

Janet Kelsey, Editor, *The Column*, spoke to Stephen Harrison, Global Head of Speciality Gases and Speciality Equipment, Linde AG about how emissions are controlled and monitored to reduce the potentially harmful risks to the environment.

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With the growing need for reducing environmental pollutants into the atmosphere, can you explain what the key elements of emissions analysis are?

In response to a burgeoning world population, 21st century industrialization has led to massive technological advances in all facets of human existence — food and textile production, medicine, infrastructure, transport and the like. Unfortunately, the flip side of these advances involves potentially harmful industrial emissions which, if uncontrolled, seriously damage the environment, plants, animals and impact on human health.

Environmental emissions occur in gaseous, liquid and solid phases and emission control interventions must be conducted in the appropriate phase. Certain uncontrolled long-term emissions can disturb the pH balance of the environment, leading to phenomena such as acid rain, while others can deplete the ozone layer. Accumulation of trace level pollutants in the environment is also a serious challenge. While many pollutants are relatively harmless in small quantities, if they are allowed to accumulate and become concentrated,

they can pose a serious threat. Together with essential nutrients, plants and animals are exposed to consuming small amounts of heavy metal compounds and these contaminants ultimately become concentrated. Some heavy metals such as lead, cadmium and mercury have been recognized to be potentially toxic when consumed by humans at the end of the food chain.

So against this background, there is a clear need to monitor and control potentially harmful emissions. Emission monitoring involves taking a representative sample from an industrial stream or the general environment and applying the correct analytical technique to identify and measure a particular constituent. Environmental analysis calculates the amount of pollution being emitted into the environment by multiplying the concentration of pollutants coming out



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industrial process stream by the flow-rate of that stream. Our business at Linde is helping companies to measure the concentration of these pollutants by harnessing high-purity gases and precision gas mixtures to identify the percentage of pollutants in the stream. Our gases are also used to assess the diluted impact of any given emission on the environment and to calibrate the instruments used during this measurement activity.

In terms of monitoring radioactive emissions, we supply the gases required to operate nuclear radiation monitoring instruments for a variety of environments. We are also one of the few companies in the world able to supply helium-3, a light, non-radioactive isotope of helium, which is used in ports to monitor containers and on motorways to monitor passing trucks for hazardous cargo.

Why is it so important to use highpurity gases?

Reliability in measurement and calibration is absolutely critical. The demand for stable, accurate measurement is the cornerstone of emissions analysis and there is an everincreasing need for reliable and sensitive techniques for testing the effects of the growing number of pollutants being released into the ecosystem.

Sound analytical protocols are at the heart of environmental analysis and testing. A

range of sophisticated instruments and next generation gas chromatography and mass spectrometry techniques play a vital role in identifying and qualifying environmental pollutants. Both techniques and equipment require high quality speciality gases for instrument operation and/or calibration, in addition to dedicated high-purity gas distribution systems.

Today's analytical instruments principally require a 'gas standard', which is the gas mixture needed to calibrate them, a zero gas to set the zero reading and a range of purge, carrier and fuel gases. The gas standard is made up of extremely sensitive high-purity gases, often intentionally containing very low levels of impurities — in some cases as low as parts per trillion — which are used in equipment calibration and gas analysis. These low impurity levels are easily compromised by a reaction with contaminants so high quality gas supply systems and equipment must be used to avoid contaminant ingress. The zero gas must also be high purity to ensure accuracy of the starting point. Once the instrument has been set up, high-purity gases are also needed to conduct the measurements. These gases are used either as purge, fuel or carrier gases to help separate components to be analysed and drive some of the detectors used. Any impurities present in these gases would skew the instruments' reading.

How important is it to conduct environmental analysis and testing at source and can you describe how 'remote' laboratories work?

Years ago production information physically resided in the laboratory but today this information can be sent — or accessed — wherever it is needed, in real time. With dedicated instruments installed right into the process and measurements being taken at specific intervals, there's no longer much need to bring samples back to the laboratory. In effect, all we need to move around these days is information. The computer is now an integral part of every laboratory, either to control processes and store data, or as an electronic laboratory log and communications medium.

Transporting emission samples to a lab is increasingly regarded as a time-consuming process that can delay production cycles and potentially compromise the integrity of the sample. The faster alternative is to place an instrument exactly where the sample is created — either in a distributed process control lab or directly into the process. Distributed labs, such as those found in petrochemical production complexes, are unmanned fixed installations primed to collect and monitor samples and feed materials and information to the central quality control or production laboratory within the complex. Their role is dedicated and inflexible, with

repeatability being the primary requirement.

In situ sampling allows for less sample handling, lower costs and rapid sample analysis — significantly reducing the traditional time lags. In turn, production teams can respond far more rapidly to optimize their processes.

Are there any international standards or legislative requirements that have to be adhered to when producing calibration gas mixtures and 'gas standards'?

In an age of global trade, analytical results have to be comparable and this requirement is addressed by a large number of international directives and standards such as DIN. EN ISO/IEC 17025 and ISO Guide 34. which provides the highest level of quality assurance and allows manufacturers to confidently state that the methods used to certify their standards are accurate, consistent, documented and validated. ISO Guide 34 defines reference materials as substances with a precise composition traceable to the International System of Units (SI) using accurate measurements. In the USA, the US Environmental Protection Agency (EPA) has established guidelines for the manufacture of US EPA protocol gases. These gases must be used for the daily calibration of continuous emissions monitoring systems (CEMS).

