UV LED-based Fiber Coupled Optical Sensor for Detection of Ozone in the ppm and ppb Range

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Abstract— **A realized novel optical sensor system to measure the concentration of ozone using the emitted light from Light Emitting Diodes in the ultraviolet range is described in this paper. The wavelength selective light interaction of the gas takes place in a fiber coupled and robust reflection cell. The control electronics are separated from the optical sensor head. Therefore it can be used in harsh environment for instance close to discharge plasma in strong electromagnetic fields or at high temperature. The sensor design is potentially low cost, quite small and well suited for a large number of applications. It can be implemented in industrial process control application or in small battery powered hand held devices. This setup is also capable for a parallel and selective measurement of nitrogen dioxide NO_2 and sulfur dioxide SO_2 – this is already implemented and proved. Further specific LEDs are utilized for this purpose in the setup. For the ozone measurements two different sensor heads where used. A small 4 cm long reflection cell with potential for handheld devices and a 40 cm one thought for high resolution stationary application. The resolution (standard deviation measured at a zero concentration of ozone) of the sensor with the small cell is about 30 ppb at 700 msec measurement time and about 3 ppb at 1,4 sec at the longer cell.**

I. INTRODUCTION

Ozone is a very oxidizing gas that can lead to irritations at the human body for concentrations above approx. 100 ppb [1]. At higher concentration it is a toxic gas. Also long time exposure of low concentrations can harm the lung function and fray the respiration system. ozone or trioxygen (O_3) is an unstable molecule that reacts as oxidizing agent in manifold way with its environment. In the nature ozone is generated mainly by cracking of air oxygen induced by ultraviolet radiation in particular in combination with exhaust gases such as hydrocarbons. In mountain regions, where the UV-radiation is stronger, also the O3 levels are much higher. Especially at summertime smog the ozone concentration levels are strongly increased so that it affects the human life. In exhaust gas polluted cities the reduction of ozone is much quicker because of the higher number of reaction partners [2] but on the other hand there are also components that support the O_3 generation. A significant higher concentration of ozone can be found in the stratosphere. Here it is an important component in the chemical ozone cycle, harmful high energy ultraviolet radiation that is emitted from the sun is absorbed by this process and therewith it protects the earthy life.

In industrial application ozone is utilized in various ways, as an active oxidation partner in chemical reaction, for bleaching substances and in food industry for killing microorganism. In the near past it is increasingly used for disinfection e.g. for water purification, because it is self degrading - this is a big advantage compared to other disinfection chemicals such as chlorine. But ozone is also unmeant generated by electric discharge scenes in air e.g. by an electric arc. In many cases this is an unwanted process but it also can be used as an indicator for a malfunction of an electrical device e.g. in power electronics.

Thus there are many applications where ozone plays an important role, so there is a need to monitor or control its concentration. The novel UV LED based fiber optical sensor system can be used in manifold application and compared to electrochemical or mercury lamp based sensors it shows advantages. The sensor concept enables a small and low cost design using standard receivers without any optical filter. So it also can be use in small hand held devices. The use of optical fibers enables the system to measure in harsh environment such as close to electromagnetic fields or high temperatures. Compared to electrochemical O_3 sensors, there is no degrading or any poisoning through the ozone and so the sensor lifetime is not limited. The LEDs have low power consumption, have potentially very long life time, are quite robust and are low cost compared to UV gas discharge lamps. Thus there are no high follow-up costs for the sensor system. The developed sensor system includes further LEDs for a selective measurement of nitrogen dioxide and sulfur dioxide.

