In PAS, the rotational and vibrational states of molecules are excited with infrared light pulses and the absorbed energy translates into kinetic energy pulses, which form an acoustic wave that can be detected with a microphone (1). Due to the nature of the direct absorption detection method of the photoacoustic effect, the instrument does not require long absorption path lengths and the background drift is virtually zero. This comes from the fact, that when no target molecules are present, no signal is detected (1, 2). The photoacoustic effect was already discovered by Alexander Graham Bell in 1880, but the sensitivity of the method was quite limited by the insensitive microphone technology until the late 20th Century. Now with the current state-of-the art MEMS fabricated cantilever microphones with optical laser readout it has been possible to achieve orders of magnitude enhancement in the sensitivity and the dynamic range compared to with condenser microphones (2,3). Additionally, the silicon cantilever withstands relatively high flow rates and external stress without stretching or breaking.

Thanks to recent development in technologies for mid-IR light sources it is now possible to run cantilever enhanced (CE)-PAS instruments with monochromatic and tunable wavelengths, broad spectral selectivity and high output powers. The joint use of these technologies bring a new level in sensitivity and selectivity with below ppb (parts-per-billion) sensitivity (4). There are a number of laser technologies now available on the market capable of providing spectrally flexible narrow-band emission in the mid IR spectral range; Quantum Cascade Lasers (QCLs), Inter-band Cascade Lasers (ICLs), DFB diode lasers and Optical Parametric Oscillators (OPOs).

In many aspects the OPO technology is the most ideal choice for driving CA-PAS instruments. OPO is a non-linear optical device that down-converts the wavelength from a pump laser into two longer wavelengths in an optical resonator.

The emission wavelengths depend on the configuration of the non-linear optical crystal (NLO) and the accessible wavelength span is ultimately limited only by the transmission window of the NLO. This very broad spectral selectivity and tuning capability is a general advantage of OPOs over other mid-IR light sources. More specifically OPOs can provide high output powers and freely selectable wavelengths in the 2.8-3.6 µm range which is an especially important wavelength range for sensitive hydrocarbon detection as it encompasses some of the strongest fundamental molecular transitions of several pollutive or poisonous industrial chemicals such as BTX, C2H2, CH4, HCN, HCL, HF etc.

This wavelength region is not readily reachable with QCL’s and the available power levels of DFBs and ICLs in this region are orders of magnitude lower than those of OPOs and not sufficient for extreme sensitivity. Moreover, the broad tuning capability of OPO compared to other mid-IR technologies allows for multi-gas detection of several components with common signal processing and chemometrics. The main draw-back of the OPO technology has traditionally been the bulkiness and complexity of available sources. However, recent advancements in OPO designs and laser packaging technology have enabled development of a new class of OPO devices of significantly smaller size.

The Cobolt Odin™ is based on a periodically poled NLO for ultimately wavelength flexible and efficient mid-IR emission. The OPO...
is pumped with a high repetition-rate 1064 nm laser and resonant for
the signal wavelength resulting in up to 100 mW output power in the
idler wavelength. The QPM crystal can be engineered for emission
anywhere between 2.5 µm and tailored for narrow-band (1 nm stan-
dard, <0.2 nm custom) emission. The emission line can also be con-
tinuously tuned over >60 nm.

Both the pump laser and the OPO resonator is assembled into a single
hermetically sealed package using the company’s proprietary HTCu-
re™ Technology for compact and robust laser assembly. The all-inte-
grated laser head package measures only 125x70x45 mm and is in-
sensitive to varying ambient conditions (e.g resistant to 60 G shocks
and exposure to -20 C to +70 C cycling), bringing the OPO technology
to a new scale of size, reliability and easy-of-use that enables inte-
gration into compact instrumentation for in-field trace gas detection.

In the first measurement setup (5), a collimated beam from the OPO
was directed through the photoacoustic cell (path length of 95 mm)
into an optical power meter. The pulsed emission from the OPO (re-
petition rate 10 kHz, pulse width 4 ns, pulse energy 5 µJ and linewidth
1.3 nm) was modulated with a mechanical tuning fork chopper op-
erating at a frequency of 135 Hz. The sample gas contained 10 ppm of
CH4 in nitrogen at 953 mbar in the photoacoustic cell. The sample gas
spectrum was collected with steps of 0.1 nm with integration time of
1 s per step. The resulting spectrum was compared to simulated HIT-
RAN spectrum and a detection limit was measured to be 3.3 ppb (2x
rms, 1 s channel integration time CIT).

The numerous promising applications for the compact OPO/CE-PAS

Figure 4. Cobolt Odin™. Complete OPO system with all-inte-
grated laser head and driver unit.

Figure 5. The OPO based CE-PAS measurement set-up. The
Cobolt Odin™ coupled into Gasera’s PA201 pho-toacoustic
detector for laser sources.

Figure 6. 10 ppm of CH4 measured with OPO/CE-OPO/CE-PAS, with 3.3
ppb DL at 1 s integration time.
In the second demonstration (6), the same OPO was used to measure benzene, toluene and 3 xylene isomers (namely, o-, p- and m-xylenes). The samples were produced by evaporating anhydrous liquid samples, with known rate, into 1200 mL/min flow of nitrogen (purity 6.0) and capturing a sample into the photoacoustic cell from the sample gas flow. The measured spectra were analyzed with Science Based Method, as described in reference (6) resulting in multi-compound detection limits (3x rms) for benzene 4.3 ppb, toluene 7.4 ppb, p-xylene 11.0 ppb, o-xylene 6.2 ppb and m-xylene 12.5 ppb.

In the third demonstration, a second OPO with tuning range from 3405 to 3463 nm, was set up to measure ethanol, methanol and methane with the PA201 photoacoustic detector. The pulsed OPO used in this experiment (repetition rate 10 kHz, pulse width 4 ns, linewidth 1.1 nm and output power 112 mW) was electrically amplitude modulated with 50:50 pulse ratio i.e. consecutively turning the 10 kHz pulse train on and off at a frequency of 70 Hz. The sample gas components were nitrogen diluted from verified gas cylinders, and the measurement pressure at the photoacoustic cell was 1060 mbar. The respective univariate detection limits obtained were (at 2x rms, with 1s CIT): for EtOH 7.7 ppb, for MeOH 11.4 ppb and for CH4 35 ppb. In this configuration, the total response time of the system was about 30 seconds, including the automatic gas exchange and the signal processing for a reduced tuning range.

With these demonstrations we conclude that the compact design and high mid-IR output power from the Cobolt Odin™, combined with Gasera’s novel cantilever enhanced photoacoustic measurement technology, allow the OPO/CE-PAS technology to offer extreme sensitivity and selectivity in reliable industrial gas analysis and monitoring. The demonstrated multi-gas detection with ppb-level performance, is reachable with a wide variety of gas components in various applications. And still, the full measurement system fits into a 19-inch, 3-unit rack mount, with possibilities for further down-scaling of the system, ultimately into handheld size.

References

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