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Supporting Information

Modified Indophenol Blue Method Enables Reliable Routine Quantification of Photocatalytic Produced Ammonia in Aqueous Sulfite Electrolyte

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Keywords: ammonia quantification, sulfite sacrificial reagent, interference effect, photocatalysis, indophenol blue method

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Section 1. Details of chemicals and materials and sample characterizations

Quantification of ammonia by the Nessler's reagent method: Add 0.1 mL of Nessler reagent and 0.1 mL of a 500 $g \cdot L^{-1}$ potassium sodium tartrate solution to 2 mL of the sample solution. Subsequently, incubate the mixture in the dark at room temperature for 10 minutes. Finally, measure the absorbance at approximately 420 nm using a UV-Vis spectrophotometer.

Quantification of ammonia by the ion chromatography method: Ion chromatography method was performed on an ICS-600 instrument (ThermoFisher Scientific). The methanesulfonic acid solution was used as eluent with a flow rate of 1 ml min^{-1}. All the samples were manually injected to prevent ammonia interference in the air.

Quantification of ammonia by ^1H nuclear magnetic resonance (^1H NMR) method.

Solution A: 50 μL of 1 mM Maleic acid was used as the internal standard; Solution B: 50 μL of DMSO-d_6 was used for a spin-lock field. Solution C: 50 μL of 0.05M H_2SO_4 was used to regulate pH of solution. Solution A, B and C were added into 900 μL of ammonia in 0.06M Na_2SO_3. After shaking up, 600 μL of above mixed solution was added into a NMR tube.

Quantification of N_2H_4 by the Watt and Chrisp method: The specific experimental procedure involves adding 2 mL of hydrochloric acid, 20 mL of ethanol, and 0.4 g of DMAB to 2 mL of the sample solution, followed by thorough mixing. After incubating in the dark at room temperature for 15 minutes, the absorbance is measured at 457 nm using a UV-Vis spectrophotometer.

Section 2. Comparative analysis of different ammonia quantification methods in aqueous sulfite electrolyte

Drawing on a thorough review of photocatalytic ammonia synthesis research, we assess ammonia quantification methods from the following perspectives (Table S1). This section primarily compares ammonia quantification methods, including nuclear magnetic resonance method (NMR)、ion chromatography method (IC)、Nessler's reagent method (Nessler)、conventional indophenol blue method (c-IB), and modified indophenol blue method (m-IB) developed in this work. The threshold in aqueous sulfite electrolyte (TASE) beyond which general ammonia quantification methods become invalid is established based on operational convenience, quantification reliability, and experimental economy. Operational convenience encompasses tolerance to chemical environments and real-time analytical capability. Quantification reliability primarily involves quantification sensitivity and quantification accuracy, especially regarding achievable detection limits and the veracity of results. Experimental economy refers to factors such as equipment and consumables cost. A fivedimensional evaluation system has been established based on the aforementioned features, with a maximum score of 10 points for each dimension, as shown in Figure S1. If any evaluation dimension scores are $\leqslant 6$, the method does not meet the threshold in aqueous sulfite electrolyte (TASE). This threshold acts as a practical benchmark for evaluating reliable ammonia quantification methods, focusing on operational convenience, quantification reliability, and experimental economy. Furthermore, it indicates the limitations of general ammonia quantification methods when applied to routine ammonia laboratory quantification in aqueous sulfite electrolyte. As details evidenced by the comparative analysis listed in Table S1 and the subsequent paragraphs, the final results are illustrated in Figure 1 of the article.

Table S1. Evaluation framework for ammonia quantification methods in aqueous sulfite electrolyte.

Comparison dimensions	Scoring	Specific aspects	Evaluation criteria	conventional ammonia quantification methods				m-IB (this work)
				NMR	IC	Nessler	c-IB	
Tolerance to chemical environments	(10)	Ion interference	Primary ions (Na^+ SO_3^{2-} S^{2-}) (5)	None (5)	Na^+ (0)	S^{2-} (0)	SO_3^{2-} (0)	None (5)
			Potential ions (2)	Organic solvent (1)	None (2)	Metal cations hydrazine, carbonyl compounds (0)	None (2)	None (2)
		pH range	Acidic (1) Neutral (1) Alkaline (1)	Neutral (1)	Neutral (1)	All (3)	Neutral Alkaline (2)	Neutral Alkaline (2)
		sub score		(7) ☼	(3) 💧	(3) 💧	(4) 💧	(9) ☼
Real-time analytical capability	(10)	Data acquisition time	Fast (3) Medium (2) Low (1)	Low (1)	Fast (3)	Medium (2)	Medium (2)	Medium (2)
		Equipment availability	Easy (7) Moderate (2) Scarce (1)	Scarce (1)	Moderate (2)	Easy (7)	Easy (7)	Easy (7)
		sub score		(2) 💧	(5) 💧	(9) ☼	(9) ☼	(9) ☼

Table S1. Continued.

Comparison dimensions	Scoring	Specific aspects	Evaluation criteria	conventional ammonia quantification methods				m-IB (this work)
				NMR	IC	Nessler	c-IB	
Quantification sensitivity	(10)	Detection limits	=0.2ppm (8)	Yes (8)	Yes (8)	Yes (8)	Yes (8)	Yes (8)
			<0.2ppm (2)	Yes (2)	Yes (2)	No (0)	No (0)	No (0)
		sub score		(10) ☼	(10) ☼	(8) ☼	(8) ☼	(8) ☼
Quantification accuracy	(10)	Linear relationship	R^2(=0.2ppm) (8)	0.999 (8)	0.999 (8)	0.999 (8)	0.999 (8)	0.999 (8)
			R^2(<0.2ppm) (2)	0.996 (1)	0.995 (1)	0.982 (0)	0.991 (0)	- (0)
		sub score		(9) ☼	(9) ☼	(8) ☼	(8) ☼	(8) ☼
Experimental economy	(10)	Quantification cost	Equipment cost (8)	High (2)	Medium (4)	Low (8)	Low (8)	Low (8)
			Consumables (2)	High (0)	Medium (1)	Low (2)	Low (2)	Low (2)
		sub score		(2) 🌢	(5) 🌢	(10) ☼	(10) ☼	(10) ☼

(1) “(number)” refers to the scores assigned to each evaluation criteria.

(2) If the scores are greater than 7, the approach is deemed feasible; if they are less than 6, it is considered ineffective.

(3) “☼” indicates that the method is feasible, while 🌢 signifies that the method is ineffective.

(4) “Yes (8)” indicates that the detection limit can achieve 0.2 ppm, while “No (8)” signifies that the detection limit fails to reach 0.2 ppm. “Yes (2)” indicates that the detection limit can achieve <0.2 ppm, while “No (0)” signifies that the detection limit fails to reach <0.2 ppm.

S2.1 Tolerance to chemical environments

Tolerance to diverse chemical environments is crucial for evaluating the suitability of a method in photocatalytic or photoelectrochemical systems. Tolerance to chemical environments in aqueous sulfite electrolyte encompasses ion interference (primary and potential ion interference) and pH range (acidic, neutral, and alkaline). Tolerance to interference from primary ions, such as sodium ions, sulfate ions, and sulfide ions, which directly disrupt the quantitative determination of ammonia in aqueous system, accounts for 5 points. Tolerance to interference from potential ions, such as metal ions or organic reagents introduced by various catalytic materials or electrolyte solutes, account for 2 points. The pH range is evaluated with 1 point each for acidic, neutral, and alkaline conditions. The chemical environment tolerance in TASE lies in the absence of reactions with the primary ions in the electrolyte, thereby enabling accurate quantification of ammonia.

