Methods Development for Low-Level Ammonia and Methane Analysis Using FTIR

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Abstract

Current methods of ambient air ammonia analysis can accomplish accurate and precise data but are inadequate at achieving detection limits below 10 ppbv. The Fourier-transform infrared spectroscopy (FT-IR) technique has not yet been reported as an analytical method for measuring ammonia in conjunction with a passive sampling device, even though it theoretically can be very precise while maintaining accuracy. The purpose of this project is to determine the viability of this technique in quantifying ammonia levels for different applications such as monitoring air quality around chicken farms. Results from this project demonstrate the feasibility of low-level ammonia analysis by the FT-IR technique. A modified set-up is required due to the memory effects of ammonia. Originally a 10 m cell was used, which was changed out with a 10 cm cell with replaceable windows. Different window materials were tested to find out what interfered the least with ammonia. A 10 cm cell with a KBr plate window shows the most promising results showing low detection limits for measuring ammonia released from indirect sampling of ammonia on sulfuric acid-treated glass wool. Real-world data from samples collected at chicken coops suggest inconclusive results.

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Introduction

Ongoing research analyzes the components and concentrations of different chemicals and elements that form our air, deciphering what exactly what amounts of these are considered dangerous. There are fluctuations in concentrations depending on different biological and chemical processes that may occur in a certain area. One major industry with air quality concerns is chicken farming. Chicken manure is nitrogen based and the breakdown of uric acid by bacteria results in ammonia and other amines. Confined feeding systems for these animals contribute the largest ammonia emissions in Europe and the United States (Simsek 2013). Concentrations within farms can vary with temperature, humidity, and airflow rate. Farmers and scientists both need to know these concentrations to provide optimal living habits for the chickens, and for the safety of people inhabiting the areas near these farms. A multitude of analytical methods, including Fourier-Transfer Infrared Spectroscopy (FTIR) have been used to determine the concentration of ammonia present in these areas.

A better idea of how this works comes from the chemical derivatization of ammonia and organic amines. Different organic amines can interfere with determining correct concentrations. Identification of amines and their concentrations requires new techniques to ensure accurate data. Many separation methods such as ion chromatography-mass spectrometry and gas chromatography allow for the separation of ammonia and amines and are very selective. Unfortunately, the detection limits are too high and not suitable for ambient air monitoring, because these techniques have relatively low sensitivity. Another technique, ion selective electrode analysis is inexpensive and has the selectivity needed but requires a large sample volume in which ammonium cation is formed from the reaction of ammonia with acidified media.

Derivatization of ammonia and amines is important for separation of these amines and overall selectivity and sensitivity. Especially in an experiment trying to deduce ammonia levels, it is important to be able to differentiate ammonia from amines. Research using ion chromatography in efforts to derive amines from ammonia demonstrated that it was hard to quantify the amounts of amines from the ammonia peak. Trimethylamine (TMA) was the only amine that was separated and quantified. Ammonia ion chromatography-mass spectrometry achieves lower detection limits by 100-fold compared to that of ion chromatography alone (Hermans 2010). Another project demonstrates how derivatization is done by multiple extra steps to separate amines from ammonia in the chromatograms while using gas chromatography mass spectrometry (GC-MS). In one case, Ammonia was derivatized onto a solid phase microextraction fiber through a reaction to form butyl carbamate. Doing this allowed for quantification of ammonia on the GC-MS (Lubrano 2016). This research shows the difficulty with analyzing ammonia in the presence of amines and points out how current methods do not consider derivatization of ammonia to avoid analytical interference from amines. FTIR does not have these issues and has already been established as a successful technique for determining whether ammonia is present. For example, it has been used in analyzing ammonia clusters within noble gas matrices (Süzer 1987). While this shows its capabilities, it does not discuss the possibility of low-level analysis. One goal of this project is to develop a technique that can provide accurate low level ammonia data with a simpler process. The FT-IR technique is able to differentiate between ammonia and amines with high sensitivity.

