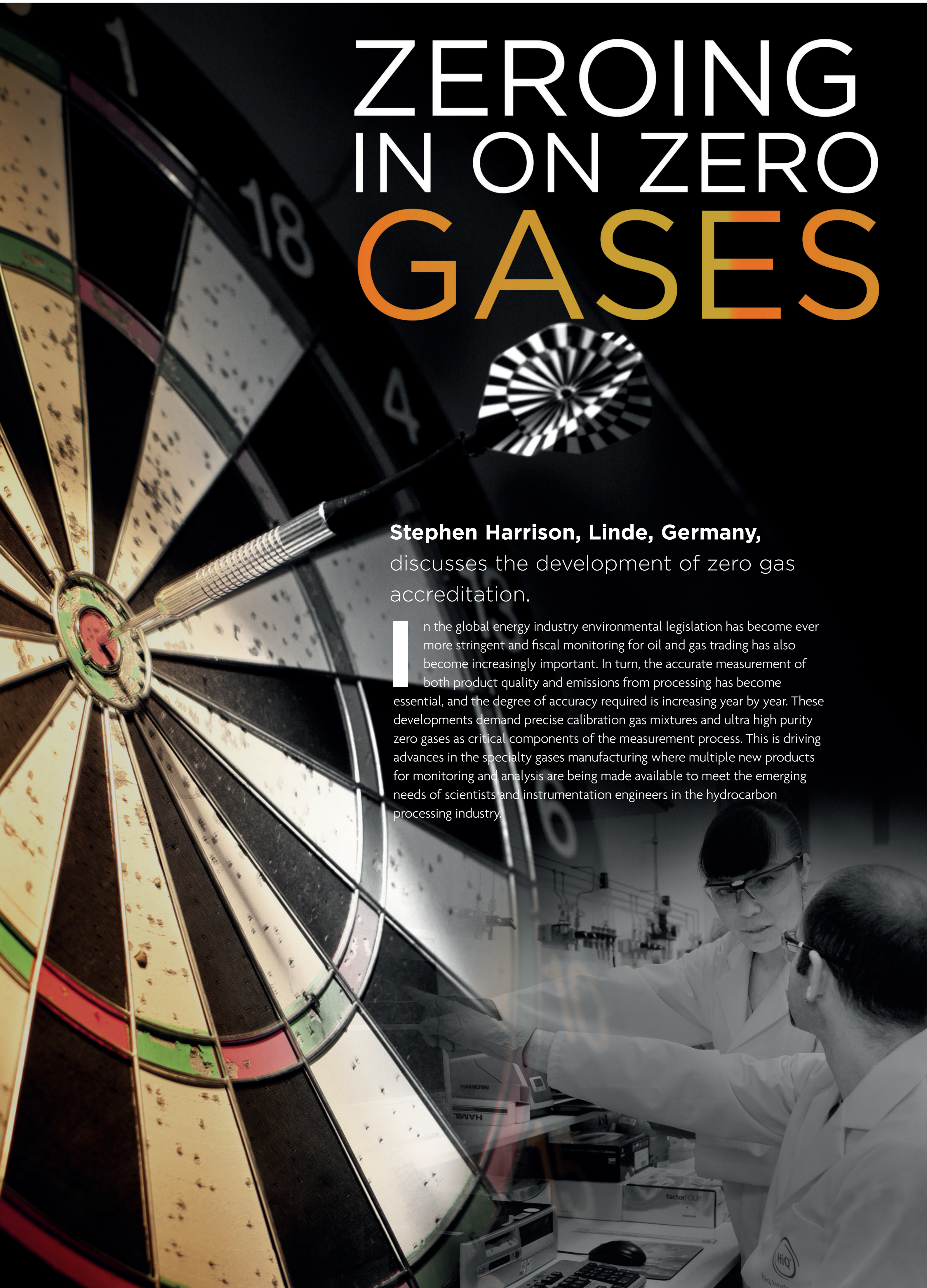
ZEROING IN ON ZERO GASES

Stephen Harrison, Linde, Germany, discusses the development of zero gas accreditation.

In the global energy industry environmental legislation has become ever more stringent and fiscal monitoring for oil and gas trading has also become increasingly important. In turn, the accurate measurement of both product quality and emissions from processing has become essential, and the degree of accuracy required is increasing year by year. These developments demand precise calibration gas mixtures and ultra high purity zero gases as critical components of the measurement process. This is driving advances in the specialty gases manufacturing where multiple new products for monitoring and analysis are being made available to meet the emerging needs of scientists and instrumentation engineers in the hydrocarbon processing industry.



