NOVEL CEM GAS DETECTION MODULE FOR SO$_2$ AND NO$_X$ MONITORING BASED ON SMALL SIZE NDUV- AND UVRAS–TECHNOLOGY

Continuous emission monitoring (CEM) is a rapidly growing market worldwide [1]. The combustion of oil, coal and natural gas is still the most important energy source for power generation. In the exhaust gas of these power facilities the content of SO$_2$, NO and NO$_2$ is significant, so that exhaust gas treatment and reduction is necessary. The emission limits for these components are decreasing and regulated by national and international guidelines. Especially in developing countries the demand for low cost CEM equipment, with sufficient measurement performance, is increasing rapidly.

Exhaust gas emissions from the maritime sources are also regulated by international law (e.g. IMO Marpol Annex VI). For this application the gas analyzer monitoring system is also based on CEM and mobile instrumentation (Marpol 73/78 Annex VI and Amendments).

Another important application is the mobile/portable flue gas analysis (e.g. PEMS[1]). In this case small size and low power operation is required. For both applications the Wi.Tec Sensorik GmbH has developed a novel CEM gas detection system based on photometric UV absorption technology.

Especially for mobile applications and rugged operation on ships the gas analyzer should have no moving parts such as a chopper blade or moving filter elements in the optical path/bench. Existing CEM gas analyzers mostly utilize rotating filter wheels and mechanical choppers.

Physical principle

In the UV-range the absorption of radiation is based on the excitation of molecular electronic levels. In Fig.1 the absorption bands of NO, NO$_2$ and SO$_2$ are shown for gas concentration of 1000ppm in a 100mm sample cell. The characteristic wavelengths λ of the maximum absorption are λ$_1$ = 405nm (NO$_2$), λ$_2$=285nm (SO$_2$) and λ$_3$=226nm (NO).

The fraction of absorbed radiation is according to the Lambert-Beer-Law:

$$I = I_0 \, exp - (\sigma \cdot d \cdot n)$$

I_0 and I are the incident and transmitted light intensities

d is the absorption path length (in cm)

n is the concentration of the absorber (in molecule/cm³)
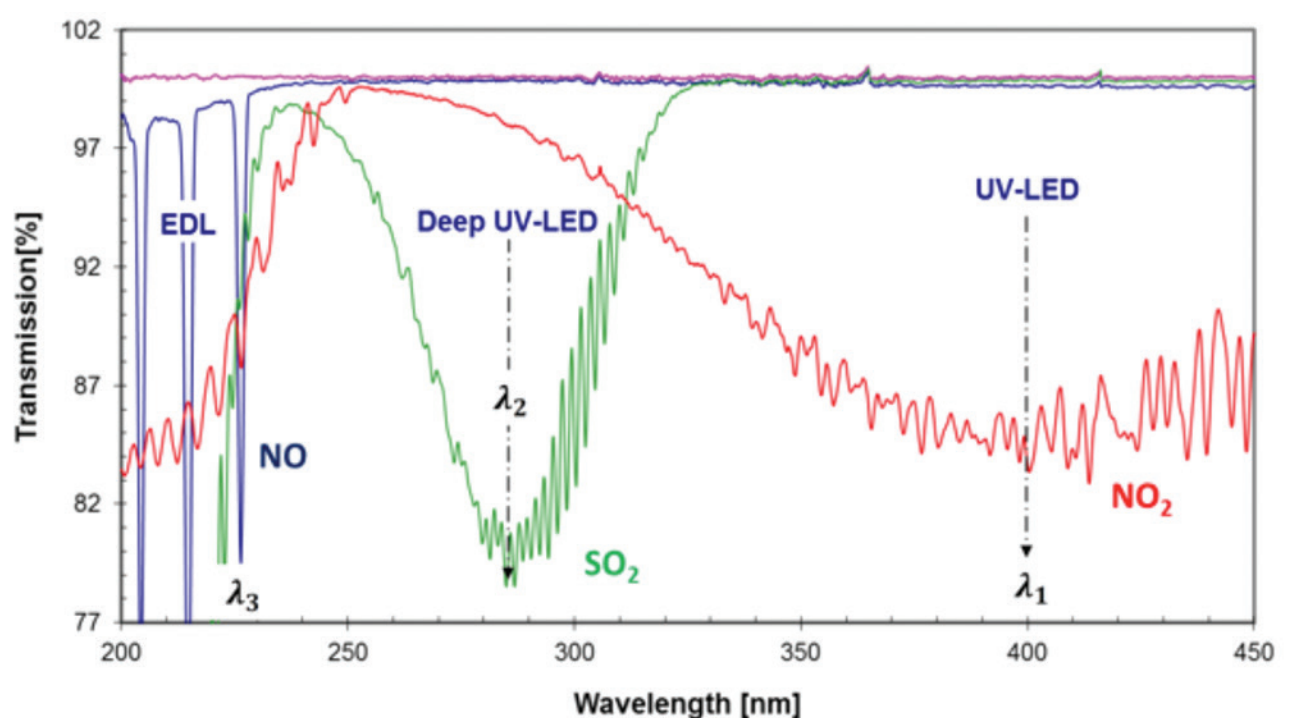
σ is the absorption cross section (in cm² molecule⁻¹)

