Environmental applications for gas analysis

Specialty gases support greenhouse gas measurement

By Stephen B. Harrison, sbh4 consulting

The Paris Agreement on climate change sets a framework for the control of greenhouse gas (GHG) emissions. It has been a catalyst for many efforts related to decarbonisation. Interestingly, it does not explicitly mention carbon dioxide (CO_2) once. Neither does it name methane, nitrous oxide, nor fluorinated hydrocarbons, known as F-Gases, which are all potent greenhouse gases.

Global warming caused by man-made greenhouse gas emissions is causing ecosystems to change. These changes can result in a higher levels of methane emissions. For example, as the tundra in Siberia thaws, trapped methane gas is released to the atmosphere. Human activity has pushed the first domino; the next ones are beginning to topple.

To understand the range of anthropogenic and natural greenhouse gas emissions, gas analysis is essential. And to ensure that gas analysers are measuring accurately and harmonise the readings around the world, high-precision specialty gases calibration mixtures are essential. As with so many cases, industrial gases might not be centre-stage, but they have a mission-critical role to play.

F-Gases: bottom up or top down, they must meet in the middle

The EU F-Gas regulations are of high relevance to industrial and specialty gases companies. Many of the refrigerant gases, foam blowing agents and electronic specialty gases that we handle are chemicals in this broad category.

The regulations govern how the gases may be traded, as new molecules or recovered molecules. They also specify which gases may be used in certain applications. For the end-users, they also prescribe leak testing checks to minimise emissions.

Reporting of F-Gas emissions is also mandated as part of many national greenhouse gas emission control strategies. Scientists involved in the Advanced Global Atmospheric Gases Experiment at the University of Bristol, have been trying to determine if the bottom-up process of emissions reporting is fully recognising F-Gas emissions. According to their top-down research where F-Gas concentrations are measured at very low concentrations in the atmosphere, their conclusion is that there must be a lot more leaks out there than we are aware of or are reporting.

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To measure F-gases such as HFCs, that are present at extremely low concentrations in ambient air, the research team at Bristol University use a combination of pre-concentration on their Medusa system followed by GC-MS. The GC-MS gas analyser requires high purity specialty gases nitrogen as a collision gas.

Older refrigerant gases (such as CFCs, which have now been phased out in many countries), nitrous oxide and sulfur hexafluoride can be measured on a GC-ECD gas analyser. That combines gas chromatography to separate the chemical species in the sample with an electron capture detector (ECD) to identify them. Gas chromatography requires carrier gases such as high purity helium or hydrogen. The ECD needs halocarbon-free high purity helium to function. These are all examples of high purity specialty gases.

Monitoring methane from the soil

Many types of bacteria exist that convert decaying plant material in the soil to gases and chemicals. Some ecosystems, such as peat bogs, are very sensitive to the presence of chemicals such as ammonia which is both an airborne and waterborne pollutant.

If the ecosystem is degraded, significant quantities of methane and carbon dioxide will likely be released to the atmosphere as a result of bacterial methanogenic digestion of plant matter and from the degraded peat itself.

Graham Leggett, a Senior Scientist in the Environmental team at LI-COR Biosciences UK Ltd, says that "measuring the flux of methane from soil is something that our gas analysers have been optimised for." Leggett is an Air Products veteran, and has worked at NPL and in the semiconductor sector, where he was also a gas analyser expert involved in airborne molecular contamination monitoring.

"Our Trace Gas Analyser platform, designed for soil flux measurements and atmospheric monitoring, is based on a OF-CEAS laser technique. In full, that is an optical feedback cavity enhanced adsorption spectroscopy method. Simply put, it uses near infrared light to detect greenhouse gases such as methane, carbon dioxide, and nitrous oxide at extremely low trace concentrations."

To measure emissions from a given surface, a soil chamber is appropriately located and the sample within the chamber is recirculated through the Trace Gas Analyser. Measurement of the increasing gas concentration within the chamber is used to calculate a flux from which the greenhouse gas emissions from a large geographic area, such as a peat bog, can be estimated.

