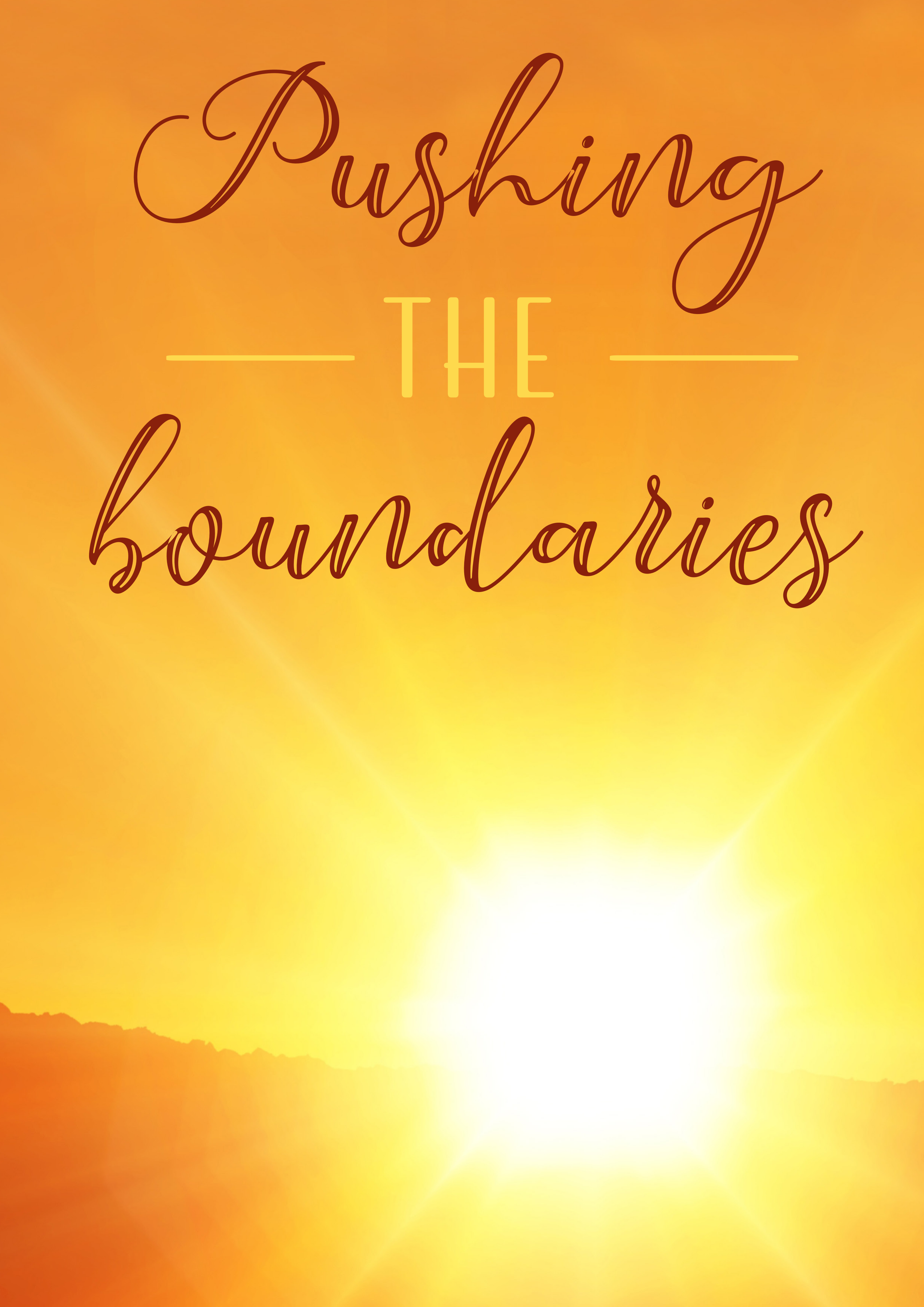
Pushing THE boundaries



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examine how tunable diode laser absorption spectroscopy (TDLAS) can aid industrial decarbonisation by pushing the limits of hydrogen measurement.

Decarbonisation of industrial processes is crucial to global efforts to minimise the impact of climate change. Governments worldwide have set aggressive targets for achieving net zero greenhouse gas (GHG) emissions by 2050, and the industry must take action to meet these objectives. Key elements of this effort include reducing the demand for primary resources by increasing the circular economy, improving energy efficiency, using carbon-free fuels, reducing the uncontrolled release of hydrocarbons and other GHGs into the atmosphere, and electrifying the heat supply using renewable energy sources such as wind, solar or hydropower. When carbon dioxide (CO_2) generation cannot be avoided, carbon capture, utilisation, and storage (CCUS) can be employed to reduce CO_2 emissions.

