this work have obtained similar sensitivity values.¹⁷

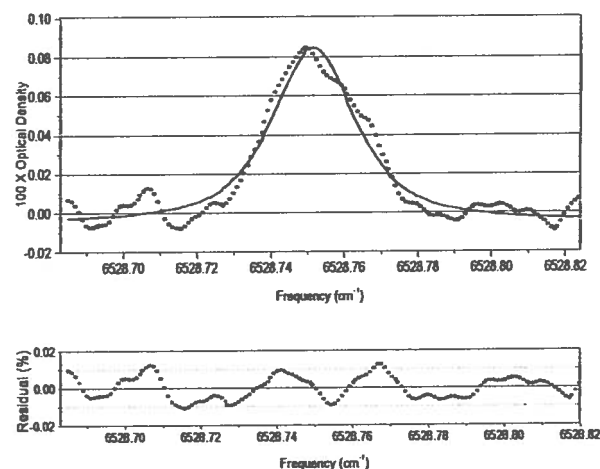


Figure 5. Typical NH_3 absorption line at 6528.76 cm^{-1} observed from the NASA-JSC bioreactor, with the detector operating in auto-balance mode. The residual obtained from the Voigt lineshape fit is shown below the NH_3 spectrum, and indicates a limiting detection sensitivity of 10^{-4} O.D. (Optical Density is given by $-\ln(I/I_0)$). The NH_3 concentration from the Voigt fit is 1.4 ppm.

Simultaneous measurements of NH_3 and CO_2 concentrations were obtained by fitting the three lines A, B and C, in real time, as mentioned in Section 1. This technique uses the fact that the three peaks can be obtained in a single diode laser scan of $\sim 0.3 \text{ cm}^{-1}$, and that peaks B and C overlap almost exactly. The algorithm begins with a Voigt fit on peak A. With the NH_3 concentration thus obtained, peak B is modeled and subtracted from the absorption feature. The remaining absorption signal at the location of peaks B and C is

fitted again to a Voigt profile, and yields the CO₂ concentration. This algorithm removes the problem of having to fit the two peaks that overlap, B and C, simultaneously. It also allows for the subtraction of the baseline in two separate sections, one for line A in the first step, and the other for lines B and C in the second step. This technique eliminates unwanted effects of spurious baseline features that may occur between the two absorption lines. Figure 6 shows an absorption spectrum of the two NH₃ and the CO₂ lines listed in Table 1, obtained in a single diode laser scan. The baseline subtraction obtained with this algorithm for the peaks A, B and C yields a fit residual of less than $\pm 0.02\%$ within the peaks. Such a residual would not have been realized if a single baseline had been adjusted across the entire scan range.

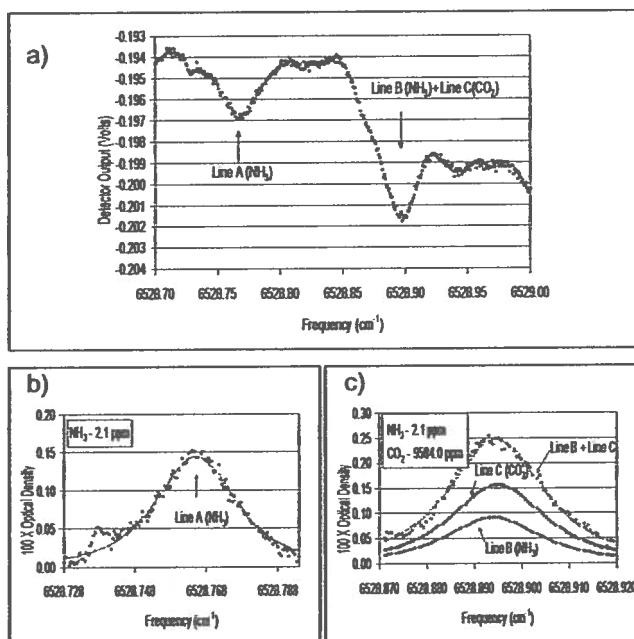


Figure 6. Measured NH₃ and CO₂ absorption lines listed in Table 1, centered at 6528.8 cm⁻¹ (1.53 μ m) observed from the BWP vent gases. Fig. 6a shows the raw data obtained from a typical laser scan over ~ 0.3 cm⁻¹. The two absorption features at 6528.76 cm⁻¹ and 6528.89 cm⁻¹ are clearly visible. Fig. 6b shows the result of applying the two-step fitting routine to line A, obtaining a NH₃ concentration of 2.1 ppm. Fig 6c shows the fit performed on the absorption feature that includes both lines B and C, showing a CO₂ concentration of 0.9%.