Multiple regulatory agencies set limits on ammonia exposure in workplace environments. OSHA's workplace exposure limit is an average of 50 ppm over eight hours, while both NIOSH and ACGIH recommend an average of 25 ppm over ten hours, with a short-term exposure limit of 35 ppm for no longer than fifteen minutes. The EPA is also actively using the National Air Emissions Monitoring Study (NAEMS, 2021) to develop emission models for ammonia and other chemicals at chicken farms. These models were drafted in August 2021, demonstrating the current need for new technologies to detect ammonia levels. Sensor technologies were recently developed for ammonia detection in chicken farms. For example, the MQ135 sensor for ammonia detection automatically turns on a fan when ammonia levels hit the threshold of 40 percent (Budiarto 2020). This sensor works by measuring the partial pressures of gases in the room. Ambient air is diffused through a liquid electrolyte in the sensor and can be applicable in many ambient air analysis situations (Vijayalakshmi 2019). Sensors connected to fans are meant for last-minute detection and remediation, when ammonia is already at dangerous levels. Determining trends at even lower thresholds can prevent the need for last-minute action. OSHA's current method relies on ion chromatography. A known volume of air is collected in a glass tube containing carbon beads and sulfuric acid. The samples are then desorbed using deionized water and analyzed for ammonium ions (Methods Development Team, 2002). 3, with the current instrument, methyl amines are detected, giving imprecise results.

Overall, more accurate ammonia analysis is necessary. Ammonia is already classified as a highly ignitable gas, so ensuring ammonia concentrations are below OSHA's regulatory standards is crucial to protect human health. On top of that, there are many short-term effects experienced by people exposed to greater than normal ammonia concentrations. This includes irritation to the skin and eyes, and potential damage to the lungs (Yarandi 2021). Other undesirable effects of ammonia include contribution to global warming, chemical reactions in the atmosphere, and higher concentrations of ammonia by-products that seep into different terrestrial and aquatic environments. The Japanese sea perch have been affected by ammonia poisoning has affected the survival and quality of these fish which have economic importance (Zhang, 2022). This is just one small example of potential hazardous effects of ammonia that affect environmental and air quality and in turn take a toll on the economy and ecological health. Developing a new technique of ammonia analysis that can help prevent these consequences has become one of the priorities in this field.

Similarly, methane has also been an interest for further regulation due to its adverse environmental and health effects. Landfills are a major source of methane emissions. Additionally, methane contributes more to global warming and other environmental factors than other major ambient gases such as carbon dioxide. Research done so far on methane concentrations has focused on maximum concentrations in the environment (Vujić 2017). A technique at analyzing lower levels of methane is also desirable as emission levels decrease.

Objective

The objective of this study is to develop and determine the commercial feasibility of a new technique to analyze low levels of ammonia in ambient air, especially in areas where levels of ammonia are high. A literature search revealed that although there have been studies on the use of FT-IR to analyze ambient air including ammonia, the technique has not yet been explored to analyze extremely low levels of ammonia via passive sampling. Therefore, we proposed to collect ammonia samples onto sulfuric acid treated glass wool to yield ammonium sulfate. The liberation of ammonia when sodium hydroxide is added to the ammonium sulfate under controlled conditions was expected to give accurate results

