

INSITU ANALYSIS OF AMMONIA SLIP AND WATER VAPOR USING A TUNABLE DIODE LASER FOR SCR/SNCR OPTIMIZATION AND BOILER TUBE SURVEILLANCE IN POWER PLANTS

Warren Dean
Business Development Manager – Lasers
Siemens Applied Automation
500 West Highway 60
Bartlesville, OK 74003

KEYWORDS

Tunable Diode Laser, Ammonia Slip Analyzer, Selective Catalytic Reduction (SCR), Selective Non-Catalytic Reduction (SNCR), Ammonia (NH₃)

ABSTRACT

Environmental Regulations driven by the 1990 Clean Air Act require Power Plants to reduce NO_x emissions. SCR's and SNCR's reduce NO_x emission by injecting ammonia into the combustion flue gas, which ideally reacts with the NO_x to form H₂O and N₂. The efficiency of the SCR/SNCR is determined by monitoring the outlet for excess NH₃, referred to as NH₃ slip. The flue gas sample at the measurement point is hot, wet and laden with dust, primarily in Coal Fired Plants (Not usually a problem in Gas Fired Plants). The sample point's harsh physical conditions coupled with the highly reactive nature of NH₃ makes reliable extractive low level analysis very difficult. The paper describes an insitu Tunable Diode Laser analyzer for measuring NH₃ and water vapor in the combustion flue gas just after the SCR in a Power plant. This paper includes performance data generated from the analyzer during a six week test on an actual coal fired Power Plant.

INTRODUCTION

This paper briefly describes the application of SCR's and SNCR's to reduce NO_x emissions. Both extractive and insitu NH₃ slip monitoring analysis systems are discussed. Actual performance data generated from an insitu tunable diode laser NH₃ slip analyzer during a six week test shows that the insitu tunable diode laser was extremely linear,

demonstrated practically no zero or span drift, was easy to install, provided 100% data capture with relative accuracy of 9.0% at 3.78 ppm NH₃.

THE SCR/SNCR DENOX PROCESS

Nitrogen oxides (NO_x) formed in the combustion process are ideally reduced to water (H₂O) and nitrogen (N₂) in the SCR process (Selective Catalytic Reduction). Ammonia (NH₃) or urea (CO(NH₂)₂) is introduced to, and mixed with, the flue gases upstream of a heterogeneous catalyst over which the reduction takes place. Depending on the amount of dust, type and concentration of acidic gas components in the flue gas, the SCR process is normally operated in the temperature range of 250° - 400°C.

The SNCR process (Selective Non Catalytic Reduction), usually uses ammonia (NH₃) or urea (CO(NH₂)₂) introduced to, and mixed with the flue gases in the hot combustion zone where the reduction of NO_x takes place. Depending on the type of reducing agent, different additives, etc., the SNCR process is usually operated somewhere in the temperature range of 800° - 950°C. The conversion of NO_x to N₂ in the presence of NH₃ is optimized at this temperature range. Temperatures below the temperature window cause the reaction rate to slow resulting in high ammonia slip, and above the temperature window the oxidation of ammonia to NO_x is too high, thus the process tends to produce NO_x instead of decreasing it.

WHY MEASURE AND CONTROL NH₃ SLIP?

Ammonia slip is measured after the DeNO_x process to control the amount of NH₃ injected so that enough NH₃ is present to react with NO_x to minimize the NO_x emissions to meet local environmental regulations. At the same time it is essential to efficient Power Plant operation not to input too much NH₃ into the combustion gas. Excess NH₃ injection can shorten the life of the SCR catalyst, cause increased corrosion, contaminate the fly ash, increase ammonia salts build up in the preheater and increase NH₃ release to the atmosphere. Some states may also have a requirement to report stack emissions.

AMMONIA BISULPHATE (ABS)

The NH₃ injected or thermally produced from injected ammonia derivate, into the flue gas can form ammonium salts from acidic gas components in the flue gas at lower temperatures. Theoretically several salts can be formed e.g. NH₄Cl, NH₄NO₃, but the main problems related to ammonium salt formation is caused by ammonium bisulphate (ABS), in the power producing industry from NH₃, H₂O and SO₃ in the flue gas. Some formation of ammonium sulphate will also occur, especially when the ammonia is in excess of the SO₂ concentration. Ammonium bisulphate has a melting point of 147° C, and will consequently be present as a liquid accumulated on surfaces or as a liquid aerosol in the flue gas at normal operating temperatures. Such an aerosol contributes to the visibility of the flue gas plume – referred to as “blue haze” phenomena. Furthermore, the ABS is hygroscopic at lower temperatures and causes a corrosive solution when absorbing moisture from the gas.