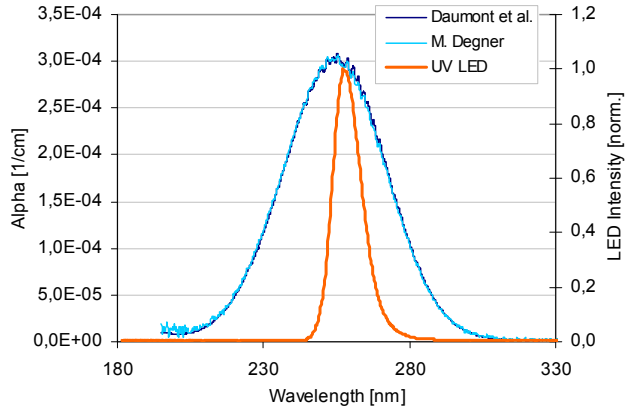

Figure 1. Spectral characteristics of ozone absorption and LED emittance

II. LED-BASED SENSOR CONCEPT

The sensor concept is based on the wavelength specific light absorption of ozone and other gases in the ultraviolet – visible (UV-VIS) wavelength range. Molecules have spatial separated charges in its structure they act as forced or stimulated oscillators while an electromagnetic wave passes. Most molecules show resonant properties in different wavelength regions. There are rotation bands in the far infrared, rotation vibration bands with its fundamentals and overtones in the mid and near infrared and there are resonances in the ultraviolet – visible range due to valence electron excitations. While almost single bands appear in the infrared – the so called finger print region, the UV-VIS absorption is often dominated by overlapping of a number of broadened electron resonances. The spectral absorption characteristic follows directly from the setup of the chemical linkage of the molecule. The total spectral composition is unique for each substance. A database spectral absorption coefficient curve [3] is plotted vs. the wavelength in dark colors in figure 1. It is superposed by a calculated spectral absorption coefficient that is based on own spectrometric measurements (in light color). The spectrometric setup that is used therefore is described in [4]. Thus the attenuation of light intensity (I) passing a sample cell is wavelength specific. The change of intensity of a light beam that is passing a homogeneous media over a path length (dx) can functional be described by the Bouguer-Lambert-Beer's law "(1)".

$$dI = -\alpha(\lambda) c\, I\, dx \qquad (1)$$

The integral form "(2)" shows the exponential relation between the total light attenuation and the path length, the concentration (c) and the wavelength (λ) depending gas specific absorption coefficient (α):

$$I = I_0\, e^{-\alpha(\lambda) x c} \qquad (2)$$

The gas specific absorption coefficient often is expressed by the equivalent cross section coefficient, it has a maximum value for ozone of about 1,14E-17 cm^{-2}. Figure 2 graphically shows the intensity dependence of the gas concentration and the path length for O_3 at its maximum absorption wavelength at 255 nm. It visualizes the challenge in designing a light absorption based sensor, that should be on the one hand small size (small x) and that also should be high concentration resolved on the other hand.

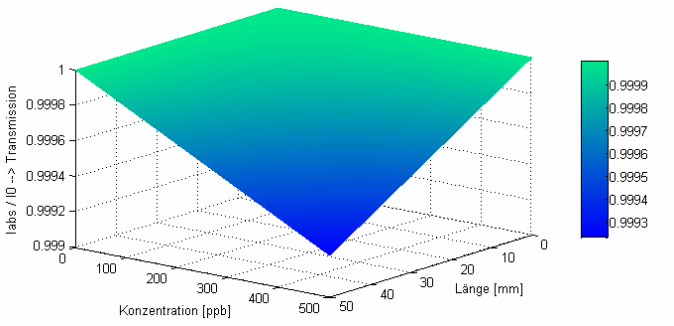

Figure 2. Transmission dependancy of ozone at 255 nm from the concentration [ppb] and the optical path length [mm]

Thus the concentration resolution for a defined molecule and a given optical path length is a function of the signal to noise ratio of the measurement system, that is a function of the temporal dynamic respectively measurement time. To resolve low concentration in the ppb – range at a small path length, tiny changes in light intensity has to be resolved robustly. Compared to the infrared the ultraviolet wavelength region was problematic to use for sensor application based on absorption spectroscopy because of the lack of available and easy to handle light sources. Except the use of the mercury lamp band at 254 nm mainly Deuterium and Xenon lamps could be used in this range. But all these lamps are gas discharge lamps, they have spectral intensity fluctuations a limited life time, are not low cost and not very robust. The approach of the concept shown here is to use novel ultraviolet LEDs as low cost, potentially long life and robust light sources. Light emitting diodes are not broadband emitters compared to superposition absorption spectra such as that of ozone (see figure 1). Thus there is no need to use expensive optical filter, mechanically moved parts or highly spectral resolved measurement techniques. Assumed there is no strong overlapping in the absorption spectra of the claimed gases. So this low cost sensor concept utilizes a spectral undersampling. At least two LEDs are required to measure one gas and at least one further LED for each additional gas component. For the ozone measurements a 255 nm LED (see figure 1) at the maximum absorption of the molecule and a LED in the visible range are used.