Fig. 1: Absorption spectra of NO, SO$_2$ and NO$_2$ in the UV-range between 200nm and 450nm

For practical purposes the Lambert- Beer-Law can also be expressed by the gas concentration c (in ppm·10⁻⁶) and the coefficient of absorption α (in cm⁻¹):

$$I = I_0 \, exp - (\alpha \cdot c \cdot d) \quad or \quad I = I_0 \, exp - (\alpha \cdot c \cdot d) \cdot \left[\frac{T_0 \cdot p}{p_0 \cdot T}\right]$$

T_0 is the temperature during gas calibration

p_0 is the barometric pressure during gas calibration

T is the temperature during measurement phase

p is the barometric pressure during measurement phase

NDUV² SO$_2$/NO$_2$ measurement

The principle arrangement of the ULTRA.sens® is shown in Fig.2. Two different UV-LEDs are used to generate the suitable UV-radiation for NO$_2$ (UV-LED1) and SO$_2$ (UV-LED 2). The LED sources are alternatingly pulsed [5]. A high efficiency beam splitter is located in front of the sample cell in order to separate the reference radiation. Using this additional information it is possible to eliminate the intensity drift of the UV-LED during the lifetime (approx. 10 years). For different gas concentration ranges sample

cells with optical lengths of 100mm (medium range) and 250 mm (low range) are available.
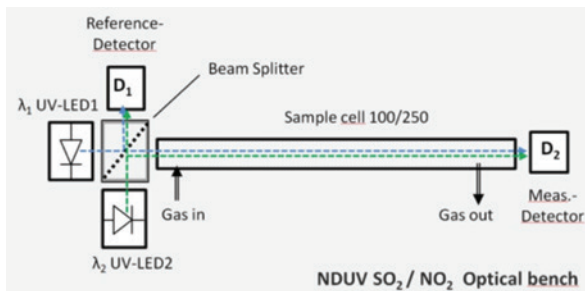

Fig. 2: Arrangement of the NDUV SO$_2$+NO$_2$ optical bench

UVRAS[3] NO measurement

The detection of NO in the UV range is a very attractive method and suitable for CEM application. Meinel [2] first described this method in 1972. The physical principle is shown in Fig. 3. The radiation coming from an Electrodeless Discharge Lamp (EDL) has three selective emission bands for NO. The lamp is filled with N$_2$ and O$_2$ [5]. In the excitation area of the lamp nitrogen oxide (NO) is generated and emits molecular resonance radiation [4]. The 226.6 nm band is mostly utilized for the NO detection since the cross sensitivity to other gases is very low. In order to select this emission band, it is necessary to integrate a narrow band pass filter. To achieve good long term stability of the measurement, a reference detector is integrated in front of the sample cell. The reference detector monitors the lamp intensity in order to simultaneously compensate for the intensity drift. The measurement detector receives the attenuated intensity I(c) due to the NO gas concentration c in the sample cell. The design is very similar to the NDUV SO$_2$/NO$_2$ measurement.
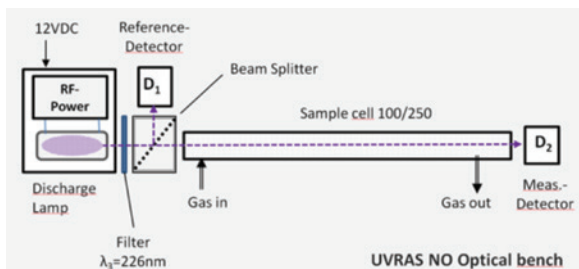

Fig. 3: Physical arrangement of the UVRAS-ULTRA.sens®

The performance of the described UVRAS-ULTRA.*sens*® is shown in Fig. 4. for different gas concentrations. The first step was started from nitrogen (baseline) to 300ppm NO. After the first step a span calibration was performed with 300ppm NO. Then the gas concentration was reduced stepwise using a precise gas blender. The deviation between the expected value and the gas reading is less than 1 ppm NO. The variation of the values is less than

[1] Portable Emission Monitoring System
[2] Non Dispersive UV
[3] UV Resonance Absorption Spectroscopy

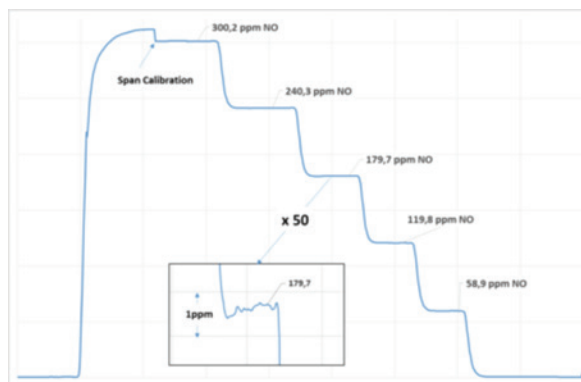300ppb as shown in the enlarged step at 180ppm NO (gas reading = 179.7ppm).

