Instrument Evaluation and Response to Laboratory Scale Ammonia Releases

CSAC 21-0XX

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For

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Science & Technology Directorate

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DISCLAIMER

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorizing documents.

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14. ABSTRACT

Transportation of industrial and agricultural chemicals pose a risk to life and environment in the event of an accidental release. Understanding detection capabilities for identifying and tracking the spill in its various phases (neat chemical, aqueous, vapor, solid, or liquid) is important to respond and mitigate additional risks.

The U.S. Army Combat Capabilities Development Command Chemical Biological Center personnel challenged four classes of instrumentation (gas, colorimetric, liquid, and spectroscopic sensors) that were readily available. These instrumentation were challenged with aqueous ammonia, liquid ammonia, and vapor ammonia. A technical overview, performance, and recommendations for the instrument's capabilities are described.

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Table 1: List of Abbreviations, Acronyms, and Notations

ABBREVIATIONS/ ACRONYMS/ NOTATIONS	DEFINITION
CASTLE	CBRNE Assessment, Science and Technology Lab
CWA	Chemical warfare agent
DEVCOM CBC	U.S. Army Combat Capabilities Command Chemical Biological Center
DHS	Department of Homeland Security
JRIII	Jack Rabbit III
PID	Photo ionization detector
ppm	Parts per million
SWIR	Short wave infrared
UAS	Unmanned aerial system
UGV	Unmanned ground vehicle
VNIR	Visible near infrared

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EXECUTIVE SUMMARY

The U.S. Army Combat Capabilities Development Command Chemical Biological Center (DEVCOM CBC) was tasked with researching and making recommendations on how to quantify and referee releases of anhydrous ammonia (NH_3) for support to the Department of Homeland security and the Jack Rabbit III program. DEVCOM CBC personnel utilized readily available instrumentation and challenged them with liquid, aqueous, and vapor samples containing NH_3.

Four classes of instrumentation were used: gas, colorimetric, liquid, and spectroscopic sensors. Gas sensors (Gasbadge Pro, MultiRAE Light) were challenged by saturating with >10,000 ppm anhydrous ammonia vapor, resulting in a long time to clear the response. These sensors are ideal for lower concentrations and are meant to be worn to notify the user of increasing concentrations of ammonia.

Colorimetric sensors (pH strips, M8 paper) were challenged with aliquots of various concentrations aqueous ammonia and neat anhydrous ammonia. The colorimetric sensors were also submerged in water and challenged by adding neat ammonia to the water. M8 paper responds to liquid ammonia and can still respond while fully submerged in water. pH paper responds to an increase in pH due to the addition of ammonia, is reversible, and does not withstand being submerged in water for extended periods of time.

The liquid sensor tested was a pH meter. The pH meter responded well to the changes resulting from addition of ammonia to the DI water, tap water, and sea water. The pH meter is limited in selectivity and capability due to its response to pH (hydronium ion content in the environment) and can change or be buffered through other competing mechanisms.

Spectroscopic sensors (Co-Aligned VNIR-SWIR hyperspectral line scanner, E8, GF77, and GF306) were challenged with aqueous ammonia, liquid ammonia, or ammonia vapor. The Co-Aligned VNIR-SWIR hyperspectral line scanner was able to spectrally differentiate ammonia hydroxide (30% ammonia) from cleaner (4% ammonia), and water. The E8 thermographic camera is not selective and provides data that is representative of the temperature of materials. The GF77 and GF306 are both more selective the E8 and the GF306 is more selective than the GF77 for ammonia. Both instruments were able to detect liquid ammonia and the plume or vapor formed from ammonia hydroxide and liquid ammonia.

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1.0 INTRODUCTION

The U.S. Army Combat Capabilities Development Command Chemical Biological Center (DEVCOM CBC) was tasked with researching and making recommendations on how to quantify and referee the release of anhydrous ammonia under various environmental conditions. The work took place on Aberdeen Proving Ground in the CBRNE Assessment, Science and Technology Lab (CASTLE) within the Advanced Chemistry Laboratory from February 2021 through Aug 2021. The overarching objectives of this work by CBC were to support the Department of Homeland Security (DHS) and the Jack Rabbit III (JRIII) program which is an extension of previous Jack Rabbit programs[1-2] that focuses on ammonia (NH_3) release.

NH_3 is used for industrial purposes, agriculture, and is a byproduct of human activities, such as driving cars.[3-5] However, ammonia's fate within the environment is complex, and ultimately toxic to plants and animals. For example, the level of ammonia that is immediately dangerous to life or health is 300ppm[6] and the National Research Council defines a lethal acute exposure guideline level that as a 10 minute exposure to 2700 ppm NH_3.[7] Therefore, the ability to sense the presence and the concentration of ammonia is important. Depending on the environmental conditions, ammonia may be present in several forms such as anhydrous (NH_3), or as an ammonium ion (NH_4^+) as well as several other species through chemical processes in the atmosphere or in the soil.[5, 8] Researching and understanding current technologies and their abilities to detect vapor, aerosol, aqueous, or liquid ammonia are the main topics described herein.

NH_3 is naturally in the vapor form in the environment or present as an ion species in aquatic environments. However, since NH_3 is often transported as a liquid, the detection of liquid NH_3 and the phase it takes on after an event that may result in the release of liquid NH_3 needs attention. These processes include rapid evaporation (liquid- vapor detection) and, aqueous detection due to ammonia's extreme solubility into water.[9] As such, detection is based on interaction with either the liquid, aqueous, or the vapor phase of NH_3. The interaction results in molecular NH_3 (or byproduct species) interacting with a photon or light, a circuit, or another molecule resulting in a change being observed. Some of these interactions are discussed in more detail herein.

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2.0 OVERVIEW

In support of the DHS and the JRIII program, DEVCOM CBC utilized instrumentation that was in their possession to better understand methods and techniques to quantify and referee liquid NH_3 releases. An overview of ammonia sensors is also available for a brief description of two main type of sensors employed within industry and their capabilities.[10] The following instruments or techniques were utilized:

- Gas sensors
  - GasBadge Pro
  - MulitRAE Lite
- Colorimetric sensors
  - pH paper
  - M8 paper
- Liquid Sensors
  - Oakton 450 PH
- Spectroscopic Sensors
  - Co-Aligned VNIR-SWIR Hyperspectral Line scanner
  - E8
  - GF77
  - GF306

The sensors were challenged with liquid NH_3, vapor NH_3 or aqueous NH_3 and their responses were noted. While no technique tested herein provides an all-inclusive capability for detecting liquid NH_3, aqueous NH_3 and vapor NH_3, each have their distinct advantages. For vapor/plume visualization, the GF306 is recommended, though it is not quantitative and is semi-selective. The pH meter is most sensitive to changes produced by liquid NH_3, but M8 paper is the in expensive and provides a visual indicator (i.e. no instrumentation necessary).

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3.0 RESULTS

General

Understanding and evaluating NH_3 vapor and the way it interacts with the surroundings is important for characterizing a potential spill or environmental threat. Therefore, CBC personnel evaluated instrumentation and devices that were rapidly available to us to evaluate liquid NH_3, aqueous NH_3, and/or the vapor that is evolved from liquid NH_3. Table 2 summarizes the various instruments that were evaluated in this effort.

Table 2: The class and type of sensors evaluated in this work.

Class	Name/Type	Quantitative (Yes/No)	Phase
Gas Sensors	GasBadge Pro	Yes	Vapor
	MultiRAE Lite	Yes	Vapor
Colorimetric Sensors	pH paper	No	Liquid/vapor
	M8 paper	No	Liquid
Liquid Sensor	Oakton 450 pH	Yes	Liquid
Spectroscopic Sensors	Co-Aligned VNIR-SWIR Hyperspectral Line Scanner	No	Liquid
	FLIR E8	No	Liquid
	FLIR GF77	No	Liquid/vapor
	FLIR GF306	No	Liquid/vapor

Table 2 is divided into four general categories: gas sensors, colorimetric sensors, liquid sensors, and spectroscopic sensors. As a method to rapidly reference these instruments, Table 2 indicates if the technique is quantitative and which phase of ammonia (liquid/aqueous or vapor) the sensor was found to be useful with. Each type of sensor has advantages and disadvantages, especially for field use. These are documented in the following sections.

Methods

The experiments that were completed to test these instruments were done in a laboratory setting and by either generating a vapor through partial and complete evaporation of liquid NH_3, by adding NH_3 to deionized water directly, or by exposing sensor to liquid NH_3. The generation of an NH_3 vapor through complete evaporation of liquid NH_3 was always completed in an environmental control chamber. For this work, the temperature within the environmental chamber was maintained 5°C (± 40%) with a relative humidity (RH) of 75% (± 10%).

Generating liquid NH_3

Liquid NH_3 was generated with an anhydrous ammonia (Prax Air) gas cylinder. The gas cylinder, with an internal educator tube, was connected directly to a jacketed addition funnel without a regulator (to allow the flow of the liquid NH_3). The 25mL jacketed addition funnel (Chemglass), was cooled with an acetone/dry ice bath in the jacket. Dry ice and acetone were added to cover the bottom half of the addition funnel and equilibrated with the funnel for at least two minutes before adding liquid NH_3. The liquid NH_3 in the addition funnel was poured into a small (25mL) beaker that was sitting in shallow acetone/dry ice bath in a Petri dish. The volume was then estimated from the 25mL beaker and used in the experiments.

