ORIGINAL ARTICLE

A pH-based method for measuring gaseous ammonia

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Abstract Cumulative emission or gaseous concentrations of ammonia (NH_3) are commonly measured by trapping gaseous NH_3 in an acidic solution that is later analyzed for total ammonia content. This traditional acid trap method is inexpensive, reliable, and accurate, but it is labor-intensive and inconvenient for high-frequency sampling. This paper describes a new acid trap method in which total ammonia concentration in a citric acid solution is calculated from measured pH by applying a speciation model. With this new method, the quantity of captured ammonia in a single acid trap can be determined repeatedly over time. Testing through titrations, laboratory emission measurements, and field measurement of gaseous NH_3 showed that the method is accurate and reasonably precise. For the most sensitive case standard deviation was 8 μmol kg^{-1} in titration results, and $10-20$ μmol kg^{-1} in the field trials. The lower quantitation limits from emission measurements and field trials were around 100 and 300 μmol kg^{-1}, respectively. Speciation modeling was used to assess the importance of interferences. Results showed that error due to minor contamination of chemicals and evaporation of water can be kept at low levels. Acidic gases may be a significant interference, but their presence is easy to recognize, and significant error can be avoided by selecting an appropriate acid concentration.

Keywords Ammonia · Manure · Measurement

Introduction

Ammonia is a major air pollutant from animal agriculture. Emission rates of NH_3 have been measured from various sources at a wide range of scales, from manure samples in the laboratory to field plots and barns. Approaches for measuring NH_3 emission generally rely on determination of NH_3 concentration or quantity in a gas phase. A common approach used for this task is to trap gaseous NH_3 in an acid solution, by bubbling the gas through the solution, and subsequently analyzing the solution for total ammonia to determine the quantity of NH_3 captured (Thompson and Meisinger 2004). Ammonia is very soluble in water (Henry's law constant is about 60 mol kg^{-1} atm^{-1} at 25°C), and once in an acidic solution, quickly forms NH_4^+ by reaction (R1) (Emerson et al. 1960).

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$$NH_3 + H^+ \rightleftharpoons NH_4^+ \qquad (R1)$$

This traditional acid trap method is reliable and has been used extensively. Assuming high capture efficiency, the quantity of ammonia captured in an acid trap provides a quantitative estimate of the mass of NH_3 originally present in a gas sample. However, the labor requirements of this method (each data point requires the analysis of a sample by wet chemistry) make high-frequency sampling challenging, which limits measurement of short-term responses. But, an acid trap does capture the cumulative effect of any fluctuations, regardless of the rapidity of concentration changes. The traditional acid trap method has been reviewed by others (Phillips et al. 2001; Ni and Heber 2001; Shah et al. 2006).

The method described in this communication is an acid trap method that allows for rapid repeated determination of captured NH_3. In it, NH_3 is captured in a solution with a known concentration of weak acid, and solution pH is monitored over time. Given the acid concentration and an estimate of H^+ activity from the measured pH, speciation of the acid can be determined, and the total NH_3 concentration can then be calculated from a charge or H^+ balance. Because pH can be measured non-destructively, multiple measurements can be made quickly, with inexpensive instruments, using a single acid solution.

Because Reaction (R1) consumes protons, solution pH increases as NH_3 is absorbed in a weak acid solution; the proposed pH-based method relies on quantification of this relationship. For a wide measurement range, it is necessary to have a well-buffered solution across a wide range in pH, and therefore strong acids, such as sulfuric, are not suitable. The ideal acid can give up multiple protons below a pH of about 7, with moderate differences between pK_a values, and the lowest pK_a well below 7. Citric acid is a tricarboxylic acid with three pK_a values between 3 and 7 (3.1, 4.8, 6.4). It also has low toxicity, and is stable and inexpensive. These characteristics make citric acid suitable for the proposed method, and it was selected for use in this work. In the following, we refer to the pH-based method with citric acid as the CA-pH method.

The relationship between solution pH and NH_3 concentration is dependent on the citric acid concentration; all else being equal, a higher concentration of citric acid will result in a smaller pH change in response to a given NH_3 addition. Therefore, highest sensitivity is attained at the lowest citric acid concentration, although at the expense of capacity. At higher concentrations, speciation calculations become less accurate. In this work, we evaluated three concentrations of citric acid: 1, 10, and 100 mmol kg^{-1} (molal basis), which all produced suitable outcomes. Interferences from acidic gases may be a significant problem for citric acid concentrations <1 mmol kg^{-1}, and concentrations >100 mmol kg^{-1} are probably not needed.

Experimental

Four approaches were used to evaluate the CA-pH method: titration of citric acid solutions with ammonia, mass balance evaluation of emission measurements from ammonium chloride solutions, measurement of emission from manure and ammonium chloride solutions, and comparison to a colorimetric method through gaseous NH_3 sampling in the field.

Titrations

For the titrations, a Metrohm 775 Dosimat dispensing unit (Herisau, Switzerland) was used to add 20−100 μL aliquots of an NH_3 titrant to about 100 g of a 1, 10, or 100 mmol kg^{-1} citric acid solution. Titrants contained about 0.05, 0.5, or 5 μmol μL^{-1} of NH_3 for 1, 10, or 100 mmol kg^{-1} citric acid solutions. The analyte solution was stirred during titrations. Titrations were carried out at room temperature (20−25°C), and solution temperature was measured using a platinum resistance thermometer (Fisher Scientific, Fair Lawn, NJ). Analyte solution pH was measured at each step as described below. We calculated the total NH_3 concentration in the analyte solution from the citric acid concentration and the measured pH using the approach described in the "Calculations" section. This calculated value was compared to the "true" concentration of total NH_3 at each step, determined from the volume of titrant added and its total NH_3 concentration.