Many of these activities require gas measurements for optimising processes and ensuring safety, as well as monitoring emissions. Tunable diode laser absorption spectroscopy (TDLAS), with its fast response time, high reliability, selectivity, and sensitivity, is a powerful tool for these applications. Thanks to its exceptional performance and flexibility, TDLAS is now widely used across many industries, from petrochemicals and chemicals, to power and steel, as a standard technology for numerous applications.[1-4] Some of the most important examples include, but are not limited to, improving energy efficiency by optimising processes to reduce fuel consumption, safety monitoring of process inertisation, detecting methane leaks in natural gas pipelines, and monitoring pollutant emissions.

Hydrogen has long been utilised in various industrial production processes, including the hydrogenation of petrochemicals, ammonia production, and semiconductor manufacturing. Recently, much hope has been put on hydrogen as a carbon-free energy source for the future, and the Ukraine crisis has accelerated efforts to switch from fossil fuels to renewable alternatives.

With the advent of a new energy sector and new carbon-free manufacturing processes, many existing production processes will have to be adapted or new processes introduced. This means that there will also be

new tasks and challenges for gas instrumentation. With its flexibility, TDLAS will play a key role and contribute to the successful and safe decarbonisation of the industry.

TDLAS – gas sensing with lasers

Photonics-based technologies for measuring gas concentrations exploit the fact that every gas, be it oxygen, carbon monoxide or complex hydrocarbons, has a characteristic infrared (IR) absorption spectrum that can be considered as its unique fingerprint. In many cases, this allows accurate identification of gas components and quantification of their respective concentration values.

Lasers are among the most important photonic devices, and they are used for numerous applications thanks to their unique properties. In the context of TDLAS, the key features include the ability to emit light with narrow bandwidth and the ability to collimate, direct and focus the laser beam. The first property makes highly selective measurements in complex gas mixtures possible, while the second is crucial for directing the laser beam over longer distances.

The use of TDLAS enables real-time, contactless measurements of gas concentrations directly in the process, known as in-situ measurements. This has several advantages:

- Instrumentation is not exposed to the process gases.
- Complex and high-maintenance sampling systems are generally not required.
- Real-time measurements greatly improve the efficiency of process control and safety monitoring.

The most commonly used configuration for TDLAS instrumentation is cross-stack, meaning that the transmitter (laser) is mounted on one side and the receiver (detector) on the diametrically opposite side of a stack, pipe or duct (Figure 1).

The transmitter is mounted on the left-hand side of the stack, and the receiver on the right-hand side.

Although the ability to perform in-situ assessments is a key feature of TDLAS, there are situations where direct in-process measurement is not possible or preferable due to system design, varying infrastructure, installed base, etc. In cases of high gas pressures or very low concentrations, extraction may be required. Multi-pass cells (MPCs) provide a well-established method for increasing the optical path. Since a TDLAS analyser's lower detection limit (LDL) is directly proportional to the distance that the laser beam travels through the gas sample, improving LDL can be achieved by folding the optical path using two mirrors. At high gas pressures, a simple extraction cell with a transmitter and receiver mounted on both sides can also be utilised.

A third principle configuration of TDLAS systems is called open path. Open path sensors can cover optical path lengths of several hundreds of metres. They are typically used for the detection of diffuse or fugitive emissions.

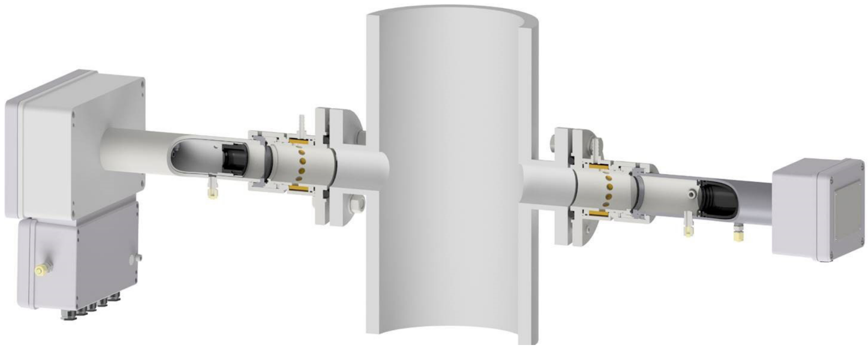

Figure 1. Sketch of a partial cross-section of a typical in-situ TDLAS installation. The transmitter is mounted on the left-hand side of the stack, with the receiver on the right-hand side.

