

AP 1002:

Understanding ammonia sensors and their applications

Different types of ammonia sensors are optimized for use in specific applications. The key to success is understanding the monitoring environment, and the specific benefits and limitations of the sensors selected.

According to the United States Geological Survey (USGS), America produces over 10 million metric tons of ammonia per year, 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, fertilizer and the oil industry to name but a few. Anhydrous ammonia (NH₃) 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 chlorofluorocarbon 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 fertilizer 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.

Smaller incidents are extremely common. A study published by the State of New York Department of Health¹ illustrates just how commonly these accidents occur. The report documents 107 serious ammonia spills that occurred in New York State between 1993 through 1998. Sixty-one people were seriously injured, and one person killed in the reported accidents. Forty-four percent of the injured persons were employees, 41% were members of the general public, and 15% were emergency responders. Seven of the nine injured emergency responders sustained serious chemical burns. Most of the releases occurred in food/beverage processing (29%) or at chemical/



Figure 1: Compact electrochemical ammonia sensors exhibit excellent linearity, are capable of low ppm range resolution, and are comparatively inexpensive.

metal/equipment manufacturing facilities (27%). Most of the accidents (101) occurred at fixed facilities; the other six releases were during transportation. Equipment failure caused 58% of the releases. More than 1,889 people were evacuated following these 107 ammonia releases.

Liquid anhydrous ammonia expands over 850 times when released to ambient air, and readily forms large vapor 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 vapor 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 vapor. In either case, the cloud may remain low instead of rising into the air.

¹A copy of "Ammonia Spills in New York State (1993-1998)" is available at the following link: <http://www.health.state.ny.us/nysdoh/enviro/hsees/ammonia.pdf>



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Figure 2: Compact electrochemical (EC) sensors are available for an increasing number of specific toxic gases. Ammonia sensors show very little response to interfering gases, are capable of low ppm range resolution, require very little power, and are comparatively inexpensive.

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 recognized 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 odor 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 vapor 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,

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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.

The four most commonly used types of fixed sensors used to detect ammonia vapor are (1) infrared, (2) chemisorption (frequently referred to as "MOS" sensors), (3) electrochemical, and (4) solid-state charge-carrier-injection (CI) sensors.

- **Infrared (IR) Sensors**

Non-dispersive infrared (NDIR) sensors measure gas as a function of the absorbance of infrared light. Molecules consist of atoms that are held together by chemical bonds. The bonds in a particular type of molecule (like ammonia) absorb energy at specific wavelengths. When a chemical bond absorbs infrared light it continues to vibrate at the same frequency, but with greater amplitude after the transfer of energy. In other words, molecules that are able to absorb energy at that wavelength are heated to a higher temperature than molecules that are not able to absorb light at that wavelength.

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. The absorbance is not linear per concentration unit, but is mathematically predictable and easily calculated by microprocessor equipped portable gas detectors.

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



Figure 3: Ammonia transmitters can be used as "stand-alone" systems that include local display of readings and alarm information, or linked together into larger multi-point arrays

absorbed at specific wavelengths. Other "photo-acoustic" infrared detectors use a microphone to measure pressure changes in the sensing chamber due to the absorbance of infrared light. In this case, the microphone is used 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

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Figure 4: Permanently installed ammonia gas detection systems offer 24-hours a day alarm notification for hazardous atmosphere

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.

- **Chemisorption (MOS) sensors**

Chemisorption sensors consist of a metal oxide semiconductor, such as tin dioxide (SnO_2) on a sintered alumina ceramic bead 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. Sensitivity to a particular gas is alterable by changing the temperature of the sensing element.

Chemisorption sensors are generally designed to respond to the widest possible range of toxic and flammable gases and vapors. 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 vapors. This non-specificity 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 chemisorption 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.

The chief limitations of chemisorption sensors are the difficulty in interpreting readings, the potential for false alarms and the effects of humidity on the sensor. As humidity increases, sensor output increases. 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. The detection technique is very straightforward in concept. 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 minimize the effects of interfering contaminants, making the readings as specific as possible for the gas being measured.

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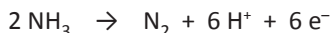
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In the case of ammonia sensors, the electrolyte includes an active ingredient that is consumed in the electrochemical reaction used to detect the ammonia. Thus, the lifespan of the sensor is directly related to its exposure to NH₃. The lifespan is 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.

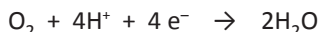
There are several variations on the specific electrochemical reaction used to detect ammonia. Some EC sensors depend on a straightforward oxidation reaction where ammonia (NH₃) is converted into nitrogen (N₂) and hydrogen “protons” (H⁺) at the sensing electrode. For every two molecules of ammonia that are oxidized, 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:



At the counter electrode:



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.

