Quantum leap

Pic 1: Horiba's exhaust testing system is based on QCLs and can detect a range of nitrogen compounds
Source: Horiba

Spectrometry equipment suppliers are starting to take advantage of the quantum cascade laser. Nadya Anscombe looks at how the market is developing

Of all the different laser sources on the market today, the quantum cascade laser (QCL) is the newest. Since its invention in the early 1990s, it was clear that this laser would have numerous applications in spectroscopy. Almost all molecules have an absorption band in the mid-IR region, making QCLs, with their continuous-wave operation in a huge range of mid-IR wavelengths (3 to 24µm), ideal for this application. And it gets better: QCLs have a narrow linewidth and relatively high power at room temperature. Traditional mid-IR laser sources either have no continuous wavelength tunability, are large in size and weight (e.g. CO and CO_2), or they require cooling (e.g. lead salt and diode lasers).

But despite many advantages and many years of development and research, there are today only a small number of commercially-available spectrometers that use QCL technology.

When compared with conventional spectroscopy techniques, such as FTIR spectroscopy, QCL-based systems are faster, more selective, more sensitive and do not need to be calibrated or cooled. So, if QCLs have so many advantages, why are there not more QCL-based systems on the market today?

'The time and effort it takes to develop a new spectroscopy system based on a new laser technology is not to be underestimated,' says Richard Cooper, sales director at UK-based Cascade Technologies. 'When we started developing our platform, mid-IR optics did not exist, so we had to design our own and have them manufactured. We also had to develop new software algorithms, sampling systems, device packaging technology and electronics to drive and pulse the laser. This all takes time.'

Andy Keay, product manager at Horiba agrees. Horiba has developed the MEXA-1400QL-NX emission measurement system for the analysis of nitrogen components in exhaust gas [see Pic 1]. 'Our product is aimed at the automotive industry and we take a long time to make sure a technology is suitable before introducing it,' says Keay. 'Our system has to work in extreme temperatures and conditions and our customers want to see proof that the system is robust and accurate.'

Unlike the industry-standard FTIR spectroscopy, the MEXA-1400QL-NX is able to analyse ultra-low concentrations of NO, N_2O, NO_2 and NH_3 accurately with virtually no interference from co-existing gases [see Figure 1]. It features four QCLs and can be used in a wide variety of applications from engine calibration to the development of after-treatment devices for complex powertrains operating on alternative fuels.

US company Physical Sciences has also developed a QCL-based system for detecting NO gas. It is designed for various applications including atmospheric monitoring, pollution emissions monitoring and breath analysis. The sensor uses room-temperature distributed feedback QCL (DFB-QCL) and balanced ratiometric detection

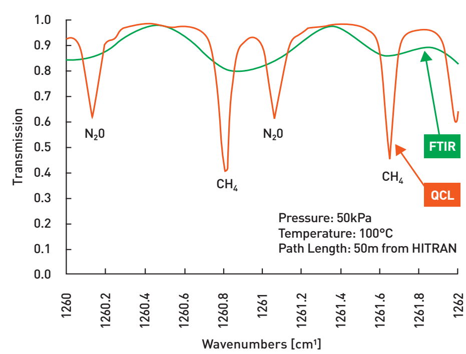


Figure 1: QCL-based spectroscopy is more sensitive and selective than traditional FTIR spectroscopy
Source: HITRAN

Pic 2: An aerosol can is rejected from the high-speed production line after a QCL-based spectroscopy system detected a leak
Credit: Cascade Technologies

Pic 3: Explosive detections systems based on QCL technology have been successfully trialled at Glasgow airport in the UK
Credit: Cascade Technologies

(BRD) technology. It has a sensitivity of 10 ppb at 1atm air pressure, 300K and 1m absorption pathlength. In single-mode laser operation it has an average linewidth of <0.3cm^{-1}, while in quasi-CW operation it features 1mW minimum average power (5ns pulse width, 1MHz pulse-repetition-rate). The system is optimised for absorption measurements using 1,900cm^{-1} NO transition to minimise interference by water vapour and other common atmospheric or industrial gases.

Another US company, Daylight Solutions, has developed a lightweight, battery-operated, portable sensor that allows recording infrared spectra of comparable quality as those of high-end FTIR spectrometers within seconds. In combination with powerful software and an application-specific database of infrared spectra permanently stored in the on-board memory, the Swept Sensor is particularly well-suited to identifying and quantifying complex mixtures of organic vapours.

