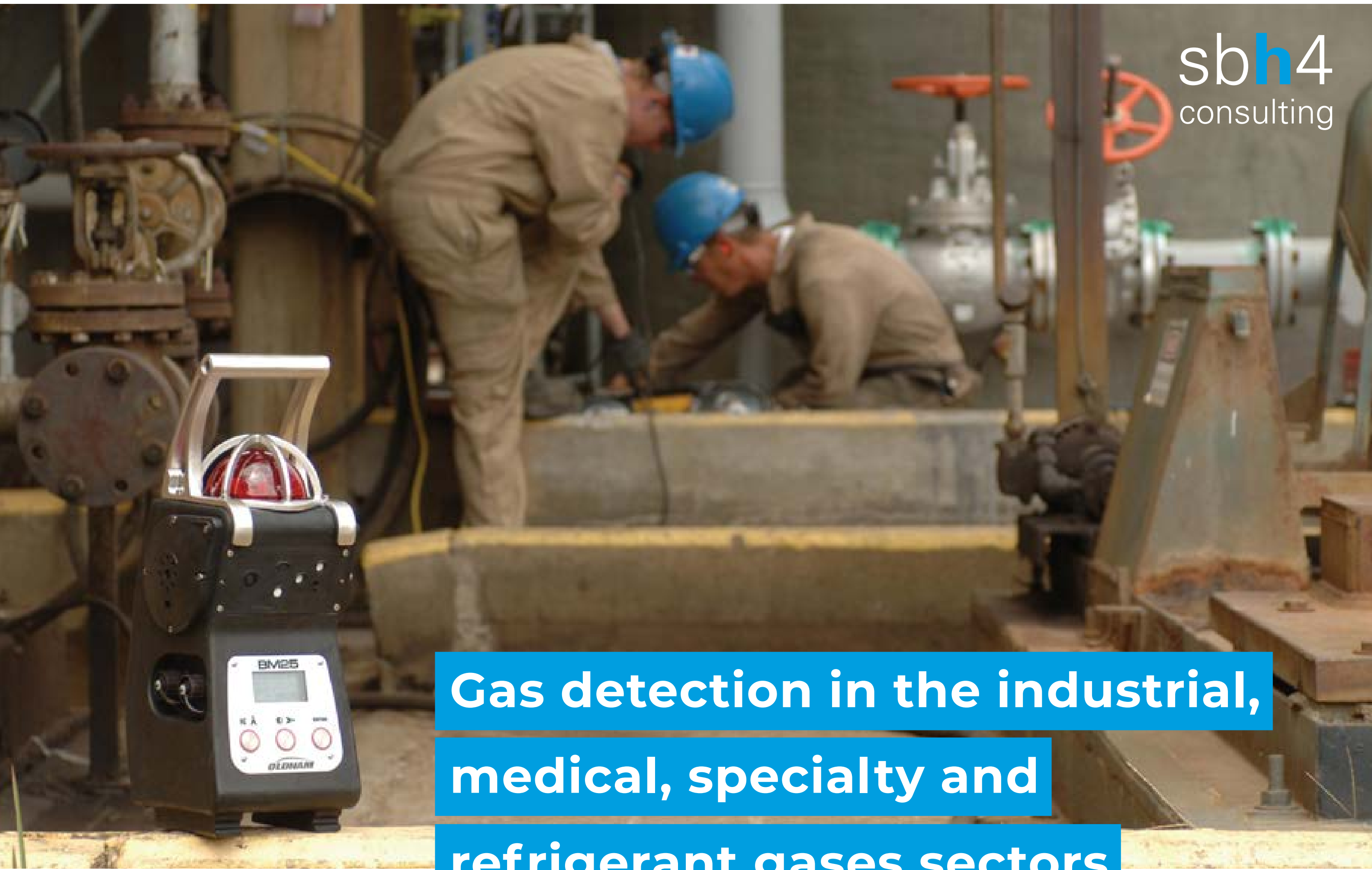

sbh4 consulting

Gas detection in the industrial, medical, specialty and refrigerant gases sectors

White Paper by
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Flammable, toxic and asphyxiant gases are processed 24 hours a day in the industrial, medical, speciality and refrigerants gases sectors. A myriad of preventative processes, such as HAZOP and risk assessments are undertaken to minimise the operational risk. Also, real-time monitoring techniques such as gas detection are used to sound the alarm if a gas leak does take place. Fixed systems can protect equipment, wearable units can protect people and portable units can support maintenance activities. The most appropriate mix of gas detection equipment on a production or end-user site will largely be influenced by the potential hazards of the gases in use and present on the site.

Safety first – prevention is a profitable mindset

Across tonnage operations, cylinder filling and customer applications, gas detection has a vital role to play in protecting both people and capital assets. And with business continuity in mind, gas detection can also play an important role in protecting profits. Investing in prevention is often money wisely spent. Identifying potential problems and proactively taking action to reduce risk is infinitely more desirable than reacting to a crisis. These are the fundamental arguments behind many proactive safety practices. Investment in safety is a mindset which can take the form of low-risk process selection, reliable equipment specification and encouraging behavioural or cultural best practices. The installation of gas detection instrumentation to raise the alarm before a situation escalates to a dangerous level can also play an essential role in a mix of mitigation and prevention strategies. The links between gas detection equipment and automated responses or human behaviour are also essential to work through. Often, an escalating approach to alarms is taken. For example, a low-level gas detection reading may result in a cautionary audible and visible alarm and automatically trigger an increase in ventilation. This could give operators the chance to investigate and rectify the situation. At a higher gas leak detection level, an automated shut-down of the process may be the appropriate response.