Generating NH_3 Vapor

Gaseous NH_3 or NH_3 vapor (used interchangeably) was produced two ways. The first way was to put either ammonia hydroxide or liquid NH_3 into a beaker and let the gaseous NH_3 evolve from the liquid. Alternately, vapor was also rapidly produced by pouring the liquid NH_3 directly onto a tray causing a rapid boiling and evaporation of the liquid NH_3.

If vapor was generated by pouring the liquid NH_3 directly out on a tray, this was completed within a chamber inside of a chemical fume hood. A picture of the climate controlled chamber is shown in Figure 1A, with the interior dimensions shown in Figure 1B. Knowing the interior dimensions provides a maximum attainable concentration when liquid NH_3 is poured out within the chamber, and is shown in Figure 1C. In this work, we produced and used less than 20mL of liquid NH_3 in any given trial and therefore all trials were below 50,000ppm.

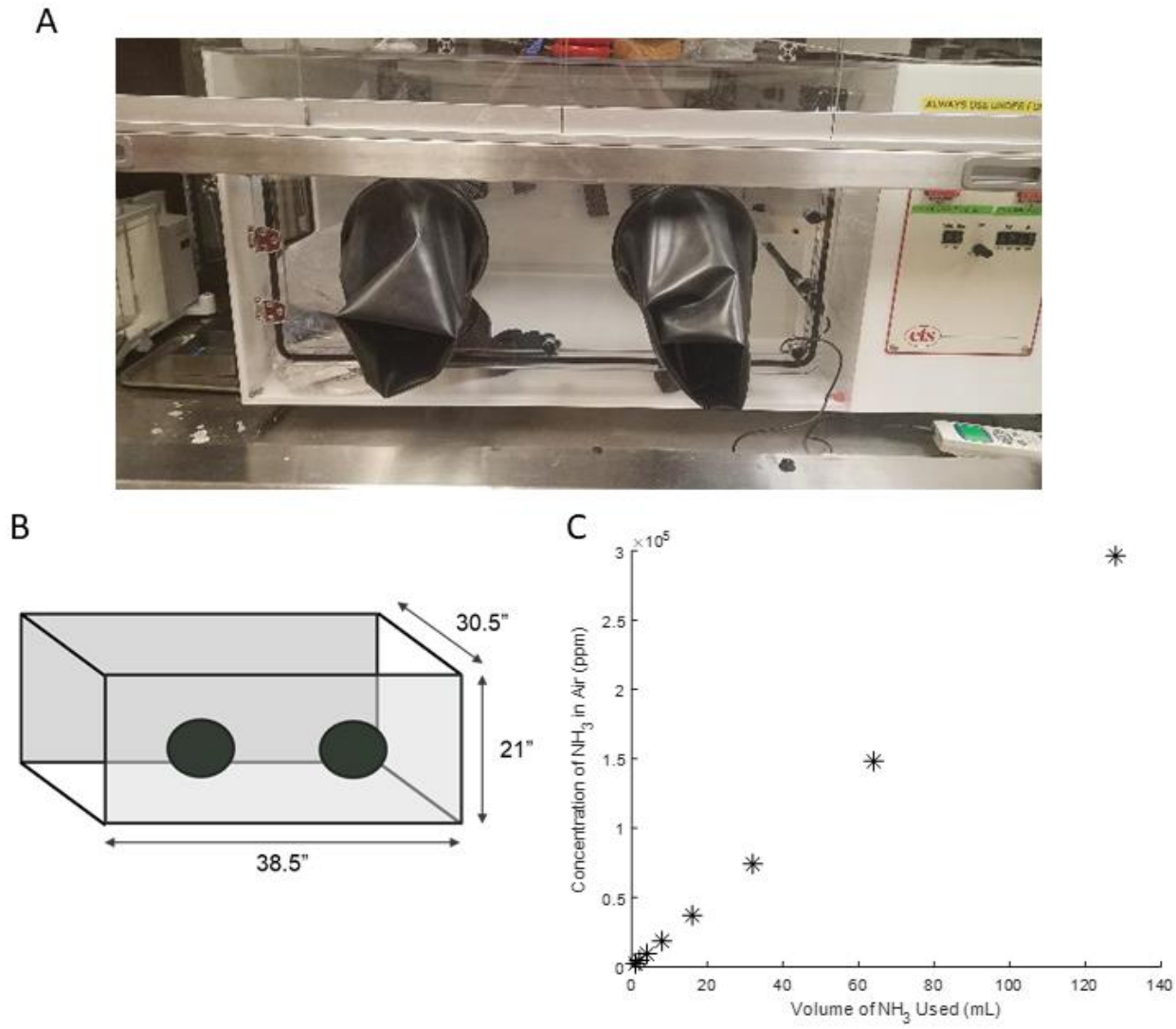

Figure 1: Digital image of environmental control chamber in a chemical fume hood (A), the dimensions of the chamber (B), and the concentration of ammonia (ppm) as a function of liquid ammonia dispensed within the chamber (C).

Gas Sensors

Gas sensors will typically detect a compound in the air through one of two methods: electrochemical and ionization. The electrochemical techniques relay on the electrochemistry of a target molecule binding to a specific material resulting in a known and predictable change in the resistance, voltage, or current after binding.[11] This can often be made very specific for a particular target molecule, and these types of sensors do exist. One disadvantage of these is that they often work as a dosimeter and can be exhausted if exposed to a concentration that is too high or exposure happens too often.[12] Alternatively, a photo ionization detector (PID) works by ionizing a compound, which produces positively charged ions and therefore an electrical current which is measured. A caveat with PIDs is that the target molecule must have an ionization potential that is below the output of the PID. For example, NH_3 has an ionization potential of 10.07eV[13] and a PID lamp that produces 10.6eV will suffice, as was employed in this work.

GasBadge Pro

Technical Overview

The GasBadge Pro (Industrial Scientific, GB60) is a single sensor that uses an electrochemistry based technology. The GasBadge Pro sensor has a range of 0 – 500ppm in 1 ppm increments for NH_3 and can work from -40°C to 60°C in 0% to 99% RH. The instrument is small and lightweight using batteries as the power source making it easy to carry.

Performance

This sensor was initially calibrated and spot-checked with 400ppm anhydrous NH_3. The sensor was subsequently employed for our in-chamber testing. We quickly determined that it responds well to NH_3 vapor, but the amount of NH_3 vapor produced during our work was well beyond the range of the GasBadge Pro. Once the sensor was saturated with a large amount (>10,000ppm) of NH_3, it took minutes for it to clear back down to baseline levels.

Recommendations

The GasBadge Pro would only be recommended for detecting "low" levels of NH_3 (up to the devices manufacturer limits), unlike our target scenario of a larger spill or accident producing large concentrations of NH_3. Alternatively, the GasBadge Pro could be useful for "edge" monitoring or for persistent monitoring in or around a location where the initial plume or cloud of vapor has dispersed.

MultiRAE Lite

Technical Overview

The MultiRAE Lite (Honeywell, PGM-6208) is multi-gas sensor instrument. A chem-resistive NH_3 sensor and a PID sensor are available within the instrument at the same time. The NH_3-specific sensor that is available has a 0 – 100ppm range in 1ppm increments. The PID sensor that is available is a 10.6eV PID can detect up to 10600ppm NH_3 (calculated). The MultiRAE Lite can operate from -20°C to 50°C, in a RH of 0 – 95%, is less than two pounds, and is battery operated making it easy to carry.

Performance

The PID was the only sensor employed because the NH_3 sensor is more likely to wear out quicker with larger concentration of NH_3. The PID was calibrated before use and checked that it worked with 400ppm anhydrous NH_3. The PID was saturated when in the chamber and took minutes to clear out. While the range of the PID is larger, the chamber we used was still contained NH_3 in concentrations larger than what could be handled with the MultiRAE Lite.

Recommendations

The MultiRAE Lite should be used for intermediate concentrations of NH_3 as prescribed by the manufacture. The MultiRAE Lite is more robust than the GasBadge Pro to higher concentrations of vapor, but is not an ideal candidate for spill-type responses. The PID that was installed is the largest range PID offered for the MultiRAE lite and therefore cannot be extended with that particular PID. The MultiRAE Lite is still recommended for carrying with the user if there is a potential for entering an area that could have NH_3 present.

Other Gas-based sensors

Other gas-based sensors could also be employed, though were outside the scope of this work to procure. Other gas-based sensors that could show some potential are:

- MiniRAE (Honeywell)
    - **Advantages:** This unit has a 5000ppm PID that can be purchased which results in a range that is suitable when the correction factor for NH_3 is employed.[14]
    - **Disadvantages:** The sensor will only clear as quickly as the pump can pull in clean air and takes time to clear out to a baseline level, even if clean air is present.
- GG-NH3-2% (Calibration Technologies Inc.)
    - **Advantages:** Can detect vapor or atmosphere containing 2% NH_3, which is equivalent to 20,000ppm.
    - **Disadvantages:** These technologies are industry-based and require networking and infrastructure to maintain.
- Solid sorbent method – carbon beads impregnated with sulfuric acid (CISA)[15-16]
    - **Advantages**: Analytical technique that is not easily saturated
    - **Disadvantages**: Not rapid – requires analysis with gas chromatography after sample is pulled from the air.