Cascade's systems also measure gasses and have a wide variety of applications, because so many molecules have absorption bands in the mid-IR region. Its systems are used for aerosol leak detection, trace gas analysis, scientific instrumentation, monitoring industrial emissions and in security and defence applications

For example, the company's CT2210 Micro Leak Detector can identify leaking aerosol cans on high-speed conveyor belts [see Pic 2]. 'One of our customers was running an aerosol production line with speeds of around 150 to 200 cans per minute and wanted to increase this up to 500 cans per minute,' explains Cooper. 'But the acoustic leak detection system the company was using could not cope with such high speeds and background noise in the facility caused false positive rejects.' Cascade's system draws in the air from around each can and tests for presence of propellant (in this case butane) at a rate of 40Hz. 'The line has now been running at 500 cans per minute for the last 15 months and our system has never been calibrated,' says Cooper.

QCL-based spectrometers are also proving valuable tools in the security industry. Together with French company Morpho, Cascade recently successfully trialled a walk-through explosives detection solution at Glasgow airport in the UK [see Pic 3]. The system, which Cooper acknowledges is similar to the aerosol system, draws air from around passengers and analyses it for breakdown components from explosives. The system works quickly, achieving a walk-through pace, without using ionising radiation or capturing passenger images. The company claims that, when compared with other technologies such as ion mobility spectroscopy and chemiluminescence its technology provides a combination of speed, low false positives and upgradeability that other technologies cannot offer.

Defence and security applications such as this have been an important driver in the development of QCL-based spectrometers.

It was support from the US Defense Advanced Research Projects Agency (DARPA) that enabled US company Pranalytica to develop its QCL-based systems. The company, which was set up in 2000 by C. Kumar N. Patel, inventor of the CO_2 laser, now offers ultra-sensitive gas sensing instruments for a variety of applications. The company is unusual in that it is the only vertically integrated supplier of turnkey QCL systems, controlling the entire QCL fabrication chain from basic QCL structure design to system integration.

Defence applications are also an important market for fellow US company Block Engineering. For example, in November 2009 Block ➤

ADVANTAGES OF QCL-BASED SPECTROMETERS

- High speed of response
- High selectivity
- High sensitivity
- Minimal cross interference
- Wide dynamic range
- Highly accurate
- Low cost of ownership (no need to calibrate)
- Non-invasive measurements possible

Engineering was awarded a $4.38m government contract to develop a handheld infrared spectrometer for standoff detection of solid and liquid explosive materials or other substances that could be used for making improvised explosive devices (IEDs). The company has now developed what it claims is the only broadly tunable QCL spectrometer on the market. 'It covers the broadest tuning range of any QCL based system (600cm^{-1}) and can be used in a standoff mode, injected into a fibre/ATR probe, used in combination with an IR microscope, or used for gas analysis,' says Adam Erlich, vice-president of marketing and business development at Block Engineering. 'The system has six orders of magnitude higher spectral radiance than an FTIR spectrometer.'

	Standoff/Noncontact			Sampling		
Detects	Solid	Liquid	Gas	Solid	Liquid	Gas
LaserScan	✓	✓	✓	✓	✓	✓
FTIR	✗	✗	✗	✓	✓	✓
Raman	✓	✓	✗	✓	✓	✗
IMS	✗	✗	✗	✗	✗	✓
Gas Chromatography	✗	✗	✗	✗	✓	✓

Figure 2: QCL-based spectroscopy has many advantages over other techniques (IMS = ion mobility spectroscopy) Source: Block Engineering

Block Engineering is currently developing its next generation system, which will have better than 0.5cm^{-1} spectral resolution and 0.1 per cent noise on the 100 per cent line. 'This can be done with about a one-second integration time, which is much faster than an FTIR,' says Erlich.

The company's QCL-based system has several other advantages over conventional FTIR spectroscopy and other spectroscopic techniques (see Figure 2). It can be used in stand-off mode and, unlike techniques such as chromatography and ion mobility spectroscopy, can be used to analyse solids.

This is particularly useful when looking at polymer degradation, for example. 'There are customers that are interested in detecting degradation in a polymer and cannot pull a small sample off to look at it in an FTIR,' says Erlich. 'There are other handheld spectroscopy systems that exist, but they require that the sample be in near-intimate contact. If the surface is rough or hard to reach, these other techniques are not viable.' With the LaserScan, a user can rapidly determine if the polymer is damaged and the extent and area of the damage at a distance of six inches (15 cm) or more.