The challenge in using LEDs is their strong temperature dependence, their limited stability and (currently) the pure output power. Especially the limited optical output leads multiplied with tiny light changes due to the gas absorption to very small absolute changes in light intensity that has to be resolved for the measurement. In addition to the here presented ozone measurements we have shown measurements of SO_2 and NO_2 at longer wavelength with resolution below 1 ppm at measurement times of 10 or 100 ms [5]. These three gases can principally (here without regarding to possible chemical reactions) be measured in parallel with one small and low cost optical sensor. In closed future this LED based

sensor concept in a modified way will also enable to measure gases such as nitrogen oxide NO and ammonia NH_3. Required LEDs for this wavelength range already have been demonstrated with adequate optical output power in laboratories of semiconductor research groups.

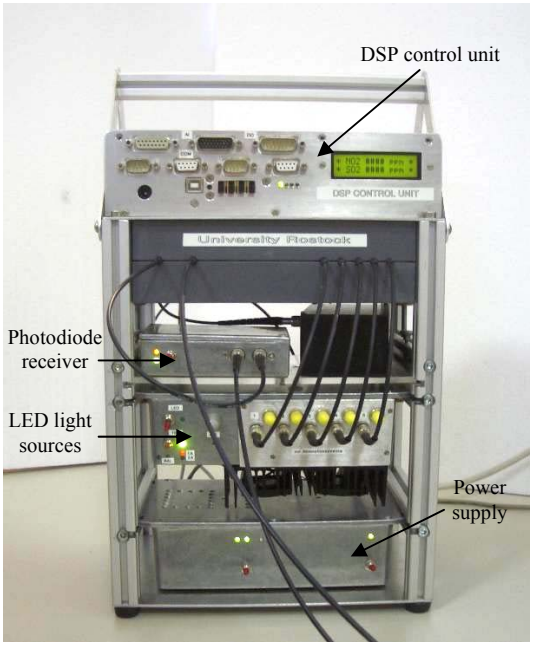

Figure 3. LED-based sensor system, optical sensor head not shown here

III. SENSOR DESIGN

The sensor design is based on a simple reflection cell without using a multi path concept. The increase of path length and therewith of resolution by using a multi path is not used, because of an easy low cost and robust setup in a possibly dirty environment. A prototype setup of the potentially low cost sensor is designed as a modular system (see figure 3). Fife fiber coupled LEDs with peak emission wavelength at 255 nm, 285 nm, 320 nm, 405 nm and 590 nm are used as spectral selective light sources. The light is guided by optical fibers through the reflection sensor cell and is finally received by broadband fiber coupled photodiodes. Two reflection cells with different length where used, a small one with an absorption path length of two times 4 cm and a bigger one with a dimension of 40 cm. The small absorption cell is shown in figure 4 in size compare with a 2 € coin. Self developed LED controller and high accuracy photodiode amplifier have been realized. The system has its own power conditioning unit and it can be battery powered also. It is controlled by a DSP that communicates via USB with a Laptop, where the online calculated data can be visualized and stored. A multitasking based program was developed on the DSP system to allow an uninterrupted signal acquisition with a variable measurement time and an independent parallel control and communication with the host PC.

The application of optical fibers provides a mechanical decoupling between the sensitive electro optical components and the possibly harsh environment where the sensor head is located. The sensor effect takes place apart from electronic signal generation. Therefore the sensor for instance is unaffected by electromagnetic fields and can operate in explosive area. Further more the sensor head and its optics are made from robust materials so it can work at temperatures up to several hundred degrees and it is resistant to chemical aggressive media.

