Setting the Standard for Automation™

Emission monitoring applications enabled by cascade lasers

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NEO Monitors AS

Standards

Certification

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Presenter

- Peter Geiser obtained his doctorate in Applied Photonics in 2006 from Clausthal University of Technology (Germany).
- Shortly after that he was employed at Norsk Elektro Optikk AS where he was responsible for research and development of gas analyzers based on mid-infrared lasers and the LaserGas™ Q product family.
- In September 2015, he joined NEO Monitors AS where is currently holding the CTO position.

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Introduction

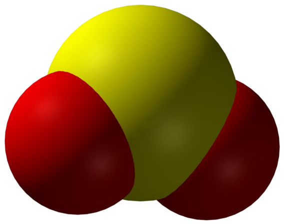
A common task in many industries like

- Oil &Gas
- Waste incinerators, and
- Glass & Metal

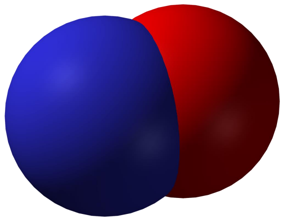
is the measurement of gases to

- Optimize processes, and
- Reduce emissions from them to protect the environment and public health.

Two real-world examples



Controlling a sulfur recovery process (H_2S and SO_2)



Emission control of a waste incinerator (NO)

Tunable diode laser spectroscopy

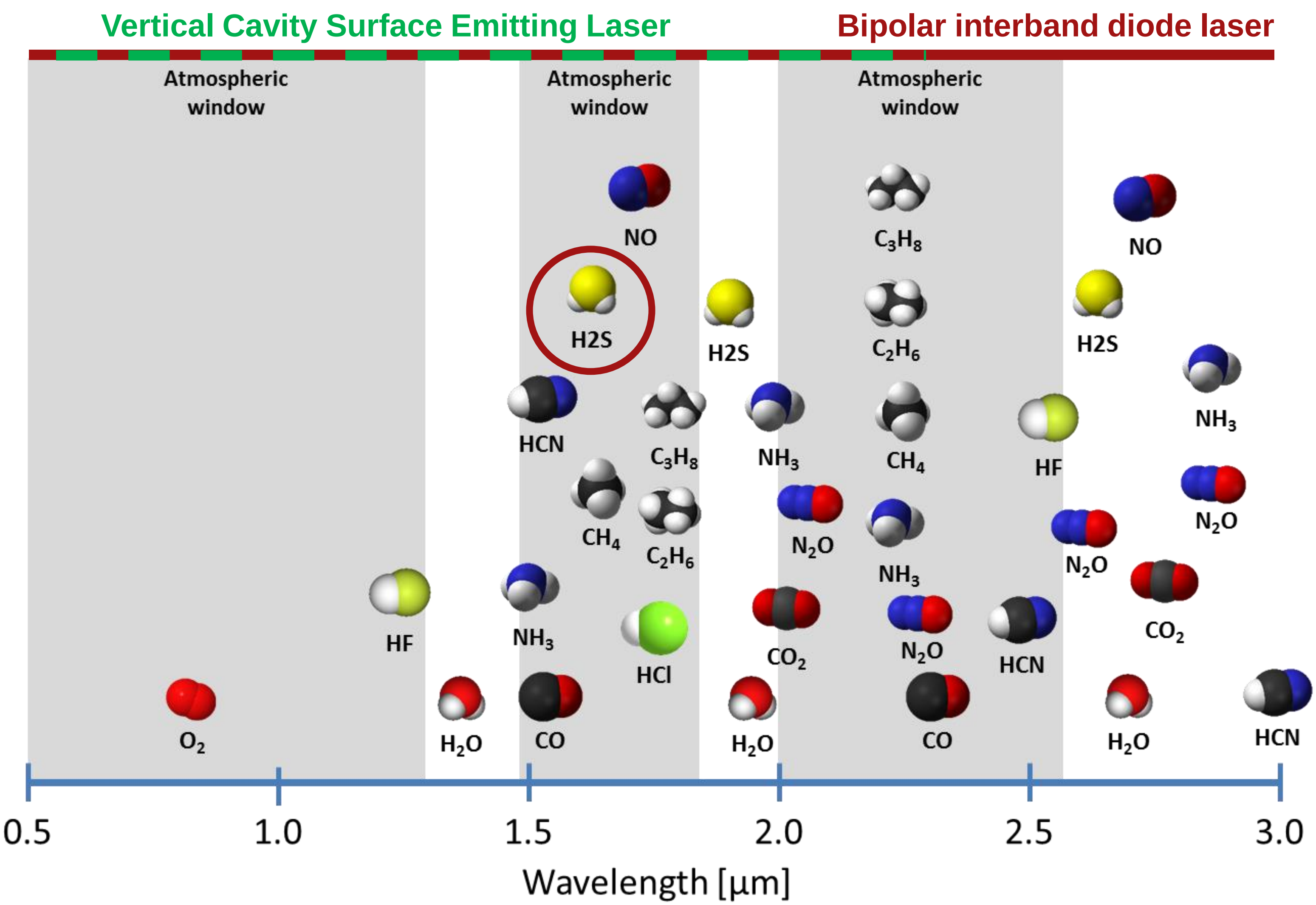
There are many measuring methods for process gases, but almost all are extractive.

