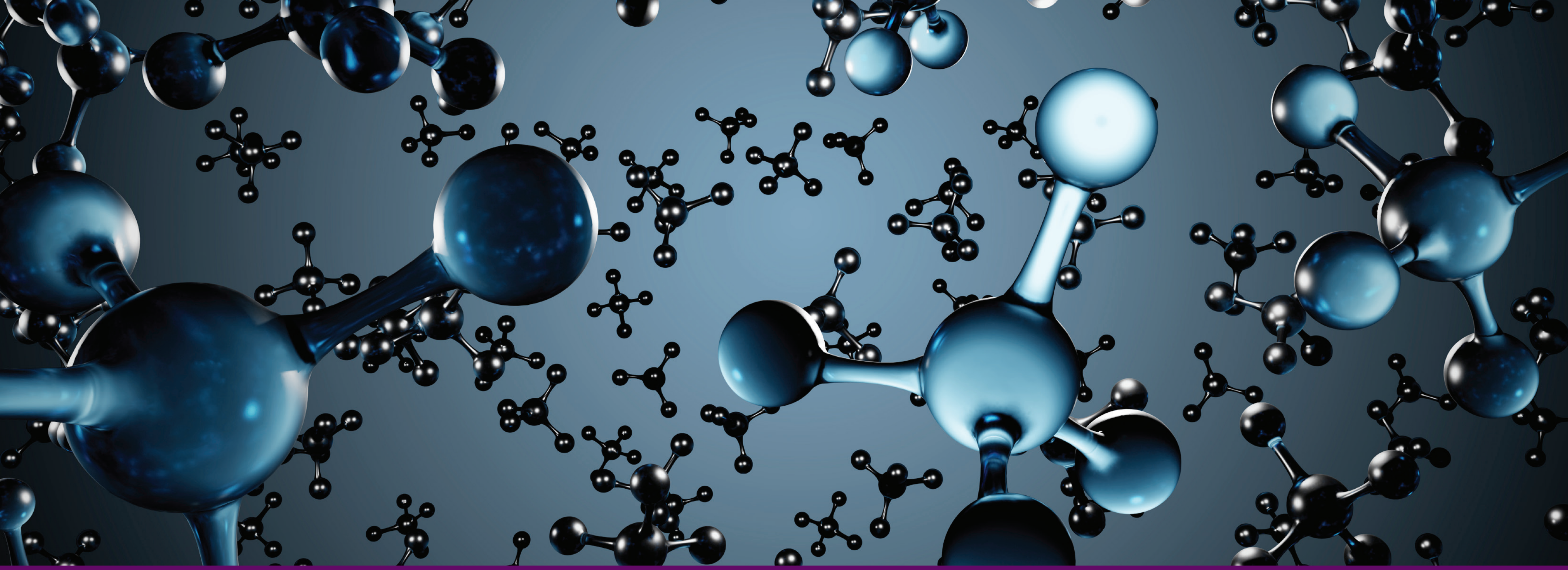


NEW PERSPECTIVES IN AMMONIA MONITORING

Regarding all nitrogen species of environmental interest, ammonia (NH_3), a reduced form of nitrogen is one of the most reactive forms in relation to natural processes and industrial activity. Ammonia contributes to the dynamism of particulate matter in the atmosphere and also the deposition of reactive nitrogen on the environment. With worldwide population growth, ammonia has been used for the last century as an industrial fertiliser, which caused concern because of the excessive deposition to sensitive ecosystems. As a consequence, ammonia is partly responsible for air quality and ecosystems health and its concentration levels have become a priority for the environmental agenda of local and territorial authorities. However, ammonia presents an alternative to conventional fuels because of its large hydrogen storage capacity and its fuel potential with the internal combustion engine. Hence, there is a growing interest to monitor ammonia levels that require versatile and reliable analytical solutions. C.I. Analytics has developed a laser based analyser able to measure from high ammonia content to trace levels found in the air and in any industrial process.

Introduction

In 1908, Fritz Haber patented the synthesis of ammonia from reaction of diatomic gases nitrogen and hydrogen in the presence of iron as catalyst at high pressure and temperature. Haber had created the foundations of high pressure chemical engineering, but it was Carl Bosch who developed an industrial scale process for ammonia production. The process called Haber-Bosch has been the lead in ammonia production for more than a century. This process has supplied agricultural fertiliser production, which dramatically increased agricultural productivity in most regions of the world. In contrast, ammonia was also used in manufacturing explosives during the First World War; ammonia was oxidised to nitric acid and then used to produce ammonium nitrate, nitroglycerine, trinitrotoluene and other nitrogen containing explosives [1].

