CONTINUOUS MEASUREMENT OF HYDROGEN SULPHIDE (H_2S) IN THE PPM AND VOL.% RANGE USING NOVEL DEEP UV LIGHT-EMITTING DIODES

Hydrogen sulphide (H_2S) is a foul-smelling, colourless and highly toxic gas. Even at very low ppm concentrations, hydrogen sulphide can be recognised by its typical smell of rotten eggs. It is corrosive, flammable, highly flammable and slightly heavier than air. For example, it is generated during the decomposition of sulphur-containing amino acids in biogas plants, where concentrations can reach up to 10,000 ppm. H_2S is also present in high concentrations in natural gas processing (Claus process). In the Kraft process (also known as the sulphate process) for the production of pulp, wood chips are boiled with an alkaline solution of sodium hydroxide (NaOH) and sodium sulphide (Na_2S). This process also produces high concentrations of hydrogen sulphide (H_2S) (vol.-%). The H_2S content must therefore be measured continuously for process control and monitoring.

Introduction

Hydrogen sulphide (H_2S) can be detected by several methods. The simplest option is to use electrochemical sensors. These gas sensors are used in gas warning systems and personal monitors in particular, as accuracy is not crucial for this application. Furthermore, these gas sensors are blinded by suddenly occurring high H_2S concentrations and must recover from this exposure over a longer period of time. Furthermore, the accuracy and reproducibility of these gas sensors is not sufficient for analytical applications. The use of UV absorption photometry has therefore become established for this application. Unfortunately, these photometers are very expensive, which means that this high-quality analysis technology has only been used in a few applications up to date. The present invention is therefore intended to open up the possibility of a broad application of this sensor technology.

UV Absorption Spectroscopy

Many research groups have already analysed the absorption spectrum of H_2S in the UV range in detail. The recognised UV spectrum of H_2S from 270 nm is shown in Fig. 1. The maximum absorption is around 195 nm. Unfortunately, many absorption lines of other gases are present in this spectral range, which can interfere with an accurate H_2S measurement. Therefore, this gas is typically measured between 255 nm and 215 nm. UV-LEDs are now available in this spectral range, which enables simple and accurate gas analysis of H_2S.

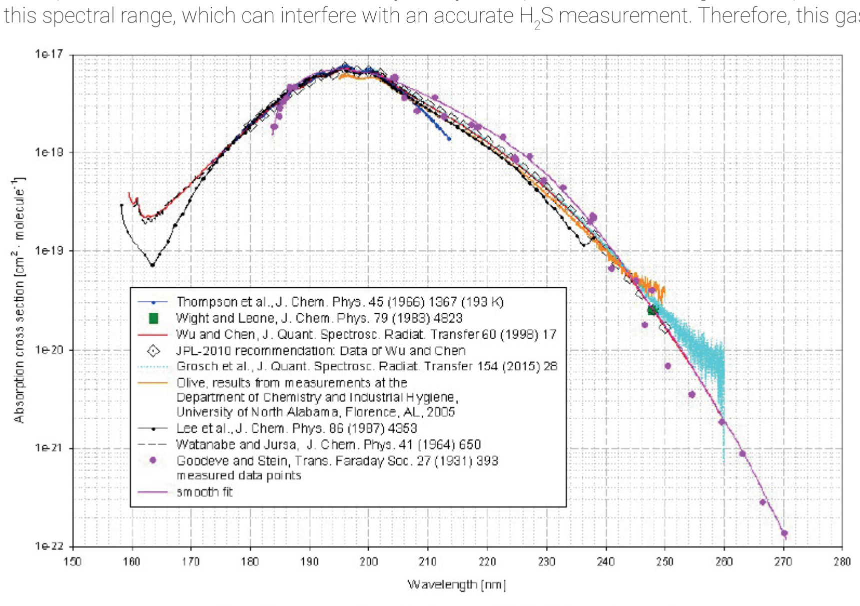

Fig. 1: Absorption spectrum of H_2S measured by different research groups [2].