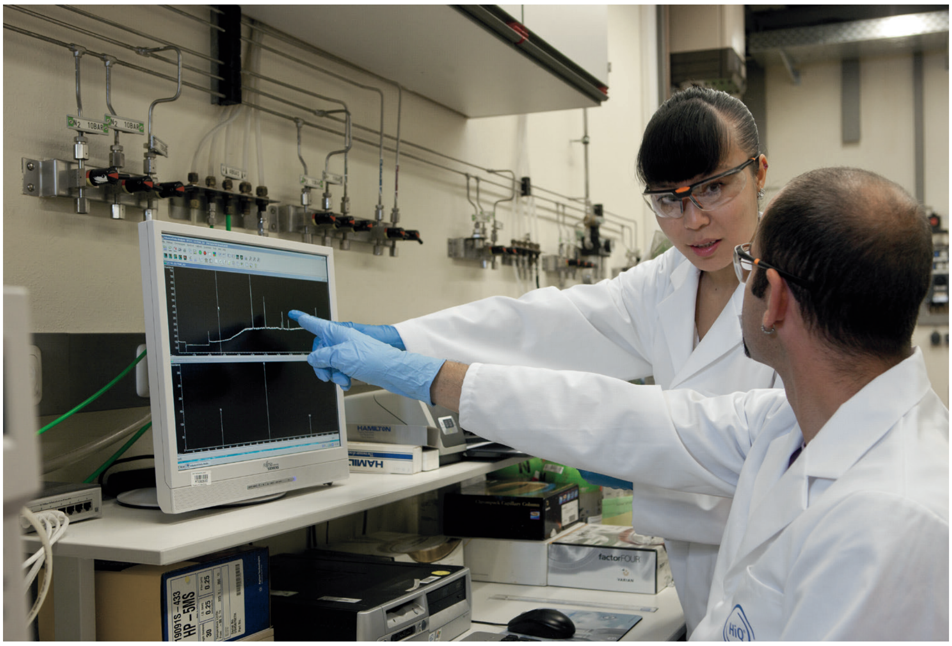


Figure 1. Gas chromatography is the most common analytical procedure used in hydrocarbon processes, particularly for natural gas measurements.

In refining, there are three main applications in which ultra high precision gases have become indispensible.

The first relates to natural gas distribution, or custody transfer. At every point where natural gas changes ownership from one organisation to another through a pipeline, or crosses an international border, ultra precise measurement is essential. This is because the exact heating value has to be established for correct invoicing and this is often also a taxable transaction when the transfer takes place across borders. Significant amounts of money are associated with these transactions, so even a small 1% measurement and billing error could translate into millions of euros per day of lost or gained revenue.

The second application involves environmental emissions monitoring, which is heavily legislated, demanding accurate and precise measurements to ensure a refinery or hydrocarbon processing facility is operating within its consent levels. High purity zero gases play a pivotal role in this measurement. Since such monitoring is a legal requirement, emissions measurements could have an impact on the hours the facility is permitted to operate over the course of the year and therefore can have a significant financial implication to the corporate balance sheet.

A spin off this environmental application is emissions trading, which is a market based approach used to control pollution by providing economic incentives for achieving reductions in the emissions of pollutants. Emissions trading is a common practice in the USA today, where facilities such as petrochemical plants are able to sell part of their emissions quota that has not been emitted within an environmental consent level. It is also an emerging practice in Europe. This means there is a direct financial consequence attached to accurate measurement. The smallest variation in accuracy could have immediate financial implications. Today greenhouse gases feature prominently in emissions trading schemes, notably carbon dioxide (CO_2), which comprises the majority of traded greenhouse gas emissions, but also methane and nitrous oxide are of notable importance in this application. In addition to achieving an extremely high degree of accuracy, results from analytical measurement must often be comparable regionally and internationally. This requirement is being enabled by an increasingly large number of international directives and standards that call for the metrological traceability of measuring results using certified reference materials as the basis for comparability.

Traceability is the verifying of results through calibration with measuring instruments of a known accuracy which are linked to acknowledged national measurement standards. In the world of physical metrology, such standard measures are the internationally recognised embodiment of the relevant SI units (international system of units).

The calibration of high precision analytical instruments used in hydrocarbon processing, such as gas chromatography (GC) and Fourier transform infrared (FTIR) spectroscopy often requires two or three set points to create a calibration curve and a zero point setting to establish the baseline reading. To create this zero point setting, a zero grade gas is needed and it is these so called zero gases that have now come under the spotlight.

