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## HYDROCARBON PROCESSING®

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# Process Controls, Instrumentation and Automation

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## Selecting the right gas analyzer to optimize monitoring of NO<sub>x</sub> and other emissions

Combustion processes of all types generate emissions of one kind or another. For example, hydrogen- and carbon-based combustion processes produce water and carbon dioxide (CO<sub>2</sub>), respectively. Some emissions, such as the sulfur dioxide produced by the combustion of sulfur-laden fossil fuels, are classified as pollutants and are regulated by environmental agencies. Pollutants can be minimized by careful combustion control, or by minimizing precursors in the fuel, such as choosing to burn low-sulfur oil and coal. Pollutants that cannot be reduced sufficiently to meet regulations must be captured or converted through an emissions control system before release, and treated to remove their problematic components before reaching the atmosphere.

Pollutants from combustion processes are regulated around the world by local environmental agencies. In the U.S., the Environmental Protection Agency (EPA) publishes and enforces regulations, including:

- 40 CFR 60, New Source Performance Standards
- 40 CFR 63, National Emission Standards for Hazardous Air Pollutants
- 40 CFR 75, Emissions Monitoring Policy Manual
- 40 CFR 96, Nitrogen Oxide (NO<sub>x</sub>) Budget Trading Program.

The European Commission (EC) also has many air quality directives and standards, including the Industrial Emissions Directive (2010/75/EU), covering integrated pollution prevention and

control to minimize or mitigate emissions in the atmosphere, water and soil, as well as in waste from industrial and agricultural installations.

These regulations become more stringent over time, so producers must stay up to date. For instance, 40 CFR 60 has expanded over the years and now incorporates minimum specifications for emissions monitoring, emission measurement methods and performance specifications. While these general environmental concepts should be basic knowledge to anyone working with combustion processes in refineries and petrochemical plants, more information is required to deal with specific emissions.

**Understanding NO<sub>x</sub> emissions.** One pollutant that often proves problematic is NO<sub>x</sub> because it can be generated by any combustion process using any type of fuel, since there are no specific precursors that can be avoided. NO<sub>x</sub> refers to a mixture of two compounds, nitric oxide (NO) and nitrogen dioxide (NO<sub>2</sub>), which can both become photochemical pollutants in the atmosphere, ultimately causing acid rain. The two compounds tend to form together, but the proportion of the two is unimportant for the purposes of monitoring. The critical measurement is the overall total.

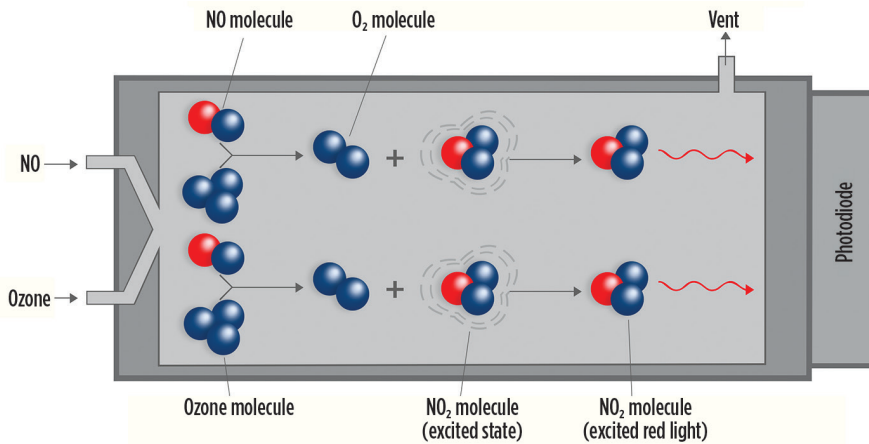
Combustion controls, such as low-NO<sub>x</sub> burners, help minimize formation to some extent, but these may result in other undesirable side effects. NO<sub>x</sub> can be reduced in the gas stream through chemical injection, but this requires accurate mea-

surement. This article will consider two different approaches for continuous NO<sub>x</sub> measurement in a combustion gas stream.

