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discuss the advantages of using
TDLAS analysers for tail gas
analysis in sulfur recovery units.

SWITCHING TO IN SITU ANALYSIS

In the May 2018 issue of *Hydrocarbon Engineering*, NEO Monitors considered refineries as "A smorgasbord of measurements."[1] The article highlighted tunable diode laser absorption spectroscopy (TDLAS) technology's ability to perform contactless real time gas concentration measurements directly into the process. In situ measurements provide several advantages compared to extractive solutions, such as the removal of complex and maintenance-intensive sampling systems, which results in a signification reduction in operational costs (OPEX).

This article will discuss the advantages of using in situ TDLAS analysers for tail gas analysis (TGA) in sulfur recovery units (SRUs) and present the results from a pilot installation. Traditionally, measurements for TGA were performed by gas chromatographs (GC), however, recently the majority of TGA have been carried out by ultra-violet (UV) analysers using heated sampling systems. UV analysers provide faster response times than GCs, which is crucial for closed-loop process control. While measurement setups are fairly simple, they have high demands on maintenance since the generated sulfur frequently clogs the sampling system. Consequently, the question arises as to whether it is possible to use in situ TDLAS to avoid issues associated with gas extraction and provide uninterrupted real time control signals, which would result in lower maintenance requirements and ultimately lower OPEX.

First, a closer look at the sulfur recovery process itself is required to understand how to tailor an in situ TDLAS analyser for a new application and why the ratio of hydrogen sulfide (H_2S) and sulfur dioxide (SO_2) is crucial for process optimisation.

Claus sulfur recovery process

The Claus sulfur recovery process was invented more than 100 years ago. Today, it is one of the most commonly used processes to recover elemental sulfur from gaseous H_2S, which

is present in numerous gaseous waste streams. Elemental sulfur is an important industrial feedstock for fertilizers, rubber, cosmetics, and pharmaceutical products.

The chemical reaction of a Claus process is best broken down into two steps, making it easier to control.[2] The first step (also referred to as the 'thermal step') involves burning one-third of the H_2S with air in a reactor furnace to form SO_2:

$$H_2S + {^3/_2} O_2 \rightarrow SO_2 + H_2O$$
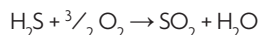
The reactor furnace is normally operated at temperatures between approximately 1000 – 1500°C. In the second step ('catalytic step'), the remaining two-thirds of H_2S reacts with SO_2 generating elemental sulfur (S) as follows:

$$2H_2S + SO_2 \rightarrow {^3/_2} S_2 + 2H_2O$$
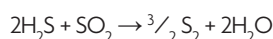
This catalytic reaction is usually done at much lower temperatures ranging between approximately 200 – 320°C. Since this is an equilibrium reaction, the sulfur is extracted from the recovery unit to avoid a back-conversion. Two or more stages are used in series to increase the yield of the recovery process.

A simplified schematic diagram of a Claus SRU is depicted in Figure 1. The reaction furnace on the left-hand side is followed by a series of condensers where sulfur is removed from the process. Since the sulfur is cooling down to its dew point in this step, it is heated up again to stay in the gas phase (re-heater). Afterward, the catalytic reaction of H_2S and SO_2 continues to generate elemental sulfur in the reactor (also referred to as converter).

Emissions from the Claus process are directly related to the recovery efficiency, meaning that higher recovery efficiency leads to less sulfur emitted in the tail gas. According to the

chemical equations, the highest H_2S-to-S conversion will be achieved if the stoichiometric ratio of H_2S to SO_2 is 2:1. Without the correct ratio, the Claus process will not run efficiently and the recovery of sulfur will decline rapidly, while the emission of SO_2 will simultaneously increase. The main purpose of TGA is to control the air to the reaction furnace. The real time 'air demand' signal that is used in the closed-loop control to the air-feed is proportional to:

