# Mirrors ring the changes in spectroscopic analysis

The first portable systems based on cavity ring-down spectroscopy will be coming on to the market this year. **Vanessa Spedding** talks to the pioneers of the technique and finds out what advantages it has over standard laser spectroscopy methods.

Lasers and spectroscopy have been partners for years. Techniques such as absorption spectroscopy, photoacoustic spectroscopy and laser-induced fluorescence are well established and successful. Often, however, these techniques cannot be used in certain environments and cannot detect or measure low concentrations of a substance.

A simple extension of laser absorption spectroscopy that has been under development for more than a decade could change all of that – and the signs are that it is just becoming commercially viable. The key to the approach is mirrors, and the technique is cavity ring-down spectroscopy (CRDS).

### Conception to inception

CRDS was conceived in 1988 when two researchers, Anthony O'Keefe and David Deacon of Deacon Research in Palo Alto, US, reported a way of determining optical absorption based on the rate – rather than the magnitude – of absorption.

The group measured the absorption of a light pulse by a gas confined in a closed optical cavity. The method, which has changed little since its inception, involves bouncing a light pulse back and forth several times between two mirrors, one at either end of the cavity. The decay rate of the light, measured at different frequencies, identifies the absorbing species in the cavity (see box). The back and forth movement of the pulse is called ringing, and the decay of the transmitted light is called ringing down.

CRDS is enormously sensitive. It picks up absorptions that are one-millionth of the strength of those that can be detected by Fourier-transform infrared spectroscopy. It is also unaffected by laser noise.

The technique has already found wide-ranging research applications, such as detecting trace amounts of volatile organic molecules, impurities and other chemical species in plasmas, flames and discharges. Calculating the area under the frequency spectrum gives the quantity of a species present, and a further refinement of the maths reveals its temperature – this information is impossible to glean from more traditional methods of laser spectroscopy.

However, all of these applications have largely taken place in the sanctuary of a research laboratory, and there is a good reason for this. The technique requires the observation of a finite amount of light decaying over a short time. This is easier using a tunable laser. A system based on optical parametric oscillation (OPO) is the natural choice, but makes the apparatus unwieldy, power-hungry, expensive and anything but portable. The more recent finding that continuous-wave lasers can be used has ▷

## Cavity ring-down spectroscopy: how it works

The intensity of transmitted light through an absorbing substance decreases exponentially with increasing absorption path length, in accordance with the Beer–Lambert law.

Cavity ring-down spectroscopy maximizes this path length by bouncing light back and forth between two mirrors in a closed cavity. The motion of the pulse is called ringing and the decay of the transmitted light is called ringing down. If the mirrors are highly reflective, clean and concave, the pulse can be sustained for several cycles, giving the light a path length of up to several kilometres.

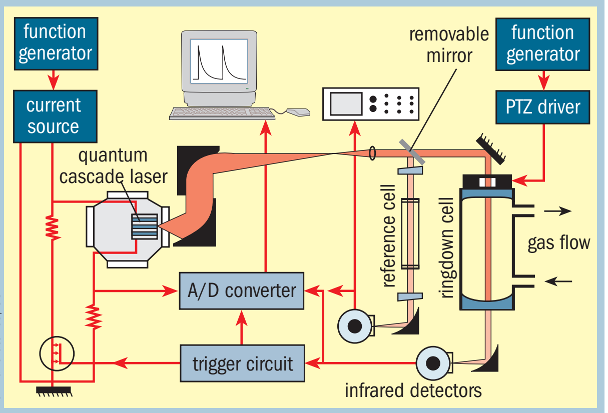
The exponential decay of the transmitted light can be plotted for extremely low concentrations of an absorbing gas, and the rate of decay calculated and compared with that of an empty cavity. Shifting the source signal through the desired frequency range gives a spectrum that shows the wavelengths at which changes in the absorption rate occur.

A tunable pulsed laser is used as the light source, where the duration of the pulse is less than the ring-down time of the cavity. Continuous-wave (CW) diode lasers can be employed if the species to be observed absorbs at one of the available wavelengths (see table).

The light beam must be able to be switched off quickly so that the decay of the signal can be observed. Andrew Orr-Ewing's group at the University of Bristol, UK, achieves this by pumping the cavity with light until the desired intensity is reached. The intensity of the transmitted signal triggers an acousto-optic modulator to cut off the light beam.

The narrow linewidth of the diode-laser source enables a highly sensitive absorption measurement because there is only one ring-down rate to measure, but it also imposes constraints. A cavity will only sustain light with wavelengths that have a particular relationship with its length – Fabry–Perot modes – so the length must be finely tuned so that one of the cavity's modes corresponds with the wavelength of the laser.

With a pulsed laser this is not a problem because its broad linewidth (10 GHz) ensures that there will always be wavelengths emitted that comply with the cavity modes. However, for a CW laser, this becomes an important issue.



Bell Laboratories, US

**The experimental set-up of a CRDS system using a QCL. While QCLs currently need cooling, their application in CRDS has potential.**

taken the technique into another league – at least for certain applications.

CRDS can now be performed using semiconductor diode lasers, offering cost, stability, power and size advantages over pulsed sources. Not only that, the narrow linewidth of the laser means it offers yet further sensitivity advantages – although not without some extra cost.