Colorimetric Sensors

Colorimetric sensors respond to a target analyte via a color change. The most ubiquitous example of this would be pH paper. The color-changing property is typically caused by either acid-base chemistry, or a reaction that causes a physical change of the molecule (typically a reduction-oxidation reaction). Specificity can be accomplished through certain types of coatings or technology used to exclude potential interferent. For example, M8 paper is a paper-based color-changing technology for identifying chemical agents on surfaces. The surface of the M8 paper is hydrophobic whereas the dyes that are imbedded in the paper preferentially interact with chemical warfare agents, causing a visible color change.

pH Paper

Technical Overview

The pH paper that was used were individual strips (VWR, BDH-35309.606) measuring from 0-14 pH units with a sensitivity of 1.0 pH units. The pH strip has several indicators on it which respond to various levels of pH, dependent on the acid/base chemistry that occurs with the indicator. When the pH paper is immersed in a liquid, the indicator may go through one or more reduction or oxidation reactions resulting in a colorimetric change thereby producing a color change on the strip.

Performance

The pH paper responded well to liquid NH_3 in both the neat form or aqueous. Figure 2 shows the pH paper (above the yellow M8 paper) in time series images that show the response to the pH paper to 4% NH_3 (right most pH strip on top of M8 paper), 30% NH_3 (middle pH strip on top of M8 paper), and neat liquid NH_3 (left most pH strip on top of M8 paper). The pH strips that flank the M8 paper are there for visual controls of the pH paper. The challenged pH strips show a clear response to liquid NH_3 and aqueous NH_3, which is likely NH_4^+. Each color on the pH strip becomes darker, especially with the aqueous aliquots, and to a lesser extent with the liquid NH_3. At the 109 minute time point, the 30% NH_3 shows the pH strip returning back to the original colors whereas the 4% NH_3 still appears wetted and not back to the original color. The liquid NH_3 rapidly boiled off and appears to have permanently changed the pH strip as it is no longer present long before the other two solutions shows signs of evaporation.

For response to NH_3 being poured directly into DI water, which simulates a spill or release into a body of water, Figure 3 shows the time series for the pH strips up to 98 minutes. 5-10 mL of liquid NH_3 was poured directly into the beaker with M8 paper and pH paper submerged. At the 0 minute time point, the top of the M8 paper is green, indicating the liquid NH_3 was poured and spattered onto the surface of the M8 paper, however no color change is seen on either the pH paper or the M8 paper (for reference). As the time progresses, the blue color becomes more vibrant (see the 10 minute time point as an example) as indicated by the 3rd test block from the top of the pH strip, as oriented in the beaker. This is expected as the liquid NH_3 rapidly forms NH_4^+ in aqueous solutions, increasing the pH.[9] At the 98 minute time point, a discoloration of the water can be seen, which is due to the pH strip leaching the dye into the water.

Additional work was completed within the chamber whereby pH paper was placed within a Petri dish, weighted with a small washer and submerged under approximately ¼ inch water. Liquid NH_3 was placed within the chamber and the total liquid NH_3 was evaporated to completion to produce >12,000ppm NH_3 in the chamber. The pH paper responded to the change in the water composition due to the absorption of NH_3 into the water resulting in an increase in pH. This data is not shown, but was observed empirically.

Recommendations

pH paper is reactive to liquid NH_3 or to water that has been exposed to liquid NH_3 either through absorption of vapor NH_3 into the water or through mixing liquid NH_3 with water. However, pH paper is not selective to NH_3. The pH strip responds to anything causing the pH to increase in the environment in which the pH strip is situated. While pH paper is inexpensive, light weight, and non-powered, the lack of selectivity makes this method of sensing NH_3 not effective. Furthermore, since the dyes are leached out of the pH strip when exposed to water for an extended period of time, these could not be placed and monitored for a color change.

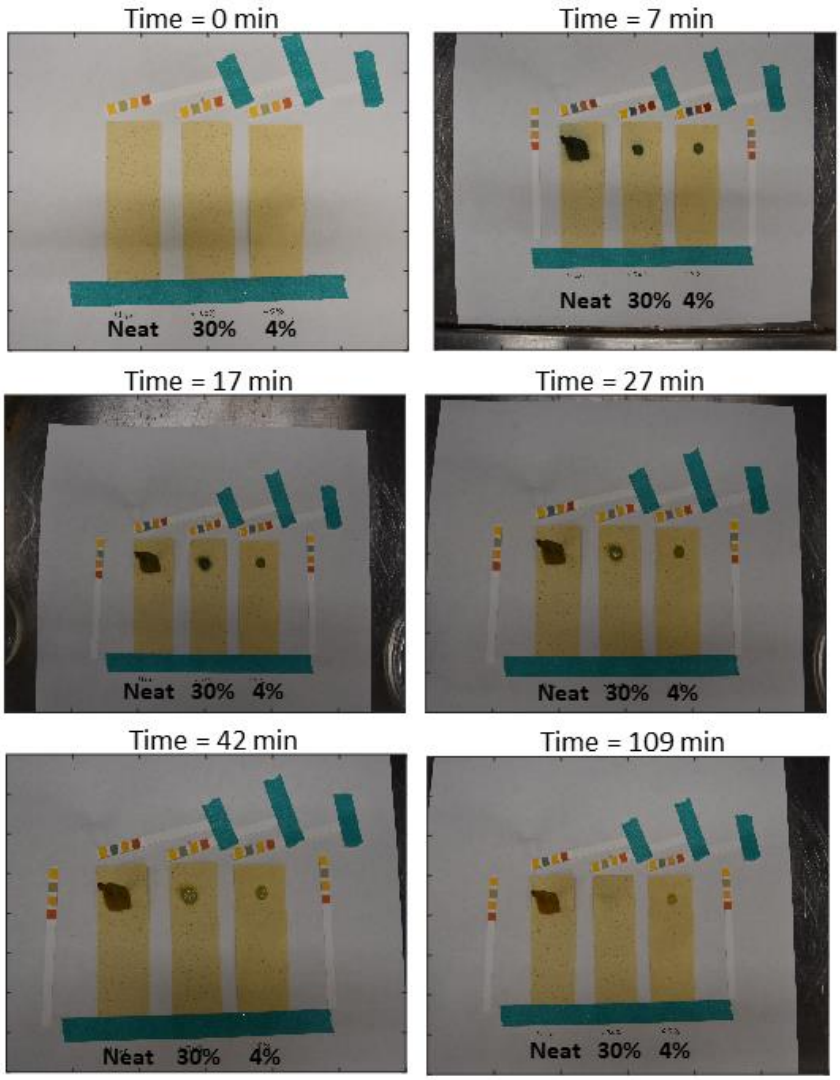

Figure 2: pH strips and M8 paper response to 4% ammonia (ammonia-based cleaner), 30% ammonia (ammonia hydroxide), and neat liquid ammonia over nearly two hours.

M8 Paper

Technical Overview

M8 paper is a paper-based colorimetric technology that changes when exposed to chemical warfare agents (CWAs). The paper is chemically treated and is impregnated with two dyes and an acid-base indicator which reacts to chemical agent.[17] The beige paper responds to liquid CWA by turning yellow or green in the presence of nerve agents and turns red in the presents of blister agents.[17] M8 paper has a hydrophobic coating allowing it to be fully submerged in water without the release of the impregnated dyes.

Performance

M8 paper produces a rapid change in color when exposed to liquid NH_3 or to NH_3/NH_4^+ in water. The tan/yellow M8 paper changes to a very dark green, which is traditionally indicative of V-type nerve agents. In Figure 2, the M8 papers are the long tan/yellow sheets of paper where, at the seven minute time interval, three spots can be clearly seen. The lower concentrations of NH_3 produces a slower change to

dark green, which can be seen in reverse as the middle M8 paper has the ammonia hydroxide evaporating off the surface, producing nearly reversible change with the paper.

At the 109 minute time interval, the liquid NH_3 (left most M8 paper in Figure 2), the spotted material changes from a dark green/black to a reddish-brown once fully evaporated. This was shown to last through at least 24 hours (no effort was made to preserve the M8 paper past 24 hours). This is in contrast to the 4% NH_3 spot on the right-most M8 paper in (Figure 2) as there was still liquid present at 109 minutes, but the green color had mostly faded away. This may be due to stabilizers or surfactants used in the solution of the 4% NH_3. If the spot is still wetted, but the color is fading, this is indicative of NH_3 evaporating preferentially compared to the surrounding water.

