Accelerating 1H NMR Detection of Aqueous Ammonia

Kolen, Martin; Smith, Wilson A.; Mulder, Fokko M.

DOI
10.1021/acsomega.0c06130

Publication date
2021

Document Version
Final published version

Published in
ACS Omega

Citation (APA)

Important note
To cite this publication, please use the final published version (if applicable). Please check the document version above.
Accelerating $^1$H NMR Detection of Aqueous Ammonia

Martin Kolen,* Wilson A. Smith, and Fokko M. Mulder*

Cite This: ACS Omega 2021, 6, 5698–5704

ABSTRACT: Direct electrolytic $\text{N}_2$ reduction to ammonia ($\text{NH}_3$) is a renewable alternative to the Haber–Bosch process. The activity and selectivity of electrocatalysts are evaluated by measuring the amount of $\text{NH}_3$ in the electrolyte. Quantitative $^1$H nuclear magnetic resonance (qNMR) detection reduces the bench time to analyze samples of $\text{NH}_3$ (present in the assay as $\text{NH}_4^+$) compared to conventional spectrophotometric methods. However, many groups do not have access to an NMR spectrometer with sufficiently high sensitivity. We report that by adding $1 \text{ mM}$ paramagnetic Gd$^{3+}$ ions to the NMR sample, the required analysis time can be reduced by an order of magnitude such that fast NH$_4^+$ detection becomes accessible with a standard NMR spectrometer. Accurate, internally calibrated quantification is possible over a wide pH range.

INTRODUCTION

Ammonia ($\text{NH}_3$) is one of the largest chemical commodities responsible for about 1.5% of global energy use and associated $\text{CO}_2$ emissions from the Haber–Bosch process. Its primary use is as a feedstock for nitrogen-based fertilizers. Electrochemical, fossil-fuel-free methods to produce ammonia are gaining significant interest for the reduction of $\text{CO}_2$ emissions, as well as enable ammonia as a carbon-free energy carrier and storage material.$^1$-$^3$ Direct electrolytic $\text{N}_2$ reduction is a renewable alternative to synthesize $\text{NH}_3$. To suppress the undesirable hydrogen evolution reaction, a selective electrocatalyst is needed.$^5$

The activity and selectivity of electrocatalysts are quantified by measuring the accumulated $\text{NH}_3$ in the electrolyte with appropriate detection methods. Recently, a number of papers were published concerning the difficulty of obtaining reproducible results in nitrogen reduction research.$^5$-$^6$ Such difficulty is related to experimental procedures and significant amounts of $\text{NH}_3$ from dust, ambient air,$^1$-$^2$ $\text{N}_2$, and desorption from cell surfaces. In addition, NOx contamination or nitrogen-containing catalyst precursors can be reduced to $\text{NH}_3$ during electrolysis, which can be falsely attributed to $\text{N}_2$ reduction.$^9$-$^10$ Reliable testing and analysis procedures including control experiments with an isotope labeled $^{15}\text{N}_2$ are necessary to avoid false positives.$^5$ Conventional spectrophotometric $\text{NH}_3$ detection methods such as the indophenol blue method cannot distinguish between isotopologues of $\text{NH}_3$ and require considerable bench time.$^9$-$^10$ $^1$H NMR spectroscopy is a fast, accessible, and isotopically selective alternative to spectrophotometric methods for $\text{NH}_3$ detection, but as we will show below, the sensitivity on a standard 400 MHz spectrometer is insufficient.$^{11}$ Here, we present a powerful liquid-state NMR method with sufficient sensitivity on relatively easily accessible NMR spectrometers, i.e., requiring limited field strength and normal sensitivity probes.