While the Nessler's reagent method offers the broadest pH range (4 to 12) among various ammonia quantification methods, it may react with sulfide ions released from sulfide catalysts in photocatalytic systems, preventing accurate ammonia quantification.[1] Additionally, the Nessler's reagent method is susceptible to interference from various metal cations (such as Fe^{3+}, Co^{2+} etc.), hydrazine, carbonyl compounds, and other substances.[2-3] Furthermore, Nessler's reagent components (K_2HgI_4) contain toxic mercury ions, posing safety challenges. In aqueous sulfite electrolyte, the inability to meet TASE due to reactions with primary ions prevents the Nessler's reagent method from achieving accurate quantification of ammonia. (Section 2.3 in Supporting Information). Regarding the IC method, aside from the risk of damaging expensive ion exchange columns in highly acidic or alkaline solutions or those containing certain organic solvents, its most critical flaw is interference from sodium and potassium ions.[4] This interference causes the IC method to fail in meeting TASE and makes accurate quantification of ammonia in sodium (or potassium) sulfite electrolyte systems unattainable (Section 2.2 in Supporting Information). In comparison, the c-IB method, despite its strong chemical tolerance, involves a complex combination of oxidants, colorimetric agents, and catalysts, imposing multiple reaction constraints. On one hand, the c-IB method operates within a pH range of 7 − 12, limiting its application to neutral and alkaline systems.[2] On the other hand, the oxidant sodium hypochlorite reacts with the reducing sulfite ions in aqueous sulfite electrolyte, preventing the formation of the essential intermediate monochloramine (NH_2Cl), failing to meet TASE and thereby hindering accurate ammonia quantification (Section 2.4 in Supporting Information). Although the NMR method imposes more stringent chemical environment requirements, such as adjusting the sample pH to approximately 7 and incorporating deuterated reagents, it achieves TASE disregarding interference from primary ions and enables accurate quantification of ammonia in aqueous sulfite electrolyte from the view of tolerance to chemical environments.[4-5]

In summary, regarding tolerance to chemical environments, the NMR method scores a total of 7 points because it does not react with primary ions and is rarely affected by interference from potential ions; however, it is only applicable in neutral systems. In contrast, other conventional methods fail to meet the TASE. The c-IB method, despite tolerance to interference from potential ions, scores only 4 points due to its reaction with the primary ion sulfite and its limited applicability to neutral and alkaline systems. The IC method is also free from potential ion interferences, scores 3 points because it reacts with the primary ion sodium and is restricted to only neutral systems. Although the Nessler's reagent method is adaptable to acidic, neutral, and alkaline systems, it scores only 3 points due to its reaction with the primary ion sulfide and its susceptibility to interference from various metal ions, hydrazine, carbonyl compounds, and other potential ions.

Comparison sequence: NMR (7) > TASE > c-IB (4) > Nessler (3) $\approx$ IC (3)

S2.2 Real-time analytical capability

Real-time analytical capability is crucial for rapid response, adjustment of reaction conditions, and experimental process monitoring. Real-time analytical capability in aqueous sulfite electrolyte encompasses data acquisition time (fast: 3 points, medium: 2 points, slow: 1 point) and equipment availability (easy: 7 points, moderate: 2 points, scarce: 1 point). The TASE in this regard refers to the simplicity of equipment availability.

Although the NMR method offers notable advantages in ^{14}N and ^{15}N isotope analysis, its lengthy data acquisition time (requiring up to 10 hours for detecting 10 μM ^{14}N without optimization), data retrieval complexity, and data processing challenges significantly limit its real-time analytical capabilities.[5-6] Furthermore, due to the scarcity of NMR equipment, the difficulty of real-time analytical capability is significantly increased, preventing it from meeting TASE standards and rendering it unsuitable as a routine laboratory method for ammonia quantification.[7] Although the IC method can deliver highly reliable analytical results and, compared to the lengthy data acquisition time of the NMR method, completes data collection in just several minutes, its scarcity of equipment prevents it from meeting TASE, severely limiting its capability as a real-time analytical method at the laboratory scale.[8] In contrast, colorimetric methods such as Nessler's reagent and c-IB methods, due to their operational convenience and rapid result acquisition, meet TASE and represent the most suitable methods for routine laboratory ammonia quantification.[9-10]

In terms of real-time analytical capability, colorimetric methods (c-IB and Nessler) achieve a comprehensive score of 9 points, meeting the TASE, despite their relatively longer data acquisition time, due to their ease of equipment availability. In contrast, IC and NMR methods fail to meet the TASE. Despite the IC method having the shortest data acquisition time, scores only 5 points due to its relative equipment scarcity, hindering its application in real-time analysis. The NMR method scores only 2 points, as it not only has the most extended data acquisition time but also presents the most challenging equipment availability for the vast majority of researchers.

Comparison sequence: c-IB (9) ≈ Nessler (9) > TASE > IC (5) > NMR (2)

S2.3 Quantification sensitivity

Quantification sensitivity refers to the ability of a quantification method to identify the minimum concentration, serving as a core metric for evaluating method performance. Quantification sensitivity in aqueous sulfite electrolyte refers to the level of the detection limit. Summarized from literature[11] that detection limits of ammonia concentration can be categorized into two conditions: a detection limit of 0.2 ppm (8 points) and a detection limit ≤0.2 ppm (2 points). TASE refers to the achievement of a detection limit of 0.2 ppm for ammonia.

The NMR and IC methods, benefiting from the advanced nature of large-scale testing equipment, hold an objective advantage in sensitivity. In photocatalytic ammonia synthesis systems, the NMR and IC methods can achieve detection limits below 0.2 ppm, whereas colorimetric methods such as c-IB and Nessler's reagent methods are generally effective only at detection limits above 0.2 ppm.[11] However, advancements in photocatalytic ammonia synthesis, particularly with catalytic material systems like PML-Cu, NH_2-MIL-125@Co(OH)2@ZIF-8 and so on, enable yields above 0.2 ppm (Table S2), ensuring that the detection limits of all four methods meet the minimum standard (TASE) for ammonia quantification.

Table S2. Summary of various ammonia quantification methods used in different photocatalytic ammonia synthesis systems

Photocatalyst	Reaction medium	NH_3 yield (ppm)	Quantification method	ref
PML-Cu	ethylene glycol	3.4	Nessler+IC+NMR(^{15}N)	[12]
NH_2-MIL-125 @Co(OH)2@ZIF-8	Ultrapure water	13.9	IB+Nessler+NMR(^{15}N)	[13]
FePc-POFs	Methanol	6.2	IB+NMR(^{15}N)	[14]
2 wt% B/TiO_2	A_2SO_4 (A = Li, Na, and K), Ethanol	0.7	Nessler+IC+NMR(^{15}N)	[15]
B/g-C_3N_4	Na_2SO_3	7.9	IB+IC+NMR(^{14}N+^{15}N)	[16]
P−Fe/$W_{18}O_{49}$	Na_2SO_3	0.3	IC+NMR(^{14}N+^{15}N)	[17]
Fe-SA/$WO_{2.72-x}$	Ultrapure water	1.6	Selective electrodes+IC+IB+NMR(^{15}N)	[18]
$FeCo_2O_4$	Methanol	0.4	IC+NMR(^{15}N)	[19]
HMOF(Fe^{II}/Fe^{III})	K_2SO_3	0.3	IC	[20]
Ultrafine Cu_2O	Ultrapure water	11.6	IC+NMR(^{15}N, IB)	[21]

In summary, regarding quantification sensitivity, the NMR and IC methods achieve detection limits below 0.2 ppm, earning a comprehensive evaluation score of 10. In contrast, colorimetric methods, including c-IB and Nessler methods, demonstrate detection limits of 0.2 ppm, achieving a score of 9. All methods meet the TASE and satisfy the lower detection threshold for ammonia in conventional systems.

Comparison sequence: NMR (10) ≈ IC (10) > c-IB (8) ≈ Nessler (8) > TASE

S2.4 Quantification accuracy

Quantification accuracy, which pertains to the accuracy and consistency of measurement results, is a critical metric for evaluating analytical methods. Quantification accuracy in aqueous sulfite electrolyte is evaluated based on the linear correlation coefficient (R^2) of calibration curves. For detection limits = 0.2 ppm (8 points), $R^2 \geq 0.999$ is required. For detection limits ≤ 0.2 ppm, the scoring criteria are: $R^2 \geq 0.999$ (2 points), $0.999 > R^2 \geq 0.995$ (1 point), and $R^2 < 0.995$ (0 point).TASE in this part denotes measurement systems demonstrating a detection limit of 0.2 ppm with linear correlation coefficients (R^2) ≥ 0.999 under standard analytical conditions.