Figure 4. Optical fiber coupled sensor head

IV. MEASUREMENT RESULTS

Various referenced gas measurements have been carried out to verify the low cost sensor system at different gas concentration and acquisition parameters such as measurement time. A setup equivalent to the schema in figure 5 was used. A xenon-flash lamp based ozone generator is utilized. The O3 generation can be varied by the total intensity of UV light interacting with the air by setting the pulse energy and repetition rate of the lamp. Further it can be regulated by the gas duration time in the generator chamber that is controlled

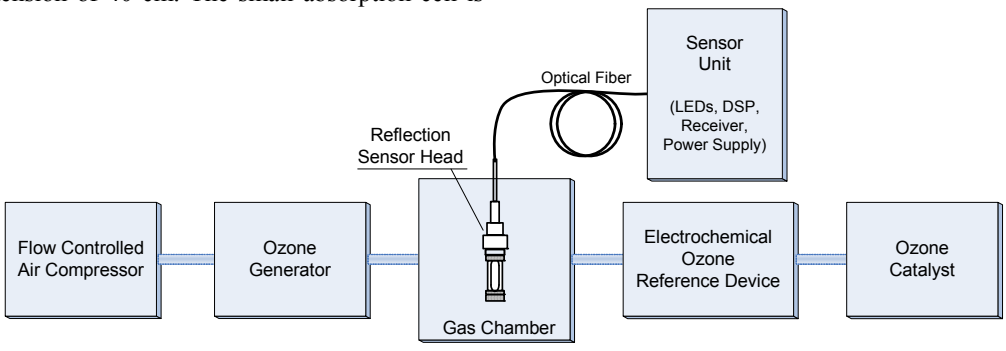

Figure 5. Schema of the ozone measurement setup with ozone generator and ozone reference device

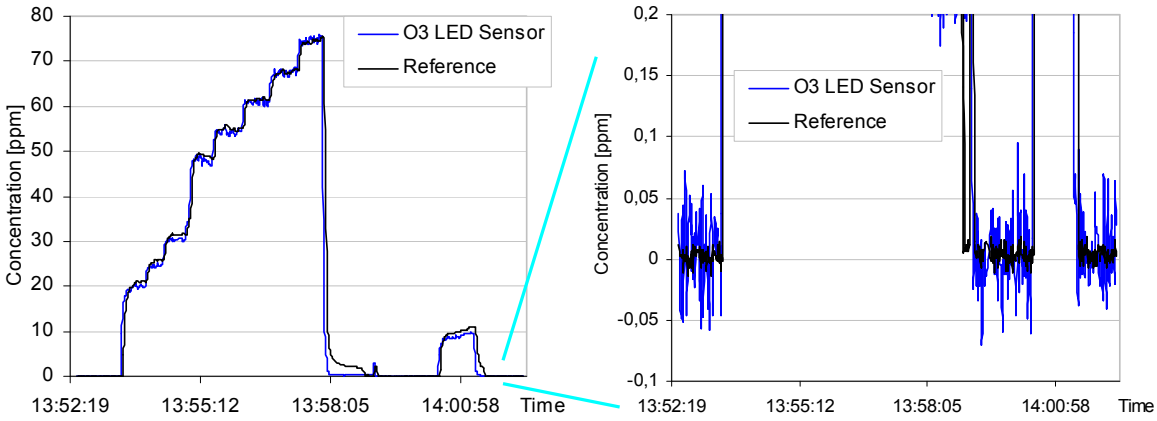

Figure 6 Referenced measurement of ozone with the UV LED sensor using the 4 cm reflection cell at 700 msec measurement time

by the gas flow of the compressor. The gas is guided into a measurement gas chamber, wherein the reflection cell is installed. Over a short path the gas is guided to an electrochemical reference device from ATi (Analytical Technology Inc.) and finally it is neutralized by a catalyst. The ozone is a quite active chemical agent. To avoid chemical reactions with the test equipment and thus an unwanted gas decomposition chemical stable components have to be used for the setup. Additionally the reference sensor is placed closed to the optical sensor to measure the same gas composition. Further more it is useful to flow the arrangement for a while with ozone to oxidize all possible reaction partners in the setup before preparing stable measurements.