ALLAN VARIANCE -

To determine the level of precision attainable with the sensor reported here, a suitable procedure is to measure the Allan variance of the concentration measurements.^{18,19} To do this, a 17 hour measurement run was performed, flowing a mixture of ammonia at a constant concentration (balanced with N₂) through the multi-pass cell, and using the detector in autobalance mode. The sample was prepared with the gas mixer mentioned above, and the results are depicted in figure 7. It is seen that, for an averaging time of less than a minute, the best precision obtained corresponds to a

standard deviation of $\sigma = 0.02$ ppm. This compares well with the values for σ obtained from the data taken in the bioreactor measurements ($\sigma = 0.1$ ppm), as shown in figure 8. Effects like the intrinsic variability of the bioreactor conditions and the fact that the measurements were carried out with a limited duty cycle of 50% (averaging time for each measurement was ~ 30 secs.) will increase the standard deviation of the measurements in the field.

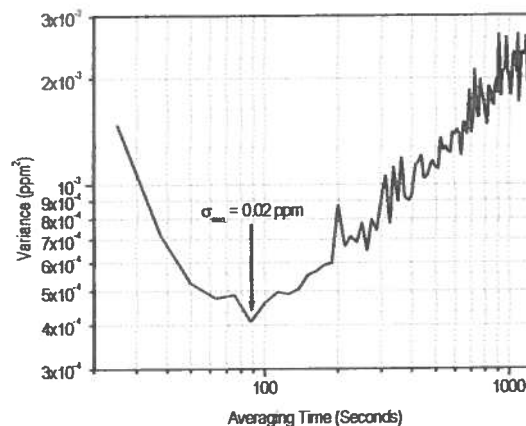


Figure 7. Allan variance of the ammonia sensor with detector operating in auto-balanced mode. The results show the minimum variance expected from the concentration measurements obtained with the diode laser based instrument described in this work. The average ammonia concentration during this data run was 0.7 ppm.

FIRST BIOREACTOR MEASUREMENT CAMPAIGN NASA-JSC -

NH₃ concentration measurements were performed at NASA-JSC for a period of 13 days, from August 25 to September 7, 2000. Figure 8 shows the overall time history of the ammonia measurements performed on the bioreactor system. The NH₃ concentration fluctuates in periods of ~ 10 hours, ranging from levels below the sensitivity of the instrument up to 5.6 ppm. Critical biochemical procedures taken on the different parts of the BWP by NASA personnel are indicated. During the period between August 30 and September 1, the 1.99 μ m diode laser was used, and otherwise the data was collected using the 1.53 μ m diode laser. From August 30 to September 7, the detection scheme was operated in the linear mode, for both diode lasers.

The standard deviation of the auto-balanced output data is calculated to be 0.1 ppm, whereas for the linear case, using the 1.53 μ m diode laser, it increases to 0.2 ppm. Such a difference is expected, since the auto-balanced scheme minimizes most common sources of noise in both signal and reference arms of the laser beam. In particular, laser amplitude fluctuations produced by electronic noise from the power supplies and temperature drifts, are removed. As mentioned in section 2.1, the linear output measurements were averaged for 1000 scans, as compared to only 500

scans for the auto-balanced measurements. The main sources of uncertainty in this experiment are the optical fringes produced in the multi-pass cell. The auto-balanced technique does not remove the fringes because they do not affect signal and reference beams simultaneously. For the data collected using the 1.99 μm diode laser, with a linear mode detection scheme, the standard deviation was also determined to be 0.1 ppm.

A background ammonia concentration measurement was performed by disconnecting the system from the bioreactor and sampling room air. The NH_3 background was measured to be ~ 0.5 ppm (see Figure 8) and is due to the residual ammonia that has accumulated on the walls of the gas line from the BWP to the ammonia sensor. During the entire measurement period the ammonia levels never exceeded 5.6 ppm after the packed bed reactor and the nitrification reactor coils were integrated. The NH_3 concentration fluctuated during the period (8/25/00–8/30/00) before the BWP was operated in the recycling mode. In this mode, no additional wastewater was added and the ammonia levels decreased.

