Laser-Based Analyzers to the Rescue

Dr. Graham Leggett and Lisa Bergson

Miffed at being ignored during the U.S. presidential campaign, Mother Earth visited her wrath upon the Atlantic seaboard one week before the election. (Some even theorize that she helped swing the vote.) It just may take a "Frankenstorm" to scare us into dealing with greenhouse gas (GHG) releases. But, the good news is that detecting and reducing GHGs and other pollutants can greatly benefit business and the economy by generating higher profits, employment and healthier living standards. For that reason, we invite you to take a close look at the instrument makers that are pioneering the shift to laser-based environmental monitoring.

Widely blamed for exacerbating global warming and climate change, greenhouse gases such as carbon dioxide, methane and nitrous oxide call for extremely fast, sensitive and accurate methods of detection. Some other pollutants—including hydrogen chloride, formaldehyde and mercury—are not directly associated with global warming but have highly toxic properties, with mercury capable of bio-accumulating over generations. "Consider how many breaths you take a day. That's how much you're exposed," says Bob Davis, vice president of Environmental and Sustainable Technologies at Airgas Inc., whose active involvement with the issue dates back to the advent of Section 608 of the Clean Air Act, which restricts the venting of hydroflourocarbons (HFCs) and perflourinated compounds (PFCs).

Now coming to the fore are laser-based monitors that offer trifold economic benefits with their fast, sensitive, yet robust performance. These revolutionary devices identify wasteful sources of pollution and greenhouse gases, such as methane leaks from natural gas pipelines. They generate savings through green-manufacturing efficiencies that reduce scrap and improve throughput, and significantly lower cost-of-ownership due to their inherently clean properties, requiring little to no consumables or maintenance.

The laser-based instruments are supplanting older technologies, some of which date to the middle of the last century. For example, wet chemical methods, while still used, have largely been replaced by direct analysis. Analyzers for specific components, such as chemiluminescence for NO and NOx, and fluorescence for SO_2, sit alongside multi-component Fourier transform infrared (FTIR) instruments. Other mature techniques include gas chromatography (GC), non-dispersive infrared (NDIR), differential optical absorption spectroscopy (DOAS) and gas filter correlation (GFC).

Isotopic ratio mass spectrometry (IRMS) is another incumbent technique that is under pressure from new advances. IRMS, often used to determine the ratio of different isotopes of carbon and hydrogen, can investigate carbon and hydrological cycles; that is, the movement of carbon and water within our ecosystem, which is critical to our efforts to stabilize the world's climate. Such measurements underpin our efforts to tackle climate change, for example, via the introduction of a price for carbon and carbon trading.

On the whole, the older techniques share a number of common attributes that can frustrate users and lead to unnecessary expenses associated with maintenance, including day-to-day running costs, and significant penalties resulting from instrument downtime in the case of continuous emissions monitoring (CEM). Typically, these legacy systems are complex, include moving parts subject to wear and tear, require consumables, and have critical components with relatively short lifetimes. In addition to the routine maintenance required to address these issues, such instruments also require frequent calibration using expensive gas mixtures, thereby imposing additional burdens of direct costs and manpower.

What we are now seeing is a remarkable convergence of timing and technology. As the need becomes more imperative to measure and reduce GHGs and pollution, photonic-based analyzers are set to meet the demand, empowered by technologies that are both effective and environmentally friendly.

To Control, You Must Measure

Key to reducing emissions is the accurate measurement of relevant pollutants, both at the source and in the wider atmosphere. Quality data allows regulators and government to effectively plan and implement emissions reduction programs with confidence. But, the atmospheric chemistry associated with these pollutants is complex, and the determination of the concentration and propagation of both primary and secondary pollutants is of paramount importance.

Increasingly, governments and non-governmental organizations (NGOs) are establishing networks for the monitoring of atmospheric greenhouse gases in response to concerns surrounding climate change. The Global Atmosphere Watch (GAW) program of the World Meteorological Organization (WMO) is a partnership involving 80 countries, which provides the scientific community with validated atmospheric composition data, helping to improve our understanding of the earth's climate and weather, and air pollution.

Monitoring stations associated with this program make continuous, precise, and accurate measurements of greenhouse gases including CO_2, CH_4, N_2O, etc. Such stations originally used traditional techniques to deliver the required measurement precision More recently, gas chromatographs (GCs) and other instruments have given way to instrumentation based on photonics-based instrumentation, such as Picarro's Cavity Ring-down Spectroscopy (CRDS) analyzers.