Materials and Methods

FT-IR technique for ammonia analysis

Over the summer of 2022, work was done to determine the utility of the FT-IR technique. A stock solution of ammonium sulfate was made, and different concentration samples were made through serial dilutions of the stock solution. Glass wool was soaked into these different concentrations and tested. An apparatus was made using a piece of glassware in which the glass wool sat, and the reaction occurred, that had a rubber stopper on one end and a cork piece on the other. Injected through the cork piece was a needle in which PTFE tubing was connected that was attached on the other end to a candy cane diffuser which was attached to a 6L gas canister. The ammonium sulfate glass wool was placed in the glass apparatus and a few drops of highly concentrated sodium hydroxide were added. The rubber stopper was quickly placed back on to ensure no ammonia gas escaped. By using highly concentrated sodium hydroxide, it ensured that the ammonium sulfate was the limiting reagent. The diffuser filled up the gas canister in approximately one hour. The gas canister was then pressurized to around 10 psig to be able to fill up the 10 m gas cell used for FT-IR. These samples were then analyzed to determine absorbance and concentration levels. Between the testing of every sample, all equipment used was cleaned intensively and warmed up with a heat gun in an attempt to desorb residual ammonia. This was important to lower the memory effects of ammonia in future samples. Controls were also done to understand technique and potential issues better. This consisted of glass wool not soaked in ammonium sulfate, but a few drops of sodium hydroxide were still added. This was done with old tubing to determine memory effects in PTFE tubing, and with new tubing to determine if ammonia was still present in results, and if so, narrowing the possibilities of where it was getting absorbed into the materials used. Another idea considered was to use urea and water to generate ammonia gas. A substantial change was the use of a 10 cm cell instead of a 10 m cell. The smaller cell could be coated with a non-polar substance that would help avoid absorbance. This process is called silization and makes the surface of the cell less porous, repelling the polar ammonia. With the use of a new cell, different “windows” were analyzed to see what produced the best spectra. Possibilities included polyethylene, polypropylene, and simple Parafilm with wire mesh. Other procedural changes for improving the ammonia testing method included directly connecting the apparatus with glass wool containing ammonium sulfate that produces ammonia gas to the gas cell for infrared spectrometric analysis. This avoided the use of tubing, passive sampler, and canister where ammonia may be adsorbed. The modified method was later established by testing the range of the technique using more serial dilutions and establishing the ammonia peaks located between 900 and 1000 cm^{-1} on the spectra.

Figure 1. Display of the original set-up used to generate and collect ammonia gas

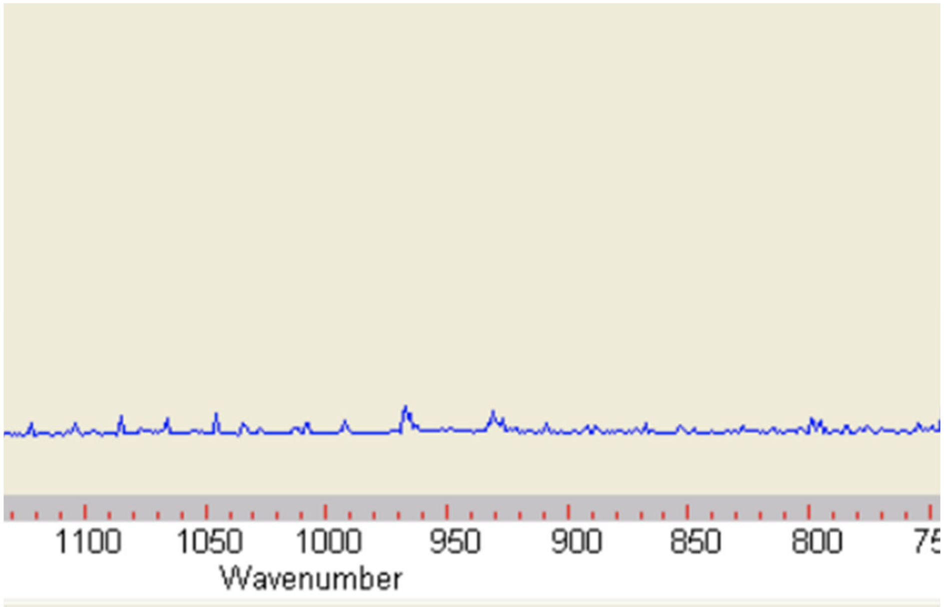

Figure 2. Example spectra is shown for the original technique of a 1000-fold dilution of 0.1M ammonium sulfate solution. Ammonia peaks are present at ~930 cm^{-1} and ~970 cm^{-1}.

Running field samples with FT-IR technique

A few changes were made to collect and test field samples. The glass wool soaked in sulfuric acid was placed in stainless-steel tea strainers and located at a site within a local chicken farm. The acidified glass wool was analyzed in the lab by using infrared spectroscopic measurements after converting the ammonium sulfate back to ammonia by adding NaOH solution. With field samples, levels of CO_2 and weather effects may influence ammonia sampling, and these effects will be analyzed when conducting these trials. The sulfuric acid will react with the ammonia in the air to generate ammonium sulfate on the glass wool. This was reacted in the lab with sodium hydroxide to release ammonia gas. Future testing will be done collaboratively at chicken farms in Oklahoma.