When submerged fully in water, as shown by Figure 3, there is no color change. It is only when NH_3 or NH_4^+ interacts with the M8 paper that there is a color change. In fact, from time point 0 min to 10 minutes, the diffusion of the NH_3 in the water can be seen as it progresses down the M8 paper. Interestingly, the liquid NH_3 that spattered off the surface of the water and hit the M8 paper above the surface of the water turned the M8 paper dark green/black instantly. M8 paper changing due to NH_3 in water was further validated when the M8 paper was fully submerged in a Petri dish and placed in an environment of >12,000ppm NH_3. The edge of the M8 paper that was closest to the surface of the water began changing to a green color quicker than the remainder of the M8 paper that was submerged deeper in the water. This is indicative of the vapor NH_3 absorbing into the water and causing the M8 paper to change.

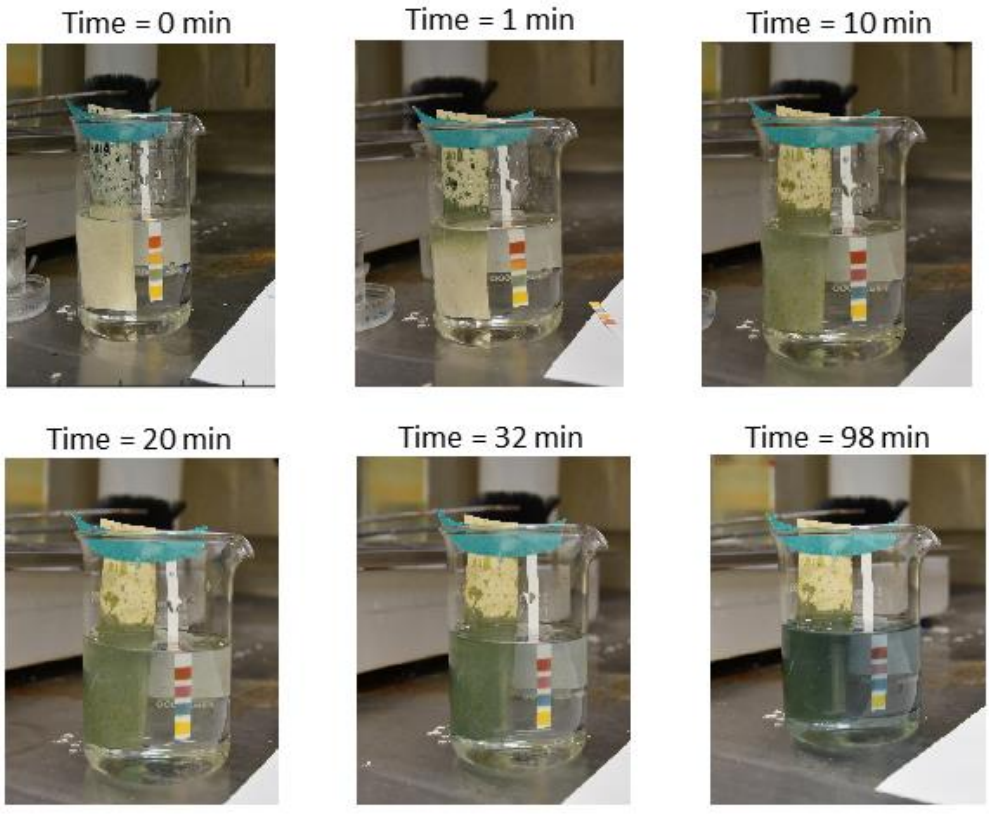

Figure 3: pH and M8 paper submerged in water and time-lapsed to show effect of the addition of neat liquid ammonia.

Recommendations

M8 paper is an inexpensive, lightweight, and easy-to-use colorimetric indicator. There may be greater selectivity than that of pH paper, but there are other compounds that change the color of pH paper (including more lethal compounds than NH_3). No color change due to vapor was observed, however color change due to liquid NH_3 spattering on it or NH_3/NH_4^+ in water was readily observed. This colorimetric paper would be best suited to be set up in advance, but the placement and monitoring of this paper for an unknown event at an unknown location at an unknown time would likely be logistically formidable.

The M8 paper could be placed on dry land or in an aquatic environment since they are hydrophobic. We have empirically observed M8 paper submerged in water over the course of days without any visual indication of water disrupting the capability of the M8 paper. Therefore, due to the low cost, M8 paper could be deployed as a visual indicator in an aquatic environment as an indicator of NH_3/NH_4^+ presence. However, to validate the selectivity in a non-controlled water source, additional research must be completed to fully understand and limit responses to false positives.

Liquid Sensors

Liquid sensors are sensors that respond to an analyte in an aqueous system. Therefore, the resulting sensors must respond to change in the ionic content which in this report is produced through the addition of liquid NH_3 into DI water or sea water. The most common liquid ion sensor is a pH meter, which responds to the amount of hydronium ion present in an aqueous environment. Generally, atmospheric waters are acidic, favoring NH_4^+ thereby increasing OH^- and increasing the pH.[9] However, naturally occurring waters, especially sea waters, are more basic and buffered thereby resulting in an equilibrium ($NH_3{\cdot}H_2O \leftrightharpoons NH_4^+{}_{(aq)}+OH^-$) producing more $NH_3{\cdot}H_2O$ complexes.[9, 18-19] Therefore, instrumentation that can measure pH and ion content are both important to use.

pH Meter

Technical Overview

The pH meter (Oakton pH 450, Oakton Instruments) measures the potential difference (mV) between two probes in the sensor when submerged in a liquid. This is most often calibrated for and read out as the pH of the solution. As the pH of the solution changes, the potential difference changes as more (or less) of the hydronium ion is available. Since NH_3 rapidly protonates to NH_4^+ in an aqueous solution, the availability of the hydronium ion and therefore the change in ions due to NH_4^+ present can be determined. The pH meter can measure ±2000mV with a resolution of 0.1mV – 1mV, operating in temperature ranges from -10°C to 100°C and has a weight of approximately one pound.

Performance

The pH meter employed responded well to the challenge of NH_3 present to it. In the initial studies, the pH meter was placed in a beaker with ~50mL of either DI or standard seawater (Sigma-Aldrich, S9148-1L). 10 mL of liquid $NH_3$was poured into the beaker while the instrument was recording to observe the change in the mV. The set-up is shown in Figure 4A. Figure 4B is the potential difference changing as a function of time when the liquid NH_3 was poured into the beaker. There is a clear indication of when the liquid NH_3 was poured into the beaker as shown by a nearly 100% change in the mV reading. Similar to the DI water, standard seawater was used to better understand how the pH meter behaves in a more naturally buffered aqueous environment. In Figure 4C, the potential difference changing as a function of time is shown clearly in the data when the liquid NH_3 was poured directly into the beaker at the one-minute mark. The liquid NH_3 being poured into the seawater resulted in about a 33% change in mV.

These data validate the functionality of using the pH meter as a measure of liquid NH_3 added to an aqueous environment but in no way quantitates an expected outcome. When the liquid NH_3 was poured into the beaker, there is a violent reaction resulting in an uncontrolled spattering of liquid NH_3 and water. Therefore, while 10mL liquid NH_3 was poured into the beaker, we are unsure of how much liquid NH_3 actually entered the water.

Multiple sensors can be employed for a better spatiotemporal understanding of a particular environment. Figure 5A is the operational set-up for this experiment whereby two pH meters were placed in a 20" x 4" stainless steel tray approximately 7" from each other as shown in figure. The tray was filled with 1L of DI water. A custom program was written to synchronize and simultaneously collect the mV readings from the two instruments (MATLAB R2017b, Mathworks) via a serial connection to a computer. After baseline readings were captured, 10-15mL liquid NH_3 was poured into the tray and data were recorded for approximately seven more minutes.

Figure 5B shows the data collected when multiple sensors were employed. Instrument 1 (black points, Figure 5B; left-most sensor in Figure 5A) was closest to where the liquid NH_3 was poured into the tray and shows a more rapid response to the diffusion of the liquid NH_3 into the water. As expected, instrument 2 (red points, Figure 5B); right-most sensors in Figure 5A) takes longer to respond to the addition of the liquid NH_3, but equilibrates to the same readings as instrument 1. Both instruments follow the same pattern whereby once OH^- ions reach the sensor, the mV reading begins to decrease until there is an equilibrium reached. An additional trail was completed (data not shown), and has similar results showing both readings beginning and ending at approximately the same readings. The additional trail was more erratic, likely due to increased spattering resulting in faster diffusion from multiple points in which the liquid NH_3 entered the water.

Recommendations

The pH meter tested works well for sensing when liquid NH_3 was introduced into a water-based environment. The pH meter senses a change in the potential difference due to a change in the hydronium ion. In aquatic systems that are highly buffered, this may not work as well. In potential situations such as a tanker that spills large volumes of liquid NH_3 into aquatic systems, this type of measurements would likely do well in sensing changes as a large volume of liquid NH_3 would likely cause a significant change in the potential difference, even in a buffered environment. A system measuring the potential difference would need to be placed in advance of an event, and therefore key locations would need to be identified, outfitted with the instruments, and set to record indefinitely.

