



# Keeping up with VOC regulations

With an ever increasing number of manufacturing and processing plants coming on stream worldwide to keep up with the product requirements of 21st century society, the focus on the release of volatile organic compounds (VOCs) into the atmosphere is coming under intense scrutiny by environmental authorities. The release of VOCs from industrial processes not only poses a potential threat to human health, but can also represent a risk of financial loss to the operator

**V**OCs are numerous, varied and ubiquitous, emanating mostly from industrial 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 cumulative and slow to develop.

There are multiple definitions of a VOC utilised by governmental agencies, researchers, industries and educators. For example, the United States Environmental Protection Agency (EPA) defines VOC to mean any compound of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates and ammonium carbonate, which participate in atmospheric photochemical reactions. The European Union describes a VOC as any organic compound having an initial boiling point less than or equal to 250°C measured at a standard atmospheric pressure of 101.3 kPa and which can do damage to visual or audible senses.

For the purpose of this article, a VOC is characterised as a compound of carbon having a boiling point less than or equal to n-dodecane ( $C_{12}H_{26}$ ), 216.2°C.

Detection and analysis of industrial VOCs demands continuous innovation to assist companies in complying with tightening legislation and to mitigate the financial implications of VOC losses from industrial processes.

A major source of manmade VOCs is solvents. In liquid phase, solvents do not pose an atmospheric pollutant hazard, but solvent vapours can and should be recovered back to the process by condensation. Solvent extraction is typically used in the pharmaceutical industry to extract pharmaceutical compounds from fermentation broths. The process also finds application in the production of vegetable oils and biodiesel. As with other VOCs, when solvents increase in temperature as part of the production process, they evaporate and enter the atmosphere where they can create a foul smell and potentially cause a variety of health problems and also require the company concerned to purchase replacement solvents.

By measuring ambient air, plants are able to determine if any of these raw materials are escaping into the air and if so, also determine the source and address it. There are several different technologies 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 in a process called low temperature or cryogenic condensation. When liquid nitrogen is used to cool the condenser, VOC emissions are reduced to low levels very rapidly, by trapping the VOCs at extremely low temperatures. They can then be reintroduced to the industrial process, saving money and protecting the environment.

Increasing regulatory requirements have created more rigorous demands in measurement and, with new compounds of concern to evaluate; laboratories performing environmental analysis of air

quality are constantly confronted with new challenges. They 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 laboratory researchers.

Stephen Harrison, Head of Specialty Gases and Specialty Equipment at Linde, says plants generally have their own unique emissions based on specific processes, the raw materials used and the final product being produced.

"With the ever-increasing awareness of the potential for negative health effects from the air we breathe, the requirements for low-level traceable calibration standards are becoming of greater importance," says Harrison. "Emerging knowledge and technologies are the driving forces behind the measurement of many more compounds and at ever-lower concentrations."

"Calibration is vital in order to accurately measure and produce reliable information about the quality of the environment around us. Technologically complex and sophisticated gas standards are becoming essential to deliver greater precision and confidence to laboratories."

"The growing demand for accurate identification and quantification of VOCs in our ambient and indoor environments has initiated requests from researchers around the world for low-level multi-component VOC calibration standards," Harrison continues.

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

The next step is to review the component's vapour pressure to evaluate if the vapour pressure 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 asked to determine the suitability of reduced pressure (volume) or a reduced concentration or a reduction in both pressure and concentration.

"Assuming that we can obtain the compound and that all of the health and safety issues are acceptable, next we address the package for the proposed calibration standard," explains Harrison.

"There are multiple cylinder materials and treatments, as well as multiple cylinder valve choices. Cylinders can be constructed of aluminium, steel, stainless steel and more exotic materials. Common materials used for specialty gas valves include stainless steel and brass. In addition to these 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 enhanced stability."

**Harrison says** that when sourcing VOC raw materials, Linde always procures the highest purity commercially available product. Once the material is received, it is assayed to confirm the purity and, if any impurities exist, they are identified and quantified.



Almost all of the VOC calibration standards Linde manufactures are produced in a balance of nitrogen. The process starts with high quality liquid nitrogen. Nitrogen is withdrawn from the supply tank, vapourised, 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, but it will normally contain some level of another inert gas, argon.

Most industrial process companies purchase a relatively small volume of the VOC standard, because the quantities needed for their work are small. Linde therefore supplies the calibration standard in a small cylinder with an internal volume of 0.9 litres that, at full pressure, contains about 104 litres of gas, or a little less than five moles. Therefore, if the requested concentration of the specific VOC were 1 ppm, a total of five  $10^{-6}$  moles of the VOC would be required.

"It is important to know what was put into the cylinder, but it is even more important to know what is coming out of the cylinder," says Harrison. "Therefore, after each cylinder is blended, we perform a complete analysis to determine the actual concentrations present in the standard."

"Since we are dealing in such low levels of constituents, the first step in the analytical procedure is to cryogenically concentrate the sample. There are several commercially available cryogenic concentrators which all operate on a similar basis. The gas is passed through a dryer to remove moisture, and then into a glass bead chamber, which is cooled with liquid nitrogen. The VOCs liquefy and freeze onto the glass beads, while the nitrogen carrier gas passes through to a vent. After a known volume of gas is passed over the beads, the flow is shut off. Then there is rapid heating of the glass beads and the vapourised sample is injected onto a gas chromatograph (GC) column."

For some of the VOCs there are reference standards available from National Metrology Institutes, but for many of the components there are no reference standards available.

"For those components where reference standards are unavailable, we utilise gravimetric techniques to provide traceability. For example, we would gravimetrically produce a series of internal standards at 1 ppm, 100 ppb, and 10 ppb. These internal standards are analysed on the GC/FID after cryogenic concentration. The plotted results are analysed for linearity. With good linearity,  $r^2 > 0.99999$ , we have confidence for both the concentrations and the peak retention time for the component of interest."

**Determining the** stability of gas mixtures is achieved by conducting stability trials, evaluating SPC data and by a technical review. The stability of a gas mixture can be affected by component concentration, chemical reactivity of the various components and raw material impurities. Of key importance with raw materials impurities is the minimisation of moisture and oxygen. The cylinder material, valve material, the cylinder cleaning, drying and passivation process also play a role in the stability of the final gas standard.

A formal technical review evaluates the physical and chemical properties of the mixture components and experience with similar mixtures, including the review of stability data for similar species and concentrations. Any relevant scientific literature and temperature conditions are also reviewed in order to make an informed decision as to the stability of the product.

"Linde's state-of-the-art capabilities allow us to produce traceable, stable, low level, multi-component mixtures," says Harrison. "We routinely supply calibration standards containing more than 60 components at 100 ppb and below. To date, the most components we have supplied in a single cylinder are 110 — earning us a Guinness World Record."

This ground-breaking 110-component 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 commercial use today and represents an extraordinary level of technological achievement.

Linde formulated the custom made 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.

"Linde Gases' development provided us the capability to have most of these compounds of interest under one analytical standard, cutting the time for set-up and calibration of our own laboratory instruments, and allowing us to run more samples," said William Elcoate, TestAmerica's Air Product Director.

While today VOC monitoring is all about emissions control — keeping within legislation and preventing the loss of valuable VOCs, Harrison suggests that in the not-too-distant future this arena could expand to include emissions trading.

"If or when this happens, it will have a direct financial impact on petrochemical companies," he says. "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 your plant open." **LN**