Results

Determining abilities of FTIR technique

The first aspect of the project was determining the linear dynamic range of FTIR method to analyze ammonia with an emphasis on lower concentrations. This is done through lab samples through serial dilutions and a 10 m gas cell. Ammonia generated from ammonium sulfate and sodium hydroxide were detectable using this method. Figure 1 shows a few of these tests compared to reference spectra. Samples were successful down to very small ppm levels. Unfortunately, blanks run after successful samples still showed ammonia peaks, leading to the conclusion that there was ammonia adsorption in the set-up for sampling and transfer of ammonia. This led to a revised set-up with a smaller gas cell and avoiding intermediate steps where ammonia could get trapped in the tubing, passive sampler, and canister.

Testing different gas cell windows

A 10 cm single-pass gas cell was used to select the best window material that would not interfere with the spectra of analytes. Methane analysis was added to the project because of the ease of obtaining methane from the gas tap in the laboratory. Different windows tested were polypropylene, polyethylene, Parafilm with wire mesh support, and KBr plates. Figure 2 shows the ammonia spectrum obtained using KBr plates compared to two reference spectra. Overall, the spectrum is clearly observed without any spectral interferences. These KBr windows would very likely be successful for analyzing samples gathered from chicken coops, because of their lack of interference. Figure 3 shows methane spectra obtained using a Parafilm window compared to reference spectra. This was somewhat successful but showed partial spectral interference by the Parafilm material. Figure 4 shows methane spectra obtained using a polyethylene window compared to reference spectra. Peaks from the polyethylene window interfered with peaks from methane leading to the conclusion that polyethylene windows are not good for methane analysis.

Field Test Sample with new gas cell set-up

Samples were collected from a chicken coop containing approximately 25-30 chickens located in Murfreesboro, Tennessee. Samples were left out for approximately 48 hours, and mild rain was experienced in the area for the last 4 hours. Figure 5 shows an ammonia spectrum obtained using the gas cell with KBr plates for the sample collected at the chicken coop. Location of sample is shown in Figure 6. The results were inconclusive leading to the conclusion that further testing of the viability of KBr plates as windows and overall set-up of gas cell/experiment needs to be done.