Emission measurements

We used a simple system to measure emission from ammonia solutions and manure. Samples were held in a 250 mL glass jar sealed with a Teflon-lined lid

(I-Chem Septa Jar, Thermo Fisher Scientific, Fair Lawn, NJ) with teflon tubes conducting dry or humidified breathing quality air (Airgas, Salem, NH) in and out (200–600 mL min^{-1}). The sample jar was submerged in a water bath $1-5°C$ below room temperature to avoid condensation in the exhaust tubing. Exhaust air was bubbled through a citric acid solution in a graduated cylinder (25–100 mL, containing 10–100 mL of solution), or a syringe body (20 mL, containing 10–15 mL of solution). Apart from using small-diameter tubing (3 mm inner diameter), no attempt was made to maintain a small gas bubble size. Solution pH was measured intermittently (15 s to >1 h sampling interval) using the equipment described below in the "Measurement of pH" section. Both automated data acquisition, where the electrode was left in the acid solution for the duration of the trial, and a manual approach, where the electrode was immersed only during measurements, were tested. Trials were carried out at $20-25°C$. For the mass balance trials, 1–3 g samples of solutions containing 100 mmol kg^{-1} NH$_4$Cl and >1 mol kg^{-1} NaOH or KOH were used. Mass balance trials were continued until the acid trap pH became stable over 0.5 h. We also measured emission from dairy manure and NH$_4$Cl solutions $(0.1-1$ mol kg^{-1}). Manure (total solids 6–7%, total ammonia 50 mmol kg^{-1}) was collected from the USDA-ARS dairy facility in Beltsville, MD.

Measurement of gaseous NH$_3$ in the field

We tested the CA-pH method for measurement of gaseous NH$_3$ at the USDA-ARS dairy facilty in Beltsville, MD by comparing CA-pH results to results from a traditional colorimetric Bertholet method using salicylate. We tested the method at low gaseous NH$_3$ concentrations of about 0.5 mg m^{-3} within the dairy barn, and also at higher NH$_3$ concentrations of about 10 mg m^{-3}, by sampling directly above a separated manure liquid pit. A citric acid concentration of 1.0 mmol kg^{-1} was used for low NH$_3$, and 10 mmol kg^{-1} was used for the higher concentrations. Gas washing bottles (125 mL) with a fritted bubbler were used for the acid traps. Each contained about 60 mL of a solution of either citric acid (1 or 10 mmol kg^{-1}) or phosphoric acid (10 mmol kg^{-1}). Air was pulled through the traps using diaphragm pumps. Flow rates were varied (1–9 L min^{-1}), as were sampling intervals (8 min to 2 h), to produce a range of aqueous total

NH$_3$ concentrations for comparing the methods. Before starting each trial, bottles were rinsed with either citric or phosphoric acid solutions, at the same concentrations that would be used in trial. Small (5 mL) solution samples were removed intermittently during trials, and taken to our laboratory for analysis. Measurement of pH was done at one time for all samples within each trial, to minimize error due to electrode drift or calibration. Samples were refrigerated (about 4°C) for up to one day prior to pH measurement (4 days prior to analysis by the salicylate method) or frozen for longer storage. Before removing samples, bottles were weighed, and lost mass, assumed to be due to evaporation, was replaced with high purity water. Citric acid samples were analyzed for NH$_3$ concentration using an automated salicylate method (Thompson and Meisinger 2004) as well as the CA-pH method. Phosphoric acid solutions were analyzed using the salicylate method.

Measurement of pH

Acid solution pH was measured using an Accumet AR15 meter, with a glass combination electrode containing an Ag/AgCl reference (Orion 91-02 or Accumet 13-6202-85). Calibration of the meter and electrodes was performed for each individual measurement trial using two buffers: the initial citric acid solution (pH 3.24, 2.63, and 2.09 for 1, 10, and 100 mmol kg^{-1}, respectively, at 20°C) and solutions of ammonium citrate, (NH$_4$)$_2$C$_6$H$_6$O$_7$, at the same concentration as the acid solution (pH 5.48, 5.31, 5.00 for 1, 10, and 100 mmol kg^{-1}, respectively, at 20°C). This approach minimizes pH measurement error by minimizing differences in junction potential between buffers and the acid solution, and minimizes the impact of error in the speciation model or errors due to contamination (see "Interferences" section). For the field trials, citric acid buffer samples were set aside at the start of each trial, stored, and handled identically to the exposed samples. Sample pH was either measured directly, with a resolution of 0.001 pH units, or else electrode potential was recorded to 0.1 mV, resulting in a resolution of about 0.002 pH units.

Chemicals

Citric acid solutions were made from anhydrous citric acid (Fisher Scientific, Fairlawn, NJ), which had a

reported purity of 100.0%, with 0.05% oxalate, <0.001% Cl, and 0.02% ignition residue. Ammonium citrate, $(NH_4)_2C_6H_6O_7$, (Fisher Scientific) had a reported purity of 99.6%, with 0.05% oxalate, <0.001% Cl, and <0.001% ignition residue. The NH_3 titrants were made by diluting a stock NH_4OH solution (25% minimum mass basis of NH_3) in water (Acros Organics, Fisher Scientific, Fairlawn, NJ). Because of inaccuracy in the reported NH_3 content of the stock solution and the possibility of volatilization losses during dilution and storage, the NH_3 content of the titrants were determined by titration (each titrant was used to titrate a citric acid solution to the pH of an $(NH_4)_2C_6H_6O_7$ solution with the same concentration of total citric acid). The effective concentration of the stock solution was determined in this way to be about 27%. Ammonium chloride, NH_4Cl, (Fisher Scientific) had a reported purity of 99.6%. All solutions were made using high purity water (18 MΩ cm deionized distilled water), and no attempt was made to remove CO_2 (speciation predictions showed that atmospheric CO_2 has a negligible effect).

Calculations

To determine the concentration of absorbed NH_3 from measured pH, the concentrations of the four citric acid species are calculated from H^+ activity (estimated from measured solution pH as 10^{-pH}) and total citric acid concentration. The NH_4^+ concentration is then calculated based on charge or H^+ balance.