Several alternatives to spectrophotometric $\text{NH}_3$ detection methods have been proposed recently. Ion chromatography can be used for ammonia detection but isotopologues cannot be distinguished and an overlap of $\text{NH}_4^+$ with other cations poses a threat to the accuracy of the method.$^{12}$ Yu et al. proposed ultrahigh-performance liquid chromatography–mass spectroscopy (UPLC-MS) to measure derivatized solutions of $\text{NH}_3$. The method is very sensitive and capable of distinguishing isotopologues of $\text{NH}_3$ but requires careful control over the pH. Quantitative $^1$H NMR has been widely adopted to quantify $^{15}\text{NH}_4^+$ from control experiments with $^{15}\text{N}_2$. The acidified form of ammonia, ammonium ($^{14}\text{NH}_4^+$), and its isotopologue $^{15}\text{NH}_4^+$ have an unmistakable fingerprint in the $^1$H NMR spectrum.$^{11}$

Quantitative $^1$H NMR is based on the proportional relationship between the signal integral $I_x$ and the number of protons $N_x$ responsible for that particular signal

$$I_x = K_x N_x$$

Received: December 16, 2020
Accepted: February 9, 2021
Published: February 19, 2021

© 2021 The Authors. Published by American Chemical Society

ACS Publications

http://pubs.acs.org/journal/acsodf

ACSM Omega 2021, 6, 5698–5704

ACS Omega 2021, 6, 5698–5704
where \( K_S \) is a proportionality factor that depends on the physicochemical properties of the sample. To achieve accurate quantification, changes in \( K_S \) have to be accounted for by a suitable quantification method.\(^{14}\) Pulse length-based concentration determination (PULCON) uses the principle of reciprocity to correlate the absolute intensity of two spectra measured in different solutions.\(^{15}\) Nielander et al. successfully applied the PULCON method to NH₄⁺ quantification.\(^{11}\)

Since fluctuations of \( K_S \) affect all resonances in the spectrum equally, the ratio of two peaks is independent of \( K_S \) and can therefore be used for quantification. Typically, an internal standard of known concentration is added as a reference. The concentration of NH₄⁺ can be quantified by either relative or absolute quantification. For relative quantification, a calibration curve is generated by measuring standard solutions of NH₄⁺ and an internal standard.\(^{14}\) The prerequisites for accurate ammonia quantification with relative quantification were recently described.\(^{16}\) Absolute quantification allows the calculation of the NH₄⁺ concentration directly from the integral of the peaks of NH₄⁺ and the internal standard without requiring a calibration curve according to

\[
C_{\text{NH}_4^+} = \frac{I_{\text{NH}_4^+}}{I_{\text{std}}} \frac{N_{\text{std}}}{N_{\text{NH}_4^+}} C_{\text{std}}
\]

(2)

where \( I, N, \) and \( C \) are the integral area, number of nuclei, and concentration of NH₄⁺ and standard, respectively. Absolute quantification requires that the total time spent to acquire one scan, the interscan delay \( t_{\text{scan}} \), is at least 5 times the longest longitudinal relaxation time \( T_1 \) in the sample.\(^{15}\) Despite the advantages of absolute quantification (calibration-free and robust) so far, no absolute quantification method has been proposed for ammonia detection. Hodgetts et al. reported that a \( d_1, T_1, \) and proton exchange-induced loss of coherence affects the NH₄⁺ peak, rendering absolute quantification not suitable for NH₄⁺ detection.\(^{16}\) By adding a suitable paramagnetic salt, accurate absolute quantification becomes possible because the \( T_1 \) values of both the internal standard and NH₄⁺ are reduced so that there is insufficient time for the proton exchange to induce a loss of coherence as we will see below.

The lower limit of quantification (LOQ) of a detection method is the lowest concentration of NH₄⁺ that can be measured within an acceptable time and with an acceptable accuracy. The LOQ depends on the sensitivity, which is calculated from the signal-to-noise ratio (SNR) at a certain interscan delay \( t_{\text{scan}} \)

\[
\text{sensitivity} = \frac{\text{SNR}}{t_{\text{scan}}}
\]

(3)