Trend in metrology

Various high precision analytical instruments are used to determine extremely small changes in hydrocarbon processes, the composition of natural gases and to monitor emissions. This calls for a carefully prepared calibration curve with low uncertainty which will require accurate calibration gas mixtures and a high purity zero gas. There is a definite trend in the realm of metrology calling attention to the importance of the zero gas. Permissible levels of impurities are falling and zero gases are being seen as part of the calibration curve. A lot of discussion is currently revolving around how to determine the minimum residual impurities after purification in zero gases.

For analytical instrumentation used in the petrochemical industry, high purity specialty gases are generally used in two ways. GC is the most common analytical procedure used in hydrocarbon processes, particularly for natural gas measurements. This instrumentation, whether the instrument is a GC with flame ionisation detector (GC-FID) or a GC with thermal conductivity detector (GC-TCD), requires a high purity carrier gas that is fit for purpose in terms of its purity. Furthermore, high purity gases are required to set the zero on most types of analytical instrument measuring gases. The increasing demands for analytical accuracy mean that only exceptionally low quantities of hydrocarbons or environmental pollutants such as NO_x or CO_2 are permitted in the carrier gas and the zero gas.

When it comes to monitoring emissions like CO_2, the most common instrument used is a nondispersive infrared (NDIR) analyser that harnesses air or nitrogen as a zero gas for continuous monitoring. NDIR analysers frequently require a constant zero gas line in order to have a zero basis for their measurements.

FTIR spectroscopy can also be used at petrochemical facilities and, in terms of detection limits, particularly in the case of CO_2, FTIR spectroscopy is more sensitive than NDIR. Furthermore, if a wide range of inorganic chemical species are being monitored, FTIR spectroscopy, which is also more sophisticated than NDIR, meets the evolving needs of the petrochemical industry as legislation is constantly updated. An FTIR will also require ultra high accuracy zero gases to prepare the calibration curve and as a purge gas during normal operation.

The lowest detection limit and the highest precision for CO_2 and nitrous oxide measurement can be achieved with a technology called cavity ring down spectroscopy (CRDS), a highly sensitive optical spectroscopic technique which has been widely used to study gaseous samples that absorb light at specific wavelengths. It can accurately determine mole fractions down to the parts per trillion (ppt) level. This technology has become more common as the cost of these analysers has decreased in recent years. CRDS is able to detect less than 0.5 parts per billion (ppb) of nitrous oxide in a background matrix of nitrogen or air and these low detection limits cannot generally be achieved currently by any other type instrumentation. Zero gases are also needed to perform these precise measurements at these very low concentrations.

MACPoll

Together with national metrology institutes and associated instrumentation companies, Linde Gases, one of the largest specialty gases suppliers in the world, has played a collaborative role in a project called MACPoll (metrology for chemical pollutants in air). MACPoll was part of a European metrology research program that focused on research and development of zero gases. Even though it was EU focused, the project attracted international participants from as far afield as Japan, indicating the importance of its work on the global stage.

The main objectives of MACPoll were to develop a measurement approach for the single and simultaneous assessment of the impurities of zero gases and to establish a protocol for the certification of the impurity composition of zero gas. Special focus was placed on reactive impurities such as nitrogen oxides, sulfur dioxide, ammonia and hydrogen sulfide, all of which are important chemical species for measurement within the hydrocarbon processing industry.

The impurity levels used in the MACPoll project refer to a set of EN standards, for example, EN 14211. These standards define very ambitious specifications for zero gases, including 0.5 ppb (or 500 ppt) nitrous oxide, 2 ppb ammonia and 1 ppb sulfur dioxide. Considering that as recently as 10 years ago, a typical impurity of nitrous oxide would have been in the order of in 100 ppb, the scale of technological development in this arena is moving at a rapid rate.

Figure 2. Environmental legislation demands accurate and precise measurements to ensure refineries are operating within its consent levels.

Preparation, packaging and supply

The production of high purity zero gases begins with careful selection of non-reactive cylinder materials, as well as a cylinder outlet valve that will prevent the ingress of atmospheric gases into the cylinder, which would contaminate the high purity zero gas.