Gas detection is all about common sensors

François Ampe, Product Line Manager EMEA at Teledyne Gas and Flame Detection in France has a depth of expertise in designing customised gas detection systems. He says that "there is a wide gulf between an off-the-shelf wearable single gas detector for oxygen deficiency and a fully integrated gas and flame detection system. In my career, I have worked with these two extremes and many solutions in between. There is a common link between a portable device, which might cost only a few hundred euros and a fixed gas detection system mounted in a rugged ATEX housing costing a few thousand Euros,

and that link is the gas sensor: every gas detection unit, large or small, will have a gas sensor.

Depending on the gases it is sniffing for, this sensor will be a very clever piece of electrochemistry, some modern solid-state electronics or a highly sensitive optical device. In each case, the technology is packed into a tiny space about the size of a few coins stacked on top of each other. The sensor is the 'nose' of the gas detector as it continuously sniffs the atmosphere.

Oxygen is generally detected using an electrochemical fuel cell. François Ampe says that "measuring oxygen enrichment and deficiency is achieved using the same sensor, so a leak of oxygen which causes oxygen enrichment or a leak of nitrogen or argon which would cause oxygen deficiency can be detected using similar devices". Oxygen, nitrogen and argon are three of the main hazardous gases processed on an ASU.

Selection of sensors to be built into gas detection equipment. Copyright Teledyne Gas & Flame Detection

Motors, gas compressors and piping – an ASU machine room has many potential gas leak hazards

A cocktail of gas detection systems is the best medicine

Portable gas detection systems which are worn by operators as they move around between locations can be effective to warn personnel to avoid areas where toxic, flammable or inert gases have accumulated. Fixed systems, on the other hand are designed to detect gas leaks as they happen or soon after. However, whether they are fixed or portable, gas detection systems based on chemical sensor technologies are limited to monitoring gases close to the location where they are situated. Open path gas and flame detection systems, on the other hand, can detect flammable gases or fire in the line of sight where they are installed and can cover a vast range.

For expansive areas an open path gas detection system might be ideal to cover the long distances involved. On the other hand, in a complex plant area or machine room where distillation columns, motors, compressors, reaction vessels and piping are obstructing the line of sight the open path system may not have the ideal surroundings to operate to its full potential. For a location that has been assessed as a high-risk leak area during a HAZOP study, such as a gas compressor, a fixed location gas detector may be more suitable.

Given the differences that exist, is there a right or wrong gas detection system? Or is it the case that each has its purpose and a combination of strategies is the most effective solution? The consensus is that an integrated array of open path gas and flame detection equipment, fixed gas detection systems, portable and wearable gas detectors and is the most effective solution.

Line of sight gas and flame detection

Air gas detection in and around the ASU

Billions of dollars of capex in the industrial gases sector is tied up in air separation units (ASUs) and steam methane reformers (SMRs). They produce oxygen, nitrogen, hydrogen and carbon monoxide for tonnage pipeline gas supplies. In these two processes alone, gas leaks have the potential to cause: oxygen enrichment from oxygen leaks; oxygen deficiency from nitrogen leaks; fires and explosions from methane or hydrogen leaks and poisoning from toxic carbon monoxide leaks.

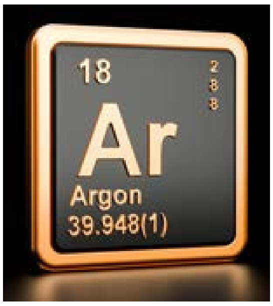
Shin Tsushima, Vice President, ASU Engineering for Matheson Tri-Gas in Texas summarises the situation for ASU gas detection: "when implementing a gas detection system on an ASU, the essential things to consider are personnel safety and equipment protection. For plant protection requirements, the most typical systems are fixed gas detectors which are located according to the results of a robust risk assessment. If these fixed detectors identify a leak, safe shutdown of the relevant equipment is the first and the best choice".

Tsushima adds that "portable type gas detectors for oxygen, toxic gas and flammable gases are also essential for protecting personnel as they move around the site. When a personal detector alarms, moving out of an enclosed space, walking across the wind direction, radioing the control room for help or donning breathing apparatus could be life-saving responses.

A merchant ASU for the production of liquified oxygen, nitrogen and argon. Copyright Matheson Tri-Gas Inc.

Furthermore, preparation and training in a suitable evacuation plan which can be executed in the event of a gas detector alarm is one of the most important site emergency procedures."

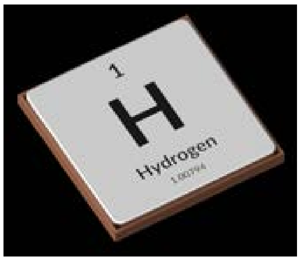
The unsung hero with some hidden hazards – the Argon Purification Unit



The Argon Purification Unit is the unsung hero of industrial gases. The 'ASU' is often in the spotlight and the acronym rolls off the tongue regularly, but how often do we hear about the smaller 'APU'? When it comes to profitable operations, the APU can make or break the P&L. And when it comes to safe operations, the APU is worthy of the same level of respect as the bigger plant items on site.