**Measuring NO<sub>x</sub> with chemiluminescence.** The first measurement method depends on a chemical effect called chemiluminescence. As the result of a chemical reaction of the intermediates NO and ozone (O<sub>3</sub>), NO<sub>2</sub> is produced in an excited energy state form. By emitting a photon in the excited state, the NO<sub>2</sub> returns to its ground state. The light emission, or chemiluminescence, can be detected and measured, and based on the amount of light emitted, the number of NO molecules can be determined.

None of the NO<sub>x</sub> molecules carried by a combustion gas stream are expected to be in an excited state, so this condition must be induced in the sample being analyzed, which requires several sequential steps. These steps include the following details:

1. All NO<sub>2</sub> in the sample must first be converted to NO. The sample gas stream passes through a heated bed of vitreous carbon, causing a reaction and turning more than 98% of NO<sub>2</sub> into NO and carbon monoxide (CO). Nearly all NO<sub>x</sub> molecules are now NO, but the overall total remains essentially the same.
2. A high-voltage corona discharge and a low-temperature, co-fired ceramics generator module in the analyzer create O<sub>3</sub> from ambient atmospheric oxygen. A pure oxygen supply is not necessary.



**FIG. 1.** A CLD analyzer determines the amount of  $\text{NO}_x$  in a sample by measuring the light given off by excited  $\text{NO}_2$  molecules.



**FIG. 2.** New CLD instruments<sup>a</sup> offer a low  $\text{NO}_x$  detection limit of 0 ppm–10 ppm.

3. The  $\text{O}_3$  and  $\text{NO}$  are fed continuously into a chamber, where they react, creating  $\text{NO}_2$  molecules. Approximately 10% of those molecules emerge from the reaction in the excited state.
4. The excited  $\text{NO}_2$  molecules emit their photon in the chamber and revert to the ground state. The spent reacted gases exit with the exhaust stream.

In a chemiluminescence detection (CLD) analyzer, the chamber in which  $\text{NO}$  and  $\text{O}_3$  react is fitted with a photodiode (FIG. 1) that can read emissions with wavelengths between 500 nanometers (nm) and 2,500 nm. The chemiluminescence in this chamber has its highest intensity around 1,100 nm. Software analyzes the excited molecule count, and extrapolates to project the  $\text{NO}_x$  content percentage for the entire gas stream.

A CLD analyzer (FIG. 2) typically requires a cold/dry sample gas stream, al-

though some CLD analyzers can work with hot/wet sample gas streams because water vapor can quench the chemiluminescence effect before it can be captured—therefore, causing an underreporting of the true  $\text{NO}_x$  level.

CLD analyzers have been available for many years, and the technology has long been accepted as the Standard Reference Method (SRM) for  $\text{NO}_x$  monitoring by the U.S. EPA (Method 7E procedure) and other regulatory agencies, including the European Standard EN 14792:2017. Over the years, the overall performance, stability and durability of commercial analyzers have improved. Among the various  $\text{NO}_x$  measurement technology alternatives, CLD analyzers offer very wide user-selectable  $\text{NO}_x$  measurement ranges from 0 ppm–10 ppm up to 10,000 ppm. They also have the lowest purchase cost—and their operational costs are minimal, since there are no consumables, with only the converter material

requiring periodic replacement at intervals of 1 yr–3 yr.

Present models do not require a pure oxygen ( $\text{O}_2$ ) supply, thus eliminating that expense. Some suppliers engineer the CLD without an internal vacuum pump, effectively removing a source of vibration that can compromise equipment integrity and reliability or add a maintenance requirement.

Some emissions monitoring applications require measurement of other gas components in addition to  $\text{NO}_x$  molecules. To expand the number of gases that a continuous emissions monitoring system (CEMS) can monitor, the CLD often needs to be packaged together with a second analyzer equipped with a non-dispersive infrared (NDIR) or non-dispersive ultraviolet photometer, and paramagnetic sensors. If the footprint and the expense of the extra analyzer are not concerns, then a CLD-based system can still be a very economical choice.

However, in other situations, another approach can be used to simplify the measurement of multiple components and to reduce the number of analyzers.

