MEASURING AMMONIA (NH_3) WITH PHOTOIONIZATION DETECTORS

Ammonia (NH_3) is a common alkaline gas. Lighter than air, it has a strong, distinctive smell and is highly reactive. Its solubility in water causes it to cauterize respiratory tracts, resulting in death at concentrations of 5000 ppm. It has the following relatively low exposure limits listed in the NIOSH "Pocket Guide to Chemical Hazards."

- **TWA** (Time Weighted Average): 25 ppm
- **STEL** (Short Term Exposure Limit): 35 ppm
- **IDLH** (Immediate Danger to Life & Health): 300 ppm
- **LEL** (Lower Explosive Limit): 15%

As an alternative to the use of ozone-depleting chlorinated and fluorinated refrigerants, the use of ammonia as a refrigerant (R717) has increased substantially over the past few years. Large quantities of ammonia can also be found in:

- Fertilizer plants
- Resin production using urea
- Explosives/munitions plants
- Nylon production
- Semiconductor production
- Water and wastewater facilities
- Clandestine drug labs

WHY MEASURE AMMONIA?

While Ammonia's distinctive smell makes it relatively easy to initially identify, the human nose is not calibrated to measure its concentration. Therefore, real-time monitors are necessary to allow continuous determination of the Personal Protective Equipment (PPE) necessary to provide proper protection from ammonia. According to the NIOSH pocket guide, protection from low levels of ammonia (up to 250 to 300 ppm) can be as little as a respirator with the appropriate ammonia cartridges. Entries into concentrations above 300 ppm or into unknown concentrations require positive-pressure supplied air or SCBAs. Even higher concentrations require full encapsulation suits (Level A) because of the highly reactive alkaline nature of ammonia gas. At concentrations above 15% (150,000 ppm), the ammonia atmosphere is potentially explosive, all activity should be stopped and all personnel should leave the area. Accurate, reliable, and continuous portable ammonia monitors are required to make these decisions.

When is Full Encapsulation Necessary?

Interviews with a wide variety of ammonia users reveals a lot of difference of opinion regarding when it is appropriate to move from supplied air respiratory or SCBA protection to full encapsulation (Level A). The best official guidance on the matter comes in an OSHA Standard Interpretation Letter of 10/1991. In it, Patricia K. Clark, Director, Directorate of Compliance Programs, OSHA says:

> *Generally, we would expect emergency responders to respond in Level A suits to unknown concentration levels and levels at or above one half the "Immediate Danger to Life and Health" (IDLH) level. The IDLH level for ammonia is 500 ppm [now 300 ppm] and one half that level is 250 ppm [now 150 ppm]. However, ammonia is an inhalation hazard at 1,000 ppm and not a skin absorption hazard. Ammonia begins to affect moist skin at exposures greater than 10,000 ppm (1%) (mild irritation) and at concentrations greater than 30,000 ppm (3%) a stinging sensation is observed. Therefore, the general procedure of using Level A equipment at 1/2 the IDLH may be unduly conservative for ammonia exposures. For ammonia, it may be more appropriate to respond in Level A gear to exposures of 1/2 the threshold for skin irritation, or 5,000 ppm.*

In discussions with numerous ammonia users (refrigeration and chemical plants), it seems that most choose to move into Level A in the range of 250 to 1000 ppm.

Ammonia Sensors Cannot Measure High Concentrations

Ammonia continues to be difficult to measure even with the latest advances in electrochemical (EC) sensors for portable monitors. Full scale for most ammonia electrochemical sensors is only 100 ppm; therefore, they do not have the range required to make appropriate PPE decisions for the high concentrations. They cannot help decide when it is necessary to make the decision to change from cartridge respirators to positive pressure supplied air or SCBAs, and electrochemical ammonia sensors certainly do not have the range required to decide when to don Level A suits. This makes users guess about high ammonia concentrations or resort to only doing "spot checks" with colorimetric ("Dräger") tubes. This causes people to chose levels of PPE that may be higher than necessary, increasing costs and making operations more difficult for the operators. Why dress-out in Level A if only SCBA is required?

