Keeping the pace

Stephen Harrison, Linde Gas, Germany, explains how keeping pace with VOCs involves continuous innovation in calibration gases.

With an ever increasing number of processing plants coming on stream worldwide in order to keep up with the burgeoning petrochemical industry, the focus on the release of volatile organic compounds (VOCs) into the atmosphere is coming under intense scrutiny by environmental authorities. For example, the US Environmental Protection Agency (EPA) regulates the emissions of VOCs to prevent ground level ozone formation: a constituent of photochemical smog. The release of VOCs from industrial processes not only poses a potential hazard to human health, but can also represent a risk of financial losses to the operator.

VOCs are effectively a variation on petrochemicals. They are numerous, diverse and ubiquitous, emanating mostly from hydrocarbon processing plants, although the natural world also emits a measure of naturally occurring chemical compounds. The risks associated with industrial VOCs are aggravated by the fact that hazardous concentrations are usually very low and the health issues they can cause can be accumulative and slow to develop.

Ensuring compliance

Detection and analysis of industrial VOCs demands continuous innovation to assist companies in complying with tightening legislation and mitigating the financial implications of VOC emissions. Certainly, the financial factor is a significant incentive to keep VOCs inside the process. If emitted, they pose possible health issues and generally become an atmospheric irritation for people working and living close to the emission source, owing to their offensive smell. However, companies are rapidly becoming aware that every gram that is lost essentially equates to money down the drain.

By measuring ambient air, processing plants are able to determine if any of their raw materials, process intermediates or end products are in the air. If this happens to be the case, measuring also allows processors to determine the emission source and address it. In the petrochemical industry, this applies to a broad spectrum of components.

Solvents are a major source of man made VOCs. As with other VOCs, when solvents increase in temperature, as in a production process exhaust stream, they evaporate and enter the atmosphere. As they enter the atmosphere, they create a foul smell and can potentially cause a variety of health problems. Another economic drawback is that the company concerned must purchase the solvents lost in the process.

There are several different technologies available to reduce or remove solvents from exhaust streams, including destruction or recovery and reuse, depending on the recovery value and concentration of the solvents.

One of the most effective ways to recover solvent vapours is to condense and capture them using liquid nitrogen as a cooling media.

Figure 1. Release of VOCs into the atmosphere is coming under intense scrutiny from environmental authorities.

This process is called low temperature or cryogenic condensation. When liquid nitrogen is used to cool the condenser, VOC emissions are reduced to low levels very rapidly, via trapping the VOCs at extremely low temperatures. Following this, they can then be reintroduced to the industrial process.

Increasing regulatory requirements have created more rigorous demands in measurement and, with new compounds to evaluate, laboratories performing environmental analysis of air quality are constantly confronted with new challenges. The laboratories find themselves under continuous pressure to expand their scope and expertise. Innovative, next generation calibration gas mixtures are essential to enable new air quality analysis technologies and meet the needs of laboratories engaged in process control, emissions monitoring and research.

Chemical processing plants generally have their own unique signature of emissions based on their specific processes, the raw materials used and the final product being produced. With the increasing awareness of the potential for negative health effects from air pollution looming large in the public psyche, the requirements for low level traceable calibration standards are becoming of greater importance. Emerging knowledge and technologies are the driving forces behind the measurement of many more compounds, at ever lower concentrations.

Calibration is vital for accurate measurement and the production of reliable information about the quality of the environment around us. Technologically complex and sophisticated gas standards for calibration are becoming essential to deliver greater efficiency and confidence to laboratories.

Adverse effects on health

Reports of the increase of asthma and the diagnosis of other respiratory diseases in both young and old are permeating the media with growing regularity. While there are many causes of these ailments, it is generally recognised that some VOCs can have severe, adverse influences on human health in several areas. These include sensory stimulation, tissue inflammation, anaphylaxis and nerve toxic reactions.

A few VOCs can also easily constrain the normal function of the central nervous system, causing headaches, fatigue, drowsiness and discomfort. Research indicates that alcohols, aromatic hydrocarbons and aldehydes have the potential to stimulate mucous membranes and upper respiratory tracts. Furthermore, a number of VOCs are proven carcinogens or potential carcinogens, such as benzene, trichloroethylene and formaldehyde.

It is a disquieting fact of life that the majority of people are routinely exposed to VOCs throughout our daily activities, from driving cars to working in offices. In fact, because of the airtight design of many buildings, the concentrations of VOCs inside can be greater than the VOCs in the ambient air outside the building, due to the fact that VOCs can be emitted from paint on the walls, carpets and furniture. Many researchers around the world have presented papers on indoor air quality, while the Japanese have even emotively labelled the phenomenon with the title 'sick building syndrome'.

The growing demand for accurate identification and quantification of VOCs across both ambient and indoor environments has initiated requests from chemical analysts around the world for low level, multi component VOC calibration gas mixture standards.

A new gaseous calibration standard

Technicians begin the process of designing a new gaseous calibration standard by determining the safety issues associated with working with the pure compound. They also check the new calibration standard, in order to establish appropriate safety procedures for personnel working in the development laboratory.

Figure 2. An effective method to recover solvent vapours is to condense and capture them using liquid nitrogen.

The next step is to review the component's vapour pressure to evaluate if it will allow for the manufacture of a gaseous standard in a cylinder under full pressure. If the vapour pressure is too low to allow full pressure at the requested concentration, the developers must determine a combination of concentration and pressure that will allow the production of the standard. If necessary, the client is consulted about the suitability of reduced pressure (volume) or a reduced concentration or a reduction in both pressure and concentration.