Citric acid can give up three H^+ ions in solution, as shown in Reactions (R2) through (R4), where A^{3-} represents the citrate anion, $C_6H_5O_7^{3-}$.

$$H_3A \rightleftharpoons H_2A^- + H^+ \tag{R2}$$

$$H_3A \rightleftharpoons HA^{2-} + 2H^+ \tag{R3}$$

$$H_3A \rightleftharpoons A^{3-} + 3H^+ \tag{R4}$$

The activity of H_3A is calculated from the total citric acid concentration and the activity of H^+:

$$a_{H_3A} = \frac{tot_{H_3A}}{\frac{1}{\gamma_{H_3A}} + \frac{K_1}{\gamma_{H_2A}a_H} + \frac{K_2}{\gamma_{HA}a_H^2} + \frac{K_3}{\gamma_A a_H^3}} \tag{1}$$

Equation (1) was derived from mass balance and mass action expressions for Reactions (R2) through (R4). In Eq. (1), a_x = activity of species x, tot_{H_3A} = total citric

acid concentration (molal scale, mol kg^{-1}), γ_x = activity coefficient of species x, and K_1, K_2, and K_3 are equilibrium constants for Reactions (R2), (R3), and (R4), respecitively. (Species charges are omitted.)

Equilibrium constants are based on expressions given in Crea et al. (2004) for citric acid, Clegg and Whitfield (1995) for ammonia, and Martell et al. (2004) for water. Activity coefficients are calculated from the extended Debye–Hückel equation (Zemaitis, 1986), with ion size parameters from Kielland (1937). (Complete equations for equilibrium constants and activity coefficients are given in the supplemental material.) Since ionic strength is calculated from species concentrations, this system of equations must be solved iteratively. Given the H_3A activity from Eq. (1), activities of remaining citric acid species are calculated from Eqs. (2)–(4), which are rearranged mass action expressions for Reactions (R2), (R3), and (R4), respectively.

$$a_{H_2A} = \frac{K_1 a_{H_3A}}{a_H} \tag{2}$$

$$a_{HA} = \frac{K_2 a_{H_3A}}{a_H^2} \tag{3}$$

$$a_A = \frac{K_3 a_{H_3A}}{a_H^3} \tag{4}$$

The activity of OH^- is calculated from the mass action expression for the self-ionization of water, assuming that the activity of water is unity,

$$a_{OH} = \frac{K_w}{a_H} \tag{5}$$

Molal concentrations (mol kg^{-1}) for all species can be calculated from

$$m_x = \frac{a_x}{\gamma_x} \tag{6}$$

Given estimates of the concentration of all charged species except NH_4^+, the concentration of NH_4^+ is calculated from Eq. (7), which can be derived from either an H^+ or charge balance.

$$m_{NH_4} = m_{H_2A} + 2m_{HA} + 3m_A + m_{OH} - m_H \tag{7}$$

(The concentration of OH^- will generally be much lower than that of other species, and could be ignored.) Then, the activity of NH_3 (aq) is calculated from the mass action expression for Reaction (R1),

$$a_{NH_3} = \frac{a_{NH_4}}{a_H K_a}, \qquad (8)$$

and used to calculate the concentration of NH_3 (*aq*), which is added to the concentration of NH_4^+ for an estimate of the concentration of total NH_3. (Although $m_{NH_3} \ll m_{NH_4}$ at pH <6, so NH_3 could be ignored as well.) For the results shown in this paper, calculations were carried out with a set of functions we wrote in the R language (R Development Core Team 2010). We have also developed a Microsoft Excel file to carry out the same calculations. Both files can be obtained by contacting the corresponding author.

Prediction of interferences

We explored potential interferences of the CA-pH method using a speciation model. Equilibrium constants for citric acid, ammonia, and water were the same as those described above. Equilibrium and Henry's law constants for CO_2 were taken from Plummer and Busenberg (1982). Henry's law constants were taken from Clegg and Brimblecombe (1989) for ammonia, and Sander (2011) for acetic acid and hydrogen sulfide. Activity coefficients were calculated as described above. The geochemical modeling software PHREEQC v. 2.17.4799 (Parkhurst 2010) was used to carry out speciation calculations. All simulation results are for 25°C. It is important to note that these speciation calculations are independent of those needed for simply using the method, which are described in the "Calculations" section.

Results and discussion

Titration results

Measured and calculated relationships between total NH_3 concentration and solution pH are shown in Fig. 1 for three citric acid concentrations. Although the slope of the titration curve is not constant for any of the cases, the three protons given up by citric acid do provide a smooth response, with a nearly linear response away from the ends. For the 1 mmol kg^{-1} case, for example, after an initial decrease in slope, pH is nearly linearly related to total NH_3 up to about pH 6.0, with the slope decreasing from 2.0 to 0.7 mmol kg^{-1} $unit^{-1}$ as pH increases. Assuming
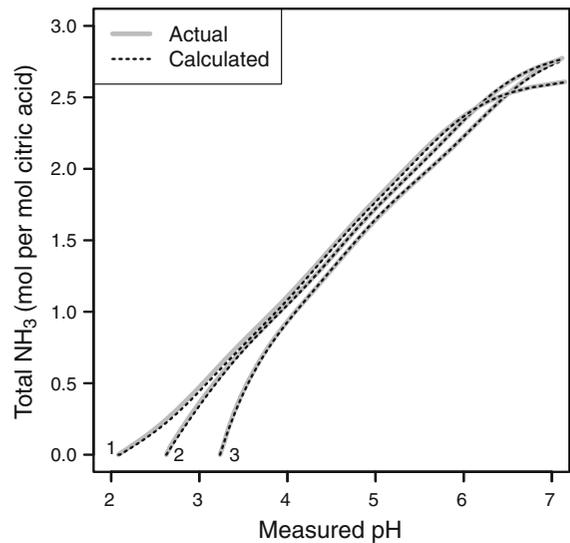

Fig. 1 Measured and calculated relationship between total NH_3 concentration and pH for titration of citric acid solutions with NH_3. The *dashed lines* show total NH_3 concentrations calculated from measured pH using the procedure described in the Calculations section. *Lines* 1, 2, and 3 are for citric acid concentrations of 100, 10, and 1 mmol kg^{-1}, respectively

the method is accurate up to pH 6.0 (depending on interferences from acidic gases—see below), it provides a measurement range equivalent to 2.8–4.0 pH units and a capacity of 2.0-fold to 2.5-fold the citric acid concentration.