Photometer Design

The photometer (ULTRA.sens®) uses electrically modulable UV-LEDs that give an emission wavelength in the range of the analysing gas. UV-LED radiation is decoupled via a beam splitter and fed to a reference detector (I_{Ref}). This reference measurement compensates for the unavoidable signal drift of the UV-LED. The sample cell (AK100) is located behind the beam splitter (BS) and is flowed with the sample gas to be analysed. The flow rate is typically between 0.2l/min and 1.5l/min. The measuring detector (I_{Meas}), which records the radiation absorption in the cuvette, is located behind the sample cell. The gas concentration can be mathematically calculated from both signals using the Lambert-Beer radiation law [3]. The calculation is done using the evaluation electronics of the ULTRA.sens® set-up.

$$I_{Meas} = I_{Ref}\, exp.[\alpha \cdot c \cdot L]$$

With

I_{Meas} = Measurement Intensity with gas concentration c

I_{Ref} = Reference Intensity

α = Coefficient of absorption in cm^{-1}

c = Gas concentration in ppm (10^{-6})

L = Sample cell length in cm

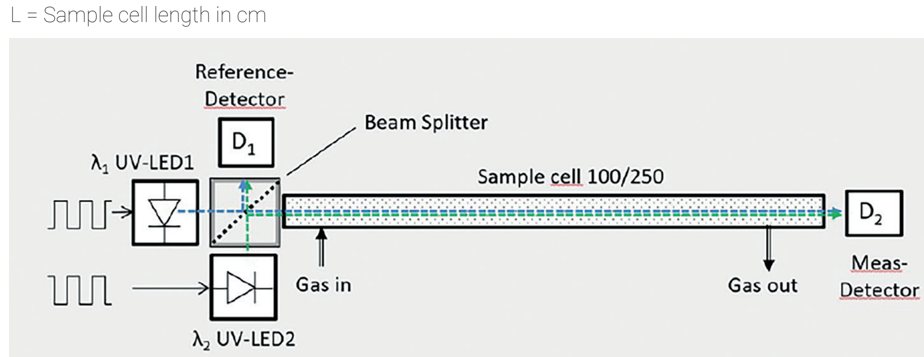

Fig. 2: Optical beam path in the ULTRA.sens® with two UV-LEDs and a beam splitter to generate a reference signal.

In principle, two different UV-LEDs can always be installed in a ULTRA.sens® photometer (see Fig. 3). This means that two different gases can always be analysed simultaneously in one setup. The UV-LED2 for measuring SO_2 is spectrally located in the area of the maximum absorption (see Fig. 4), while the H_2S measurement (UV-LED1) occurs in the absorption minimum of SO_2. This is also very helpful for the possible compensation of cross-sensitivities. The residual cross-sensitivity of SO_2 is offset against the H_2S measurement in the evaluation electronics. To do this, the ULTRA.sens® must be supplied with the interfering gas (SO_2) and the cross-influence measured. In the simplest case, the cross-calculation is performed with a linear factor and can also be performed with a polynomial for more complex correlations.

