LASER ABSORPTION SPECTROSCOPY: A NEW PERSPECTIVE IN EMISSION MONITORING

According to the World Health Organization (WHO), poor air quality conditions were responsible of 4.2 million premature deaths in 2016. Air pollution has been associated to high levels of numerous diseases including cancer, heart disease, stroke and respiratory infections, besides having a harmful effect in the natural ecosystems. For this reason, worldwide governments are committed to establish clear policies to ensure clean, safe and a sustainable environment for present and future generations.

Although it is too soon to conclude the global situation with Covid -19, the scientific community is concentrating efforts to study the correlation between high levels of mortality and atmospheric pollution. For this reason, it is ever more important to develop reliable analytical techniques able to measure the atmospheric levels of air pollutants and their dynamism in short periods of time. C.I. Analytics has developed a laser based analyzer able to measure trace levels of gas impurities commonly found in the air. This paper presents an overview of the laser product and offers a solution to the stringent environmental monitoring at the forefront of new emerging technologies.

Introduction

Environmental policies have been implemented worldwide to reduce greenhouse gas emissions due to human activities, combustion of fossil fuels for energy generation, transportation and industry. Emissions sources include the residential, commercial and institutional, industrial, transportation and solid waste sectors. Community greenhouse gas emissions for 2014 are estimated to have totalled 1.9 million tonnes of CO_2, or more than 8.8 tonnes per person. The main contribution to greenhouse gas emissions are CO_2, H_2O, CH_4, and NO_x. Due to human activity in an industrial era, their composition went from traces to an exponential increasing from the 1800s to 2000s.

Within the gases contributing to atmospheric pollution, we may find ground level ozone (O_3), sulfur oxides (SO_2 and SO_3), nitrogen oxides (also known as NO_x; NO_2 and NO), volatile organic compounds (VOC), carbon monoxide (CO) and ammonia (NH_3) [1].

NH_3 is mainly produced from livestock waste management and fertilizer production. It has a pungent odour that if inhaled in great quantities generates irritation of the mucous membranes. NH_3 combines with sulfates and nitrates in the atmosphere to produce secondary particulate matter ($PM_{2.5}$), which is known to present harmful effects on human health and the environment. NO_2, a highly reactive pollutant substance is an indicator of the traffic pollution levels since this gas is emitted specially from the combustion of fossil fuels. NO_2 has become one of the most monitored substances since it is highly lethal to human health with either short or long term exposure. It is responsible for causing respiratory diseases at all stages of life. Methane (CH_4) has an indirect human health effect since it is a precursor to ground-level ozone, which causes respiratory deceases and a significant contributor to air pollution related deaths [2,3].

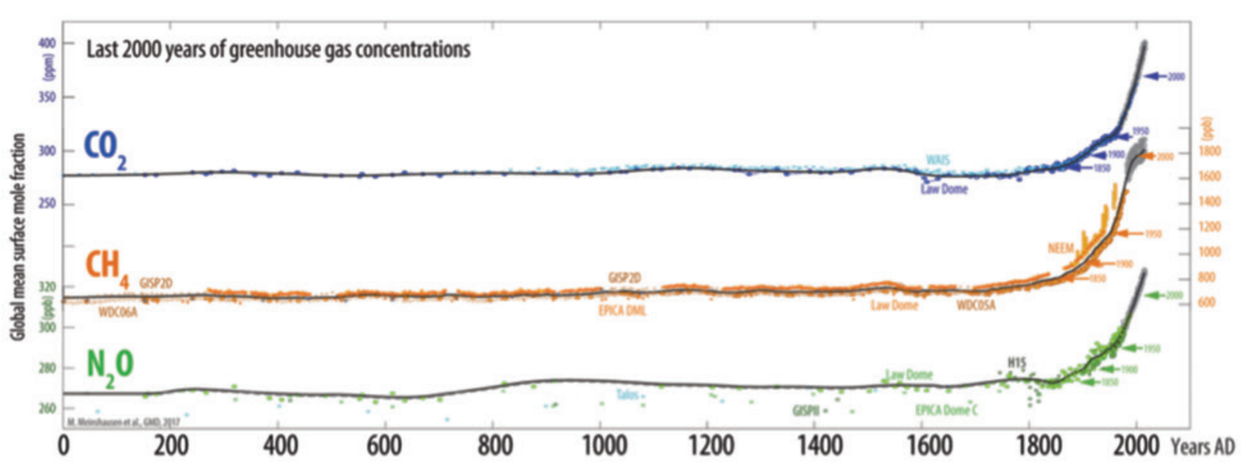

Figure N.1 Supplied "Global stocktake shows the 43 greenhouse gases driving global warming" The Conversation, May 31st, 2017, CSIRO & University of Melbourne, P.Canadell & al.

