Revealing Ammonia Quantification Minefield in Photo/Electrocatalysis

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Abstract: Photo/electrocatalytic ammonia synthesis—a low carbon and sustainable process has developed fast over the past decade while the ammonia yield over state-of-the-art photo/electrocatalysts are still very moderate (typically < 1 mmol g⁻¹ h⁻¹, roughly ~1 ppm taking xx volume solution and xx mass of catalyst used as one example). Such low concentration of NH₃ synthesised brings about a challenge on the reliable quantification of the product in both photocatalysis and electrocatalysis. Notably, we found that the quantitative detection of ammonia concentration below 0.2 ppm is error-prone, which is likely the case happening in the majority of photocatalytic or electrocatalytic NH₃ synthesis, thus arising concerns about the rationality and accuracy for low-concentration ammonia quantification in these processes. Herein, we discuss the methodology used and analyse the reliability of various detection methods (e.g., indophenol blue method, nessler’s reagent method, ion chromatography method and ¹H nuclear magnetic resonance method) for the detection of trace ammonia in aqueous media. By regulating the parameters of detection methods, the experimental detection limitation can be expanded from 0.2 ppm to 0.1 ppm, even lower. The challenges facing in detection of low concentration of ammonia in photo/electrocatalysis can be overcome by integration of multiple detection methods. According to the data presented, we also propose an effective criteria for precise quantification of ammonia, avoiding the unreasonable comparisons in photo/electrocatalytic ammonia synthesis.

Introduction

Ammonia (NH₃) is one of the essential commercial chemicals in today’s chemical industry.[5] The industrially artificial catalytic reduction of nitrogen (N₂) to ammonia via the Haber-Bosch process over a metallic Fe-based catalyst needs harsh reaction conditions (200-250 bar, 400-500 °C).[6] Conversely, the enzyme nitrogenases in nature containing cationic Fe and FeMo active sites can fixate N₂ to NH₃ under ambient conditions.[7] Taking inspiration from these biocatalytic systems, more and more researchers work on Ni≡N bond activation under ambient conditions through photo/electrocatalytic routes.[4] The photo/electrocatalytic ammonia synthesis driven by sunlight or electricity over the catalysts was widely explored and investigated, revealing the possibility of the nitrogen fixation under ambient reaction conditions.[5] As shown in Figure 1a, publications about photo/electrocatalytic nitrogen reduction reaction (NRR) research had been increasing during the past 5 years, indicating that the noticeable promise and potential of NRR.

Whilst significant fundamental advancements have been made in recent years regarding the photo/electrocatalytic ammonia synthesis, production rates and selectivity of the current catalytic systems still fails to warrant industrial interests.[6] At present, the evaluation of photo/electrocatalytic activity based on the production rate (µmol g⁻¹ h⁻¹) or coulombic efficiency possibly causes a misunderstanding on exploiting low current/overvoltage or low usage catalyst to attain attractive ammonia yield. Thus, how to reasonably evaluate the activity of synthetic ammonia is still a controversial issue. Besides, owing to the low catalytic ammonia production rates and environmental ammonia contamination problem, more attention has to be paid to the accurate and reproducible quantification of ammonia,[7] which is highly desirable and vital though technically challenging.

Results and Discussion

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Table 1. The $R^2$ values of different detection methods for quantifying ammonia concentration in pure water.

<table>
<thead>
<tr>
<th>Ammonia Detection Methods</th>
<th>$R^2$ (lower than 0.2 ppm)</th>
<th>$R^2$ (lower than 0.2 ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nessler’s reagent method</td>
<td>0.9990 ± 0.0029</td>
<td>-0.208 ± 70.419</td>
</tr>
<tr>
<td>Indophenol blue method</td>
<td>0.9995 ± 0.0007</td>
<td>0.9799 ± 0.0431</td>
</tr>
<tr>
<td>Indophenol blue method</td>
<td>0.9989 ± 0.0009</td>
<td>0.9376 ± 0.0373</td>
</tr>
<tr>
<td>Ion chromatography$^{[b]}$</td>
<td>0.9952 ± 0.0013</td>
<td>0.8047 ± 0.4946</td>
</tr>
<tr>
<td>Ion chromatography$^{[c]}$</td>
<td>0.9989 ± 0.0021</td>
<td>0.9033 ± 0.3529</td>
</tr>
<tr>
<td>NMR$^{[d]}$</td>
<td>/</td>
<td>0.9985</td>
</tr>
</tbody>
</table>

