

Detecting Nitrous Oxide in Complex Mixtures Using FTIR Spectroscopy: Silage Gas

Yongjing Zhao¹, Anthony S. Wexler¹, Frank Hase², Yuee Pan¹, Frank M. Mitloehner³

¹Air Quality Research Center, University of California-Davis, Davis, USA

²Karlsruhe Institute of Technology, Institute of Meteorology and Climate Research, Eggenstein-Leopoldshafen, Germany

³Department of Animal Science, University of California-Davis, Davis, USA

Email: yjzhao@ucdavis.edu

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Abstract

Nitrous oxide (N₂O) is a greenhouse gas with about 300 times the global warming potential (GWP) of carbon dioxide (CO₂). It is emitted from a wide range of sources and is responsible for about 6% of anthropogenic US greenhouse gas emissions. Analytical techniques are needed that can measure concentrations of N₂O rapidly and inexpensively in sources that are also emitting other compounds that may interfere with the analytical process. In this work, we demonstrate the use of Fourier Transform Infrared (FTIR) spectroscopy to analyze N₂O in the complex mixture of gases produced during the early phase of the silage making process. Silage gas samples were collected into Tedlar bags from the bucket silos during the first week of corn ensiling. A bag of the silage gas was analyzed using a Bruker FTIR spectrometer coupled with a long optical path length White Cell. First, N₂O infrared absorption bands were identified in the FTIR spectra of the silage gas by comparing them to both standard N₂O gas and simulated infrared spectra which confirmed that N₂O was present in the silage gas. Then, N₂O concentration in the silage gas was derived from the FTIR spectra using LINEFIT program. It was demonstrated that FTIR spectroscopy is a viable method for measuring N₂O concentrations in the silage gas.

Keywords

Corn Silage, Nitrous Oxide, FTIR, LINEFIT

1. Introduction

Nitrous oxide (N₂O) is an important long lived greenhouse gas (GHG) with a global warming potential (GWP) of 265 compared to carbon dioxide (CO₂) (GWP = 1) and methane (CH₄) (GWP = 28) [1]. Unlike CO₂ and CH₄, the inventory of N₂O emissions

remains largely uncertain because some of the N₂O emission sources have not yet been systematically quantified, such as those from agricultural sources, landfills, and waste water treatment systems. More importantly, some N₂O sources may not have even been discovered yet.

The California Global Warming Solutions Act of 2006 (AB 32) requires California to reduce its GHG emissions to 1990 levels by 2020 [2]. In order to achieve this goal, accurate GHG emission budgets are needed, in which an improved estimation of N₂O emissions from California agriculture is essential. Various gas emissions, except for N₂O, from silage have been investigated by various laboratory and field experiments [3] [4] [5]. The N₂O emissions from silage corn cropland, but not from the corn silage, have been estimated worldwide [6] [7] [8]. Wang and Burries monitored nitrogenous gases produced by silage in both field and laboratory silos using a mass spectrometer [9]. They reported a maximum N₂O concentration of 4.35% in the farm silo gas at about 54 hours after ensiling. Because N₂O and CO₂ both have a mass of 44, the N₂O signals were obtained by differentiating them from CO₂ peaks in the mass spectra, which may have introduced measurement uncertainty. Little information has become available on N₂O produced by silage since the Wang and Burries measurements, because in the interim silage gases produced during the early phase of ensiling were studied mostly for toxicity [3]. Insufficient attention has been given to N₂O as an important GHG gas emitted during the silage making process.

The present paper demonstrates that FTIR (Fourier Transform Infrared) spectroscopy can be used to measure N₂O concentration in the complex mixture that comprises silage gas, because some of the N₂O absorption peaks are isolated from other gas absorptions in the FTIR spectra. Since the FTIR spectroscopic technique has been used for real-time measurements of N₂O and other gas species [10] [11], it is an excellent tool for real time monitoring of N₂O in silage gas and may also be suitable for measuring N₂O emissions in other anthropogenic emissions mixtures.

