# Solutions for Ammonia Gas Detection: A Comparison Summary

The measurement of low ammonia ($NH_3$) concentrations is a key objective for the safety of personnel and industrial infrastructures.

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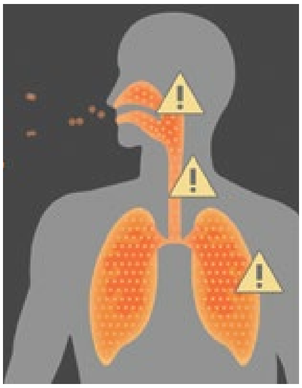
# Introduction

The hazardous, toxic, and combustible nature of ammonia is well-known in industrial settings. Undetected ammonia leaks in production plants and storage facilities can have devastating consequences, including accidental yet catastrophic explosions, fires, and loss of life at the plant level, with damage potentially extending to nearby communities.

# Exposure

Many gases in industrial settings can adversely affect worker health. Acute exposure to ammonia can result in corrosive injury to the mucous membranes of the eyes, lungs, and gastrointestinal tract and to the skin due to its alkaline pH and its hygroscopic nature. Chronic exposures may cause prolonged irritation of the respiratory tract, resulting in chronic cough, asthma, and lung fibrosis *(Agency for Toxic Substances and Disease Registry, Centers for Disease Control and Prevention)*.

There are industry-wide exposure limits established for more than 700 chemical substances globally. For ammonia, the Occupational Safety and Health Administration (OSHA) suggests an 8-hour exposure limit of 25 ppm and a short-term (15-minute) exposure limit of 35 ppm in the workplace. Recommendations and regulations vary globally and are updated periodically as more information becomes available, so limit values should be confirmed with respective national agencies and/or organizations before proper usage.



# Ammonia Gas Detection

When evaluating sensors for use in occupational exposure assessment, there can be several competing types from which to choose. For many industrial hygienists, a best practice for plant safety is to follow a multi-sensor layered approach with strategic detection positioning that provides a highly secure web of coverage to guard against accidental gas releases.

Selecting the right sensor(s) for a specific application can be difficult and requires an understanding of the conditions in which they will be operated *(e.g. settings prone to humidity, temperature swings, or interferant gases)* as well as the specific benefits and limitations of each sensor type. Several performance characteristics should be evaluated and prioritized prior to purchasing a sensor like sensitivity, response time, selectivity, calibration requirements, and limits of detection, to name a few.

The most commonly used ammonia sensing technologies, their operating principles, and advantages and disadvantages are described below:

## Laser-based Gas Detection Technologies

Laser-based technologies, such as photoacoustic infrared (PAIR) and open-path laser (OPL), are grounded on the specificity and the quantitative nature of absorption spectroscopy. More specifically, the physical basis on which this system operates is infrared absorption of molecular gases, which utilizes the ammonia absorption spectral signatures of infrared radiation. A laser-based solution should principally aim at a selective, sensitive, and fast detection of ammonia; otherwise, the relative costly laser is likely not a well-suited choice. They have a wide dynamic range and are not degraded or consumed by exposure to high concentrations of ammonia.

Absorption spectroscopy is based on a unique signature attenuation of spectral intensity caused by the gas to be monitored. It happens when light radiation interacts with molecular species and it is represented by the Beer-Lambert Law:

$$I_t (\lambda) = I_0 (\lambda)\ e\text{-}\alpha (\lambda)\ L$$

where $I_t(\lambda)$ and $I_0(\lambda)$ are the transmitted and incident light intensities at wavelength, $\lambda$, of the laser, respectively, and $L$ is the path length.

The absorption coefficient $\alpha(\lambda)$ is determined by:

$$\alpha (\lambda) = C \times \varepsilon (\lambda)$$

where $C$ is the concentration of gas, and $\varepsilon(\lambda)$ is the specific absorptivity of the gas.