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How important is traceability for measurement certainty?

All the regulations mentioned require the metrological traceability of measuring results using certified reference materials as the basis for comparability. Traceability is the ability to verify measurements through calibration with measuring instruments of a known accuracy that are linked to acknowledged measurement standards. Traceability represents a path back to one single unique internationally accepted standard — "an unbroken chain of comparison."

In the world of physical metrology, such standard measures are the internationally recognized embodiment of the relevant SI units. These principles form the basis for the analytical results of test and calibration laboratories.

In producing calibration gas mixtures, Linde traces back to the most reliable reference materials from international entities such as NIST (National Institute of Standards and Technology) in the USA, the VSL (Van Swinden Laboratorium, formerly NIMi) in the Netherlands and the NPL (National Physical Laboratory) in the UK.

Have there been any recent developments in emissions monitoring and detection?

An interesting trend in this arena is the change taking place in the developing world. For gases

emissions monitoring, we're seeing a definite transition from traditional 'wet' chemistry
— which is chemistry conducted in the liquid phase — to the use of CEMS analytical devices that are *in situ*. This change is largely complete in mature economies but emerging nations are still moving from manually intensive chemistry to modern instruments that are small, compact and quick and easy to operate.

The world in general is becoming more conscious about the chemicals around us and the damage they're capable of doing. Some chemicals that were originally hailed as scientific breakthroughs in the advancement of society, in time have actually proved to be environmentally destructive. Chlorofluorocarbons (CFCs) are a prime example. Mercury is another. In decades gone by, mercury was freely handled in the classroom to educate children about physical properties of materials. Later we became aware that it was hazardous to touch, so we let school children handle it in a bottle — we still didn't realize that the hazard went beyond touching this liquid metal and that the vapour emanating from the bottle was also toxic. These days we are fully aware of the multiple hazards of mercury and its emission sources. The mercury hasn't changed but our understanding of the hazards associated with it has undergone great advancements.

So we're forever finding out that more emissions need to be measured and

also at increasingly lower levels. These developments are driving a reduction in detection limits — our ability to detect pollutants at extremely low levels of dilution— and so significant advances in detection technology are taking place.

A great example is testing for performance enhancing drugs in the sports world. In the past we were looking for high amounts of these chemicals in the body but these days such drugs are becoming very sophisticated and they leave far smaller residues.

Camouflage chemicals are also being used to mask their presence. The same principles apply in forensic science.

In terms of air pollution, years ago we measured many of these pollutants as percentages. Today single digit parts per million and parts per billion tend to be the rule rather than the exception. We keep moving down this scale and it wouldn't surprise us if, within the next decade, the measurement norm for certain components becomes parts per trillion.

Look at what's going on in the automotive sector. A great deal has been done to reduce exhaust emissions — improved engine efficiencies, smarter aerodynamics and the introduction of catalytic converters that reduce overall emissions and emission toxicity.

Not so long ago we were talking about

'low emission' vehicles and measuring exhaust fumes in hundreds of the parts per million range. About 20 years ago the industry moved on to 'ultra-low emission' vehicles — a step change in clean burning engines. Now we're talking about 'super ultra-low emission' vehicles, where the emissions of acid gases and hydrocarbons are cleaner than the ambient air present in the local atmospheres of many countries of the world. Notwithstanding the inevitable CO₂ emissions from combustion, it can be said that the noxious gases emitted are actually cleaner than the air sucked into the engine. So today the automotive technology measures emissions at parts per billion and we at Linde continue to support these advances with calibration gases and gas standards to measure emissions at these progressively lower levels.

Developing countries are also progressively increasing their own automotive industry standards in line with EU standards for public and private vehicles again calling for lower levels of emissions measurement.

Intensified efforts to protect our environment are successfully reducing the amount of pollutants being emitted. In developed countries today, the ambient environment is generally clean, despite the heavy industrialization taking place in these regions. This is because environmental

awareness campaigns and successful implementation of environmental protection programmes have improved the world around us and detection and environmental controls are actually working well.

This wasn't always so. Many years ago, for instance, the Rhine was considered as one of the most polluted rivers in Europe. Even as recently as 1986, the river was severely polluted by a chemical factory fire and within 10 days, the pollution had travelled the length of the Rhine and into the North Sea. After the chemical spill in 1986 the Rhine Action Programme (RAP) was developed and adopted by all the countries bordering the Rhine. Today it's a clean river. Pollution levels are still monitored and controlled but now at extremely low concentration levels.

These pollutants will always need to be monitored and measured and this is the challenge facing the industries that we support with high-purity gases and extremely precise gas mixtures at very low concentrations. Measurement has moved into a whole new level of complexity. As a company, we're excited to be right at the forefront of these advances.

Stephen Harrison is a chartered chemical engineer, born and educated in the UK. He has worked in industrial gases for the past 20 years — initially in customer applications and technlogy in the UK and more recently in business and marketing for speciality gases globally. He now lives and works in Germany.



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