To reduce the minimum LOQ by a factor of 2, the analysis time has to be quadrupled.\(^{17}\) Nielander et al. could detect 1 \( \mu \)M NH₄⁺ in ethanol within 1 h (\( t_{\text{scan}} = 2 \) s) with a 900 MHz NMR and cryo-probe.\(^{11}\) The sensitivity difference between a 900 MHz NMR and a standard laboratory NMR (400 MHz) is substantial. The type of probe and the field strength difference lead to 1 order of magnitude lower sensitivity, which leads to 2 orders of magnitude longer analysis time to achieve the same LOQ on a 400 MHz NMR without cryo-probe.\(^{18}\) To compensate for the lower sensitivity, longer experiments (typically several hours) are necessary to accumulate enough NH₄⁺ in the electrolyte to reach the detection limit, which is unfavorable and which in addition increases the risk of false negatives due to deactivation and of false positives due to contamination. Higher \( ^1\)H NMR sensitivity is needed to enable laboratories with more standard NMR spectrometers to quantify NH₃ efficiently.

The type of the pulse sequence influences the NH₄⁺ sensitivity strongly.\(^{11,16}\) The signal from the hydrogen atoms of the solvent has to be suppressed to avoid baseline distortions and low receiver gain. Nielander et al. showed that pulse sequences that utilize pulsed field gradients in combination with selective excitation pulses are very effective at suppressing water without removing the NH₄⁺ signal.\(^{11}\) These pulse sequences use pulsed field gradients to dephase the water resonance and selective pulses to ensure that during acquisition water is completely out of phase while NH₄⁺ is in phase.\(^{19}\)

The \( T_1 \) of a molecule influences the sensitivity, because for a given interscan delay \( t_{\text{scan}} \), \( T_1 \) determines the percentage of spins that can relax back to equilibrium in between scans. A smaller percentage relaxation leads to less acquired signal per scan according to

\[
M_z = M_0(1 - e^{-t_{\text{scan}}/T_1})
\]

(4)

where \( M_z \) and \( M_0 \) are the magnetization in the \( z \)-axis following \( t_{\text{scan}} \) and at full relaxation, respectively. The interscan delay \( t_{\text{scan}} \) is composed of the recycle delay \( d_1 \) and the acquisition time. It is noteworthy that for some pulse sequences, the percentage relaxation only depends on the recycle delay, not on the acquisition time, as will be discussed in more detail below. Reducing the interscan delay, for example, by fast sampling is a well-known strategy to improve the \( ^1\)H NMR sensitivity.\(^{20}\) Another strategy to lower the interscan delay is to shorten the \( T_1 \) of the analyte, which has the advantage that the same percentage relaxation can be achieved at a lower interscan delay.\(^{14}\) \( T_1 \) is determined by the fluctuating magnetic interactions due to nearby magnetic moment fluctuations and due to positional changes of surrounding nuclei and moments. Interactions with unpaired electrons of paramagnetic substances are 1000 times larger than typical interactions between nuclear magnetic moments. Therefore, a small amount of a paramagnetic substance is sufficient to lower \( T_1 \) drastically.\(^{21}\) This concept is applied in contrast agents for medical magnetic resonance imaging (MRI). The so-called paramagnetic relaxation enhancement (PRE) is also a common strategy to overcome sensitivity barriers for small organic molecules and proteins, because as \( T_1 \) decreases, more scans can be acquired in the same amount of time.\(^{9,22,23}\)