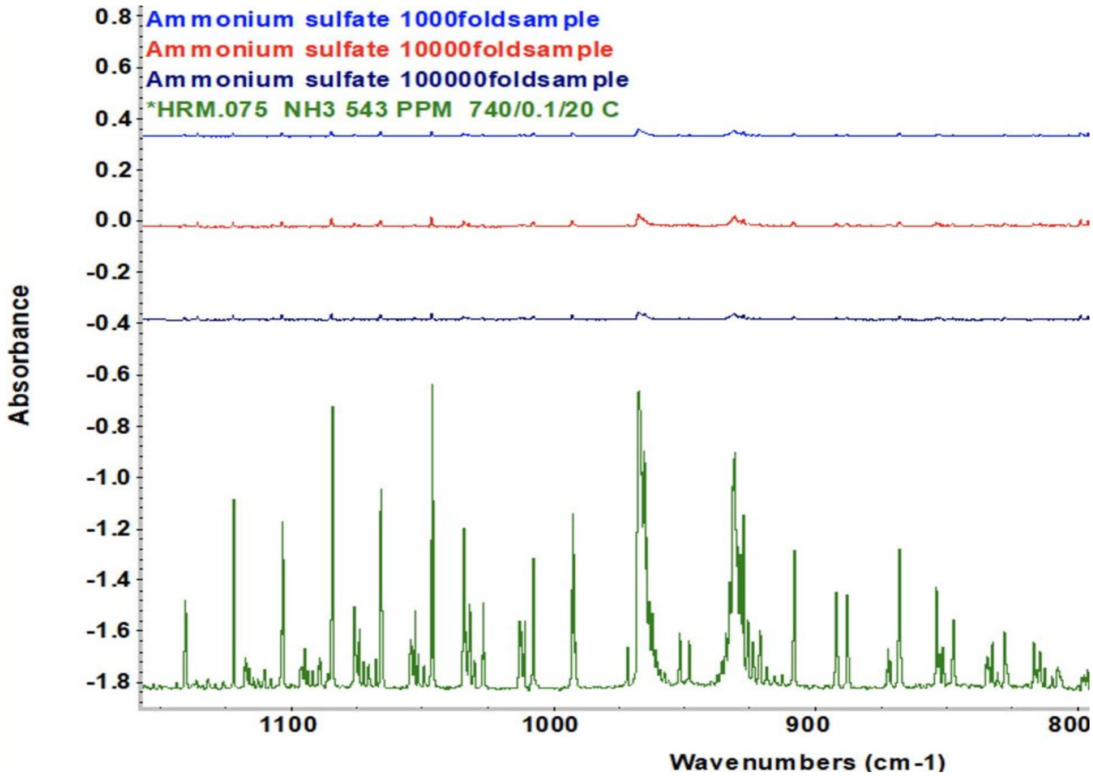

Figure 3. Ammonia spectra resulting from serial dilutions of ammonium sulfate reacted with sodium hydroxide using the 10 m cell. These samples are depicted by the peaks in light blue, red, and dark blue (top 3 spectra). Reference peaks of ammonia are shown in green at the bottom. All samples show ammonia peaks in the 900-1000 cm^{-1} range.

