Specialty gases

New applications for sustainable development

By **Stephen B. Harrison**

The 17 Sustainable Development Goals (SDGs) were adopted by all Member States of the United Nations (UN) in 2015. Specialty gases are enabling many new applications which underpin the SDGs and are thereby making these goals a tangible reality.

PRMs for decarbonisation

The Paris Climate Change Agreement of 2016 has placed the topic of decarbonisation at the heart of the UN 2030 Agenda for Sustainable Development. Decarbonisation will be key to achieving both SDG 7 (Affordable and Clean Energy) and SDG 13 (Climate Action).

In past decades, the production of biogas and its conversion to biomethane for use as a decarbonised, renewable energy source has grown exponentially. In the year 2000 there were approximately 1,000 biogas plants in Germany; there are now more than 9,500. When biogas is upgraded to biomethane, it can be used for natural gas grid injection, as a vehicle fuel (CNG), for decentralised electrical power generation or for heating.

EN 16723 – Part 1 declares the technical specifications for injecting biomethane into the natural gas grid in Europe. These specifications include heating value and maximum levels for undesirable components such as siloxanes, ammonia and BTEX chemicals that could damage equipment or cause health risks. To perform these measurements, primary reference materials (PRMs) are required to ensure that the required analytical instrumentation is calibrated correctly. These PRMs are highly sophisticated specialty gases. They must be traceable to international standards and are prepared with utmost attention to materials compatibility, so that the very low concentrations of highly reactive components remain stable in the mixture.

Hydrogen also plays a central role in decarbonising energy supplies and the product specification for hydrogen as a fuel is harmonised internationally through the set of ISO 14687 standards. Arul Murugan, Senior Research Scientist at NPL in the UK, explains why such a standard is required. "The fuel cells in cars, lorries and buses which convert hydrogen to motive power contain catalysts that are very sensitive to sulfur. The total sulfur content in the fuel grade hydrogen is therefore capped at only four parts-per-billion (ppb)."

"Nitrogen provides no energy value and can reduce fuel cell performance, so it must be present at less than 300 parts-per-million (ppm). The energy gases team within the Gas and Particle Metrology group at NPL produce reference materials that enable implementation of ISO 14678 globally. These are a new generation of specialty gases which support traceable measurement of fuel purity to ensure that hydrogen-powered vehicles will perform for prolonged periods without damage to sensitive system components."

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Beyond the equipment to produce PRMs, NPL also has additional resources. Murugan confirms, "We use our onsite hydrogen refuelling station (operated by ITM Power) and fuel cell vehicle to validate sampling and hydrogen purity analysis methods. Having such convenient access to the station has facilitated NPL to become one of the leading organisations in the development of relevant standards at international level and as a result, it enables the UK to move forward with alternative clean fuels."

CCU for medical cannabis

The recovery of carbon dioxide (CO_2) from industrial processes and its use for greenhouse crop growth is an established Carbon Capture and Utilisation (CCU) application which supports SDG number 13, referred to as 'climate action'.

This technique is being stretched to a new application for the growth of medical cannabis. Several therapeutic uses of cannabis are under investigation, including the treatment of epilepsy in children which is the heart of SDG number 3, 'Good Health and Well-Being'.

Chris Dolman, Business Manager – Analytical and Pharmaceuticals at BOC in Australia, has been preparing for this opportunity and is enthusiastic about its potential. "A major CO_2 source that we use in Australia is carbon capture from an ammonia plant, where CO_2 is produced as a by-product. In New Zealand, we recover and purify CO_2 from a steam methane reformer at the Marsden Point Oil Refinery," he said.

Steam methane reformers (SMRs) are used on refineries to produce hydrogen which is essential for upgrading heavy

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fuels in hydrotreating and hydrocracking operations and for desulfurisation of sour fuels to minimise environmental emissions of sulfur dioxide when they are burned. SMRs convert hydrocarbons to a mixture of carbon monoxide, hydrogen and CO_2 through a high temperature catalytic process. The BOC CO_2 plant at Marsden Point started up three years ago and represented a $40m investment with a production capacity of more than 50,000 tonnes per year.

Dolman continues, "We purify CO_2 to high quality grades that are compliant with international food and medical standards. Beyond the acceleration of crop growth in the greenhouses, high purity CO_2 is also used as a solvent to extract cannabis oil from the plant crop".