The NMR and IC methods, leveraging their advanced technological features, exhibit adequate precision in trace-level detection scenarios compared to laboratory-scale colorimetric methods such as c-IB and Nessler's reagent methods. For ultratrace ammonia detection (< 0.2 ppm), the NMR and IC methods demonstrate acceptable analytical accuracy, with R^2 values of 0.996 and 0.995, respectively, and 95% confidence intervals. [22] In comparison, colorimetric methods using Nessler's reagent and the c-IB methods exhibit R^2 values of 0.982 and 0.991, respectively, with 90% confidence intervals.[11,23] However, at higher ammonia concentrations, all four conventional ammonia quantification methods achieve an R^2 of 0.999 with 99% confidence intervals, surpassing the TASE and enabling accurate measurement.[11]

In terms of quantification accuracy, the NMR and IC methods achieve a comprehensive score of 9 points, as they exhibit a linear correlation coefficient (R^2) ≥ 0.999 for detection limits of 0.2 ppm but show slight limitations ($R^2 > 0.995$ but < 0.999) at detection limits ≤ 0.2 ppm. Similarly, colorimetric methods (c-IB and Nessler) score 8 points, meeting the requirement for $R^2 > 0.999$ of 0.2 ppm but demonstrating reduced precision at extremely low concentrations. All methods exceed the TASE, fulfilling the required quantification accuracy.

Comparison sequence: NMR (9) $\approx$ IC (9) > c-IB (8) $\approx$ Nessler (8) > TASE

S2.5 Experimental economy

Experimental economy is a critical consideration in experimental design. Experimental economy in aqueous sulfite electrolyte encompasses equipment cost (high: 8 points, medium: 4 points, low: 2 points) and consumables cost (high: 2 points, medium: 1 point, low: 0 points). TASE in this dimension is defined as the equipment cost falls into the low-cost category.

The NMR method incurs prohibitive operational costs, including expensive deuterated reagents and cryogenic cooling systems, failing to reach TASE and rendering it impractical for routine laboratory detection.[24] The IC method, while exhibiting lower capital costs than NMR method, still requires moderate equipment cost and incurs recurrent consumable expenses (e.g., chromatography columns), thus failing TASE compliance.[7-8] In contrast, colorimetric methods (e.g., Nessler's reagent and c-IB methods) demonstrate minimal equipment cost and superior experimental economy, fully satisfying TASE as the primary approach for routine ammonia quantification in laboratory.[25]

In terms of experimental economy, colorimetric methods (c-IB and Nessler) achieve a perfect score of 10 points, due to their minimal equipment and consumables costs. In contrast, the IC and NMR methods fail to meet the TASE. The IC method scores 5 points, with medium costs for both equipment and consumables. The NMR method scores only 2 points, as it involves expensive equipment and high-cost consumables.

Comparison sequence: c-IB (10) $\approx$ Nessler (10) > TASE > IC (5) > NMR (2)

S2.6 Section summary

Comprehensive comparative analysis across five evaluation dimensions (tolerance to chemical environments, real-time analytical capability, quantification accuracy, quantification sensitivity and experimental economy) reveals that nuclear magnetic resonance (NMR) method and ion chromatography (IC) method fail to meet the threshold in aqueous sulfite electrolyte (TASE) due to lack of operational convenience (limited chemical environments tolerance and real-time analytical capability) and experimental economy, despite demonstrating acceptable quantification reliability. While colorimetric methods balance operational convenience and experimental economy, the Nessler's reagent method exhibits inadequate chemical tolerance in sulfide-catalyst systems due to S^{2-} interference. Though the conventional indophenol blue (c-IB) method avoids this limitation, its sulfite reactivity compromises tolerance to chemical environments. The modified IB (m-IB) method, which involves the controlled introduction of oxidants to neutralize sulfite to unavailing levels, overcomes limitations of Nessler's reagent method while retaining the benefits, such as reduced experimental uncertainty and lower health risks for operators. This establishes the modified indophenol blue method exceeding the threshold for reliable routine laboratory ammonia quantification in aqueous sulfite electrolytes.

Section 3. The failure of different ammonia quantification methods in aqueous sulfite electrolyte

NMR, IC, and colorimetric methods (c-IB and Nessler's reagent methods) are presently the most widely used techniques for quantifying ammonia. Each method has distinct advantages and disadvantages, depending on the specific application. However, in aqueous sulfite electrolyte, each of these methods exhibits significant limitations, rendering them unsuitable as routine laboratory methods for ammonia quantification. Details are discussed in this section.

S3.1 Nuclear magnetic resonance (NMR) method

As an advanced method for quantitative analysis of ammonia content, the NMR method is regarded as one of the most accurate methods for isotopic-labeling ammonia quantification due to its capability to effectively differentiate between $^{14}NH_4^+$ and $^{15}NH_4^+$ by splitting the ammonium proton signals into a triplet (J = 52 Hz) peaks and a doublet (J = 72 Hz) peaks, respectively.[24] In photocatalytic and photoelectrochemical systems, the NMR method exhibits a detection limit for ammonia below 0.2 ppm, demonstrating acceptable quantification sensitivity and accuracy.[11] However, when the ammonia production in the reaction system falls below 0.2 ppm, the sensitivity, which is proportional to the signal-to-noise ratio (SNR) and inversely proportional to the acquisition time, requires prolonged NMR acquisition.[26] This leads to a sharp decline in SNR, severely interfering with NMR signals and reducing sensitivity

(Figure S1).[6,27] Moreover, longer acquisition times, spanning several hours, increase the risk of false positives, compromising operational convenience.[6] Additionally, expensive spectrometers are essential to meet sensitivity requirements.[4] The NMR method also demands specific chemical environmental conditions; maintaining a pH around 7 is crucial for ammonia stability and accurate quantification.[11,28] In aqueous sulfite electrolyte, the need for specialized high-end equipment, expensive deuterated reagents, and liquid nitrogen for cooling further restricts the use of the NMR method[25], thus excluding it as a routine laboratory method for ammonia quantification.

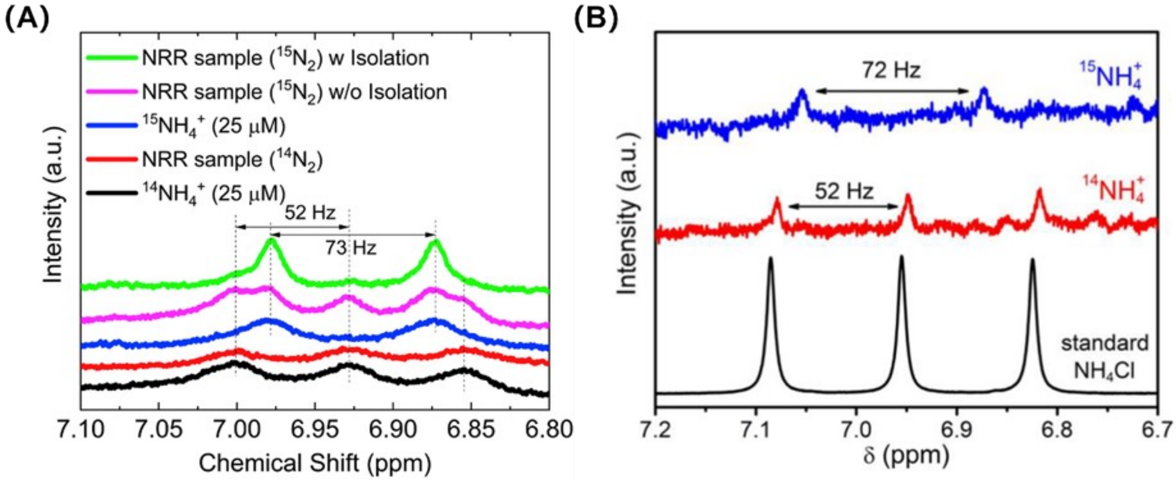


Figure S1. The phenomenon of poor signal-to-noise ratio (SNR) in ^{1}H-NMR spectra. A) ^{1}H-NMR spectra of Ag_2O-Au-685 nanocages.[26] and B) Mo-doped $W_{18}O_{49}$ ultrathin nanowires.[27]

