Understanding Ammonia Sensors and their Applications

According to the European Environment Agency (EEA), almost 10 million metric tonnes of ammonia are produced and used per year in Western Europe, making it one of the most common of all High Production Volume (HPV) industrial chemicals. Ammonia is commonly used in many industries, including petrochemical, pulp and paper, fertiliser and the oil industry to name but a few. Anhydrous ammonia (NH_3) is also very widely used as a coolant in large industrial refrigeration systems. In fact, the use of ammonia as a refrigerant (R717) has increased substantially over the past several years as a replacement for environmentally unfriendly chloro-fluorocarbon refrigerants. While ammonia refrigeration has long been a standard in the food/beverage industry, it is also now found in pharmaceuticals production, in air-conditioning equipment for many public buildings and in electric power generation plants.

Ammonia is rightly regarded as a highly hazardous chemical. According to the EEA, the worst industrial accident of the last twenty years occurred on 21 September, 2001, when an ammonia / ammonium nitrate explosion at a fertiliser plant in Toulouse, France killed 30, and injured more than 2,000 workers and nearby residents. According to the government investigation, as horrific as the accident was, it could have been much worse if intervening buildings had not broken the force of the explosion, preventing the potential detonation of 20 more railroad tank cars full of anhydrous ammonia.

Liquid anhydrous ammonia expands over 850 times when released to ambient air, and readily forms large vapour clouds. These clouds are normally lighter than air and tend to rise. However, liquid anhydrous ammonia may also form an aerosol consisting in part of small liquid droplets. As an aerosol, the droplets of ammonia are heavier than air and sink toward the ground. The sudden drop in temperature due to release of ammonia may also cause water vapour in the air to condense, forming a visible white cloud. Convective air currents due to the heavier than air cloud may carry the ammonia downwards as well. Therefore, when anhydrous ammonia is released to the air, it may rise and disperse as a gas, or it may travel along the ground as an aerosol, or because it has trapped water vapour. In either case, the cloud may remain low instead of rising into the air.

Ammonia is a highly toxic gas, and proper safety monitoring procedures and equipment must be in place at all times to avoid serious accidental injury or death. The most widely recognised exposure limits for ammonia are an eight-hour TWA (Time Weighted Average) of 25 ppm, with a 15-minute STEL (Short Term Exposure Limit) of 35 ppm. Ammonia is also corrosive to the skin, eyes, and lungs. Exposure to 300 ppm is immediately dangerous to life and health. Fortunately, ammonia has a low odour threshold (20 ppm) with good warning properties, so most people seek relief at much lower concentrations.

Besides its toxic properties, ammonia is also an explosively flammable gas, with a lower explosive limit (LEL) concentration of approximately 15% volume. Although ammonia vapour is not flammable at concentrations of less than 15%, it can easily explode or catch fire throughout its flammability range of 15% to 28% by volume. Ammonia contaminated with lubricating oil, however, can catch fire or explode at concentrations as low as 8%.

In Europe the installation of gas warning systems for ammonia refrigeration systems is required as part of EN 378, "Refrigerating Systems and Heat Pumps - Safety and Environmental Requirements". EN 378 explicitly requires the installation of fixed leak monitors in refrigeration and air-conditioning machinery rooms, as well as other areas where a sudden leak into an occupied space would cause a hazardous condition.

Ammonia sensor capabilities and limitations

Almost anyone who has used ammonia sensors in refrigerated areas is aware of the limitations of the sensors. The environment is just plain tough on sensors. Temperatures can range from – 40° (in some flash freezing operations) to + 40° C (during defrost periods). Strong jets of water, steam and detergents used during wash-down procedures can potentially damage sensors and other system components. Interfering contaminants from propane powered forklifts, alcohol based disinfectants, or even the products being stored or manufactured can have an adverse affect on the performance of the sensors. Most importantly, different types of ammonia sensors have different limitations. The secret to choosing and installing a trouble free system is understanding the limitations of the sensors, and choosing the correct sensors for the locations and conditions in which they will be operated.

• Infrared (IR) Sensors

Non-dispersive infrared (NDIR) sensors measure gas as a function of the absorbance of infrared light. When infrared radiation passes through a sensing chamber containing a specific contaminant, the only wavelengths that are absorbed are the wavelengths that match the chemical bonds in that contaminant. The rest of the light is transmitted through the chamber without hindrance. Since most chemical compounds absorb at a number of different frequencies, IR absorbance can provide a "fingerprint" for use in identification of unknown contaminants. Alternatively, for some molecules it may be possible to find an absorbance peak at a specific wavelength that is not shared by other molecules likely to be present. In this case absorbance at a particular wavelength can be used to provide substance-specific measurement for a specific molecule. For instance, ammonia has a usable absorbance peak at a wavelength of about 1.53 microns (μm). Absorbance at this wavelength is proportional to the concentration of NH_3 present in the sensing chamber of the sensor.