### Direct absorption spectroscopy for $\text{NO}_x$ and other pollutants.

This second measurement method uses an entirely different approach. Direct absorption spectroscopy utilizes a given compound's capability to absorb specific wavelengths of electromagnetic radiation. The absorption at a given wavelength is measured, allowing an analyzer to detect and quantify the presence of various compounds of interest. Using this technology, a single analyzer can monitor a range of pollutants in a gas stream.

The tell-tale spectral fingerprints for many polluting flue gas components can be observed in the near- and mid-infrared sections of the electromagnetic spectrum. The ability to create radiation with wavelengths ranging from 800 nm to 12,000 nm depends on a mix of different types of lasers, each of which can be optimized and combined to generate outputs within specific segments of that larger range. One current technique is using tunable and multiple individual cascading lasers to cover this wide wavelength band, which is not possible with a single laser. Multiple lasers working together permit measurements of a longer list of specific chemical components.

Quantum cascade laser (QCL) technology offers fast, high-resolution spectroscopy to detect and identify a range of molecules in the mid-infrared wavelength range. Coupled with tunable diode laser (TDL) spectroscopy to cover the near-infrared band, a single instrument can provide greater insight and monitoring in both the near- and mid-infrared range of spectroscopic light.

QCL and TDL narrow line width (FIG. 3) allows scanning of individual peaks of identified components with minimum interference and without filtration, reference cells or chemometric manipulations. No consumables are necessary, ensuring low lifecycle costs.

QCLs are fabricated to scan a desired wavelength spectrum, using a laser “chirp” technique. To start the process, a QCL is pulsed with electrical energy and heats up. As the temperature increases, the wavelength of the emitted light also increases. The duration of a chirp is about 1 microsecond ( $\mu\text{s}$ ), and, in this time, it scans a spectrum of between one and three wavenumbers. This act is performed with all the laser modules, in sequence, to cover the full range of critical frequencies to monitor each of the desired chemical components.

Internal signal-processing software takes the raw detector signal and converts it into a spectrum from which it can calculate the concentration of each analyte. QCLs can be chirped at a frequency of up to 100 kHz, gathering many thousands of spectra in a few seconds. Advanced signal processing enables real-time validation of measurements and reduces the need for calibrations. Multi-reflection cells enable absorption pass lengths of 2 m up to 5 m, compared to 200 mm for conventional NDIR photometry. This technology is capable of very high sensitivity, allowing it, in some situations, to reach into parts-per-billion (ppb) ranges.

This approach offers many advantages for CEMS in refineries and petrochemical plants (FIG. 4).  $\text{NO}_x$  is certainly a major area of concern, but other pollutants may be added to the list, including:

- Carbon monoxide ( $\text{CO}$ )
- Carbon dioxide ( $\text{CO}_2$ )
- Ammonia ( $\text{NH}_3$ )
- Sulfur dioxide ( $\text{SO}_2$ )
- Water vapor ( $\text{H}_2\text{O}$ )
- Oxygen ( $\text{O}_2$ )

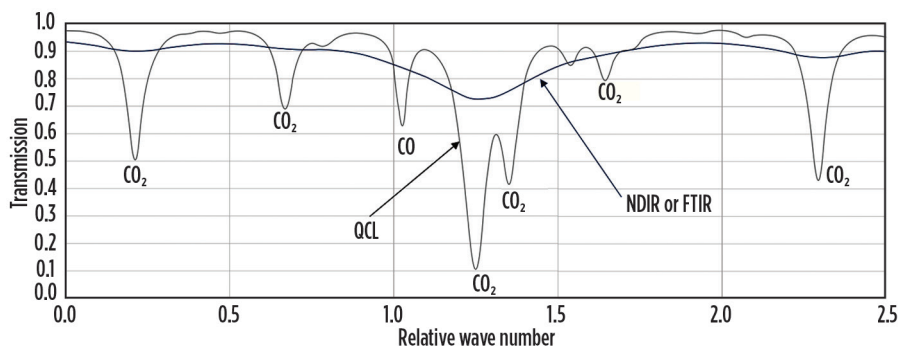


FIG. 3. This graph compares QCL detection to a conventional broadband technique, such as nondispersive infrared (NDIR) or Fourier-transform infrared (FTIR) analysis. In this example, the  $\text{CO}_2$  peaks are more pronounced and are easier to see with QCL detection.