S3.2 Ion chromatography (IC) method

Ion chromatography (IC) is a method that utilizes the ionic property of substance for separation and detection, making it a common method for ammonia quantification.[29] The IC method demonstrates both commendable quantification accuracy and sensitivity.[11] Additionally, unlike the NMR method, which requires prolonged data acquisition, the IC method can deliver quantitative results in a short time, offering acceptable real-time analytical capabilities.[29] However, from an equipment perspective, the IC method exhibits limitations in terms of experimental economy and operational convenience.[8,30] A common interference in the IC method arises from sodium and potassium ions, whose retention times are similar to that of ammonia, complicating separation.[31] Furthermore, due to the currently low ammonia production rates in photocatalysts, which are significantly lower than the cation concentrations in electrolytes, accurate quantification of ammonia remains unachievable (Figure S2 A). In aqueous sulfite electrolyte, the detection limit for ammonia is determined to be 20 − 40 ppm, which is notably higher than the ammonia yields achievable in current photocatalytic ammonia synthesis systems. Additionally, the linear correlation coefficient of approximately 0.93 fails to meet the required accuracy standards (Figure S2 B−D). Consequently, the IC method is unsuitable for photocatalytic ammonia synthesis experiments in aqueous sulfite electrolyte.

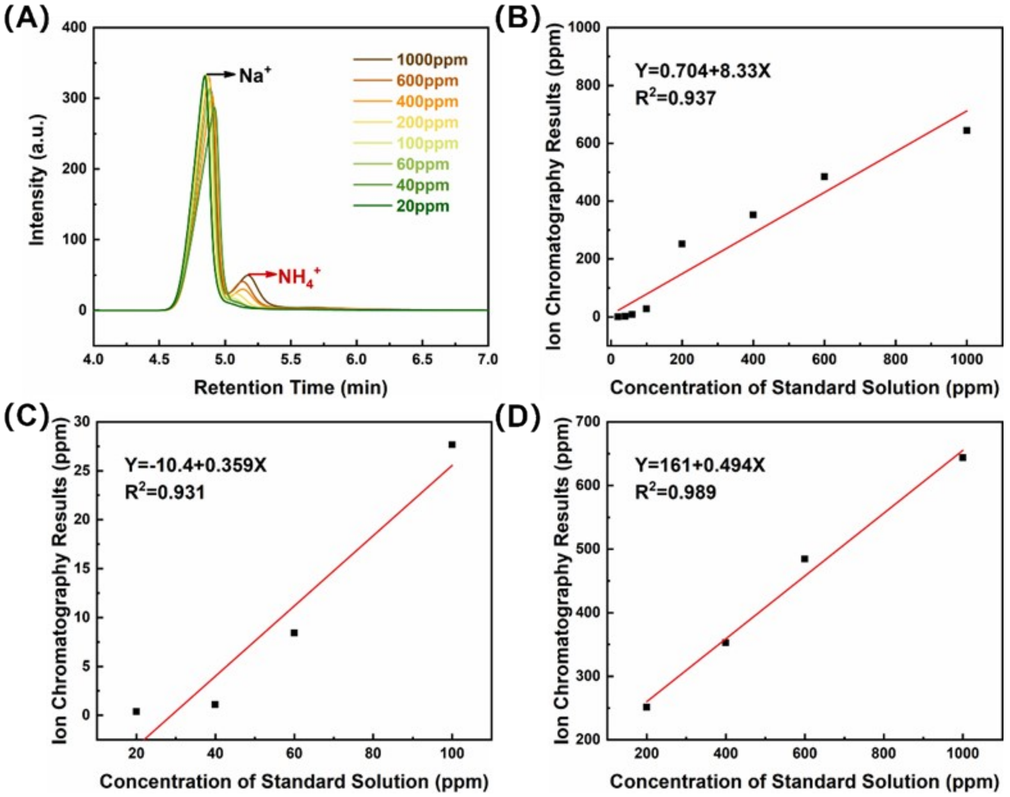


Figure S2. Failure phenomena of ammonia quantification using sodium sulfite solution as the background in the ion chromatography (IC) method. A) The normalized results of different concentrations of ammonia standard solutions (1000, 600, 400, 200, 100, 60, 40, 20 ppm) measured by ion chromatography method. B−D) The fitting standard curves based on this data.

The raw data for IC method quantification of varying ammonia concentrations are liested in Table S3.

Table S3. Raw data related to standard ammonia solution concentrations determined by ion chromatography method.

Concentration of Standard Solution (ppm)	Ion Chromatography Results (ppm)	Peak Area (Na$^+$)
1000	643.74	49.847
600	484.09	50.818
400	352.53	49.758
200	251.56	49.315

100	27.66	48.174
60	8.43	49.399
40	1.1	49.815
20	0.37	49.531

S3.3 Nessler's reagent method

The Nessler's reagent method is widely used for determining the ammonia content in samples.[8] This method is based on the principle of the reaction between ammonia and the Nessler's reagent, which produces a yellow or brown (at high concentrations) precipitate, serving as a standardized reagent for ammonia quantification in samples. The specific chemical reaction involved is as follows:

$$NH_4^+\ (aq)\ + 4[HgI_4]^{2-}\ (aq)\ + 8OH^-\ (aq) \rightarrow 2Hg_2NI\cdot H_2O\ (l)\ + 14I^-\ (aq)\ + 8H_2O\ (l)$$

(S1)

The Nessler's reagent method combines the operational convenience and experimental economy typical of colorimetric techniques.[7] Compared to the NMR and IC methods, which are limited to accurate quantification within a pH around 7, Nessler's reagent offers a broader pH range of 4 − 12.[2] However, its tolerance to chemical environments is significantly compromised due to interference from various cations such as Fe^{3+}, Co^{2+}, and Ni^{2+}, as well as sulfide ions potentially released in sulfide photocatalytic systems, thereby preventing accurate quantification of ammonia.[32] Additionally, the presence of toxic mercury in Nessler's reagent further restricts its application.[29] Moreover, in systems with various aldehyde sacrificial agents, the Nessler's reagent method exhibits significantly higher ammonia yields compared to other methods, suggesting potential interference with other sacrificial agent systems.[3, 33-34] While the Nessler's reagent method demonstrates good linearity in pure water, its accuracy is significantly compromised, or even entirely invalidated, in aqueous sulfite electrolyte (Figure S3). Consequently, due to these limitations, the Nessler's reagent method cannot be employed as a routine laboratory method for ammonia quantification in aqueous sulfite electrolyte.