Also if the ABS is formed on a low temperature catalyst, it will plug parts of the catalyst, increasing the pressure drop over the catalyst causing catalyst deactivation.

ABS ON AIR PREHEATER SURFACE

The temperature of the flue gas decreases as it passes the air preheater and the ABS condensation temperature is reached somewhere inside the air preheater. Most of the ABS is formed and accumulated on, the cold heat exchange surfaces, but a part of it will be formed in the flue gas thus producing a liquid aerosol.

Increasing NH₃ slip increases the ABS. The ABS accumulates in the preheater. This ABS accumulation causes a pressure drop decreasing the air preheater efficiency and eventually clogging the unit. It has been reported that by monitoring and controlling the NH₃ slip at 2-3 ppm in the duct just after the SCR, that the time between outages due to ABS accumulation has been extended from 2 years to every 4 years. Also an accurate measurement of the NH₃ slip gives the possibility to predict or plan a maintenance outage for preheater cleaning and/or catalyst replacement.

Some power plants sell their fly ash to cement manufacturers. Too much NH₃ slip may contaminate the fly ash. Too much NH₃ in the fly ash can weaken the cement and also smells strongly of NH₃ making the fly ash unmarketable.

THE MEASUREMENT PROBLEM

The sample in the duct just after the SCR is hot, 250-400°C, saturated with water and laden with dust (usually about 20-25 g/Nm³). The sample in the stack is a little cooler and contains less dust but the NH₃ analysis problem still remains. How does one get all the NH₃ in the duct to the analyzer? Extractive analysis systems have historically used the differential chemiluminescent technique. This technique employs a heated probe, heated filter and a NH₃ to NO converter at the stack. The NH₃ is converted to NO. NO is relatively stable and transported via heated line to a cooler and pump then to the chemiluminescent analyzer for analysis. This gives a value for NO, NO₂ and NH₃. Bypassing the converter the reactive NH₃ in the sample is not converted to NO and ideally not measured by the chemiluminescent analyzer. This gives NO + NO_x. The NH₃ is inferred by subtracting the two values i.e. $(NO + NO_2 + NH_3) - (NO + NO_2) = NH_3$.

The extractive method relies on the assumption of constant conversion efficiencies of the NH₃ → NO converter and the NO₂ → NO converters in the CLD's. Also calibration with NH₃ blends has been difficult and costly due to the reactive nature of NH₃. The uncertainty of the NH₃ measurement and the cost of maintenance of the extractive sample handling system over time lead to a search for a more reliable analysis technique. The force driving the search for a more reliable and repeatable analysis technique is that the plant operators need to monitor NH₃ after the SCR at 2 ppm and below. Some plants want to measure NH₃ at 0.5 to 1 ppm to monitor their catalyst performance to predict/forecast an outage date to coincide with long lead time catalyst delivery.

Extractive systems have been unable to provide repeatable, reliable NH₃ measurements at these levels.

THE SOLUTION – INSITU TUNABLE DIODE LASER

By using an insitu type analysis system the sample never leaves the process. The NH₃ concentration is not affected by sample transport. There is no sample handling system components to fail due to heat, dust, water, and everyday “wear and tear”.

The tunable diode laser measures NH₃ across the duct resulting in an average, not a point source, as in extractions sampling. It has been demonstrated in coal fired Power Plants that the NH₃ concentration is highly stratified in the duct. Across the duct diode laser analysis provides a true average NH₃ concentration in the duct.

THE ANALYZER – SIEMENS LDS 3000 TUNABLE DIODE LASER

OVERVIEW

There are five basic components to the tunable diode laser.

1. A central control unit - contains the operator control panel, display, system computer, laser, reference cell and input/output cards.
2. Hybrid cable – connects the control unit to the laser Transmitter.
3. Laser Transmitter Box located on the duct.
4. Laser Detector Box located on the duct.
5. Loop cable – connects the Laser Detector Box to the Transmitter Box.