Employing a device such as a pH meter that measures the potential difference of the water-based environment will sense *any* change in potential difference. Therefore, the sensor is not selective to NH_3 influencing the aquatic equilibrium. Decreased selectivity may not necessarily be a negative characteristic of the instrumentation if the intent is to monitor for an event, *not necessarily NH_3 only*.

In addition to an instrument such as the pH meter, different models of pH meters and some standalone instrumentation provide the capability to measure the electrical conductivity (EC). The EC of a system changes with respect to any change in ion content that can carry electric charge, such as NH_4^+, which is rapidly formed when liquid NH_3 enters water. Furthermore, there is a known relationship between the EC and the concentration of NH_3 in an aqueous environment at different temperatures.[20] Therefore, additional research should be carried out to understand the use of EC or combination of pH meter and EC for deployment in an event.

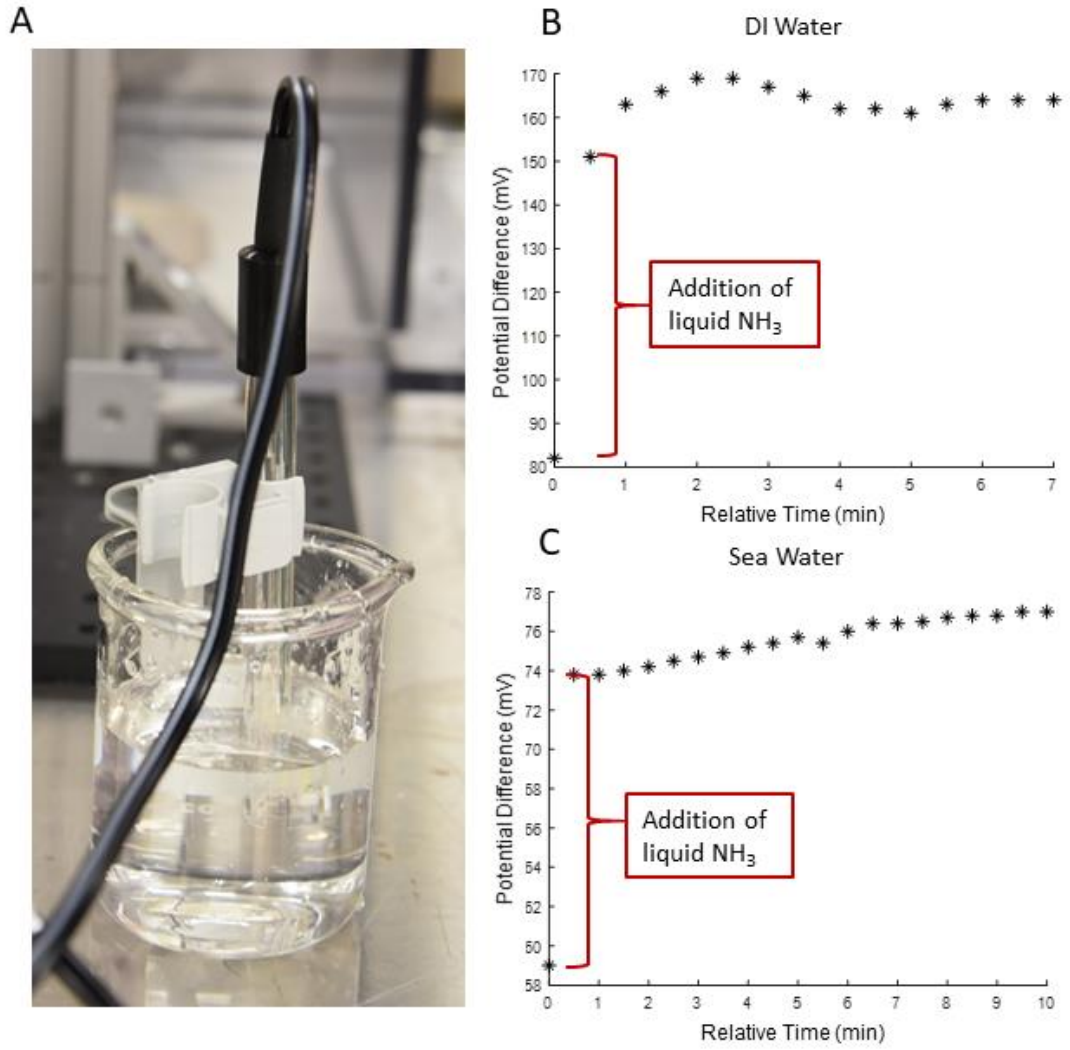

Figure 4: Experimental set up for use of a pH meter in a beaker (A) and the addition of liquid ammonia in DI water (B) or sea water (C).

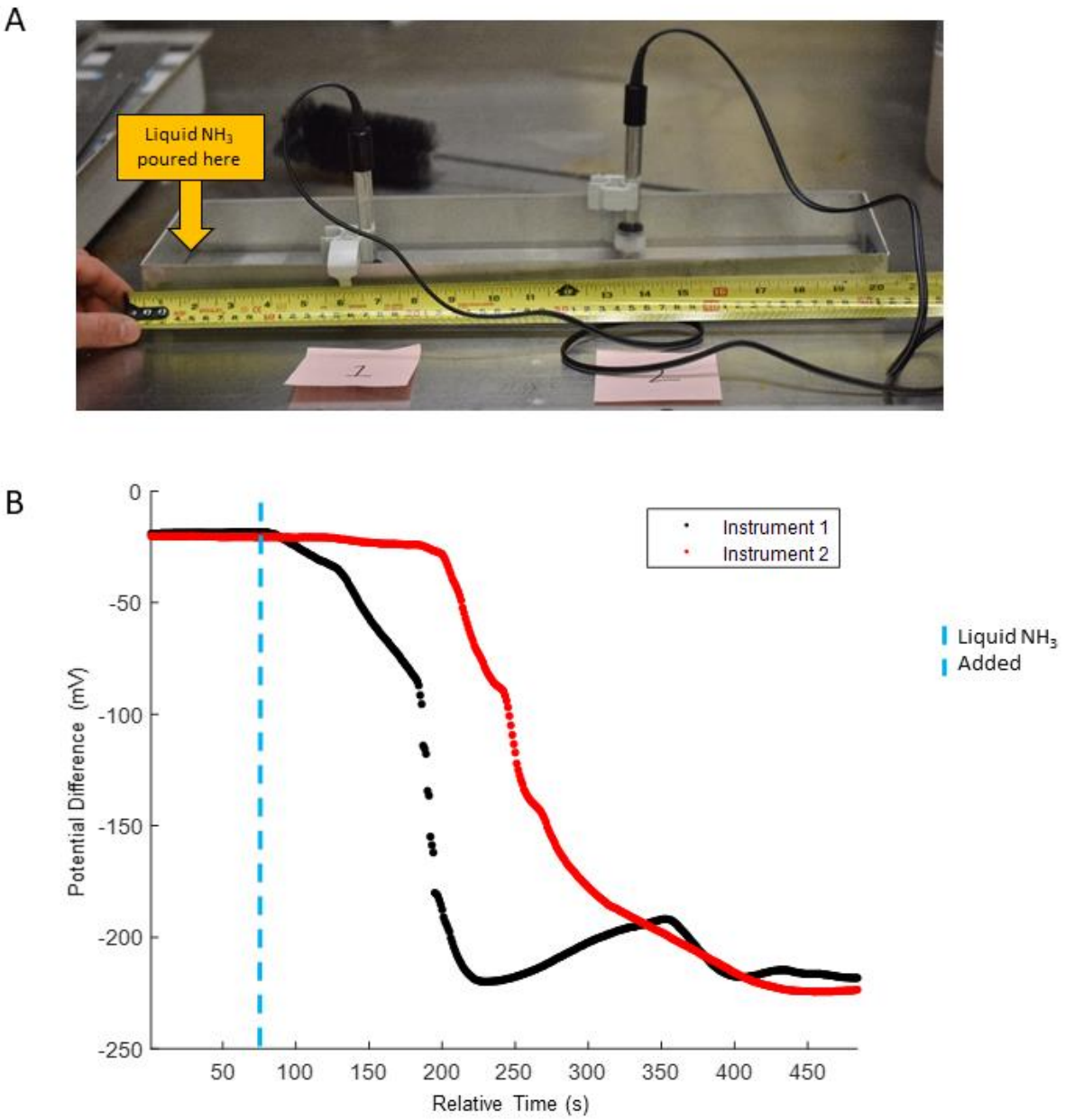

Figure 5: Multiple pH meters employed to map the flow of liquid ammonia through water from where the liquid ammonia was poured into the tray (A) and progressing past pH instrument 1 to pH instrument 2. The time-series data clearly show the liquid ammonia affecting change in the read-out of the pH meter from pH instrument 1 (black points) prior to affecting change in the read-out from pH instrument 2 (red points) after the liquid ammonia was added (blue dashed line) (B).

Spectroscopic Sensors

Spectroscopic sensors respond to a stimulus from the electromagnetic spectrum. These stimuli can be produced by various mechanisms such as reflected visual light or thermal emission. Different sensors are employed for different portions of the electromagnetic spectrum. In this report, sensors are employed that span the visible through shortwave infrared and the mid through long range infrared regions.