$$2[SO_2] - [H_2S]$$

In situ TDLAS of H_2S and SO_2

In situ, extractive and open path TDLAS measurements of H_2S have been demonstrated in a large variety of applications using lasers in the near-infrared (NIR) spectral region. One of the most important applications is the measurement of H_2S in processed natural gas. Since H_2S is a corrosive gas it ultimately poses a safety issue by corroding pipelines and other equipment. The break-through level of H_2S in processed natural gas is approximately 4 ppm so that a detection limit of below 1 ppm is required. This can be challenging since H_2S is a relatively weak absorber in the infrared region and absorption arising from high concentrations of methane and ethane lead to cross-interference. A careful selection of laser wavelengths and proper signal processing resulted in the utilisation of the TDLAS technology for this challenging application. For a long time, laser-based measurements of SO_2 were considered to be impossible since SO_2 does not have any absorption bands with sufficient strength in the NIR. In the mid-infrared (MIR), however, several strong absorption bands are available. Until recently, no suitable MIR laser sources were available so that SO_2 measurements with TDLAS were mainly limited to proof-of-principle investigations in laboratory environments. The advent of the interband cascade laser (ICL) technology has opened the opportunity to extend the measurement capabilities of TDLAS from the NIR to the MIR region, even in industrial environments. This was already demonstrated in many applications, e.g. in the recycling of activated charcoal where an in situ ICL-based SO_2 analyser provides a real time control signal to regulate and protect a downstream filter system.[3]

Tailoring a TDLAS analyser for a new application has to start with a careful investigation of the process itself. Information about the typical gas composition and process conditions at the installation point (marked TGA in Figure 1) are gathered. Based on this input, spectroscopic databases like HITRAN are used to compute transmission spectra to identify suitable absorption lines.[4] In this context, suitable means that the absorption line is interference-free from other species in the process and allows a quantification of the target species with the required sensitivity.

Table 1 provides an overview of a common TGA gas matrix. Depending on the implementation and amount of converter stages, the gas matrix can vary slightly. In some installations the H_2S concentration can be up to 3% and the SO_2 concentration up to 2%. The pressure is typically ambient, and the temperature is kept at approximately 145°C in order to keep the sulfur in the gas phase.
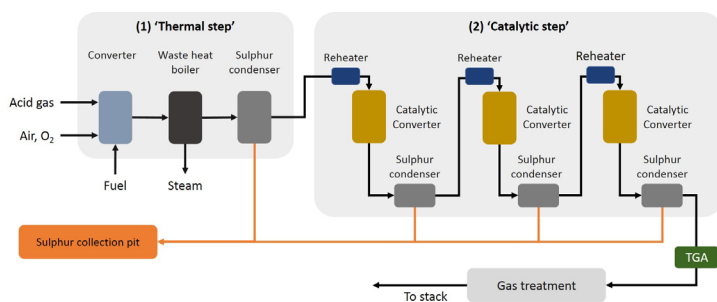

Figure 1. Schematic flow diagram of a Claus sulfur recovery unit (SRU).

Table 1. Generic gas matrix of a TGA application

| Species	Chemical formula	Concentration range (%)
Water vapour	H_2O	30 – 50
Carbon dioxide	CO_2	4 – 15
Hydrogen sulfide	H_2S	0.6 – 1.2
Sulfur dioxide	SO_2	0.03 – 0.3
Carbon monoxide	CO	0.6 – 1.2
Hydrogen	H_2	2 – 6
Nitrogen	N_2	40 – 50

Figure 2 shows the result of a transmission simulation in the NIR and MIR region. The high water vapour (H_2O) content in the tail gas makes TDLAS measurements of H_2S and SO_2 challenging due to its dense absorption spectrum and strong broadening effect on both gases. The absorption bands used are indicated by orange and red arrows: H_2S is measured in the NIR around 1590 nm (6289 cm^{-1}) and SO_2 in the MIR around 4000 nm (2500 cm^{-1}). Since the absorption lines are well-separated and typical distributed feedback (DFB) lasers have a limited tuning range of approximately $5 - 10$ cm^{-1}, using a single laser source is not feasible. For this application, two separated analysers were used.
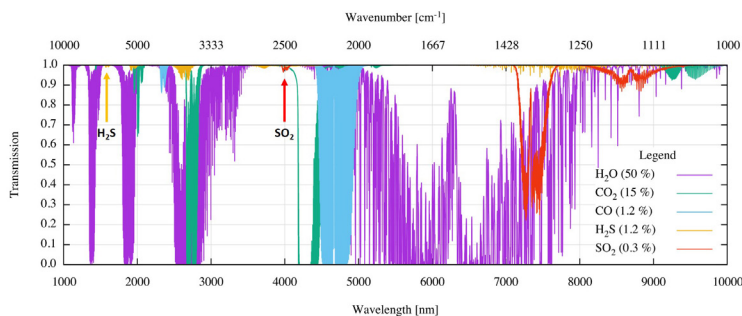
Figure 2. Transmission simulation of a typical TGA process based on the HITRAN database.[4]
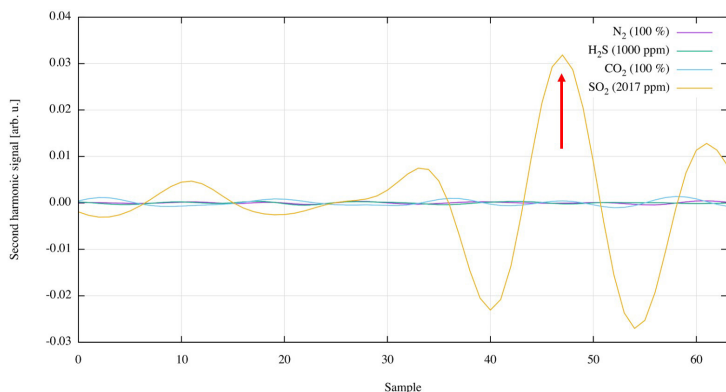
Figure 3. Second harmonic spectra of 100% N_2, 100 ppm H_2S, 100% CO_2, and 2017 ppm SO_2.
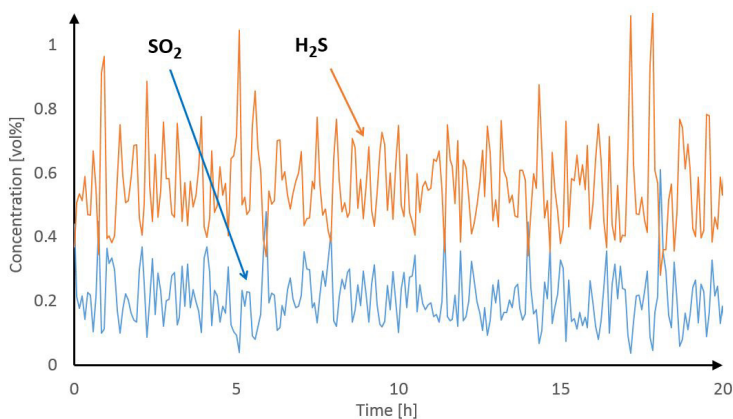
Figure 4. Field-results of in situ H_2S and SO_2 measurements.