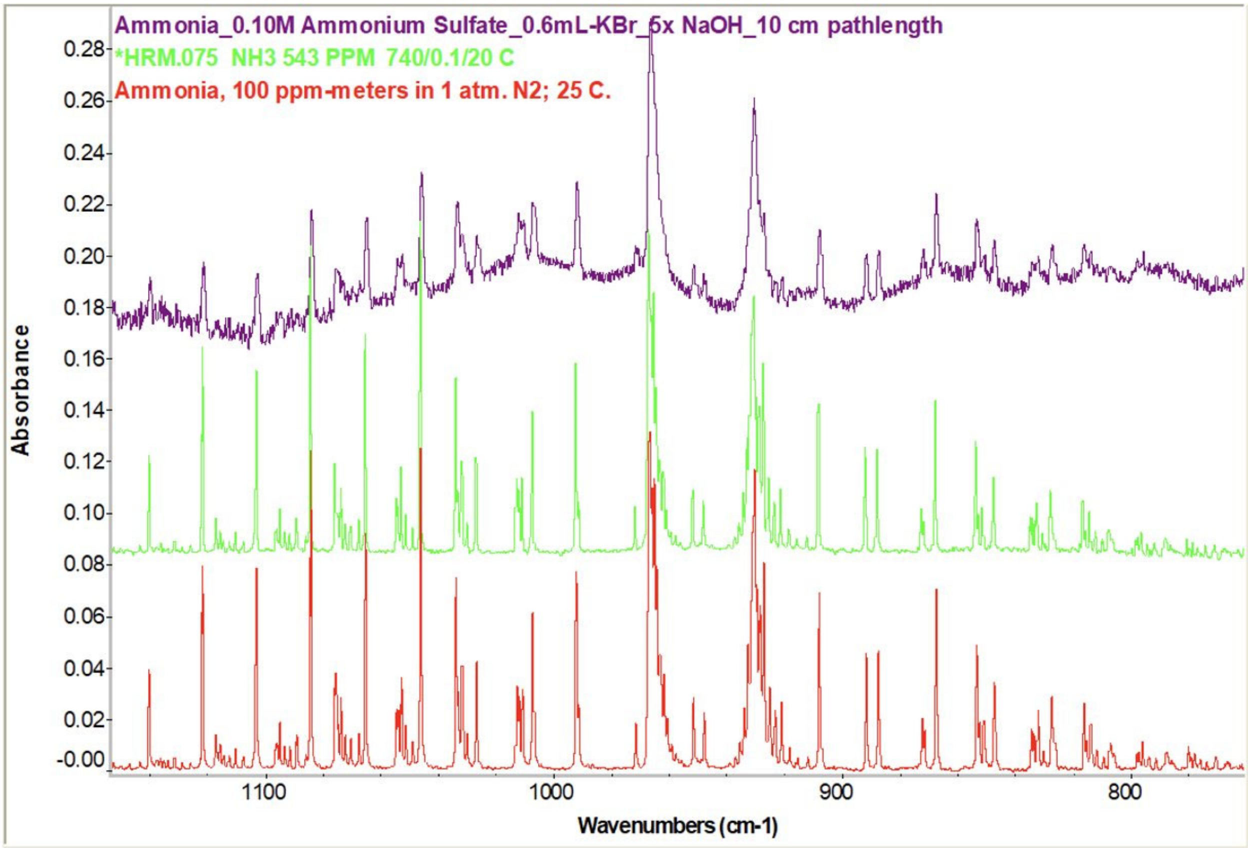

Figure 4. Shown in purple (top spectrum) is ammonia spectrum resulting from 0.1 M ammonium sulfate reacted with sodium hydroxide using the 10 cm cell and KBr plates as windows. Shown in green and red (bottom two) are two different reference spectra of ammonia. Distinctive ammonia peaks are seen in the 900-1000 cm^{-1} region.

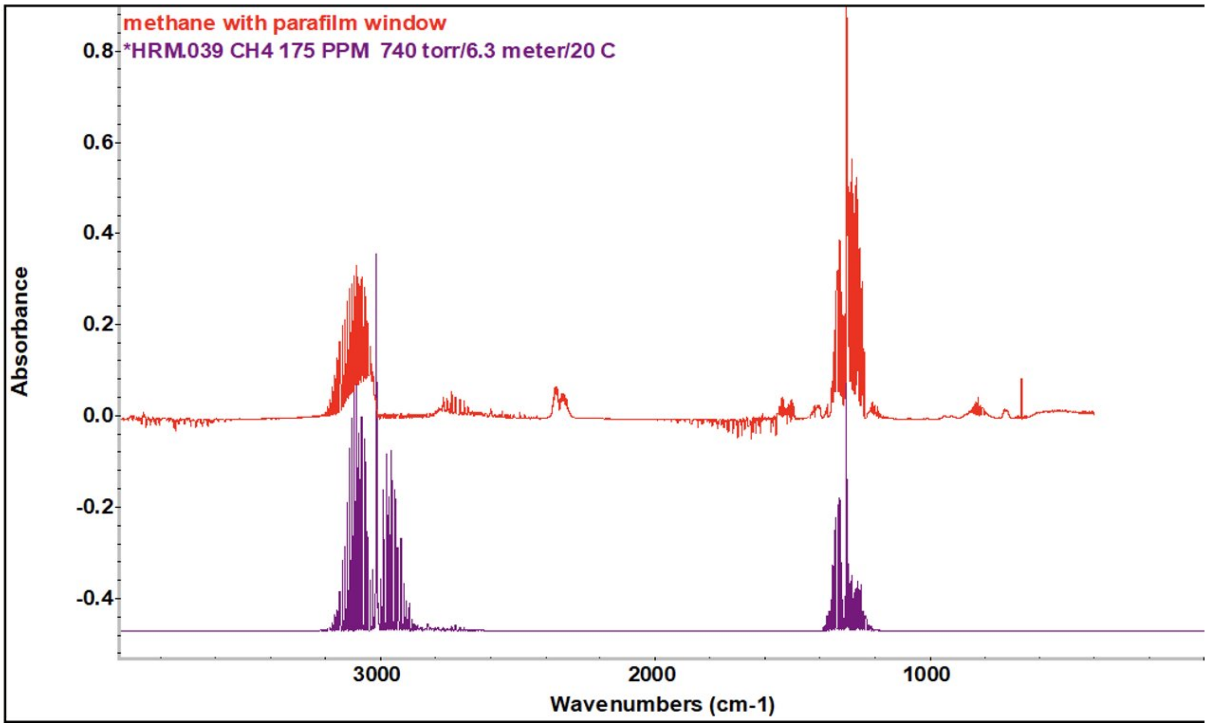

Figure 5. Methane spectrum using the 10 cm cell with a Parafilm window is shown in red (top spectrum). Reference methane spectrum is shown in purple (bottom spectrum).

