A Novel NO_x Gas Sensor based on Resonance Absorption Technique in the UV-Range

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Introduction

Measurement of Nitrogen oxides (NO_x) is very important for many industrial applications involving combustion processes like power plants, burner control, internal combustion engines etc. In these applications it is necessary to measure the concentration of NO_x very precise (< 1% Accuracy). The ranges vary from less than 100 ppm NOx (Stack gas monitoring) to 1500 ppm NOx (Diesel Exhaust gas). For the total NO_x detection it is also necessary to measure NO_2. The currently accepted technologies (e.g. CLD[1] and NDIR[2]) employ a catalytic converter in order to convert NO_2 to NO. This technique has some disadvantages:

- Conversion rate is not 100% and can change over time and usage
- Simultaneous detection of NO and NO_2 is not possible
- The converter operating at approximately 500°C increases power consumption

A novel technique for simultaneous detection of NO_2 (along with NO) based on UV absorption of NO_2 in the range at 360 nm and NO in the range of 227 nm is described here. Since the technique does not require a use of dispersive element (such as grating or prism), it is called NDUV[3]. The new Sensor (see Figure 3) is designed to be rugged, vibration-resistant (no moving parts, solid state detectors) and compact to accommodate on-vehicle emission monitoring applications. The detection limit is < 1ppm NO_x with a sample rate of 1 second. The cross sensitivity to other gases like water vapor, CO, CO_2, SO_2 and C_nH_m are negligible. We compared the test results with a CLD and electrochemical gas sensors (see Figure 4 and 5).
For the detection of NO an electrodeless discharge lamp (EDL)[4] is used generating an optical DC signal. The detection of NO_2 is realized by using a pulsed LED[5] that generates an AC signal. To distinguish between both signals and calculate the gas concentration a microcontroller based signal conditioning electronics is adapted. This electronic creates an output of four signals showing information about the behavior of each lamp (reference signal) as well as the actual measurement of NO/NO_2.

Based on this sensor design we developed a new analyzer for on road measurements taking samples directly from the exhaust under real condition.
The design of the bench is very flexible (modular) and can be used for different gas applications like H_2S in Biogas or Ammonia in the future.

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[1] Chemiluminescense Detector
[2] Non Dispersive Infra Red
[3] Non Dispersive UltraViolet
[4] Electrodeless Discharge Lamp
[5] Light Emitting Diode

Principle of Operation

Nitric oxide has some strong absorption bands at 226,5 nm, 214 nm, 206 nm and 194 nm. In Fig. 1 the absorption spectra of NO in Nitrogen is shown. The cell length is 10 cm. Since the cross sensitivity to other gases like SO_2, NO_2, H_2S and aromatic hydrocarbons (gasoline vapor) is significant between 190 nm and 225 nm, the preferred wavelength for the NO detection is about 226,5 nm.

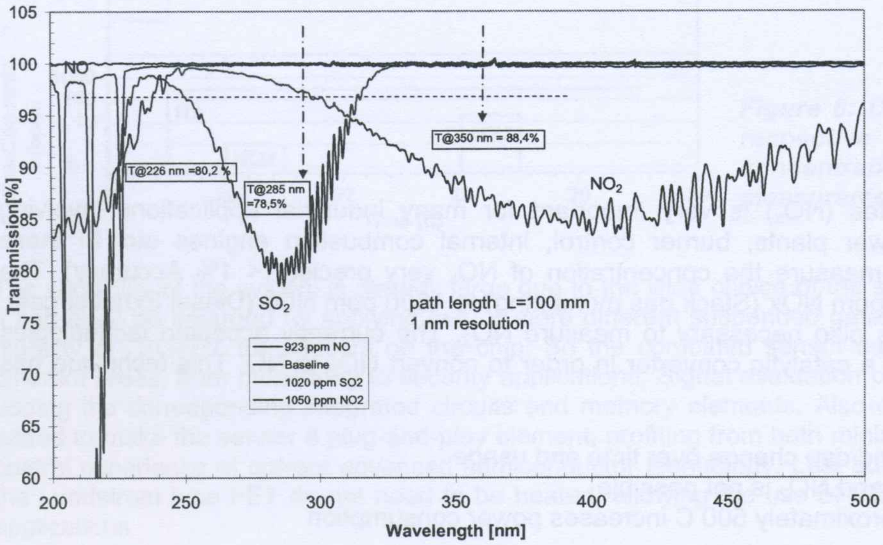

Figure 1: Transmission spectra of UV-NO/NO_2/SO_2

The Sensor uses an EDL as a source for UV radiation. The fused silica bulb filled with a mixture of nitrogen and oxygen at low pressure (~1 mbar). The gas mixture in the bulb is excited by a controlled RF oscillator. Due to the strong electromagnetic field strength in the coil of the oscillator, plasma is generated inside the bulb. In the plasma, exited NO radicals at different states (electronically, and rotation-vibration) are generated by a reaction of nitrogen and oxygen (See Equation 1).