An example result for a stepwise increase of the O_3 concentration captured with the 4 cm cell at a sample time of 700 ms is shown in figure 6. The measurement results from the ozone LED-based sensor are plotted in blue colours while the simultaneously logged reference signal is shown in dark colour. An extended view of this test is visualized on the right side in figure 6. The optical measurement shows a good correlation to the reference. The arrangement but also the higher time constant of the electrochemical sensor let its values delayed appear although they are simultaneous logged. Especially the regeneration of it is quite slow, as it can be seen after the time mark 13:58:05, this effect of ozone releasing is flow depending. The extended plot displays the resolution of the LED sensor for O_3 with the small sensor head and 700 ms measurement time. The standard deviation for a probe around this zero concentration is 0,03 ppm.

The figure 7 shows a measurement result of the O3-LED sensor with the long (40 cm length) sensor head at a measurement time of 1,4 sec. The display of the curves is identical to them of figure 6. In conformity to the absorption theory, the sensor resolution increases with the absorption path length and also the signal to noise ratio reduces with the sampling time. Practical issues such as the higher attenuation due to the light coupling of real but not ideal collimated beam over a longer path length counteracts the resolution increase. The measurements show that the sensor resolution increases to a standard deviation at zero concentration of O_3 of 0,003 ppm – as it is visualized on the right side in figure 7. The bigger measurement volume of the long cell results in a bigger time shift between the optical and the electrochemical measurement.

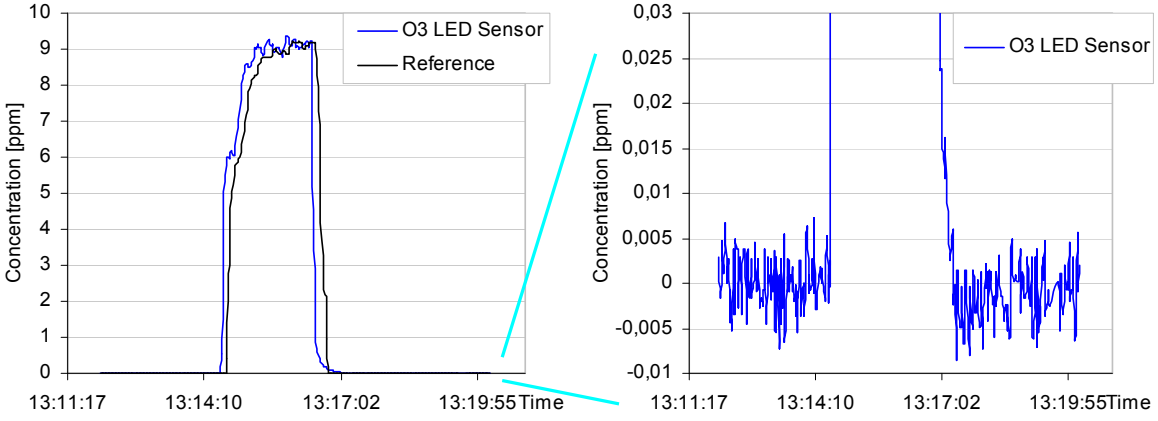

Figure 7 Referenced measurement of ozone with the UV LED sensor with the 40 cm reflection sensor head at 1,4 sec measurement time

V. CONCLUSION

A UV LED based optical gas sensor system for high resolution measurement of ozone has been described in this paper. This spectroscopic sensor development is novel as it uses low cost and compact components without utilizing optical filter or mechanically moved parts. Therewith it also has potential as a hand held device. The realized prototype setup works with fiber coupled free path absorption cells to create an all optical sensor head that is thought for the use in harsh environment (e.g. high temperature, aggressive media, strong electromagnetic field). The gas measurements are in close agreement with simultaneously captured data from a laborious reference device. The optical measurement principle provides a fast response. A dynamic range from some ppb to about 10 ppm a long sensor head (40 cm) respectively from some tenth of ppb to about 100 ppm for a small sensor cell (4 cm) is documented here, but the upper dynamic limit was measured also above a factor 10 higher. The realized sensor system is also capable to measure other gases separately and simultaneously. Based in the indirect principle of light absorption measurement technique the quantitative concentration measurements are relative ones related to a zero measurement and it has to be considered that the sensor accuracy is not equal to its resolution.

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