Comparison of measured and calculated total NH_3 from the titrations demonstrates that the CA-pH method is accurate and precise. Calculated ammonia concentration closely matched the actual concentration (Fig. 1), with error generally less than 20 and 200 μmol kg^{-1} for 1 and 10 mmol kg^{-1} trials (Fig. 2). Results from three trials with 100 mmol kg^{-1} showed a similar response, with error generally less than 2 mmol kg^{-1} (supplemental material). This response leads to significant relative errors only at the lowest total ammonia concentrations for each citric acid concentration. For the three citric acid concentrations examined, relative error was <10% for ammonia:citric acid ratios >0.25:1 (about 10% of the total trap capacity). Below this value, relative accuracy and precision both declined. Variability among trials was quantified using the difference from the mean error, which was taken as a fifth-order polynomial fit to all titrations for each citric acid concentration (Fig. 2). Since the slope of the titration curves increases with the citric acid concentration
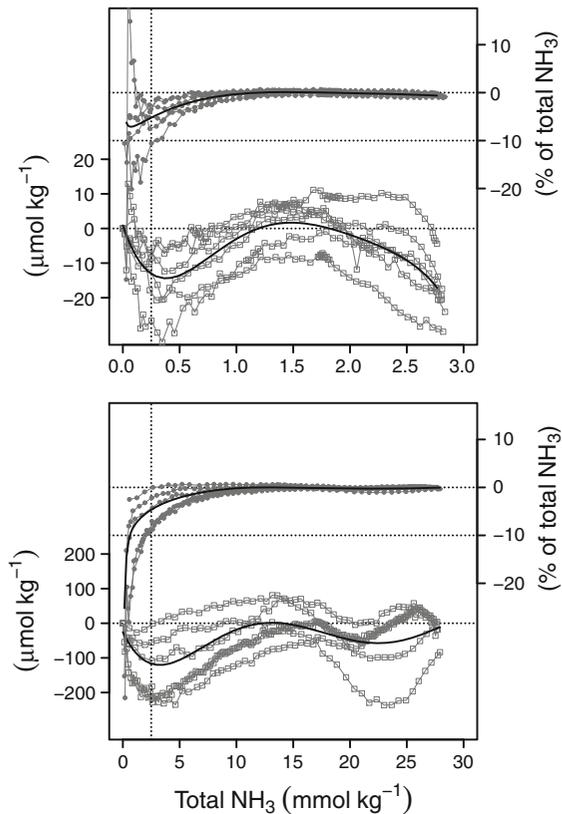
Fig. 2 Error in the calculation of total ammonia from measured pH for titrations of 1.0 (*top*) and 10 (*bottom*) mmol kg^{-1} citric acid with NH_3. The smooth line is a fifth-order polynomial fit to data from all trials, with equal weight given to each trial

(Fig. 1), variability increased with the citric acid concentration; within-titration standard deviation was 2.9, 15, and 200 μmol kg^{-1} for 1, 10, and 100 mmol kg^{-1}, while among-titration standard deviation was 7.6, 64, and 1,000 μmol kg^{-1}. Variability within single trials was lower than variability among trials, probably due to electrode drift and variability among pH meter calibrations. Therefore, ammonia measurement by difference with a single acid trap solution will be more precise than comparisons between separate traps. For comparisons between two NH_3 concentrations in the same trial, differences as low as 1% of the trap capacity were measured with error <10%. For 1 mmol kg^{-1} citric acid solutions, for example, a difference of 20 μmol kg^{-1} was measured with <2 μmol kg^{-1} error in about 90% of cases. This difference is equivalent to a pH change of 0.01–0.03 units. More details are given in the supplemental material.

Taking three times the standard deviation as the detection limit gives a minimum value of 9 μmol kg^{-1}, which is comparable to reported detection limits of other methods for ammonia in acid solutions, such as indophenol colorimetry and ion chromatography, which range from about 0.7–70 μmol L^{-1} (National Research Council 1979; Shah et al. 2006). However, quantitation limits will be higher than this detection limit. Even the 20 μmol kg^{-1} limit described above is probably attainable only under ideal conditions. This discussion does not assign any error to the determination of NH_3 additions using the Dosimat dispensing unit.

Emission measurements

Measured cumulative emission in the mass balance trials showed consistent high recovery (97–99% for five trials), confirming the accuracy of the measurement method (see supplemental material for an example). Using a 1 mmol kg^{-1} citric acid solution, we were able to measure NH_3 flux from a concentrated (1 mol kg^{-1}) NH_4Cl solution with a 90 sec sampling interval (Fig. 3). The method was sufficiently precise to allow for quantification of the effect of a change in flow rate on NH_3 emission rate; a doubling in flow rate caused a 1.9-fold change in flux (95% confidence interval 1.7–2.0). Variability was, however, greater than in the titrations; residual standard error from linear regression models for total NH_3 versus time (which includes variability in emission) was 20 and 19 μmol kg^{-1} for low and high flow, respectively. A 90 s sampling interval resulted in an increase in total NH_3 at each step of about 100 μmol kg^{-1}, and a coefficient of variation of about 6% for NH_3 flux for the low flow case.