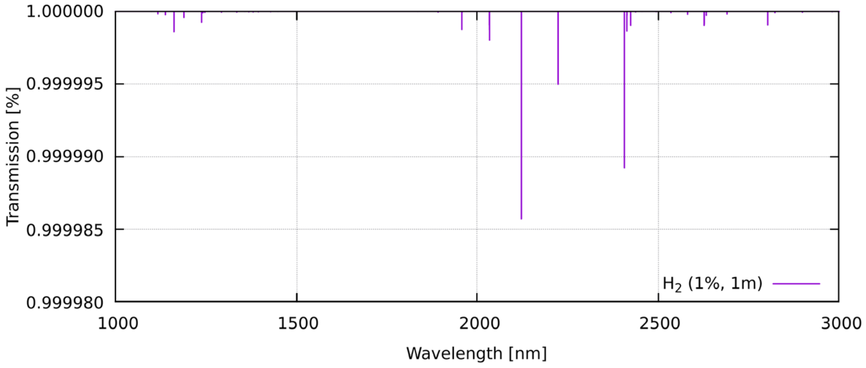

Figure 2. Simulated IR transmission spectrum of 1% hydrogen.

TDLAS for hydrogen

As mentioned above, TDLAS is used today for many applications and gases. Nevertheless, there are some important gases that were considered impossible to measure with this technology, and hydrogen is probably the most prominent example. This perception was based on the misconception that hydrogen does not have an IR absorption spectrum. There are, however, absorption lines spread throughout the IR region (Figure 2). These lines are very weak, so a high-quality gas analyser is required in order to obtain results that are useful in an industrial operation.

When taking safety applications as an example, hydrogen has a lower explosive limit (LEL) of 4%; end-users usually require alarm levels of 1% or even lower. For many applications, a fast response time (T90) is essential, and typically a T90 of 1 second is demanded by customers. Finally, the analyser shall not have any cross sensitivities with other gas components in the process or in the air to avoid false alarms.

NEO Monitors developed the world's first hydrogen TDLAS analyser for in-situ applications in 2017.[5] The latest version – LaserGas™ III H_2 – is designed for Zone 1 applications, with the laser beam allowed to penetrate a Zone 0 and meeting IEC 61508 functional safety requirements (SIL2).

One of the key figures of a TDLAS analyser is worth a closer look. The lower detection limit (LDL) of a TDLAS analyser can be determined by mounting it on an absorption cell filled with ambient air, placing it in a climatic chamber, and measuring the noise level over approximately 20 hours.

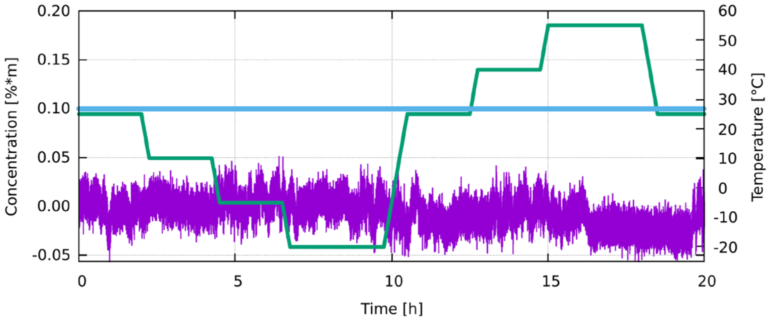

Figure 3. Noise measurement in a climatic chamber (T90 = 1s). Left y-axis: measured hydrogen concentration (purple) and lower detection limit (blue). Right y-axis: climatic chamber temperature (green).

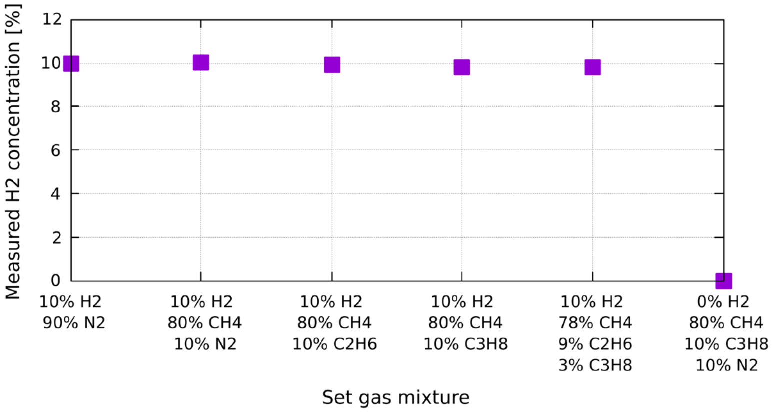

Figure 4. Set vs measured hydrogen concentrations in various hydrocarbon backgrounds.

