IET INTRODUCES... LASER DISPERSION SPECTROSCOPY FOR GAS ANALYSIS & LASER ISOTOPE RATIOMETERY

A cursory glance through the pages of this issue of International Environmental Technology reveals a myriad of measurement applications, and associated solutions. These solutions have been developed and refined over decades, employing a range of measurement principles, from complex wet-chemical analysis, incredibly versatile gas chromatography, through to optical techniques, including the more recently mature, laser absorption spectroscopy.

Perhaps nowhere are measurement requirements more complex than for in-the-field, environmental measurements. Complex and harsh sample conditions within combustion process stacks for example, or extremely high accuracy and precision demands associated with long-term background measurements of greenhouse gases. Gas analysers for these applications must be robust, accurate, and stable, delivering traceable measurements for scientific, regulatory, and process control tasks. Ideally transportable, increasingly users are seeking to take analytical instrumentation out of the laboratory, and to the source, requiring analysers of lower power consumption, and lower weight, while still maintaining performance expected from instruments operating in controlled conditions.

To this end, MIRICO is bringing the next generation of laser-based gas analysis instrumentation to market, targeting a range of industrial and scientific applications with its mid-infrared technology, designed originally for space applications.

Figure 2: The Laser Spectroscopy Team

Introducing MIRICO, the Mid-InfraRed Instrumentation Company

MIRICO's technology portfolio is based on research carried out by Dr. Damien Weidmann and the Laser Spectroscopy team at the Rutherford Appleton Laboratory, part of the Science and Technology Facilities Council (STFC), a national laboratory in the UK - http://www.ralspace.stfc.ac.uk/RALSpace/Areas+of+expertise/Technology/Laser/37444.aspx.

The Laser Spectroscopy team consists of 10 senior researchers focused on developing unique spectroscopic techniques primarily for atmospheric science, earth observation, and planetary landers for space missions. The team's work has resulted in new analytical instruments for gas analysis that deliver laboratory standard performance in a highly compact, field deployable form factor, and offer highly unique capabilities. These powerful techniques enable a host of exciting applications, by bringing measurements out of the laboratory and into the field. Benefitting from over 10 years of research and development, MIRICO has turned these innovative technologies into a suite of products, delivering the requisite tools for industry and research professionals. Our innovative engineering team works with our customers to meet the requirements for different applications.

Over the coming months, MIRICO will be launching the first of its products based on two of the Laser Spectroscopy team's technologies; the Laser Isotope Ratiometer (LIR), and open path sensing variants based on the Laser Dispersion Spectroscopy (LDS) platform.

Laser Dispersion Spectroscopy

Laser Dispersion Spectroscopy (LDS) is a new gas sensing technique that applies a novel approach to tuneable diode laser (TDL) spectroscopy. "Traditional" TDL techniques depend on measuring detected intensity to derive concentration. This significantly impacts measurements in "dirty" environments where detected intensity of the transmitted light fluctuates (e.g. soot, dust, rain, smog, etc). MIRICO's LDS instrument derives concentration using the phase of light. This makes it highly immune to intensity fluctuations received at the photodetector. The instrument enables precise, real time measurements of trace gases molecules in demanding environments. Furthermore, and unlike TDL, LDS exhibits linear response over a wide dynamic range, and the analyser can therefore measure gas concentrations from parts per billion all the way to 90% without the requirement for dilution.

Figure 4 presents the operating principle of LDS in a long-range, open-path configuration. Equally, LDS can be applied in a shorter range, cross-stack arrangement for continuous emissions monitoring (CEM) applications. The technique will also be applied for extractive measurements. When combined with MIRICO's novel multi-pass cell, sensitivity can be increased to parts per trillion concentrations for trace gas measurement applications. Such sensitivity is achieved without the need for a high-finesse cavity, commonly required to achive low concentration measurmenets, for example as is required