$$N_2 + O_2 \rightarrow NO^* \text{ (exited NO) (1)}$$

After the recombination NO* molecules return back to the ground level and emit a specific photon ($h\nu$)(See Equation 2).

$$NO^* \rightarrow NO + h\nu \text{ (2)}$$

Since the NO molecules are exited to different energy states, the lamp emits photons with different wavelengths. There are two different lines emitted which are used in the measuring principle. All molecules, which return back to ground level, emit “Cold Lines”. The energy from the cold emission lines [NO-γ(0,0)] is absorbed by NO molecules in the sample gas. Since these lines are generated by NO and absorbed by NO it is called resonance absorption.
Other transitions, which result in return to states other than the ground level, are called “Hot Lines”. The energy from the hot emission lines cannot be absorbed by NO molecules in the sample gas. Therefore the hot lines can be used for reference measurement.
In Figure 2 the emission spectrum of the EDL is shown.

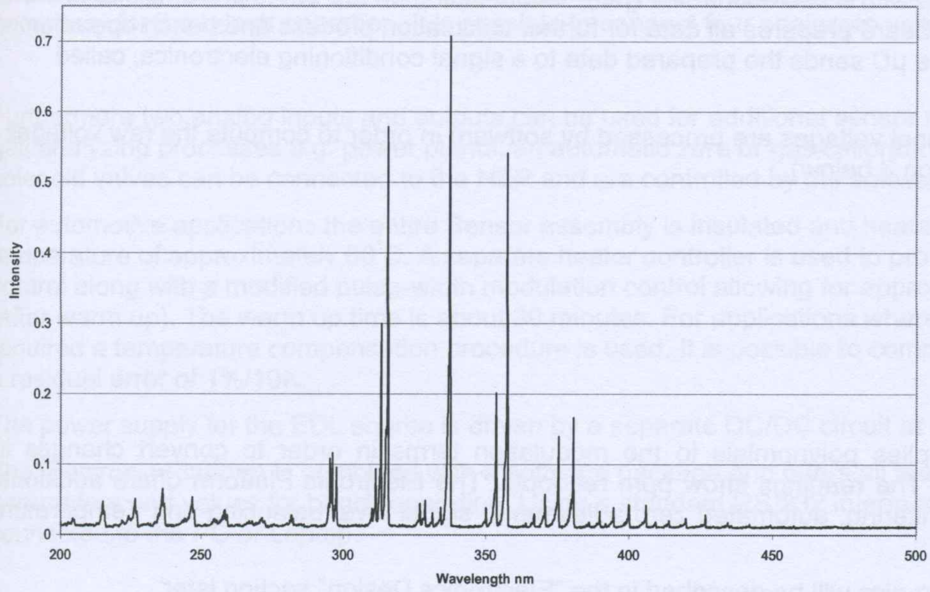

Figure 2: Electrodeless discharge lamp emission spectrum.

Design and Performance of the UV-Sensor

The UV Sensor has a very modular design. It is possible to use the Sensor for different gas applications other than NO/NO_2 by changing the detector and filter characteristics. For the mobile use the complete bench is designed with no moving parts.
The UV Analyzer measures NO/NO_2 based on the resonance absorption technique. The defined wavelength is selected by an ultra-violet interference filter, which includes both cold and hot emission lines.
The radiation of the EDL passes through focusing optics through the sample cell. The lens produces approximately parallel light over the entire cross sectional area of the sample cell. For the NO_2 measurement a pulsed high power LED is used. A beam splitter separates the light for reference and measurement detection. As shown in the Figure 3 below the detector 1 is used for the reference and detector 3 for the measurement channel of NO_2.

