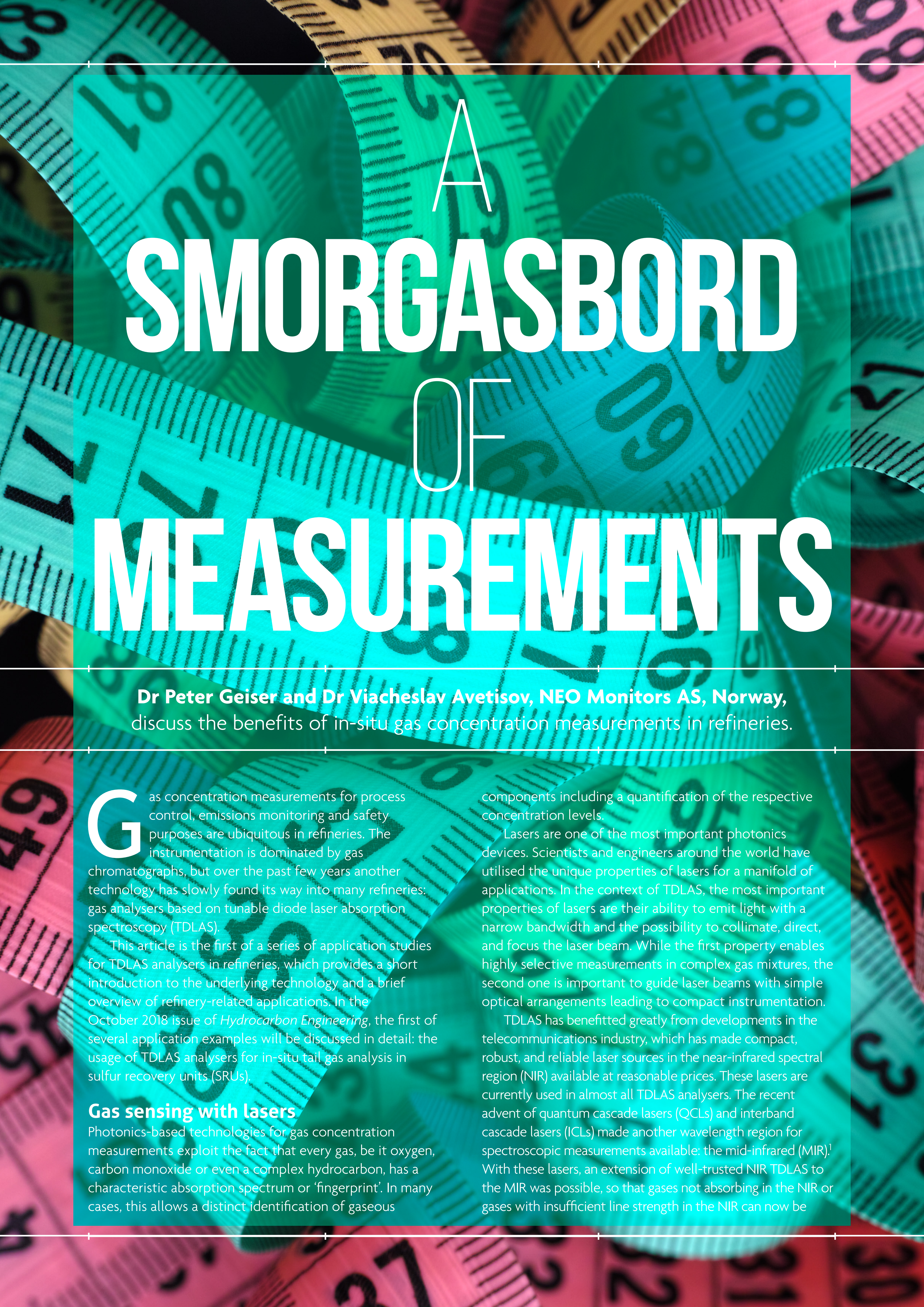

A SMORGASBORD OF MEASUREMENTS

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discuss the benefits of in-situ gas concentration measurements in refineries.

Gas concentration measurements for process control, emissions monitoring and safety purposes are ubiquitous in refineries. The instrumentation is dominated by gas chromatographs, but over the past few years another technology has slowly found its way into many refineries: gas analysers based on tunable diode laser absorption spectroscopy (TDLAS).