To consider the gas detection requirements on the APU, the process is the same as every other process unit – consider the risks which are presented by the gases being processed. Quite obviously, we have argon. We sometimes refer to nitrogen as the 'silent killer' because it can cause oxygen deficiency and anoxia, and the same phrase would be equally valid for argon. It is similarly inert, and an argon gas leak can displace oxygen in the atmosphere which can be very hazardous, especially if the leak takes place in a confined space with inadequate ventilation. This hazard can best be detected with several fixed gas detectors which are permanently sniffing for oxygen deficiency.

Thinking beyond the obvious presence of argon, we must dig deep into the workings of the APU to identify other potential hazards. The crude argon feed to the APU contains oxygen and nitrogen. The main function of the APU is to remove the nitrogen and oxygen to yield high purity argon.



The ASU's distillation process has done as much of the oxygen and argon separation job as reasonable possible and we must now turn to other technologies to get the residual gases out. The most common technique is to use a 'deoxo' unit: a reactor fed with hydrogen gas. The deoxo reactor is filled with a palladium catalyst which triggers the reaction of the oxygen and hydrogen. This reaction releases heat and the temperature at the outlet will be about 150° C. The flow of hydrogen to the deoxo reactor is controlled so that a small excess of hydrogen (around 1%) is present in the outlet gas stream. The resulting argon, nitrogen and hydrogen mixture is distilled to yield high purity argon and the residual hydrogen and nitrogen mixture is generally flared.

In this scenario we have: a source of pure hydrogen (perhaps a gas line or a high-pressure bank of hydrogen cylinders); the presence of heat; a combustion-type reaction taking place in the deoxo reactor and an open flare. Putting these things together, it becomes obvious that a leak of hydrogen near the APU could be very hazardous. One or more fixed gas detectors sniffing for Hydrogen are therefore required.

Example gas detection requirements to be considered on air gases production facilities

Air Gases	Oxygen enrichment / deficiency	Flammable gases	Toxic and other hazardous gases
Air Separation Unit (ASU) and other cryogenic air gases production	Both	H_2 for Analyser room [*7]	Potentially CO_2 or NH_3 as refrigerants
Argon Purification Unit (APU)	Deficiency	H_2 for deoxo unit	
Nitrogen liquefaction unit (NLU)	Both	Potentially hydrocarbon refrigerants	Potentially CO_2 or NH_3 as refrigerants
PSA or VSA units for onsite air gases production	Deficiency		

Safety with Specialty Gases

Whilst ASUs and SMRs are high value assets, they are also highly automated and relatively few people are in contact with the process equipment during normal operation. However, many of the people employed in the industrial gases sector work on cylinder filling plants. These are often highly manual operations where the workforce spends much of their day in proximity to potentially hazardous gases. The hazards are similar to ASU and SMR operations: oxygen is core to medical cylinder gases; hydrogen and nitrogen are used in industrial cylinder gases; and carbon monoxide is commonly used on specialty gases cylinder filling sites, where a plethora of other exotic toxic, flammable and pyrophoric gases might also be processed.

Jorge Duarte Guimarães, an industrial and specialty gases consultant in São Paolo, Brazil who has spent more than 30 years in the sector with most of that time with AGA and Linde, says that :”when implementing a gas detection system in an SG plant, the critical points are those related to the toxicological characteristics and the risks associated with any leakage of the products that will be produced and handled on the site. Oxygen and inert gases such as nitrogen, helium and argon, despite being almost 99.9% of the air around us, when pure, have high risks. For example: the release of oxygen can enhance combustion or even lead loss of consciousness for personnel. Therefore, fixed oxygen detectors are requirements in specialty gases and medical cylinder filling plants”.

He continues to say that “flammable gases such as hydrogen and methane demand specific attention due to the danger of fire and explosion. Explosimeters and flame detection systems should be considered in areas where these products and handled.

Jorge Duarte Guimarães

Special consideration should be paid to gas mixing rooms where different gas lines cylinders are handled involving a range of products with a mix of risks such as: oxidizing, inert, toxic and flammable. In these cases, a system with multi-gas detectors is necessary”.

The use of multi-gas portable detectors is also common in special gas plants, as many areas of the plant, such as: laboratories, filling stations, compressor rooms and warehouse are confined spaces. Duarte continues: "fixed and portable gas detectors require occasional re-calibration using high precision gas mixtures. They should also be bump-tested frequently – before and after each shift, according to standard operating procedures in some industries".

PS200 portable Multi Gas detector – Copyright Teledyne Gas & Flame Detection

Gas detector bump testing and calibration gas mixtures

The quality requirements for daily use functional test gas mixtures (bump test gases) are generally not as high as the gas mixtures used for the detector and sensor calibration. For the functional test gas a general certificate of analysis can be appropriate. Alternatively, a higher quality ISO17025 accredited gas mixture might be specified.

For the quarterly, half yearly or annual calibration of the gas detector, it is often required to use a traceable and accredited calibration gas mixture. For the highest levels of confidence an ISO 17034 accredited reference material calibration gas mixture would be selected. Steve Abbott, the National Operations Manager at Coregas Pty Ltd in Australia comments on his experience with accredited specialty gas mixtures. "Our specialty gases accreditation journey began in 1997 when we achieved ISO17025 accreditation as a calibration laboratory for gas mixtures. Subsequently, Coregas achieved ISO Guide 34 accreditation in 2002 which made us the first accredited gases reference material producer in Australia. Furthermore, the updated version of ISO Guide 34, which is called ISO 17034, was implemented in 2018 and we achieved accreditation for that new standard in December 2018. One of the main purposes of these accreditations is to demonstrate traceability and our reference materials that we use at Coregas are traceable to Australian National Standards of weights and thus to the International System of Units (SI)".