Tunable diode laser spectroscopy (TDLS) is now a mature technology for in-situ measurements.

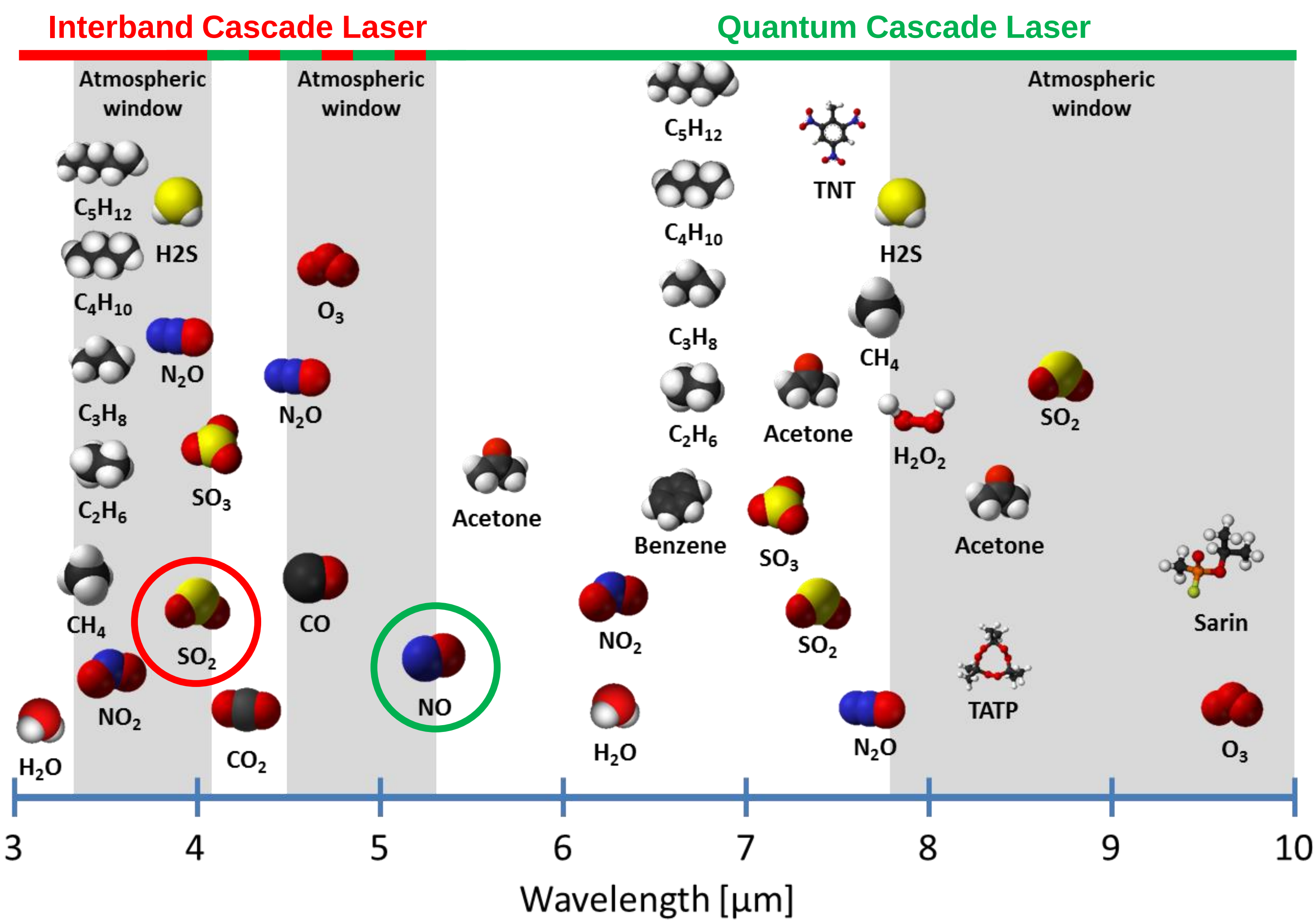
Industrial partners prefer in-situ measurements, because they

- provide real-time measurements,
- require less maintenance than extractive systems,
- and have a low cost-of-ownership.