CEMS for IMO 2020

The International Maritime Organization (IMO) is the UN agency with responsibility for the prevention of marine and atmospheric pollution by ships. According to their vision statement, a fundamental role of the IMO is to support Member States in their implementation of the 2030 Agenda for Sustainable Development.

The next major milestone where IMO policy will influence the SDGs will be the implementation of IMO 2020, which aims to reduce sulfur emissions from shipping by 77% over the period from 2020 to 2025. It is estimated that this will result in a reduction of 570,000 premature deaths due to illnesses such as stroke, lung cancer and asthma which are related to air pollution. So, it will have a significant contribution to SDG number 3: 'Good Health and Well-Being'.

One of the main routes of implementation will be the production of marine fuels with a lower sulfur content, which will consume additional hydrogen on refineries. LNG, methanol and battery power are also emerging as alternative marine fuels with fewer emissions at sea. However, whilst refiners invest to change their fuels mix and shipping operators adapt their propulsion systems, many ships will operate scrubbing systems which allow them to use traditional high-sulfur bunker fuel whilst simultaneously minimising atmospheric emissions of sulfur dioxide (SO_2).

On-board Continuous Emissions Monitoring Systems (CEMS) are increasingly being used to analyse the gases emitted from funnels and ensure compliance to the SO_2 emissions targets. The use of CEMS to monitor power plant and waste incinerator emissions is common. Their use on the oceans brings some additional challenges, for example the ship is a high vibration environment and it is not easy to replace empty specialty gases calibration gas mixture cylinders at sea.

Steve Gibbons, Head of Factory Sales & Product Management for ABB's Continuous Gas Analysers division in Frankfurt, says that "our GAA330-M instrumentation is ideal for marine CEMS. At its heart is an ABB Uras26 NDIR Spectrometer. Our service engineers can commission the analyser in port using specialty gas cylinders."

"Thereafter, the instrument has a self-calibration capability using a gas-filled calibration cell. We have experienced tremendous interest in our marine CEMS systems and this is a high growth application that will also pull for additional specialty gases – even though they are only required in the initial phases of instrument setup for the GAA330-M."

Car exhaust emissions

The issue of sulfur emissions from cars has been addressed internationally in recent years using low-sulfur fuels. In Europe, the maximum sulfur content in gasoline and diesel has been 10 ppm since 2009. Because sulfur is present in the fuel at very low concentrations, SO_2 emissions are minimised. IMO 2020 will apply a similar approach to the marine fuels sector.

The focus of recent automotive emissions regulations in Europe and the US has been control of pollutants derived from combustion of ethanol, which is being used at increasing concentrations in gasoline fuel blends and the reduction of NOx (oxides of nitrogen) emissions. For example, the EURO 6 legislation implemented a cap on ammonia emissions from heavy vehicle engines at 10 ppm. Ammonia is a toxic by-product of the selective catalytic reduction (SCR) systems that are installed in modern engines for NOx reduction.

In the US, E85 and E15 are enabling sustainable road transportation because the ethanol which they contain can be produced in a renewable way through the fermentation of crops such as maize. This touches SDG 7 (Affordable and Clean Energy) and is also related to SDG 13 - Climate Action. However, the combustion of ethanol yields a different emissions footprint to that of gasoline and the toxic gas formaldehyde must be monitored in support of SDG number 3: 'Good Health and Well-Being'.

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The calibration of automotive emissions testing analysers is stipulated in the relevant European and US EPA regulations. EURO 6 specifies that the calibration of the ammonia analyser should take place with a specialty gas mixture which is certified to a measurement uncertainty of plus or minus 3%. Unlike the calibration gases for NOx emissions, there is no requirement for traceability and the measurement uncertainly is also less precise. These differences reflect the reality of the current situation: the production of ammonia calibration gas mixtures for this new application is not as advanced as the mature supply of NOx specialty gas mixtures.

The challenges associated with the production of formaldehyde calibration gas mixtures for this emerging application are perhaps even greater than for ammonia mixtures. Formaldehyde can polymerise under certain conditions and many suppliers choose to cap the concentrations in gas cylinders at approximately 30 ppm. This ensures that the calibration gas mixture remains stable and the certified value is consistent throughout the shelf-life of the product. gw