The insitu tunable diode laser NH₃ slip analyzer consists of a central unit, hybrid cables and sensors. The hybrid cable contains optical fibers and a low voltage electrical cable (24 V), and connects the sensors with the central unit.



FIGURE 1. INSITU TUNABLE DIODE LASER NH₃ SLIP ANALYSIS SYSTEM

CENTRAL UNIT

The Central Unit incorporates a control panel with display, built-in keyboard, control computer, laser, reference cell, electronics for the laser and slots for up to three receiver channels. A PC-card (PCMCIA card) is used to hold the software and necessary files for the operation. This simplifies the software updating which can be done remotely through the serial port. No moving media like hard drives are used.

The control computer (an industrial X86 PC) is mounted in a computer housing together with a display driver, a data acquisition card and a TPU (Time Processing Unit). The last two units handle the timing and acquisition of data. The control computer measures up to three points at a speed of 24 times/second. Response time down to 0.1 s is achievable. The central unit also handles a large number of I/O-units for 4-20 mA input/output and relay output. The I/O setup is completely flexible and configured to the application.

HYBRID CABLE

The hybrid cable is constructed for very harsh environments and consists of two optical fibers, one for transmission of the laser light to the detector and one for the return of the detected signal. The cable is suitable for operation between -50°C and +80°C. It also contains two electrical wires used for powering the electronics in the sensors (24 VDC).

SENSORS

The sensors consist of a transmitter and a receiver intended to work Cross Duct. In the transmitter there are provisions for connection of a fiber optic connector and in the receiver there is a photo detector and some electronics.

The sensor optics requires protection from the measurement environment. There is a number of ways to accomplish this. The standard approach is to use pressurized instrument air. The sensor can be equipped with a number of options such as heater for the instrument air, in line calibration path, fan purging, steam purging, etc. Sensor maintenance is easy by removing it from its flange by means of a quick connect. The removal and relocation of the sensor does not require realignment. Thus the sensor optics can very easily be cleaned if needed.

MEASUREMENT PRINCIPLE

The tunable diode laser NH₃ slip analyzer measures the gas concentration by using line absorption spectroscopy. Plotting the absorption of a gas mixture versus the wavelength, it can be seen that absorption only takes place at certain wavelengths in the spectral region. The extremely narrow absorption peaks are referred to as absorption lines. See Figure 2 below.