Increasingly, these devices play a role in field campaigns as well. "In very general terms, we use laser and other spectroscopic methods, including CRDS, for several reasons," explains Steve Brown, a Research Chemist at the National Oceanic & Atmospheric Administration (NOAA), Earth System Research Laboratory. "First, they provide analytical devices with an absolute and specific response for atmospheric trace gases. They can serve either as standards for calibration of other devices, or as a detection method for trace gases that cannot be measured easily or sensitively by other methods. Second, they are a direct measurement of optical properties of aerosols, for which there are no alternative methods."

"Relative to other methods, spectroscopic instruments tend to be more robust in field environments," continues Brown, who specializes in tropospheric chemistry. "They are smaller, lower in power consumption, require less frequent calibration and often do not have requirements for high vacuum."

These days, more and more variations of laser-based analyzers—most falling under the broad category of Cavity Enhanced Absorption Spectroscopy (CEAS)—are coming into the market from around the world. Among the leaders are companies such as Picarro Inc., LI-COR Biosciences, Ap2e and Los Gatos Research Inc. (LGR), as well as Tiger Optics, LLC. There are also intriguing products from new start-ups, like Cascade Technologies Inc., and, by now, practically ubiquitous Tunable Diode Laser devices offered by everyone from GE Company to Ametek Inc. to COSA Xentaur Corp and Mettler-Toledo.

Tiger Optics was the first to introduce powerful Cavity Ring-Down Spectroscopy to commercial markets in late 2001. CRDS is based on absorption spectroscopy and works by attuning a laser's wavelength to the unique molecular fingerprint of the sample species. By measuring the time it takes for the light intensity to fade or "ring-down", the analyzer delivers an accurate molecular count in milliseconds. The time of light decay, in essence, provides an exact, non-invasive and rapid means to detect specific contaminants in a gas sample.

Moreover, Tiger analyzers are low-power and low-flow, with no consumables, no replacement parts and no need for calibration. At Tiger, we're proud of the fact that our technology not only helps our customers reduce the waste generated by their processes, but also has a low carbon footprint. All of these factors add up to cleaner, greener manufacturing, nipping pollution at the source.

Cost of Complacency

Many scientists concur that extreme weather events—termed "global weirding" by New York Times columnist Thomas L. Friedman—are linked to climate change, warming the ocean just enough to induce more evaporation, hence and ultimately, precipitation. To that point, the U.S. National Research Council recently released a report on the consequences of climate change, including rising sea levels, more frequent and severe floods, droughts, forest fires, and insect infestations, concluding that they represent serious security threats. Superstorm Sandy, with its toll in lives, disruption and some

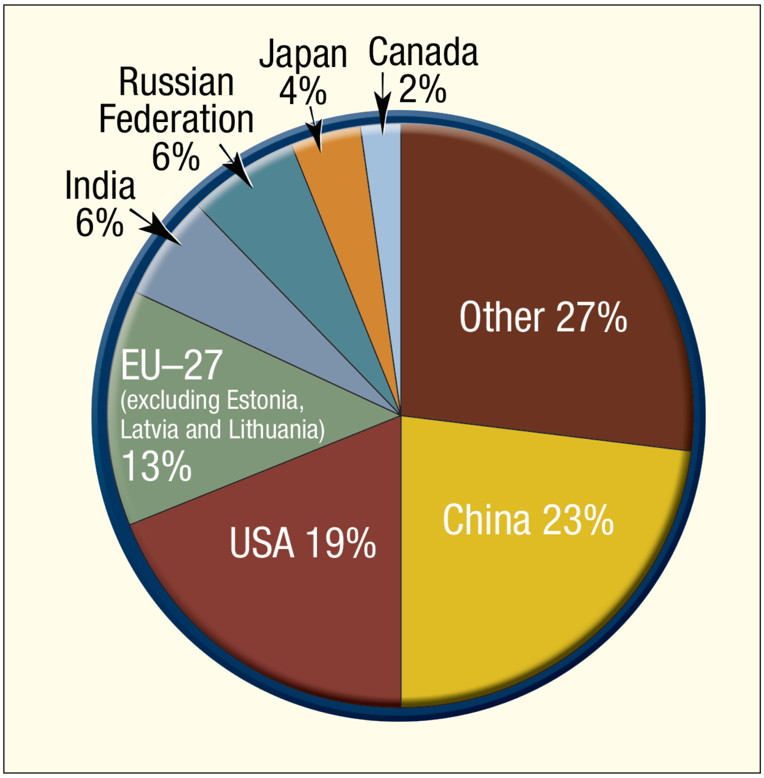

Figure 1. Global GHG emissions by country (Source: EPA)

$50 billion in estimated damages, is a harsh reminder of the havoc that can be wreaked on a densely populated and advanced region of the world.