Coregas calibration gas mixture filling and analysis

The accreditation authority responsible for Coregas production and testing operations is NATA, the National Association of Testing Authorities Australia which is the sole accreditation body in Australia. Their reputation is global, and they currently hold the secretariat for the International Laboratory Accreditation Cooperation (ILAC).

When it comes to gas mixtures filling it is possible to prepare general certified (non-accredited) specialty gases calibration mixtures in small batches for speed and economy. However, most ISO Guide 34 mixtures must be prepared as single cylinders which involves more labour input per cylinder and results in higher costs of production. Coming back to Steve Abbott at Coregas, “there are four members of our Specialty Gases laboratory team who are NATA signatories for our accredited ISO Guide 34 certificates. Between them, they have 40 years of experience as NATA signatories for reference material production.”

For a deeper insight into these quality considerations, it should be noted that under the correct usage and interpretation of the ISO Guide 34 standard for reference material producers, each individual cylinder must be prepared and validated for stability and homogeneity. Coregas offers cylinders from 2.8 to 48 litres capacity that have been individually analysed with full ISO 17034 certification. Abbott says that “our biggest cylinder, the G size is popular in laboratories where gas detection equipment is manufactured and recertified. Smaller portable refillable cylinders are ideal for in-situ bump testing or calibration. This is especially useful for servicing gas detectors located in diverse locations around industrial gases production facilities or customer sites where they are using industrial gases”.


NATA
NATA Accredited
Reference Materials Producer
National Association of Testing Authorities, Australia
has accredited
Coregas Pty Ltd
Special Gas Laboratory
ISO 17034

Coregas ISO17034 NATA Accreditation certificate

Portability is essential for many gas detection applications but there is a limit to the size of cylinder that can be used for high quality gas mixtures. Production of ISO 17034 accredited mixtures in very small low-pressure disposable cylinders is not possible for technical and quality reasons. The problem is that there is not enough content to conduct several check analyses after filling to prove homogeneity and stability of the gas mixture. These tests are required to comply with the ISO17034 standard.

Abbott concludes, "at Coregas, our pedigree has grown from serving customers in Australia. In recent years, both our reputation and our specialty gas cylinders have been travelling abroad. For example, we are proud to be a supplier to many multi-national gas detection device manufacturers and local gas detection equipment servicing companies in Brazil."

Coregas specialty gas mixture cylinders for gas detector bump testing and calibration

Cause and effect: cylinder filling process evaluation, gas detection and mitigation

"The use of a cause and effect matrix is really powerful" says Robert Lee, Managing Director at iGAS Technology Solutions in the UK. "When we design industrial, specialty and medical gases cylinder filling plants for operating companies they want us to deliver a fully engineered solution. So, we bring in specialist gas detection companies to select the right

Cylinder gases operations

technology to sense for the gases that are being used in the process. We work together to identify the hazards and scope the most cost-effective gas detection system".

"Beyond the hardware design and construction, what my team can offer is the engineering expertise and operational insight to devise safety management systems that link the gas detection alarms with likely causes of the leak and appropriate mitigation. For some gas alarms a simple intervention like shutting a flow control valve may be all that is required to eliminate the hazard. In the other extreme, an emergency shut down of the entire process and evacuation of the plant building would be required. This is where the process of working through the 'cause and effect matrix' comes in to play".

Flammable and toxic gas detection on the SMR

Flammable energy gases such as hydrogen and methane demand specific attention due to the danger of fire and explosion. For a leak to air, hydrogen has a lower explosive limit of 4% and an upper explosive limit of 75% - that is an extremely wide range. And spark ignition from electrical components or maintenance activities is an ever-present risk. The combination of these hazards adds up to a high-risk situation and the need for explosimeters and flame detection systems becomes clear in

Teledyne Gas and Flame Detection MX43 control unit

Steam Methane Reformer (SMR), Lima hydrogen cluster, Ohio – copyright Matheson Tri-Gas

areas where hydrogen is processed. The SMR also produces carbon monoxide, which is both flammable and toxic. So, the use of a system with multi-gas detectors including sensors that are specific to carbon monoxide might be appropriate. Wearable gas detectors as part of the operator's daily PPE would also be common practice around hydrogen plants. This is partly because plant facilities, such as: laboratories, filling stations and compressor rooms are generally indoors in confined spaces. These enclosed buildings may also present the risk of oxygen deficiency if the inert gas nitrogen is used to drive pneumatic process control systems. Ventilation, in addition to gas detection is an appropriate mitigation.

For many flammable gases with a carbon atom in the molecule, such as methane which is a common feedstock for SMRs and propane which can be used as a refrigerant gas, an infrared sensor can be used. François Ampe of Teledyne Gas and Flame Detection explains that "hydrogen is also a flammable gas, but unlike hydrocarbon gases, the hydrogen molecule contains no carbon atoms and is therefore not infrared active. So, for hydrogen gas detection a specialist catalyst bead type of sensor must be used. This is the kind of essential knowledge that we offer to our customers when we help them select the most appropriate gas detection system".