This article is the first of a series of application studies for TDLAS analysers in refineries, which provides a short introduction to the underlying technology and a brief overview of refinery-related applications. In the October 2018 issue of *Hydrocarbon Engineering*, the first of several application examples will be discussed in detail: the usage of TDLAS analysers for in-situ tail gas analysis in sulfur recovery units (SRUs).

Gas sensing with lasers

Photonics-based technologies for gas concentration measurements exploit the fact that every gas, be it oxygen, carbon monoxide or even a complex hydrocarbon, has a characteristic absorption spectrum or ‘fingerprint’. In many cases, this allows a distinct identification of gaseous components including a quantification of the respective concentration levels.

Lasers are one of the most important photonics devices. Scientists and engineers around the world have utilised the unique properties of lasers for a manifold of applications. In the context of TDLAS, the most important properties of lasers are their ability to emit light with a narrow bandwidth and the possibility to collimate, direct, and focus the laser beam. While the first property enables highly selective measurements in complex gas mixtures, the second one is important to guide laser beams with simple optical arrangements leading to compact instrumentation.

TDLAS has benefitted greatly from developments in the telecommunications industry, which has made compact, robust, and reliable laser sources in the near-infrared spectral region (NIR) available at reasonable prices. These lasers are currently used in almost all TDLAS analysers. The recent advent of quantum cascade lasers (QCLs) and interband cascade lasers (ICLs) made another wavelength region for spectroscopic measurements available: the mid-infrared (MIR).[1] With these lasers, an extension of well-trusted NIR TDLAS to the MIR was possible, so that gases not absorbing in the NIR or gases with insufficient line strength in the NIR can now be

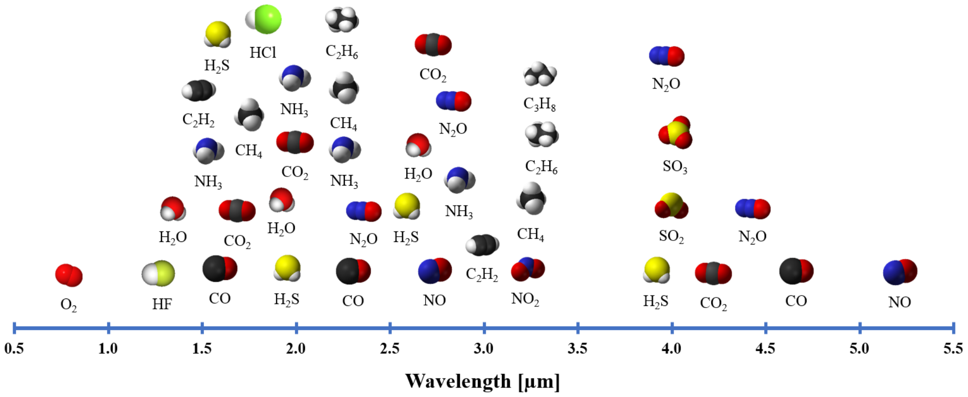

Figure 1. Overview of absorption band positions in the near and mid-infrared region.

Figure 2. Transmitter unit of an in-situ TDLAS gas analyser.

Figure 3. Fence-line monitoring using an open path TDLAS instrument.

measured in the MIR: sulfur oxides, nitrogen oxides, and a series of hydrocarbons are important examples (Figure 1).

In addition to advancements in laser technology, new developments in digital signal processing, accompanied by significantly increased computing power, have enabled the integration of more complex mathematical algorithms into TDLAS analysers. The recently developed IROSS technique (in-situ real time overlapping spectral separation) combines multi-variate analysis (MVA), a well-known chemometric method, and traditional TDLAS methodology.[2] This allows the analysis of complex spectra for multi-gas sensing in real time and finds their appropriate application, e.g. in the separation of overlapping and thus interfering spectra of CO and CH_4 in the 2.3 µm wavelength region.

Contactless measurements

TDLAS has become one of the most important industrial applications of lasers, enabling a contactless measurement of gas concentrations directly in processes, or 'in-situ measurements'. This has several advantages:

- Instrumentation is not exposed to corrosive gases.
- Complex and maintenance-intensive extractive systems are in general not required.
- Real time measurements enable much higher efficiencies of process regulations and safety monitoring.