"As scientists who study sea level change and storm surge, we fear that Hurricane Sandy gave only a modest preview of the dangers to come, as we continue to power our global economy by burning fuels that pollute the air with heat-trapping gases," wrote Benjamin Strauss and Robert Kopp in a somber full-page "opinion" article in the New York Times on November 25. Strauss is the chief operating officer of Climate Central, a research group; Kopp is an assistant professor of earth and planetary sciences at Rutgers University and associate director of the Rutgers Energy Institute.

The harmful effects of atmospheric pollutants have long concerned many public health and policy leaders. Indeed, the World Health Organization estimates that urban outdoor air pollution leads to 1.3 million deaths worldwide per year. Surges in ground-level ozone concentrations are responsible for increased hospital admissions, and other pollutants, such as hydrogen chloride (HCl), have a range of quantifiable, negative effects on the wider environment. High levels of ozone, in combination with associated photochemical smog, can result in respiratory tract irritation in healthy folks, and pre-existing conditions, such as asthma and emphysema, are exacerbated by inhalation of air containing these pollutants. Furthermore, atmospheric HCl is responsible for the accelerated erosion of building materials, such as concrete. It is also linked to reduced crop yields and the formation of photochemical smog.

Savings Through Compliance

The move toward a cleaner environment is not a zero sum game. In addition to environmental monitoring and modeling, we foresee economic expansion in remediation, recycling and the development of cleaner processes, such as innovations at coal-fired utilities and in automotive design. The upshot: new technologies and new businesses, with exciting new job opportunities in fields with long-term potential in the United States and overseas.

Taking an example from our work, Tiger serves the National Institute of Standards and Technology (NIST) and gas suppliers, such as Airgas, in the development and fabrication of an HCl standard for the 2012 Boiler MACT (Maximum Achievable Control Technology) rules recently promulgated by the U.S. Environmental Protection Agency for industrial, commercial and institutional boilers and process heaters. Fuels, such as coal, oil, natural gas and biomass, are burned by industrial boilers and process heaters to produce heat and electricity.

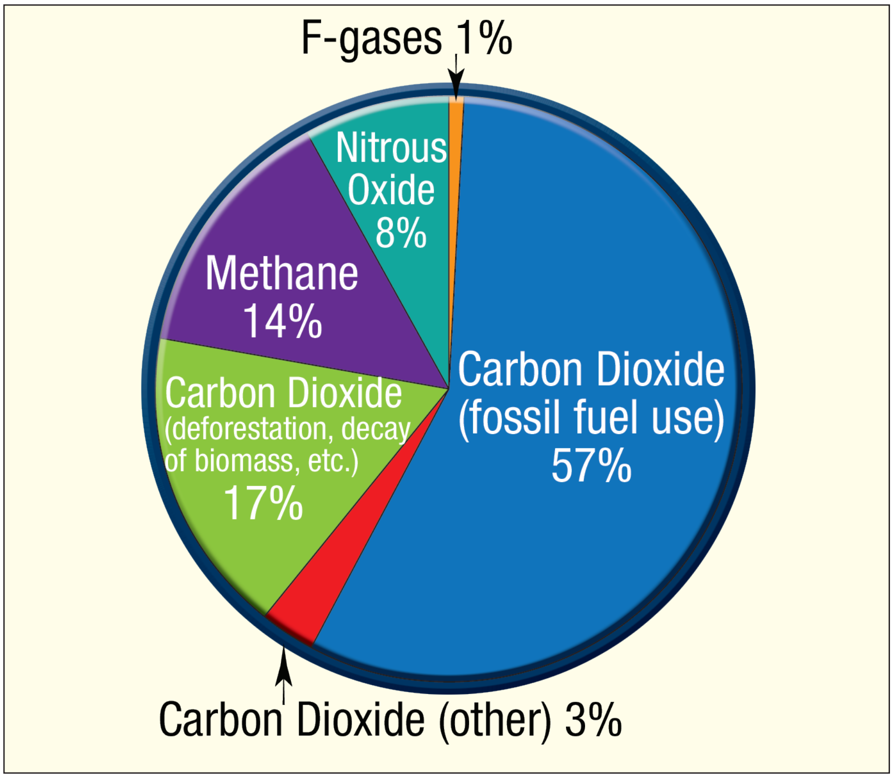

Figure 2. Global GHG emissions by gas (Source: EPA)

Here, too, fresh economic benefits can materialize. "What people don't realize about things like the EPA's Boiler MACT is that if you burn hotter and inject your fuel appropriately you're going to save a tremendous amount of money on your industrial boiler—30 percent just on fuel," says Bob Davis. MACT standards are based on limits of emissions that can be delivered using the latest control technologies—a combination of optimized manufacturing processes, abatement technologies and work practices. As industry and utilities become more efficient, Davis anticipates the need for more new hires and manufacturing equipment, thereby creating a virtuous cycle of economic development.