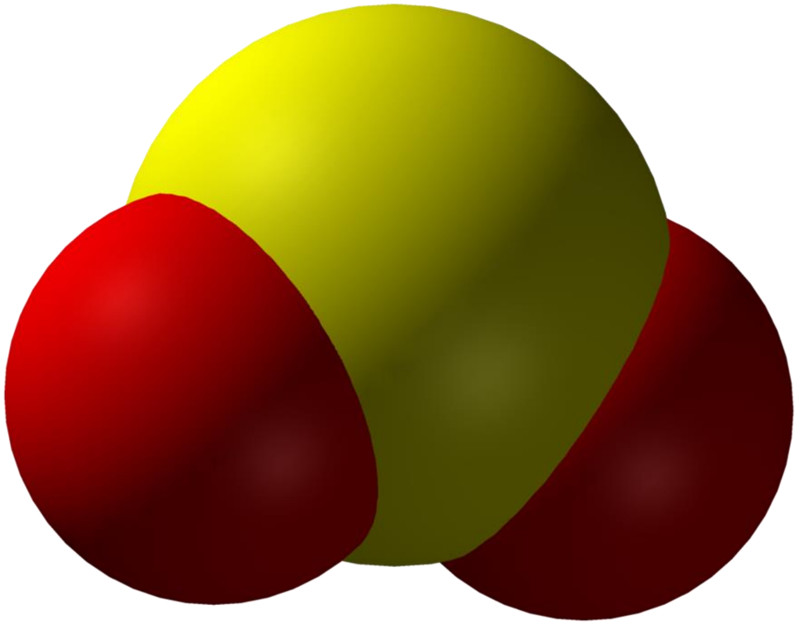
Near-infrared spectral region (NIR)



Mid-infrared spectra region (MIR)



Sulfur dioxide (SO_2)



Sulfur recovery process

The Claus sulfur recovery process is one of the most commonly used processes to recover elemental sulfur from gaseous hydrogen sulfide (H_2S). H_2S is present in numerous gaseous waste streams from, for example, natural gas plants and oil refineries.

Chemical reaction broken down into two steps

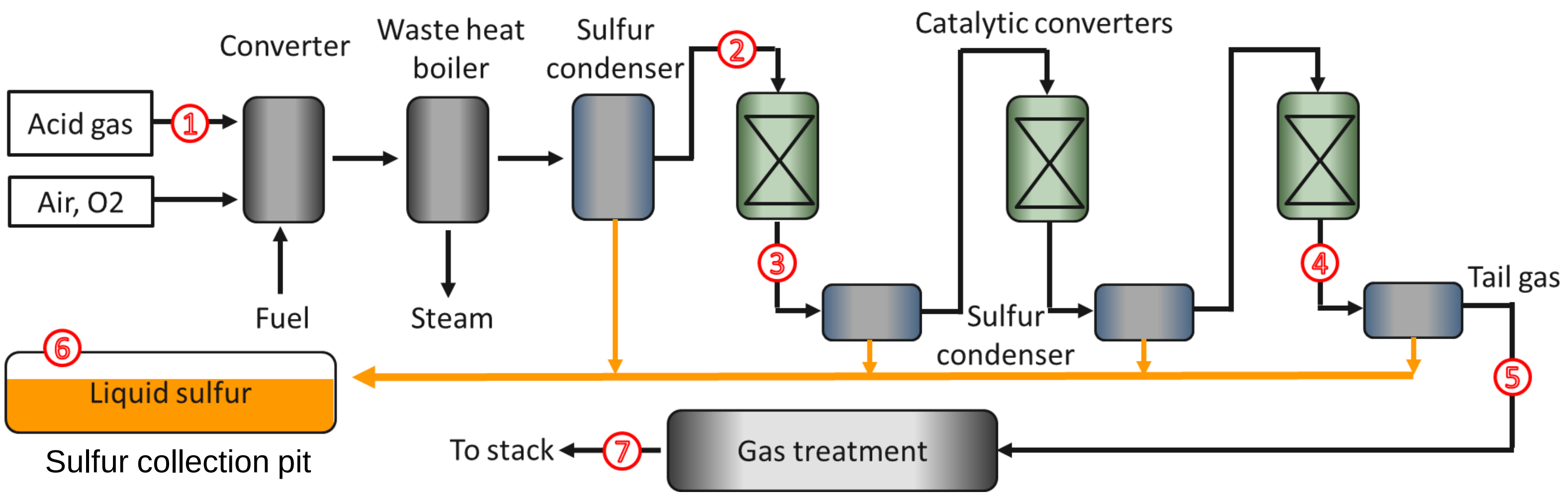
1. Thermal step (between 1000 °C and 1500 °C):

$$H_2S + 3/2\ O_2 \rightarrow SO_2 + H_2O$$

2. Catalytic step (between 200 °C and 315 °C):

$$2\ H_2S + SO_2 \rightarrow 3/2\ S_2 + 2\ H_2O$$

Schematic of a sulfur recovery plant



Measuring point		Target gases
1	Process gas feed	H_2S，SO_2，CO_2，HC
2	Inlet of the first catalytic converter	H_2S，SO_2
3	Outlet of the first catalytic converter	H_2S，SO_2
4	Outlet of the last catalytic converter	H_2S，SO_2
5	**Tail gas downstream the last condenser**	**H_2S，SO_2，COS，CS_2，N_2，H_2O，O_2**
6	Sulfur collection pit	H_2S，SO_2
7	Before/at the stack	SO_2，CO，NO_x，O_2