Ammonia Sensors are Easily Exhausted

Electrochemical sensors can "see" relatively small amounts of ammonia without being exhausted. Like a dry-cell battery, an electrochemical ammonia sensor only lasts a fixed period of time, measured in ppm/hours. Suppose an ammonia cell is rated for 20,000 ppm/hours. That means it can be exposed to 10,000 hours of 2 ppm ammonia or 1000 hours of 20ppm. In this example, once 20,000 ppm/hours is reached, the cell is dead. Unfortunately, it is not even this simple. In addition to fixed life expectancy, electrochemical sensors have maximum over range ratings that are relatively low. A maximum overrange rating is the highest concentration of ammonia that the cell can see before it is potentially irreversibly harmed. This rating is like a "sensor IDLH." For many ammonia sensors, this "sensor IDLH" is only 200 ppm. This is the root of the reliability problem with electrochemical ammonia sensors. They are quickly used up in the presence of large ammonia leaks and cannot be used to help locate a leak. They are also expensive to purchase and calibrate.

MEASURING AMMONIA WITH A PID

Ammonia has an Ionization Potential (IP) of 10.18eV and can be readily measured with a Photoionization detector (PID) with a standard 10.6eV lamp. Portable PIDs have considerable advantages for measuring ammonia in ranges above the TWA and STEL of ammonia (25-35 ppm):

- A PID is an optical system that is not damaged by overranging.
- With a scale up to 10,000 ppm, the PID will not easily overrange and therefore can be used for all PPE decisions and for leak detection.
- Isobutylene calibration gas for the PID is stable relatively inexpensive ($65 for 35 liters with a 2- year shelf life)
- Ammonia calibration gas is less stable and expensive ($280 for 58 liters with only A 1-year shelf-life).
- A replacement 10.6eV lamp for RAE PIDs is $195 and will last up to 2 years, yielding a cost per a year of approximately $100.
- An ammonia sensor is much more expensive ($395) and has a life of 1 year yielding a cost per year of $395. But ammonia electrochemical sensors can die quickly when exposed to high concentrations of ammonia, yielding sensor lives of one to three months.
- Because the PID is not harmed by high concentrations of ammonia, it can be used as an accurate leak detector so that leaks can quickly be located and fixed. This reduces worker exposures and facilitates prompt repairs.
- PIDs provide nearly instantaneous response to ammonia. Ammonia sensors respond in 150 seconds. The MiniRAE 2000 PID responds in 3 seconds or less. Fast response makes it easier to assess changing conditions. Fast response makes it easy to detect leaks.

2-Year Cost Comparison of PID vs EC Sensor

While the PID has a higher cost of purchase than an electrochemical ammonia sensor, the 2-year cost of ownership for a PID is substantially less than that of the electrochemical ammonia sensor.

PID Specificity to Ammonia

A PID is not specific to ammonia and it will respond to a variety of other compounds. For example, if someone happens to spill ammonia and mineral spirits at the same time, the PID will provide a total combined reading for both compounds spilled. However, when responding to a major ammonia leak one can often assume that only ammonia is present because the presence of ammonia is easy to establish due to its distinctive smell. In these cases, a PID provides an accurate, reliable and cost effective means of measuring ammonia so that PPE decisions can be made to decide when it is necessary to:

1. Put on a respirator (over 35 ppm for 15 minutes).

2. Put on positive-pressure supplied air or SCBA (over 250 to 300 ppm).

3. Put on Level A suits (over 250 to 5000 ppm).

USING LEL SENSORS FOR MEASURING AMMONIA

Wheatstone bridge LEL sensors (also known as catalytic bead combustible gas sensors) also provide a means of measuring anhydrous ammonia and other hydride gases. LEL sensors are slightly more sensitive to ammonia than to methane. However, LEL sensors still do not have the sensitivity necessary to make toxicity decisions for anhydrous ammonia gas. Finally, hydride gases are a chronic toxin to Wheatstone bridge LEL sensors. So while they provide good initial warnings of very high ammonia levels (~10,000 ppm), their life in these high concentrations is limited to minutes or hours, depending on the concentration of ammonia.