Before the Haber-Bosch process, nitrogen-fixing bacteria were responsible for most of the ammonia production. However, Haber-Bosch was the most efficient route to feed the growing possibilities of ammonia. Nowadays, we still see the benefits of industrial scale processes to feed the exponential population growth, but the environmental effects require new alternatives for ammonia production since hydrogen supply is highly dependent on the natural gas industry. In addition, carbon dioxide is produced with fossil fuels being used to generate the high temperature and pressure that the Haber-Bosch process requires. Electrochemical processes are a good alternative to ammonia production towards a ‶green‶ pathway. At Monash University in Melbourne, researchers are working on a fuel cell able to convert renewable electricity into ammonia. These fuse cell can be fed using renewable power and the main feedstock coming out from air (for nitrogen supply) and water (as the hydrogen source). The ambition here is that this renewable ammonia could serve as fertiliser or as an energy carrier fuel [2].

Ammonia as an alternative fuel

Recent technological advances have shown ammonia as a sustainable fuel alternative. Ammonia – made of one nitrogen atom bonded to three hydrogen atoms- is a good hydrogen carrier because of its physical and chemical properties, making it easier for storage and transport compared to hydrogen in its liquefied form. Liquefied hydrogen transportation requires ultralow refrigeration conditions, because its boiling point is -253 °C, ammonia stores and handles as a regular LPG (e.g. propane, the main component of LPG with a boiling point of -42.1°C) with a boiling point of -33.3°C. Given the small molecule size, hydrogen molecules are more susceptible to leak out from hoses and the leakage rate is higher compared to larger molecules such as ammonia and short chain aliphatic hydrocarbon based compounds. Ammonia has a distinct smell easily detectable by the human nose in case of a leak [3].

Since ammonia does not contain any carbon atom, it would produce mainly water and nitrogen gas as combustion products replacing conventional fuels reducing carbon dioxide emissions. Even though ammonia was not initially being used as a fuel for vehicles, it has proved to work as a fuel for buses in Belgium in the 1940s. In 2015, Iki et al. manufactured a combustion prototype enabled liquid kerosene and gaseous ammonia to be fed, and ammonia was combusted in a gas-turbine unit[4,5].

Ammonia monitoring techniques

Wet classic chemistry methods were initially used to quantify ammonia in animal houses. Sampling was carried out by continuously drawing air samples trough an acid solution (during a defined period of time), for a subsequent laboratory analysis of the dissolved ammonia. The advantages of this method is that it is inexpensive and accurate and became the method of choice for many studies carried out in the early ammonia monitoring days at pig farms. However, the wet chemistry methods result was impractical for timely monitoring of ammonia levels in a dynamic emission process since the methods measure accumulative quantities and the results are not immediately available.
In addition, the methods require multiple steps for sample preparation which make it more susceptible to human errors incidence. To overcome these issues the dry colorimetric method to detect ammonia became available. Its ability to monitor ammonia down to 32ppb become the method of choice and is still available from one manufacturer. The dry colorimetric method also reduced the analysis to seconds (level dependent) and always provided proof-positive results every time, a characteristic not common with other technologies.

Electrochemical (EC) sensors result a low cost option for ammonia measurements. Nonetheless, low accuracy, high drift and poor selectivity of these devices are not accepted when considering reference values of ammonia. Even though, improved EC sensors have shown improvement with accuracy, when comparing the performance with wet chemistry techniques, cross-sensitivity with other inorganic volatile gases such as hydrogen sulphide and other volatile organic compounds have been observed.

More recent technologies based in spectroscopic methods and suited gas analysers have been developed. Within these techniques, we can include chemiluminescence analysers, photo acoustic spectroscopy (PAS) analysers, Fourier transform infrared spectroscopy (FTIR) analysers and tunable diode laser absorption (TDLA) analyser. Relatively fast time response, real time and low sample manipulation requirements of the samples are the main advantages that these new automated systems offer to ammonia monitoring. However, these are costly analysers that were not design to operate in harsh environments [6].

Laser technology

Laser absorption spectroscopy has become the foremost used technique for quantitative assessments of atoms and molecules in 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. Miniaturised 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 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.