Tail Gas Analysis (TGA)

To achieve the highest H_2S-to-S conversion, the best stoichiometric ratio of H_2S and SO_2 is obviously 2:1.

Without the correct ratio, the Claus process is not running efficiently and the recovery of sulfur declines rapidly while the emission of SO_2 increases.

Traditionally, measurements of H_2S and SO_2 for TGA were performed by gas chromatographs. In recent times, the majority of TGA is done by heated UV analyzers.

The measurement setups are fairly straight-forward, but have high demands on maintenance and the generated sulfur is frequently clogging the extraction pipes.

Typical gas composition and conditions

Species	Chemical Formula	Concentration range
Water vapor	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 %

Gas temperature: about 145 °C
Pressure: slightly above ambient
Optical path length: 35 cm (insertion tubes)

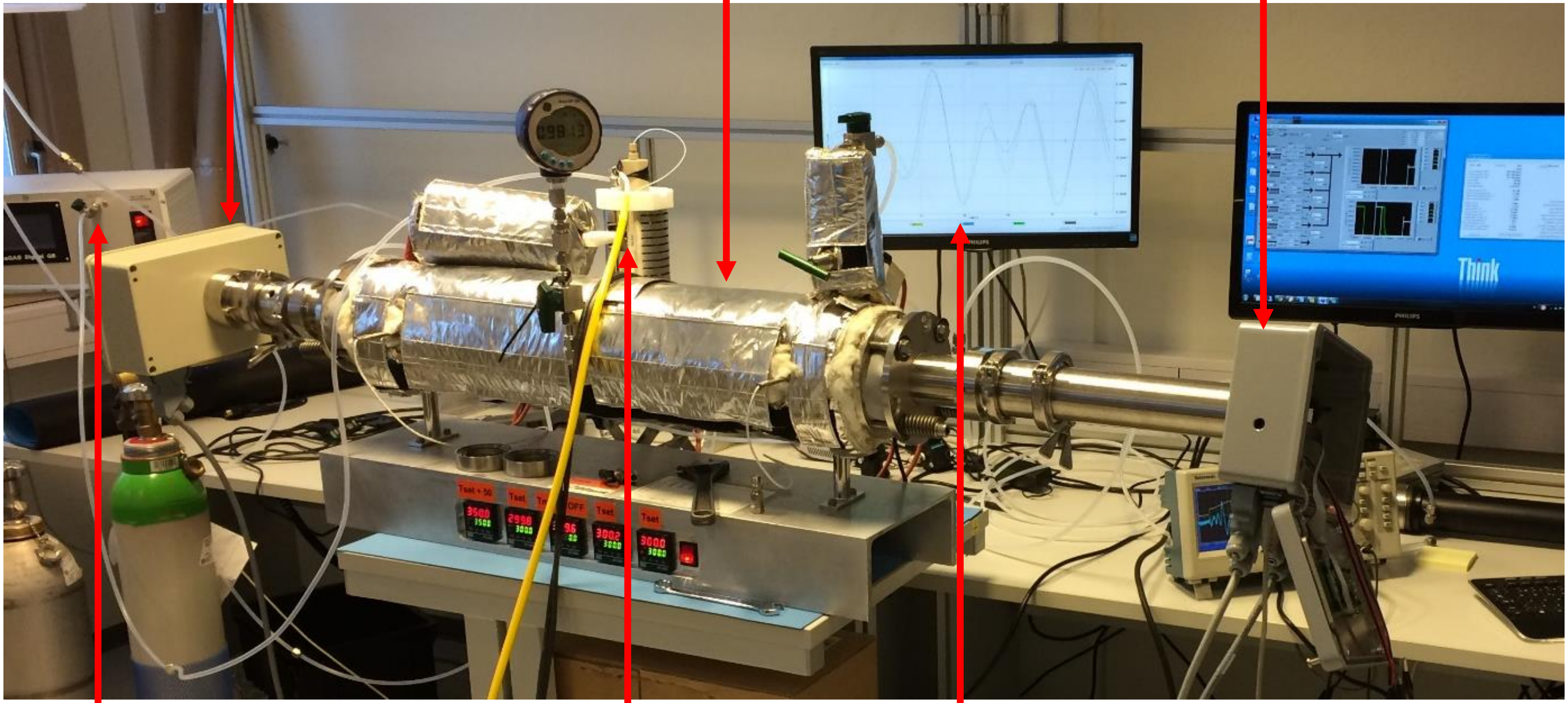
Information provided by our customer. Other Claus process applications may have other gas compositions (e.g. up to 3 % H_2S and 2 % SO_2).