Headwall Co-Aligned VNIR-SWIR

Technical Overview

The Co-Aligned VNIR-SWIR hyperspectral line scanner (Headwall Photonics, MA) is a combination of two hyperspectral spectrometers that rely on reflected light from a material to understand a chemical's absorption bands. The spectrometers span a range of 400nm – 2500nm resulting in the ability to sense absorption bands within that region. The Co-Aligned VNIR-SWIR instrument is a commercially available UAV-mountable instrument that often uses solar illumination to capture the reflected light from surfaces. The relative absorption bands of NH_3 or NH_4^+ are 1033nm, 1538nm, and 2008nm which are related to the vibrations of N-H bonds.[21]

Performance

Four samples where illuminated and their reflected light was captured with the Co-Aligned VNIR-SWIR instrument. The four samples were contained in four different Petri dishes and were a blank, water, ammonia-based cleaner, and ammonia hydroxide which resulted in concentrations of 0% NH_3/NH_4^+, ~4% NH_3/NH_4^+, and ~30% NH_3/NH_4^+. This is shown in Figure 6A where the green box is the blank (an empty Petri dish), the blue box is the water, the yellow box is the ammonia-based cleaner, and the red box is the ammonia hydroxide. The locations of the materials are the same in Figure 6B and Figure 6C. This work was completed prior to receiving the liquid NH_3 and therefore does not have liquid NH_3 as one of the components in the test.

Figure 6A is a white-light digital image to show that there is visually no difference between any of the Petri dishes and to differentiate between them a sensor of some capacity is required. Figure 6B is a composite RGB image from the hyperspectral line scanner from the VNIR (400nm – 1000nm). The VNIR spectral data does not have any differentiating absorption bands within it (spectra not shown). That is why each of the four Petri dishes visually appear the same with the selected composite spectral bands. Figure 6C does show visually different Petri dishes from the blank, and the ammonia hydroxide petri dish is different from the water and ammonia-based cleaner Petri dishes in the SWIR (900nm – 2500nm).

The data in Figure 6D clearly show the spectral differences between the contents of the Petri dishes. The spectra in Figure 6D were derived by the average spectral content within each of the individual Petri dishes. The blank (top-most spectrum in Figure 6D) has no material in the Petri dish. The resulting spectrum is very similar to that of background that the Petri dish is sitting on top of (data not shown). The water spectrum (second from the top in Figure 6D) is the expected spectrum as water has absorption bands between 1400nm – 1500nm and from 1800nm – 2100nm,[22-23] which are where the major differences between the blank and water spectra are. The water and the 4% NH_3 spectra (second from the top and third from the top of Figure 6D, respectively) are very similar indicating that the ammonia-based cleaner is mostly water. The ammonia hydroxide (30% NH_3/NH_4^+, bottom spectrum in Figure 6D) shows clear absorption lines at 1037nm, 1223nm, and 1301nm and aligns well with what is reported in the literature for vibrational bands of NH_4^+.[24] Therefore, we are confident that the differences in the spectral content in Figure 6D is explicated due to the presence of NH_4^+, which is the main component of aqueous NH_3.

Recommendations

The instrumentation the data was obtained with can be mounted on a UAS or UGV and is relatively lightweight. The data must be analyzed post-acquisition, and therefore cannot provide real-time feedback. While this is not necessarily "man portable", the instrument is rapidly deployable in the event that it is needed. Further investigation is recommended for differentiation between aqueous NH_3 and liquid NH_3. Additional research would also be required to validate use of this instrumentation in the field at a natural

aquatic environment. The rapid deployment of the instrument in the event that it is needed followed by the post processing can provide temporal information of NH_3 in an aquatic environment or boundaries to affected areas.

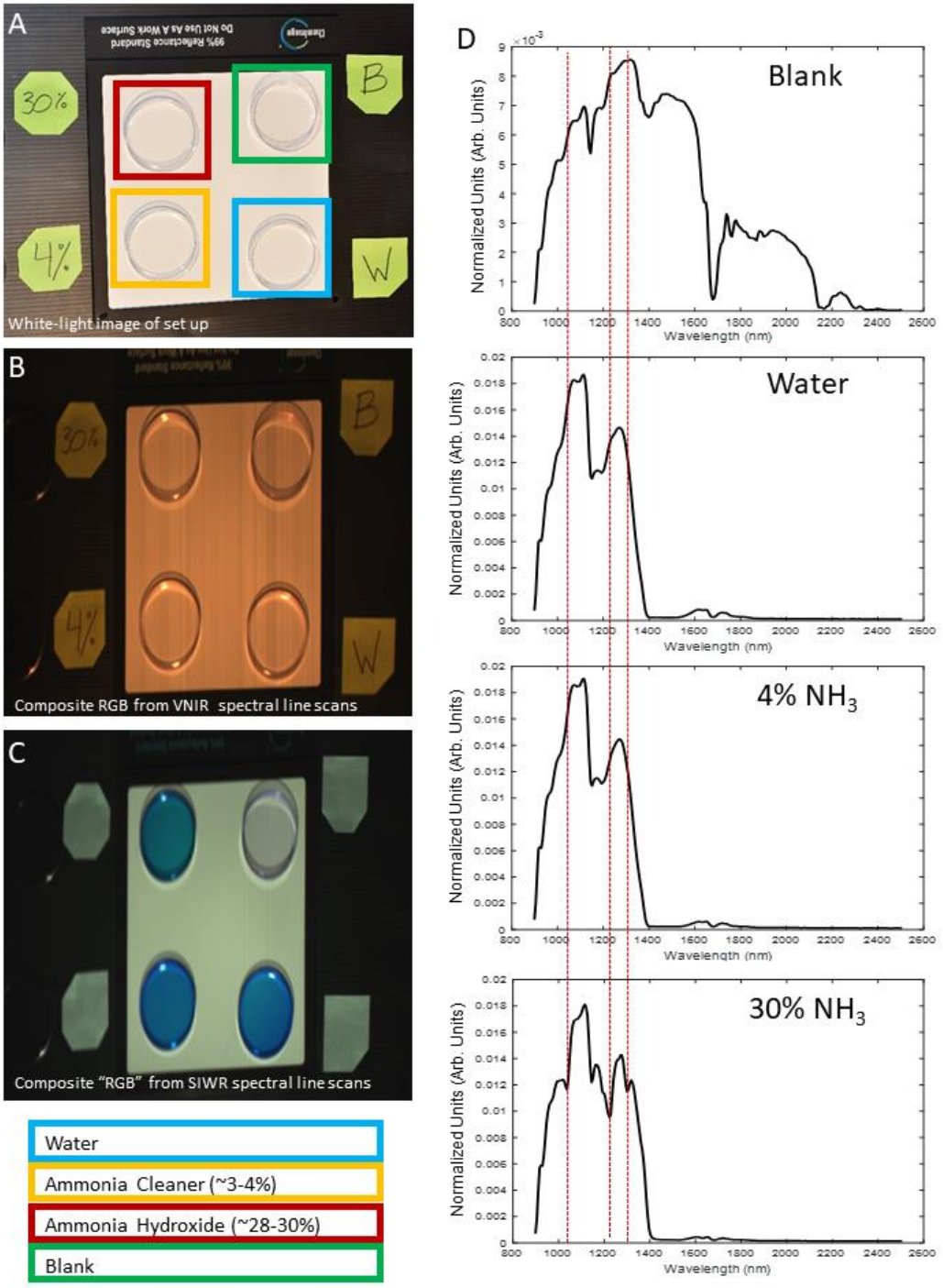

Figure 6: White light image of four Petri dishes on a 99% reflective surface filled with nothing (blank, green box), water (blue box), ammonia-based cleaner (orange box), and ammonia hydroxide (red box) (A) and the corresponding composite VNIR (B) and SWIR (C) images. The average spectral intensities within the center of the Petri dishes (D) and the highlighted absorption bands that are unique to ammonia hydroxide (red-dashed lines).

FLIR E8

Technical Overview

The FLIR E8 (referred to as the E8; FLIR Systems, USA) is a thermographic camera that provides chemical inference based on temperature differences. The infrared bands that are reflected (7.5µm - 13µm) to the E8 are not selective as the camera uses all the IR bands that it is capable of using to create the thermographic image. The E8 provides a 320 x 240 pixel image with temperature measurement range of -20°C to +250°C. The total weight of the E8 is 1.27lb.

Performance

The performance of the E8 is limited in scope as it is only thermographic and not selective for NH_3. Liquid NH_3 is colder than the minimum temperature measurements range on the E8 and is therefore not suitable for the differentiation of liquid NH_3 with respect to other evaporative or endothermic processes within an environment.