## RESULTS AND DISCUSSION

The Gd⁴⁺ ion is widely used for PRE in medical MRI due to its large magnetic moment from seven unpaired electrons.\(^{24}\) We investigated the influence of paramagnetic Gd⁴⁺ ions on the sensitivity for aqueous ammonia detection to enable \( ^1\)H NMR as a routine analysis tool for NH₄⁺ quantification, with the use of an internal standard (absolute quantification). In agreement with Nielander et al., we found that pulse sequences that are suppressing the water resonance by dephasing it during acquisition are well suited for NH₄⁺ detection.\(^{11}\) With excitation sculpting (ES), the water resonance is suppressed effectively and a flat baseline is obtained around the NH₄⁺ triplet. However, at 40 \( \mu \)M NH₄⁺, the SNR is only 13.6 for a 12.8 min measurement on a 400 MHz NMR with room-temperature probe (see Figure 1a). With this sensitivity, it takes 4 h until the accumulated ammonia in the electrolyte
produced by a catalyst with intermediate activity becomes quantifiable by NMR (calculation in the Supporting Information, SI). Therefore, we sought to improve the sensitivity by adding 1 mM paramagnetic Gd\(^{3+}\) to the NMR tube. Maleic acid (MA) was added as an internal standard to quantify the amount of NH\(_4^+\) with absolute quantification. The singlet of maleic acid at ca. 6.21 ppm is sufficient separated from the NH\(_4^+\) triplet at ca. 6.9 ppm. The \(T_1\) values of both NH\(_4^+\) and MA decrease drastically after the addition of Gd\(^{3+}\). \(T_1\) decreases from 2.16 to 0.14 s and from 2.05 to 0.13 s for NH\(_4^+\) and MA, respectively. This 15.4-fold reduction of the \(T_1\) of NH\(_4^+\) enables a reduction of the interscan delay by the same factor, which, according to eq 3, leads to a potential 3.9-fold sensitivity increase (\(1/\sqrt{15.4} = 3.9\)). The linewidth of NH\(_4^+\) increases only slightly with the addition of Gd\(^{3+}\) from 3.6 to 4.2 Hz.

To show that the measured sensitivity gain matches the sensitivity gain predicted from \(T_1\) measurements, we measured a sample of 40 \(\mu\)M NH\(_4^+\) with and without 1 mM Gd\(^{3+}\) using different acquisition parameters (Figure 1a–c). In Figure 1a, the total analysis time is identical in both measurements and \(d_1\) is set to 5\(T_1\) so that NH\(_4^+\) has the same percentage relaxation in both cases. With 1 mM Gd\(^{3+}\), the sensitivity is significantly higher but not as much as expected from the \(T_1\) decrease (factor 3.9). We will later show that a sensitivity gain close to the predicted value can be measured directly by removing an additional 90° pulse that is by default included in the ES pulse sequence. With the default version of ES, the sensitivity gain is lower than expected from the \(T_1\) decrease because the additional 90° pulse removes the contribution of the acquisition time to the percentage relaxation. Consequently, the acquisition time only adds time to the total analysis time without improving signal strength and the percentage relaxation depends only on \(d_1\). Since the acquisition time makes up a larger fraction of the interscan delay at low interscan delays, the decrease of sensitivity is more pronounced with 1 mM Gd\(^{3+}\) where the acquisition time makes up 0.75 s of the total 1.5 s interscan delay. Without Gd\(^{3+}\), only 2 s out of 12 s interscan delay is the acquisition time that leads to a smaller sensitivity loss. In other words, the interscan delay could be factors 1.2 and 2 smaller for 0 mM Gd\(^{3+}\) and 1 mM Gd\(^{3+}\), respectively. Therefore, the sensitivity gain with 1 mM Gd\(^{3+}\) would increase by a factor 1.3 (\(\sqrt{1/1.3} = 1.3\)) from 2.4 to 3.1 if the sensitivity loss would have been equal in both cases. Taking into account \(\approx 15\%\) sensitivity loss due to line broadening, the sensitivity gain is 3.6, which is close to the predicted value.

The experiment shown in Figure 1a is not sufficient to prove a sensitivity gain because it only shows that with a higher recycle delay, less scans can be acquired in the same amount of time. Less scans will always lead to lower SNR. To prove a sensitivity increase, it is necessary to show that a larger recycle delay is necessary with 0 mM Gd\(^{3+}\) but not with 1 mM Gd\(^{3+}\). This is shown in Figure 1b, where both 0 mM Gd\(^{3+}\) and 1 mM Gd\(^{3+}\) were measured with low recycle delay (0.5 s) and identical total acquisition time. The sensitivity without Gd\(^{3+}\) is 3.9 times lower, indicating that a large fraction of the signal is lost due to low percentage relaxation. The percentage relaxation at a recycle delay of 0.5 s is 20.7% and 97.2% for \(T_1\) of 2.16 and 0.14 s, respectively. Therefore, 4.7 times more signal can be expected with 1 mM Gd\(^{3+}\) in the same amount of time. We assume that 15% of that signal increase is lost due to line broadening with Gd\(^{3+}\), which results in sensitivity improvement by a factor of 4.08. This value agrees well with the experimentally observed value of 3.9.