First tests have been performed in the laboratory (here SO_2)

Receiver

Heated-cell

Transmitter

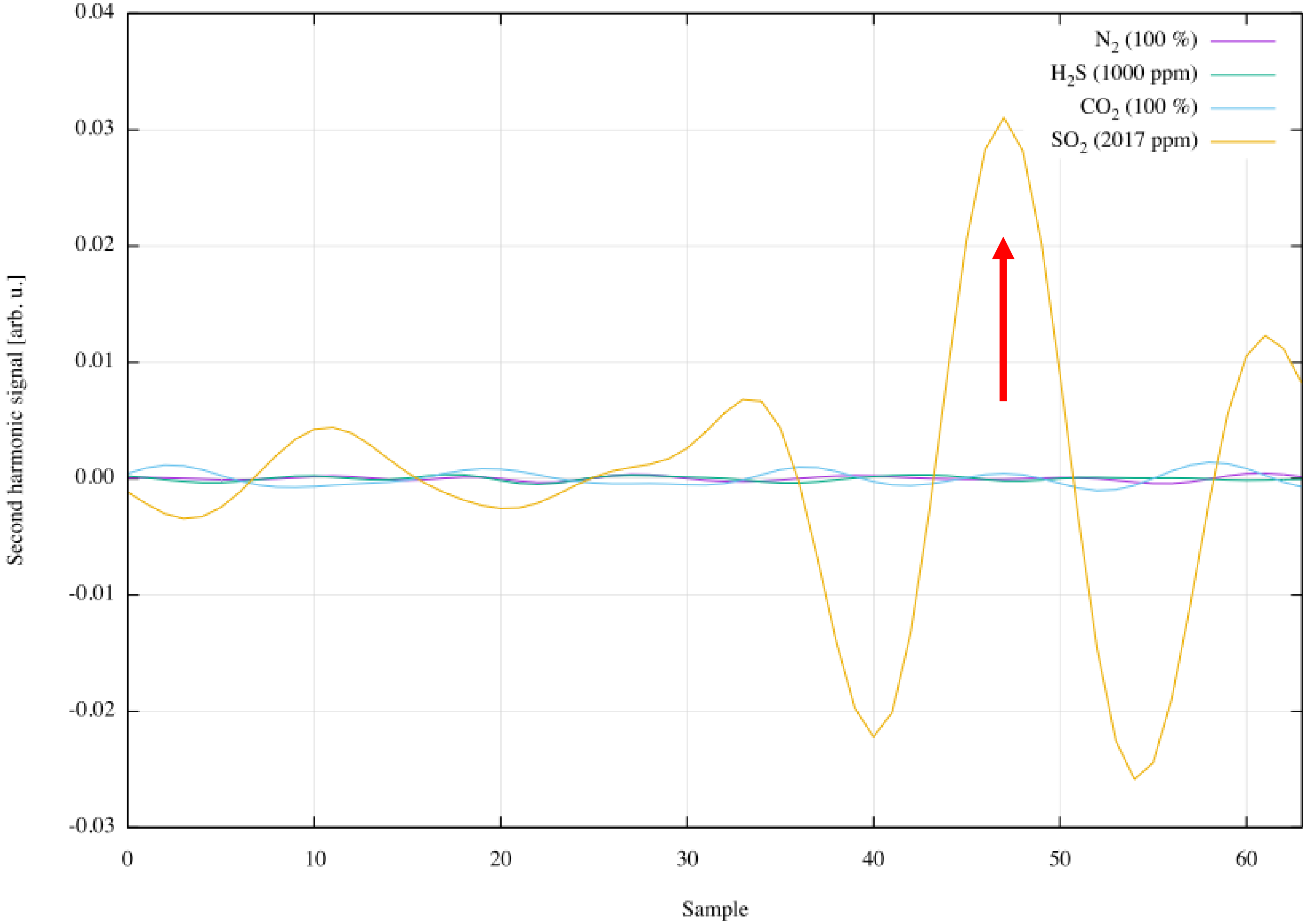


Gas mixer

Evaporator

Spectrum

No interference with H_2O, CO_2, …



Summary of laboratory evaluation

Performance under simulated application conditions

H_2O concentration	40 %
CO_2 concentration	15 %
Temperature	150 °C
Pressure	1 atm