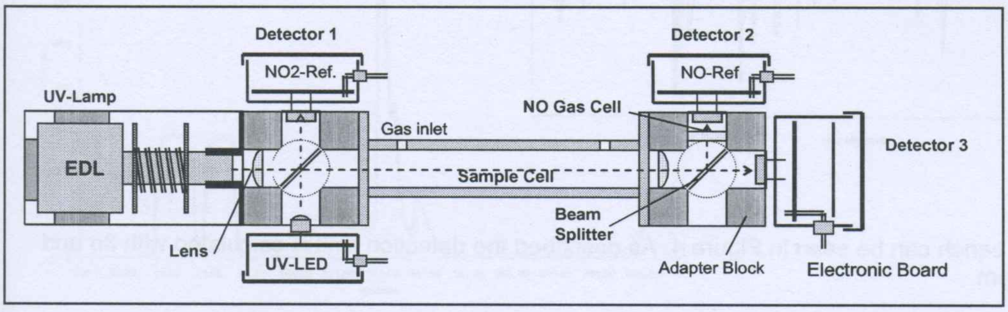

Figure 3: Design of UV Sensor

After passing the sample cell the light beam is divided into two halves for reference and measurement channel for NO detection. Detector 3 is dedicated to the Nitric Oxide (NO) measurement and detector 2 is serving as a reference.
The total radiation incident on the measuring detector includes hot and cold emission lines. When Nitric Oxide is introduced into the sample cell, some of the cold lines are absorbed and a signal from the measuring detector changes accordingly. The signal from the reference detector does not vary when the concentration of nitric oxide in the sample cell changes. However, exhaust from combustion processes also includes gas species, other than nitric oxide, which absorb both the hot and the cold bands and cause a proportional change in the signal from the measuring and reference detector.

Each detector communicates with a Microcontroller (μC) - board sitting on top of the pre-amplifier in the detector 3 housing. The μC-board prepares all data for further calculation process and bench operation. Using a SABus[6] protocol, the μC sends the prepared data to a signal conditioning electronics, called Electronic Platform.

The gas and reference channel voltages are processed by software in order to compute the raw voltages into modulation (See Equation 3 below).

$$Mod = \frac{R - M}{M} \quad (3)$$

Mod=Modulation

R=Reference Signal

M=Measurement Signal

Then the control board applies polynomials to the modulation terms in order to convert changes in modulation linear readings. The readings show ppm readouts. The Electronic Platform offers additional capabilities such as digital filtering, automated zero adjustment, signal level balancing and Temperature compensation.

Further features of the electronics will be described in the "Electronics Design" section later.

Detection Limit

The detection limit is defined with 3σ. The actual bench shows a detection limit of less than 1 ppm.

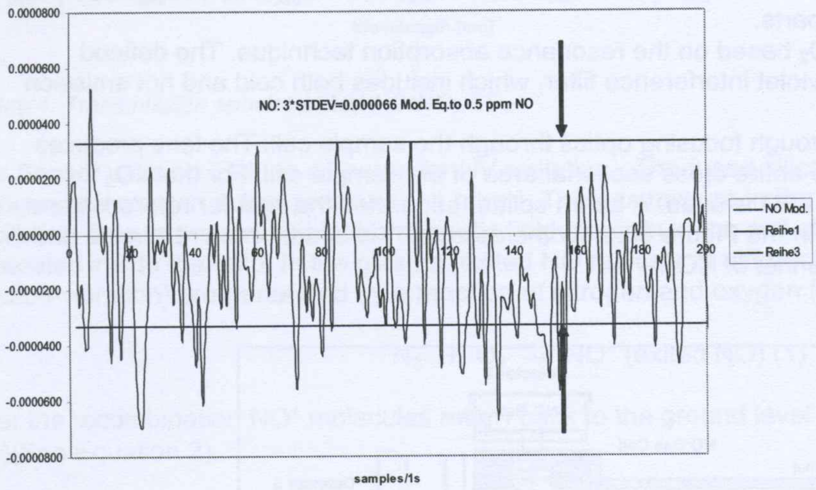

Figure 4: Detection limit

The detection limit of the bench can be seen in Figure 4. As described the detection limit is calculated with 3σ and shows an output of 0.5 ppm.

Electronics Design

The electronic system includes a pre-amplifier circuit for each channel. The pre-amplifier is designed for very low noise and stable signal conditioning. Because of a sheet metal housing design the pre-amplifiers are protected against electromagnetic interference (EMI). The amplification factor is adjusted in order to produce 1.0 volt at the output. As described in the bench design section, the μC sends the conditioned signal to the Electronic Platform which has a 24 bit AD converter.

6 SABus Sensor Actor Bus

The Electronic Platform has a broad functionality and implies all algorithm procedures which are necessary for the bench operation. It is possible to connect four analyzers using the SABus protocol.