2. Materials and Methods

2.1. Fourier Transform Infrared (FTIR) Spectrometer

An FTIR spectrometer (Bruker Optics, Inc., Tensor 27, Germany) with spectral resolution of 1 cm⁻¹ was used in the present study, which covers the spectral range from 850 to 7000 cm⁻¹ with a mid-infrared (MIR) source, a KBr beam-splitter, and a Cryo-cooled MCT detector. A White Cell with variable optical path length between 3.2 - 64 meters and a volume of 16 liters was coupled to the FTIR spectrometer to increase gas absorptions in the White Cell.

2.2. LINEFIT Program

An instrumental line shape retrieval program, called LINEFIT, developed by Hase [12] at the Karlsruhe Institute of Technology in Germany was used to analyze the FTIR spectra to derive the gas concentrations inside the White Cell. The LINEFIT code is in wide use within the FTIR group of the NDACC (Network for Detection of Atmospheric

Composition Change, <http://www.ndsc.ncep.noaa.gov>) and TCCON (Total Carbon Column Observing Network) [11] for the analysis of reference gas cell spectra recorded with high-resolution [13] [14], but has also been used for the analysis of spectra observed with low-resolution spectrometers [15].

2.3. Laboratory Bucket Silos

Various types of laboratory silos had been used for decades to simulate the conditions of large scale silos for different purposes [16] [17] and references therein]. Procedures to make corn silage in laboratory bucket silos and collect gas samples from the bucket silos have been described by Hafner *et al.* [5]. In summary, for this study, twelve kilograms of corn forage were manually compressed in 18.9-liter buckets. Excess gases produced in bucket silos were collected and filled 5-liter Tedlar bags (SKC-West Inc., Fullerton, CA) during the first week after ensiling. A bag of the silage gas was analyzed by the FTIR spectroscopy to investigate what compounds were present in the silage gas. Since the properties of the silage produced in the bucket silos were similar to typical values [5], the silage produced in the bucket silo was normal so the gas sample collected should be representative of the complex mixture that is silage gas.

3. Results

3.1. FTIR Spectra of the Silage Gas and Verification of N₂O Peaks

Gas samples were analyzed with Bruker Tensor 27 FTIR spectrometer coupled with a long-path White Cell. When switching gas samples in the White Cell, the White Cell was flushed three times by alternatively evacuating the chamber down below 1 hPa and filling with pure nitrogen (N₂) to 1013 hPa. When analyzing pure N₂ and standard N₂O gas samples, the White Cell was filled with either one to 1013 hPa. To analyze the silage gas, 5 liters of silage gas from one 5-liter Tedlar bag plus 11 liters of high purity N₂ were added to the White Cell to bring the pressure up to 1013 hPa in the 16-liter White Cell. The White Cell was operated at ambient pressure to prevent any contamination to gas samples due to possible leaks. Therefore, the air samples from the bucket silos had been diluted by a factor of 3.2 in the White Cell.

The optical path length of the White Cell was adjusted close to its maximum of 64 meters in order to maximize instrument sensitivity and therefore to detect weak absorption signals. First, the FTIR spectrum of the high purity N₂ was recorded as background. Then, the FTIR spectrum of the silage gas plus N₂ mixture was recorded. Significant N₂O absorption peaks were found in the FTIR spectra of the silage gas. In order to confirm that N₂O absorptions were identified correctly, the FTIR spectrum of a 5-ppm standard N₂O gas was also recorded.

Figure 1 shows four spectra in the 1850 - 2850 cm⁻¹ spectral region at 1 cm⁻¹ spectral resolution: 1) FTIR spectrum of air samples from the bucket silo; 2) FTIR spectrum of 5-ppm standard N₂O gas in N₂ balance; 3) FTIR spectrum of pure N₂; and 4) simulated spectrum of N₂O, CO₂, CO, and H₂O gases generated by the LINEFIT program and Hitran 2008 spectral lines parameters [18]. The first three spectra in **Figure 1** were measured