To study if adding Gd\(^{3+}\) also improves the sensitivity with other pulse sequences, we measured the sensitivity gain with the double pulsed field gradient spin echo (DPFGSE) pulse sequence (Figure 1c) using the same acquisition parameters as in Figure 1b. The sensitivity gain with DPFGSE (2.1) is lower than with ES (3.9). The reason for this is that with DPFGSE, the percentage relaxation has to be calculated using the full interscan delay including acquisition time, not just the \(d_1\) as for ES. Using the same methodology as in (b), we calculate the percentage relaxation with and without Gd\(^{3+}\) and arrive at an expected sensitivity gain of 1.8, which agrees well with the experimentally measured value. The sensitivity gain is lower than in (b) because with 1 mM Gd\(^{3+}\), the chosen \(t_{\text{escan}}\) of 1.25 s is almost 9 times longer than the \(T_1\) of NH\(_4^+\), which means that \(t_{\text{escan}}\) is much longer than the necessary 5\(T_1\), and as a result, sensitivity is lost. The previous examples demonstrate that after addition of 1 mM Gd\(^{3+}\), a significant sensitivity gain is observed with different acquisition parameters and pulse sequences, and this sensitivity gain agrees well with the expected values predicted from \(T_1\) measurements.

We measured the accuracy of NH\(_4^+\) quantification with 1 mM Gd\(^{3+}\) by calculating the NH\(_4^+\) concentration from the intensities of MA and NH\(_4^+\) using eq 2 and comparing it to the gravimetrically measured concentration (Figure 2a,b). The method has very good linearity (\(R^2 = 0.999\)) and an acceptable relative error (\(\leq 10\%\)) in the NH\(_4^+\) concentration range of 30–388 \(\mu\)M with the ES pulse sequence. The relative error is randomly distributed around the abscissa, which suggests that it is caused by integration errors. Higher accuracy (relative error \(\leq 5.3\%\)) was obtained with an isotope labeled \(^{15}\)NH\(_4^+\) (see Figure S2). \(^{15}\)NH\(_4^+\) can be quantified with higher accuracy because it appears in the NMR spectrum as a doublet, which has inherently higher SNR than the \(^{14}\)NH\(_4^+\) triplet.
The pH of the catholyte, which is used for detection, can vary over time due to acidic or alkaline species produced in the electrochemical reaction or because of migration of ions induced by the electric field.\(^{25,26}\) \(\text{N}_2\) reduction experiments are especially prone to pH changes because the electrolyte volume is minimized to maximize the signal for ammonia detection. Both UPLC-MS and the indophenol method are sensitive to pH changes because the pH in the electrolyte volume varies over time due to acidic or alkaline species produced in the electrochemical reaction or because of migration of ions induced by the electric field.\(^{25,26}\) Both UPLC-MS and the indophenol method are sensitive to pH changes because the pH influences the reaction that is carried out prior to analysis.\(^{9,13}\) Therefore, additional dilution steps can be necessary to measure accurately with these methods.

To investigate if the accuracy of our \(^1\text{H} \)NMR method depends on the pH, we acidified a sample of 388 \(\mu\text{M} \text{NH}_4^+\) with different concentrations of \(\text{H}_2\text{SO}_4\) (Figure 3a). Based on the previous finding that the \(T_1\) values of \(\text{NH}_4^+\) and MA are very close to each other, we chose a recycle delay of 0.5 s \((3T_1)\) for this experiment. For acid concentrations above 37 mM \(\text{H}_2\text{SO}_4\), the relative error continuously increases when more acid is added. To investigate if the growing relative error might be caused by changing \(T_1\) values, we measured the \(T_1\) values of \(\text{NH}_4^+\) and MA at 370 mM \(\text{H}_2\text{SO}_4\) (Figure 3b). The gap between the \(T_1\) values of \(\text{NH}_4^+\) and MA is slightly larger at 370 mM \(\text{H}_2\text{SO}_4\) than at 37 mM \(\text{H}_2\text{SO}_4\) which might explain the larger error. After increasing the recycle delay from 0.5 to 1.5 s to compensate for the increased \(T_1\) gap, the relative error decreases to \(<2\%\) between 37 and 222 mM \(\text{H}_2\text{SO}_4\). This suggests that the detection method is accurate over a wide pH range if a higher \(d_1\) is chosen to compensate for \(T_1\) changes.