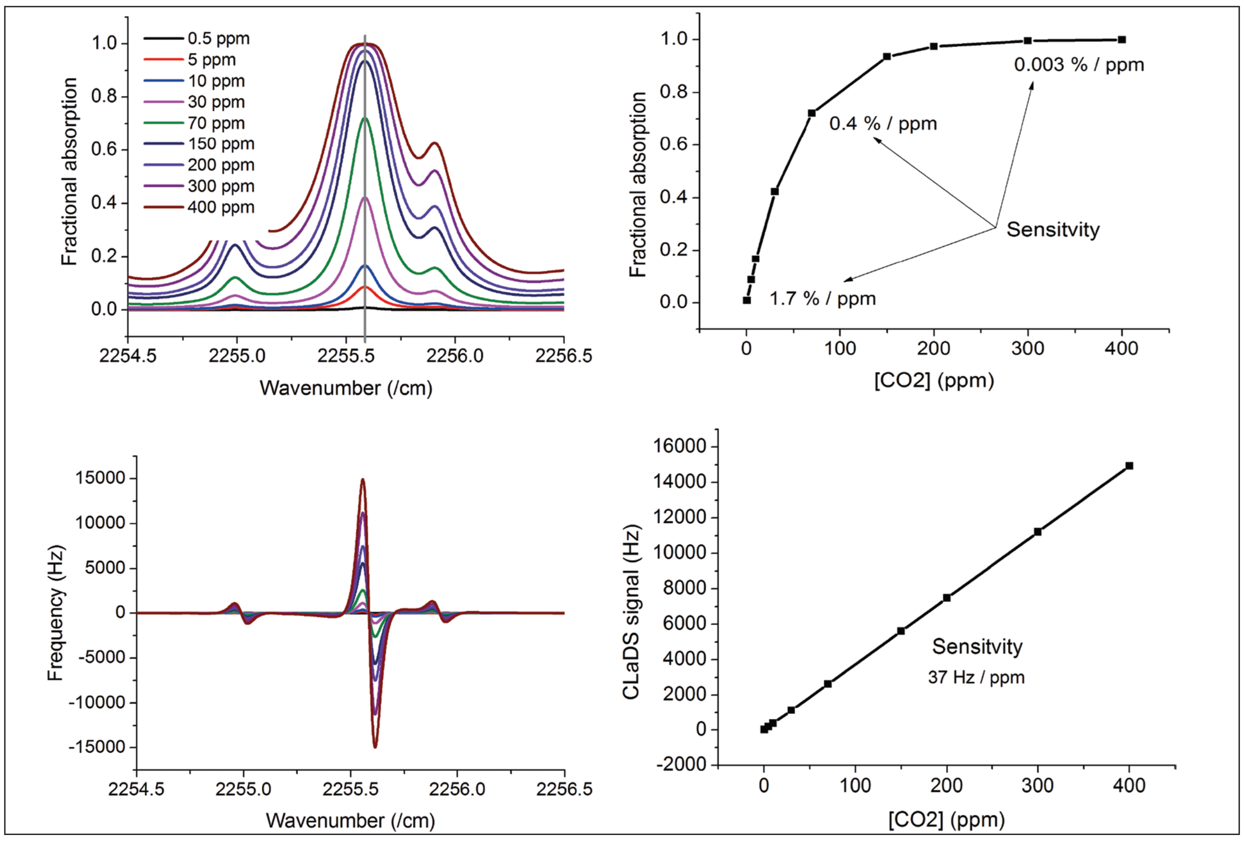

Figure 4. Absorption Vs Dispersion: Top left & right: absorption spectrum showing drop in selectivity & sensitivity over concentration dynamic range, Bottom left & right: dispersion spectrum showing baseline free measurement & maintaining sensitivity & selectivity over dynamic range.

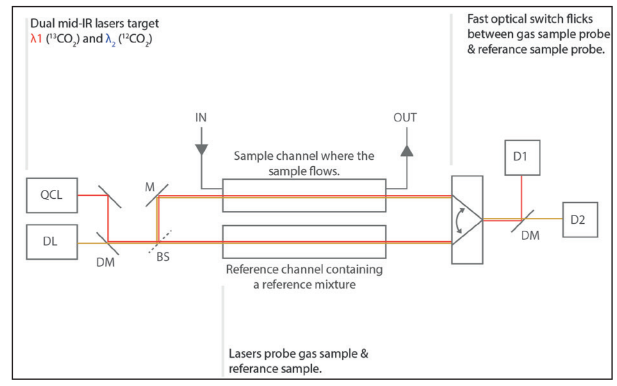

Figure 1. Schematic of the Laser Isotope Ratiometer.