Basically, the Law states that for a constant path length, the intensity of the incident light energy traversing an absorbing medium diminishes exponentially with concentration, as illustrated in Fig. 1 *(CLU-IN, EPA)*.

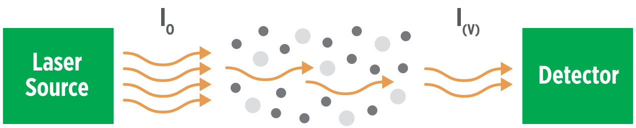
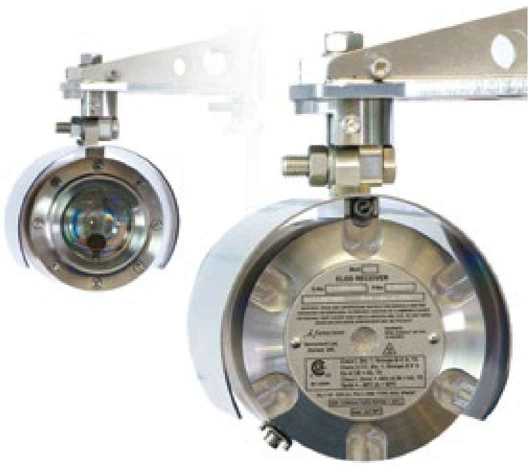


Figure 1. Illustration of Beer's Absorption Law.

In a laser-based IR instrument *(pictured below)*, a gas sample is introduced into the measurement chamber of the monitor, and the sample is exposed to a specific wavelength of IR light. If the sample contains the gas of interest, it will absorb an amount of infrared light proportional to the concentration of gas present in the sample.

In this paper, an optical and a non-optical laser-based detection scheme are investigated with respect to a potentially suited ammonia detection application. The two different detection schemes are based on tuneable diode laser absorption spectroscopy (TDLAS) with a photodetector *(optical)* and photoacoustic spectroscopy (PAS) with a microphone as a detector *(non-optical)*.



## Photoacoustic Infrared (PAIR)

In photoacoustic detection, the selectivity of traditional infrared gas spectrometry is further enhanced by the high sensitivity of photoacoustic spectroscopy, which utilizes a gas-microphone method to detect the presence of ammonia. The basic structure of this system is shown in Fig. 2 *(Applied Engineering in Agriculture, ASABE)*.

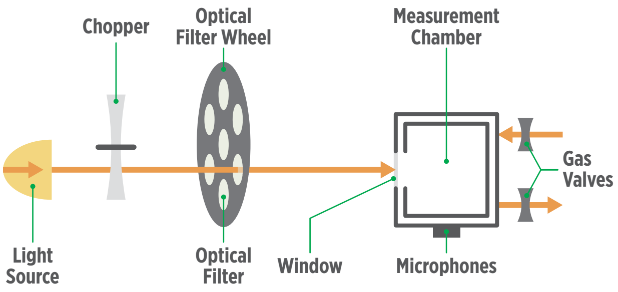


Figure 2. Schematic of a photoacoustic gas detector's operation.