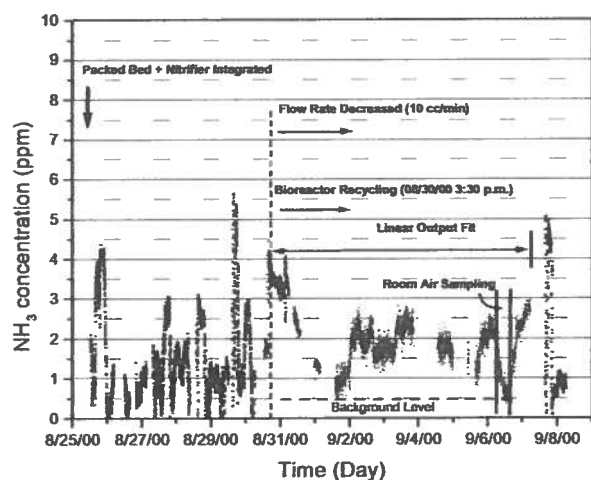


Figure 8. Ammonia concentration measurements for the first NASA-JSC campaign. Solid circles correspond to data points obtained in auto-balance mode, and triangles correspond to data obtained in the linear mode of the detector. Measured ammonia levels never exceeded 5.6 ppm during this period.

NH_4^+ aqueous phase concentration measurements were performed each morning by NASA personnel using standard wet-chemical techniques, taking a bioreactor effluent sample after the GLS. From this and the pH of the aqueous solution, the concentration of NH_3 in solution can be calculated. An estimate of the NH_3

concentration in the gas phase was determined using Henry's Law.²⁰ The resulting values are shown in Table 2. It is observed that the calculated values from the wet-chemical measurements are somewhat larger than the measured concentrations with the laser based sensor. However, it should be noted that these values provide an order of magnitude estimate of the overall ammonia concentration expected in the gas phase. An accurate calculation would require a precise account of all the ions in solution, the pH of the solution, and the variation of these quantities in the various subsystems of the bioreactor.

Figure 9 shows the simultaneous NH_3 and CO_2 concentration measurements for a portion of the overall measurement time, obtained by applying the triple Voigt fit algorithm described in Section 3.1. The two measurements are clearly anti-correlated, which is to be expected from the fact that ammonia and carbon dioxide gas-phase concentrations should have opposite dependence on the pH in the BWP water solution. The CO_2 concentration shown in Fig. 9 provides information that can be used to improve the BWP operation by monitoring the efficiency of the BWP in performing TOC reduction. Throughout the time periods when CO_2 concentrations were measured, largely fluctuating values were obtained. CO_2 levels from less than 1000 ppm to 20,000 ppm were observed, with values decreasing after the BWP was set into its recycling mode on August 30, 2000.

Table 2

Date	NH_3 Aqueous [mg/L]	NH_3 Gas [ppm]
8/25/00	32.5	13.0
8/26/00	12.5	5.0
8/27/00	8.7	3.5
8/28/00	8.6	3.4
8/29/00	20.7	8.3
8/30/00	19.9	8.0
8/31/00	10.0	4.0
9/01/00	14.5	5.8
9/02/00	6.1	2.4
9/03/00	11.0	4.4
9/04/00	5.2	2.1
9/05/00	3.7	1.5
9/06/00	4.4	1.8

Table 2. Aqueous and gas phase NH_3 concentrations calculated from measurements of $[\text{NH}_4^+]$, pH and using Henry's Law.

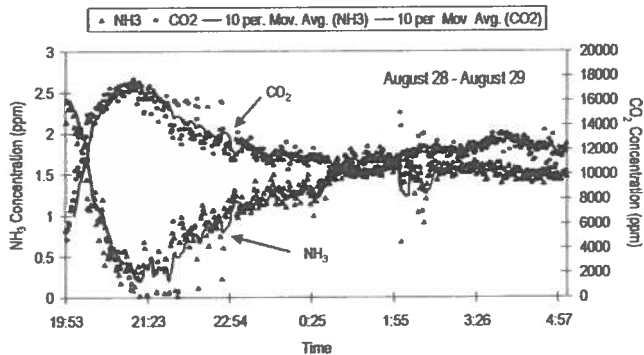


Figure 9. Simultaneous CO₂ and NH₃ concentration measurements. The CO₂ levels do not exceed 20,000 ppm. The time period can be related to the ammonia measurements reported in Fig. 8.