Furthermore two analog inputs and outputs can be used for additional sensor modules. For continuous gas analyzing processes e.g. power plants, an automatic zero or gas calibration is needed. Therefore solenoid valves can be connected to the NEP and are controlled by the software.

For automotive applications the entire Sensor assembly is insulated and heated to an operating temperature of approximately 60°C. A separate heater controller is used to provide proportion and integral control along with a modified pulse-width modulation control allowing for approximately 0.1°C stability (after warm up). The warm up time is about 30 minutes. For applications where no heated bench is required a temperature compensation procedure is used. It is possible to compensate the temperature to a residual error of 1%/10K.

The power supply for the EDL source is driven by a separate DC/DC circuit at a constant voltage of 12 V.

The Electronic Platform is combined with a software package and offers all feature adjustments to set up parameters and values for bench operation. Using a standard RS 232 interface the bench can be directly connected to the PC or Laptop.

CLD Correlation

The following Figure 5 shows the UV Sensor correlation to the CLD used with real sample gas from a vehicle (exhaust gas). Usually, the engine cold start condition produces enough hydrocarbon gas components to cause serious interference on the UV NO channel. In this test the hydrocarbon content is measured using an NDIR gas analyzer (Hexane equivalents).

The test is made using a typical sample system to extract the exhaust gas from the vehicle and provide some particulate filtering. The sample is applied to the UV Sensor and CLD instruments at a constant flow and pressure. However, the UV Sensor in this test is not temperature controlled (worst case scenario).

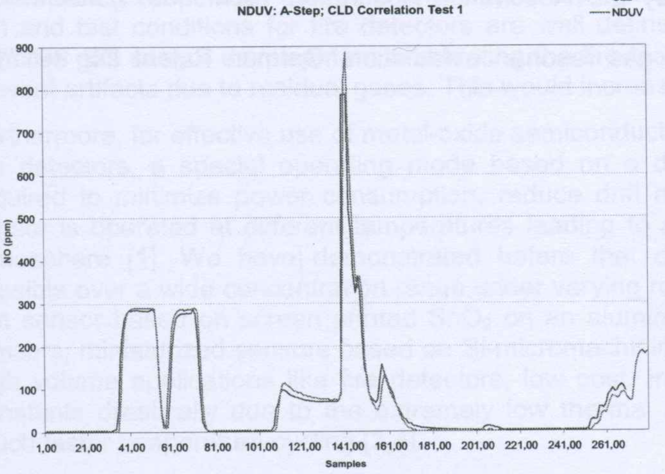

Figure 5: CLD Comparison

The test result in Figure 5 shows that the UV Sensor correlates very well with the CLD instrument. Furthermore a correlation to an electrochemical cell is shown in Figure 6.

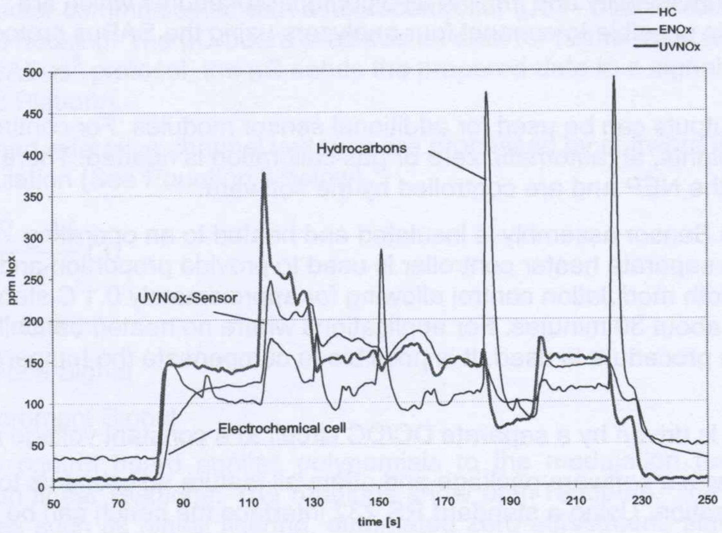

Figure 6: Comparison with Electrochemical Gas Sensor

References

1 H. Meinel: Detection of Nitric Oxide by the Resonance Absorption Technique. Zeitschrift für Naturforschung 30a (1975) 232-328

2 G. Wiegleb: Source for generating of gas resonance radiation. German Patent DE 3617110 (1984)