WHAT MEASUREMENT TECHNIQUE DO I USE?

Users of ammonia have a number of techniques available to them for measurement: detector tubes, electrochemical ammonia sensors, PIDs, and LEL sensors. The choice of which technique is the best is driven by the expected ammonia concentration and sometimes the solution is using multiple techniques. For example, the combination of PID with ammonia detector tube is an affordable way of combining inexpensive ammonia specificity (detector tube) with continuous monitoring.

SUGGESTED MEASUREMENT TECHNIQUES

Always 0 to 50 ppm ammonia:

- Ammonia-specific sensor in MultiRAE Plus or ToxiRAE II or RAE Systems Gas Detection tubes

Frequently over 50 to 100 ppm ammonia:

- MultiRAE Plus with PID and ammonia sensor or RAE Systems Gas Detection tubes.

Frequently over 100 ppm ammonia:

- MultiRAE Plus with PID, MiniRAE 2000 PID and ToxiRAE PIDs or RAE Systems Gas Detection Tubes.

RAE SYSTEMS PRODUCTS FOR MEASURING AMMONIA

MultiRAE Plus: The only portable monitor available that offers users the option of applying three complimentary ammonia measurement solutions in one compact monitor: PID, electrochemical ammonia sensor, LEL sensor. The MultiRAE Plus provides accurate real-time monitoring of ammonia so that all PPE decisions can be made:

1. Put on a respirator (over 35 ppm for 15 minutes).

2. Put on an SCBA (over 250 to 300 ppm).

3. Put on Level A suits (over 250 to 5,000 ppm).

4. Evacuate the area (over LEL of ammonia).

The PID detector, in addition to Oxygen, LEL, two toxic gas sensors and internal pump, allows it to accurately measure ammonia in concentrations from TWA through LEL.

- A user-selected response factor in the MultiRAE Plus easily adjusts the PID sensitivity (up to 2,000 ppm) to ammonia.
- The MultiRAE can be configured with an electrochemical ammonia sensor for a low range of ammonia (1 to 50 ppm), PID for a high range of ammonia (50 to 2,000 ppm), and an LEL sensor for explosivity of ammonia (over 15% ammonia).
- A user-selected response factor in the MultiRAE easily adjusts the LEL sensitivity (0 to 100% LEL) to ammonia to provide protection when ammonia concentrations exceed the 2,000 ppm full scale of the PID.

ToxiRAE Plus Pocket PID: An affordable "personal" PID that fits into a shirt pocket, the ToxiRAE PID provides the benefits of PID measurement of ammonia (up to 2000 ppm) in a compact package.

MiniRAE 2000 Professional PID: With a strong internal pump the MiniRAE 2000 is our best PID instrument for pure ammonia leak detection.

ToxiRAE II: A personal ammonia monitor using an electrochemical sensor, the ToxiRAE II provides an affordable solution to those with only low concentrations of ammonia (less than 50 ppm).

RAE Systems Gas Detection Tubes: Colorimetric tubes are an inexpensive way to make spot checks of ammonia concentrations. Colorimetric tubes are also helpful in substantiating PID readings of ammonia.

REFERENCES

OSHA: OSHA Standard Interpretation and Compliance Letter, from Patricia K. Clark, Director, Directorate of Compliance Programs to Mr. Thomas A. Valente, Jr., 10/2/1991.

NIOSH: *Pocket Guide to Chemical Hazards*, NIOSH Publications, Cincinnati, OH 1994

RAE Systems: Correction Factors and Ionization Potentials (Technical Note TN-106)