APPENDIX D:

DRAFT MANUSCRIPT:

**A COMPARISON OF NH₃ POINT
MONITORING AND DIODE LASER
BASED PATH INTEGRATED MEASUREMENTS**

Proceedings of the AWMA/SPIE International Symposium
on Optical Sensing for Environmental and Process Monitoring

To be Held 6-10 November 1994
McLean, VA

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A comparison of NH_3 point monitoring and diode laser based path integrated measurements

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ABSTRACT

Measurements made using two different types of ammonia monitors during a two-month field study in the summer of 1994 are discussed. The first was a diode-laser based open path monitor designed for automated operation in an industrial environment. The second is a monitoring analyzer based on thermal decomposition of ammonia to NO and subsequent analysis by O_3 - NO chemiluminescence. The two monitors provided consistent measurements of ammonia concentration during weeks of continuous unattended operation.

1. INTRODUCTION

The measurement of gas phase ammonia is important in a number of applications where it poses environmental safety and air quality concerns. The applications can be grouped in two categories; ambient monitoring and process control. Fenceline monitoring of the emission of ammonia from fertilizer production plants and pipeline leak detection are examples of ambient applications. One important example of a process control application is the use of ammonia to reduce oxides of nitrogen (NO_x) emission from power generation facilities utilizing selective catalytic reduction (SCR) technologies. The amount of ammonia injected in the exhaust stream must be carefully controlled to achieve efficient NO_x reduction and to control NH_3 emission from the stack.

Traditionally, monitoring of ammonia for ambient applications has been achieved by passing the sample through a high temperature oven which thermally decomposes and oxidizes the ammonia to form nitric oxide (NO), nitrogen dioxide (NO_2), and water. The oxides of nitrogen are then measured using a NO_x chemiluminescence analyzer.¹ As long as the converter has high and stable conversion efficiencies over the range of ammonia concentration encountered, this process works well. There are two drawbacks associated with this approach. To successfully monitor a large facility requires several analyzers to achieve proper coverage. Secondly, the response times of these analyzers are generally on the order of a minute and thus are too slow for mobile applications such as airborne pipeline leak detection.

Several groups have tried to extend traditional ambient ammonia monitoring techniques to process control applications. One of the primary difficulties in monitoring gas phase ammonia in process control applications is in handling the sample to be analyzed. For instance, to measure the ammonia at many power generation facilities, a portion of the stack or duct effluent is drawn from the stack and either directly analyzed or diluted and then analyzed. These techniques require heated sample lines as well as heated valves and manifolds which are expensive and require continuous maintenance.

Other techniques are available and have been used for monitoring ammonia. For example, differential absorption spectroscopy in the ultraviolet (uv) has been used to monitor both ambient levels of ammonia in an open path configuration and in a slightly different configuration to do source monitoring.² Cryogenically cooled lead-salt diode lasers operating near $7\text{ }\mu\text{m}$ have been used in conjunction with second harmonic spectroscopy techniques to monitor ammonia in several applications.^{3,4} These systems can be operated as point monitors or open path devices. They are expensive, and require regular maintenance by skilled personnel. They are sensitive and well suited to scientific studies but are not well suited to most industrial applications. Differential absorption lidar has also been used to measure NH_3 .⁵ These sensors have the advantages of fast response and range resolved measurements.

Unfortunately, pulsed laser technology has not sufficiently progressed such that this technique is cost competitive in comparison to traditional methods.

Commercial near infrared tuneable diode lasers (TDL) have significant promise for industrial process control and ambient monitoring applications. Reliable lasers are being produced which are narrow band tunable in wavelength regions that overlap with absorption features of many important pollutants. When used in combination with derivative spectroscopy techniques, sensitive and reliable measurements are possible. Automated sensor systems based on these techniques are now being developed for applications in industrial environments.⁶⁻¹⁰

This paper presents results of a field study in a line-of-site TDL based ammonia monitoring was compared to a traditional point monitor. The study was conducted at a large cattle feedlot in the northern Colorado area during a two month period. Measurements made using two different types of ammonia monitors are discussed. The point monitoring analyzer is based on thermal decomposition of ammonia to NO and subsequent analysis by O_3 - NO chemiluminescence. Path integrated measurements were accomplished using a near infrared distributed feedback diode laser and second harmonic spectroscopy. A comparison of the measurements shows generally high correlations. When correlations between the instruments was poor, it is shown to be due primarily to the different nature of a path-integrated measurement and that of a point monitor. Of particular interest is the high degree of reliability of both instruments under harsh environmental conditions.