Block Engineering's technology can also been used in cancer research. An FTIR microscope often does not give the spectral and spatial resolution necessary in a reasonable amount of time. Many researchers have turned to synchrotrons to power their IR microscope in order to get better performance. 'But waiting for synchrotron time is problematic – and a synchrotron is typically the size of a football field and impractical as a tool for the lab,' says Erlich. By combining Block Engineering's QCL technology with a microscope, researchers can achieve performance that in some cases is better than a synchrotron. 'These researchers are excited about using a tool that they coin a "synchrotron in a box",' says Erlich.

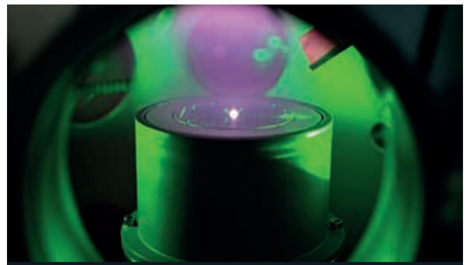
Another novel application of mid-IR spectroscopy is in the monitoring of plasmas [see Pic 4]. German company Neoplas Control was set up in 2006 as a spin-off from the Institute for Plasma Science in Greifswald, Germany. 'Monitoring plasmas using conventional techniques, such as mass spectrometry, is difficult,' explains Henrik Zimmermann, CEO of Neoplas. 'A sample needs to be extracted from the gas chamber and this can disturb the plasma.' Neoplas's system enables remote monitoring of plasma conditions with lasers that are of low enough power so as not to stimulate any reactions in the plasma. The company has developed a multi-channel laser supply enabling the use of up to eight lasers simultaneously. 'This means customers can detect and monitor up to eight molecular species at any one time without any cross interference from other vapours,' says Zimmermann.

Neoplas has also sold systems for various other applications, such as for monitoring sinter processes in industrial ovens, combustion engine development and OEM parts for breath analysis.

With so many exciting applications, the QCL's future in the spectrometer market looked assured. But why has this seemingly ideal technology only now managed to break into the commercial market? As usual, the driving factor is cost.

'Although research on QCLs has been ongoing in the lab for a while, it is only within the last few years that the QCL chips are being made well enough, and their performance good enough, that they can make the leap from the research lab to industry,' says Erlich.

Spectrometer developers have played an important part in this trend, driving a growth in the number of applications and therefore volumes. Cascade's Cooper explains: 'When we started, we



Pic 4: QCL-based spectroscopy systems can be used to monitor plasmas Source: INP Greifswald

were paying prices that were not affordable. So we worked to find applications that had the volume that was needed to drive the prices down. We also helped our suppliers improve their yield, because this also contributes to cost.'

The resultant price drops have been significant. According to Craige Palmer, assistant sales manager at QCL supplier Hamamatsu, 'prices of QCLs have dropped 50 per cent since 2006'.

Similar figures are quoted by fellow QCL supplier Alpes Lasers. 'The volume of lasers sold has increased three-fold since 2006,' says Olivier Landry, customer relations manager at Alpes Lasers. 'We expect similar growth in coming years. It is true the price of lasers has come down in the recent years, by more than 50 per cent in certain common cases, although not for more exotic [research] lasers.'

So with prices dropping and performance improving, the future looks bright for QCL-based spectrometry. Equipment suppliers are constantly looking for new applications and improving their equipment. For example, Block Engineering has plans to shrink its system down to the size of a bar-code scanner, while Cascade Technologies is looking at putting four QCLs on a chip.

Zimmermann believes the price of QCLs needs to drop further and performance needs to improve before the market can really take off. 'Everyone is looking for that killer application, but no one has found it yet. When they do, the market will really take off and prices will come down even further. There is definitely room for improvement.' ●

SUPPLIERS OF QCL-BASED SPECTROMETERS/SENSORS

Aerodyne (www.aerodyne.com)

Block Engineering (www.blockeng.com)

Cascade Technologies (www.cascade-technologies.com)

Daylight Solutions (www.daylightsolutions.com)

Horiba (www.horiba.com)

Neoplas Control (www.neoplas-control.com)

Physical Sciences Inc (www.psicorp.com)

Pranalytica (www.pranalytica.com)