It stands to reason that public perception ties emissions with smokestack industries like coal. It's true that shale gas fracking and landfill sites for waste disposal are major contributors of methane. Yet methane also derives from sources as diverse as serene rice paddies and ruminant livestock, as well as permafrost and methane clathrates[1], emissions that can be exacerbated by global warming.

Opportunities abound as a result. By monitoring methane from livestock, for example, farmers are optimizing feeds and other parameters to promote more efficient digestion and better yields. And, as anyone who has ever sat for hours in traffic in China, Korea or New Jersey will attest, vehicle emissions are on the rise worldwide. There is, however, hope in sight via the development of cleaner, more efficient combustion engines, combined with new pollution abatement technologies, hybrid and full electric drive, and perhaps most promising, fuel cell technology.

Clean Technologies for Clean Air

The new laser-based technologies offer the performance, the low cost-of-ownership and the ease of use to make compliance not just possible, but, more often than not, profitable. As a whole, they are part of a vast paradigm shift that is fundamentally changing the way measurements are made.

Many research institutions, including

NIST and NOAA as prime examples, have developed their own analytical systems, including variants of CRDS, for niche applications requiring performance characteristics beyond those offered by commercial instruments. Such refinements come at a significant cost and, often, size and weight premium, prohibiting commercial use at present. Nevertheless, they are essential tools for revealing the nature of complex processes relating to atmospheric chemistry and other, equally demanding applications.

Such CRDS instruments are able to probe the chemistry of short-lived species, for example the hydroxyl radical, OH-, offering unrivalled sensitivity, precision, and stability, coupled with fast measurement rates. NIST's Frequency Stabilized CRDS (FS CRDS) instrument has been used for ultra-sensitive isotopic ratio CO_2 measurements, while NOAA investigates the tropospheric chemistry of NO_2, NO_3, and N_2O5 using their home-grown Cavity Ring-down instrument, in addition to the many Picarro devices employed.

While CRDS instruments offer a technique essentially free from calibration, consumables, and service gases, making them extremely transportable and well-adapted to field measurements, there are limitations to consider. Requiring an extractive sample, they do not provide the remote sensing capability of open-path FTIR and other such techniques. Diffuse sources, therefore, require that the instrument be moved through the region of interest.

It is, however, straightforward to transport such analytical equipment on a road vehicle or even a plane to provide a sweep of large areas for possible emissions sources. As Picarro and LGR have aptly demonstrated, CRDS instruments excel in the initial detection of emissions and thereafter, locating point source emissions within a large site, complementing remote sensing techniques to offer a complete picture. As NOAA's Brown reports, "Our analytical instrument portfolio for field measurements from a platform, such as the P-3 aircraft, normally incorporates a variety of analytical devices, including laser spectroscopic instruments."

CRDS offers specific, interference-free measurements with excellent sensitivity, but a single laser is required for each analyte, thereby limiting broadband measurements for multi-species analysis. Until recently, multi-species measurements required both multiple lasers and optical cavities due to the limited wavelength range of the highly reflective mirrors required. New offerings from Tiger, Picarro and LGR now feature so-called multi-species mirrors, with expanded capabilities. Beyond that, the development of prism-based optical cavities by Tiger Optics affords broadband coverage, negating the need for multiple optical cavities and providing better sensitivity than multi-species mirrors allow.