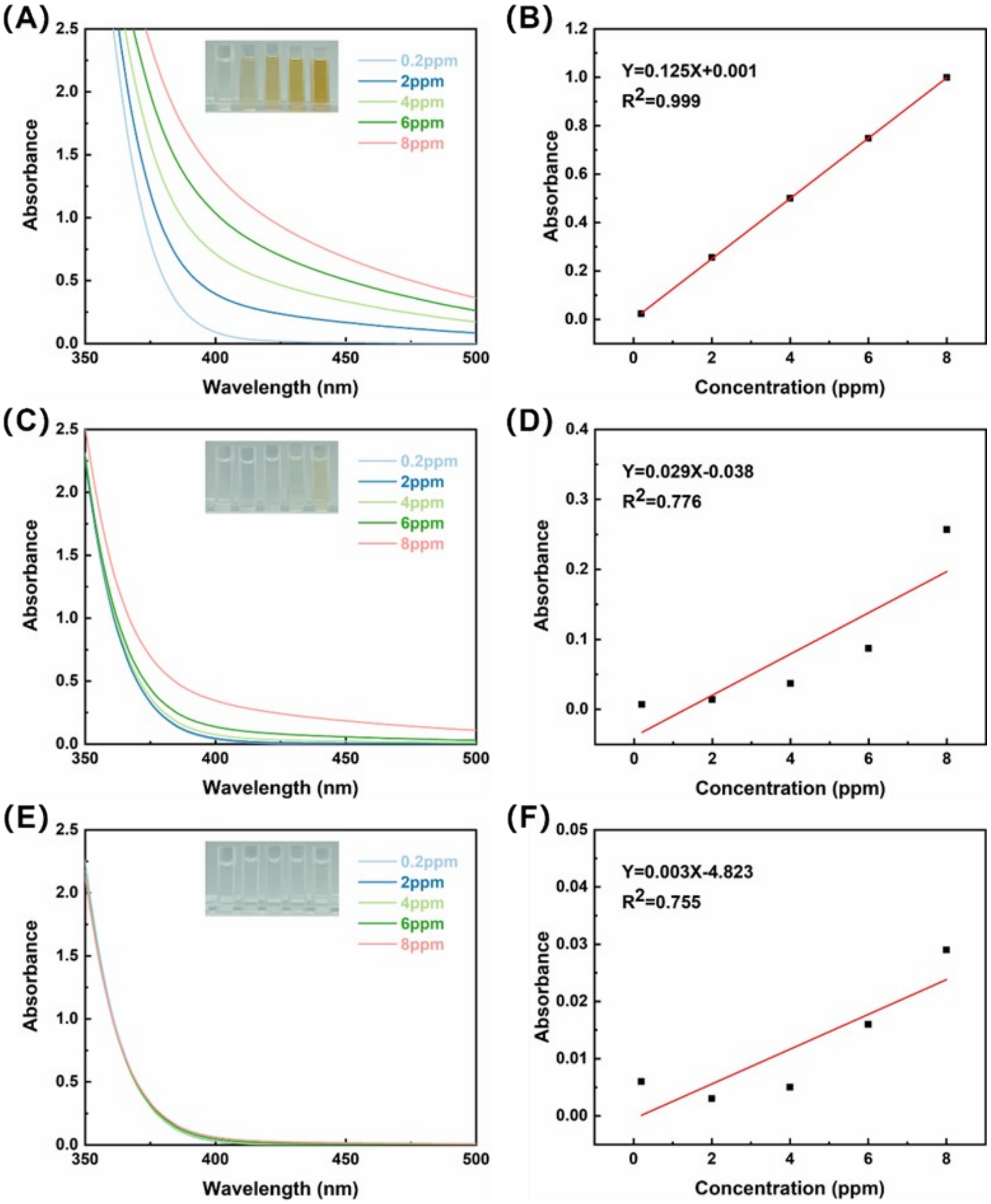


Figure S3. UV-visible absorption spectra of ammonia standard solutions (0.2 − 8 ppm) treated with Nessler's Reagent method: A−B) ultrapure water as background and corresponding calibration curve, C−D) addition of sodium sulfite post-coloration with ultrapure water background and corresponding calibration curve, E−F) sodium sulfite as background and corresponding calibration curve.

S3.4 Conventional indophenol blue (c-IB) method

Compared to methods such as NMR and IC, colorimetric methods (Nessler's reagent and conventional Indophenol Blue methods) are the most commonly used methods for ammonia quantification in the field of ammonia synthesis due to their operational convenience and experimental economy.[35] In recent years, the c-IB method has gained increasing preference over Nessler's reagent method among researchers.[9] While the Nessler's reagent method is susceptible to interference from various ions such as sacrificial agents, cations, and aldehydes, the c-IB method demonstrates a certain degree of chemical environmental tolerance, particularly within specific pH ranges.[2] In aqueous sulfite electrolyte, the c-IB method fails due to the reaction between sulfite and the strong reducing agent sodium hypochlorite (Figure S4). However, through the synergistic action of multiple specific reagents and appropriate pretreatment of the test solution, excess sulfite can be neutralized without compromising ammonia products, enabling accurate quantification of ammonia. Consequently, the c-IB method is rendered impractical for detecting ammonia in aqueous sulfite electrolyte, owing to the constraints previously outlined.

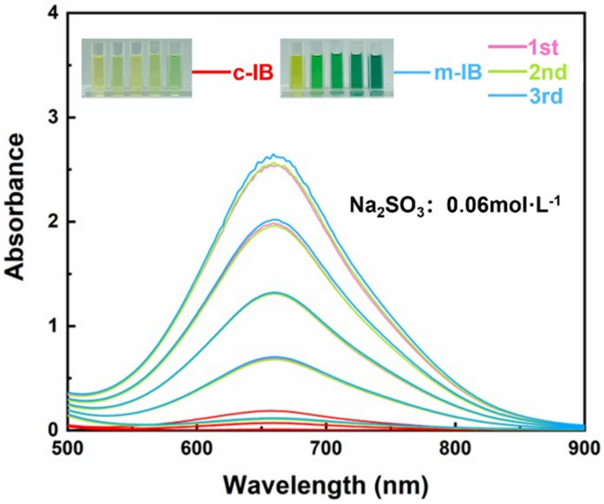


Figure S4. Comparison of ammonia quantification phenomena using sodium sulfite solution as background solutions in c-IB and m-IB methods.

Section 4. Investigation of pretreatment agents based on reaction mechanism

S4.1 Arrhenius acid-base theory

Based on Arrhenius acid-base theory, this method intended to neutralize excess sulfite using sulfuric acid. However, as indicated by the absorption peaks, compared to the results obtained with potassium monopersulfate treatment, the use of sulfuric acid for neutralization resulted in extremely low absorption intensity and a non-linear relationship (Figure S5). Therefore, employing sulfuric acid as a pretreatment fails to achieve accurate quantification of ammonia.

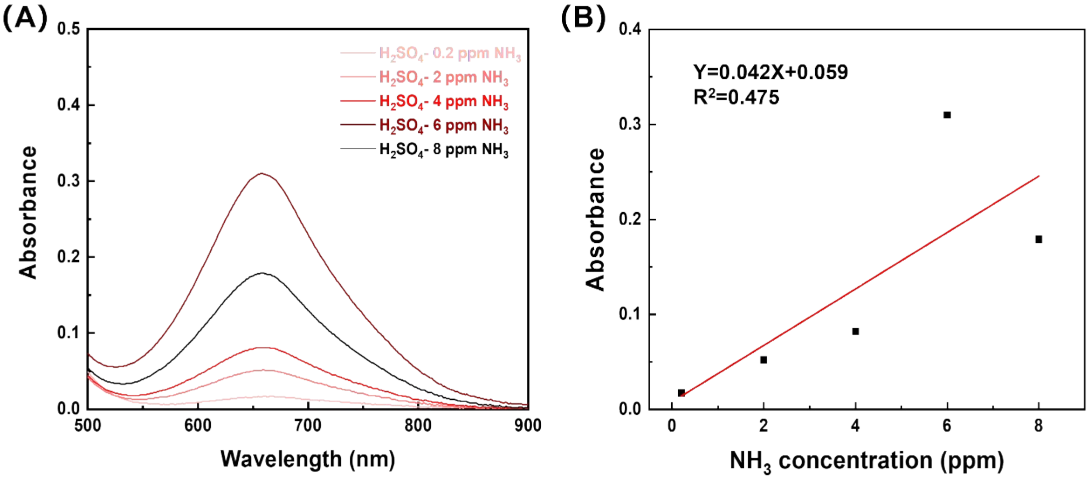


Figure S5. A) UV-visible absorption spectra obtained via the c-IB method after pretreatment with dilute sulfuric acid. B) Corresponding external standard curves.