2. EXPERIMENTAL SETUP

Figure 1 is a block diagram of the instrumentation used for the ammonia monitoring field study. The laser transceiver for the open path monitor and the ML9842 point monitor were co-located in a small utility trailer. A retroreflector for the open path monitor was mounted in several positions during the course of the study. The sample stream for the point monitor was drawn from a sampling cane on the roof of the trailer into a manifold and then pulled through a convertor into the analyzer. Wind speed and direction were monitored using a commercially available anemometer system. All of the instruments were interfaced to a custom data acquisition system based on personal computer.

2.1 Path integrated TDL monitor

Path integrated measurements were made with the Diode Laser Absorption Concentration Sensor (DARCS). DARCS is a member of the Diritgas⁸ family of TDL gas sensors which include portable point samplers and fiber-optic multiple sensor systems. All of the Diritgas sensors are capable of long term untended operation. All use a common line-locked detection technology⁶⁻⁸ and microprocessor control of the laser operating temperature and current to automatically find and lock to a predetermined absorption line.

Figure 2 illustrates the operating principles as applied to path integrated measurements. The laser, electronics, and reference cell containing the gas to be measured (Species A) are contained in a transceiver unit (Figure 3b). A laser beam transmitted to a distant retroreflector and back is used to monitor the column density, or path integrated concentration, of Species A in the atmosphere. The laser frequency is modulated over a wavelength range of the same order as the line width of the absorption feature of the species of interest (Figure 3a). The third harmonic, $3f$, of the radiation transmitted through the reference cell is used to generate an error signal to lock the laser wavelength to the peak of the absorption line. The second harmonic, $2f$, of the radiation through the gas sample is then proportional to the species concentration according to a previously established analytical relationship.⁶ The first harmonic signal, $1f$, is used to normalize the $2f$ signal to the returned laser intensity, I_0 .⁷ The ratio of the second to first harmonic is independent of transmitted radiation intensity and insensitive to transceiver alignment and atmospheric transmission effects. An onboard microprocessor is used to identify and lock to the preselected line, maintain appropriate gain levels over a four order of magnitude range in I_0 and a four order of magnitude range of concentration, monitor status variables, adjust operating parameters, and process the harmonic signals into concentration values.

Figure 1. Schematic Diagram of Instrumentation Used During the Ammoniac Field Study.

Figure 2. Schematic of DARCS Path Integrated Measurements Approach.

Figure 3 is a photograph of the DARCS system. It is designed for automated, unattended operation for extended periods of time and can be installed and operated by unskilled personnel. The system consists of a weather resistant transceiver box mounted on a standard surveyors tripod and connected to a weather tight electronics box by an umbilical. The 1.5" retroreflectors mounted in weather resistant enclosures can be mounted permanently to telephone poles or on portable tripods for surveying applications. The sighting scope is used to align the transceiver with the retroreflectors. Concentration can be accurately measured if a portion of the 1.5 mrad laser beam exiting the transceiver falls on a retroreflector. No other user adjustment or calibration is necessary in normal operation.

2.1.1 Calibration of path integrated monitor

For ammonia monitoring, the laser is locked to a strong absorption line at 1540.49 nm with a modulation amplitude approximately 1.5 times the pressure broadened line width. The system was calibrated by placing a 14.6 cm cell containing 10-10,000 ppm-m of ammonia in air in front of the retroreflector. As expected, the system response is linear, and in good agreement with the theoretical calibration function based on estimated spectral coefficients taken from FTIR spectra¹¹ and the known functional form of the second harmonic absorption signal.⁶

The instrument zero and calibration were periodically checked for various target distances at the urban site and at the feedlot. The returned laser signals from retro-reflectors located at two distances were alternatively monitored with an instrument time constant of 0.5 sec and with a dwelling period about 2 minutes. Five repetitive cycles were performed for each measurement. At the end of each measurement sequence, a calibration cell containing a mixture of 1.25 torr NH₃ and ambient air corresponding to 240 ppm-m NH₃ was placed in front of the 5 m retro-reflector for calibration. The mean and standard deviation for each sequence are summarized in Table 1 for the instrument zero at three target distances. Instrument calibration on five different days is reported in Table 2.