Fig. 4.: Gas test with different NO concentrations (0ppm→300ppm → 240ppm → 180ppm → 120ppm → 60ppm → 0ppm)

Combined Module

Figure 5 shows both optical benches integrated into a single module. They are shown with 100mm sample cells. The total arrangement is very handy and suitable for integration into a 19" CEM gas analyzer or a mobile instrument (e.g. PEMS).
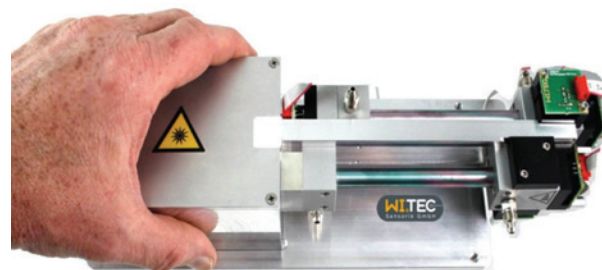

Fig. 5: Combination of LED based NDUV detection of SO$_2$+NO$_2$ and EDL based UVRAS for selective NO detection in a single handy ULTRA.sens® OEM module

The signal conditioning main board can run both optical benches simultaneously with a 16 bit digital resolution. The data interface is based on RS232 and CANopen. The operation voltage is 24VDC with a power consumption of less than 4 Watts (without temperature controller).

Conclusion

The presented combination of an LED based NDUV optical bench (SO$_2$+NO$_2$) and an EDL based UVRAS (NO) is very unique. Since the ranges (100ppm/300ppm/2000ppm/3000ppm) and the detection limits (<0.5ppm) are sufficient for many applications such as CEM, Marpol and PEMS the market potential is very high.

The ULTRA.sens® OEM module is easy to integrate and the power consumption is low (<4W). The cross sensitivity to other gases such as H$_2$O, CO, CO$_2$ and hydrocarbons is negligible. Furthermore it is possible to integrate a CO$_2$ NDIR gas sensor (e.g. 0-20 Vol.-%) into the system for SO$_2$/CO$_2$ ratio monitoring (e.g. Marpol application). Based on the direct NO$_2$ gas concentration measurement it is possible to use this as a substitute for the costly catalytic NO$_2$→NO converter (indirect measurement) used in regular CEM/PEMS systems.

Specifications

NO - range:	**0-300 ppm (low)**	**0-3000ppm (high)**
NO$_2$ - range:	**0-100 ppm (low)**	**0-3000ppm (high)**
SO$_2$ - range	**0-100 ppm (low)**	**0-3000ppm (high)**

Linearity:	± 1% F.S. (Full Scale)
Repeatability:	< 0.5% F.S.
Barometric pressure influence:	± 0.1% F.S. / mbar (without pressure compensation)
Zero point stability:	± 2% F.S. / day
Span drift:	± 1% F.S. / month
Detection limit (3·σ):	< 0.5% of span
Water vapor Interference:	< 1 ppm
Operating temperature:	5-45°C (with temperature controller @50°C)
Temperature influence zero:	< 1% F.S. / 10K
Temperature influence span:	< 1% F.S. / 10K
Operating pressure:	800-1200 hPa
Permissible gas flow:	0.2-1l/min.
Influence of gas flow:	< 0.5% F.S.
Response time:	t$_{90}$ < 3 s
Warm-up time:	30 Minutes
Storage temperature:	-10°C up to 70°C
Power supply:	24VDC
Dimension:	W=100mm, H=100mm, L=300mm

Literature

(1) Pattison, M.: Growing market for CEM in developing countries. International Environmental Technology, September 2017

(2) Meinel, H.: Detection of Nitric Oxide by Resonance Absorption Technique. Zeitschrift für Naturforschung 30a, 323-328 (1975)

(3) Wiegleb, G.: Lamp for producing resonant gas radiation. German Patent DE 3617110, 21.5.1986

(4) Wiegleb, G.: Gasmesstechnik in Theorie und Praxis, Springer Vieweg Verlag 2016

(5) Wiegleb, G.: German Patent Application DE 10 2016 108 267 (9.11.2017)

Author Contact Details
Prof. Dr. Gerhard Wiegleb, Dipl.-Ing. Sebastian Wiegleb.Wi.Tec-Sensorik GmbH • Schepersweg 41-6, 46485 Wesel, Germany • Tel +49 281 206578-20 •
Email: ge.wiegleb@witec-sensorik.de • Web: www.witec-sensorik.com

Read, Print, Share or **Comment** on this Article at: **envirotech-online.com/article**