Environmental monitoring after the pandemic in 2020

The pathogenic agent of Severe Acute Respiratory Syndrome CoronaVirus 2 (SARS-CoV-2) causing the infectious disease Covid -19, first reported in Wuhan, in the Hubei province in China at the end of 2019, has been a public health concern worldwide. Its effects have been reflected in drastic changes of the contemporary human life. Global governments have had to take political and sanitary decisions to contend with the spread of the virus given the easy transmission amongst humans. The most significant measure was the world-wide quarantine of cities and countries, which caused a radical reduction in travel to places of study or work, as well as a reduction of international flights. The travel restrictions reduced the fossil fuels consumption of civilizations and the result was less global environmental emissions.

Due to Covid-19 spreading fast during the first two months of 2020, the WHO declared a global health emergency, forcing the local and central administrations to undertake drastic policies; for instance, imposing lockdown protocols controlling the movement of their citizens outside their domiciles to avoid the community transmission. As a result of the general paralysis of non-essential industries, industrial waste emissions released to the environment have decreased to a large extent. For the first time, inhabitants of big cities experienced clear skies and an improvement of the air quality.

Using cutting edge technology and satellite tracking, NASA (National Aeronautics and Space Administration) and ESA

Figure N. 2 C.I. Analytics Laser laboratory unit

(European Space Agency) observed an environmental quality improvement and a reduction up to 20-30% of NO_2 emissions throughout the pandemic early stages. Monitoring before and after the lockdown demonstrated large fluctuations of the gases due to Covid-19 in countries with high infection rates such as China, Spain, France, Italy and USA (NASA & ESA, 2020) [4,5,6]. There may be a correlation that has not as yet been identified.

On a global scale, intensive research has been conducted to evaluate the impact of the pandemics in the environment. For instance, a study carried out at Rio de Janeiro, Brazil, where the partial lockdown effects were analyzed resulted in changes of the CO levels with a significant reduction (30.3-48.5%) [7]. In Delhi, an Asian megacity with a population close to 16.8 million inhabitants, they experienced important changes in the air quality during the lockdown. Amid the most common pollutants, NO_2 levels decreased 52.68%, whereas, CO emissions decreased 30.35% during the 24th March to 14th April, 2020 shutdown. The same study concluded a general 40 to 50 % improvement in air quality when comparing the emissions with the preceding year [8].

The challenge analysing environmental pollutants

With continued improvements in industrial processes and more stringent environmental regulations, many industrial applications require fast and accurate analytical methods. In general, industrial analyzers use gas chromatography, electrochemical, optical and mass spectrometry techniques to measure trace contaminants and key species.

Gas chromatography (GC) is the most widely used technology and provides simultaneous, sensitive detection of several species. However, GC requires frequent calibration, operational consumables (e.g., carrier gases and column replacements), hands-on maintenance, and is often too slow for active industrial process control (e.g. measurement every 2–4 minutes). Although electrochemical sensors are inexpensive, they typically cannot provide the necessary accuracy (often due to cross-interferences) and fast measurement time for industrial applications and emission monitoring.

Mass spectrometry provides very sensitive detection of multiple species, but is expensive and insufficiently robust for process control and emissions monitoring needs. Conventional optical methods (e.g. NDIR and FTIR) can quantify several species and provide fast time response, but also require frequent calibration and exhibit substantial cross-interferences between species.

Recent advances in small and compact monochromatic laser diodes and high reflective multi-pass cavities mirrors have resulted in instrumentation that meets sensitive and accurate detection requirements. Thus, compared to conventional sensors, analyzers based on laser absorption spectrometry technology provide fast (> 1 Hz), sensitive and accurate readings in complex gas mixtures with minimal calibration or drift.

Laser technology

Laser absorption spectroscopy has become the foremost used technique for quantitative assessments of atoms and molecules in the gas phase. Laser-based techniques have a great potential for detection and monitoring of constituents in gas phase. They combine a number of important properties, e.g. a high sensitivity and a high selectivity with non-intrusive and remote sensing capabilities. Miniaturized and affordable new optical components (laser, cavity, and mirrors) yield to small, compact and cost-effective product for different applications in field, continuous emission monitoring, laboratory or process measurements.

The principle of the technique relies on a light beam from a tuneable laser passing through a gas sample and then being focused onto a detector. Typically, telecommunications-grade, near-infrared (1200 – 2000 nm) diode lasers and InGaAs detectors are used due to their robustness, availability and cost. The laser wavelength is tuned over a small range (typically 0.5 nm) by varying its injection current or laser temperature. This can be done by a laser controller (dual laser current and temperature control). Specific molecules absorb IR light at particular laser frequencies, resulting in a decrease in transmitted intensity at those frequencies. The measured transmission trace can then be converted to an absorption spectrum, and the integrated area under the absorption peak can be directly related to the concentration of the targeted species via Beer's Law.

C.I. Analytics Laser

The new CI Analytics laser-based analyzer is designed for high precision and accurate trace gas measurements at ppm and ppb levels. High sensitivity and selectivity (interference-free) make this analyzer a robust analytical instrument suitable for stable operation in laboratories, continuous emission monitoring, industrial process or any stringent environment. With the combination of stable laser, multi-pass cavity, 24 bits analog to digital data conversion and processing software, lower detection limits can be achieved in few seconds compared to conventional TDL and associated techniques.