Secondly, cylinder preparation is an important preparation step. Cylinders are initially heated in an oven while cycles of purging with a dry gas and evacuation to a high vacuum are used until all residual gases are completely removed from the cylinder and the inner cylinder surface is dry. After this preparation, the cylinders are filled using a high purity gas, typically with product from a liquid storage tank which is vaporised, pressurised and supplied via a high purity gas distribution system which will often integrate various purification technologies such as chemical adsorption purifiers, chemical reaction purifiers and particulate filters. The most common downstream purification methods for high pressure cylinder gases involve a combination of activated carbon, molecular sieve and chemical adsorption using a catalyst. These methods are able to achieve grade 7.0 (99.99999%) purity zero gases.

Finally, the high purity zero gases are analysed using state of the art instrumentation and the results declared on a certificate, typically in form of a 'less than' value.

A new international standard

The MACPoll project has proposed the creation of a new international standard called ISO/DIS 19229 'Gas analysis - purity analysis and the treatment of purity data' for the assessment of impurities.

ISO/DIS 192299 sets requirements for the purity analysis of materials used in the preparation of calibration gas mixtures, and this standard is also applicable for purity analysis of zero gases. The hypothesis of ISO/DIS 19229 is quite straightforward. If an impurity is critical and significant, then a traceable analysis or indicative purity analysis should be carried out.

The new draft standard ISO/DIS 19229 defines a significant impurity as an impurity that contributes more than 10% to the target uncertainty. ISO/DIS 19229 provides guidelines on how to handle data derived from impurities that are measured and detected and how to handle analytical data that originated from specifications or specification limits. The evaluation of these analytical data is carried out in accordance with the 'Guide to the uncertainty in measurement' that distinguishes between Type A evaluation by means of statistics and Type B evaluation for manufacturer's specifications.

The future

Higher accuracies in calibration mixtures enable better certainty, accuracy, standardisation and precision of measurement internationally. This brings measurement in different countries onto a more level playing field. With higher accuracy comes a greater degree of confidence in the analytical data being reported. And, because the mix is traceable back to a national or international standard, all gas producers, end users and environmental agencies can have a higher degree of confidence that the analytical data being reported is accurate and uniform across the world. This principle, which has been applied to calibration gas mixtures in the past, is now being introduced for zero gases in a step that will further harmonise measurement around the world and result in an even fairer playing field for international trade.

Many technological challenges have been successfully tackled through the MACPoll project and its achievements are highly regarded, providing good preparation for the high quality calibration gas mixtures and zero gases of the future. Work on accreditation of zero gas began about five years ago is said to be about three years away from implementation.

This trend towards national and international specifications is being driven by atmospheric monitoring stations and metrological institutes who have recognised the value of having accurate reference points when measuring impurities anywhere in the world, and this is the task of zero gases. However, the spin off application to custody transfer or cross border measurement for hydrocarbons and natural gas is evident.

The USA, through its Environmental Protection Agency (EPA) has also been focusing on accreditation of zero gases in the past five years. Three years ago the country's ambient air environmental legislation, or 'Green Book' contained the first ever references to a metrological standard for synthetic air as a zero gas.

Maintaining zero gases purity

The purity of the zero gas used to set zero point on analytical instrumentation is critical. Impurities occurring in concentrations as low as parts per billion can have serious consequences, particularly if the impurities are part of the sample to be analysed or if the analyst is not sure which molecules are present in the sample.

Leading gas producers like Linde guarantee the purity of the zero gas in the cylinder. Linde's gases range in purity up to 7.0, which is the highest commercially available grade, being 99.99999% pure with 0.1 ppm of total impurities. The company also provides certificates of analysis on its own gases to assure customers of these exceptional quality attributes.

While the reliability of the analysis is only as good as the quality of gas being used, specialty gas distribution systems and equipment for high purity gases and calibration gas mixtures must also meet increasing demands for high standards of performance and new analysis methods. The demand on regulators and valves in today's sophisticated analytical environment is extremely high and components must be capable of dealing with high and low pressures, large and small flows. They must also be suitable for high purity inert gases as well as reactive, flammable, corrosive or toxic gases.

In addition to the use of high precision gas delivery equipment, laboratory personnel must follow the correct operating procedures in terms of purging, to ensure the required gas is delivered to its point of use in its original high purity form. Any chink in the high purity gas delivery chain can compromise the purity of the gas.

Conclusion

Debate surrounds the benefits of using a gas cylinder to zero an analytical instrument, as opposed to a generator to create zero gas. The main concern here is that while a gas generator might perform very well for a given period, at some point its function may fall below par as the equipment ages. By comparison, gas supplied in cylinders comes with a certificate of purity that relates to its prescribed shelf life. Therefore as zero gas accreditation is well on its way, the supply options favour cylinder delivery.