S4.2 Redox reaction theory

Based on redox reaction theory, the self-sacrificial oxidation strategy using NaClO as a pre-treatment oxidizer was then explored. Sulfite ions (SO_3^{2-}) are oxidized to sulfate ions (SO_4^{2-}), while chlorine in sodium hypochlorite (NaClO) is reduced, demonstrating their roles as reductant and oxidant respectively. However, in addition to reacting with SO_3^{2-}, excess hypochlorite (ClO^-) may follow the breakpoint chlorination mechanism, reacting with ammonium ions (NH_4^+) (Reaction S2). In this mechanism, ammonia initially reacts with active chlorine (ClO^-) to form chloramine species (e.g., monochloramine, dichloramine, and trichloramine) and ultimately producing nitrogen gas, leading to underestimated or even undetectable ammonia yields due to the failure to form indophenol blue.[36] Besides, this strategy involves complex reaction pathways, violating Principle (iv) of reaction pathway controllability.

$$2NH_3\cdot H_2O\ (l)\ +3ClO^-\ (aq) \rightarrow N_2\ (g)\ +5H_2O\ (l)\ +3Cl^-\ (aq) \tag{S2}$$

S4.3 Lewis acid-base theory

Based on Lewis acid-base theory, $KMnO_4$ could act as an oxidant. However, by comparing the UV-Vis absorption spectra of the reaction reagents and electrolyte components, it was observed that the absorption wavelength of $KMnO_4$ is close to that of ammonia at 525 nm, which would interfere with the ammonia detection results (Figure S6). Therefore, $KMnO_4$ cannot be used as a pretreatment agent in this system.

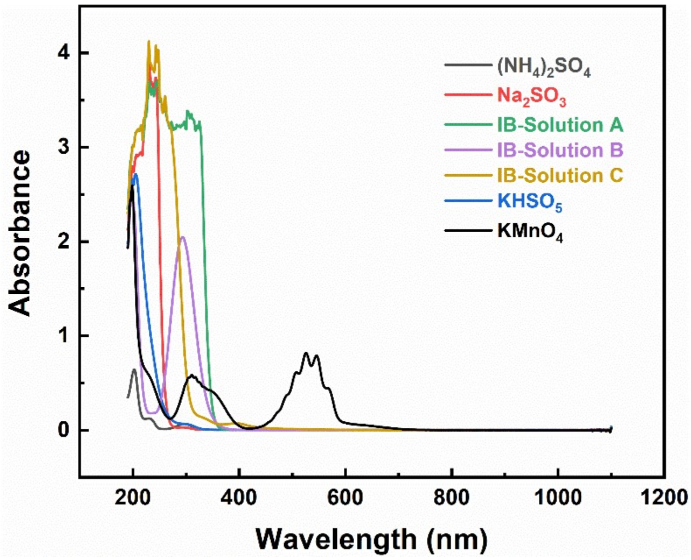


Figure S6. UV-visible absorption spectra of the components of IB method and oxidants of AOP method.

Hydrogen peroxide (H_2O_2), another common AOP oxidant, aims to eliminate sulfite interference in a mild and effective oxidation environment (Reaction S3).[37] However, commercial H_2O_2 solutions (3% − 30% concentration) gradually decompose into water and oxygen during storage. This method suffers from stability issues, violating Principle (iii).

$$SO^{2-}_{3}\ (aq) + H_2O_2\ (l) \rightarrow SO^{2-}_{4}\ (aq) + H_2O\ (l)$$

(S3)

Section 5. Assessing the reactivity of $KHSO_5$ based on thermodynamic calculations

The method for calculating the Gibbs free energy of the reaction between sulfite ions (SO_3^{2-}) and peroxymonosulfate ions (HSO_5^-) is described below.

$HSO_5^-\ (aq)\ + 2H^+ + 2e^- \rightarrow HSO_4^-\ (aq)\ + H_2O\ (l)$ $E^0 = +\ 1.82\ V\ (vs. NHE)$ (S4)[38]

$S_2O_8^{2-}\ (aq)\ + 2H^+ + 2e^- \rightarrow 2HSO_4^-\ (aq)$ $E^0 = +\ 2.12\ V\ (vs. NHE)$ (S5)[39]

$S_2O_8^{2-}\ (aq)\ + 2e^- \rightarrow 2SO_4^{2-}\ (aq)$ $E^0 = +\ 2.01\ V\ (vs. NHE)$ (S6)[39]

$HSO_5^-\ (aq)\ + H^+ + 2e^- \rightarrow SO_4^{2-}\ (aq)\ + H_2O\ (l)$ $E^0 = +\ 1.76\ V\ (vs. NHE)$ (S7)

$2\Delta G_{S7}^0 = 2\Delta G_{S4}^0 - \Delta G_{S5}^0 + \Delta G_{S6}^0$

According to $\Delta G^0 = -nEF$, $2E_{S7}^0 = 2E_{S4}^0 - E_{S5}^0 + E_{S6}^0$, $E_{S7}^0 = +\ 1.76\ V\ (vs. NHE)$

$H_2O\ (l)\ \rightarrow H^+ + OH^-$ (S8)

$\Delta G^0 = -RTlnK_w$, $K_w = 1 \times 10^{-14}\ (298K)$, $\Delta G^0 = 79.9\ kJ \cdot mol^{-1}$

$SO_4^{2-}\ (aq)\ + H_2O\ (l)\ + 2e^- \rightarrow SO_3^{2-}\ (aq)\ + 2OH^-$ $E^0 = -0.93\ V\ (vs. NHE)$ (S9)[39]

$HSO_5^-\ (aq)\ + SO_3^{2-}\ (aq)\ \rightarrow 2SO_4^{2-}\ (aq)\ + H^+$ (S10)

$\Delta G_{S10}^0 = \Delta G_{S7}^0 + 2\Delta G_{S8}^0 - \Delta G_{S9}^0$

$\Delta G_{S10}^0 = -2E_{S7}^0F - 2 \times 7.99 \times 10^4 J \cdot mol^{-1} + 2E_{S9}^0F$, $\Delta G_{S10}^0 = -678.97\ kJ \cdot mol^{-1}$

The method for calculating the Gibbs free energy of the reaction between ammonium ions (NH_4^+) and peroxymonosulfate ions (HSO_5^-) is described below.

$HSO_5^-\ (aq)\ + H^+ + 2e^- \rightarrow SO_4^{2-}\ (aq)\ + H_2O\ (l)$ $E^0 = +\ 1.76\ V\ (vs. NHE)$ (S7)

$H_2O\ (l)\ \rightarrow H^+ + OH^-$ (S8)

$N_2\ (g)\ + 6H^+ + 2H_2O\ (l)\ + 6e^- \rightarrow 2NH_4OH\ (aq)$ $E^0 = +\ 0.092\ V\ (vs.NHE)$ (S11)[39]

$HSO_5^-\ (aq)\ + 2NH_4^+\ (aq)\ \rightarrow N_2\ (g)\ + SO_4^{2-}\ (aq)\ + H_2O\ (l)\ + 7H^+ + 4e^-$ (S12)

$\Delta G_{S12}^0 = \Delta G_{S7}^0 + 2\Delta G_{S8}^0 - \Delta G_{S11}^0$

$\Delta G_{S12}^0 = -2E_{S7}^0F - 2 \times 7.99 \times 10^4 J \cdot mol^{-1} + 2E_{S11}^0F$, $\Delta G_{S12}^0 = -481.72\ kJ \cdot mol^{-1}$