Example gas detection requirements to be considered on energy gases facilities

Hydrogen and energy gases	Oxygen enrichment / deficiency	Flammable gases	Toxic and other hazardous gases
Steam Methane Reformer (SMR) for hydrogen or syngas production	Perhaps*1	CO, H_2 & CH_4	Potentially CO_2 or NH_3 as refrigerants
Electrolytic hydrogen or oxygen production	Potentially enrichment*9	H_2	
LPG & CNG fuel gases cylinder filling	Perhaps*1	CH_4, propane	Potentially CO_2 or NH_3 as refrigerants
Distributive LNG*3	Perhaps*1	CH_4	

Flame detection is also advisable when handling flammable gases. Ampe says that "in the industrial gases sector, flame detection can be used as a second line of defence, in combination with gas detectors. An example might be a high-pressure methane compressor on CNG tube-trailer filling system. Using multiple gas detection devices and flame detectors, the operator can use a 'voting system' to escalate between a visual alarm, an audible alarm and an automated system shutdown, according to the number of gas and flame detectors that have been activated. This can help to minimise disruptive 'false-alarms' and simultaneously ensures that a truly hazardous situation is flagged as quickly as possible – to protect lives and plant assets".

Gas detection works very well in enclosed buildings where there is no wind to disperse a gas leak. But in open outdoor spaces a leak can be diluted to an undetectable level by a strong wind current. Ampe explains how flame detectors can help in those situations: "on a steam methane reformer there is generally a natural gas pipeline feeding the plant and a hydrogen pipeline exporting product from the plant. We are surrounded by flammable gases. Flanges and valves in the pipework are potential gas leak points and the plant risk assessment may have determined that each one should be fitted with a gas detector close by. However, prevailing atmospheric conditions might mean that the methane or hydrogen gas leak is blown away from the gas detector and no alarm is registered – it can happen. This is where a flame detector might spot the problem before it escalates to a major explosion. In French, we call this complementary approach 'ceinture et bretelles'. I think that in English it is known as 'belt and braces'".

Hydrogen electrolyser gas detection

Throughout history, there have been some high-profile safety incidents related to Hydrogen. The crash of the airship Hindenburg in 1937 is an oft cited example of how this gas has the potential to be extremely dangerous. And the recent explosion at the OneH2 hydrogen plant in North Carolina on 7th April 2020 is a pertinent reminder that the hazards associated with this gas have not diminished over time. But, with good safety management systems we can do many things to minimize the risks from the hazards that are inherent in the production and distribution of hydrogen.

Steam methane reformers have been the default technology for large scale hydrogen production for several decades. However, electrolysers are now scaling up and making inroads into this space. These plants have a specific set of gas detection considerations. Christopher Braatz from McPhy in Germany says that "hydrogen electrolysers are often located indoors in an enclosed space. This makes a combination of passive measures such as ventilation and active systems such as gas detection especially important".

Hydrogen gas grid admixing. Copyright TÜV SÜD.

0.5 MW, 200 cubic metres per hour McPhy Hydrogen Electrolyser. Copyright RAG & Karin Lohberger Photography.

There are various international technical standards that we follow when considering the safety of our electrolyser installations, for example the 'ISO 22734-1: Hydrogen generators using water electrolysis process – Industrial, commercial, and residential applications'. On the topic of gas detection for safety, in section 4.2 it stipulates that: 'Hydrogen generators shall be designed and manufactured such that where a release of flammable gas occurs during normal operation, the formation of a flammable atmosphere is prevented, minimized, detected, and/or controlled'. In section 4.4.1.9 it continues to specify the standards to which the gas detectors must be manufactured, installed and maintained. The requirement to evaluate the reliability of the gas detection system is stipulated. It also specifies that: 'The hydrogen gas detector(s) shall be installed in optimum location(s) to provide the earliest detection of hydrogen gas, such that their protective function can be proven'.

Braatz adds that "we use these international standards in combination with a detailed risk assessment which our engineers conduct with the electrolyser operator. The first lines of defense are to implement good ventilation and install a hydrogen gas detector. We might even go further to consider oxygen gas detection. Furthermore, automated safety control systems at our installations invoke the appropriate actions in the event of a gas leakage alarm. For example, a severe alarm would trigger an emergency shutdown of the electrolyser. This shutdown follows the same procedure that would also be used to make the electrolyser safe for routine maintenance. Quite simply, the electrical power supply is isolated, and the inert gas nitrogen is used to purge the internal space of the electrolyser. The nitrogen, oxygen and hydrogen gases are then vented to a safe location."

Certification of hydrogen electrolyser equipment and facilities

Many types of hydrogen electrolyser operate at elevated pressures in the order of 20 bar. This has the benefit of reducing their footprint and increasing the electrical current density to produce more hydrogen from a smaller unit. As such, this type of electrolyser comes under the scope of the European Pressure Equipment Directive (PED) 2014/68/EU. One of the consequences of this is that they must be certified by a Notified Body before they are sold from the manufacturer to the operator.

Founded in 1866 as a steam boiler inspection association, TÜV SÜD is a prime example of such a Notified Body with a long-standing pedigree in pressure vessel inspection and certification. Through rigorous internal qualification management and training procedures, a Notified Body such as TÜV SÜD, will employ several experts who are competent to carry out the inspections and certification according to the PED. Guntram Schnotz of TÜV SÜD Industrie Service in Filderstadt, Germany is one such person.

According to Schnotz, the equipment certification must be followed by a review of the installation at the operator's site. He says that "TÜV SÜD are approved by the European Union to certify equipment under the PED which is to be put into service anywhere in the EU. The next stage in the process becomes national. As a German entity, we are authorised to conduct the inspection and certification of the final installation which the operator is responsible for, if it is installed in Germany".