In Figure 3, even with a high recycle delay of 1.5 s, an unusually high error remains at the highest and lowest acid concentrations. The error at the lowest acid concentrations is in agreement with the results by Hodgetts et al. and is caused by deprotonation of MA below 20 mM \(\text{H}_2\text{SO}_4\).\(^{16}\) Spectra acquired at the highest acid concentration had phasing issues, which had to be corrected by postprocessing the spectrum using the autophasing algorithm in the software package MestReNova. We suspect that the phasing issues are caused by tuning and matching, which become more difficult at high salt concentrations.\(^{14}\) To achieve maximum accuracy, the acid concentration should not exceed 222 mM.

As discussed previously, with the default settings of the ES pulse sequence, the acquisition time does not contribute to the percentage relaxation so that sensitivity is lost. To determine the maximum sensitivity for \(\text{NH}_4^+\) detection with 1 mM \(\text{Gd}^{3+}\), we deactivated the additional 90\(^\circ\) pulse at the beginning of the pulse sequence so that both acquisition time and recycle delay contribute to the percentage relaxation. This leads to a significant increase in sensitivity (see Figure 4). The sensitivity can be further increased by reducing the interscan delay from \(3T_1\) to \(3T_1\), which is feasible in this case because the \(T_1\) values of \(\text{NH}_4^+\) and MA are very close to each other. The SNR of a 40 \(\mu\text{M} \text{NH}_4^+\) sample measured for 14.6 min (interscan delay \(3T_1\)) is 47.4. This corresponds to a 1.4-fold sensitivity increase compared with the activated 90\(^\circ\) pulse. The relative error is similar to an interscan delay of \(3T_1\) and \(3T_1\) (<6\%), indicating that the interscan delay can be reduced without sacrificing accuracy. As discussed above, at high acid concentrations, a higher recycle than \(3T_1\) might be necessary to compensate for \(T_1\) changes.

We remeasured the sensitivity gain after addition of 1 mM \(\text{Gd}^{3+}\) to obtain a direct measurement of the sensitivity gain without the interference of the additional 90\(^\circ\) pulse. Sensitivity increases of 3.9- and 3.6-fold are measured with 1 mM \(\text{Gd}^{3+}\) for interscan delays of \(3T_1\) and \(3T_1\), respectively. These values are consistent with the predicted sensitivity gain from the \(T_1\)
NMR tubes, postprocessing methods, etc. We attempt to magnitude because of di

Hodgetts et al. by calculating a standardized sensitivity that compare our sensitivity with the sensitivity measured by
di

The sensitivity can be increased by a factor of 3.5 mM Gd3+, which corresponds to an order of magnitude less

standardized sensitivity is signifi
cantly higher than the value calculated from Figure 1a (3.1), we estimate that the sensitivity can be increased by a factor of 3.5 ± 0.4 with 1 mM Gd3+, which corresponds to an order of magnitude less analysis time or several hours less ammonia accumulation to reach the detection limit. This sensitivity improvement makes fast 1H NMR NH4+ quantification accessible with a standard NMR spectrometer and reduces the cost of essential control experiments with expensive (∽$500 euros/L) 15N2.

It is difficult to compare the sensitivities of two different NMR detection methods if these methods were applied using different spectrometers. The sensitivity can vary an order of magnitude because of different field strength, probe hardware, NMR tubes, postprocessing methods, etc. We attempt to compare our sensitivity with the sensitivity measured by Hodggets et al. by calculating a standardized sensitivity that takes into account the influence of field strength and type of probe (cryo- or room-temperature probe) on sensitivity (Figure 4). The calculation of the standardized sensitivity can be found in the SI. As expected, with 1 mM Gd3+, the standardized sensitivity is significantly higher than the value reported by Hodggets et al. without Gd3+.