Optical filters or "choppers" are used to limit the wavelengths of the infrared light passing through the sensing chamber to the specific frequencies at which absorbance by the target molecules occur. Some NDIR detectors use "thermopile" detectors to directly measure the amount of infrared light absorbed at specific wavelengths. Other "photo-acoustic" infrared detectors use a microphone to measure pressure changes in the sensing chamber due to the heating effects of the absorbance of infrared energy by the ammonia molecules.

The chief benefits of infrared sensors are high specificity of the sensor to ammonia, long term stability and reduced need for calibration adjustment. Infrared detectors have a wide dynamic range, and are not degraded or consumed by exposure to high concentrations of ammonia. The chief limitations are the physical size of the detector assembly, the need to protect the detector against the potential effects of fluctuating temperature and humidity, and the substantially higher cost compared to other detector types.

Ammonia transmitters can be used as "stand-alone" systems that include local display of readings and alarm inform-ation, or linked together into larger multi-point arrays

Charge carrier injection (CI) ammonia sensors are not adversely affected by exposure to high concentrations of gas, and are ideal for installation in environments subject to high background concentrations of ammonia

• Chemosorption (MOS) sensors

Chemosorption sensors consist of a metal oxide semiconductor (MOS) sensing element contained within a flame arrestor. In clean air the electrical conductivity is low. Oxidation of the measured gas on the sensing element increases conductivity. An electrical circuit is used to convert the change in conductivity to an output signal which corresponds to the gas concentration.

Chemosorption sensors are generally designed to respond to the widest possible range of toxic and flammable gases and vapours. The idea is to provide a "broad range" response to the presence of contaminants. MOS sensors are able to detect chlorofluorocarbon refrigerants as well as other contaminants that are difficult to detect by other means, as well as ammonia, carbon monoxide, hydrogen, alcohols and many other gases and vapours. This nonspecificity can be advantageous in situations where unknown toxic gases may be present, and a simple go/no go determination is sufficient. However, since the sensors are not specific to ammonia, this can lead to false alarms if the sensors are installed in environments subject to the presence of interfering contaminants.

The chief benefits of chemosorption sensors are their long operational life and low cost. MOS sensors are by far the least expensive type of fixed ammonia sensor, and are not damaged or consumed by chronic exposure to ammonia. MOS sensors can be used to detect ammonia from concentrations as low as 30 ppm, all the way up to flammable range concentrations. However, because the output signal is highly non-linear, they need to be calibrated and adjusted for use in the desired range. Adjustment for use in high concentrations is at the expense of reduced accuracy and resolution at lower concentrations.

Other limitations stem from the effects of humidity on the sensor. As humidity increases, the sensor output increases, which can lead to higher than actual readings or false alarms. As humidity decreases to very low levels, sensor output may fall to zero even in the presence of the contaminant being measured. The extremely low humidity seen in many refrigerated areas (especially flash freezers) may make it effectively impossible to use this type of sensor. In addition, the user must exercise caution in assumptions about other contaminants that may be present in the area being monitored. The best use for MOS sensors is as a "go / no go" alarm device which is adjusted for maximum accuracy near the hazardous condition or "take action" threshold, or for use in measuring refrigerant gases (such as Freons®) that are difficult (or more expensive) to detect by other means.

• Electrochemical (EC) Sensors

Substance-specific electrochemical sensors are available for many of the most common toxic gases. EC sensors are compact, require very little power, exhibit excellent linearity and repeatability, and are comparatively inexpensive. Gas that enters the sensor undergoes an electrochemical reaction that causes a change in the electrical output of the sensor. The difference in the electrical output is proportional to the amount of gas present. EC sensors are designed to minimise the effects of interfering contaminants, making the readings as specific as possible for the gas being measured.

In the case of ammonia sensors, the electrolyte includes an active ingredient that is consumed in the electrochemical reaction used to detect the ammonia. Thus, the lifespan of the sensor is directly related to its exposure to NH_3. The lifespan is generally listed in parts-per-million exposure hours (ppmh). For instance, a "17,520 ppm hour sensor" has a lifespan of one year when continuously exposed to a constant concentration of 2 ppm of ammonia, (2 ppm x 365 days x 24 hours = 17,520 ppm hours). The same sensor would last only six months if continuously exposed to 4 ppm, three months when exposed to 8 ppm, etc.

There are several variations on the specific electrochemical reaction used to detect ammonia. Some EC sensors depend on a straightforward oxidation reaction where ammonia (NH_3) is converted into nitrogen (N_2) and hydrogen "protons" (H+) at the sensing electrode. For every two molecules of ammonia that are oxidised, six electrons (e–) of electricity are also produced. This electrical current output is what is used by the instrument to determine the concentration of ammonia present. The second half of the electrochemical reaction occurs at the "counter" electrode, where the hydrogen protons produced in the first half of the reaction react with oxygen to produce water.

