OPO-based optical analyzer monitors multiple gases in real time

BERTRAND HARDY-BARANSKI, OLIVIER LE MAUGUEN, and FLORENT THIBAULT

A new gas analyzer based on a compact doubly resonant optical parametric oscillator pumped by a pulsed laser can monitor multiple gases in real time with a very wide dynamic range at ppb levels.

Gas measurement instrumentation is necessary to control and monitor industrial process in the oil and gas, chemical, pharmaceutical, and food industries. Under constraints to save costs and energy and to further reduce the emission of pollutants, these industries are continuously seeking more sophisticated gas-measurement techniques that provide real-time quantification of multiple gases from very low- to high-concentration levels.

While laser-based optical gas analyzers are a natural solution for real-time quantification of trace gases, it has been difficult to develop systems capable of measuring more than three to four gases accurately enough because of limited wavelength tunability (typically a couple of wavenumbers). However, a new gas analyzer based on an optical parametric oscillator (OPO) pumped by a pulsed microchip laser—capable of measuring eight gas species in real-time with quantification limits as low as 30 parts per billion (ppb)—is responding to these new industrial requirements.

Laser-based gas-sensing methods

When excited by a laser source in the infrared (IR) region, a molecule emits a unique signal that is representative of the gas species and its concentration in the measured sample. This spectral "fingerprint" is created by interaction of the molecule's vibration modes with the light probe. The best region for easy discrimination of the majority of gas species is found in the mid-IR range, typically in the 2 to 5 µm window.

To date, two main families of gas analyzers are based on this principle. Fourier transform IR (FTIR) spectrometers scan a wide range of the IR spectrum (typically several thousands of cm^{-1}) from a broadband optical source. The signal that represents the sum of all signatures of the gases present in the sample is interpreted via an interferometer to give concentrations of each of the gas species in the sample. Although this family of spectrometers is well-suited for the complete identification of the gases in a sample, its detection limits are typically at the part-per-million (ppm) level in commercial versions.

Tunable diode laser absorption spectroscopy (TDLAS) instruments target a peak in the IR signature of a gaseous species (typically 1 to 10 cm^{-1}). They are generally powered by distributed-feedback diodes or quantum-cascade lasers (QCLs), or more recently using vertical-cavity surface-emitting lasers (VCSELs).

These spectrometers can monitor a gas at very low concentrations (ppb and below) in a very short timeframe (typically milliseconds). However, TDLAS instruments are only capable of monitoring a handful of gases (from one to three typically) and as such, are largely environment-specific; that is, a different environment might require targeting another spectral absorption band of the target gas species in order to cope with interfering species, thus requiring a different laser source.

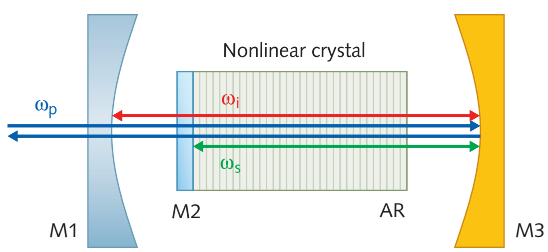

FIGURE 1. The double-nested OPO or NesCOPO used in the VHR-TL broad-tuning-range source uses double-pass pumping (blue) and two different resonant cavities for the signal (green) and the idler (red).

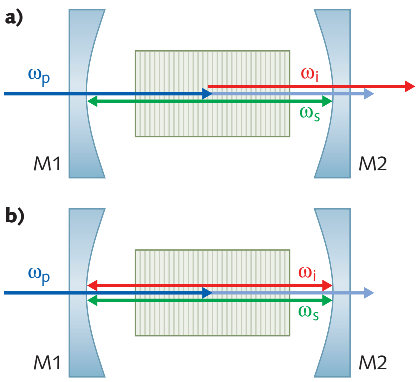

FIGURE 2. In singly resonant (a) versus doubly resonant (b) OPOs, the resonant waves build gain during each travel through the nonlinear crystal.

High resolution and wide tuning range

Using an optical technology patented by the French Aerospace Lab ONERA (www.onera.fr/en) and a pulsed microchip laser from Teem Photonics, Blue Industry and Science developed a very high resolution tunable laser source (VHR-TL) that combines a very wide tuning range (between 2350 and 3125 cm^{-1} in the current version) with very high resolution (0.01 cm^{-1})—broad tunability and narrow linewidth in a single optical source.[1] For comparison, the VHR-TL source spans 775 cm^{-1} while QCLs are limited to 10 cm^{-1} at similar resolution.

The heart of the VHR-TL is the so-called nested-cavity doubly resonant OPO (NesCOPO) design (see Fig. 1). As for any OPO, the NesCOPO converts an input pump wave ω_p into two output waves: the signal wave ω_s and the idler wave ω_i. This conversion is operated in a nonlinear crystal within one (or more) resonant cavities, with $\omega_p = \omega_s + \omega_i$ according to the principle of energy conservation. By changing physical parameters of the OPO it is possible to command the value of the ω_s;ω_i couple within the accessible spectral range, with the idler wave only being used for IR spectroscopy measurements.

A key advantage of the doubly resonant OPO design is its lower lasing threshold compared to the standard singly resonant scheme, basically because both parametric waves are resonant in the cavity (see Fig. 2). The VHR-TL OPO also has a double-pass pump scheme that subsequently lowers the lasing threshold and allows pumping with inexpensive pulsed microchip lasers. These passively Q-switched lasers provide few-nanosecond pulses—at a duration fitted to the OPO gain settling time—with kilowatt-level peak power at 1064 nm to efficiently drive parametric-wave generation.

Contrary to the singly resonant OPO, the idler wave ω_i exhibits a laser-like quality at output. Superior beam quality, higher energy density, and spectral purity combine to provide higher sensitivity and spectrally resolved measurements.