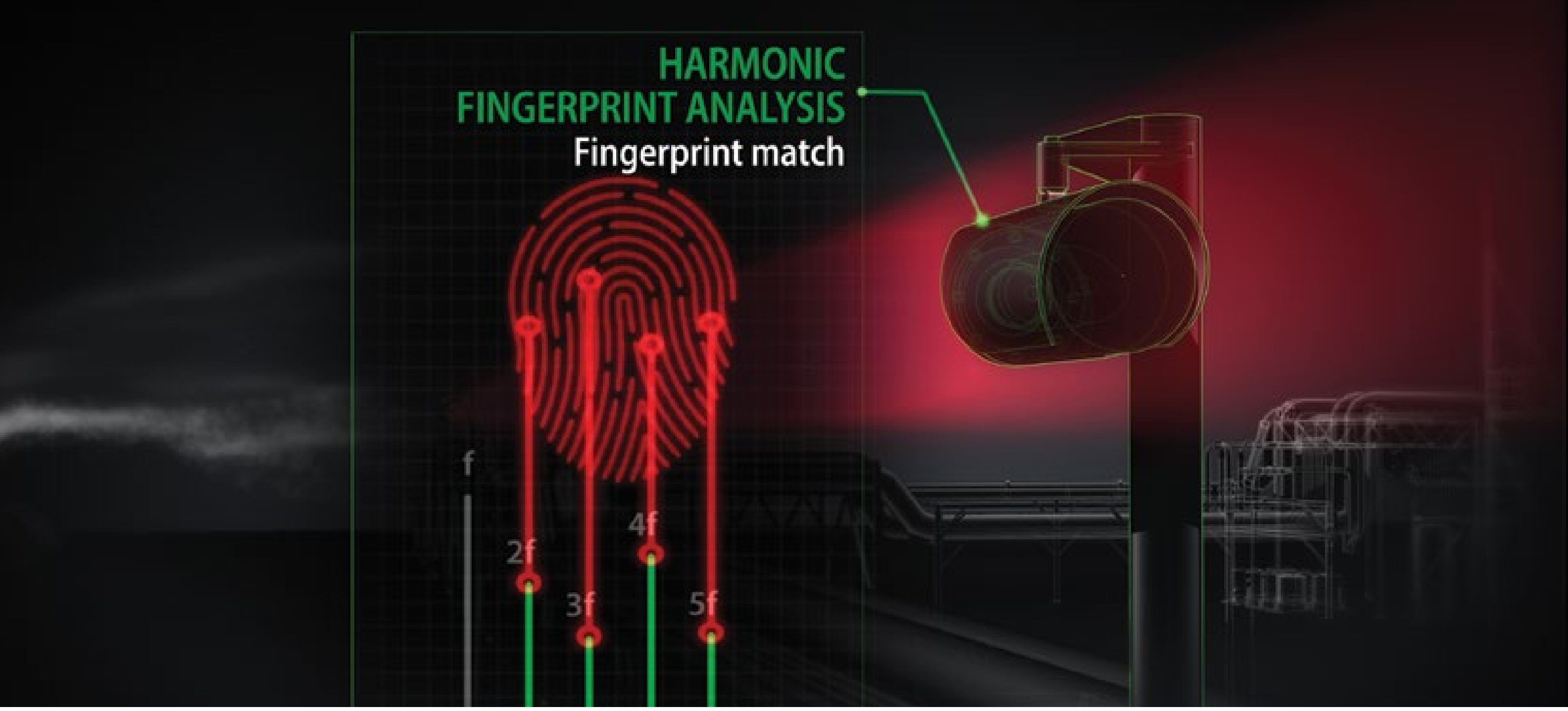
The IR light from a tungsten lamp is first modulated by a mechanical chopper and then passed through a narrow-band optical filter to remove all wavelengths except for the "measuring wavelength" characteristic of a target gas. In the measurement chamber, the target gas molecules become energized upon light absorption, and dissipate the absorbed energy in the form of heat. The chopper-modulated pulsed light results in periodic heat expansion and contraction of the sample air, forming a standing pressure or sound wave. The resulting acoustic signal is recorded by an extremely sensitive microphone and converted to an electrical signal correlated to gas concentration, which can be written by the following equation:

$$S = M \cdot P_v \cdot (C_\omega \cdot \eta \cdot c \cdot \alpha_v + A_b)$$

where $S$ is the microphone signal at the light modulation frequency $\omega$, $M$ is the microphone sensitivity, $P_v$ describes the optical power for the excitation, the photoacoustic cell constant is given by $C_\omega$, and the conversion efficiency of the absorbed light energy into heat is described by $\eta$. The frequency-dependent gas-specific absorption coefficient according to Beer and Lambert is described by $\alpha_v$ and $c$ is the gas concentration. Furthermore, $A_b$ describes the "zero-gas" background signal that should be ideally zero or at least close to zero.