The instrument zero shows a consistent zero offset due to optical interference effects. The instrument zero is +50 ppm-m for a 5 m distance, and decreases to near zero for distances greater than 100 m. Therefore no background subtraction was required for long path measurements. The calibration checks demonstrate a consistent calibration over the entire field test period.

Table 1. Instrument Zero Measured at Three Different Target Distances

<u>L (m)</u>	<u>I_{2f}/I₀</u>	<u>σ(I_{2f}/I₀)</u>	<u>ppm-m</u>	<u>σ(ppm-m)</u>
5	7.50x10 ⁻⁵	0.60x10 ⁻⁵	52	4
60 ¹	4.73x10 ⁻⁵	0.35x10 ⁻⁵	32	3
340 ¹	-2.12x10 ⁻⁵	0.71x10 ⁻⁵	-14	5

¹ Values were measured at the urban site

Table 2. Instrument Calibration on Four Different Days

<u>Date</u>	<u>ppm-m</u>
06-17-94 ¹	246
06-23-94 ¹	236
06-27-94 ²	257
06-30-94 ²	249
08-22-94 ²	231

¹ Values were measured at the urban site

² Values were measured at the feedlot

Figure 3. Photograph of DARCS System Showing Transceiver (Foreground on Tripod), Electronics Box, and Retroreflector (Background on Tripod).

2.2 Point monitor

The point monitor used in this field study was based on a Monitor Labs ML9842 analyzer, which is a conventional chemiluminescent NO_x analyzer specifically modified to measure ammonia. The thermal converter used in this study was manufactured by Measurement Technologies and consists of a stainless steel oven heated to 450 C. The conversion process is aided by a proprietary catalyst. The monitor was calibrated before and after the field study. The converter efficiency was measured to be 98.5 % over a range of 0 to 20 ppm ammonia. Figure 4 illustrates the response of the monitor to ammonia as a function of concentration. The response is linear, indicating stable and efficient conversion over the entire range.

Figure 4. Point Monitor Response to Input Ammonia Concentration. The Solid Line Represents a Linear Least Squares Fit to the Calibration Data. This slope is 0.9858 and Intercept is 0.0563.

2.3 Physical layout of the field study

Figure 5 illustrates the physical layout of the field instrumentation. A trailer was parked in a field directly to the south of a cattle feedyard. The anemometer was mounted, at a height of 6 feet, approximately 40 meters from the trailer. While this height does not eliminate boundary effects in wind measurement, it was similar to the height of the inlet for the point monitor. For the majority of the results presented here, the retroreflector for the open path monitor was mounted on a telephone pole approximately 260 meters to the west. Several pens of the feedyard were directly under the optical path of the open path monitor. For upwind measurements, a second retroreflector was mounted 133 m to the south and between the cow pens. Additional data were obtained at an urban site proximate to the Spectral Sciences laboratories in Burlington, Massachusetts. For these studies, the monitoring path was 340 m over parking lots to the edge of a major interstate highway, Interstate 95.

The environment of a cattle feedyard is one of extreme levels of dust and activity. Cattle moving about on bare ground in the pens continually raise the particulate density of the ambient air. Cattle moved from pen to pen also aggravated the situation. At the onset of the study, one concern was that such an environment might present reliability problems for both analyzers. However both instruments performed well for approximately two months

with only minor maintenance. In one instance power to the instruments was disrupted by power connections being broken as cattle were moved. A lightning strike in the vicinity did disable the data acquisition system and the anemometer after approximately two months, at which point the study was terminated. The instruments suffered no ill effects from the lightning strike.

Figure 5. Physical Layout at Feedlot Site.

3. RESULTS AND DISCUSSIONS

3.1 Path Integrated Monitor

3.1.1 Spectral Scans

Two spectral scans using the path-integrated instrument are shown in Figures 6a and 6b: one is from an urban site in Massachusetts covering a distance of 340 m, the other is from the feedlot in Colorado and covers a distance of 403 m. The spectral scans were accomplished by tuning the laser diode temperature from 18 to 28 °C. The data is plotted in terms of the normalized second harmonic signal (I_{2f}/I_0 , where I_0 is the returned laser intensity). The top trace, which corresponds to the 3f spectrum of NH_3 in the reference cell serves as a line marker for NH_3 absorptions, is in arbitrary units and offset from the bottom 2f trace. Absorption lines due to H_2O , CO_2 and NH_3 within the path are also identified in the figures. The NH_3 line at 26.2 °C (1540.49 nm) is seen to be relatively clear of interfering absorptions and is used for all line-locked measurements. An increase of NH_3 concentration by 1.1 ppm from the urban site to the feedlot is observed from the figures.