For the NesCOPO nested cavities' design, the signal and idler waves are resonant in different cavities. The frequency combs of the two cavities overlap in the nonlinear crystal, where the longitudinal modes with better phase matching will define the actual spectral output characteristics (see Fig 3). With careful design, single-mode operation is obtained for any frequency over the nonlinear crystal effective gain bandwidth.

The two cavity concave mirrors (M1 and M3) are translated with piezoelectric actuators to provide continuous tuning of the output frequency. Mirror command is entirely software controlled over the 775 cm^{-1} range with a resolution better than 0.01 cm^{-1}. The system is easily customized to the application without any hardware changes, for example, to reduce the measurement cycle or to add or delete gas species analyzed in a particular environment.

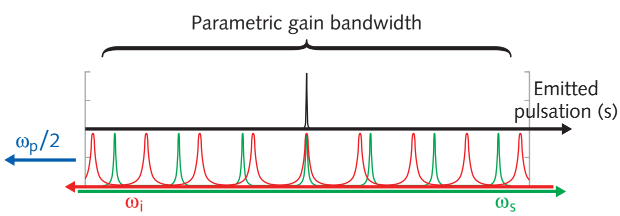

FIGURE 3. Unique frequency selection in NesCOPO design is achieved by overlapping the two different frequency combs created by the two cavities (signal and idler).

Industrial performance

Integral to the Blue X-FLR8 gas analyzer, the VHR-TL source delivers performance metrics similar to those of TDLAS while providing real multigas analysis possibilities with detection limits in the ppb range. For example, the system is able to continuously monitor eight gases in real time: five light hydrocarbons at low ppm, as well as propane, nitrous oxide, and carbon dioxide from low ppb to ppm levels. Thanks to the high resolution of the equipment, it is even possible to resolve the shape of the absorption transition.

Graphical output from the analyzer for four gases over a >700 cm^2 scan range appears similar to what can be achieved with FTIR technology (see

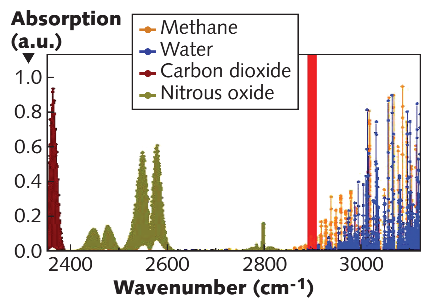

FIGURE 4. A gas absorption spectra covering a >700 cm^2 wavenumber range is graphed from the Blue gas analyzer (the red window indicates the zoomed-in portion shown in Fig. 5).

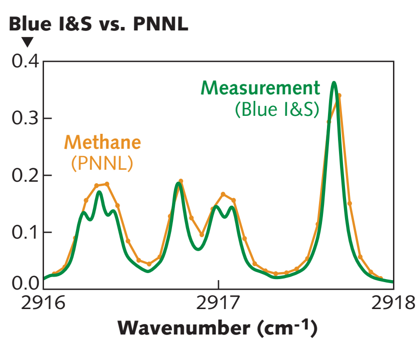

FIGURE 5. The zoomed-in region from Fig. 4 is displayed; the Blue X-FLR8 curve (green) shows much better resolution than the cutting-edge FTIR system used by the Pacific Northwest National Laboratory (PNNL, orange curve) to constitute their set of infrared reference data.

Fig. 4). However, the Blue X-FLR8 analyzer measurement is superior to advanced FTIR systems as it shows a multipeak structure when measuring methane that is not present in conventional FTIR-based scans (see Fig. 5).

Fiber-coupled microchip laser pumping enables a compact (dimensions 40 × 30 × 17 cm, weight 12 kg) and robust design for the VHR-TL, making the Blue gas analyzer itself compact and reliable enough to be used in-line or in mobile applications, where it is operational in minutes.

Implemented for process-control monitoring by a large industrial gas company, the instrument triggers just-on-time maintenance cycles by calculating real-time soiling of the process by scanning seven different IR windows (see Table).[2] The windows were chosen to offer a good compromise between the time required for the measurement and the ability to accurately quantify the gas species by deconvolving the spectra in real time. The current measurement cycle time is 5 min., with a consistent cycle reduction to come by early 2015 when the analyzer is deployed at the production site.

Infrared spectroscopic technologies are increasingly used in industrial applications because they provide fast, reliable, and unattended measurements at trace levels. Compared to the incumbent and widely established gas chromatography or mass spectrometry techniques, they are also easier to implement because they require virtually no consumables and minimize hands-on time. Adding multigas capabilities to existing TDLAS performance metrics, the Blue Gas Analyzer with VHR-TL source technology has the potential to foster new applications in the realms of real-time industrial process monitoring.

Seven different infrared windows scanned

Wavenumber (cm^{-1})	Scan width (cm^{-1})
2,383.78	1.00
2,554.53	1.00
2,577.50	1.00
2,701.20	1.00
2,901.80	2.00
2,964.60	2.00
3,032.00	2.00

REFERENCES

1. B. Hardy et al., Opt. Lett. 36, 678–680 (March 2011); doi: 10.1364/OL.36.000678.
2. S.W. Sharpe et al., Appl. Spectrosc. 58, 1452–1461 (July 2004).

Bertrand Hardy-Baranski is chief scientist, and **Olivier Le Mauguen** is business development manager at Blue Industry and Science, 208 Bis Rue La Fayette, 75010 Paris, France; email: bhb@blueindustryandscience.com; www.blueindustryandscience.com. **Florent Thibault** is new business development manager at Teem Photonics, 61 Chemin du Vieux Chêne, 38246 Meylan, France; email: f.thibault@teemphotonics.com; www.teemphotonics.com.