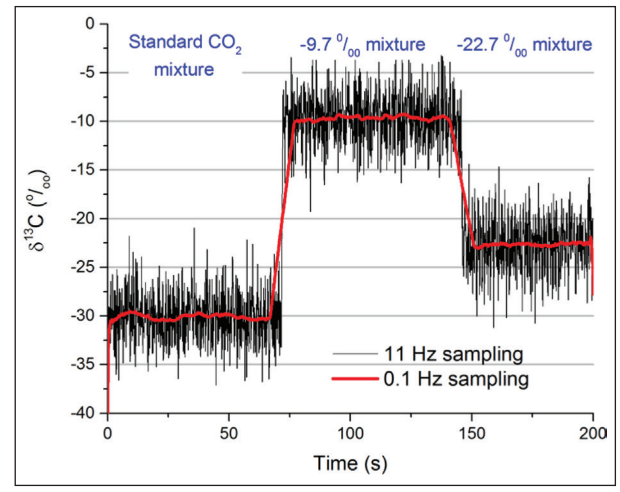

Figure 2. Temporal record of δ13C value while swapping between different CO2 samples.

for cavity ring-down spectroscopy, and other, cavity-enhanced techniques. The end result is reduced complexity, and a more robust, reliable, and lower-cost system.

How it works

The output from a laser is directed to a frequency shifter, which splits the beam into a fundamental and the frequency shifted wave. These beams are combined into a single dual-frequency laser beam. The dual-frequency beam is sent through a gas sample and is focused onto a fast photodetector that extracts the beat-note between both frequency components. When the dual-frequency beam interacts with a molecular transition both wavelengths experience slightly different refractive indices. As the laser is frequency-chirped, the difference in propagation velocities impacts the instantaneous frequency difference between the two optical waves, and this effect (that is proportional to the chirp rate) can be directly measured as an instantaneous frequency of the heterodyne beat-note signal. This signal enhancement due to the frequency chirp rate is central to the concept of LDS signal generation.

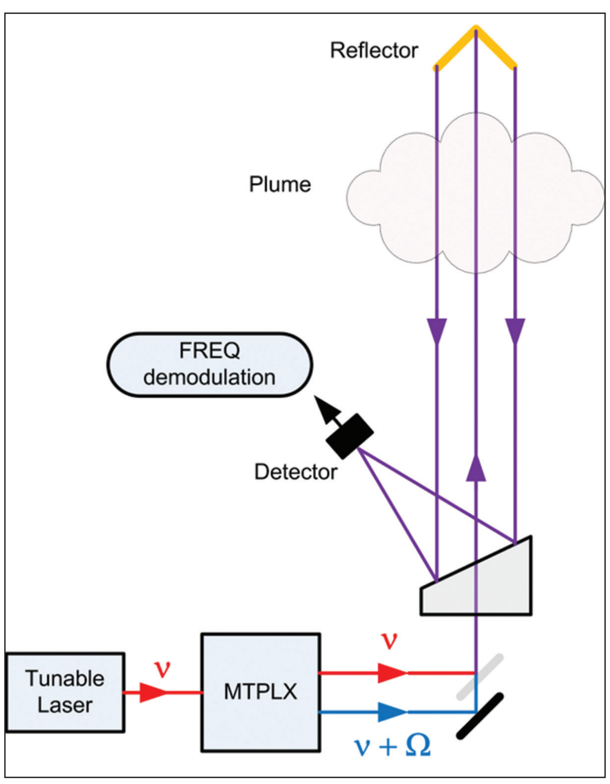

Figure 4. Basic schematic of long-range, open-path Laser Dispersion Spectroscopy analyser