Diode lasers may not have the frequency range of OPO-based lasers, but their advantages are attracting commercial enterprise to the technology, shown in part by the launch of "the world's first commercially available gas analyser to incorporate CRDS" – the MTO-1000 from Tiger Optics in the US. The system is designed to detect trace levels of moisture in the atmosphere. Tiger Optics is aiming the system at cleanroom and other industrial environments.

The origin of this product lies in the work of Kevin Lehmann at Princeton University, US. He claims that he was the first to demonstrate continuous-wave excitation in CRDS in the mid-1990s. His discovery, which he patented, precipitated interest from US instrumentation firm Meeco. A joint development effort resulted in the Tiger Optics spin-off that has since focused on the commercial applications of CRDS.

"For excitation, we use distributed feedback diode lasers in the near-infrared," said Lehmann. "These lasers have some excellent properties. They are robust, small, stable, have a monolithic cavity and a low power consumption. We designed a system that can be shipped across the world and arrive still aligned." Tiger Optics claims that the portable instrument demands only modest maintenance and offers straightforward, plug-and-play operation.

## Obstacles to success

Others doubt that CRDS systems are ready to be packaged in this way. Andrew Orr-Ewing of Bristol University, UK, has been conducting CRDS research for some years and operates pulsed and continuous-wave-based CRDS systems in his laboratory. He agrees that diode lasers are more stable, more portable and can offer greater sensitivity, but they present other challenges.

For example, in a continuous-wave CRDS system the electronics that are required to cut off the beam are delicate and highly tuned. More importantly, the cavity-mode constraints due to the narrow linewidth of the source necessitate a precision operation to tune the cavity length to the wavelength of the laser. If the mirrors become soiled and have to be removed for cleaning, replacing them without destroying the alignment is no trivial feat, cautions Orr-Ewing.

**Tiger Optics's CRDS system in action: the MTO-1000 can measure moisture levels of 100 ppt.**

But Lehmann does not foresee any problems. "In the analysis of ultrapure gases, the mirrors do not become contaminated at a significant rate," he countered. "Also, the Tiger design differs from most laboratory-based systems in that the mirrors are held in a mount that does not allow their alignment to be altered. Mirror replacement can take place with only a minor change in the alignment of the input beam."

He is not the only one with a confident outlook. Hot on the heels of Tiger Optics is another US firm, BlueLeaf Networks, formerly Informed Diagnostics. Its founder and chief technology officer, Barbara Paldus, received the 2001 Adolph Lomb Award from the Optical Society of America for her contribution to the development of CRDS, making her the first woman to receive the award since its inception in 1940.

Paldus, whose CRDS work stems from research at Stanford University, US, has no doubts about the commercial potential of CRDS. Already her research has resulted in seven patents, with another three pending.

"I am certain that several companies are currently focused on commercializing the various applications of CRDS," she said. "We have secured solid financial backing for our business plan." Paldus considers CRDS a disruptive technology that is about to prove its value in a number of new application areas – for example, in medicine for the diagnostic testing of patients' breath; in forensics for detecting trace amounts of vapour from concealed explosives; and in test, measurement and diagnostics in the fibre-optics industry.

## Proliferation

Regardless of maintenance issues, there can be no doubt that commercial detectors using continuous-wave CRDS will proliferate in the coming years. The first raft of these is likely to comprise single-purpose instruments, such as the MTO-1000, dedicated to picking up traces of one species only. This is owing to the limited tunability of diode lasers, coupled with the fact that each set of mirrors has a narrow spectral range of operation, typically 50 nm.

Eventually the technology will probably move towards a more flexible version of CRDS based on a broadband approach, where several wavelengths are fired in unison through the cavity to produce a simultaneous reading of the decay rates of individual species at different wavelengths.

Lehmann is already on the broadband case and has devised a technique based on Brewster's angle-prism retroreflectors – a method for generating polarized light. He expects to receive funding from the US National Science Foundation to take this project towards a commercial product.

## Broadband applications

Roderic Jones and colleagues at Cambridge University, UK, are also producing results in this area. Stephen Ball, a researcher in the group, described the team's successful implementation of broadband CRDS for observing the $NO_3$ radical using a YAG-pumped dye laser. The grating in the source was removed to provide radiation at wavelengths of between 650 and 670 nm.

"Light exiting the ring-down cavity is imaged onto a two-dimensional detector. We follow the ring-down in 'time' and in 512 'wavelength bins' simultaneously. We can unambiguously identify and quantify the absorption of $NO_3$ in the presence of different overlapping absorbers and can follow absorptions [and absorber concentrations] that change with time," said Jones.

Ultimately, the chances are that CRDS will become even more sensitive, because of the relatively untapped potential of quantum cascade lasers (QCLs). Conventional diodes and OPO-based CRDS cannot operate in the mid-infrared where the strongly absorbing transitions are seen.

QCLs are tunable across exactly this range. However, they require considerable cooling and so CRDS applications of QCLs are currently confined to the laboratory. However, with the announcement of the first room-temperature continuous-wave QCL (p5), we can expect to see another major shift in the evolution of CRDS. □

---

**For more information**

University of Bristol **www.bris.ac.uk**
Princeton University **www.princeton.edu**
Tiger Optics **www.tigeroptics.com**