	H_2S	SO_2
Detection limit	20 ppm·m	25 ppm·m
Range	5 %·m	2 %·m
Max Temperature	200 °C	200 °C
Max Pressure	1.2 bar	1.2 bar
Max OPL	2 m	2 m

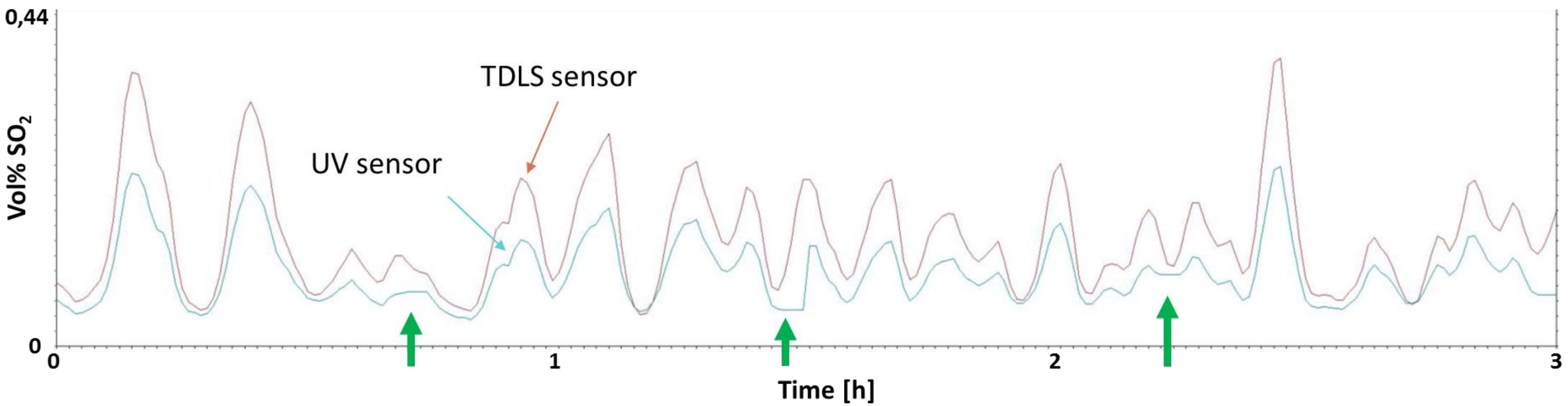
Field campaign at a German sulfur recovery plant

In October 2016, the H_2S and SO_2 sensors were installed at a German sulfur recovery plant (Coke oven plant, *Betriebsgesellschaft Schwelgern* in Duisburg/Germany).

A co-located extractive UV analyzer was used as reference system.

PROOF-OF-PRINCIPLE!!!!

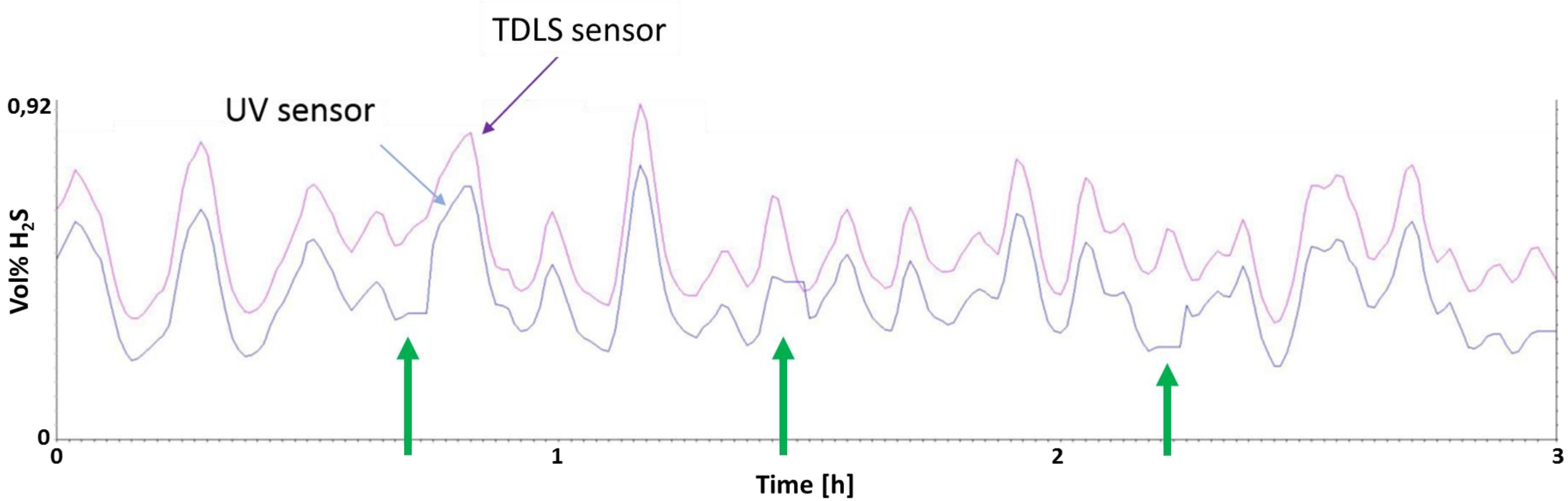
Comparison
Extractive UV vs in-situ TDLS: SO_2



The UV analyzer has to be recalibrated every hour and purged for several minutes (green arrows).