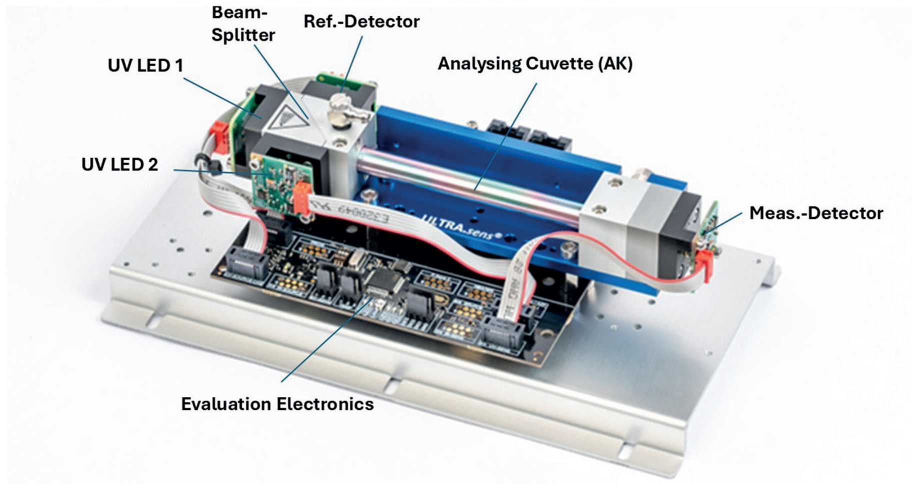

Fig. 3: ULTRA.sens® design with two different UV-LEDs for measuring two different gases in one module with a cell length of L=100mm (AK100).

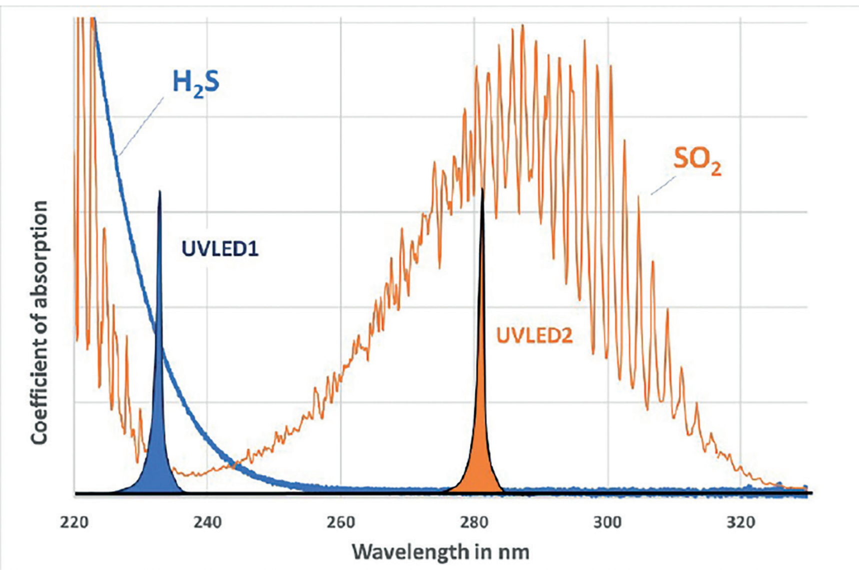

Fig. 4: Simultaneous measurement of H_2S and SO_2 in an ULTRA.sens setup.

In order to be able to detect the lowest possible H_2S concentrations with a high degree of accuracy, the detection limit must be as low as possible (LDL lower detection limit). The detection limit is typically determined as 3 times the standard deviation of the noise signal at the zero point (N_2 flow). In Fig. 5, this signal was recorded and analysed over a period of 1 hour. The LDL value in this case is ±0.5ppm H_2S.