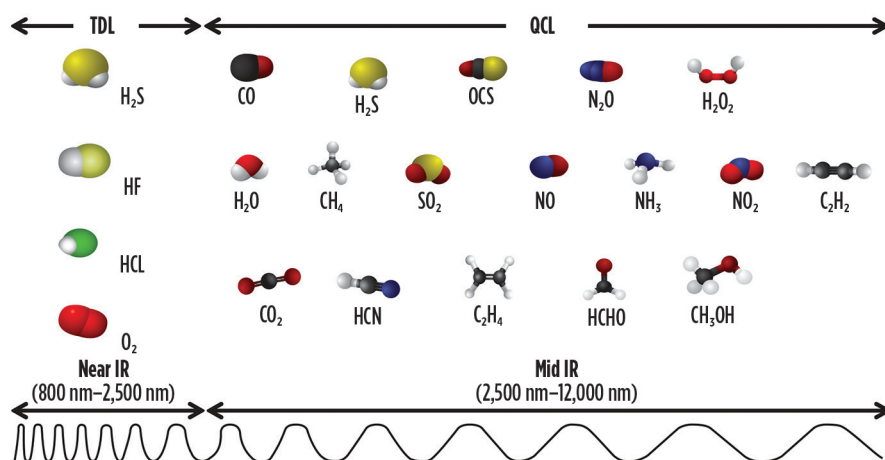


FIG. 4. QCL/TDL systems include up to six high-resolution lasers to measure both the near- and mid-infrared spectral regions for real-time, optimal gas measurement and analysis down to sub-ppm concentrations.



FIG. 5. One analyzer<sup>b</sup> is a purpose-built hybrid QCL/TDL process gas analyzer designed to enhance performance and reduce costs, particularly in  $\text{NO}_x$  measurement and CEMS applications.

Where it is necessary to monitor a list of components in a gas stream, a particular analyzer<sup>b</sup> can make all the required measurements (FIG. 5). Sophisticated models can monitor up to 12 gases, so that fewer analyzers may be necessary. Naturally, not all analyzer models are designed to handle all of these measurements, as such capabilities are costly and few applications need that degree of flexibility. More frequently, 3–5 components might require monitoring, so a user can choose the model that can measure only the components of interest to minimize analyzer cost and complexity.

QCL/TDL-based analyzers can take a variety of forms, making them easy to install in plant environments. Many are now robust enough to be mounted in the field without a traditional analyzer shelter. These field-mountable housings minimize the distance between the analyzer and the duct sampling point, reducing the lag time to capture a measurement. Some housings are even certified for hazardous areas, eliminating the need for a purged shelter. Internal components are

often highly modular, allowing field replacements of major subsystems, including the actual laser module—thereby ensuring high availability.

Some analyzers can take the sample stream directly from the stack in the hot/wet state to keep acid gases from condensing. These types of analyzers often need some internal adjustment of the reading when the limitation value is stated on a dry basis, but they have the advantage of not requiring gas conditioning to convert the stream to cold/dry. This conditioning, by necessity, removes water-soluble components from the sample stream, which is a drawback in certain applications.

A hot/wet stream also sends particulates into the analyzer, which can create deposits if not captured separately. Treating the sample stream beforehand to cool it and remove moisture creates a cold/dry stream that is free of particulates, providing pollutant level readings as specified in regulations, with no adjustment required.

Many tools are available to measure NO<sub>x</sub> and other pollutants from combus-

tion processes in refineries and petrochemical plants. Given the full range of available options, plant personnel can select an approach that is ideally suited for a given application. **HP**

#### NOTES

<sup>a</sup> Emerson's Rosemount X-STREAM Enhanced XECLD continuous gas analyzer

<sup>b</sup> Emerson's Rosemount CT4400 continuous gas analyzer



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