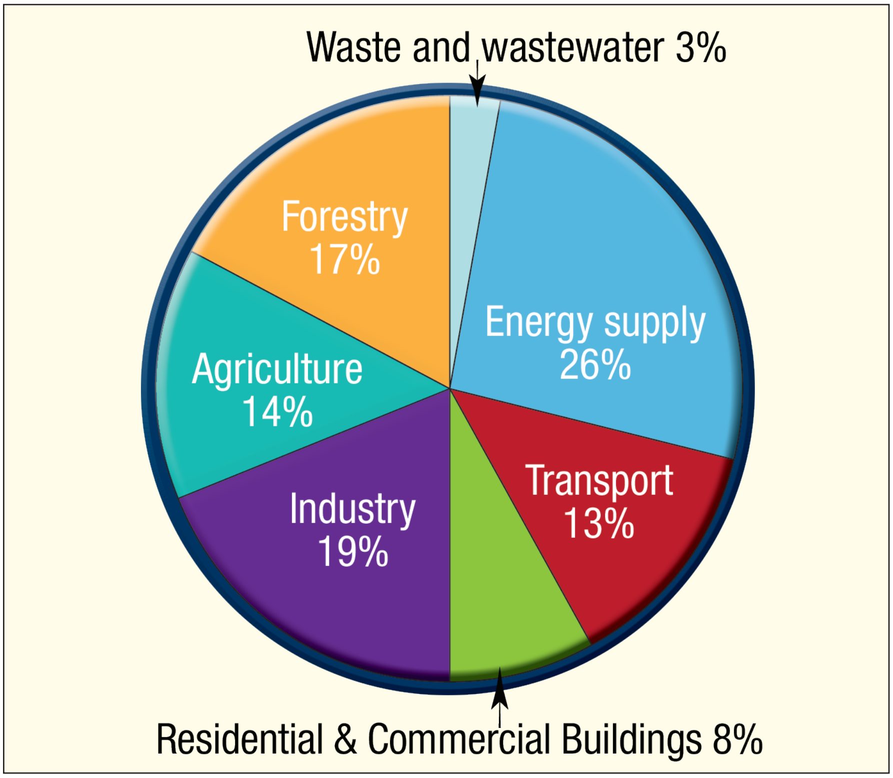

Figure 3. Global GHG emissions by source (Source: EPA)

It is worth noting that conventional CRDS analyzers cannot measure certain major pollutants—NOx, SO_2, and O_3 as examples. Other compounds related to climate change, such as CFCs (chlorofluorocarbons, commercially known as Freon) and SF6, require higher sensitivity than is available at these wavelengths. The likely answer lies in the use of higher-cost new laser technology operating at mid-infrared wavelengths. (See "Quantum Cascade Lasers Provide Wide Range of Applications," feature article, page XX) In this region of the spectrum, significantly more intense absorptions offer the enhanced sensitivity needed for these emerging applications.

The first such commercial instruments are already available, such as LI-COR and LGR's Off-Axis Integrated Cavity Output Spectroscopy (OA-ICOS) instrument for the measurement of N_2O, CO, and H_2O. Although prices are currently prohibitive for many users, you might expect to see many more established techniques replaced by CRDS mid-IR instrumentation as the mid-IR photonics technology develops and the cost of components decreases.

CEAS methods include the aforementioned CRDS, as well as ICOS, and optical feedback cavity enhanced absorption spectroscopy (OF-CEAS) commercialized by Ap2e of France. CEAS systems use a high-finesse optical cavity to provide path lengths of tens of kilometers. CEAS systems can also, in certain configurations, take advantage of broadband light sources to provide multi-component analysis, while offering improved sensitivity when compared with shorter path-length methods, such as tunable diode laser absorption spectroscopy (TDLAS).

Currently addressing the challenge of automotive emissions: Sensors Inc.'s LASAR, incorporating Ap2e's OF-CEAS technology, and Cascade Technologies' Quantum Cascade Laser (QCL) system (sold by Horiba), as well as CRDS and TDLAS analyzers from various makers. Ap2e, Cascade and other direct absorption techniques typically have a limited dynamic range, particularly compared with the four to six orders of magnitude found in CRDS analyzers. Further, there can be issues with laser intensity noise, which must be carefully addressed. At the same time, Ap2e's OF-CEAS offers sensitive multi-species detection with a single laser, but its feedback mechanism imposes considerable complexity.

For continuous emissions monitoring, analysis can be obtained via CEAS and CRDS, as well as TDLAS, which is the most widely used laser-based technique for gas-phase measurements. Here, a laser at a single wavelength is used to determine the concentration of the desired analyte, using what is essentially a traditional absorption measurement. Manufacturers of open-path, cross-stack, and extractive systems include Aero Laser, Neo Monitors, PKL Technologies, and SICK. Detection limits tend to be restricted by the relatively short path-length available, although some makers, such as Aerodyne, have developed multi-pass cells to compensate. Also, this technique suffers from the "ambient effect", i.e. influence from the surrounding medium, which must be zeroed out.