Another key first step is to determine the availability of the compound. It is especially important to ascertain whether or not it is commercially available in a relatively pure form. Occasionally, if a specific compound requested by a client is not available commercially, specialty gases companies may ask the client to supply the compound to allow them to potentially manufacture a gaseous standard.

Assuming that the compound can be obtained and that all of the health and safety issues are acceptable, the next step is to address the package for the proposed standard. There exist multiple cylinder materials and treatments, as well as multiple cylinder valve choices. Cylinders can be constructed of aluminium, steel and stainless steel, as well as more exotic materials. Common materials used for specialty gas valves include stainless steel and brass. In addition to the traditional stainless steel or brass cylinder valve, there are now new coating processes that can assist in developing a cylinder and valve package that will provide stability.

Once the several different methods of cylinder preparation are added to the equation, there is a potentially large number of cylinder, cylinder preparation and valve combinations that need to be considered and investigated. This will provide a package that will ensure the stability of the gas standard.

Standard preparation

When sourcing VOC raw materials, specialty gases companies generally procure the highest purity commercially available product. Once the material is received, it is assayed to confirm the purity; if any impurities exist, they are identified and quantified.

Almost all of the VOC calibration standards manufactured are produced in a balance of nitrogen. The process starts with high quality liquid nitrogen from the supply tank. It is vaporised, pressurised and passed through various stages of purification equipment before it is used in a standard. The resultant nitrogen is typically 99.99999% pure and free of chemicals that will react with the VOCs in the mixture or interfere with the analysis. However, the nitrogen will normally contain some level of another inert gas, argon.

Most hydrocarbon processors purchase a relatively small volume of the VOC standard, because the quantities needed for their work are small. The standard is typically supplied in a small cylinder with an internal volume of 0.9 ltrs. At full pressure, these cylinders will contain approximately 104 ltrs of gas, or a little less than 5 moles. Therefore, if the requested concentration of the VOC were 1 ppm, a total of 5×10^{-6} moles of the VOC would be required.

Given that it would be difficult to produce an accurate standard in this very small amount, the manufacturing process begins using a larger 30 ltr water volume cylinder, containing approximately 4000 ltrs of gas at full pressure, or 170 moles. After the VOC standard is produced in the larger cylinder, the mixture can be decanted into a number of smaller cylinders for final analysis and shipment to the client. Very small quantities of chemicals are involved and leak tight connections, elimination of reactants, precision in preparation and analysis are all key to the success of the process.

Multi component mixtures

Linde's capabilities allow the production of traceable, stable, low level, multi component mixtures. The company routinely supplies calibration standards containing more than 60 VOC components at 100 ppb and below.

To date, the most components Linde have supplied in a single cylinder is 110. This calibration gas mixture was granted Guinness World Record status for the greatest number of separate chemical components in a single gas mixture. The calibration standard, part of Linde's HiQ® specialty gases range, comprises the largest number of components (including more than a hundred VOCs) of any known calibration gas in contemporary commercial use.

Linde formulated the custom 110 component mixture for TestAmerica, who are using the standard in their laboratory for environmental analysis in Austin, Texas. The gas calibration standard will be used to detect and assess VOCs in samples of indoor and ambient air to determine safety levels and even to identify the potential source of pollution.

Gases in action

Emissions and pollution control issues are a priority the world over, both in developed and developing economies. As a constituent part of these issues, VOC emission control is high on the global agenda.

Authorities are also becoming far stricter than ever before on calibration standards used for environmental emission measuring. In China, for example, the general rule is that calibration standards must align with GBW, the official Chinese quality standard. GBW accreditation is a requirement for gas production facilities wishing to supply specialty calibration gas mixtures to both domestic and foreign owned companies operating in China. The country does not generally allow the import and use of any calibration gas mixture not conforming to GBW standards, although there are some notable exceptions relating to gas mixtures beyond its technology thresholds for local manufacture within the country, such as the most complex VOC calibration gas mixtures.

Linde Gases has been granted important GBW certification by the Chinese State Bureau of Quality and Technical Supervision for a wide range of mixtures to be manufactured in China. This approval has led to Linde's production of gas reference materials from its plant in Suzhou, Jiangsu province in eastern China. The plant produces Linde's HiQ high purity gases, as well as HiQ gas mixtures for the calibration of measurement instrumentation for environmental monitoring purposes, including the detection and control of combustion emissions for power generation. These gases will enable Linde to better support the growing emphasis being placed by China on tackling its CO_2 emissions.

In order to achieve the GBW certification, Linde made significant investment in plant operations through the appointment of both Chinese and expatriate scientists, engineers and other technical specialists. The company also proceeded with the installation of top of the range laboratories and advanced gas filling facilities. Additionally, a mass comparator (a specialised weighing device) was installed, capable of measuring the mass of a gas cylinder (up to approximately 401 kg) with a resolution of 0.002 g and repeatable to within 0.003 g. To draw an analogy, this level of accuracy in measurement is the equivalent of a normal bathroom scales being able to determine if someone is holding a piece of paper or not.

The future

VOC monitoring in the contemporary market is all about emissions control: namely, keeping within legislation and preventing the loss of valuable VOCs. However, it appears likely that in the near future this arena could expand to include emissions trading. If and when this happens, emissions trading will have a direct financial impact on petrochemical companies. As soon as VOCs become molecules included in emissions trading programmes, the focus will shift dramatically beyond just keeping emissions within legal limits, to embrace trading good environmental behaviour for money; or for the right to keep a particular plant open and operational.