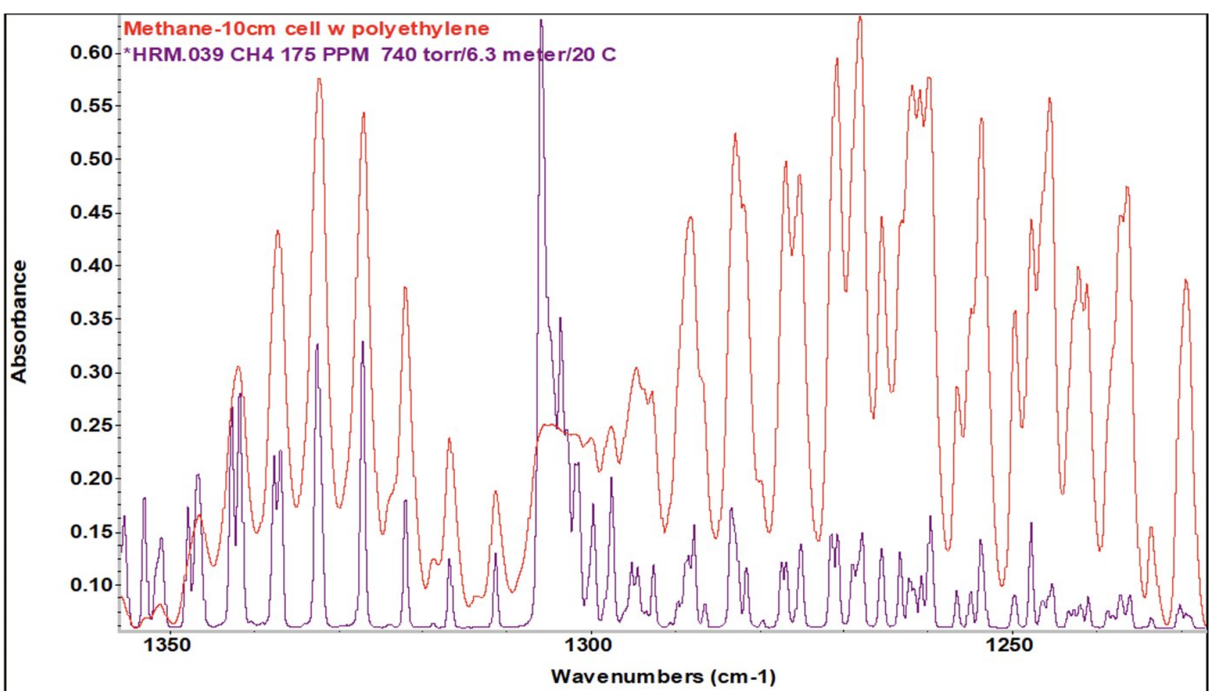

Figure 6. Methane spectrum acquired with the 10 cm cell and polyethylene windows is shown in red (top spectrum). The methane reference spectrum is shown in purple (bottom spectrum).