The E8 was tested in conjunction with the Co-Aligned VNIR-SWIR hyperspectral line scanner described in the previous section. Figure 7A shows a white-light image of the test set-up with a blank (green; top right corner of Figure 7A), water (blue; top left corner of Figure 7A), ammonia cleaner (yellow; bottom right corner of Figure 7A), and ammonia hydroxide (red; bottom left corner of Figure 7A). The liquids were contained within the Petri dishes. Figure 7B shows the thermographic image of the test set up with the area illuminated with a stage light, which was necessary for testing the Co-Aligned VNIR-SWIR system. This resulted in a large temperature gradient (45.5°C to 8.4°C) and some key observations are that the ammonia hydroxide (30% aqueous NH_3) is cold (near the lower limit of 8.4°C) which is partially due to the fact that it is kept at 5°C storage. This is contrasted to the ammonia hydroxide appearing warmer (15.4°C) in Figure 7C, after about 20 minutes of warming under the light.

Recommendations

The E8 is not recommended for characteristically differentiating liquid NH_3 from other areas. Since the E8 is a thermographic technique with the lower range of -20°C, there will be no ability to differentiate between where the liquid NH_3 is and where it *was* as the liquid NH_3 necessarily cools the material it is touching. While this is an inexpensive, lightweight device, this instrument cannot selectively identify liquid NH_3 or a system that has NH_3 in it. It can, however, identify colder areas, which may be useful in the event of a large spill from NH_3 as the NH_3 will rapidly cool what has touched or is touching.

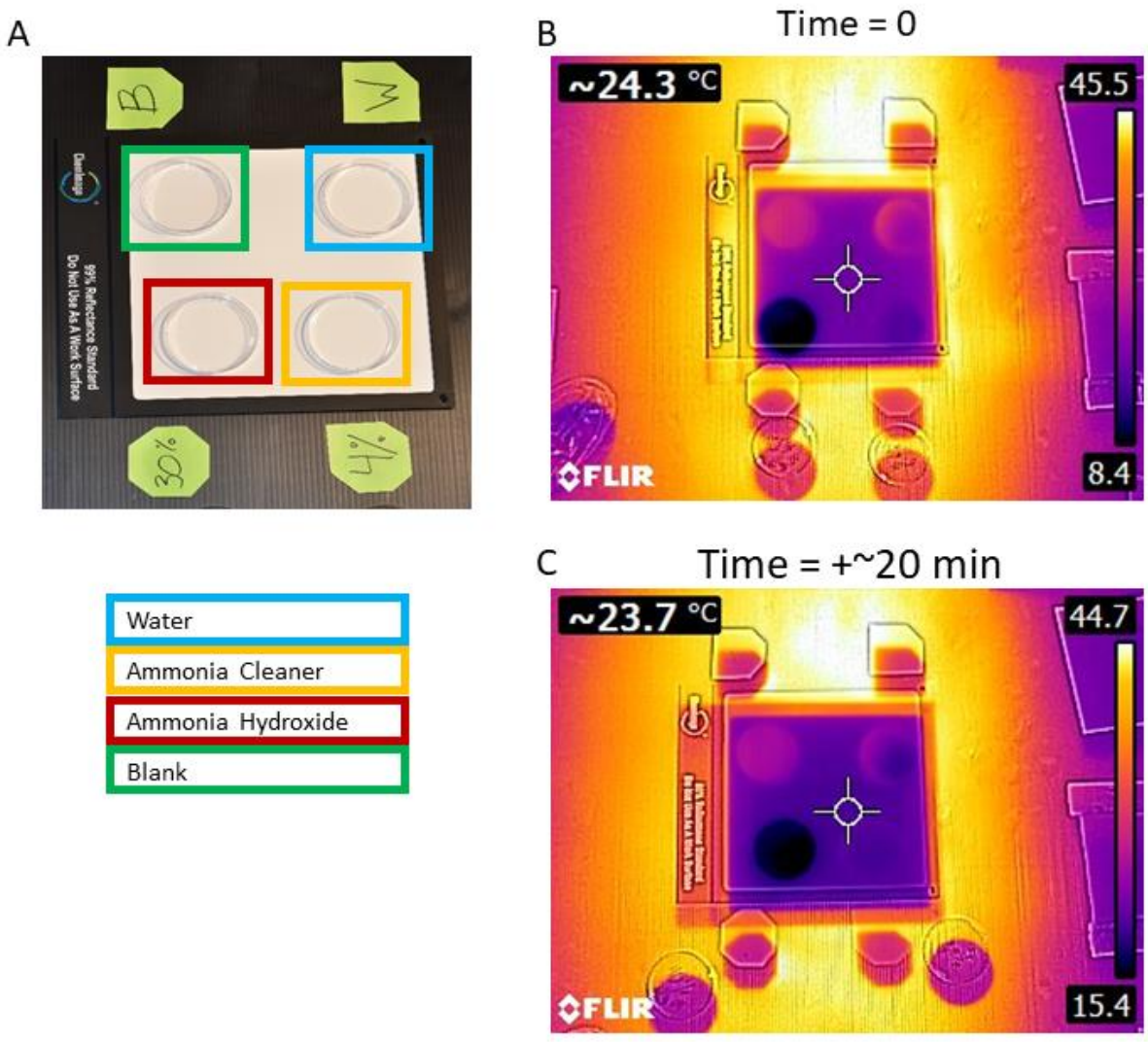

Figure 7: A white light image of four Petri dishes with nothing in it (green box), water (blue box), ammonia-based cleaner (orange box), and ammonia hydroxide (red box) (A) and corresponding thermographic images at zero minutes after addition of liquids (B) and after approximately 20 minutes while illuminated with a stage light (C).

FLIR GF77

Technical Overview

The FLIR GF77 (referred to as the GF77; FLIR Systems, USA), is an infrared detector with two lens options. The 25° HR 9.5 - 12µm lens was chosen as the manufacturer specifies sensitivity to NH_3 at > 20 ppm. This system is semi-specific as it can detect multiple gases that have absorption profiles within the range of the lens. The GF77 is lightweight (3.4 lbs.) and can operate from -15°C to 50°C.

Performance

The GF77 responded to fumes produced from ammonia hydroxide and liquid ammonia. Ammonia hydroxide was placed in a beaker (~30-50mL) and placed inside of a chemical fume hood. The GF77 was hand-held in place monitoring the beaker. A plume from the fumes could be seen, as shown in a still frame from a video, in Figure 8A. A different beaker was used to add liquid NH_3 to it and the plume

could also be seen, as shown in Figure 8B. The dynamic range of the GF77 makes it difficult to detect the fumes (i.e. plume) from the ammonia hydroxide and the liquid NH_3 *at the same time*. However, the GF77 performed well in visualizing the plumes from either individually. When adding the liquid NH_3 (not pictured) there were clear large plumes of NH_3 emanating from the mouth of the beaker. It is clear from the full video that the GF77 could detect large amounts of vapor with relative ease in a laboratory setting.

In addition to detecting plumes from beakers, liquid NH_3 was poured directly onto a 2" x 2" concrete coupon. The plume and the bulk liquid could be visualized in/on the concrete coupon, as shown in Figure 8C. The darker area indicated by "Liquid NH_3" on Figure 8C is the liquid NH_3 in/on the concrete coupon, and can be visualized decreasing in the video by the dark area decreasing in size over approximately 30 seconds. The porous structure of concrete allows the liquid NH_3 to intercalate and become entrapped within the micro structures of the concrete. There is rapid evaporation within the first couple seconds, but as the concrete cools due to the liquid NH_3, the evaporation from the interior will be slower. This is partially seen as the majority of the concrete becomes dark from the liquid NH_3, and then the dark area recedes from the bottom up and maintains a layer towards the top of the concrete coupon.

Recommendations

The GF77 is a relatively inexpensive instrument to visualize liquid and gaseous NH_3 in a semi-selective capacity. According to the manufacture, the GF77 detects sulfur hexafluoride, ammonia, and ethylene gases, though these are just the major manufacturing gases that can be detected in the 9.5µm - 12µm range and should not be confused as an exclusive list of detectable liquids and gases. This instrument could be valuable in determining where a gaseous plume of NH_3 is located and/or where liquid NH_3 has spilled and is still off-gassing on the ground. Further testing would be required to better understand liquid NH_3 entrapment within different media (i.e. concrete coupons, soil, gravel, etc.) and the ability for the instrument to selectively detect NH_3 in a real-world event.