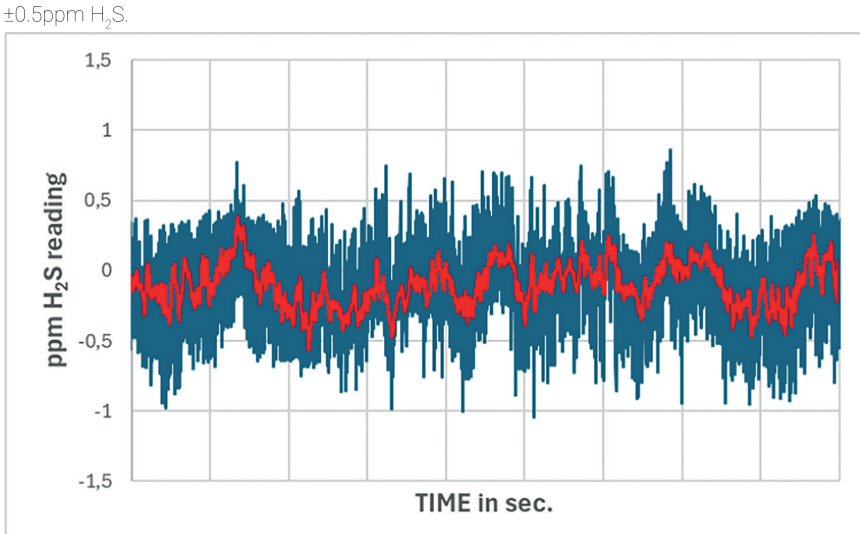

Fig. 5: Zero Noise (±0.5ppm) with a sample cell length L=250mm (AK250) measured during a time interval of app. 1 hour.

UV-LED Lifetime extension

As the service life (LT_0) of the UV-LED for H_2S measurement is limited to a few thousand hours, the evaluation electronics have an algorithm to extend the service life. For this purpose, the UV-LED is periodically switched off in a cycle time to increase the service life. A duty cycle of 50 % ($t_{on} = t_{off}$) therefore doubles the service life. This makes it very easy to determine a service life extension factor:

$$f_{LEF} = 1 + \frac{t_{off}}{t_{on}}$$

During the time in which the UV-LED is switched off, the last H_2S measured value is saved and displayed for the entire off time (frozen value, see Fig.6). This can be used without any problems for slow processes such as in biogas plants.

Example: With an on time of 10 seconds and an off time of 50 seconds, this extends the service life by a factor of $f_{LEF} = 6$. This means that the service life of LT_0=3,000 hours is then increased to 18,000 hours, i.e. more than 2 years (see Fig.7).

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Since the service life specification of LT_0>3,000 hours refers to a decrease in the UV-LED's radiation intensity by a factor of 2, the measurement setup is still measurable after these 2 years. It is only subject to a higher statistical probability of failure. The times ton and toff can be set as required by the customer using the MARS light software that comes with the ULTRA.sens®, so that service life expectations of > 10 years are also possible.

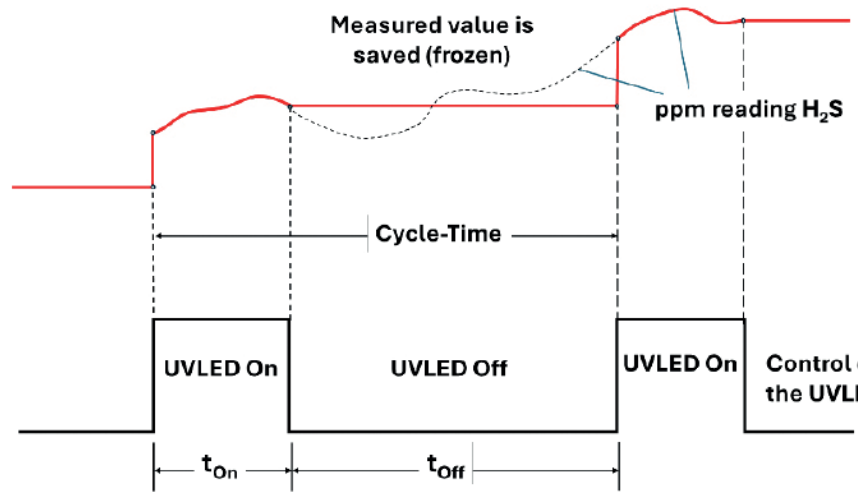


Fig. 6: Definition of the cycle time and course of the H_2S measurement signals during this time.