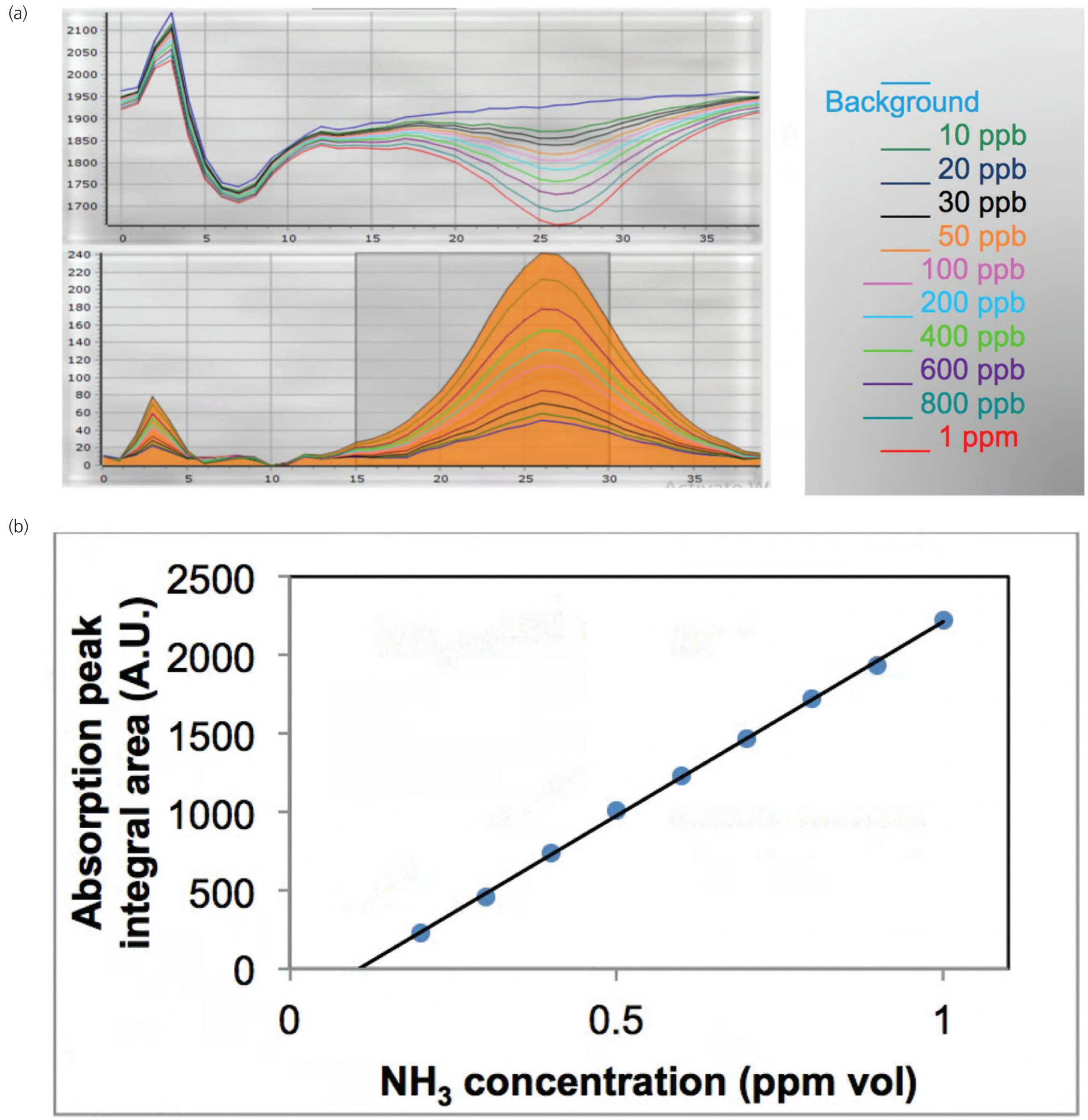
C.I. Analytics Laser

This new CI Analytics laser-based analyser is designed for high precision and accuracy trace gases measurements at ppm and ppb levels. High sensitivity and selectivity (interference-free) make this analyser 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 TDLA and associated techniques.

C.I. Analytics Ammonia Laser analyser can measure from very low ppb levels (LDL 6ppb vol) to ppm and percentage concentration. The results are accurate and repeatable offering a response in less than 1 minute. Figure 1 represents an example of the analyser performance for ammonia measurements at concentration level below 1ppm vol. The results suggest a lineal correlation at low ammonia content.

Conclusions

Ammonia is a molecular entity of relevance for the worldwide industrial development. On the other hand, ammonia is an environmental indicator of anthropogenic effects in the environment affecting the air quality and the natural equilibrium of ecosystems. Hence, monitoring of ammonia is important to comply with quality standards, and to fulfill the environmental policies. Since the measurements require a cost effective and practicality compromise, C.I. Analytics has developed a new Laser analyser able to report ultralow levels of ammonia hand held with the vanguard of new analytical needs.



Figuren 1 NH_3 measured at different concentrations ranging from 0 ppm vol to 1 ppm vol. (a) Laser transmitted intensity (top graph) and absorption peak (bottom graph) NH_3 sample gas. Vertical axis Arbitrary unit and horizontal axis wavelength around center value; data collected in CILaser®. (b) Calibration curve built with the normalised absorption peak integral area. Gas supplied from a permeation device (183 ng/min) and dilution system through analyser sample cell at constant flow (200 sscm) and a constant vacuum pressure (-12.2 psi). Each absorption peak is averaged for 30 seconds at 1 khz laser scanning frequency (30000 samples).

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