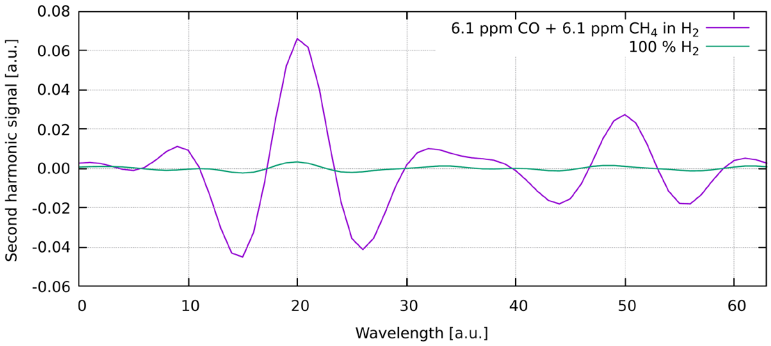

Figure 5. Recorded spectra of (1) 6.1 ppm CO (sample 20) and 6.1 ppm CH_4 (sample 50) in hydrogen background, purple trace, and (2) pure hydrogen, green trace.

To simulate real ambient conditions, the set temperature of the climatic chamber is changed in several steps, from room temperature to -20 °C, up to 55°C, and back to room temperature.

In general, the temperature changes lead to a drift of the optical fringes that are caused by reflections from optical components, such as lenses and windows in the beam path between the laser and the detector. Since such a climatic chamber test covers the entire operating temperature range of the analyser, it can be considered a 'worst case scenario' and the actual LDL is lower in many cases due to smaller temperature variations.

From Figure 3, a noise level of less than 0.05 %·m (3σ) or 0.1 %·m (peak-to-peak) at a response time of 1 second was derived; the latter corresponds to a sensitivity of less than $3 \cdot 10^{-6}$ (rel. abs.) when related to the absorption line strength reported in spectroscopic databases. These sensitivities are close to the theoretical limit of TDLAS analysers. The results show that the sensitivity is dominated by stochastic noise and only a few optical fringes are visible. Faster response times are also possible, but with a certain penalty on the sensitivity as the stochastic noise level will increase while the level of optical fringes will be maintained.

In summary, hydrogen measurements using TDLAS also meet the fundamental requirements for successful use in many process control and safety applications.

Hydrogen in natural gas

Hydrogen is becoming increasingly used as a fuel for vehicles, trains, ships, aeroplanes, and many other applications. In addition, blending hydrogen with natural gas through existing pipeline networks is seen as a possible first step in decarbonising natural gas systems.

Accurate metering is a critical task in supplying energy to end users; they want to determine the energy content they are receiving, and the supplier wants to bill accordingly. Gas chromatographs are commonly used to measure key indicators such as calorific value or Wobbe index. However, this expensive, slow, and complex technology does not meet the needs of most users. Hence, there is also a desire to use optical technology for this purpose.

Figure 4 shows results of hydrogen measurements in various hydrocarbon gas mixtures. For this purpose, a LaserGas™ II analyser with MPC was used in combination with a gas mixer to generate different gas compositions under well-controlled conditions. For the first five measurement points, 10% hydrogen was mixed with different ratios of methane (CH_4), ethane (C_2H_6), propane (C_3H_8), and nitrogen (N_2). The last measurement point represents a zero measurement of a hydrocarbon mix without hydrogen. The respective gas mixture is indicated on the x-axis and the measured hydrogen concentration on the y-axis.

The results demonstrated that there were no cross-sensitivities, and deviations of 1 - 2% relative from the expected hydrogen value were observed. This shows that the setup is very well suited to measure hydrogen in hydrocarbons with the required degree of precision.

Hydrogen impurities

When using hydrogen, the quality or purity of the supply can be critical. Impurities in hydrogen can interfere with the proper functioning of equipment that stores, distributes, or uses hydrogen as fuel. When hydrogen is blended with natural gas and used in boilers, the tolerance for impurities is generally higher than when hydrogen is used in vehicles powered by polymer electrolyte membrane fuel cells. The presence of impurities in hydrogen depends on the production process used. Carbon monoxide (CO) and CH_4 may be present in hydrogen from steam methane reforming (SMR), while oxygen (O_2) is present from chlor-alkali or water electrolysis.

TDLAS can also be used for these types of applications. For hydrogen generated from SMR processes, a combined impurity measurement of CO and CH_4 with low ppm ranges is often desired. By carefully selecting an IR wavelength, these two components can be measured with a single laser. This is illustrated in Figure 5, which shows a combined measurement of these two gases. In real installations, LDLs of 0.05 ppm for CO and 0.2 ppm for CH_4 have been achieved.

Conclusion

In summary, the innovative TDLAS technology has become a valuable tool to push the limits of hydrogen measurement in various industrial applications. As the world strives to achieve ambitious decarbonisation goals and transition to a sustainable future, TDLAS will play a key role in optimising processes, ensuring safety, and monitoring emissions in both established and emerging industrial sectors. Despite initial misconceptions about the feasibility of measuring hydrogen with TDLAS, advances in the field have led to the development of specialised analysers that can accurately and rapidly measure hydrogen in industrial environments.

TDLAS technology also offers the advantage that it can be transferred very easily to other applications, from CCUS, to ammonia as an energy carrier, and much more.

References

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