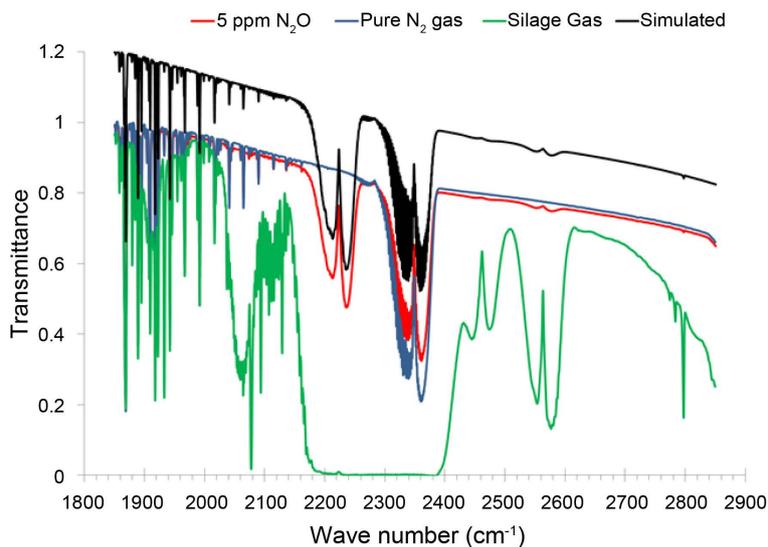


Figure 1. FTIR spectra of air samples from the bucket silos (green), 5-ppm standard N_2O with N_2 balance (red), and pure N_2 gas (blue) in white cell recorded by a Bruker tensor FTIR spectrometer. A simulation spectrum of gases N_2O , CO_2 , CO , and H_2O by LINEFIT program is also shown (black) and upward shifted.

using the Bruker FTIR spectrometer coupled with a White Cell. The simulated spectrum takes into account not only the transmittance of all four gases but also the FTIR instrumental parameters.

The N_2O absorption bands can be identified in the FTIR spectrum of the 5-ppm N_2O standard gas and the simulation spectrum. The N_2O absorption bands in the region of 2130 - 2270 cm^{-1} are the fundamental ν_3 and associated “hot bands”, which are strong absorptions [19]. The N_2O absorption bands located between 2400 - 2600 cm^{-1} include a harmonic band of $2\nu_1$ and a combination band of $\nu_1 + 2\nu_2$ [20] which are relatively weak absorptions. These N_2O absorption bands cannot be seen in the spectrum of the pure N_2 gas. **Figure 1** shows that the absorption of the silage gas in the region of 2130 - 2270 cm^{-1} was saturated while the absorption of the 5-ppm N_2O in the same region was not, indicating that the N_2O concentration in the silage gas were much higher than 5 ppm. On the other hand, the absorption of the silage gas in the region of 2400 - 2600 cm^{-1} were not saturated and, by comparison, the absorption of the 5-ppm N_2O gas in this region were much weaker, further confirming that N_2O concentration in the bucket silos was much higher than 5 ppm.

A CO_2 fundamental ν_3 absorption band [21] located at 2349 cm^{-1} is shown in **Figure 1** in the spectra of both the 5-ppm N_2O gas and the pure N_2 gas. Because CO_2 should not be present in the White Cell in either case, this CO_2 absorption came from CO_2 gas outside the White Cell between 1) the FTIR MIR source and the White Cell, and 2) the White Cell and the FTIR MCT detector, because these two areas were exposed to ambient conditions. In the spectrum of the silage gas, the saturation between 2200 and 2400 cm^{-1} was due to the combined strong absorptions of CO_2 and N_2O . The CO_2 $3\nu_2$ harmonic band at 2077 cm^{-1} is a weak absorption [21] that can be seen in the spectrum

of the silage gas but not presented in the spectra of the 5-ppm N₂O gas and the pure N₂ gas.

3.2. Retrievals of FTIR Spectra Using LINEFIT Program

3.2.1. Selection of the Spectral Windows

The 5-ppm standard N₂O spectrum in **Figure 1** showed that 1) N₂O absorption at the fundamental ν_3 and associated “hot bands” was not saturated between 2130 and 2270 cm⁻¹ and 2) the absorption of CO₂ at the fundamental ν_3 band located at 2349 cm⁻¹ was not saturated either. Therefore, three spectral windows can be used to retrieve the 5-ppm N₂O spectrum: i) 2140.0 - 2285.0 cm⁻¹, ii) 2130.0 - 2650.0 cm⁻¹, and iii) 2510.0 - 2615.0 cm⁻¹.