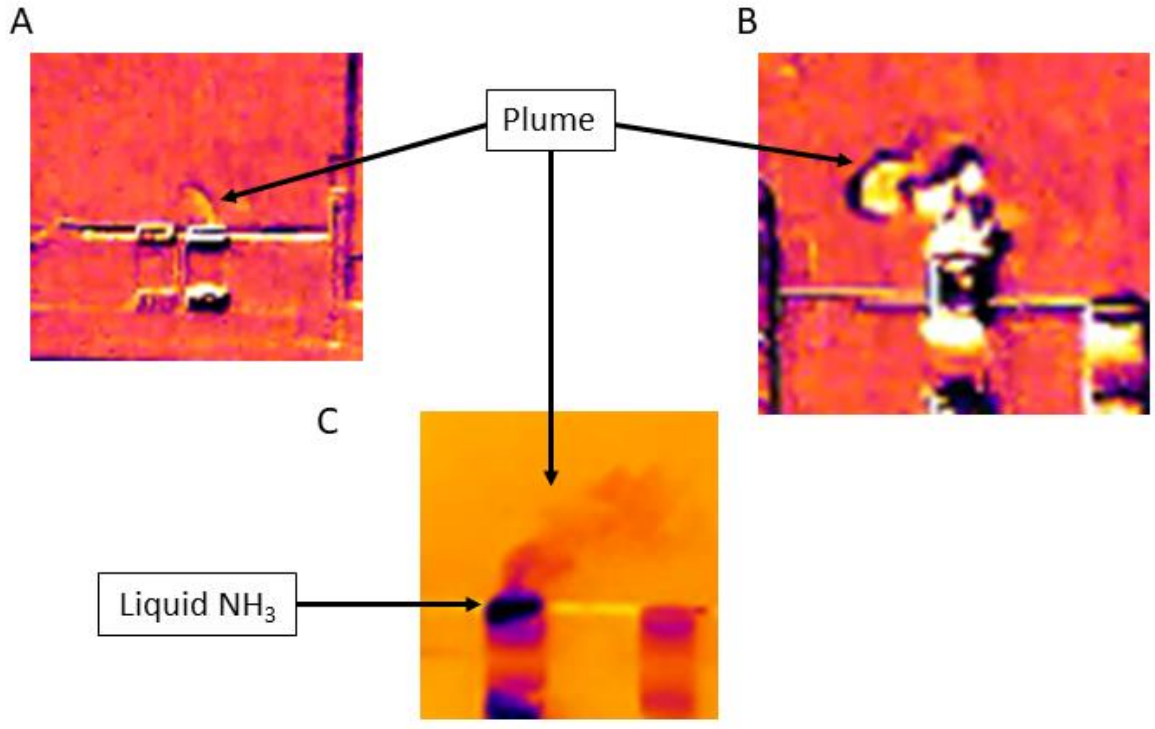

Figure 8: Plumes generated by ammonia hydroxide in a beaker (A), a beaker containing liquid ammonia (B), and liquid ammonia after it was poured directly onto a concrete coupon (C) with the GF77.

FLIR GF306

Technical Overview

The FLIR GF306 (referred to as the GF306; FLIR Systems, USA) is an infrared detector that has a single lens that is cooled along with the detector. The field of view of the GF306 is 14.5° x 10.8° and can be easily used at 10 or more meters away. The GF306 detects in the 10.3µm – 10.7µm range, which makes this detector more selective than the GF77. The GF306 is 5.47lbs, can be operated -20°C to 40°C, and is easily mounted on a tripod. The GF306 can also be utilized in a high sensitivity mode which uses image processing techniques to improve the sensitivity of the measurements.

Performance

The GF306 provides both normal sensitivity and high sensitivity modes. Utilizing the normal sensitivity mode makes identifying large plumes of vapor or liquid easy. The data presented in Figure 9 are from the high sensitivity mode, and the lower concentrations of gaseous NH_3 is easily seen. The GF306 was challenged against fumes/vapor from ammonia hydroxide and liquid NH_3 in a chemical fume hood. The ammonia hydroxide was placed in a beaker (~30-50mL) with the GF306 monitoring from approximately 3m away on a tripod. Figure 9A clearly shows a plume above and surrounding the mouth of the beaker. Figure 9B shows the vapor/fumes above the beaker with liquid NH_3 present, indicating that the GF306 can detect vapor from liquid NH_3 as well. When adding the liquid NH_3 to the beaker, the vapor was so great that there was no clear image of the beaker or surrounding areas. The data in Figure 9B was after the vapor plume had subsided and a clear image with the beaker in view could be obtained.

Liquid NH_3 was also poured directly onto a 2” x 2” concrete coupon to determine the how well the GF306 could visualize the liquid NH_3 in/on the concrete coupon and resulting fumes/plume. As seen in Figure 9C, there are fumes emanating from the concrete coupon, along with a darkening of the coupon its self. Similarly to described for the GF77, the GF306 was able to visualize the liquid NH_3 being poured onto the concrete coupon and evaporating out. After three minutes, NH_3 vapor was still clearly seen evolving from the surface of the concrete; we did not record past three minutes.

Recommendations

The GF306 is a mountable instrument capable of detecting large releases of liquid NH_3 as well as smaller volumes of vapor or plumes in high sensitivity mode. The GF306 is recommended for visualization of plumes or vapor from a test event or an incident. In addition to the capability of visualizing the plum/vapor itself, the instrument is also capable to detecting liquid NH_3 that has intercalated into a material and is still off-gassing. As the wavelength range that the GF306 operates in is narrower than the GF77, the GF306 is more selective, though is still capable of sensing more than just NH_3. Therefore, additional research is recommended to fully understand the instrument’s selectivity in detecting NH_3 in a real-world event and to better understand the instrument’s capability of detecting liquid NH_3 entrapment within different media (i.e. concrete coupons, soil, gravel, etc.).

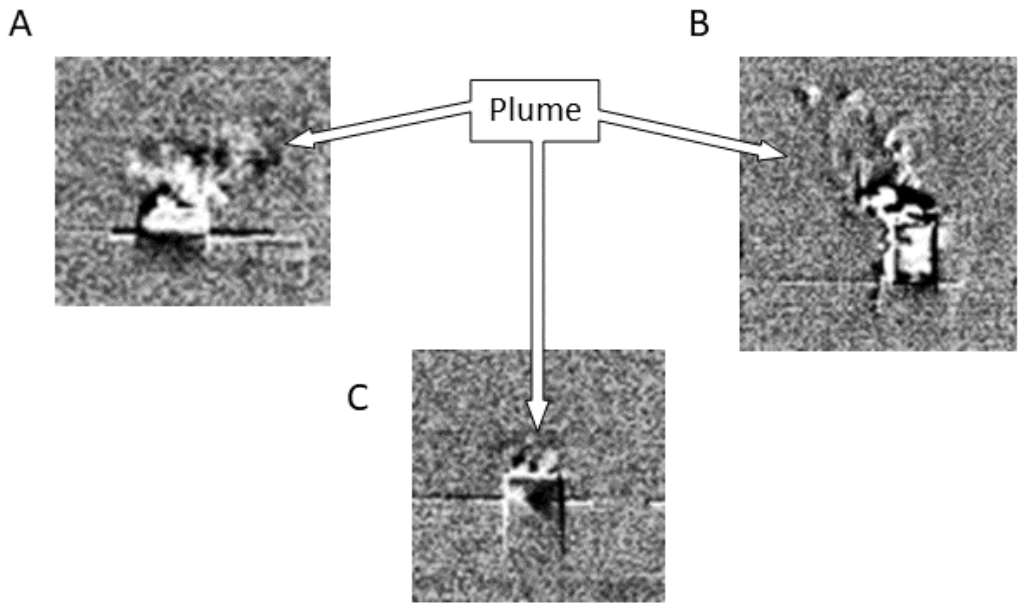

Figure 9: Plumes generated by ammonia hydroxide in a beaker (A), a beaker containing liquid ammonia (B), and liquid ammonia after it was poured directly onto a concrete coupon (C) with the GF306.

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4.0 SUMMARY AND CONCLUSIONS

Three different classes of technologies were utilized to sense and detect NH_3 in a liquid or vapor state. The classes were:

- **Gas sensors** consisting of the electrochemical-based or ionization based vapor sensors
- **Colorimetric sensors** consisting of pH paper and M8 Paper
- **Liquid sensors** consisting of a pH meter
- **Spectroscopic sensors** consisting of a hyperspectral line scanner, and three optical gas imagers

Gas sensors are capable of detecting gaseous NH_3 but are easily overwhelmed and take significant time to off-gas the NH_3 that is present in the sensor. **Colorimetric sensors** were able to detect both aqueous and liquid NH_3 to varying degrees. Notably, M8 paper produces an irreversible color change (dark green changing to a permanent brown/burnt orange) when exposed to liquid NH_3. **Liquid sensors**, such as the pH meter utilized can detect changes due to NH_3 affecting the surrounding aqueous environment. **Spectroscopic sensors** were able to detect NH_3 in an aqueous environment or in the vapor form, depending on the instrument.

For visualization of gaseous NH_3 or NH_3 plumes, the FLIR GF306 is recommended for further distances (10's of meters) whereas the GF77 would also be recommended if closer and the leaks are large. Gas sensors should be worn by individuals if they may be in or around an environment with NH_3 vapor present as it presents a hazard to health. Colorimetric sensors such as the M8 paper can be used to detect liquid NH_3 or NH_3 in an aqueous environment. The hyperspectral line scanner can be used to identify NH_3 present in an aqueous environment based on a characteristic absorption band of NH_3. Liquid sensors could be deployed in or around an area that may be at risk for an event, but unless a NH_3 selective sensor is deployed (not tested in this document), the changes are relative.

This work was meant to rapidly test instrumentation on hand as a non-bias evaluation of the sensors and techniques that CBC personnel had available. Additional research into interferents and capabilities of NH_3 detection in/on different media is necessary. Additionally, full market research of the instruments and devices available was outside the scope of this work and there may be some capabilities not outlined herein that meet the requirements for sensing NH_3 in the event of a spill.

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