SECOND BIOREACTOR MEASUREMENT CAMPAIGN AT NASA-JSC –

From November 10 to November 14, 2000, a second measurement campaign took place, using only the 1.53 m diode laser. The sensor was operated with the detector in the linear mode scheme. The operating conditions of the bioreactor had changed such that no ammonia could be measured by the laser based gas sensor. Instead, larger amounts of CO₂ were observed with respect to the first measurement campaign in August-September, by using absorption line C. Figure 10 shows the results obtained from an uninterrupted monitoring of CO₂ from November 11 to November 14.

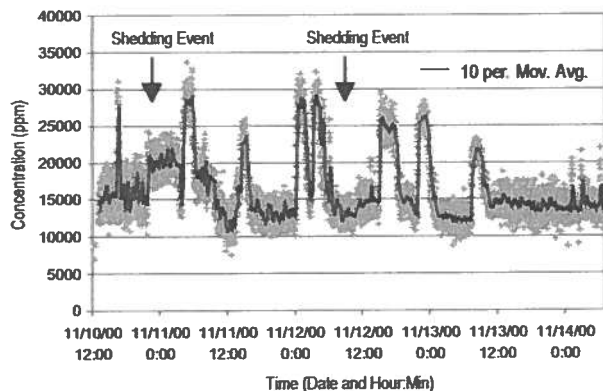


Figure 10. CO₂ concentration measurements in packed bed bioreactor, during the second NASA-JSC campaign. The CO₂ levels this time reached up to 35,000 ppm. Shedding events are listed at the approximate time that they occurred (± 6 hrs.). The solid line is a moving average of 10 measurements per point.

In a background concentration of about 10,000 ppm (or 1%), several outbursts of CO₂ concentrations of up to 3.5 % are evident. The onset of these outbursts was a series of 4 “shedding” events in the bioreactor, two of them indicated by arrows in figure 10 (the other two occurred one and two days earlier). A “shedding” event consists in the sudden de-foliation of the bacterial layer

within the nitrifier reactor, due to the over-size thickness of the bacterial film. The reactor loses the bacterial population, which is carried away by the flow and accumulates in the filters that separate the packed bed and the nitrifier reactors. The evidence of the occurrence of such an event is the accumulation of biomass in these filters.

CONCLUSION

The present work describes the performance of a trace gas sensor based on overtone absorption spectroscopy at 1.53 and 1.99 μm , applied to ammonia detection in a bioreactor exhaust line, with a time resolution of 30 seconds and a sensitivity of 0.7 ppm at a SNR of 3. The advantages of this sensor compared to other methods are compactness, portability, and simplicity of operation, and the ability to perform real-time measurements. The NH₃ concentration measurements reveal a dynamic behavior of the bioreactor that could not be detected and measured otherwise. The ammonia concentration measurements have established that during the period of this study, ammonia emissions into the environment remained below harmful levels. This evaluation may have to be revised when considering longer periods of operation in a closed environment. The ability to perform simultaneous NH₃ and CO₂ measurements in real-time has been demonstrated. A clear anti-correlation between the concentrations of these two gases is observed, in agreement with the expected operating conditions of the NASA-JSC bioreactor. The CO₂ concentration measurements were almost an order of magnitude smaller than estimated (up to $\sim 50\%$). Further measurement of these chemicals by the bioreactor operating crew will have to resolve this question. Shedding events, followed by a CO₂ spike have been observed; however, some CO₂ spikes were not correlated to a shedding event. To better understand this phenomena, further testing should be done over longer periods of time.

The diode laser based ammonia sensor can be used to measure other gases of environmental importance such as CO₂, HF, HCl, NO, CH₄ and H₂O. These can be monitored by the appropriate wavelength selection of the DFB diode laser or a tunable multi-wavelength DFB diode laser source, which provide additional wavelength channels for multi-species gas detection.