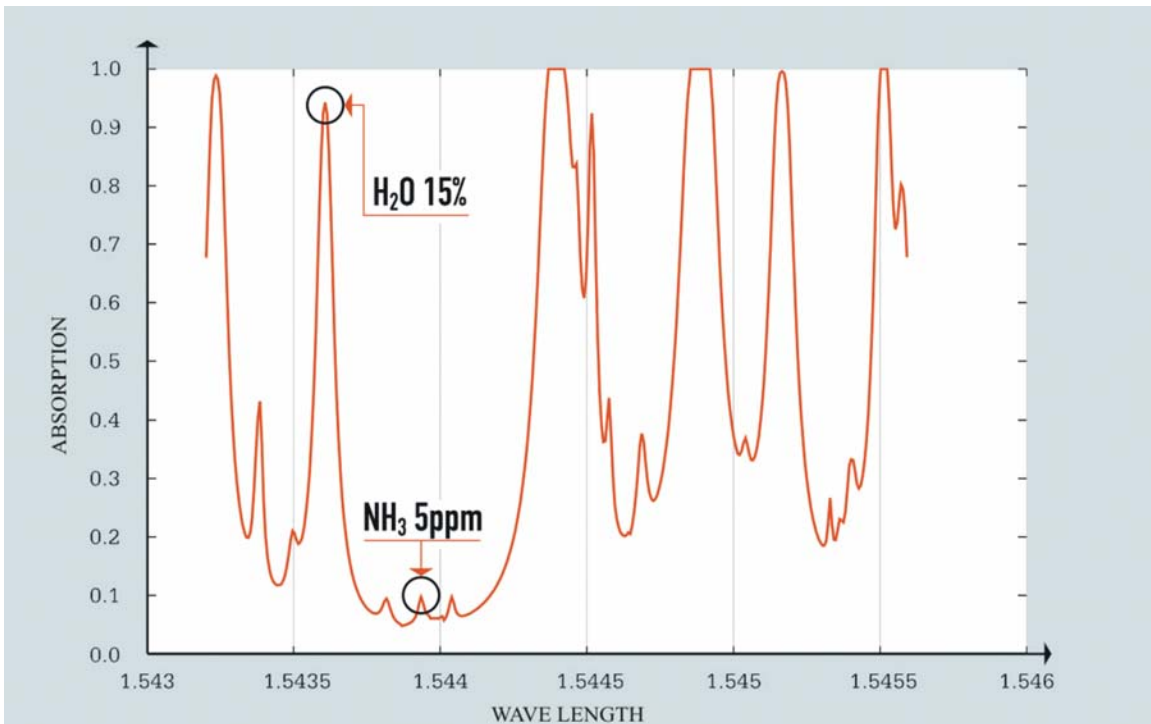


FIGURE 2. NIR SPECTRUM NH₃/H₂O

The NH₃ is identified by comparing the sample with the spectrum from a built in reference cell. The analyzer performs line spectroscopy by using a diode laser as the light source. The laser's spectral width is much narrower than the width of the NH₃ absorption line. Furthermore, the wavelength of the laser can be selected to be near one absorption line of the gas to be measured. Varying the current and temperature, the laser wavelength is tuned to cover the required narrow spectral range. The tuned range includes the absorption line. The laser light is partially absorbed when it is tuned over the absorption line. The area beneath the absorption line can be extracted from the laser signal received. The area beneath the absorption line is a measure of the gas concentration. To provide H₂O concentration with the same laser, the laser is tuned past the NH₃ spectral range to a near by H₂O absorption line.

The light emitted from the laser is split into five beams. The first beam passes through a reference gas and is then detected. This reference signal is used for continuous self-calibration and zero point determination of the system, taking temperature and pressure into account. The second beam is used for measuring the intensity of the laser and

provides the control unit with information relating to the state of the laser. The third, fourth and fifth beam is conducted via the optical fiber to the respective sensor head, where it enters the measuring section. When the laser light passes through the gas in the measuring section it is partially absorbed. The receiver detects the laser light and after signal conditioning the signal is converted to an optical signal and returned to the central unit using the multimode optical fiber.

A block diagram of analyzer is shown in Figure 3 below.

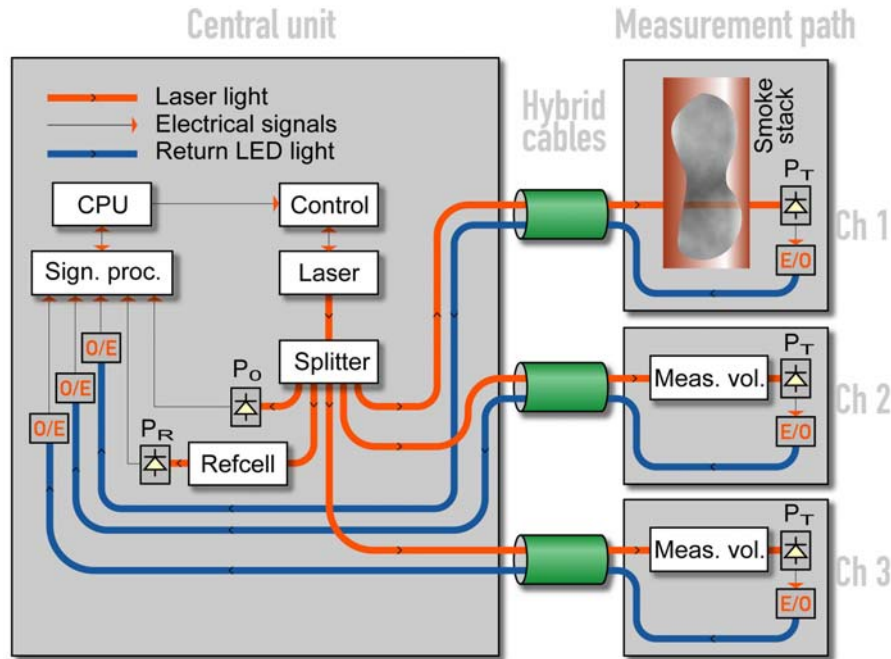


FIGURE 3. BLOCK DIAGRAM OF THE MEASUREMENT SYSTEM

The concentration of the measured gas is calculated from the absorption spectrum for the measurement channel (PT). Any change in the measurement conditions, for example as a result of a higher dust load in the flue gas or contamination of the optical components, is compensated for automatically to guarantee accuracy of the measurement results under a wide range of operating conditions.