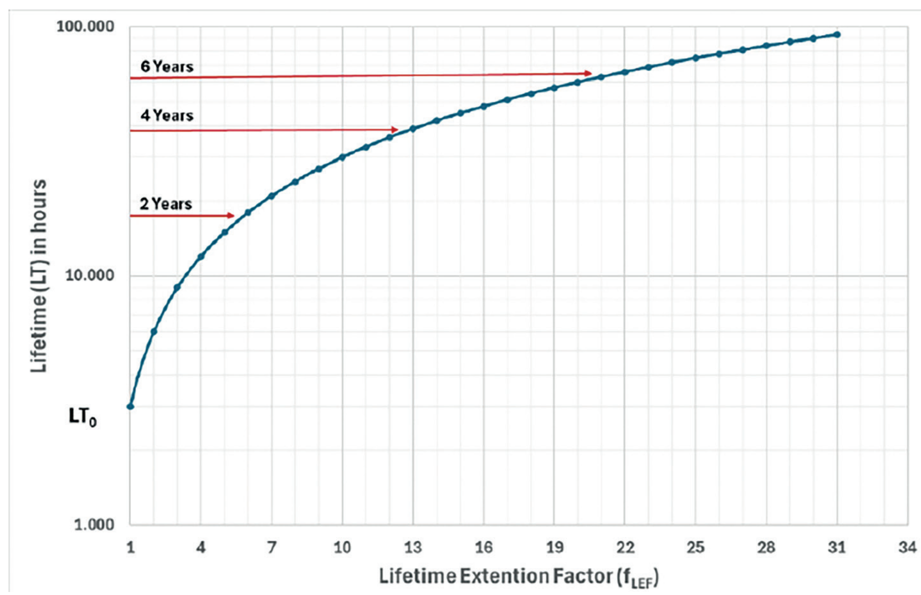


Fig.7: Progression of the service life as a function of the f_{LEF}. Note that the y-axis is shown in logarithmic form. If the LT_0 value is improved, this leads to a further significant improvement in life expectancy during operation.

Conclusion

The use of innovative UV-LEDs opens up new possibilities with the proven ULTRA.sens® concept. In particular, the selective gas analysis of H_2S in biogas plants and chemical processes becomes much easier with this measurement technology. Compared to conventional electrochemical cells, the UV-based physical methods are much more precise and accurate and are not damaged by high H_2S concentrations [4]. Furthermore, the ULTRA.sens® can be used to measure other gases simultaneously with H_2S gas analysis in a single setup. This feature also opens up completely new measurement possibilities for further applications in gas analysis. The previously limited-service life of these UV-LEDs is significantly extended by efficient cyclical control, so that all practical requirements can be met.

The ULTRA.sens® is available for trace gas analysis (1 ppm detection limit) and high process gas concentrations in the vol.% range [5]. The photometer is offered with a 100 mm stainless steel sample cell (AK100) and an amorphous silicon coating. The sample cell is also available in a process-compatible version featuring a gas measurement cell encapsulated in stainless steel with inert silicon coating. This version is suitable for H_2S concentrations exceeding 5,000 ppm [6].

References

[1] Lobo-Ploch, N. et. al.: Milliwatt power 233 nm AlGaN-based deep UV-LEDs on sapphire substrates. Appl. Phys. Lett. 117, 111102 (2020)

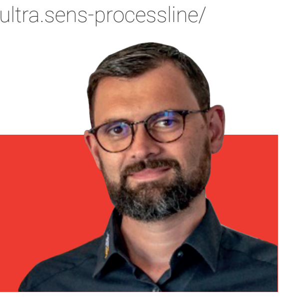
[2] Keller-Rudek, K., Moortgat,G., Sander R., Sörensen, R.: The MPI-Mainz UV/VIS Spectral Atlas of Gaseous Molecules of Atmospheric Interest

[3] Wiegleb, G.: Gas Measurement Technology in Theory and Practice, Springer Verlag Wiesbaden 2023 (https://doi.org/10.1007/978-3-658-37232-3)

[4] ETG Biogas Product line https://etgrisorse.com

[5] Data Sheet ULTRA.sens® H_2S, Wi.Tec-Sensorik GmbH: https://www.witec-sensorik.de/downloads/data-sheet-ultra.sens-ak100-led/

[6] ULTRA.sens® processline : https://www.witec-sensorik.de/produkte/ultra.sens-processline/



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