Both analysers were calibrated in the laboratory using a heated cell. The latter can be interfaced with a gas mixer and a water evaporator. This allows industrial conditions to be recreated as close as possible in a controlled environment to optimise analysers for new applications. The selected absorption line has to be verified as interference-free. Even though the database used has become more reliable over time, an experimental validation is mandatory. For this purpose, the heated cell is filled with different gases and the resultant spectra are recorded. Figure 3 shows the results obtained at a gas temperature of 200°C. No interference with the 1000 ppm H_2S and negligible interference with the 100% CO_2 is visible. The latter poses no issue since, in a Claus application, the CO_2 concentration is much lower. Spectra of other important gases generated during the Claus process are not plotted since they do not absorb in this wavelength region: water vapour (H_2O), which is generated in higher percent-levels during the process; carbon disulfide (CS_2) and carbonyl sulfide (COS).

Field demonstration

In October 2016, both analysers were installed at a German sulfur recovery plant to perform first in situ measurements. The measurement path length was 35 cm for both analysers, the gas temperature was approximately 150°C and the pressure slightly above ambient. To prevent sulfur from coating the TDLAS optics and clogging the insertion tubes, constant air purging was used. It was expected that occasional steam purging would be needed to clean the insertion tubes from sulfur deposit. However, after two years of continuous operation (at the time of writing), there has so far been no need for this procedure.

Figure 4 displays the obtained results of the two in situ analysers. The expected opposing trend can be seen of both gases at the measurement point due to changes in air control to the reaction furnace. Unlike UV analysers, TDLAS does not require regular purging and calibration, but delivers continuous concentration readings without interruption.

Conclusion

The case study presented in this article demonstrates the performance and advantages of in situ TDLAS measurements. To the best of NEO Monitor's knowledge, this was the first time a Claus sulfur recovery process was solely controlled by this technology, eliminating the need for frequent maintenance due to clogging of extraction pipes. Following the pilot installation, this technology is currently being used in several other Claus plants around the world.

References
1. GEISER, P. and AVETISOV, V. 'A smorgasbord of measurements', *Hydrocarbon Engineering*, pp. 81 – 84, (May 2018).
2. GOAR, B. et al, 'Sulfur Recovery Technology', Energy Process, Vol. 6, No. 2. pp. 71 – 71, (1986).
3. GEISER, P., 'New Opportunities in Mid-Infrared Emission Control', SENSORS 15, pp. 22724 – 22736, (2015).
4. ROTHMAN, L. S., GORDON, I. E., BABIKOV, Y., BARBE, A., BENNER, D. C., BERNATH, P. F., et al, 'The HITRAN 2012 molecular spectroscopic database', Journal of Quantitative Spectroscopy & Radiative Transfer, 130, pp. 4 – 50, (2013).