FEATURE

Laser-Based Analyzers—Shining New Stars

By Paul Nesdore

A look at the technology and the players in the laser-based gas analysis arena

In certain high-flying circles the phrase "disruptive technology" gets tossed around a lot for inventions that often prove to be more hype than hardware. Here at G&I, we think we've homed in on the real goods in laser-based trace gas analysis. If, a decade ago, the first sensors were rarities in the field and on the factory floor, the new-generation analyzers are taking the market by storm. At the prestigious GAS 2011 International Gas Symposium and Exhibition in Rotterdam this February, vendor after vendor, from conglomerates like GE to tiny start-ups, flaunted their laser-based wares and spoke of "sharp demand" across a range of markets. Displacing incumbent technologies in markets as disparate as natural gas, semiconductors, and environmental monitoring, these smart new devices are literally transforming the way we measure.

Figure 1. SpectraLase SS2000e Moisture Analyzer

Here, we will review the rapidly growing and widespread impact of a new league of instruments that derive their measurement from laser-based absorption techniques. Within this category, the leading commercial technologies fall into two camps: Tunable Diode Laser Absorption Spectroscopy (TDLAS), including single-pass, dual-pass, and multi-pass cells, and Cavity Enhanced Absorption Spectroscopy (CEAS), epitomized by Cavity Ring-down Spectroscopy (CRDS) and Integrated Cavity Output Spectroscopy (ICOS). For most customers the differences between these acronyms blur, but to manufacturers and technologists in the field, the distinctions are dramatic.

Let's start with the commonalities and address the fine points further on. This generation of laser-based analyzers uses a narrow-bandwidth light source otherwise known as a semiconductor diode laser, first developed in the 1960s. The advent of room temperature, tunable diode lasers (TDL) in the 1980s spurred research on a new way to conduct molecular analysis. The upshot is that both techniques measure by using temperature controlled lasers tuned to the characteristic absorption for a particular molecule. Unlike FTIR and UV visible spectrometers, the newer technologies exploit their high frequency resolution, which results in enhanced sensitivity and selectivity.

Utilizing such laser-based techniques, the newer instruments provide eye-popping speed of response and wide dynamic range that can run as much as four or more orders of magnitude in some cases. Despite a higher upfront price, the benefits are proving irresistible: faster throughput, extremely precise measurements, and low cost of ownership. Indeed, the stability of some devices has won kudos. Dr. Paul Brewer, a scientist from Britain's National Physical Laboratory, has praised the LaserTrace analyzer from Tiger Optics LLC by saying, "We've run it continuously for five years, and it's remained within 2 percent of the standard moisture level."

The new devices are at work in scientific laboratories, the petroleum and natural gas industries, and the bulk and packaged gas markets. Gas analyzers are needed at the "fill zone" where refrigerated trucks load merchant product in liquid form; they're in demand at semiconductor fabrication plants, where chip makers require ever-lower detection of contaminants. The devices are used in medical applications and breath analysis; they go aloft with atmospheric testing. Laser-based instruments helped test the waters of the Gulf of Mexico in the wake of the Deepwater Horizon oil spill.

New Techniques in Practice

With wide applicability, TDLAS is enjoying great popularity, as entities as disparate as GE Panametrics and Germany's national metrology institute, the Physikalisch-Technische Bundesanstalt (PTB), exploit its amiable qualities. Chief among the pioneering manufacturers: SpectraSensors Inc., a 1999 spinoff of the NASA/Caltech Jet Propulsion Laboratory, and Delta F Corp., the older Massachusetts company that licensed New Mexico-based Southwest Science's patent permitting sub parts-per-billion measurement of contaminants in semiconductor grade ultra-high-purity gases. SpectraSensors, after its first sale to El Paso Products, seized market share from stunned, long-time suppliers to the natural gas industry, despite the relatively high price of its new-technology moisture meters (See Figure 1).

By contrast, CEAS involves a sensor cell or "cavity" formed with highly reflective mirrors that allow the laser beam to bounce back and forth, creating an effective path length on the order of 50 kilometers. This results in tremendous sensitivity for detecting analytes at extremely low levels, generally in the parts-per-billion to parts-per-trillion realm. The catch is that this method takes considerable technical know-how to commercialize.

The more widely known CEAS technology, CRDS, is challenging to develop, with strong patent protection. As a result, it remains in the custody of the smaller companies that fostered its development -- chiefly Tiger Optics LLC, which introduced the first such commercial analyzer in 2001 with Continuous Wave (CW) CRDS, and Picarro Inc., which launched its ESP-1000 series in 2005 with the technology it calls Wavelength-Scanned (WS) CRDS.

In the semiconductor market, Tiger joined Delta F in unseating conventional technologies such as Ametek's oscillating crystal moisture analyzer and MEECO Inc.'s Coulometric-based technology. Picarro, for its part, made a strategic decision in 2007 to switch its focus from the semi market to greenhouse gas monitoring. In 2010, the company was selected as a vendor to a global network that pledges to install 100 sensors to measure atmospheric greenhouse gas concentration.