Section 6. Threshold analysis of redox ion pairs

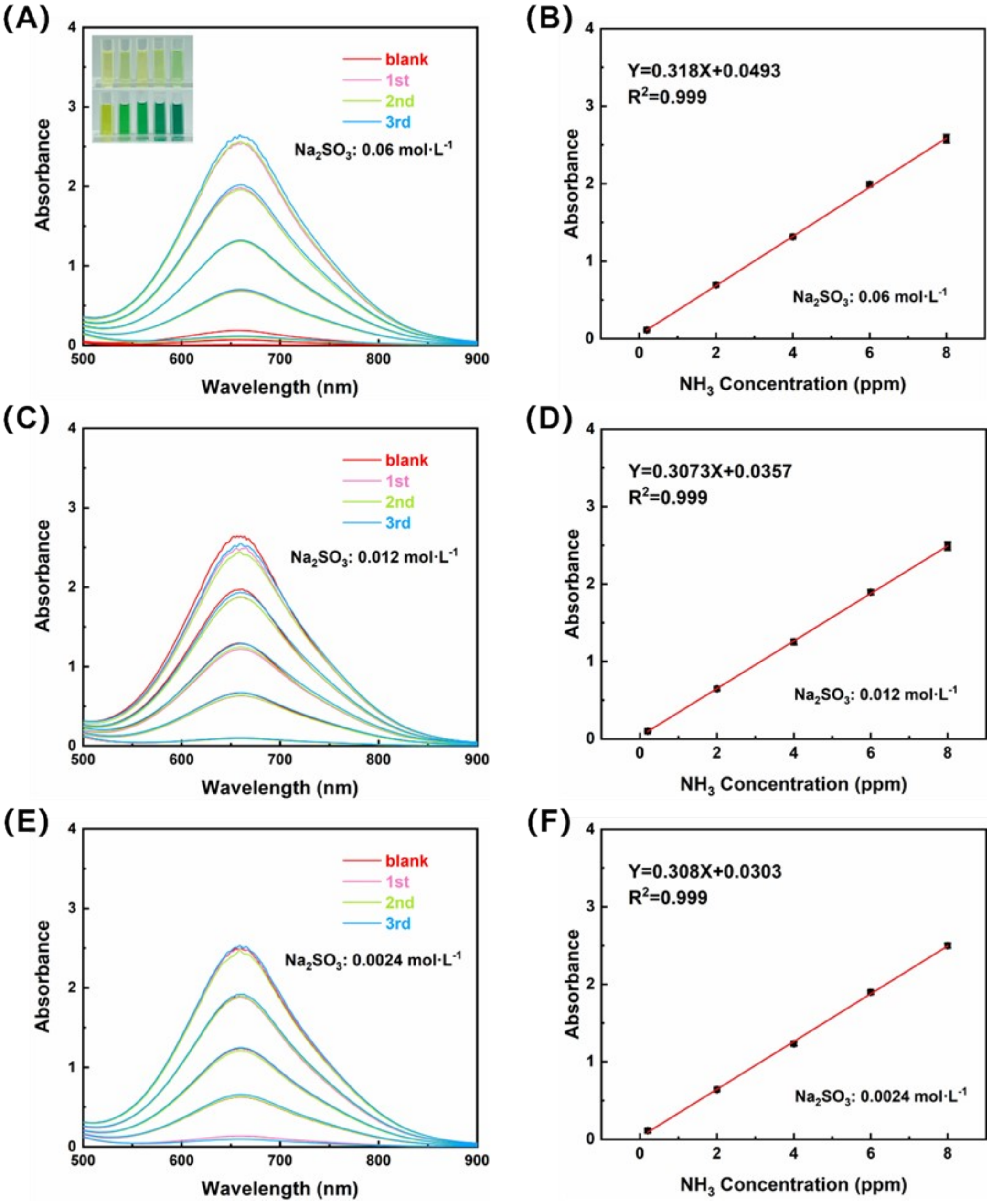


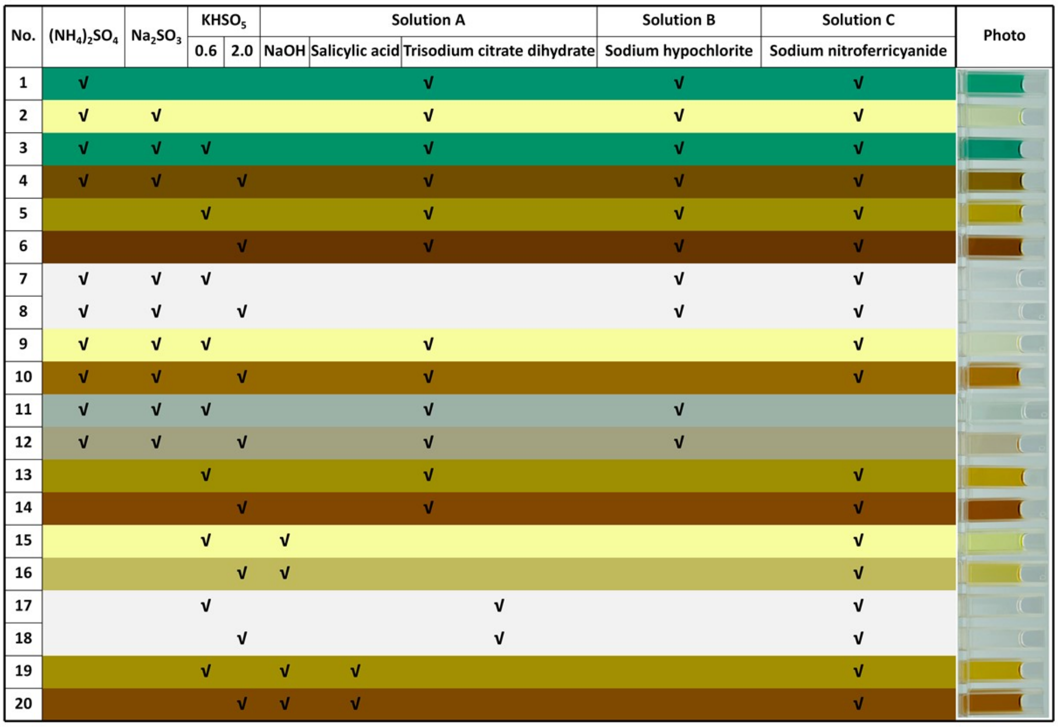
Figure S7. Comparative analysis of UV-Vis absorption spectra and calibration curves using m-IB and c-IB methods in aqueous sulfite electrolyte at varying concentrations: A-B) 0.06 mol·L^{-1} Na$_2$SO$_3$, C-D) 0.012 mol·L^{-1} Na$_2$SO$_3$, E-F) 0.0024 mol·L^{-1} Na$_2$SO$_3$.

Section 7. Key influencing factors of the m-IB method

The effectiveness of the (m-IB) modified indophenol blue method is influenced by multiple reaction conditions, including strategic optimization of reagent types and stoichiometric ratios, reagent concentration, precise execution of pretreatment steps, investigation of reagent stability, impact of impurity ions and interference on side reactions. To ensure accurate quantification of ammonia content, these factors must be meticulously considered during experimental design.

S7.1 Strategic optimization of reagent types and stoichiometric ratios

The colorimetric results are closely related to the type and ratios of reagent addition. The presence or absence of specific reagents and the order in which they are added directly determine the accuracy of ammonia quantification. The different colour development effects of the modified indolphenol blue method after varying the addition amounts of each component separately proved that normal colour development results could only be obtained when the calibration test was carried out in accordance with the appropriate ratios (Figure S8).



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<tr><th>0.6</th><th>2.0</th><th>NaOH</th><th>Salicylic acid</th><th>Trisodium citrate dihydrate</th><th>Sodium hypochlorite</th><th>Sodium nitroferricyanide</th></tr>
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Figure S8. The effect of changes in the components of indophenol blue on the color development of the calibration.

S7.2 Investigation of reagent stability

This experiment compared the effects of different storage durations and incubation times of ammonia standard solutions to investigate the reagent stability of ammonia quantification. The reagent demonstrates excellent stability, as evidenced by its negligible impact on the colorimetric detection of ammonia content within a 3-hour timeframe (Figure S9). This m-IB method is validated as a reliable and effective laboratory method for ammonia quantification.