Because the optical filter will only pass the particular wavelength of light for the gas in question, a pressure pulse indicates that the gas is present. If no pressure pulse occurs, then no gas is present. Therefore, temperature or pressure changes will not change the zero reading on the unit. Additionally, this zero reading will not be affected by aging of the IR source or microphone since the zero is based upon a true zero reading and not the difference between two readings as in traditional IR.

For installations that require detection of ammonia at low levels, particularly in an environment where cross-sensitivity is an issue, photoacoustic infrared monitors are an excellent choice, as they provide precise, high-performance monitoring for a variety of gases.



## Tunable Diode Laser Absorption Spectroscopy (TDLAS)

Another technology that uses the effect of light absorption by ammonia is laser-based open path gas detection. This sensor technology utilizes Enhanced Laser Diode Spectroscopy (ELDS) by measuring the concentration (ppm.m) over the full distance between the transmitter unit and receiver unit. The absorption signal is analyzed using a technique called Fourier transform. This converts the signal from a time domain into a frequency domain. The resultant component frequencies are then compared to a predetermined pattern *(Harmonic Fingerprint)* to confirm the presence of ammonia. This technology helps to eliminate false alarms from interference gases and is less prone to water vapor interference, providing greater reliability and performance in challenging environments such as rain or fog.

It is best suited for outer perimeter monitoring along property fence lines to guard against a specific toxic gas passing beyond the facility's boundaries.

## Traditional Gas Sensing Technologies

Depending on the application, other sensing technologies, such as electrochemical (EC) sensors and catalytic bead sensors for combustible gas detection, should be considered to either supplement laser-based sensors or used instead for appropriate facility safety.

Compared to their laser-based counterparts, these sensors typically offer a smaller size and much lower unit cost, but have various limitations as well.

## Electrochemical (EC) Sensors

Electrochemical sensors function on principles similar to those found in batteries. The basic structure typically consists of a gas-permeable hydrophobic membrane *(barrier)*, an electrolyte, a sensing electrode *(or working electrode)*, a counter electrode *(or auxiliary electrode)*, and sometimes a third reference electrode, as shown below in Fig. 3 *(Chemical Exposure Evaluation)*.

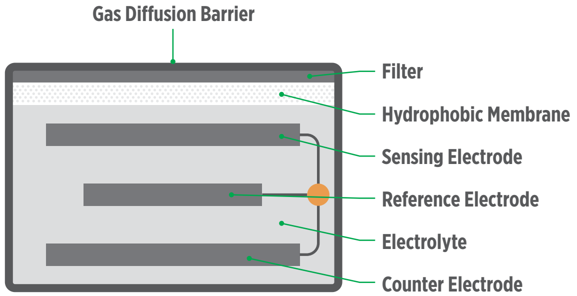


Figure 3. The basic structure of an electrochemical sensor.

When the target gas enters the sensor through the membrane, a chemical reaction occurs at the sensing electrode, which is facilitated by a catalyst and electrolyte solution. This reaction causes a release of electrons, whereby the flow of the electrons is measured as current within the sensor. Consequently, the current is proportional to the gas concentration and the reaction is measured in parts-per-million (ppm) of the gas. This process is demonstrated by the following electrochemical reactions:

Ammonia ($NH_3$) oxidizes at the anode (sensing electrode) to produce nitrogen ($N_2$) and hydrogen "protons" ($H^+$). For every two molecules of ammonia that are oxidized, six electrons ($e^-$) of electricity are produced:

$$2\,NH_3 \rightarrow N_2 + 6\,H^+ + 6\,e^-$$

The counter electrode operates as a cathode for the purpose of completing the circuit to allow the charge to flow. This second step *(reduction reaction)* occurs where hydrogen protons produced from the first half of the reaction react with oxygen to produce water:

$$O_2 + 4\,H^+ + 4\,e^- \rightarrow 2\,H_2O$$

EC sensors can facilitate sensitive and selective analyses of numerous gas-phase species at a high time resolution *(typically on the order of seconds)* and are relatively low cost compared to other sensors. Their small size also permits detection in a versatile range of locations.