Green Manufacturing

With over $50 million worth of instruments in the field, Tiger Optics has largely focused its technology on reducing GHGs and pollution at the source. On that score, Tiger has achieved powerful results. Much as Tiger's industrial customers value its technology for its performance and versatility, they also find there are no trade-offs when it comes to ease of use and cost-of-ownership. Through improved throughput and reduced waste, as well as freedom from costly, fossil fuel-based calibration gases, Tiger offers users a path toward cleaner manufacturing.

Thus, by helping our industrial customers worldwide manufacture more efficiently, Tiger and its competitors are at the forefront of a new era. We have proven that laser-based analysis can be used to monitor and to model sinks (temporary or permanent stores for pollutants, the ocean being the largest for CO2) and sources of GHGs and pollutants. Beyond that, our technologies' inherently clean and beneficial properties can actually aid in their reduction.

Having garnered ISO 9001 certification consistently since 2008, Tiger is now addressing the challenges posed by new, highly stringent CEM regulations. "No other analyzer meets the levels and the accuracy," observes Davis, whose company uses Tiger analyzers to develop protocols. Airgas—along with NIST and 16 other national metrology institutes developing and manufacturing standards—depends on Tiger analyzers for their consistent, precise and sensitive performance.

That said, Tiger analyzers are robust enough to provide the continuous emissions monitoring required for coal-fired utilities, cement manufacturers, automakers, and glass, paper and aluminum production to comply with increasingly stringent regulations. Following initial lab tests at the EPA in Research Triangle Park, Ty Smith, the president of Cemtek Group, a leading maker and integrator of continuous emissions monitoring systems, says that: "The EPA folks were very happy to see the Tiger measure the HCl so accurately with excellent stability, and with no adjustments or corrections." Working in parallel, the Electric Power Research Institute (EPRI) has also completed a successful lab test of the Tiger-i HCl at UC Riverside. Next up: field tests at one of the major U.S. coal-fired utilities.

Role Models

The good news is that, in recent years, efforts to curb emissions have resulted in many success stories. The ozone layer is gradually recovering following the ban on production of CFC compounds. The significant reduction of SO2 emissions from the combustion of coal and other fossil fuels has all but eliminated the incidence of large-scale deforestation events that were previously common in certain regions due to acid rain. Monitoring has also shown direct, sometimes surprising, economic benefits.

As a result of the 2000 Texas air quality field study (TexAQS2000), scientists found an unexpected factor that caused the Houston area to experience the highest ozone levels in the United States. They learned that wasteful leaks of reactive gases from the petrochemical refineries in the area were a "much larger factor in Houston's poor air quality than was previously expected," according to NOAA. As a result, Texas revised its plan for air quality management, leading to reductions in emissions, based on data gathered during the 2006 TexAQS/GoMACCs campaign, using a range of traditional and laser-based analyzers.

Creative Construction

One last point: there is healthy competition among most of the companies engaged in commercializing this work, along with many of our scientific counterparts. As an active player and one of a handful of pioneers in this realm, Tiger is proud of the advances and the benefits to society, research and industry our field has spawned. Through our shared efforts, the prospect of a better future is heightened, if far from assured. G&I

Reference:

1. Clathrates, also known as gas hydrates, are crystalline solids which look like ice, and which occur when water molecules form a cage-like structure around smaller "guest molecules". The most common guest molecules are methane, ethane, propane, isobutane, normal butane, nitrogen, carbon dioxide and hydrogen sulfide, of which methane occurs most abundantly in natural hydrates. Source: http://ethomas.web.wesleyan.edu/ees123/clathrate.htm

Graham Leggett *joined Tiger Optics in May 2011 as product manager of its environmental division. Dr. Leggett has more than 15 years of experience in gas analysis, ranging from research science at the United Kingdom's National Physical Laboratory, to the measurements of specialty gases in semiconductor manufacturing and environmental applications. Prior to joining Tiger Optics, Dr. Leggett served as a project director and manager at AEA Technology plc, the international environmental consulting firm, where he oversaw such projects as the UK's National Atmospheric Emissions Inventory, the UK's Greenhouse Gases Inventory, and the European Topic Centre on Air Pollution and Climate Change Mitigation. Earlier in his career, he managed a portfolio of projects at the National Physical Laboratory relating to atmospheric environmental measurements, for a total of nine years' experience in the greenhouse gas and air quality sectors. He can be reached at gleggett@tigeroptics.com*

Lisa Bergson *is a Founder and CEO of Tiger Optics*