"Before we ship these analysers to customers, we test them with specialty gas mixtures", says Leggett. "These lasers are very sensitive to the background matrix that the calibration gas mixture is in. So, the calibration gas cannot use a synthetic air mixture of 20% pure oxygen in pure nitrogen. The traces of methane must be filled into a cylinder with 'whole air'." That is clean dry air with the argon and carbon dioxide present at normal atmospheric concentrations.

"It takes the meaning of 'specialty gases' into a new dimension. These 'whole air' mixtures are truly very special gas mixtures," confirms Leggett.

During operation, these gas analysers require calibration gas mixtures as specified by the testing programme they are engaged in. Soil flux measurements ▶

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require infrequent calibration since absolute concentration is not critical, while some international atmospheric research protocols call for daily drift tests using commercial specialty gas mixtures with weekly calibration using named traceable reference materials.

Some stringent test standards require the gas analyser to be returned to the instrument manufacturer for an annual service. That will involve calibration using sophisticated standards, such as specialty calibration gas mixtures produced by the Carbon Cycle Greenhouse Gases group (CCGG) of the US National Oceanic & Atmosphere Administration (NOAA).

"Cavity enhanced laser spectroscopy in the near infrared range is an established technique and the lasers are robust, reliable, and economical," says Leggett. "LI-COR recently introduced a new Trace Gas Analyser for nitrous oxide soil flux and atmospheric measurements based on the same technology. Given its high global warming potential and interest in research of the nitrogen cycle, it is an important addition to this family of products."

CO_2 atmospheric flux measurement

In the atmosphere, flux measurement is also important for atmospheric research. A flux measurement determines the exchange of carbon dioxide, methane, water, and potentially other gases, between the ecosystem and the atmosphere.

When studying how forests breathe, the eddy covariance technique is now standard. With this technique, a relationship is found between atmospheric gas concentrations, and wind speed and direction by measuring the gas molecules being carried by wind eddies. During the night forests consume oxygen and release CO_2 through respiration. During the day, this process continues and the photosynthesis

Lake Baikal in Siberia, where methane gas bubbles frozen in ice

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process, which consumes CO_2 to produce plant biomass and oxygen, also kicks in.

Measuring the flux of CO_2 above or around the forest gives scientists insights into atmospheric conditions and clues about potential long-term changes in air composition. The instrumentation uses a three-dimensional anemometer to record wind speed and direction. It also has an infrared gas analyser capable of measuring carbon dioxide concentration changes.

"Similar configurations of the instrument are used for methane and moisture measurements to give a comprehensive view of the biosphere," says Leggett. "The gas analyser in this instrument must be fast. It operates at 10 Hz, meaning that 10 gas analysis readings are taken each second."

Speed is the key for eddy covariance. Wind can move air quickly with rapid changes in speed and direction. To measure the carbon dioxide gas transport flux accurately, both the wind speed and CO_2 concentration must be monitored at high frequencies. LI-COR has designed analysers capable of measuring at the high speeds necessary to capture the high-frequency of this natural phenomenon, something that until recently has been difficult for gas analysers to do. Researchers operate these systems in exceptionally challenging environments, from the Amazon to the arctic, and the instruments have been designed to cope with these extremes, with low power requirements for remote, unmanned operation, 24/7/365.

In rainy locations, or where the atmosphere is heavily polluted with dust a closed-path gas analyser is preferred for the eddy covariance equipment. Calibration of this equipment is achieved by connecting the specialty gas cylinder to the calibration gas injection port – just like any other gas analyser.

Leggett concludes by saying that, "An open-path version of the eddy covariance infrared gas analyser is also available. Calibration is achieved by inserting a small shroud into the analysers optical path and purging it with the gas mixture. This can be done in the field or in the laboratory."

As with the LI-COR trace gas analyser, the calibration gases used will range from commercially available specialty gas mixtures to exotic preparations from NOAA and other international research programmes. gw

ABOUT THE AUTHOR

Stephen B. Harrison is Managing Director of sbh4 consulting. Harrison has over 30 years' experience of the industrial and specialty gases business and was previously global head of Specialty Gases & Equipment at Linde Gases. He also spent more than 15 years with BOC Gases.