ACTUAL INSTALLATION DATA

Figure 4 below illustrates the typical insitu NH_3 slip analysis set up for a coal fired power plant.

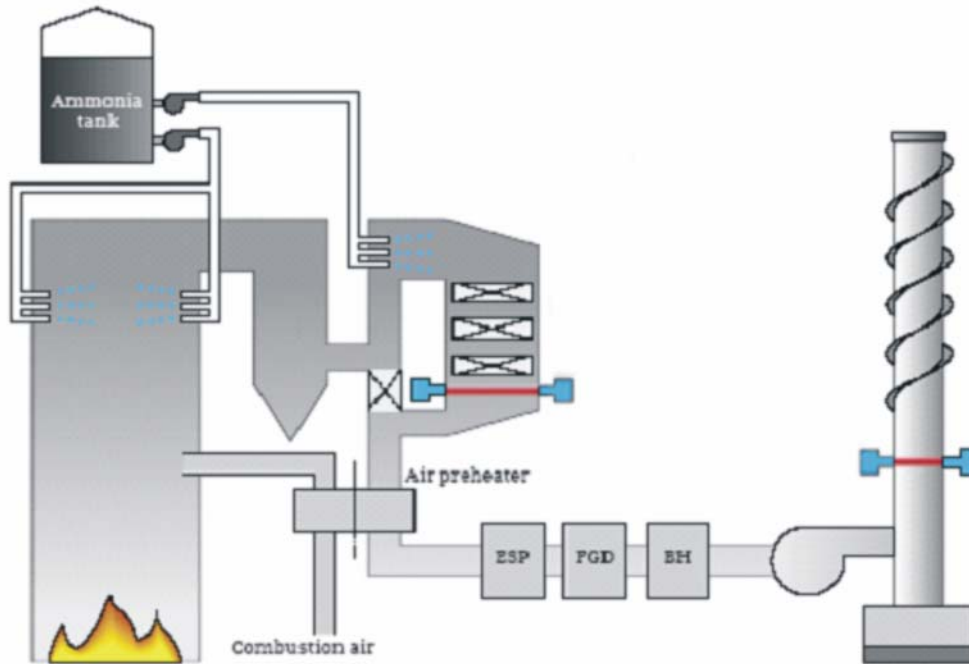


FIGURE 4. TYPICAL INSITU NH_3 SLIP ANALYSIS SET UP

ACTUAL TEST SUMMARY ON A FULL SCALE COAL FIRED POWER PLANT

A recent test on a full-scale coal fired power plant performed under the US EPA's Environmental Technology Verification Program demonstrated that the insitu NH_3 slip analyzer performed quite well. A summary of results follows. (See Table 1) For complete test protocol and raw data see "Environmental Technology Verification Report Continuous Emission Monitor for Ammonia" prepared by Battelle under a cooperating agreement with the U.S. Environmental Protection Agency. 1

TABLE 1. SELECTED SUMMARY OF RESULTS

PARAMETER	PERFORMANCE RESULTS	COMMENTS
Relative Accuracy	9.0% at 3.78 parts per million on a wet volume basis (ppmwv) 9.1% at 9.20 ppmwv 7.0% at 14.4 ppmwv	Based on 12 data points at each concentration
Linearity	Regression slope = 1.059 (\pm 0.014) ppmwv, r2 = 0.9937	Calculated over three concentration levels with 12 data points each.
Precision	4.4% relative standard deviation (RSD) at 4.85 ppmwv 3.8% RSD at 10.5 ppmwv 1.9% RSD at 16.3 ppmwv	Variability due primarily to the variability of background ammonia concentration in the duct
Calibration and Zero Drift	No zero drift Span RSD values – 0.12 to 0.26%	Minimal drift over the five-week test
Ease of Use	Generally easy to use	
Completeness	100% data capture	

CONCLUSION

The measurement and control of NH₃ slip at 2 ppm and below is necessary to optimize SCR performance to reduce NO_x emissions and increase power plant efficiency. Historically extractive systems have been used to measure NH₃ at much higher levels. Some extractive NH₃ analysis systems are not a direct NH₃ measurement, but require multiple converters (Modified NO_x Analyzer) and high maintenance compared to insitu tunable diode laser NH₃ slip monitors and have not been able to reliably measure NH₃ in 1-2 ppm range in the duct just after the SCR. Extractive analyzers utilizing Ion Mobility Spectroscopy (IMS) technology have also been used in this application.