[a] Ion chromatography$^{[a]}$: the loop size is 10 $\mu$L, ICS 600, Thermo Fisher Scientific.
[b] Ion chromatography$^{[b]}$: the loop size is 20 $\mu$L, 930 compact IC Flex, Metrohm.
[c] NMR: $^1$H nuclear magnetic resonance spectroscopy method (0.02-0.5 ppm).

d, 1

Generally, the qualitative and quantitative analysis of ammonia depends on various methods, such as colorimetric methods (indophenol blue and Nessler’s reagent method),$^{[8]}$ ion chromatography method (IC),$^{[9]}$ fluorescence method,$^{[10]}$ ammonia ion-selective electrode and$^{[11]}$ nuclear magnetic resonance (NMR) method.$^{[11]}$ All of these methods theoretically show considerable consistency and high accuracy in wide-ranging ammonia concentrations under ideal conditions. However, when it comes to a complicated chemical environment (such as harsh pH conditions, impurity ions and other N-containing contaminations), the validity and accuracy, especially at nano/micromolar concentrations, need to be verified carefully.$^{[12]}$ Additionally, the detection and quantification of low-concentration ammonia (particularly below 0.2 ppm) become the pressing priority, considering that they are involved in the majority of the reported photo/electrocatalytic ammonia synthesis. Unfortunately, the accurate detection of low-concentration ammonia using typical methods is not optimistic as shown in Figure 1b. The detection errors for standard NH$_3$ solution (0.1 ppm) increase, ranging from 20.5% for Nessler’s reagent method to 71.2% for the ion chromatography method. Almost all testing methods exhibit unsatisfactory reproducibility when the ammonia concentration is below 0.2 ppm, leading to more inaccurate and unreliable detected results. The standard curves of NH$_3$ in pure water with indophenol blue, Nessler’s reagent and ion chromatography methods are presented in Figure S1 (supporting information) and Table 1. In the case of high ammonia concentration ($>0.2$ ppm), strong linear relationships are established between intensity and the concentration in aqueous media (pH = 7) (the coefficient of determination value ($R^2$) = 0.9990 for Nessler’s reagent method, 0.9995/0.9996 for indophenol blue methods and 0.9952/0.9989 for IC, respectively), which are in accordance with reported results. With the ammonia concentration decreases less than 0.2 ppm, the poor correlation coefficient of the three methods can be observed (Figure S2) probably due to the practical detection limitation of three different methods. It hints that the measured ammonia concentration lower than 0.2 ppm using normal quantification methods would be questionable.
In addition to the testing requirement of low-concentration ammonia in neutral water (pH = 7), other aqueous media (pH = 1 or pH = 13) are extensively employed in electrocatalysis. Considering the interference of ions on the ammonia quantification, we selected the electrolytes with different concentrations as a comparison, including 0.05 M H₂SO₄, 0.1 M KOH and 0.5 M Na₂SO₄ (Table 2 and Figure S5-B). For Nessler’s reagent method, it showed a great linear relationship between absorption intensity and the concentration of ammonia in 0.5 M Na₂SO₄ (R² = 0.9960), whereas the linearity is unsatisfactory in 0.05 M H₂SO₄ and 0.1 M KOH. Compared with Nessler’s reagent method, the indophenol blue method presented a remarkable correlation coefficient in three different pH solution (R² = 0.9999 for 0.05 M H₂SO₄, R² = 0.9987 for 0.5 M Na₂SO₄ and R² = 0.9901 for 0.1 M KOH). Nevertheless, the reproducibility of spectrophotometric/colorimetric assessment is unsatisfactory in the low ammonia concentration range, thus each examination needs to be recalibrated rigorously. The IC method would be more suitable for acidic and neutral aqueous media at low ammonia concentration (R² = 0.9953 for 0.05 M H₂SO₄) since the interference of Na⁺/K⁺ ions in different electrolytes. Alternatively, the NMR method exhibited dramatical reproducibility and stability in different electrolytes and a considerable R² of 0.9961 for 0.05 M H₂SO₄ and 0.9960 for 0.5 M Na₂SO₄. We also found that the high-concentration electrolytes present the higher challenge under the same test parameters. The brand new test parameters and specific NMR tubes are required (such as shape tube), otherwise it would cause damages to NMR instrumentation if we need to quantify low ammonia concentration dissolved in high-concentration electrolytes.