Ammonia emission rates from agricultural sources will often be lower than from this concentrated solution. We used the CA-pH method to quantify the effect of exposure time and mixing on NH_3 emission from diluted dairy manure [1:1 dilution with high purity water (18 MΩ cm deionized distilled water)] over about two days, using a 45 min sampling interval. A citric acid concentration of 10 mmol kg^{-1} was used to avoid interferences from acidic gases. The CA-pH method captured a distinctive pattern in NH_3 flux from still manure: an increase over the first few hours, followed by a gradual decline (Fig. 4). The CA-pH method was able to capture a >10-fold drop in flux
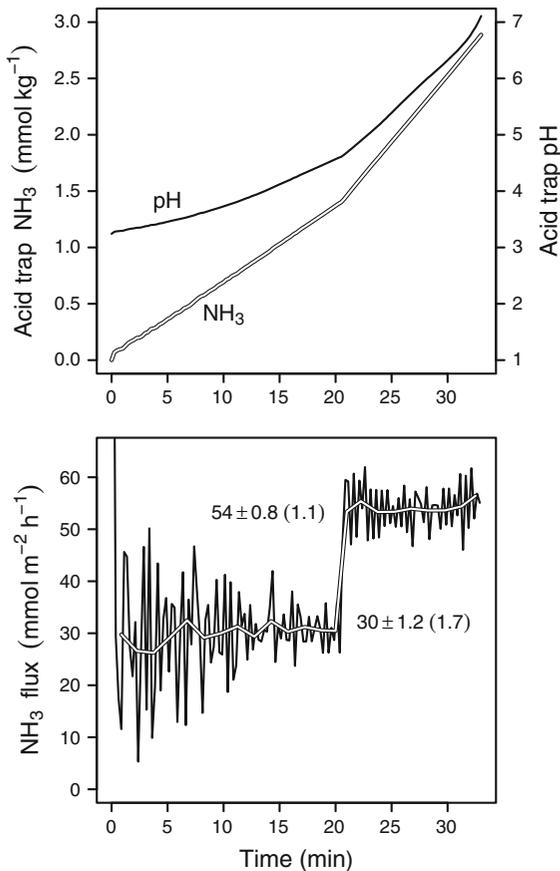
Fig. 4 Measurement of NH_3 emission from diluted dairy manure (initial conditions: NH_3: 25 mmol kg^{-1}, total solids: 3.4%, pH: 6.58) in the laboratory using the CA-pH method, with 10 mmol kg^{-1} citric acid and a 45 min sampling interval. A 140 g sample was held in a 250 mL jar (20 cm^2 area) at about 23°C, and 250 mL min^{-1} of humidified air flowed through the headspace. The *gray bars* at the *bottom* of the plot show when stirring occurred. The acid trap solution was replaced about 1 h before the second stirred period. Residual standard error from polynomial regression models fit to total NH_3 concentrations in the first and second unstirred periods was 54 and 19 μmol kg^{-1}, respectively. The increase in acid trap solution total NH_3 at each step ranged from 310 to 1,100 μmol kg^{-1} for the unstirred periods, and 49 to 130 for the stirred periods (excluding a single zero)

Fig. 3 High-frequency measurement of high NH_3 emission from a solution of NH_4Cl and $NaOH$ (1 mol kg^{-1} NH_4Cl, initial pH 7.7) in the laboratory using the CA-pH method with 1 mmol kg^{-1} citric acid, at 19°C. The *top* plot shows acid trap solution pH and calculated total NH_3 concentration. The *bottom* plot shows NH_3 flux, calculated from the rate of change in acid trap total NH_3. Air flow rate through the headspace was initially 300 mL min^{-1}, and was doubled to 600 mL min^{-1} after 20 min. Two sets of flux calculation results are shown, based on a 15 and 90 s sampling interval. Residual standard error from linear regression models fit to total NH_3 concentration vs. time was 20 and 19 μmol kg^{-1} for low and high flow, respectively. The increase in acid trap solution total NH_3 at each step (90 s interval) ranged from 96 to 110 μmol kg^{-1} for low flow and 120 to 180 μmol kg^{-1} for high flow. Values printed on the *bottom* plot are mean flux ±95% confidence interval, with SD in parentheses ($n = 11$ or 9 points)

caused by stirring. (The difference between stirred and still conditions is most likely caused by interactions among CO_2 emission, manure pH, and NH_3 emission (Ni et al. 2000); here the results are presented simply as an example application of the method.) Variability in this and similar trials was also greater than in the titrations. Residual standard error of a sixth-order
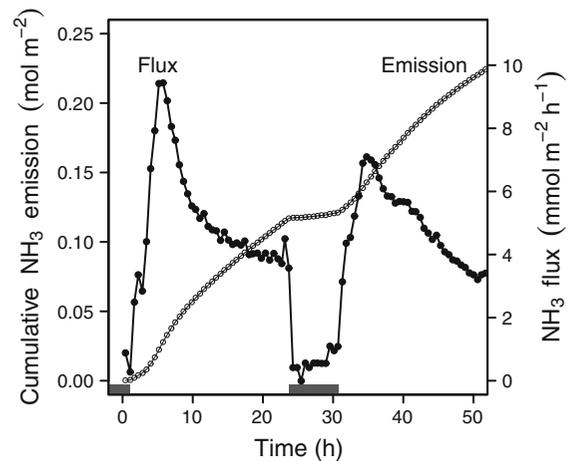
polynomial regression model for total NH_3 versus time during the unstirred periods (which includes variability in emission) was 54 and 19 μmol kg^{-1} for the first and second periods, respectively. The increase in acid trap solution total NH_3 at each step ranged from 0 to 1,100 μmol kg^{-1}. Additional examples of emission measurements are given in the supplemental material.