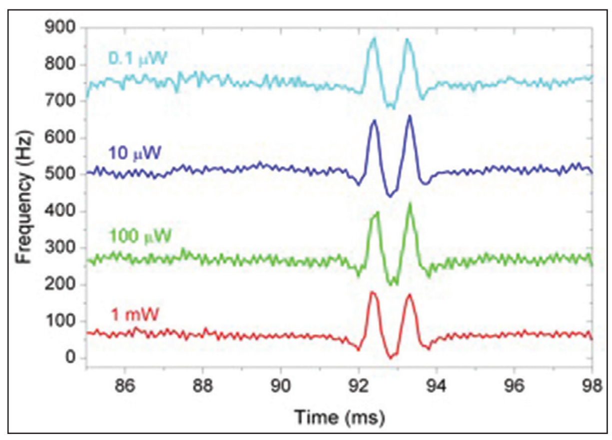

Figure 5. LDS signal versus detected power intensity

Figure 5 shows with great clarity how the LDS signal is independent of detected power intensity

Applications

The variety of configurations for LDS open up a tremendously wide range of target applications. A cross-stack system can measure pollutants from combustion processes, and in abatement facilities, while a long-range open-path system offers solutions for both industrial fenceline monitoring, and emissions monitoring over large-area sources; landfill sites, refineries, carbon capture and storage, etc. It should also be noted that MIRICO's open-path systems have been successfully tested over distances in excess of 1 km; a far greater distance than is currently possible with standard TDL systems. Finally, the extractive, multi-pass cell system presents options for trace measurements such as those required by semiconductor fabrication, pharmaceutical, and specialty gas industries.

Laser Isotope Ratiometer

The Laser Isotope Ratiometer (LIR) offers a new technique to measure the ratio of stable isotopes of a given molecule. The instrument is designed to offer high precision, real time measurements in a compact and robust package. Furthermore, the system is equipped with an on-board calibration system for autonomous operation and enhanced stability and accuracy in a simple package. Overall the LIR brings simplicity to stable isotope analysis, whether in the field or in a laboratory environment. The instrument's design originated as part of a European Space Agency programme to demonstrate the LIR for space applications, specifically a Mars planetary lander. Overall the design offers a compact form factor, robustness and precision without the need for a skilled operator or consumables.

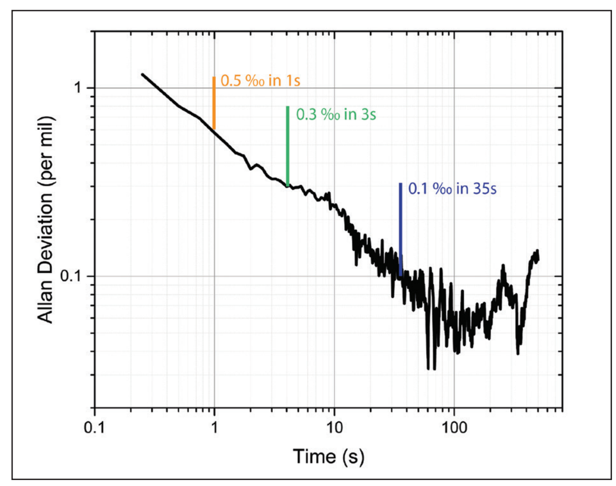

Figure 3. LIR Allan deviation plot.

How it works

The operating principle of the LIR for CO_2 is outlined in Figure 1.

1. Two lasers of wavelength λ1 and λ2, probe $^{13}CO_2$ and $^{12}CO_2$. The wavelengths are selected for optimum measurements of the isotopes and equal temperature dependence.
2. Lasers probe the gas sample, at the same time lasers probe a reference mixture.
3. A fast optical switch flicks the beam between the gas sample probe and reference chamber probe at a rate greater than 10 KHz. Detectors measure the beams, λ1 and λ2 measuring the reference channel and sample channel simultaneously. Signal processing then calculates concentration profiles and the stable isotope ratio is derived.

Figure 2 demonstrates the speed with which the LIR can measure a sample of changing $\delta^{13}C$, while Figure 3 presents an Allan deviation plot establishing achievable precision with the instrument.

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