However, they do have recognizable limitations and are challenged by environmental conditions and relatively short life expectancies when compared to other plant safety equipment.

Most traditional electrochemical sensors have a 1-2 year life, but actual lifetimes can be on the order of months or weeks when ammonia concentrations are high or extremes in temperature or humidity are encountered. It can be difficult to predict when a sensor will begin to lose sensitivity, so frequent calibration of EC sensors may be needed to ensure accurate readings. They frequently degrade at a faster rate when exposed to heavily polluted conditions. For example, the lifespan of ammonia EC sensors is directly related to its exposure to ammonia because the electrolyte is consumed as the reaction occurs. Exposures to high temperatures can accelerate the evaporation of the electrolyte, thus reducing sensitivity and lifespan.

Another limitation of EC sensors is cross-sensitivity to interfering gases, or non-targeted gases, that will also be detected by the sensor, resulting in skewed measurements of the desired gas. It is vital to understand the effects of potential interferants on each type of EC sensor in operation. Depending on the reaction, the interfering effect can create a false lower or higher concentration than the actual measurement *(Chemical Exposure Evaluation)*.

## XCell® Electrochemical Sensing Technology

MSA's patented XCell technology utilizes the same principles found in traditional electrochemical sensors but employs a number of significant physical design advancements.

Instead of a typical water-based electrolyte, XCell Sensors employ a unique class of ionic electrolyte liquids that features an evaporation-resistant profile capable of withstanding extreme environments with large humidity and temperature fluctuations *(-40°C to +60°C)*.

Another differentiator is the choice of catalyst in the electrode material. Unlike traditional electrochemical sensors, the XCell catalyst is not consumed by the gas reaction. Contact with ammonia has virtually no effect on the lifespan of the sensor. They can withstand background gas concentrations without reducing the sensor's life.

The mechanical design of the sensor is also optimized for operational efficiency. Every arrangement and placement of the sensor components have been strategically positioned to develop the most efficacious interaction between the electrolyte, electrode catalyst, and target gas regardless of environmental conditions to overcome.

With these enhanced features, XCell ammonia sensors have an expected lifespan of more than five years and are supported with a three-year warranty. These design advancements are instrumental in heightening sensor performance and lifetime which can help keep plants safe from ammonia gas leaks, while lowering the cost of maintenance for the user.

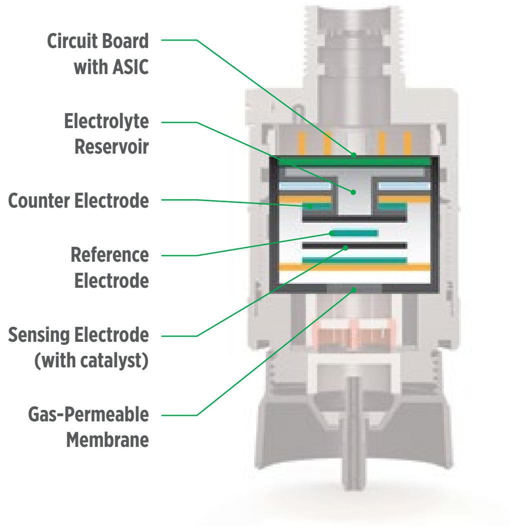


Figure 4. The basic structure of an XCell electrochemical sensor.

## Catalytic Bead Technology

The operating principle of catalytic bead gas sensors employ catalytic combustion to measure combustible gases in air at LEL *(lower explosive limit)* concentrations. A heated catalyst *(a coated wire coil)* burns the selected gas. As the temperature of the wire increases, so does its electrical resistance. A standard Wheatstone bridge circuit uses two wire coil elements *(one for detection and one for compensation)* to transform the raw temperature change to signal the presence of combustible gas.