**CONCLUSIONS**

In summary, the 1H NMR analysis time required to quantify NH4+ in aqueous samples can be reduced by an order of magnitude by adding 1 mM paramagnetic Gd3+. This improvement makes 1H NMR NH4+ quantification more accessible and reduces the cost of control experiments with 15N2, which enables faster, more reliable N2 reduction research. A large reduction of the T1 of NH4+ and MA without significant line broadening causes the sensitivity increase. The method has very good linearity (R2 = 0.999) and is accurate over a wide pH range if the interscan delay is increased to compensate for small T1 changes.

**MATERIALS AND METHODS**

**Materials.** 15NH4Cl (99.995%), 15NH4Cl (≥98 atom %, 1N ≥ 99 % CP), maleic acid (≥99%), and H2SO4 (≥97.5%) were obtained from Sigma-Aldrich. Gadolinium(III) nitrate hexahydrate (99.9%) was obtained from Fisher Scientific. DMSO-d6 (99.9% D, 0.03% V/V Tetramethylsilan) was obtained from Cambridge Isotope Laboratories. Ultrapure water was produced with a Milli-Q Advantage A10 water purification system (resistivity: 18.2 Ω at 25°C).

**Sample Preparation.** Ammonia standard solutions (40–500 μM) were prepared fresh daily by adding a suitable amount of NH4Cl to ultrapure water and performing serial dilutions to the required standard concentrations. In a typical experiment, 525 μL of NH4+ standard solution was mixed with 50 μL of 0.5 M H2SO4, 50 μL of DMSO-d6, 25 μL of 12.5 mM maleic acid, and 25 μL of 27 mM Gd3+ solution inside a 1.5 mL Eppendorf tube. This solution (600 μL) was transferred into a 5 mm thin-wall NMR tube (Wilmad). All NH4+ concentrations are reported as concentration in the NMR tube unless otherwise noted. The NMR tube was closed with Norell Sample Vault NMR tube caps (Sigma-Aldrich). The tube was cleaned with ultrapure water and ethanol using an NMR tube cleaner. After cleaning, the NMR tube was dried at 60°C for 1 h and stored in a dust-free environment.

**1H NMR Data Acquisition and Processing.** 1H NMR spectra were acquired on a 400 MHz pulsed Fourier transform NMR spectrometer equipped with an autosampler. An autotunable, temperature-regulated Agilent OnenMR room-temperature probe was used for all measurements. The temperature was set to 25 °C, and the receiver gain was optimized automatically. To avoid baseline distortions and low receiver gain, the water resonance has to be suppressed by a suitable pulse sequence. Good water suppression was obtained with pulse sequences that use pulsed field gradients to dephase the water magnetization and selective pulses to flip the NH4+ magnetization back into phase during acquisition. Two pulse sequences that were preinstalled in the software of our NMR system (vNMRj) were used in this work: Excitation Sculpting (vNMRj: “waterES”) and double pulsed field gradient spin echo (vNMRj: “selexcit”). The waterES pulse sequence has the following structure:

waterES: G1-P90-G1-d1-P90-G2-S180-P180-G2-G3-S180-P180-G3-aq

where G1–G3 are the z-ge

Bullet points for the main text are included in the text to highlight important points.
strengths of 0.85 and 1.28 G cm⁻¹, respectively, and a duration of 1 ms. The selected 180° pulse was defined as a "q3" pulse shape with a width of 5 ms and a power of 0 dB. The position and width of the selective pulse in the frequency domain were set to 6.63 ppm and 540 Hz, respectively, so that the pulse is positioned between the resonances of NH₄⁺ and maleic acid. The pulse shapes q3 and "Wsupp" that were used to create the shaped pulses in waterES and seleexcit are standard pulse shapes available in the software package vNMRj. Equivalent pulse shapes should be available in other software packages.