ICOS, also under the CEAS umbrella, initially appeared to lag CRDS in market acceptance. Today, however, we see new entrants, such as ap2e, that developed the ProCeas Trace Gas Analyzer, selected by R&D Magazine (USA) as one of the 100 most significant technological innovations in the world in 2010. The venerable Los Gatos Research Inc. is also keeping pace (with one of its devices used in the Gulf of Mexico to measure methane and carbon dioxide after the 2010 oil spill).

ICOS differs from CRDS in that its measurement is intensity-based, like TDLAS, as opposed to time-based. In general, intensity based measurements are more sensitive to environmental conditions, as well as noise and drift derived from certain key components, such as the laser source and detector. However, ICOS enjoys the advantage of alignment insensitivity.

A New Paradigm

Part of what makes these new laser-based techniques so revolutionary is the fact that they have toppled the conventional business model that has governed instrumentation for over half a century. For decades, plant owners needed not only to buy monitoring equipment, but invariably paid fees for installation and post-sale support. Calibration, replacement parts, consumables, and repairs were required regardless of the technique, be it electrolytic, chilled mirror, gas chromatography, piezoelectric quartz technology, FTIR or others. Maintenance and operating costs were generally 50 to 70 percent of the total

Figure 2. Tiger Optics' HALO

long-term cost of ownership. Indeed, in the late 1990s, DuPont identified the expenditure on process equipment maintenance in its plants as its largest controllable expense.

But, with many of the laser-based techniques, especially Continuous Wave Cavity Ring-down Spectroscopy, nearly all but the initial investment goes away. Part of the beauty of these new analyzers is there is no trade-off between powerful performance, low cost-of-ownership, and operational simplicity. Users relish the savings in consumables, time, and labor that such benefits as freedom from calibration confer. Tiger Optics was the first to market the benefits of its products' built-in zero capability and innovative laser-locked cell; such savings are now touted by almost all laser-based manufacturers, from GE Panametrics to Ametek.

There has to be a Catch

To be fair, the laser-based technologies do have certain notable limitations. First and foremost, they are considerably more expensive than many incumbent techniques. Also, some are quite bulky, confining them to fixed installations and applications where space is not at a premium. Exceptions include the sleek new bright red analyzer from LSE Monitors, the breadbox-sized HALO from Tiger Optics (see Figure 2) and the compact VCSEL laser-based, low pass oxygen sensor from Oxigraf Inc., among others.

Furthermore, the laser-based technologies can typically only detect one species without sacrificing performance. And, as opposed to qualitative methods, such as FTIR, the new laser-based manufacturers must select their lasers for pre-determined analytes of interest, obviating the possibility of using them to scan a host of components, known and unknown. Further, they generally operate in the near-IR, which limits their sensitivity and access to a wider spectrum of molecules. There are exceptions here too, such as LSE Monitors, the joint venture of Sensor Sense B.V. and Synspec B.V., which employs a mid-IR quantum cascade laser, in conjunction with a photo-acoustic detector, for sub-ppb ammonia and nitrous oxide analysis in environmental applications.

QCL: How it Works

Cascade Technologies uses Quantum Cascade Laser (QCL) technology. Quantum Cascade Lasers (QCL) operate on a principle whereby electrons cascade down a series of quantum wells, which result from the growth of very thin layers of semiconductor material. Whereas (in standard semiconductor diode lasers) a single electron-hole recombination can only ever produce a single photon, the Quantum Cascade Laser electron can cascade down between 20 and 100 quantum wells producing a photon at each step. This electronic waterfall provides a step change in performance in terms of lasing efficiency enabling QC lasers to emit several watts of peak power in pulsed operation and tens of milliwatts CW.

The lasing wavelength for QCLs is determined not by the choice of semiconductor material as with conventional lasers, but by adjusting the physical thickness of the semiconductor layers themselves. This removes the material barriers commonly associated with conventional semiconductor laser technology and opens up the possibility of near-infrared through to THz spectral coverage.

Now an infrared spectroscopic laser source, which has no need for cryogenic cooling, can also achideve high output powers, large spectral coverage, excellent spectral quality and good tuneability.

Technology Implementation

The practical implementation of QCLs started in the late 1990s with an industry eager to harness the power of a spectroscopic source spanning the full spectrum of the technologically significant mid-IR wavelengths (3 - 25 µm). A patented technique developed by Cascade Technologies known as Intra pulse spectroscopy, uses the laser in pulsed mode to facilitate its use over the wide range of environmental conditions typically associated with industrial monitoring. Pulsing the laser for up to a microsecond at a time causes instantaneous localised heating within the device, which results in a large frequency chirp. This chirp is harnessed to provide a near instantaneous frequency sweep through many spectroscopic features of interest.

This rapid sweep combined with high duty cycles provides the technology with many key advantages. These include:

- Up to a million measurements a second
- Sub-parts per billion sensitivity
- Room temperature operation
- Multiple gases simultaneously
- No consumables

In addition, the ultra fast chirp rate can also be used in conjunction with optical design to prevent laser feedback noise and optical fringing, which tends to be the most common noise floor for most practical implementations of optical spectrometers. The removal of this noise floor, without the need of complex fringe removal techniques or optical isolators, enables the laboratory performance of this technology to be easily transferred to real world applications.