Traditionally such sensors have a long life and are less sensitive to temperature, humidity, condensation, and pressure changes. However, they are also subject to sensor poisoning and shortened life with frequent or continuous exposure to high measured gas concentrations. Another limitation is that they monitor a wide range of combustible gases and vapors in air and are therefore not ammonia gas specific.

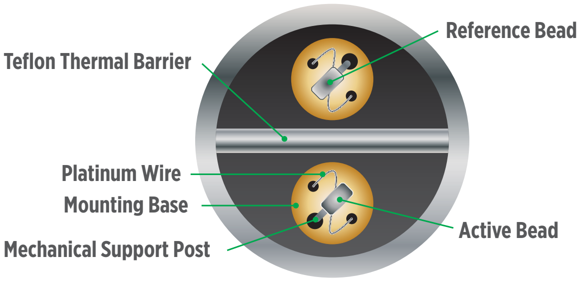
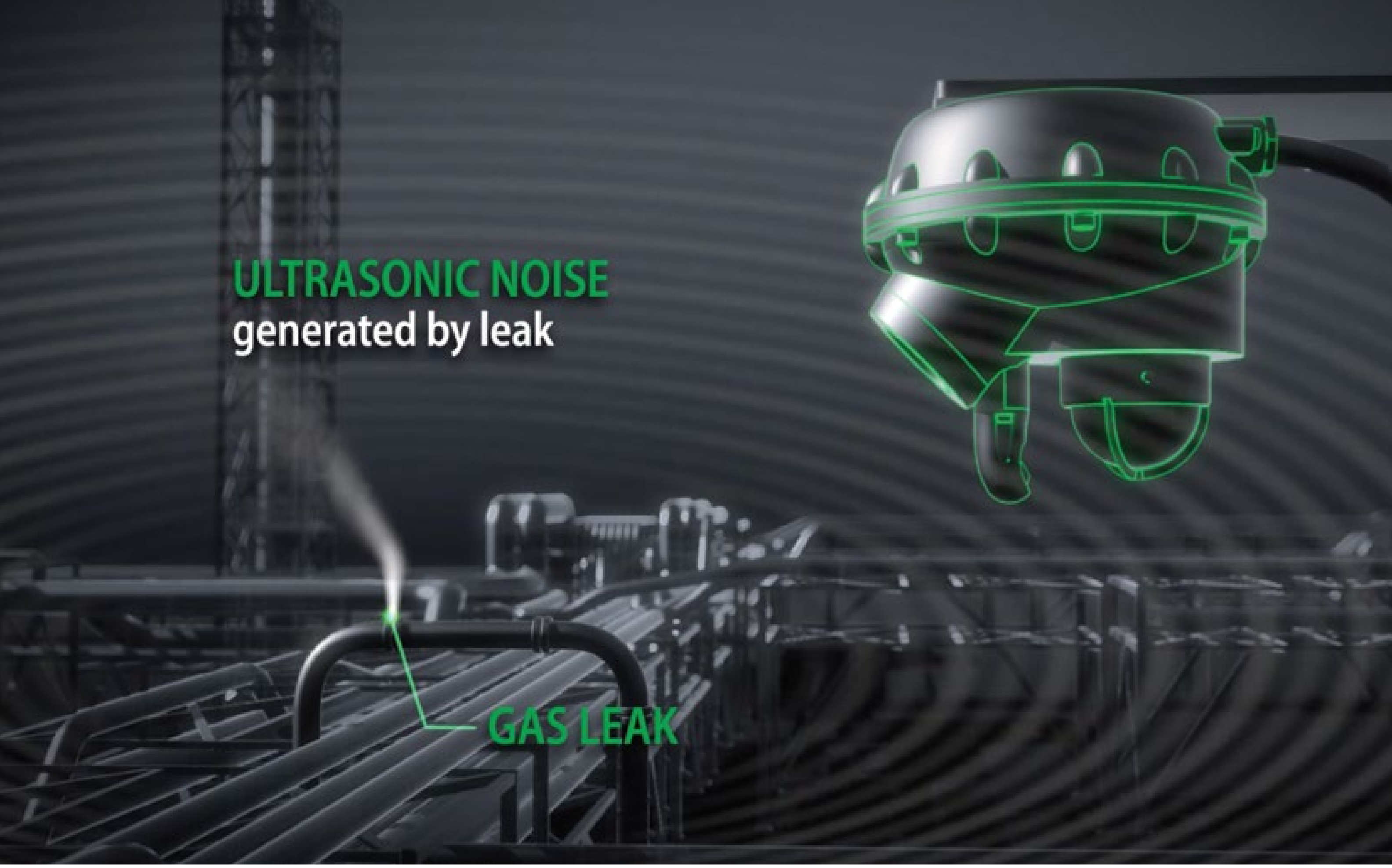