In the spectrum of the silage gas, two spectral windows at 2140 - 2615 and 2510 - 2615 cm⁻¹ were selected to retrieve the N₂O concentrations. When fitting the spectral window at 2410 - 2615 cm⁻¹, a special technique in the LINEFIT program, called “de-weighting”, was applied to the sub-window between 2300 and 2510 cm⁻¹ because of the complexity of CO₂ absorptions in this region.

3.2.2. Retrieval of FTIR Spectra of the 5-ppm Standard N₂O Gas

Retrieval of the 5-ppm N₂O spectrum was to confirm that the selected spectral windows can be used to accurately derive the N₂O gas concentrations from the FTIR spectra. The retrieval of the 5-ppm N₂O spectrum was also used to calibrate the optical path length of the White Cell. The retrieval of FTIR spectra using the LINEFIT program does not need any calibration when the total columns (in m⁻²) of the species are derived, but in order to convert from total columns to gas concentrations, the optical path length of the White Cell is needed. Because it is difficult to accurately estimate the White cell’s path length, calibration of the White Cell’s optical path length was performed using the 5-ppm N₂O standard gas mixture.

Figures 2-4 show the retrieval results of the 5-ppm N₂O spectrum at three spectral windows. Both FTIR and fitted spectra are shown on the low portion of the figures in red and blue, respectively. The differences between FTIR and fitted spectra, called “Residuals”, are shown on the upper portion of these figures. In principle, the LINEFIT program simulates a transmittance spectrum of all species at the given spectral window and fits it to the observed FTIR spectrum by scaling the total column of each species until the residuals fall in a preset threshold. The N₂O columns in the White Cell along the optical path derived from the three spectral windows were 6.99×10^{21} , 6.69×10^{21} , and 7.18×10^{21} m⁻², respectively. The optical path length of the White Cell was calibrated to be 57.6 m. The converted N₂O concentrations were 4.94, 4.91, and 5.08 ppm respectively, which were -1.2%, -1.8%, and 1.7% different from the expected values of 5 ppm, resulting in an average of 4.98 ± 0.09 ppm. The ± 0.09 ppm error bar was the standard deviation of the retrieved values from the three spectral windows. Uncertainties caused by general spectroscopic error (line intensities and broadening coefficients) and experimental error (temperature, pressure, instrument line shapes, etc.) were not accounted in the error bar; these contribute less than 10% to the error estimate for

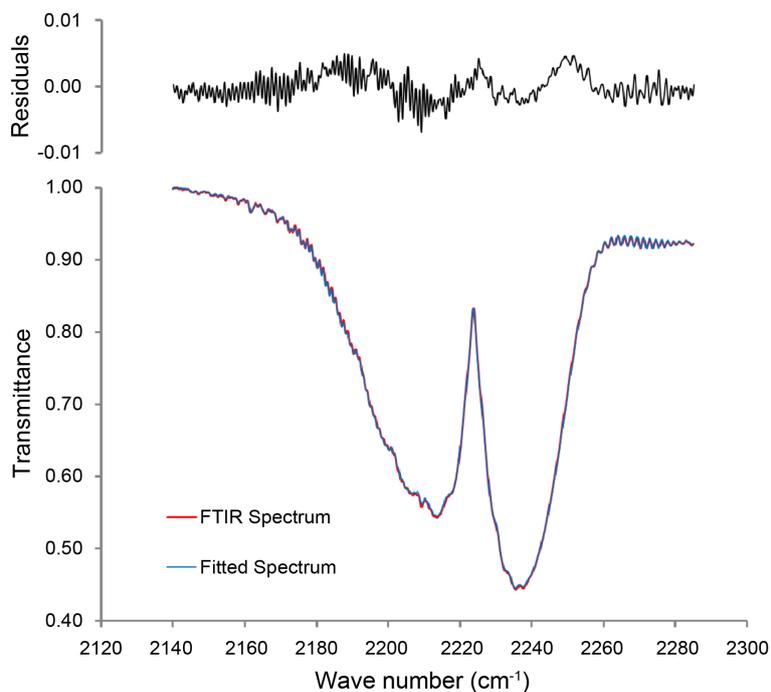


Figure 2. Retrieval of the 5-ppm N_2O spectrum at window 2140 - 2285 cm^{-1} . The FTIR spectrum (red) and the fitted spectrum (blue) are shown on the bottom panel. The differences between FTIR and fitted spectra (residuals) are shown in top panel in black.