Applications

The C.I. Analytics laser laboratory analyzer can measure H_2S, CO_2, NH_3, acetylene (C_2H_2) and mixtures with no interference. The laser emission narrow band makes it very selective to these impurities. Table N.1 presents the Low Detection Limits (LDL) for some impurities:

Table N.1 LDL table for C.I. Analytics Laser

Gas impurity	Range (Minimum- Maximum)	LDL	Response time for LDL
H_2S	0-30 ppm	1ppb	15 seconds
NH_3	0-5ppm	6ppb	30 seconds
	0-30ppm	66ppb	1 second
CO_2	0-400ppm	150 ppb	15 seconds
	0-5%	100 ppb	1 second
C_2H_2	0-100ppm	1 ppb	1 second

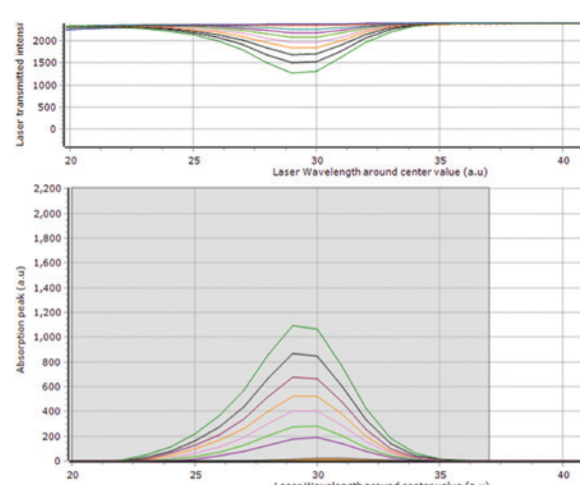

Figure N.3 Laser transmitted intensity (top graph) and absorption peak (bottom graph) NH_3 sample gas at different concentration levels from 0 to 1 ppm. Vertical axis is an arbitrary unit and horizontal axis wavelength around center value.

The CI Analytics CI SMART LASER software processes and integrates at very high frequency to give stable measurements for long periods of time.

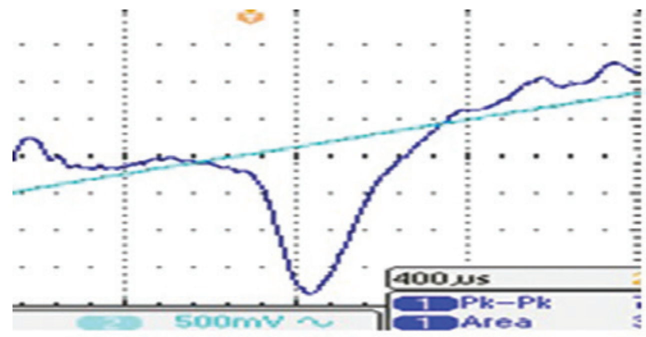

Figure N.4 1ppm of acetylene (C_2H_2) in nitrogen and in ethylene. Absorption peak is obtained by scanning the laser around the central absorption wavelength. Vertical axis is an arbitrary unit and horizontal axis wavelength around center value.

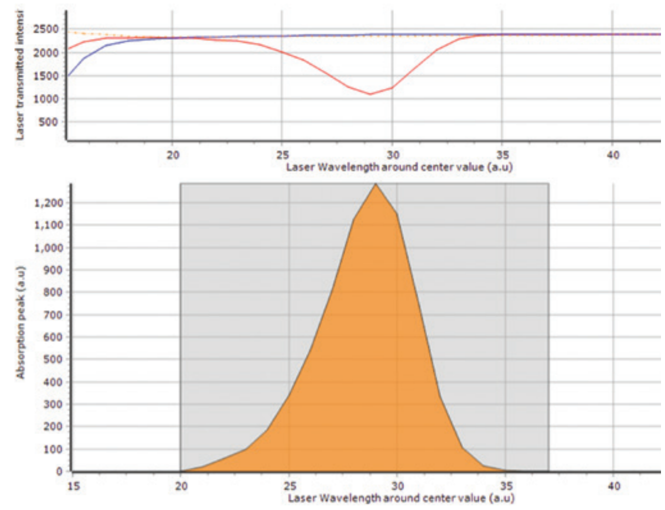

Figure N.5 1 ppm of Ammonia in pure nitrogen, measured in 1 second. Top graph shows nitrogen background in blue (No absorption) and transmitted intensity in red with presence of Ammonia. The bottom graph in orange is the absorption peak which is obtained by subtracting transmitted light from sample cell to the background signal. Vertical axis is an arbitrary unit and horizontal axis wavelength around center value.

Conclusion

C.I. Analytics new Laser analyzer offers an analytical solution for trace gas monitoring. Whether to comply with environmental standards or to control process efficiencies, CI. Analytics Laser analyzer is a versatile automatic unit designed to respond in a fast and appropriate way to the analytical needs of a changing world.

References

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