These advances in both QC laser technology and spectrometer hardware when combined with novel spectroscopic techniques such as intra pulse spectroscopy offer not simply a small improvement on other methods of gas detection but provide a major step change in sensitivity, speed of operation, fingerprinting capability, size and cost.

Long and Winding Road

Perhaps not surprisingly, the laser-based technologies were developed and commercialized first by small, innovative instrument makers, often spin-offs from university and government labs. Theirs was often a hard road to success. In the case of Tiger Optics, its technology was first licensed from Princeton University in 1993. Invented by Professor Kevin Lehmann, CW CRDS pioneered the use of small (contact lens-sized) and relatively low-cost communications grade lasers, instead of conventional pulsed lasers. Notably, the significant price, performance limitations, and bulk of pulsed lasers had nixed the possibility of commercializing this powerful technique.

It took nine years of challenging development to bring CW CRDS to market. Much to the developer's disappointment, its debut device, the 100-pound MTO-1000, was frequently met with shrugs and skepticism. Early adopters were few and far between, with the Dutch national lab, Air Products & Chemicals, and Germany's BASF among the first to spring for its then-novel technology.

More commercially mature than CRDS by a few years, TDLAS-based instruments found acceptance among marquee semiconductor manufacturers, petrochemical companies, and natural gas producers and distributors alike. Consider Analytical Specialties Inc., a Houston, Texas company founded in 1994. Five years later, Dow Chemical Company formed a strategic partnership with the company and Los Gatos Research, which provided the technology. So great was its success that Analytical Specialties attracted Yokogawa Electric Corp. as its buyer in 2008. At the time, the Japanese company predicted that it would claim the largest share of the TDLAS market with sales of $30 million by 2013. Yokogawa said it expected the market to be worth $150 million by that year. Regardless of whether Yokogawa achieves its target, the forecast of the overall market's growth may be apt.

Market Momentum

Financial results are hard to come by, since most of the pioneers are closely held private companies or are now part of large conglomerates. Nonetheless, evidence suggests that both the TDLAS and CEAS wings of the movement have taken off. In 2008 and 2009, SpectraSensors ranked on Inc. Magazine's list of the 5,000 fastest-growing private companies in the United States, with nearly 324 percent revenue growth from 2005 through 2008. Also on the Inc. list and ranked the 20th fastest growing company in the Philadelphia area in 2009, Tiger Optics experienced a whopping 177 percent jump in sales in 2010, tallying over 1,000 measurement points in the field since its inception. Picarro, in Sunnyvale, California, announced in late 2010 that its workforce had more than doubled in 18 months, spurring its move to a much larger facility.

The overwhelming success of the pioneers has prompted a host of new entrants, from small start-ups to multi-billion-dollar behemoths. Seeing their market share increasingly erode is prompting "make or buy" decisions among the world's major instrumentation companies, from Switzerland to Southern California.

Two acquisitions were announced before the close of 2010. Finland-based Vaisala agreed in September to sell its laser-based oxygen measurement technology and business to SICK Maihak GmbH, a unit of the SICK Group, a sensor technology company with more than 100 offices worldwide. Delta F Corp., the Woburn, Massachusetts maker of oxygen and moisture analyzers, was sold for US $25 million; the new owner is Spectris plc, the United Kingdom's largest manufacturer of production-testing equipment and the parent company of Servomex, a leading maker of industrial oxygen monitors.

Meanwhile, a few major players have opted to develop their own TDL-based devices. With their formidable marketing capabilities and distribution channels, companies such as Ametek and GE may expand aggressively and could someday dominate the market for TDLAS analyzers.

Broad Applications

Until now, the versatility of the laser-based techniques has allowed the pioneers to secure strong positions in their respective markets, with very little overlap. Thus, SpectraSensors cornered the market for natural gas analysis in the United States. Picarro garnered accolades for its dedication to greenhouse gas monitoring around the world. Tiger Optics and Delta F continued to vie for the affection of the semiconductor market. Meanwhile, companies are finding fresh ways to serve fields as disparate as diagnostic breath analysis, homeland security, and quality control for aerosol can production.

The Future Looks Bright

Users and manufacturers alike have much to look forward to as the market for laser-based analyzers matures. Prices will drop and footprints will shrink as capabilities grow.

As Lisa Bergson, Tiger Optics' founder and CEO, observes, "In the decade that we have been working with them, many of our optical components have undergone significant improvement in performance specifications, while prices have either decreased or remained steady. We really feel that we're only beginning to see the benefits of scale our customers will enjoy."

On top of that, instrument developers are pushing the boundaries of the technology. Ap2e, Picarro, Block Engineering, and Cascade Technologies (see sidebar), as examples, are working in or close to the mid-IR, which promises to greatly expand both detection and sensitivity.

Taking a different approach to expanded range detection, Tiger Optics' Prismatic, winner of Gases & Instrumentation's Golden Gas Award in 2010, spearheaded the advent of broadband analysis for the detection of up to sixteen species with a single sensor cavity.

Laser-based measurement, once the dream of scientists, looks like a bonanza for end-users and their suppliers. G&I

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