Figure 5. Catalytic bead sensor.



### Ultrasonic Gas Leak Detection (UGLD)

UGLD technology detects leaks from pressurized gas systems by sensing the airborne ultrasound produced by the escaping gas. This means that the ultrasonic gas leak detectors detect gas leaks at the speed of sound in a detection radius up to 28 meters (92 ft.) depending on the gas, leak size, and leak rate.. Unlike gas detection methods like point or open path mentioned above, ultrasonic gas leak detectors do not have to wait for the gas to accumulate into a potentially dangerous gas cloud and come into physical contact with the detectors. They instantaneously raise an alarm if a leak is detected. The ultrasonic acoustic gas leak detector picks up the leak without being affected by conditions such as changing wind directions, gas dilution, and the direction of the gas leak—conditions relevant for most outdoor gas installations.

The limitations with UGLD are that they are not suitable for low pressure leaks and are unable to determine the concentration of ammonia being released. They are a good choice as a first line of defense due to their rapid response time, minimal maintenance requirements, and environmental versatility.

## Conclusion

Compared to just 20-30 years ago, ammonia sensor technology has substantially improved, with the new design and introduction of ionic liquids in the chemistry of electrochemical (EC) sensors. Moreover, they can be supported by other ammonia detection technologies such as Enhanced Laser Diode Spectroscopy (ELDS) open path gas detectors, Photoacoustic IR monitors, and Ultrasonic gas leak detectors.

As these new technologies improve, combining them for individual applications is becoming more commonplace. When assessing a plant's safety requirements, users should consider a layered strategy to design the most comprehensive gas detection system for the facility. There is no single perfect solution, so understanding the monitoring environment and the specific benefits and limitations of the sensors selected is paramount to ensuring optimal plant safety.

## References

*Strahl, T., Herbst, J., Maier, E., Rademacher, S., Weber, C., Pernau, H.-F., Lambrecht, A., and Wöllenstein, J.: Comparison of laser-based photoacoustic and optical detection of methane, J. Sens. Sens. Syst., 10, 25–35, https://doi.org/10.5194/jsss-10-25-2021, 2021.*

*Open Path Technologies: Measurement at a Distance (Tunable Diode Lasers). CLU-IN, EPA. 2021. https://clu-in.org/programs/21m2/openpath/tdl/*

*Duarte VIVEIROS, João FERREIRA, Susana O. SILVA, Joana RIBEIRO, Deolinda FLORES, José L. SANTOS, et al., "Ammonia Sensing System Based on Wavelength Modulation Spectroscopy," Photonic Sensors, 2015, 5(2): 109–115.*

*Li, Hong; Zhang, Chen; and Xin, Hongwei, "Performance of an Infrared Photoacoustic Single Gas Analyzer in Measuring Ammonia from Poultry Houses" (2015). Agricultural and Biosystems Engineering Publications. 651. https://lib.dr.iastate.edu/abe_eng_pubs/651*

*Misti L. Zamora, Christopher Zuidema, Kirsten Koehler, "Chemical Exposure Evaluation" (2020). John Wiley & Sons, Inc. https://doi.org/10.1002/0471435139.hyg144*

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