Hydrogen electrolyser installation. Copyright TÜV SÜD.

Biogas plant with biomethane upgrade and CHP units

The critical link in the chain between the production of a hydrogen electrolyser and its use will be the hand-over documentation which will include a user manual. Schnotz adds that "many of the safety management cases will be implemented into the equipment design. However, some residual risks will exist, and these must be identified in the operating manual so that the user of the equipment is able to implement appropriate mitigation. Gas leak hazard mitigation is one such example. The operating manual is likely to refer to the requirement for ventilation and gas detection. When we are inspecting an installation prior to certification, we review the hand-over documentation and check that all the required precautions have been correctly in corporated into the final installation. Our goal is to make sure that nothing is left to chance because we know how hazardous hydrogen can be".

Relying on our senses – biological gas detection

The production purification and distribution of biomethane from biogas upgrades is increasingly considered to be within the scope of industrial gases. Anaerobic sludge digesters process either domestic wastewater or a biomass feedstock such as grass or maize to produce biogas. Biogas is a crude gas mixture that contains carbon dioxide, methane and a range of other gases in trace quantities. The tiny cpA neuron in a mosquito's nose can detect an elevated level of carbon dioxide in the air that results from human breathing from more than 20 metres away. Human beings, on the other hand, have no sensory perception for carbon dioxide and the same can be said for other colourless, odourless gases such as methane.

The first step in a biogas upgrade will be to remove these impurities which might include toxic or corrosive gases such as hydrogen sulphide. The next step is to separate the methane, which is the target energy vector. Some plants then go one stage further to purify the carbon dioxide for use in welding, water treatment, beverage dispense or food processing applications. When it comes to gas detection, there are a range of flammable, toxic and other hazards to consider.

Involvement in biomethane brings industrial gases directly into the heart of the natural gas distribution network. For many years, the natural gas pipeline grid has added very low concentrations of 'stenchants' to the gas. These are generally mercaptans: hydrocarbons that contain sulphur.

Methyl mercaptan can be detected by the human nose at levels in the order of 2 parts per billion (ppb). Our noses are approximately one order of magnitude more sensitive to Ethanthiol, or ethyl mercaptan, can be detected at only 0.36 ppb. So, only an extremely low concentration needs to be added to natural gas to enable a gas leak to be detected by people who may be using natural gas in their homes or maintenance teams working on the gas grid. It might come as a surprise that modern gas detection has its origins in the biology of mosquitos and human beings.

Customer site safety

Cylinder and bulk liquid gas storage areas at customer sites, eg specialty gas cylinder stores at universities, toxic gas cabinets at semi-conductor producers or the medical cylinder gases stores at a hospital may also require gas detection equipment. Industrial gases field service personnel, such as customer engineering services teams working on tank maintenance or drivers making bulk liquid deliveries will also need gas detection equipment. Bulk carbon dioxide deliveries to a brewery or beverage bottling plant may warrant the use of a CO2 detector. Liquid oxygen deliveries to local hospital bulk storage tanks may call for the use of an oxygen gas detector. And, applications specialists visiting from the industrial gases provider for process optimisation will most probably have an appropriate wearable gas detector as part of their PPE kit.

Ammonia refrigeration system evaporators

Bulk liquid nitrogen vapourisers

As an example of a customer application, food freezing factories using cryogens such as liquid nitrogen or liquid carbon dioxide will also require gas detection equipment. A combination of wall mounted sniffers close to the processing equipment and wearable devices is often used. Beyond these cryogens, gases for use in mechanical refrigeration systems are also supplied by many industrial gas companies. The use of hydrocarbon refrigerants in this area is becoming increasingly popular due to their low environmental impact and excellent thermodynamic performance. Their application stretches from food processing factories to small domestic refrigerators, super-market food display cabinets and world-scale natural gas liquefaction systems.

The main risk introduced with hydrocarbon refrigerants such as isobutane, propane, propylene and ethylene, compared with alternative fluorine-based refrigerants, is flammability. Speaking on this topic from his role as Global Product Manager Specialty Gases & Equipment at The Linde Group in Germany, Roberto Parola says that “flammable and explosion hazards should be properly assessed – both for new systems and when hydrocarbons are used as retrofit gases in existing refrigeration equipment. The implementation of adequate measures, including a proper gas detection system, ventilation, safety signage and the designation of Ex-proof areas should be considered as actionable outcomes of the risk assessment”.

Natural refrigerants such as carbon dioxide and ammonia must also be used with appropriate precautions. Parola adds that “ammonia is used extensively in large scale commercial and industrial refrigeration equipment. It has zero global warming potential, which is a major reason for its selection. However, the gas is both toxic and flammable. An ammonia leak might be detected through our sense of smell, but we should not rely exclusively on our nose as a warning system: gas detection equipment should also be considered”.

Leaking ammonia gas cylinder

Carbon dioxide for carbonated beverages

Maintenance – special considerations are required

The safety issues referred to in this White Paper are not simply theoretical; they are very real. As an example of the hazards involved, consider that on the 5th of November in 2005 at the Delaware City Refinery in the USA two maintenance contractors died by suffocation. They were raising a pipe onto a reactor which was inerted with nitrogen. One of the technicians fainted and fell into the reactor; the second victim was also asphyxiated in trying to save his colleague. Whilst this case study is from the oil and gas sector, nitrogen is also present extensively in industrial gases plants during normal operation, construction and maintenance.