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REFERENCES

1. K.P. Petrov, Y. Mine, T. Topfer, R.F. Curl, F.K. Tittel and J.C. Graf; Proceedings of the International Conference on Environmental Systems, ICES '97, 1997.
2. F.K. Tittel, D. G. Lancaster, D. Richter, R.F. Curl, and J.C. Graf; Proceedings of the International Conference on Environmental Systems, ICES '99, Denver, CO July 12- 15, 1999.
3. D. Richter, F.K. Tittel, J. Bahr, D. Wickham, J. Wright and J.C. Graf; *Proceedings of the International Conference on Environmental Systems, ICES '00*, Toulouse, France, July 10-13, 2000.
4. R. Claps, F.V. Englich, D. Leleux, D. Richter, F.K. Tittel, R.F. Curl; "Ammonia detection using near infrared diode laser based overtone spectroscopy", submitted to Appl. Opt. 2001.
5. M.E. Webber, R. Claps, F.V. Englich, F.K. Tittel, J.B. Jeffries, R.K. Hanson; "Measurements of NH_3 and CO_2 with DFB Diode Lasers Near $2.0 \mu m$ in Bioreactor Vent Gases", submitted to Appl. Opt. 2001.
6. P.C.D. Hobbs; "Ultrasensitive laser measurements without tears" Appl. Opt. **36**, 903-920 (1997).
7. L. Lundsberg-Nielsen, F. Hegelund, F.M. Nicolaisen; "Analysis of the High-Resolution Spectrum of Ammonia ($^{14}NH_3$) in the Near-Infrared Region, $6400-6900 \text{ cm}^{-1}$ ", J. Molec. Spectrosc. **162**, 230-245 (1993).
8. M.E. Webber, D.S. Baer, R. Hanson; "Ammonia Monitoring Near $1.5 \mu m$ with Diode Laser Absorption Sensors", submitted to Appl. Opt.
9. L.S. Rothmann, et al; *The HITRAN molecular spectroscopy database and HAWKS (HITRAN atmospheric workstation): 1996 edition*. J. Quant. Spectrosc. Radiat. Transfer, **60**, 665-710, 1998.
10. R.M. Mihalcea, M.E. Webber, D.S. Baer, R.K. Hanson, G.S. Feller, W.B. Chapman; "Diode-Laser Absorption Measurements of CO_2 , H_2O , N_2O and NH_3 near $2.0 \mu m$ ", Appl. Phys. B, **67** 283-288 (1998).
11. M.E. Webber, S. Kim, S.T. Sanders, D.S. Baer, R.K. Hanson, and Y. Ikeda; "In situ combustion measurements of CO_2 using a distributed feedback diode laser sensor near $2.0 \mu m$ ", Appl. Opt. To be published, Feb. 20, 2001.
12. A.A. Kosterev, F.K. Tittel, C. Gmachl, F. Capasso, D. L. Sivco, J. N. Baillargeon, A. L. Hutchinson, A. Y. Cho; "Trace-gas detection in ambient air with a thermoelectrically cooled, pulsed quantum-cascade distributed feedback laser", Appl. Opt. **39**(36), 6866-6872 (2000).
13. D.G. Lancaster, D. Richter, R.F. Curl, F.K. Tittel; "Real-time measurements of trace gases using a compact difference-frequency-based sensor operating at $3.5 \mu m$ ", Appl. Phys. B **67**, 339-345 (1998).
14. E.E. Whiting, "An empirical approximation to the Voigt profile", J. Quant. Spectrosc. Radiat. Transfer, **8** 1379-1384 (1968).
15. D.J. Brassington, "Tunable diode laser absorption spectroscopy for the measurement of atmospheric species", pp. 85-147, in *Spectroscopy in Environmental Science*, edited by R.J.H. Clark and R.E. Hester, John-Wiley & Sons (1995).
16. C.H. Townes, A.L. Schawlow; *Microwave Spectroscopy*, ch. 13. p. 364, Table 13.4. Mc Graw-Hill, NY (1955).
17. G. Durry, I. Pouchet, N. Amarouche, T. Danguy, G. Megie; "Shot-noise-limited dual-beam detector for atmospheric trace-gas monitoring with near-infrared diode lasers", Appl. Opt. **39**(30) 5609-5619 (2000).
18. P. Werle, R. Mucke, F. Slemr; "The Limits of Signal Averaging in Atmospheric Trace-Gas Monitoring by Tunable Diode-Laser Absorption Spectroscopy (TDLAS)", Appl. Phys. B **57**, 131-139 (1993).
19. D. G. Lancaster, A. Fried, B. Wert, B. Henry, F. K. Tittel; "Difference-frequency-based tunable absorption spectrometer for detection of atmospheric formaldehyde", Appl. Opt **39**(24), 4436-4443 (2000).
20. P. Brimblecombe, S.L. Clegg; "Solubility of Ammonia in Pure Aqueous and Multicomponent Solutions", J. Phys. Chem. **93** 7237-7248 (1989).

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