The insitu tunable diode laser has demonstrated that this measurement can be made reliably with minimal installation and maintenance cost.

REFERENCES

1. Hand, Kelly, MacGregor, Ian , Carvitti, Joseph, Rectanus, Mike, Cowen, Ken, and Riggs, Karen, “Environmental Technology verification Report, ETV Advanced Monitoring Systems Center, Siemens Laser Analytics LDS 3000 Continuous Emission Monitor for Ammonia, Battelle, Columbus, Ohio, January 2004. Available from the US EPA.

2. H. Ahlberg, S. Lundqvist, R. Tell and T. Andersson, "Laser spectroscopy for *in situ* ammonia monitoring", *Spectroscopy Europe*, vol. 6, pp. 22-26, March/April 1994.
3. H. Ahlberg, S. Lundqvist, T. Andersson, and R. Tell, "Near-IR diode laser system for emission and process control", Int. Congress on Optical Science & Engineering, Hague, Netherlands, March 12-15, 1990.
4. H. Ahlberg, S. Lundqvist, R. Tell, and T. Andersson, "Industrialized high sensitivity fiber-optic near-IR diode laser based gas analysis system", Optical Sensing for Environmental Monitoring, Atlanta, Georgia, USA, October 11-14, 1993.
5. L. Sandström, H. Ahlberg, S. Lundqvist, R. Tell and T. Andersson, "The influence of the FM tuning characteristic on wavelength modulations spectroscopy" *Advances in Optical Imaging and Photon Migration*, pp. 259-261, Orlando, Florida, USA, March 8-11, 1998.
6. M. Walter, W. Schäfer, M. Markus, and T. Andersson, "Analysis and Control of Combustion in a Waste Combustion Plant by Means of Tunable Diode Lasers" 5th International Symposium on Gas Analysis by Tuneable Diode Lasers, Freiburg, Germany, February 25- 26, 1998.
7. S. Lundqvist, T. Andersson, and J. Grimbrandt, "Photonics in advanced process control applications", Photonics East, Boston, USA, November 1-5, 1998.
8. S. Sandström, S. Lundqvist, and T. Andersson, "In-Situ monitoring of O₂ and temperature in a pelletizing process", Int. Symposium on Optical Science, Engineering, and Instrumentation, Denver Colorado, USA, July 18-23, 1999.
9. M.W. Markus, S. Semer, M. Walter, W. Schäfers, and L. Sandström, "Feuerungsregelung einer Hausmüllverbrennungsanlage mittels In-Situ-Diodenlaser-Spektroskopie - Betriebserfahrungen und Ausblicke", *VDI Berichte* Nr. 1551, 67-72 (2000).
10. D. Malmberg, L. Sandström, „In-situ monitoring Of Oxygen Concentration and Gas Temperature in a Metallurgical Process by using Diode Laser Spectroscopy“, The 6th Japan-Nordic Countries joint Symposium, The Iron and Steel Institute of Japan, Nagoya, 2000, pp. 145.
11. D. Malmberg, L. Sandström, J. Nygren, and C. Sandberg, ICS 2001, 2nd International Congress on the Science & Technology of Steelmaking, Swansea 2001, vol. 1, pp. 299.
12. L. Sandström and D. Malmberg, "On-line and In-Situ monitoring of oxygen and gas temperature in a reheating furnace utilizing tunable diode-laser spectroscopy", *Spectrochimica acta part A*, 58, (2002), pp. 2449.
13. G. Haeffler, "Laser Based Gas Analysis for Process Control in Waste Incineration Applications", *VDI Berichte* Nr. 1667, 1-7 (2002).

14. M. Markus, "Optimierungspotential in Mullverbrennungsanlagen mittels In-Situ Gasanalytik", VDI-Seminar BAT- und preisorientierte Dioxin/Gesamtemissionsminimierungstechniken 2000, Munchen, 14/15 Sept. 2000.
15. C. Sandberg, L. Sandström, G. Haeffler, and J. Nygren, "Self-induced Pressure-Broadening measurements of oxygen transitions in the A-band with vertical-cavity surface-emitting lasers", 3rd Int. Conf. on TDLS, Zermatt, July 8-12 , 2002, p. 76.