One might wonder if these fatalities could have been avoided if the maintenance workers had been better informed of the risks and had been issued with a portable gas detector, or wearable gas detectors that could have been sniffing for oxygen and making an audible alarm in the case of oxygen deficiency.

BM 25 Wireless and BM 25 Transportable Multi Gas Monitors for area gas detection and the MX40 Wireless controller – Copyright Teledyne Gas & Flame Detection

Confined space entry can be extremely hazardous

The examples in this White paper generally relate to normal process operation. Construction, start-up (eg running in an SMR with nitrogen), decommissioning, purging and maintenance activities should all be subject to case-specific risk assessments and gas detection is likely to be specified under an appropriate 'permit-to-work'. This permit may specify the use of portable or wearable gas detection equipment.

Gas detection for confined space entry

Fixed gas detectors are ideal for monitoring leaks from process units, such as gas compressors. However, gas detection during maintenance must be mobile. Kevin O'Donnell, EMEA Business Development Manager at Teledyne Gas and Flame detection explains: "gas detection is about protecting people in addition to plant assets. Maintenance can take place in just about any plant location and will generally involve people – and their safety must be protected".

Area gas detectors, such as the BM 25 from Teledyne Gas & Flame detection can be carried to the maintenance location to provide localised monitoring of hazardous gases. Going one step further, the BM 25 Wireless area gas monitor can communicate with the MX 40 controller to enact various safety mitigations, such as the automated closure of an actuated valve.

Entry into confined spaces presents an additional risk due to reduced ventilation and the potential for hazardous gas accumulation. Kevin O'Donnell says that "wearing a portable gas detector as part of their PPE is routine for many maintenance teams on industrial gases plants. One of the benefits of our PS200 is that it can be configured to include an internal sample pump. That means that a gas sample can be drawn safely from up to 30 metres using quickly connected flexible tubing. This eliminates the need to lower the detector into a pit or empty tank prior to entry and it's a much better way to monitor the atmosphere inside the tank". If the tank has been purged with nitrogen, it will be essential to ventilate the tank with air prior to entry. The PS200 can validate that a safe oxygen concentration has been achieved in the tank to avoid asphyxiation of the maintenance team.

Cryogenic gases present additional risks. In some gases, there may be a bund or pit around a liquid oxygen, liquid argon or liquid nitrogen storage tank. If liquefied gases or cold vapours are released, they will sink to the bottom of the pit and entry can be extremely hazardous. "Operators will certainly want to wait before entering a pit that has been filled with cold oxygen, argon or nitrogen vapours – but they will not want to wait indefinitely. The oxygen sensor in the PS200 gas detector can measure both elevated and depleted oxygen concentrations which can help them to make an informed decision about when it will be safe to resume work in that area" concludes O'Donnell.

Example gas detection requirements to be considered on medical, specialty and refrigerants gases facilities

Cylinder filling, medical gases and specialty gases	Oxygen enrichment / deficiency	Flammable gases (eg H_2, CH_4)	Toxic and other hazardous gases (eg CO_2, CO, H_2S)
Specialty and Electronic Gases cylinder filling	Both	Wide range of gases	Wide range of gases
Refrigerant gases cylinder filling	Deficiency[*5]	Perhaps[*6], potentially pentane, propane, R32	Perhaps[*6], potentially CO_2 and NH_3
Liquid Helium trans-fill and cylinder filling	Deficiency		
Medical Gases cylinder filling	Both[*4]		N_2O[*4]
Nitrous oxide production	Perhaps[*8]		N_2O
Industrial Gases cylinder filling	Both	Potentially CO, H_2	Potentially CO, CO_2
Acetylene production and cylinder filling	Perhaps[*1]	Acetylene	
Beverage dispense gases cylinder filling (CO_2 / N_2)	Deficiency		CO_2
Dry ice production	Perhaps[*2]		CO_2 and potentially NH_3 as refrigerant

Further reading

Some extracts of this White Paper will also be published in gasworld and H2 View during 2020.

This White Paper is a high-level summary with some example gas detection considerations. For more detailed information, the following documents may be of value.

- HYCO Plant Gas Leak Detection and Response Practices - Doc 215/18 (EIGA)/CGA H-14-2018
- Safe Practices Guide for Cryogenic Air Separation Plants - IGC Document 147/13/E/CGA P-8 -2013/ JIMGA-T-S/91/14
- Unmanned Air Gas Plants: Design and Operation - Doc.132/15 (EIGA)/CGA P-8.6-2015
- Fire Hazards of Oxygen and Oxygen Enriched Atmospheres Doc 04/18 (EIGA)
- Hazards of Oxygen-Deficient Atmospheres Doc 44/18 (EIGA)
- Safe Handling of Electronic Specialty Gases - Doc 199/15 (EIGA)
- The Safe Storage, Handling and Use of Special Gases, BCGA Code of Practice 18
- ISO 22734-1: Hydrogen generators using water electrolysis process

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Specific notes to the tables

*1 A flammable gas leak (for example methane, acetylene, or hydrogen), which may result in oxygen deficiency in extreme cases, should be detected by flammable gas detectors at low concentrations of the flammable gas before an oxygen-deficient atmosphere is reached.

*2 A CO_2 leak, which may result in oxygen deficiency in extreme cases, should be detected by CO_2 detectors before an oxygen deficient atmosphere is reached.