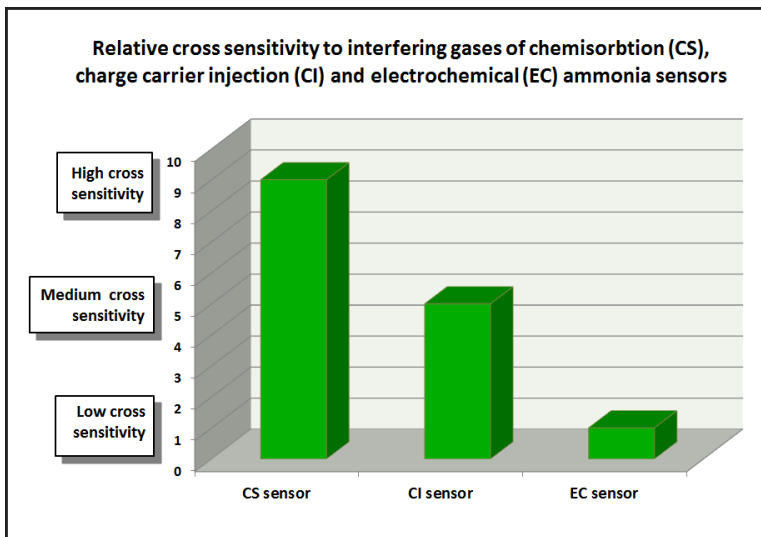


Figure 5: Chemisorption (CS) sensors are very cross sensitivity. Charge carrier injection (CI) are less cross sensitive. Electrochemical (EC) sensors show very low cross sensitivity to other gases.

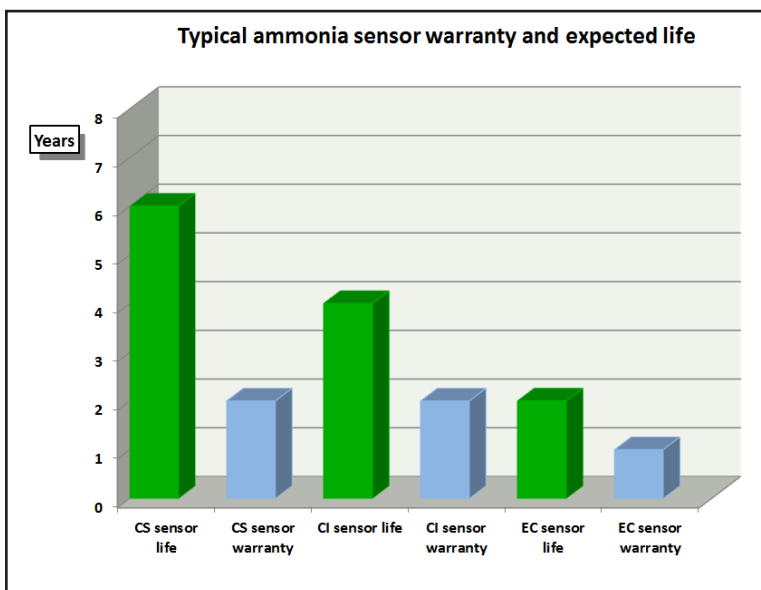


Figure 6: The operational life of ammonia sensors depends on the monitoring environment, but usually exceeds the warranty period. CS sensors can last up to 8 years or longer. CI sensors usually last 3 to 5 years. EC sensors generally last between 1 and 2 years.

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Once again, the electrical output of the sensor is proportional to the amount of ammonia oxidized at the sensing electrode. 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 fertilizer 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) ammonia sensors are based on an entirely different detection principle. 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 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 minimizing the effects of interfering contaminants. CI sensors are able to be used over an extremely wide detection range, from as low as 20 ppm concentrations to 10,000 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.

Most importantly, the sensor is not “consumed” or permanently altered by exposure to ammonia.

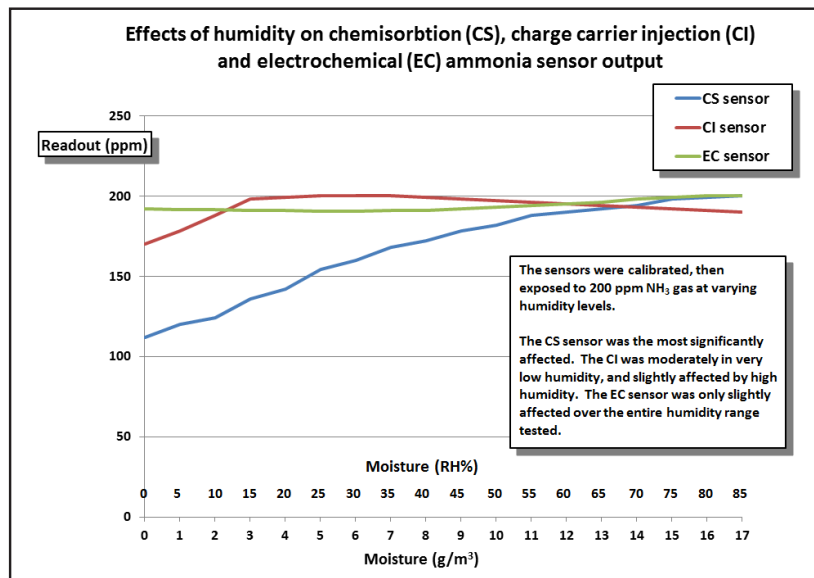


Figure 7: Chemisorption sensors are strongly affected by changes in humidity. CI sensors are modestly affected, but still work well in low humidity. EC ammonia sensors are largely unaffected by even major humidity changes, and work well even in extremely low humidity.

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 minimize the effects of interfering contaminants, they may still respond to volatile organic solvents (such as the limonene in citrus oil cleansers) 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.