The data were processed in the software package MestReNova (version: 12.0.1–20560) using the automated tools provided in this software. Unless otherwise noted, an apodization of 4 Hz was applied followed by phase and baseline correction. The peaks of NH₄⁺ (t, ≈6.99 ppm, 4H) and MA (s, ≈6.21 ppm, 2H) were integrated using the line fitting tool. Using the line fitting tool instead of directly integrating the peaks leads to an approximately 2-fold decrease of the relative error. The three integrals of the NH₄⁺ peaks were added together to calculate the total NH₄⁺ integral. From the ratio of the integral of NH₄⁺ and MA, the concentration of NH₄⁺ was calculated with absolute quantification according to eq 2. The linewidth of NH₄⁺ is calculated by averaging the full width at half-maximum (FWHM) of the three NH₄⁺ peaks. The signal-to-noise ratio (SNR) was calculated using the "SNR calculation" tool in MestReNova with the noise region defined from 11 to 13 ppm. The SNR values were calculated by averaging three measurements of the average SNR of the three peaks of the NH₄⁺ triplet. The relative error was calculated according to

$$\text{relative error} = \frac{c_{\text{calcd}} - c_{\text{grav}}}{c_{\text{grav}}} \times 100$$

where c_{calcd} and c_{grav} are the concentrations of NH₄⁺ calculated from absolute quantification and from the weight and purity of the NH₄Cl that was added to prepare the standards, respectively.

The T₁ values of NH₄⁺ and MA were measured using the ES pulse sequence with default settings. Spectra were acquired at six different recycle delays, and the function $y(x) = a \times (1 - \exp(-bx))$ was fitted to the integrated peak intensities of NH₄⁺ and MA as a function of $d_i$ using the software OriginPro 2015. The parameter $b$ from the fitting function was inverted to calculate $T_1$. An example of the $T_1$ determination using this method can be found in the SI.

### ASSOCIATED CONTENT

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c06130.

Experimental details, calculations, and accuracy and linearity with $^{15}$NH₄⁺ and $T_1$ determination (PDF)

### AUTHOR INFORMATION

**Corresponding Authors**

Martin Kolen — Materials for Energy Conversion and Storage (MECS), Department of Chemical Engineering, Delft University of Technology, 2629 HZ Delft, The Netherlands; orcid.org/0000-0002-6309-4521; Email: m.kolen@tudelft.nl

Fokko M. Mulder — Materials for Energy Conversion and Storage (MECS), Department of Chemical Engineering, Delft University of Technology, 2629 HZ Delft, The Netherlands; orcid.org/0000-0003-0526-7081; Email: f.m.mulder@tudelft.nl

**Complete contact information is available at:**

https://pubs.acs.org/doi/10.1021/acsomega.0c06130

**Notes**

The authors declare no competing financial interest.

### ACKNOWLEDGMENTS

This work is part of the Direct Electrolytic Ammonia Production project with project number 15234, which is financed by The Netherlands Organisation for Scientific Research (NWO). The authors thank Dr. Stephen Eustace and Zhiyu Liu for helpful discussions about paramagnetic relaxation agents.

### REFERENCES


(13) Yu, W.; Lewis, N. S.; Gray, H. B.; Dalleska, N. F. Isotopically Selective Quantification by UPLC-MS of Aqueous Ammonia at University of Technology, 2629 HZ Delft, The Netherlands; orcid.org/0000-0003-0526-7081; Email: f.m.mulder@tudelft.nl

本文内容是一个化学研究，在文档中提到了氨的生产和检测方法，以及相关的化学反应和实验技术。文章还讨论了氨作为潜在的间接氢存储材料的应用，并对日间和季节变化对可再生能源生成的影响进行了研究。研究还涉及了氨的合成协议，通过定量同位素测量。文献涵盖了从氨的合成到其在不同介质中的测定方法的研究，以及在二氧化氮还原中的应用。文章还提到了氨的光化学和催化合成方法，并讨论了铁掺杂二氧化钛和其他金属氧化物的光催化作用。