3.1.2 Comparison between urban and feedlot operations

A comparison of daily concentration variations of NH_3 and associated operation conditions between the urban site and feedlot was made using the path-integrated instrument in normal line-locked operation. Figure 7 shows the NH_3 column density and returned 1f signal as a function of clock times, with a time constant of one minute.

During the 60 hr period of urban NH_3 monitoring (Figure 7a), 20 min averaged signal varied from 0 (-0.00) to 25 ppm-m (0.076 ppm) and the returned laser intensity, 1f, varied over a factor of two with weather conditions. While the observed signal shows the characteristic diurnal variation in NH_3 concentration, we have no independent confirmation of ammonia concentration. Therefore, this small variation of observed NH_3 concentrations defines an upper bound for the detection-limit of the technique. The decrease of laser intensities at 4 pm on the second day and between 9 pm and 5 am on the third and the fourth days was due to rainy weather and moisture condensation inside the retro-compartment.

Figure 6. Spectral Scans from Urban Site (a) and Feedlot (b).

(a)

(b)

Figure 7. Column Density (ppm-m) and 1f Signal at the site (a) and in Feedlot (b).

In contrast to the urban operation, the feedlot operation (Figure 7b) shows a large span of these values over a 24 hour period on 7/22/94. The NH_3 concentration varied from 280 (1.1 ppm) to 1680 ppm-m (6.5 ppm) except for a period near 20:00 when the returned signal approached zero with a corresponding increase in noise. This noise is decreased with further time averaging. The large variation in the 1f signal is due primarily to flexure of the trailer floor with thermal expansion, and secondarily to air quality at the feedlot. Examination of the status parameters of laser temperature, current, and power, which are logged along with the data presented, showed that the laser was well controlled throughout the measurement period.

3.1.3 Comparison of upwind and cross wind measurements

Comparison of upwind and crosswind data allows a direct measurement of the ammonia emitted from the source. Two retro-reflectors were set up to define measurement paths across the feedlots (West at 259 m) and between the feedlots (South at 133 m). For a southerly wind, the later path samples nearly pure ambient air. The two paths were monitored for alternating two minute periods following the procedure described previously for instrument zero and calibration measurements. Results are presented in Figure 8. The path integrated concentration along the upwind path was 0.01 ± 0.04 ppm, in reasonable agreement with the point monitor concentration of 0.04 ppm. The crosswind integrated path concentration was 1.23 ± 0.14 ppm.

Figure 8. Repetitive Upwind Cross Wind and Measurement.

3.2 Comparison between point-monitor and path-integrated instrument

A comparison of concentration measurements between the point-monitor instrument and the path-integrated instrument was also made for the data of 7/22/94. The NH_3 concentrations (ppm) measured by these two instruments are plotted in Figure 9 together with the environmental temperature (T_{trailer} , $^{\circ}\text{C}$), wind speed (WS, miles/hr) and wind direction (WD, north = 0°). The time constant for the concentration and temperature measurements is approximately one minute. The two monitors recorded similar concentration time histories on a time scale of tens of minutes. There are substantial differences however in the detailed time history on a minute time scale and in the relative intensities of each feature. These, no doubt, reflect the difference in sampling for the

point monitor and path integrated monitor. For example, the point monitor, located between the feedlots measured as low as 0.1 ppm when the wind was from the south. The integrated monitor measuring cross wind directly above the feedlots monitored 1 ppm. These differences are consistent with the upwind/cross wind measurements discussed above.

Figure 9. Typical Daily Data with One Minute Time Casting.

3.2.1 Time history of ammonia concentrations

Figure 10 presents data for the entire 18 day measurement period averaged over one hour intervals. Midnight of each day is indicated by a dotted line. The experiment was started on July 21 and ended by a lightening-strike on August 11. The disruption of the experiment on the eighth day was caused by cattle breaking the power connection to our instruments. A diurnal temperature variation of 12 °C is apparent from the figure.

Figure 10. Complete Data Set with One Hour Averaging Time.

The two ammonia monitors show similar ammonia time histories, characterized by ammonia peaks in the early nighttime hours. Between 20:00 and 23:00, the ammonia concentration over the cow pens exceeds 2 ppm 40 % of the time, while between 03:00 and 15:00 it is less than 2 ppm 99 % of the time.