*3 The case considered here is distributive liquefied natural gas (LNG), meaning downstream LNG storage and distribution operations. The production and purification of LNG in midstream natural gas processing operations will require H_2S and other gas detection.

*4 The most common medical gases filling considered here are: pure oxygen, pure nitrogen, medical air (which may be blended from oxygen and nitrogen) and the blending of oxygen / nitrous oxide mixtures and helium / oxygen mixtures. The filling of specialty medical gas mixtures, such as mixtures CO_2 / oxygen mixtures or lung function test gases containing CO or acetylene may require additional gas detection precautions, see the relevant section of the table. The production of nitrous oxide from ammoni um nitrate will require process-specific gas detection precautions see the relevant section of the table.

*5 Many fluorinated refrigerant gases are not readily detected by common gas detectors and for those that are non-toxic and non-flammable an oxygen gas detector sniffing for oxygen deficiency may be an appropriate precaution.

*6 Refrigerant gases is a broad product group which may include inert HFC or HCFC gases like R134a; flammable HFO gases like R32 and R1234yf; flammable hydrocarbons like propane and toxic gases like Ammonia and CO_2. Some refrigerant gas cylinder filling operations focus on a few products with a limited range of hazards, others process a broad range of products for which a wider range of precautions are necessary.

*7 A flame ionisation detector (FID) gas analyser is generally used for ASU condenser total hydrocarbons analysis for process safety. The FID uses hydrogen as a fuel gas. The hydrogen is generally supplied by specialty gas cylinders or from an on-site laboratory scale hydrogen generator. Since the instrumentati on-shack is generally an enclosed space, gas detection is required despite the comparatively small quantities of hydrogen gas involved.

*8 An N_2O leak, which may result in oxygen deficiency in extreme cases, should be detected by an N_2O gas detector before an oxygen deficient atmosphere is reached.

*9 The electrolyser produces hydrogen on the cathode and simultaneously produces oxygen on the anode. If the oxygen leaks, it can result in oxygen enrichment.

General notes to the tables

Each site is unique and gas detectors and alarm systems must be located according to the risk assessment evaluation for the site in question.

Portable or wearable gas detectors must also be considered for personnel when they are in areas that could expose them to a hazardous atmosphere.

It is common practice to install gas detectors based on the most severe hazard presented by a gas leak. If a gas presents two potential hazards, detection should be based on the first hazard that would materialise. For example, a small methane leak could cause an explosion and fire. A severe methane leak may also cause oxygen deficiency. In this example, detection of methane at 50 % LEL (2.5 % methane in air) would occur before the detection of oxygen deficiency at 19 % oxygen in air using an oxygen sensor.

The selection of the sensor technology may be influenced by the anticipated frequency of exposure. For example an IR detector is more expensive than a catalytic bead, but it will withstand repeated exposure to high concentrations of the gases to be detected better and have a longer lifetime. The use of two gas detectors based on different technologies to detect the same hazard, for example IR and catalytic bead for methane leak detection could be good practice, if the project budget allows. This builds in redundancy to the system and should detect the leak and trigger mitigation before a hazardous situation is reached.

It is common practice to use different gas detector sensor technologies in an escalating automated safety mitigation regime. For example, in an ammonia compressor house an electrochemical type sensor may trigger ventilation fans at low levels of ammonia. A catalytic detector may then initiate a full electrical shut down at higher concentrations of ammonia. This avoids over reliance on one single gas detection technology. In this example, a lower-cost electrochemical type sensor could be located close to the compressor room entrance door, further from the compressor, where the risk of exposure to high concentrations of ammonia gas is lower. This would extend the electrochemical sensor life and allow the use of cost-effective technologies to reduce the overall system cost.

Enclosed spaces (eg plant buildings, process control instrumentation shacks and gas analysis laboratories) require additional precautions, compared to well ventilated outdoor areas.

General notes to the tables

In many of the above processes, Nitrogen is sometimes used as an alternative to compressed air as a service gas for pneumatic systems. Where this is the case, there may be the need for gas detection to identify oxygen deficiency if the nitrogen is used in confined spaces.

Indoor and outdoor gas storage areas or gas cabinets at industrial gases production facilities, eg flammable or toxic gases cylinder storage compounds may also warrant gas detection.

The most suitable location of the gas detection sensors must also be considered. Some gases such as methane and hydrogen are lighter than air and a gas detector located in the roof of an enclosed space may be advisable. Other gases such as carbon dioxide are heavier than air and a location close to floor level may be appropriate. Similarly, build-up of inert cryogens, such as liquid nitrogen, might best be detected at ground level since the cold gas is denser than ambient air.

The examples in this table relate to normal process operation. Construction, start-up (eg running in an SMR with nitrogen), decommissioning, purging and maintenance activities should all be subject to case-specific risk assessments and gas detection is likely to be specified under an appropriate 'permit-to-work'. This permit may specify the use of portable or wearable gas detection equipment.

Carbon dioxide (CO_2) and Nitrous oxide (N_2O) have some documented toxic effects, however, they are not classified as toxic gas according to GHS.

About the author

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He was previously global head of Specialty Gases & Equipment at Linde Gas and spent more than 15 years with BOC Gases in global leadership and national management roles. He is now the owner and manging director at sbh4 GmbH. He offers business and strategy development consultancy, M&A advisory, marketing and PR services to the gas detection, gas analysis instrumentation and industrial, medical, specialty gases and refrigerants sectors.

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