Many advantageous recommendations regarding ammonia quantification in photo/electrocatalysis have been made in reported work. On the basis of the foregoing and to further enhance the consistency and accuracy of measurement at low ammonia concentration (especially lower than 1 ppm or even 0.2 ppm), particular attention should be paid as summarized in Figure 3: i) Firstly, the quantitative measurement with ammonia concentration below 0.2 ppm is error-prone. The detection minifeild should be realized and valued in the photocatalytic and electrocatalytic experiments; ii) For the accuracy and scientific rigor, it is recommended that the detection of ammonia concentration below 0.2 ppm requires two different quantitative methods to cross check; iii) The appropriate ammonia determination method should be derived from the concentration of NH₃ production in photo/electrocatalysis (> 0.2 ppm or < 0.2 ppm). Additionally, the choice of NH₃ quantification methods is also dependent on the pH of electrolytes. For neutral electrolytes, three methods (NMR, Nessler’s reagent and indophenol blue methods) are consistent to achieve accurate detection of NH₃ concentrations below 0.2 ppm. The indophenol blue method is also suitable for alkaline and acid electrolytes. For photocatalysis, the ammonia concentrations (< 0.2 ppm) are recommended to be confirmed using IC or NMR methods. It is certainly more rigorous to confirm these quantitative results of ammonia by more than two different detection methods. Meanwhile, as the existence of trace ammonia in the air, the ammonia rates generated (especially lower than 0.2 ppm) with quantitatively isotopically labelled NMR would make this measurement more convincing (Figure S9).

Table 2. The R² values of different detection methods for quantifying ammonia concentration in different electrolytes.

<table>
<thead>
<tr>
<th>Ammonia Detection Methods</th>
<th>Electrolytes</th>
<th>R² (lower than 0.2 ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nessler’s reagent method</td>
<td>0.05M H₂SO₄</td>
<td>0.8979 ± 0.3424</td>
</tr>
<tr>
<td>Nessler’s reagent method</td>
<td>0.5M Na₂SO₄</td>
<td>0.9960 ± 0.0761</td>
</tr>
<tr>
<td>Nessler’s reagent method</td>
<td>0.1M KOH</td>
<td>0.9818 ± 0.0019</td>
</tr>
<tr>
<td>Indophenol blue method¹</td>
<td>0.05M H₂SO₄</td>
<td>0.9999 ± 0.0093</td>
</tr>
<tr>
<td>Indophenol blue method¹</td>
<td>0.5M Na₂SO₄</td>
<td>0.9987 ± 0.0062</td>
</tr>
<tr>
<td>Indophenol blue method¹</td>
<td>0.1M KOH</td>
<td>0.9901 ± 0.0172</td>
</tr>
<tr>
<td>Ion chromatography¹</td>
<td>0.05M H₂SO₄</td>
<td>0.9953 ± 0.0004</td>
</tr>
<tr>
<td>Ion chromatography¹</td>
<td>0.5M Na₂SO₄</td>
<td></td>
</tr>
<tr>
<td>Ion chromatography¹</td>
<td>0.1M KOH</td>
<td></td>
</tr>
<tr>
<td>NMR¹</td>
<td>0.05M H₂SO₄</td>
<td>0.9961</td>
</tr>
<tr>
<td>NMR¹</td>
<td>0.5M Na₂SO₄</td>
<td>0.9960</td>
</tr>
</tbody>
</table>

[a] Ion chromatography¹: the loop size is 100 μL, IGS 600, Thermo Fisher Scientific.
[b] ¹H NMR: ¹H nuclear magnetic resonance spectroscopy method.