Measurement of gaseous NH_3 in the field

In general, the three methods used in the field trials gave similar results. Total aqueous NH_3 concentrations determined by the CA-pH method were close to those determined in the same solutions by the salicylate method, and those measured in phosphoric acid solutions by the salicylate method (Fig. 5 shows results from one trial; additional results are given in the supplemental material). We saw no consistent biases among the methods, although the CA-pH measurements showed positive bias more often than negative bias. Contrary to the titration results, there
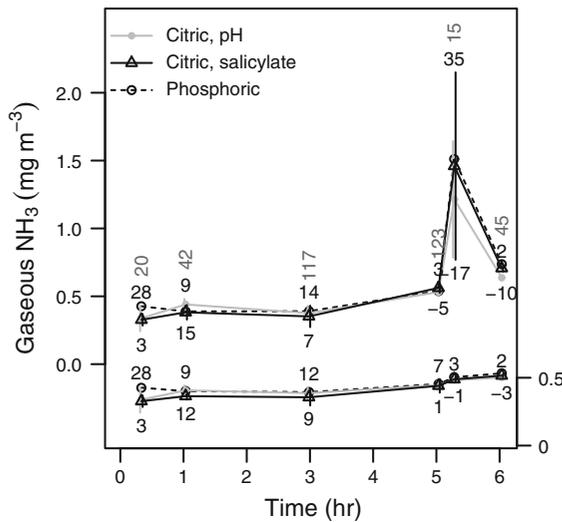
Fig. 5 Gaseous NH_3 concentrations measured in a dairy barn using the CA-pH method and the traditional colorimetric Bertholet method using salicylate. The CA-pH method was carried out using 1 mmol kg^{-1} citric acid, which was analyzed for total NH_3 by both pH and the salicylate method. Phosphoric acid traps were also used, and were analyzed for total NH_3 using the salicylate method. The *upper data* (which correspond to the *left y*-axis) show results based on the increase in aqueous NH_3 and the sampled air volume for each step (consecutive calculation). The time interval in minutes used for each point is given as the upper-most number, printed vertically. The *lower data* (which correspond to the *right y*-axis) were calculated using cumulative aqueous NH_3 and cumulative air volume (cumulative calculation). *Vertical bars* show ±one SD. *Numbers* printed below the *error bars* are the apparent error (difference between mean pH-based and salicylate results, as a percentage), and numbers printed just above the *error bars* are coefficients of variation among the three replicates for pH-based results (as a percentage)

was not a tendency for low accuracy below ammonia:citric acid ratios of 0.25:1. Standard deviation among replicates was higher than in the titrations, and was similar for both the CA-pH and salicylate results (10−20 μmol kg^{-1} for 1 mmol kg^{-1} acid traps and 200−550 μmol kg^{-1} for 10 mmol kg^{-1}), which suggests that differences among replicate solutions was a greater source of error than error inherent in the laboratory analyses. However, the CA-pH method did not consistently perform well with 1 mmol kg^{-1} citric acid at the lowest total NH_3 concentrations in the field. Below about 200 μmol kg^{-1}, results within some individual trials showed signicant positive bias (supplemental material). We have not identified the source of this error, which was not apparent in the titration results. This response was not present in the 10 mmol

kg^{-1} trials, for which the CA-pH method was accurate as low as 800 μmol kg^{-1}. The salicylate method was much more sensitive than the CA-pH method, and appeared to be accurate below 10 μmol kg^{-1}.

Gaseous NH_3 concentration can be calculated based on the increase in total aqueous NH_3 between any two sample points, but we focused on consecutive points and cumulative changes. Concentrations of gaseous NH_3 calculated from aqueous concentrations in the acid traps are shown in Fig. 5 for a single trial from within the barn. As expected, both relative accuracy and relative precision generally improved as the size of the sampling interval increased. For this trial (referred to as trial B in the supplemental material), a sampling interval of about 1 h appeared to be sufficient for reasonable accuracy and precision. Some trials carried out at the lowest gaseous NH_3 concentrations (e.g., trial A in the supplemental material) had less accurate CA-pH results, and the effect of the positive bias at low aqueous concentrations described above was clear. Even with the positive bias present at the start of these trials, the difference between CA-pH and salicylate results dropped to <25% with long sampling intervals (>2 h).

Quantitation limits

Quantitation limits for gaseous concentration and emission rate are dependent both on the aqueous phase quantitation limits and operating parameters, such as the acid trap mass. The upper limits of gaseous NH_3 or emission rate are not clearly defined but are very high. For example, with 100 mmol kg^{-1} citric acid, a gas flow rate of 1 L min^{-1}, an acid trap mass of 1 kg, and a sampling interval of 15 min, a gaseous concentration as high as 300 g m^{-3} (about 50% NH_3 by volume at 1 atm and 20°C) could be measured in theory. Conversely, limited sensitivity of the CA-pH method makes measurement of low emission rates or gas phase concentrations more difficult. Results from measurement of gaseous NH_3 in the field suggest quantitation limits of about 300 and 1,000 μmol kg^{-1} for 1 and 10 mmol kg^{-1} citric acid, respectively. Variability was generally lower in laboratory emission trials, and quantitation limits based on these results are about 100 and 500 μmol kg^{-1}, respectively. Because the sensitivity of the method depends on operating parameters, there is no clearly-defined lower limit on the concentration or emission rate that can be mea-

sured. However, an estimate can be made by assuming the gas flow rate is 5 L min^{-1}, acid trap solution mass is 100 g, that measurements are needed every 5 h, and a concentration change of 300 µmol kg^{-1} can be quantified. In this case a gaseous concentration of 340 µg m^{-3} (about 500 ppb) could be reliably measured.

Measurement of emission rate is not directly constrained by gaseous NH$_3$ concentration. With a quantitation limit of 100 µmol kg^{-1}, a 20 g acid trap solution, and a 1 h sampling interval, an emission rate of 2 µmol h^{-1} could be measured. Longer sampling interval, smaller acid trap volume, or, in the case of gaseous concentration measurements, a higher gas flow rate, would result in lower limits. Acid trap methods based on more sensitive analyses (e.g., salicylate method or ion chromatography) will always be more sensitive. Some denuders and automated instruments for direct gaseous measurement have detection limits below 1 µg m^{-3}, although the sensitivity of denuders is also dependent on sampling time (National Research Council 1979; Shah et al. 2006). More information on selection of operating conditions can be found in the supplemental material.

Interferences

In addition to pH measurement errors and inaccuracy in the speciation model, there are three general groups of interferences: contamination of citric acid or (NH$_4$)$_2$C$_6$H$_6$O$_7$ solutions, acidic or basic gases in the sample gas, and evaporation of water from the acid trap. Evaporation is relatively unimportant except for some cases with low citric acid concentration (i.e., 1 mmol kg^{-1}), and is discussed further in the supplemental material.