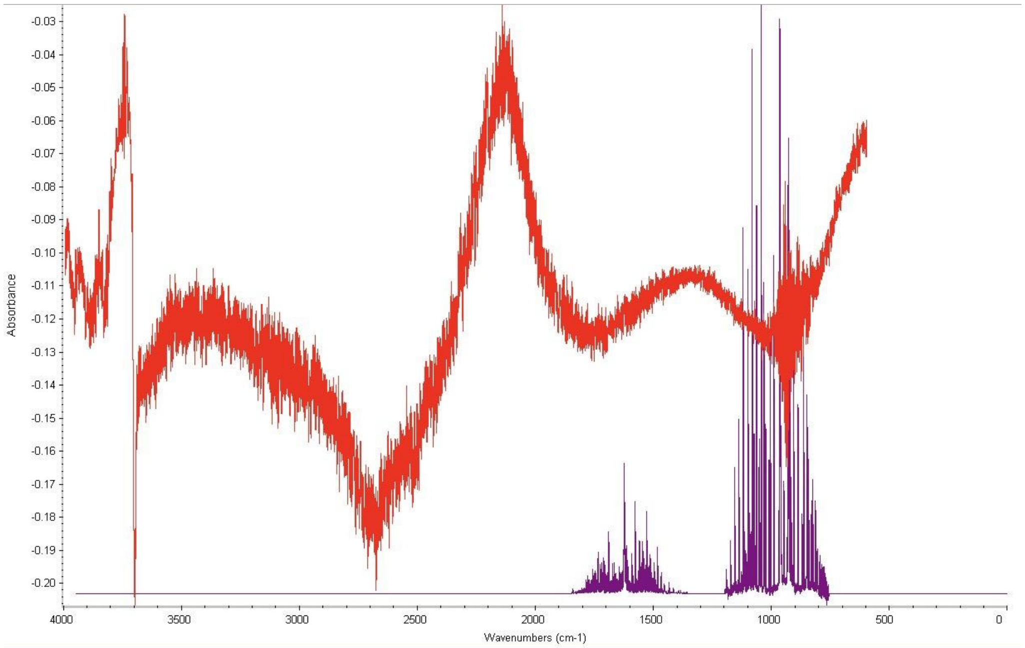

Figure 7. Supposed ammonia spectrum from chicken coop using the 10 cm cell and KBr plates as windows is shown in red (top spectrum). Reference spectrum is shown in purple (bottom in 500-200 cm^{-1} range).

Figure 8a and 8b. Photograph of location of sample around chicken coop used to produce spectra in Figure 7. Close-up of sampler to display acidified glass wool in mesh container

Discussion

The original experimental set-up helped determine the viability of FTIR to evaluate the presence of ammonia at levels down to 0.041 ppmv. Spectra shown in figure 3 contain 3.250 ppmv, 0.407 ppmv, and 0.041 ppmv concentrations of ammonia. Numerous tests of different concentrations of ammonium sulfate allowed for the determination that ammonia could be detected to these levels. Running blank control experiments after many trials led to the conclusion that ammonia is adsorbed onto the sampling set-up. To try to resolve this issue, new PTFE tubing was used. Ammonia was suspected of being adsorbed in the 10 m gas cell, reaction apparatus, and/or 6 L gas canister. To resolve this, the gas canister went through a more thorough cleaning after samples that included a heating jacket, and the gas cell was heated using a heat gun. Ammonia still was detected after all these changes, which led to a new set-up that avoided using the gas canister. Instead, the reaction apparatus containing ammonium sulfate was connected with a short piece of tubing directly to the gas cell. The gas cell was then changed to a smaller 2.4 m cell, which would give less surface area for the ammonia to absorb, and therefore less memory effect. With the adaption of the new cell came a different issue, as separate transmission windows are needed for the cell. This means that the next step of the project was to determine what windows would provide the best spectra for ammonia with minimal interference. Different windows considered were polypropylene, polyethylene, Parafilm with wire mesh support, and KBr plates. At this point, methane analysis was also considered and tested with the different windows. The most common issue encountered was getting the different window materials to hold a vacuum seal, especially the Parafilm that would collapse and pop sometimes even with wire mesh when the cell was evacuated. Although, Parafilm™ was seen to produce good spectra with methane when able to get a vacuum seal. After multiple tests, it was determined that KBr plates are the most suitable for ammonia analysis and are the easiest to assemble and capable of holding a vacuum when evacuated. However, KBr windows break easily and utmost care in not over-tightening the windows is necessary. The KBr windows would then be used with samples of ammonia gathered at a chicken coop. After the first sample from the coop was tested, it was determined that the set-up used still produced some errors, as the results came back inconclusive. This reinforced the fact that more testing of windows and revised set-up had to be done before field samples could be continued.

Conclusions

FTIR is a viable technique for testing ammonia and methane. It allows the detection of ammonia down to very low ppm levels. Unfortunately, ammonia is also highly adsorptive on the glass wall of the gas cell such that the method is very prone to memory effects. Therefore, accommodation for heating the gas cell to reduce the adsorption of ammonia during infrared analysis is needed. With a smaller gas cell, different infrared-transparent windows can also be used to observe ammonia and methane, with KBr windows being the most successful for ammonia analysis so far. More testing of cell window materials and the set-up for conversion of ammonium to ammonia is still needed to further justify FTIR as a viable testing resource for ammonia and methane. Future research for this project includes more testing of windows and set-up modification. It also requires more local field tests at chicken farms once the set-up is finalized, and then finally tests done at bigger, more commercial style farms.

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