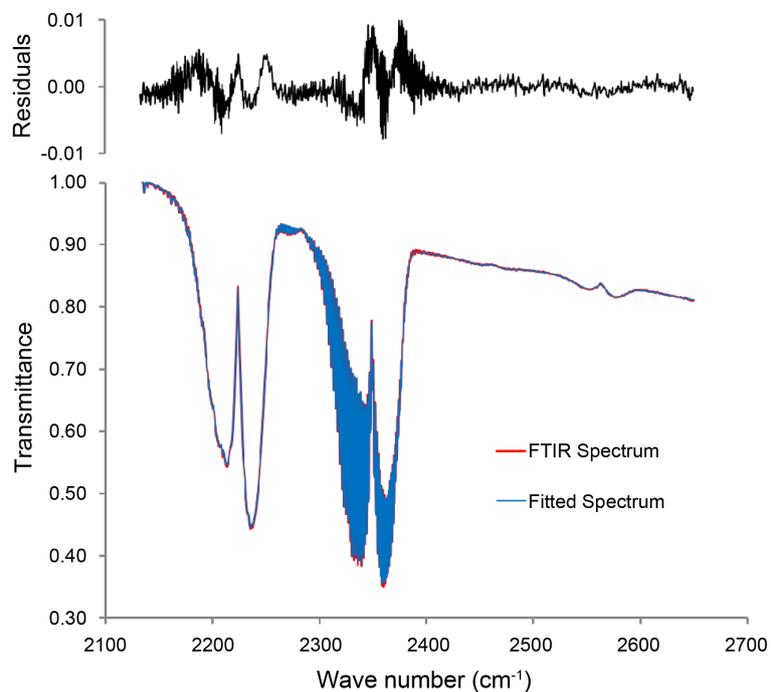


Figure 3. Same as **Figure 2** except for window at 2140 - 2650 cm^{-1} .

open-path FTIR measurements [22]. Similar uncertainty estimates apply to the error bars of the retrieval results in the rest of this paper so will not be repeated.

3.2.3. Retrieval of FTIR Spectra of the Silage Gas

The N_2O FTIR spectrum of the silage gas was retrieved at two spectral windows 2140 - 2615 and 2510 - 2615 cm^{-1} . The spectral fitting results are shown in **Figure 5** and **Figure 6**.

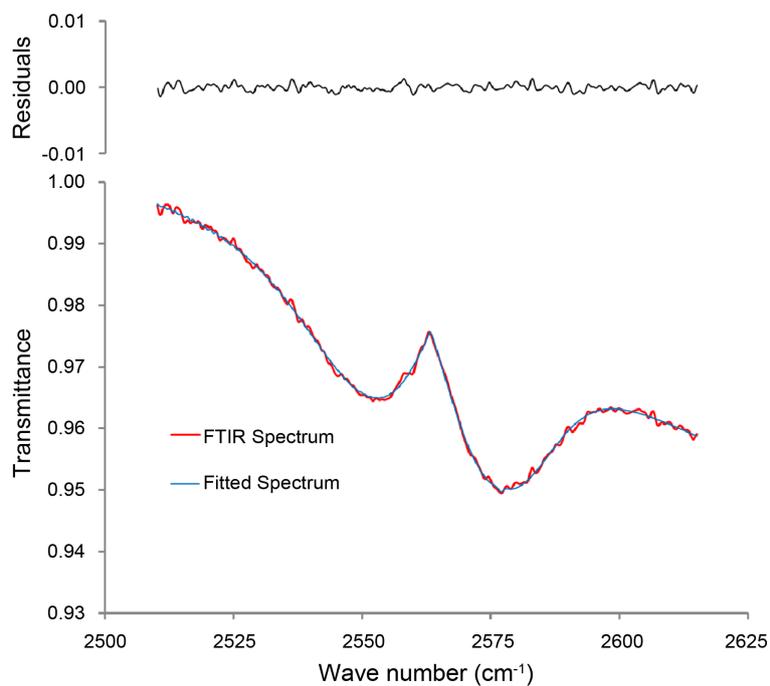


Figure 4. Same as **Figure 2** except for window at 2510 - 2615 cm^{-1} .

