Increasing Regulatory Requirements Demand Rigorous Measurement of VOC Emissions

A Special Report from Linde Gases Division

Volatile Organic Compounds (VOCs) 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 complicated 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 VOCs utilized 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 our purposes here, a VOC is characterized as a compound of carbon having a boiling point less than or equal to n-dodecane ($C_{12}H_{26}$), 216.2°C.

The Need to Meet New Challenges

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

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 to meet the needs of laboratory researchers.

"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 Stephen Harrison, Global Head of Specialty Gases and Specialty Equipment, Linde Gases Division. "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," Harrison continues. "Technologically complex and sophisticated gas standards are becoming essential to deliver greater precision and confidence to laboratories."

Adverse Influences on Health

While not quite a daily event, it is becoming a common occurrence when local newspapers, television, and radio report that asthma and other respiratory diseases are on the rise, affecting both young and old. While there are many causes of these ailments, it is generally recognized that some VOCs can have severe, adverse influences on human health in several areas. These include sensory stimulation, tissue inflammation, anaphylaxis, and toxic nerve 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's a disquieting fact of life that we are routinely exposed to VOCs throughout our daily activities, from driving our cars to working in our offices or even just sitting at

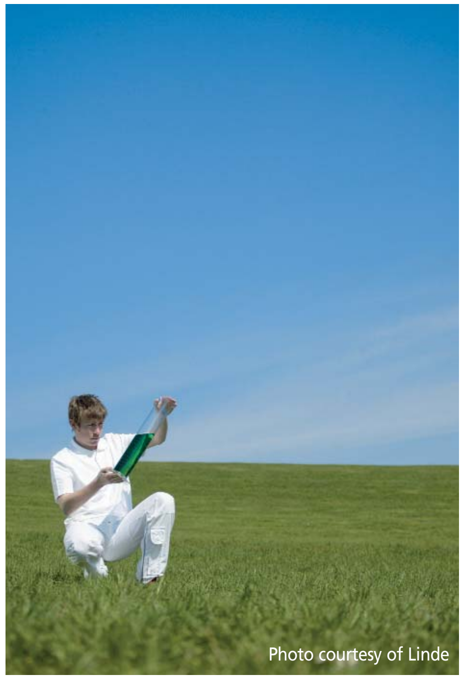

Photo courtesy of Linde

home," says Mike Hayes, Assistant General Manager, Environmental and Calibration Products, Linde Gases Division. "Just about every activity we participate in has the potential to put us into contact with VOCs. In fact, because of the airtight design of many buildings, the concentrations of VOCs inside are often greater than the VOCs in the ambient air outside the building. Many researchers around the world have presented papers on IAQ (Indoor Air Quality). The Japanese even have a more descriptive name for this—Sick Building Syndrome."

Designing a New Gaseous Calibration Standard

"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," Hayes continues.

"There are multiple steps and procedures involved in producing a new gaseous VOC calibration standard, whether a single or multiple analytes. The first step is to determine the availability of the compound and whether it is commercially available in a relatively pure form. Occasionally, we find that a specific requested compound is not available commercially and we may then ask the customer to supply the compound to allow us to manufacture a gaseous standard."

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 vapor pressure to evaluate if it will allow for the manufacture of a gaseous standard in a cylinder under full pressure. If the vapor 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 customer 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 Hayes. "There are multiple cylinder materials and treatments, as well as multiple cylinder valve choices. Cylinders can be constructed of aluminum, 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 valves, there are now new coating processes that can assist in developing a cylinder and valve package that will provide enhanced stability.

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

Calibration Standard Preparation

Hayes says that when sourcing VOC raw materials, Linde always procures the highest purity commercially available product. Almost all 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, vaporized, pressurized, and passed through various stages of purification equipment before it is used in a standard. The resultant nitrogen is typically 99.99999 percent 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.

Analysis

"Although important to know what was put into the cylinder, it is even more important to know what is coming out," says Hayes. "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. The gas is passed through a dryer to remove moisture, 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 vaporized sample is injected onto a gas chromatograph (GC) column."

Traceability

For some 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," Hayes explains, "we utilize 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 analyzed on the GC/FID after cryogenic concentration. The plotted results are analyzed for linearity. With good linearity, $r2 > 0.99999$, we have confidence for both the concentrations and the peak retention time for the component of interest."

Stability

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 minimization 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.

Guinness World Record

"Linde's state-of-the-art capabilities allow us to produce traceable, stable, low level, multicomponent mixtures," says Hayes. "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 groundbreaking 110–component calibration standard 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," commented William Elcoate, TestAmerica's Air Product Director.

The Future

While today VOC monitoring is all about emissions control and keeping within legislation and preventing the loss of valuable VOCs, Stephen 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 programs, the focus will shift dramatically beyond just keeping emissions within legal limits, to embrace trading good environmental behavior for money—or for the right to keep your plant open." ■

For more information on Linde's Specialty Gases and Specialty Equipment, please contact press@linde-gas.com.