Contamination of chemicals

Contamination of the citric acid solution used in the acid trap may prevent the accurate determination or specification of citric acid concentration, and introduce compounds that affect solution pH. By using the initial citric acid solution as the low pH buffer, the relative error can be kept near or below the relative error in the citric acid concentration for the entire range. This approach effectively incorporates an error into the pH calibration that mostly negates the effect of solution composition error. Unaccounted-for acids

and bases distort the relationship between pH and total NH$_3$. Simulations showed that, if the initial citric acid solution is used as the low pH buffer for calibration, relative error will not exceed the relative concentration of a strong acid or base (mole basis) across the entire pH range. Contamination of (NH$_4$)$_2$C$_6$H$_6$O$_7$ is even less significant. Since high purity citric acid (>99%) and (NH$_4$)$_2$C$_6$H$_6$O$_7$ (>98%) can be purchased, and high purity water is easy to produce, contamination of solutions at the point of production will generally not be a significant source of error.

Microbial growth that occurs in acid traps can be a problem. Microbial growth in citric acid or (NH$_4$)$_2$C$_6$H$_6$O$_7$ solutions will consume citric acid, elevating pH. We found that citric acid solutions were stable for more than three months at room temperature, as determined by pH. However, some solutions from field trials carried out on a hot day (air temperature about 30°C) showed turbidity and an increase in pH after being left at room temperature (about 25°C) for five days. To avoid this problem, we refrigerated samples for up to one day, and froze them for longer storage. Additionally, we found that (NH$_4$)$_2$C$_6$H$_6$O$_7$ standards showed a slow increase in pH whether stored at room temperature or under refrigeration (up to 0.2 pH units over 5 weeks). Therefore, maintaining fresh standards, and checking standard quality through pH is important.

Gaseous interferences

Acidic gases present in the sample gas may be an important source of error. Although acidic gases do not dissociate to a large degree in acidic solutions, even low amounts of dissociation generate enough H$^+$ to cause significant errors in some cases. For emissions from animal manure, carbon dioxide (CO$_2$), acetic acid (CH$_3$COOH), and hydrogen sulfide (H$_2$S) are acidic gases that may be present. The effect of these gases was evaluated with simulated titrations using a defined gas phase in equilibrium with the solution.

Three acidic gas scenarios were evaluated: a gas phase in equilibrium with typical dairy manure, typical air in a dairy barn, and clean air with only 4 × 10^{-4} atm of CO$_2$ (i.e., 400 ppm at 1 atm of total pressure). We calculated gas partial pressures for a manure gas phase by applying Henry's law to typical manure composition [pH of 7.5, total CO$_2$ and CH$_3$COOH concentrations of 0.1 mol kg^{-1}, and a

total sulfide concentration of 0.01 mol kg^{-1} (Sommer and Husted 1995; Hafner and Bisogni 2009)], which results in partial pressures of about 0.2, 0.03, and 3×10^{-8} atm for CO_2, H_2S, and CH_3COOH, respectively. Typical dairy barn air partial pressures were taken as $5 \times 10^{-4}, 1 \times 10^{-8}$, and 2×10^{-8} atm for CO_2, H_2S, and CH_3COOH, respectively (Zhao et al. 2007; Martensson et al. 1999).

Predicted acidic gas interference was most important at higher acidic gas partial pressures, lower citric acid concentrations, and higher pH values (Fig. 6). Simulations showed that clean air has only a small effect, even for the 1 mmol kg^{-1} case. However, dairy barn air will cause >10% error in measurements for 1 mmol kg^{-1} acid traps for pH >5.0, and gas in equilibrium with manure causes significant error through most of the range for this citric acid concentration. For barn air, the majority of the predicted error (>99%) is caused by acetic acid. For gas in equilibrium with manure, significant error can be avoided only by using a citric acid concentration of 10 mmol kg^{-1} (and then only for pH <5.5) or by using a higher citric acid concentration (error for the 100 mmol kg^{-1} case reaches −6% only at the highest pH, where the total NH_3 concentration is three-fold the citric acid concentration). For manure gas, acetic acid and CO_2 contribute approximately equally to the error, with H_2S contributing <5%.

The potential error from acidic gases must be evaluated for each type of sample, and may be the limiting factor in selecting the concentration of citric acid. The presence of interferences from acidic gases can be assessed by sparging an acid trap with an unreactive gas at the end of a trial, when the highest pH that will be used is attained. If acidic gases are present in solution, the solution pH will increase and ultimately stabilize after they have been removed. The difference in calculated total NH_3 at the pre- and post-sparging pH values will be the maximum error in the data, assuming that partial pressures of acidic gases were constant throughout the trial. Where it is not possible to select operating conditions that avoid significant errors from acidic gases, it may be possible to remove them upstream of the acid trap using a denuder (Lawrence and Koutrakis 1994; Rasmussen et al. 1996).

Basic gases present in the sample gas will also cause error. In this case, relative error in determination
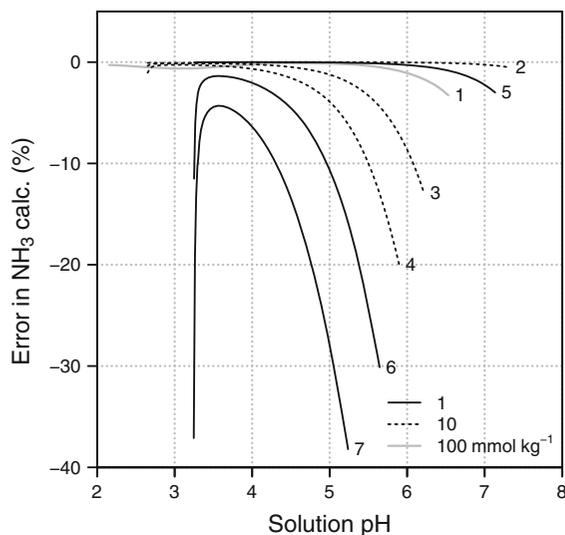
Fig. 6 Predicted error in calculation of total NH_3 in citric acid solutions in equilibrium with one of three gas phases. Lines are as follows: (1) 100 mmol kg^{-1}, manure gas; (2) 10 mmol kg^{-1}, clean air; (3) 10 mmol kg^{-1}, barn air; (4) 10 mmol kg^{-1}, manure gas; (5) 1 mmol kg^{-1}, clean air; (6) 1 mmol kg^{-1}, barn air; (7) 1 mmol kg^{-1}, manure gas. All results are for 25°C

of NH_3 will be equal to the relative concentration of basic gases in the sample gas. Fortunately, NH_3 is the dominant basic gas emitted from agricultural systems. Volatile amines are present in agricultural emissions, but at much lower levels than NH_3 (Schade and Curtzen 1995; Rappert and Muller 2005; Huang et al. 2009).