Significant differences are seen between the two monitors which reflect the differences in the sampling geometry. For example, the concentration measured at the point monitor is more highly variable, and generally lower than that observed over the integrated path. The mean and deviation for the one hour averages are 0.6 ± 0.4 for the point monitor and 1.2 ± 0.5 the path integrated measurement. The point monitor measured less than 0.1 ppm ammonia 25 % of the time, while the path integrated monitor never measured less than 0.5 ppm over the cow pens.

3.2.2 Wind effect

Figure 11 illustrates the fundamental difference between the point monitor and the open path monitor. To generate this plot the compass was divided into four quadrants as shown in the inset of the figure. The hourly concentration averages for both instruments were categorized into these quadrants according to the average wind direction for that hour. The result is four time series each representing a quadrant. The correlation coefficient between the analyzers and the average reported concentration for each quadrant was calculated. The ratio of the average reported concentration is shown in Figure 11a. The result of the correlation calculation is shown in Figure 11b. When the wind is out of the south, the two instruments show poor correlation due to the fact that ammonia coming off of the feedlot is carried away from the point monitor towards the north. However, the optical path for the laser device is directly over the cattle and consequently continues to interact with the ammonia. Measurements from the other three quadrants, where cattle are present upwind of the point monitor show strong correlation. When the wind is from the north, the two monitors measure the same ammonia concentrations.

Figure 11. Correlation of the Point and Path Integrated Ammonia Concentration by Wind Direction.

3.2.3 Frequency analysis of ammonia concentrations

To examine possible periodicities within the ammonia concentration due to either meteorological or photochemical phenomena, a brief study was undertaken. Figure 12 contains a plot of the Fourier transform of approximately 10 days of data for the open path and point monitors as well as the wind speed and wind direction. Both monitors have spectral components at frequencies which are near multiples of an inverse day. This reflects the tendency towards higher concentrations over a 2-6 hour period in the early nighttime and is consistent with a photochemical reduction in the NH_3 concentration during the extended daylight hours of midsummer. The point monitor however, has much larger low frequency components corresponding to 24 and 12 hour periods ($1-2 \text{ day}^{-1}$). Both wind speed and wind direction show significant 24 hour periodicity in Figures 12c and 12d. This is probably the reason for the periodicity observed in the point monitor's measured concentration. On the eastern slope of the Rocky Mountains afternoons are generally breezy as a result of a steady outflow from the mountains. In the area of the study the wind is from the northwest and can be strong. This type of wind would carry ammonia from the cattle pens to the point monitor at nearly the same period of the day each day, explaining the 24 hour periodicity. However the open path monitor would be exposed to a more constant concentration.

Figure 12. Fast Fourier Transform of Data from 7/30/94 to 8/10/94.

4. CONCLUSIONS

Both the chemiluminescence-based point monitor and the diode-laser based path integrated monitor provided reliable, accurate, and trouble free monitoring of ammonia concentrations for an extended time in a hostile environment. It is particularly significant that the prototype DARCS path integrated sensor worked automatically with no adjustments or alignments from the time it left the Burlington, MA laboratory until its return 3 months later.

The two monitors give consistent results if and only if they sample air with the same fractional ammonia concentrations. Under most circumstances however, the ammonia concentration several meters from the cow pens do not give a fair indication of the total ammonia produced over the cow pens. The path integrated measurement indicated that the average concentration over the cow pens varies over only a small range of 0.5-2 ppm during the daylight hours, with occasional excursions into the 2-4 ppm range during the early portion of the night. The concentration measured by the point monitor just 30 meters from the cow pens is likely to be substantially lower due to transport effects. These measurements approach the path integrated measurements only under favorable wind conditions.

The choice of monitoring technique is dependent on the quantity of interest. Point monitors work best for monitoring the concentration at a single point of interest, such as a smokestack, or workstation. The path integrated DARCS system would be appropriate for any application where a more complete sample of concentration over a larger area is required. These include: remote monitoring of emissions from an extended source, fence-line monitoring of gases entering or leaving the perimeter of a facility, surveys of ambient concentrations, or chemical surveying.

5. ACKNOWLEDGEMENTS

The authors would like to acknowledge U. S. Department of Energy as the sponsor of the Diode-Laser Absorption Remote Concentration Sensor (DARCS) Program under SBIR Phase II Grant No. DE-FG02-91ER81196.A001.

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