Figure 2. (a-b) ¹H NMR spectra of NH₄⁺ (0.1 ppm) in aqueous media included a stand reference (maleic acid) and repetitive experiments using DMSO-d₄. (c) NMR spectra of NH₄⁺ (0.1 ppm) solution in DMSO-d₄, D₂O, CD₃OD and CD₃CN. One ppm equals 1 mg of NH₄⁺ in 1 L of H₂O.

Figure 3. Flow diagram of suggested protocols to rigorously conduct ammonia quantification (IB = indophenol blue method, NS = Nessler’s reagent method, IC = ion chromatography method, and NMR = ¹H nuclear magnetic resonance method).
Moreover, we give prominence to the significance of accurate and reproducible quantification of ammonia, especially lower than 1 ppm or even 0.2 ppm (Figure 4). The previously reported catalysts are systematically summed up in accordance with the mass-normalized ammonia evolution rates and produced ammonia concentration (Table S2). Regrettably, in 65% electrocatalytic statistics, the generated NH3 concentration is unable to be calculated due to deficient information provided. For another 35% electrocatalytic reported results and all photocatalytic statistical results, most of the mass-normalized ammonia production ranges from 0.013 to 1.0 mmol g⁻¹ h⁻¹ [14]. Notably, the generated ammonia concentrations are still at the ppm level (mg L⁻¹), or even the ppb level (μg L⁻¹), which puts forward a higher quantitative requirement for ammonia detection. Furthermore, the production rate (μmol g⁻¹ h⁻¹) or coulombic efficiency could be unreasonably raised, exploiting low usage catalyst or low current/overvoltage. [15] The obtained data are challenging to reflect actual catalytic performance directly, sometimes would cause misunderstanding. Reporting quantitative ammonia concentration can assist in providing another reference standard for comparison, thereby advocating researchers to provide the final NH₃ concentration and absolute ammonia yield (μmol or μmol h⁻¹) for appraising the catalytic performance of a new catalytic system.

**Conclusion**

In summary, we present the advantages and detection limitation and application scope of various detection methods (indophenol blue method, Nessler’s reagent method, ion chromatography method and ¹H nuclear magnetic resonance method), especially when ammonia is below the detection limitation of 0.2 ppm in photo/electrocatalytic ammonia synthesis. On the basis of the data presented, a rigorous ammonia detection flow diagram and another reference standard were proposed for more accurate and reliable NH₃ quantification (especially lower than 1 ppm or even 0.2 ppm), together with the positioning and evaluation of the catalytic activity. It is highly recommended that the low-concentration ammonia quantification should be paid sufficient attention, so as to bypass detection minefield and push the development of the online and fast characterization techniques for accurate and reliable ammonia quantification in the future.

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**Keywords:** ammonia • detection • photo/electrocatalysis • quantification • 0.2 ppm.

![Figure 4. Ammonia concentration and mass-normalized NH₃ production rates of reported NRR photo/electrocatalysts. The NH₃ evolution rates, ammonia concentration and other detailed information are from the literature and summarized in Table S2.](image)


The analytical methods for the detection of ammonia concentration below 0.2 ppm in photo/electrocatalytic \( \text{N}_2 \) fixation are evaluated rigorously, reliably and insightfully. We motivate to indicate the low-concentration ammonia quantification minefield and conclude a rigorous ammonia detection flowchart as well as another reference standard to achieve a more accurate and responsible ammonia detection in photo/electrocatalysis.