Conclusions

Titrations, laboratory emission measurements, and measurement of gaseous NH_3 in the field all indicate that the proposed pH-based citric acid trap (CA-pH) method is an accurate and precise approach for measuring NH_3 emission or gaseous NH_3 concentration. The sensitivity is lower than other methods for measurement of NH_3 in acid solutions, but the new method is inexpensive, data collection is simple and rapid, and repeated measurements can be made on the same solution over time. The method is best suited for measurement of NH_3 emission in the laboratory, or high gaseous NH_3 concentrations in the field, but can be used to measure gaseous NH_3 down to 340 μg m^{-3} and possible lower. In applying the method, it is

important to evaluate the potential for bias due to interferences, especially from acidic gases.

References

Clegg S, Brimblecombe P (1989) Solubility of ammonia in pure aqueous and multicomponent solutions. J Phys Chem 93(20):7237–7248

Clegg SL, Whitfield M (1995) A chemical-model of seawater including dissolved ammonia and the stoichiometric dissociation-constant of ammonia in estuarine water and seawater from −2°C to 40°C. Geochim Cosmochim Acta 59(12):2403–2421

Crea F, De Stefano C, Millero F, Crea F (2004) Dissociation constants for citric acid in NaCl and KCl solutions and their mixtures at 25°C. J Solution Chem 33(11):1349–1366. doi:10.1007/s10953-004-1046-z

Emerson MT, Grunwald E, Kromhout RA (1960) Proton-transfer studies by nuclear magnetic resonance. i. diffusion control in the reaction of ammonium ion in aqueous acid. J Chem Phys 33(2):547. doi:10.1063/1.1731182

Hafner SD, Bisogni JJ (2009) Modeling of ammonia speciation in anaerobic digesters. Water Res 43(17):4105–4114. doi:10.1016/j.watres.2009.05.044

Huang G, Hou J, Zhou X (2009) A measurement method for atmospheric ammonia and primary amines based on aqueous sampling, OPA derivatization and HPLC analysis. Environ Sci Technol 43(15):5851–5856. doi:10.1021/es900988q

Kielland J (1937) Individual activity coefficients of ions in aqueous solutions. J Am Chem Soc 59:1675–1678

Lawrence J, Koutrakis P (1994) Measurement of atmospheric formic and acetic-acids—methods evaluation and results from field studies. Environ Sci Technol 28(5):957–964

Martell A, Smith R, Motekaitis R (2004) Database 46: NIST critically selected stability constants of metal complexes. URL http://www.nist.gov/srd/nist46.cfm

Martensson L, Magnusson M, Shen Y, Jnsson J (1999) Air concentrations of volatile organic acids in confined animal buildings-determination with ion chromatography. Agric Ecosyst Environ 75(1–2):101–108. doi:10.1016/S0167-8809(99)00072-9

National Research Council: (1979) Ammonia. Medical and biological effects of environmental pollutants. University Park Press, Baltimore

Ni J, Hendriks J, Vinckier C, Coenegrachts J (2000) A new concept of carbon dioxide accelerated ammonia release from liquid manure in pig house. Environ Int 26(1–2):97–104

Ni JQ, Heber AJ (2001) Sampling and measurement of ammonia concentration at animal facilities: a review. Adv Agronom 98:201–269

Parkhurst D (2010) PHREEQC: a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. URL http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/

Phillips V, Lee D, Scholtens R, Garland J, Sneath R (2001) A review of methods for measuring emission rates of ammonia from livestock buildings and slurry or manure stores, part 2: monitoring flux rates, concentrations and airflow rates. J Agric Eng Res 78(1):1–14

Plummer L, Busenberg E (1982) The solubilities of calcite, aragonite and vaterite in CO_2–H_2O solutions between 0°C and 90°C, and an evaluation of the aqueous model for the system $CaCO_3$–CO_2–H_2O. Geochim Cosmochim Acta 46(6):1011–1040

R Development Core Team (2010) R: a language and environment for statistical computing. URL http://www.R-project.org

Rappert S, Muller R (2005) Odor compounds in waste gas emissions from agricultural operations and food industries. Waste Manag 25(9):887–907. doi:10.1016/j.wasman.2005.07.008

Rasmussen RA, Lewis CW, Stevens RK, Ellenson WD, Dattner SL (1996) Removing CO_2 from atmospheric samples for radiocarbon measurements of volatile organic compounds. Environ Sci Technol 30(4):1092–1097. doi:10.1021/es9501979

Sander R (2011) Henry's law constants. In: Linstrom P, Mallard W (eds) NIST Chemistry WebBook, NIST Standard Reference Database Number 69, National Institute of Standards and Technology, Gaithersburg. URL http://webbook.nist.gov

Schade G, Curtzen P (1995) Emission of aliphatic-amines from animal husbandry and their reactions—potential source of N_2O and HCN. J Atmos Chem 22(3):319–346

Shah S, Westerman P, Arogo J (2006) Measuring ammonia concentrations and emissions from agricultural land and liquid surfaces: a review. J Air Waste Manag Assoc 56(7):945–960

Sommer SG, Husted S (1995) The chemical buffer system in raw and digested animal slurry. J Agric Sci 124(01):45–53. doi:10.1017/S0021859600071239

Thompson R, Meisinger J (2004) Gaseous nitrogen losses and ammonia volatilization measurement following land application of cattle slurry in the mid-Atlantic region of the USA. Plant Soil 266(1–2):231–246

Zemaitis JF (1986) Handbook of aqueous electrolyte thermo-dynamics: theory and application. Design Institute for Physical Property Data sponsored by the American Institute of Chemical Engineers, New York

Zhao L, Brugger M, Manuzon R, Arnold G, Imerman E (2007) Variations in air quality of new ohio dairy facilities with natural ventilation systems. Appl Eng Agric 23(3):339–346