Thus, at the sensing electrode:

$$2\ NH_3 \longrightarrow N_2 + 6\ H+ + 6\ e-$$

At the counter electrode:

$$O_2 + 4H+ + 4\ e- \longrightarrow 2H_2O$$
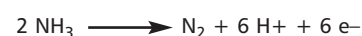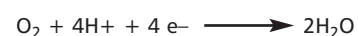
The sensor is filled with an organic gel electrolyte mixture in which the reaction occurs. Active ingredients in the electrolyte are incrementally used up as the sensor is exposed to ammonia. Once the "ppm hour" exposure life of the sensor is exceeded, it is no longer capable of detecting gas, and will need to be replaced. The positive benefits for this type of sensor include excellent low ppm range resolution, and excellent cold temperature performance down to – 40° C.

In other sensors a patented "pH shift sensitive" set of electrochemical reactions is used to detect ammonia. These sensors are based on a hydrous electrolyte system that, while slightly less able to withstand cold temperatures, provide extended measurement ranges of up to 5,000 ppm, with exposure life of up to 50,000 ppm hours.

Electrochemical ammonia sensors should be used only when the normal ambient background concentration of ammonia is sufficiently low to allow a reasonable operational life. For example, this type of sensor would not be recommended for use at a poultry farm or nitrate fertiliser plant where the routine ambient concentration of ammonia might be as high as 20 to 30 ppm. In this environment the life span of the sensor could be a matter of weeks. On the other hand, the high specificity to ammonia, and low cross sensitivity to other interfering contaminants that may be present (such as the carbon monoxide) makes these sensors the preferred approach in many environments.

• Charge carrier injection (CI) sensors

Charge carrier injection (CI) sensors depend on the adsorption of ammonia by "charge carrier" molecules in a solid state substrate. By absorbing ammonia the charge carriers are "injected" into the sensor element, causing a change in resistance that is


Compact electrochemical ammonia sensors exhibit excellent linearity, are capable of low ppm range resolution, and are comparatively inexpensive.

proportional to the concentration of ammonia present.

The materials, morphology and layering of the substrate are all carefully selected to maximize the affinity of the sensor to ammonia while minimising the effects of interfering contaminants. CI sensors can be used over an extremely wide range of concentrations, from as low as 20 ppm to 30,000 ppm or higher. Because the sensing element is operated at an elevated temperature, the sensor functions as its own "heater", and is an ideal candidate for operation in flash freezers and other environments subject to extreme cold (– 40°C or colder) temperatures. Because the detection principle is not based on the oxidation of ammonia, the sensor can also be used for the measurement of ammonia in oxygen free environments. Most importantly, the sensor is not "consumed" or permanently altered by exposure to ammonia. In the presence of ammonia the charge carriers are "injected" into the sensor element, while in fresh air the ammonia is desorbed. CI sensors are extremely stable, with operational life spans of five years or even longer. CI sensors are not affected by shifts in humidity, and offer excellent performance in the extreme low humidity associated with flash freezing operations.

While CI sensors have been designed to minimise the effects of interfering contaminants, they may still respond to volatile organic solvents (such as the limonene in citrus oil cleaners) and high concentrations of carbon monoxide due to engine exhaust. CI sensors are optimized for detection at higher concentration ranges, and should not be used for applications that require taking action at very low concentrations (less than 20 ppm).

No single type of ammonia sensor is perfect for all applications. The key to success is understanding the monitoring environment, and the specific benefits and limitations of the sensors selected.
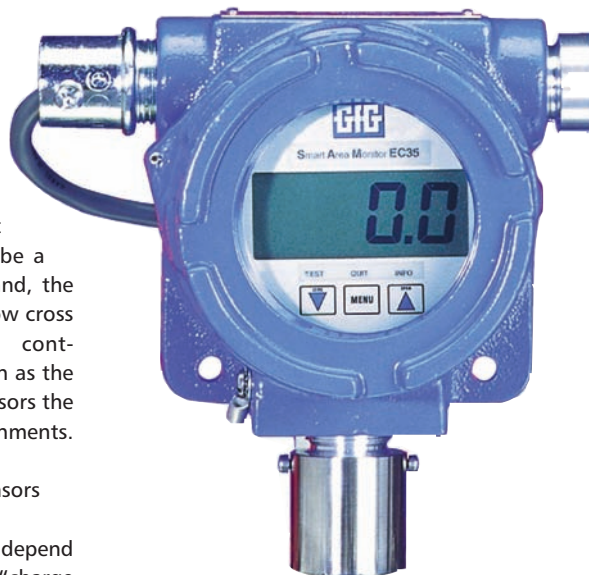
Permanently installed ammonia gas detection systems offer 24-hours a day alarm notification for hazardous atmospheres

AUTHOR DETAILS

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