All of this consequently reduces the OPEX of measurement systems drastically.

Different configurations

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 or duct (Figure 2). Transceiver setups are also possible, integrating a laser and detector in a single unit. In this case, a retro-reflector is used to bounce the beam back to the transceiver so that the beam is passing the investigated gas sample twice.

While the ability to perform in-situ measurements is one of the outstanding features of TDLAS, in some cases it is simply not possible to measure directly in the process. High gas pressures or the necessity to quantify very low concentrations can make an extraction necessary. This can be done either by simple extraction cells with a transmitter and receiver mounted on each side or extractive multi-pass cells (MPCs) can be used. MPCs are a well-proven approach to fold the optical path and thus increase the sensitivity since the latter is proportional to the optical path length.

A third 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 fence-line monitoring to detect fugitive emissions (Figure 3).

Application examples

Applications for all three configurations can be found in refineries, as summarised in Table 1. Some important examples where TDLAS has proven to be a suitable alternative to other technologies will be briefly described in the following.

Oxygen

The oxygen (O_2) absorption band around 0.76 µm is well isolated from bands of almost all other gas molecules. It is, therefore, well-suited for interference-free measurements of oxygen in almost any given gas matrix and for wide pressure and temperature ranges. TDLAS measurements of O_2 directly in the combustion zone have proven to be efficient for process optimisation. This is the best known and the largest application area for O_2 TDLAS analysers, particularly in refineries with a great variety of heaters and boilers. The technology is also expanding gradually to other processes. Replacing zirconium oxide and paramagnetic O_2 analysers with TDLAS analysers is beneficial in terms of better process control with faster response time and less maintenance. There are many different hydrocarbons and hydrogen streams where continuous O_2 monitoring is required for safety purposes. Below is a short list of units and processes where O_2 TDLAS analysers have been successfully used for process optimisation and process safety:

- Fluid catalytic cracking unit (FCCU) regenerator flue gas.
- Vacuum distillation columns.
- Tail gas in SRUs.
- Alkylation units.
- Petroleum coke calcining.
- Flare gas.

FCCU

Heavier hydrocarbons are converted in FCCUs to more valuable, lighter hydrocarbons. Carbon residue (coke) generated in the cracking reactions decreases the activity of catalysts. Therefore, a regeneration of the catalyst is required. The catalyst is routed to a regenerator where a coke burning process occurs at high temperatures of approximately 650 – 750˚C (920 – 1020˚F) and medium-high pressures of approximately 2.8 – 4.2 bar abs (26 – 46 psig). Afterward, the regenerated catalyst is routed back to the reactor. Since the quality of the catalyst is a key factor that influences the cracking reaction's efficiency, the efficiency of the regeneration process should be controlled. In-situ TDLAS offers several opportunities to optimise the regenerator performance in FCCUs by measuring carbon monoxide (CO), carbon dioxide (CO_2) and O_2. Analysers installed on top of the regenerator provide crucial data. Measurements of O_2 in the regenerator flue gas are important to regulate the combustion efficiency, while the CO-to-CO_2 ratio is used to control the coke formation in the reactor. The ratio can also be used to regulate the regeneration process temperature to protect the catalyst from overheating, which would reduce its lifetime.

Steam decoking furnace

Furnaces of different types require periodical decoking due to coke deposition in the furnace tubes. The process is known as steam-air decoking and maintenance intervals may vary from days to weeks. Reducing the maintenance requirements is increasingly important for modern refineries. The progress in decoking can be controlled by measuring CO_2 in the process offgas. The most important is to be able to measure CO_2 during the final stage of decoking when the offgas is mainly steam and the CO_2 concentration gradually falls well below 1 vol.%. At a predefined CO_2 level, the decoking can be terminated and the furnace can be returned to normal operation. The application is challenging since the required measurement range is at least 0 – 20 vol.%, while the detection limit should be less than 0.01 vol.% in almost pure steam (>90 vol.%). Nevertheless, TDLAS provides a solution. The laser wavelength is carefully selected for an optimum CO_2 absorption line in terms of the required measurement range and sensitivity, which is also spectrally well isolated from water vapour (H_2O) absorption lines. With TDLAS, CO_2 can be measured in-situ, thus providing valuable real-time data to control the decoking process.