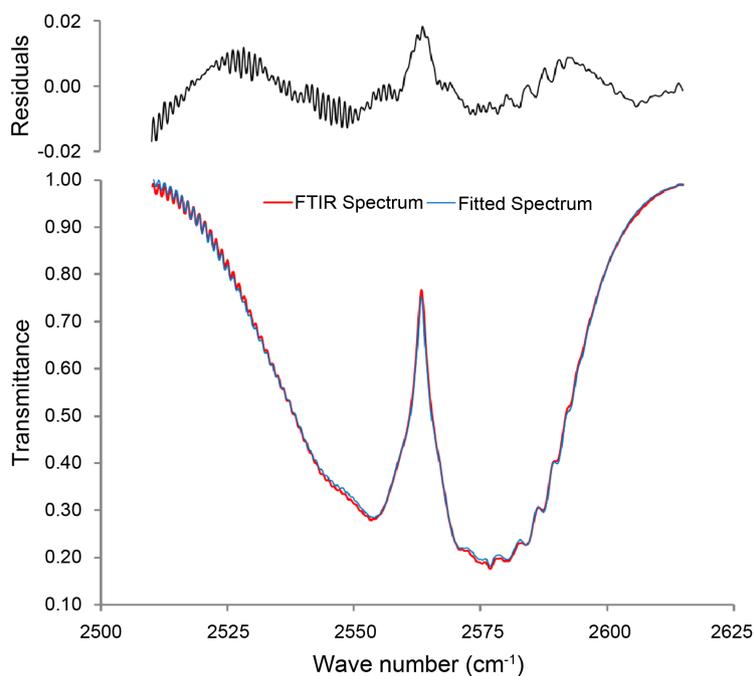


Figure 5. Retrieval of the bucket silos samples spectrum at window 2510 - 2615 cm^{-1} . The FTIR spectrum (red) and the fitted spectrum (blue) are shown on the bottom panel. The differences between FTIR and fitted spectra (residuals) are shown in top panel in black.

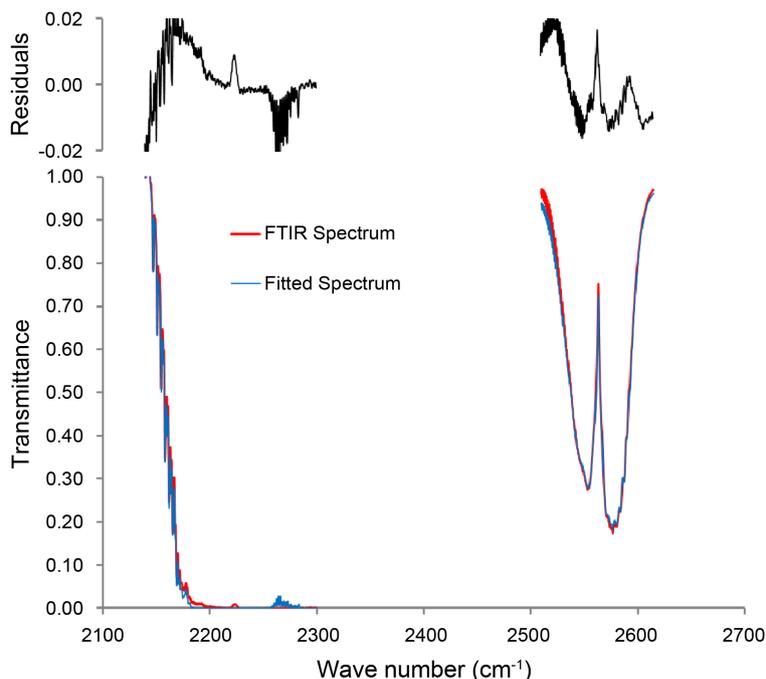


Figure 6. Same as **Figure 5** except for at 2140 - 2615 cm^{-1} window with a sub-window at 2300 - 2510 cm^{-1} de-weighted (not shown).