For TDLS analyzers this is not necessary and concentration readings are continuously available.

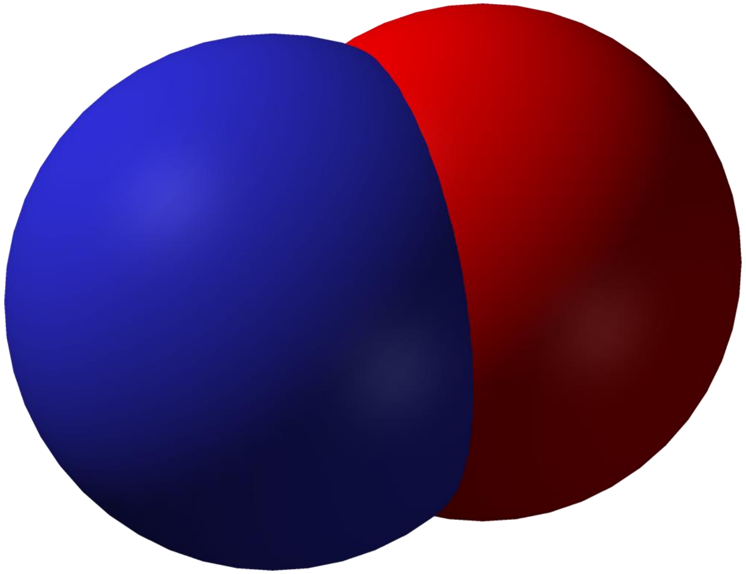
Comparison
Extractive UV vs in-situ TDLS: H_2S



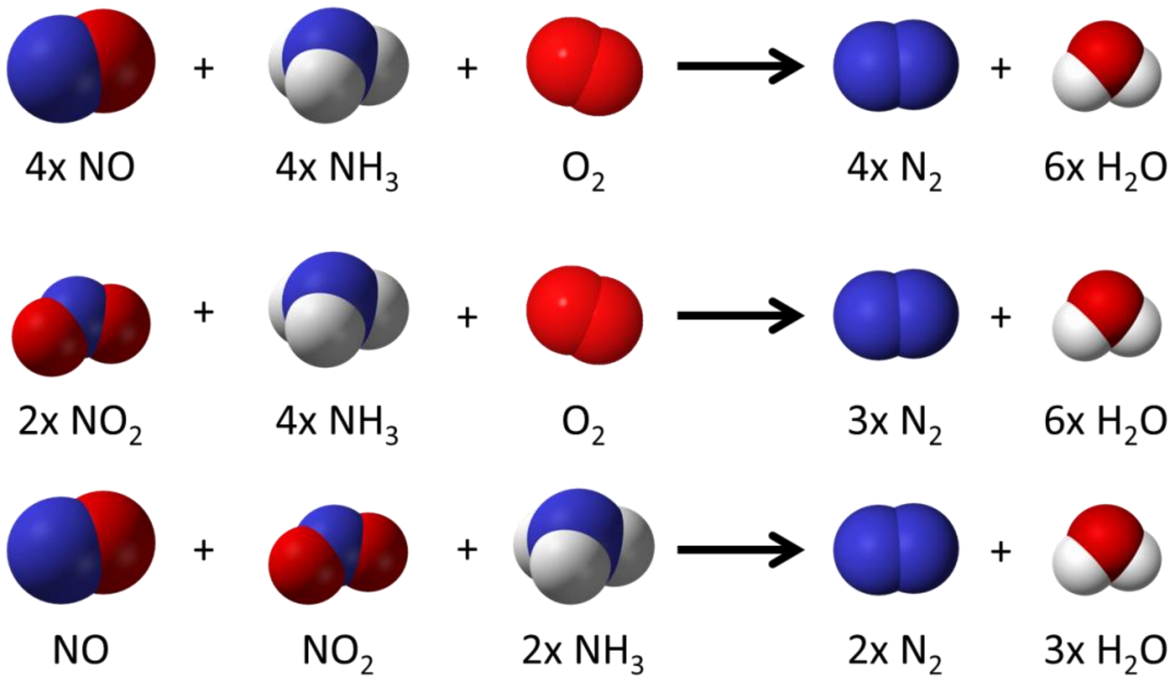
Explanations for deviation:

- Interference with CO_2 in the process
- Instrument has been retuned so that the offset was removed