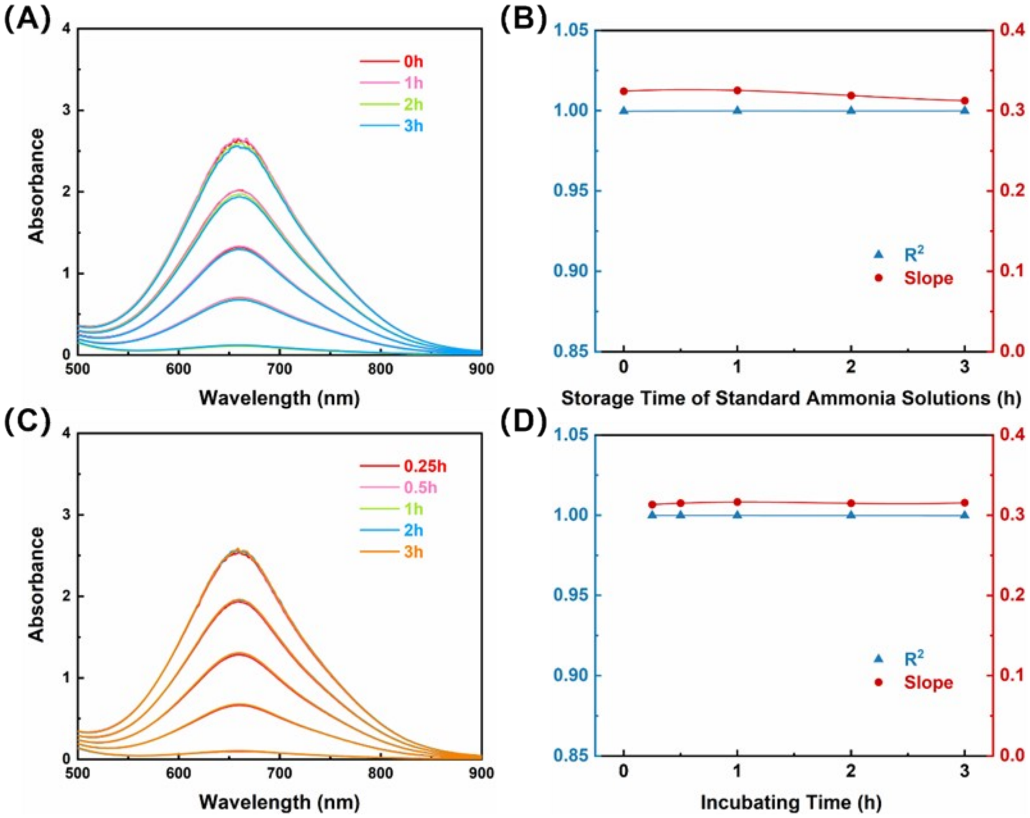

Figure S9. The effect of the storage time of the solution to be tested and its incubation time. A) Impact of varying storage time. B) Corresponding external standard curves and the R^2 and slopes of the obtained curves. C) Impact of varying incubation time. D) Corresponding external standard curves and the R^2 and slopes of the obtained curves.

S7.3 Impact of impurity ions

Considering that the use of sulfide catalysts may introduce a certain amount of sulfide ions contamination, this study conducted verification experiments to assess the impact of sulfide ions on the optimized colorimetric method. Due to the presence of ferrous ions in the sodium nitroprusside catalyst, a characteristic colorimetric reaction occurs with sulfide ions, interfering with the final calibration colorimetric results (reaction S2 and S3). However, there is a certain degree of tolerance for sulfate ion concentrations in the solution. This method can still maintain good calibration performance when the sulfate ion concentration does not exceed 0.006 mol·L^{-1} (Figure S10).

$$S^{2-}(aq) + Fe^{2+}(aq) \rightarrow FeS(s)$$

(S2)

$$3S^{2-}(aq) + 2Fe^{3+}(aq) \rightarrow Fe_2S_3(s) \quad (S3)$$

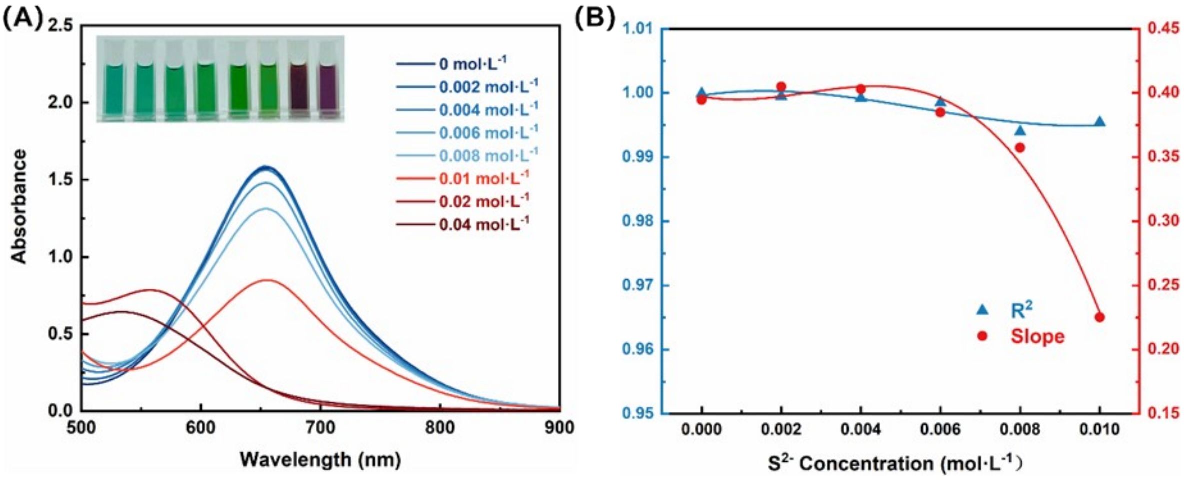

Figure S10. The effects of S^{2-} on the modified indophenol blue method. A) UV-visible absorption spectra obtained using the modified IB method with different concentrations of sulfite ions. B) Corresponding external standard curves and the R^2 and slopes of the obtained curves .

S7.4 Interference on side reactions

The experiment utilized the Watt and Chrisp method to calibrate hydrazine standard solutions. The introduction of sulfite ions exhibits no interference with the detection of hydrazine, enabling accurate quantification of the byproduct hydrazine (Figure S11).

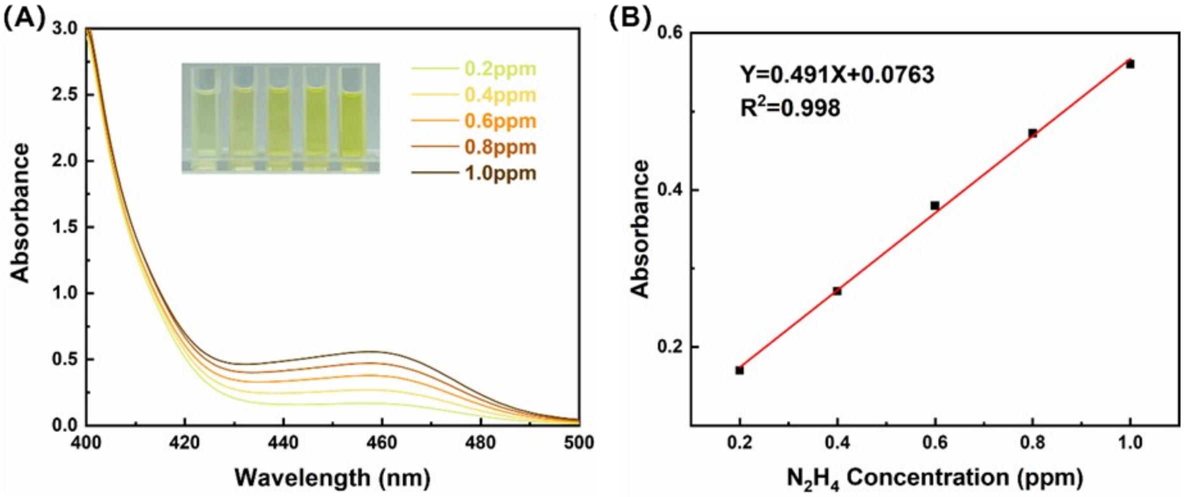

Figure S11. The effects of sulfite on hydrazine quantification. A) UV-visible absorption spectra obtained with sodium sulfite solution (0.06 mol·L^{-1}) as the background using the Watt-Chrisp method. B) Corresponding external standard curves.

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