Similar to **Figures 2-4**, both FTIR and fitted spectra are shown on the low portion of the figures in red and blue, respectively. Their residuals are shown on the upper portion of the figures. In **Figure 5**, the N_2O column in the White Cell retrieved from 2510 - 2615 cm^{-1} window was $8.11 \times 10^{23} \text{ m}^{-2}$, equivalent to 573.8 ppm N_2O in the White Cell. **Figure 6** shows the 2140 - 2615 cm^{-1} window without the 2300 - 2510 cm^{-1} sub-window because this region was de-weighted. In the de-weighting spectral regions, the LINEFIT program neglects the residuals between observed and simulated spectra in order for the residuals from other spectra regions to fall below the pre-set threshold. This technique is usually used when there is a particular absorption feature that the LINEFIT program cannot handle correctly. The N_2O column in the White Cell retrieved from this window without the sub-window was $7.98 \times 10^{23} \text{ m}^{-2}$, or 564.5 ppm. Because the N_2O concentration in the Tedlar bag was diluted by a factor of 3.2 when the samples were introduced into the White Cell, the N_2O concentrations in the silage gas are estimated to be 1836 and 1806 ppm, respectively, retrieved from the two spectral windows, resulting in an average of 1821 ± 21 ppm. These two estimates agree within 1.7%, similar to the uncertainty in retrieving concentrations from the 5-ppm N_2O standard gas mixture spectrum.

4. Discussion

FTIR spectroscopy was used to analyze N_2O in a complex gas mixture produced in corn silage. The corn silage was made in laboratory bucket silos and silage gas samples were collected during the early phase of ensiling. A 5-liter Tedlar bag of the silage gas was

analyzed with a Bruker FTIR spectrometer at 1 cm^{-1} spectral resolution coupled with a long-path White Cell. N_2O absorption peak fingerprints were identified in the FTIR spectra of the silage gas using both standard N_2O gas spectra and simulated spectra from the IR spectral database. This observation verified that N_2O was produced in the bucket silos at the early phase of ensiling. To quantify the N_2O concentration, the FTIR spectra were retrieved using the LINEFIT program. N_2O concentrations retrieved from three spectral regions of the 5-ppm N_2O spectrum were 4.98 ± 0.09 ppm confirming that N_2O can be accurately retrieved from FTIR spectra using LINEFIT program. An N_2O concentration of 1821 ± 21 ppm was derived from two spectral regions of the silage gas FTIR spectra indicating that N_2O concentration in the silage gas was very high. Wang and Burries [9] measured N_2O concentrations in the farm silos using mass spectroscopy and reported that N_2O varied from 10,000 to 43,500 ppm in the first 66 hours and peaked at about 54 hours after ensiling, which was about 5.5 - 23.9 times greater than the N_2O concentration in the laboratory bucket silos measured in the present study. The difference between the two measurements could be due to several factors: 1) N_2O and CO_2 both have a mass of 44, so the N_2O signals were obtained by differentiating them from CO_2 peaks in the mass spectra, which might have introduced uncertainty in the mass spectroscopic measurements, 2) The differences in sampling locations and methods between the two measurements, and 3) The N_2O concentrations between farm silos and laboratory bucket silos might be truly different.

5. Conclusion

The primary goal of this work was to 1) verify that N_2O was present in silage gas during the early phase of ensiling based on FTIR spectroscopy, 2) demonstrate that N_2O concentrations in silage gas can be accurately retrieved from FTIR spectra using the LINEFIT program, and 3) confirm that FTIR spectroscopy is a viable method for measuring N_2O concentrations in complex gas mixtures, such as the silage gas. Since only one bag of silage gas was analyzed by FTIR for this study, the concentrations measured should be considered preliminary. Due to limited amounts of silage and silage gas sampled, the concentrations measured in this work should not be construed a quantitative estimate of N_2O emissions from silages. In order to quantitatively investigate the N_2O emissions from silage, an extended study is needed, including measurements of representative silage mixtures and ages of gas samples during silage making process. Most importantly, research is needed on methodology to reduce the N_2O emissions during the silage making process. This work is intended as a pilot work to demonstrate the efficacy of using FTIR to measure N_2O concentrations in complex mixtures such as emissions from silage.

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