Nitric oxide (NO)



Reduction of NOx emissions from combustion processes



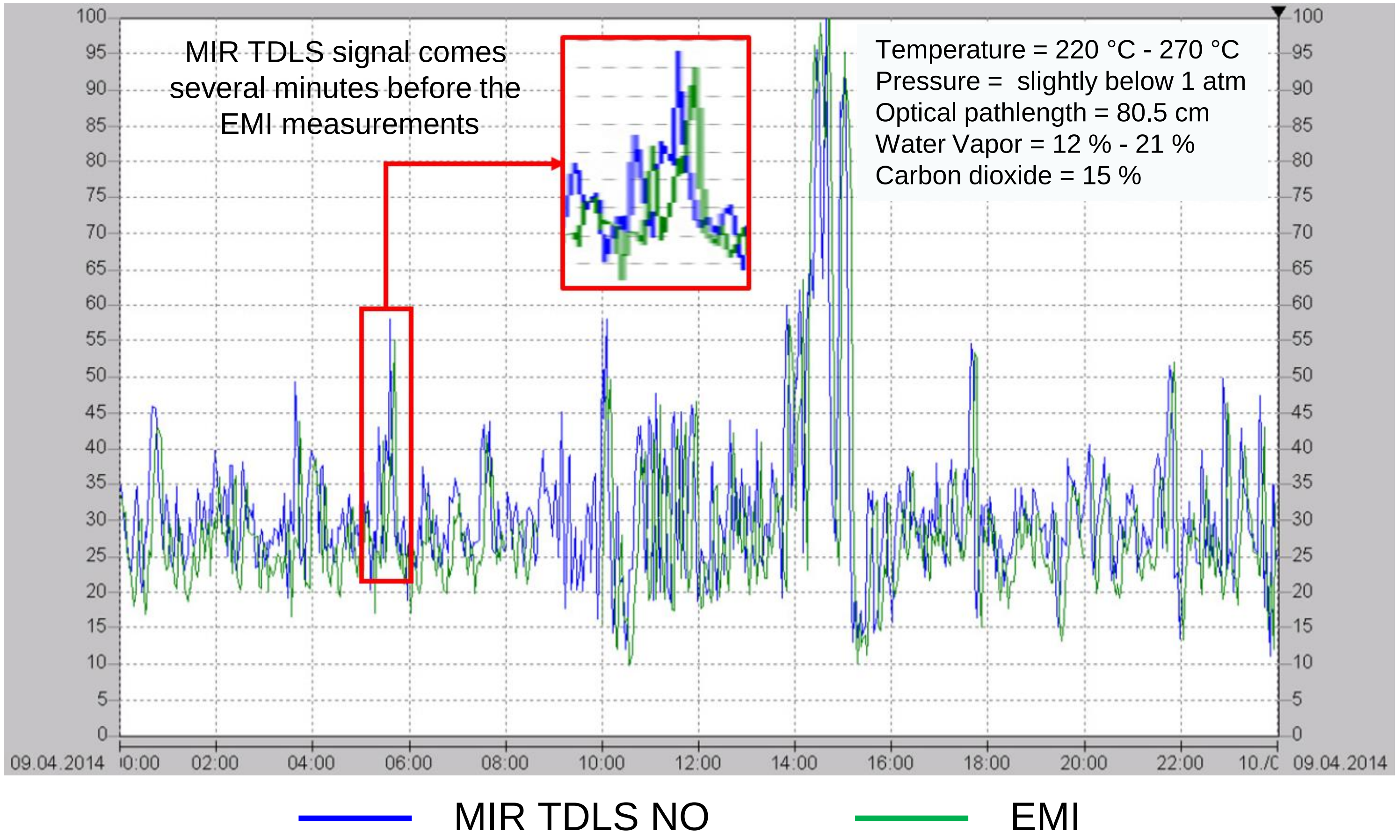
Near-Infrared NO sensors cannot be used due to strong interference with water vapor and low sensitivity at higher temperatures. Currently, ammonia measurements are used to control the deNOx-process, and NO emissions are merely monitored. However, it is desirable to use a direct NO measurement as control signal early in the process.

Waste incinerator

To demonstrate that mid-infrared TDLS is suitable for this kind of applications, a sensor has been installed at a waste incinerator in Germany.

Comparison of MIR TDLS and EMI

A comparison of measurements performed with MIR TDLS (raw gas) and the final emission monitoring (clean gas) is shown here:



Conclusions

- Cascade lasers have opened up new and exciting possibilities for emission monitoring applications.
- The technology is now being used in many challenging applications and customer acceptance and satisfaction is very high.
- Combination of near- and mid-infrared technologies has proven to be feasible and very powerful.
- There will be more applications coming in the future enabled by cascade lasers and the combination with their near-infrared counterparts.