Fence-line monitoring

One of the most crucial applications in refineries is the detection of gas leaks, which can be dangerous to both people and environment, inside and nearby the facility. A gas leak must be detected as quickly as possible so that necessary safety measures can be initiated immediately. TDLAS sensors in open path configuration can also be used as simple gas detectors and trigger an alarm if the gas concentration is rising above a defined level. A significant advantage of TDLAS is its ability to cover long distances with a single detection unit, making the usage of many point sensors obsolete.

For fence-line monitoring, the TDLAS detectors are typically placed around or in close proximity of equipment that poses a risk of a gas leak. Open path TDLAS detectors have already been used in many industrial installations to detect, for example, hydrogen sulfide (H_2S), ammonia (NH_3), hydrogen fluoride (HF), and methane (CH_4).

Combustion

Boilers, furnaces, and heaters in refineries all generate heat and power by combusting diverse hydrocarbons. Although application conditions and fuels can vary, the general principle is very similar: hydrocarbons are oxidised in an exothermic reaction to water vapour, carbon dioxide and an abundance of other gaseous species. Combustion processes are characterised either as lean or rich, depending on whether there is an excess of either air (oxygen) or fuel. Both conditions are leading to a poor energy efficiency. Additionally, in a rich combustion, high concentrations of CO are generated, while in a lean combustion the generation of nitrogen oxides (NO_X) is high. The highest efficiency can be achieved with a small amount of excess air, i.e. a lean combustion. This ensures that fuel is burnt completely under all conditions and thus the potential of high CO concentrations and unburnt fuel in the flue gas is minimised. Otherwise, fuel would be wasted and unsafe combustion conditions could potentially occur.

For a long time, O_2 concentration measurements were used to control excess air to maximise efficiency, and CO measurements were used to provide a feedback on the O_2 set point and to monitor CO breakthroughs to avoid fuel-rich operation. In recent years, safety has become a prime concern and, therefore, additional CH_4 measurement might be required as well.

Table 1. Overview of TDLAS applications in refineries

Application	Type	Gases
DeNO$_X$	In-situ process control	NH_3, NO, NO_2
Continuous emissions monitoring system (CEMS)	In-situ emission monitoring	NO_X, CO_X, SO_X
FCCU	In-situ process control	CO, CO_2, O_2
Steam decoking furnaces	In-situ process control	CO_2
Alkylation units	Safety open path	HF
Fence-line monitoring	Safety open path	$H_2S + CH_4$
Combustion	In-situ process control/safety	O_2, CO, CH_4
Tail gas analysis in SRU	In-situ process control	H_2S, SO_2
Hydrogen recycle gas	Extractive process control	H_2O, H_2S, CH_4
Vacuum column/tower	In-situ process safety	O_2

Multi-gas TDLAS, using a dual-laser approach in combination with the IROSS technique, allows O_2, CO, and CH_4 to be measured, as well as H_2O and process gas temperature in a single transceiver analyser. This provides the whole palette of control signals required for efficient and safe operation of a combustion process in-situ and in real time.

A DeNO$_X$-process is typically following the combustion zone to remove any NO_X still generated. Here, NH_3 is added to convert NO_X to water vapour and nitrogen. In-situ measurements of NH_3 are predominantly used for so-called ‘ammonia-slip’ measurements to regulate the NH_3-feed. Lately, NO_X can also be measured in the raw gas through MIR absorption bands of NO and NO_2; this information can be used as additional input to the control loop.

Conclusion

Considering the need for gas concentration measurements for a manifold of applications, refineries can truly be regarded as a smorgasbord for measurement instrumentation. While extractive measurements are currently dominating, application examples show the usefulness and feasibility of in-situ measurements, and in particular TDLAS, as it is providing highly sensitive and selective measurements in real time and at low OPEX. Progress in laser technology and data processing will make even more applications possible in the future, improving efficiency and safety of many processes. More detailed descriptions of specific applications will follow in future issues of *Hydrocarbon Engineering*.

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