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On-line gas diffusion membrane separation-flow injection analysis with spectrophotometric detection for the automated determination of ammonia nitrogen in complex industrial wastewater

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The determination of ammonia nitrogen (NH_3–N) in industrial wastewater is often challenged by complex matrix interference, and traditional laboratory analysis cannot provide timely feedback for dynamic process regulation. To address these issues, an automated online gas diffusion membrane separation-flow injection analysis system coupled with salicylate spectrophotometric detection was developed for the rapid determination of NH_3–N in complex industrial wastewater. This method employs a hollow-fiber membrane contactor to selectively separate volatile NH_3 from the complex matrix, effectively eliminating interference. Under optimized conditions, the method exhibited a linear range of 1.0–50.0 mg L^{-1} (R^2 = 0.9997), with a limit of detection of 0.22 mg L^{-1} and limit of quantification of 0.72 mg L^{-1}. Precision was excellent, with relative standard deviations below 3.0%. The system showed a strong anti-interference performance against salinity up to 35, common co-existing ions, and various organic nitrogen compounds. When applied to real industrial wastewater samples from an ammonia-stripping process, the proposed method showed good agreement with the reference salicylate method (HJ 536-2009) and exhibited higher spike recoveries (86.0–96.7%) compared to the reference procedure. With a sample throughput of 14 samples per hour, the developed method offers a rapid, accurate, automated, and practical solution for the high-frequency monitoring of NH_3–N in complex industrial effluents, supporting improved process control and regulatory compliance.

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1. Introduction

Ammonia nitrogen (NH_3–N) is a key water quality parameter in environmental monitoring and wastewater management. The excessive discharge of NH_3–N from industrial sources can cause eutrophication, oxygen depletion in receiving waters, and toxicity to aquatic organisms.[1,2] In industrial wastewater, NH_3–N concentrations often range from several mg L^{-1} to several thousand mg L^{-1}, depending on the production process.[3] To meet stringent discharge regulations and minimize environmental impact, high-ammonia industrial effluents typically undergo ammonia stripping (or ammonia removal) prior to the final discharge. This process involves adding alkali (*e.g.*, NaOH) to convert ammonium ions (NH_4^+) into volatile free ammonia (NH_3), which is then transferred from the liquid phase to the gas phase in a stripping tower.[4] The precise and timely monitoring of NH_3–N during the stripping process is essential for optimizing alkali dosage, improving treatment efficiency, and reducing operational costs. However, complex industrial wastewater, such as that generated by chemical, petrochemical, pharmaceutical, or fertilizer plants, contains high levels of suspended solids, turbidity, color, organic matter, heavy metals, and salinity. These matrix components severely interfere with conventional analytical methods, resulting in inaccurate measurements and operational difficulties.

Traditional offline laboratory analysis, which relies on manual sampling followed by batch spectrophotometric determination, provides good accuracy but suffers from significant time delays. This approach cannot capture rapid fluctuations in NH_3–N concentrations during dynamic treatment processes and is labor-intensive. To overcome these limitations, automated flow analysis techniques, particularly flow injection analysis (FIA), have been developed for NH_3–N monitoring in wastewater.[5–7] When coupled with spectrophotometric detection, FIA offers high sample throughput, low reagent consumption, and excellent reproducibility. Among spectrophotometric methods, the salicylate–hypochlorite method

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(based on a modified Berthelot reaction) has gained wide acceptance as a greener alternative to the classical phenol-hypochlorite (indophenol blue) procedure.[8] In this reaction, ammonia reacts with hypochlorite to form monochloramine, which then couples with salicylate in the presence of a catalyst (*e.g.*, nitroprusside) to produce a stable blue-green complex measurable at approximately 660–700 nm. Compared with phenol-based methods, the salicylate approach provides comparable sensitivity and precision while offering lower toxicity, reduced odor, and greater safety and convenience in reagent handling. It has been adopted in national standards and is compatible with automated systems.[9–11]

Despite these advantages, the direct application of the salicylate method to complex industrial matrices remains challenging because of interferences. Gas diffusion membrane separation coupled with FIA provides an elegant solution by selectively converting NH_4^+ into NH_3 gas under alkaline conditions, allowing the volatile ammonia to diffuse across a hydrophobic microporous membrane (commonly polytetrafluoroethylene (PTFE) or expanded PTFE (ePTFE)) into an acceptor stream.[12–14] This online separation effectively eliminates non-volatile interferences, such as particulates, colored substances, and metal ions, before color development, significantly enhancing selectivity and accuracy without extensive sample pretreatment. Hollow-fiber membrane contactors (HFMC) are particularly advantageous due to their high surface area, compact design, and efficient mass transfer.[15,16] Nevertheless, fully integrated online systems optimized specifically for highly complex industrial wastewater using gas diffusion-FIA with salicylate detection remain limited.

In this study, an online gas diffusion membrane separation-flow injection analysis system with spectrophotometric detection was developed for the automated determination of NH_3–N in complex industrial wastewater. The proposed method integrates the high selectivity of gas diffusion, the efficiency and automation of FIA, and the environmental friendliness of the salicylate reagent. Key analytical performance parameters—including linear range, limit of detection, precision, interference tolerance, and applicability to real industrial samples—were systematically evaluated. The proposed system provides a practical, robust tool for high-frequency monitoring, which can support optimized ammonia stripping operations, improve wastewater treatment efficiency, and ensure regulatory compliance.

2. Materials and methods

2.1 Reagents

Sodium dichloroisocyanurate (NaDTT) was purchased from Sigma-Aldrich (Saint Louis, Missouri, USA). Boric acid was purchased from Xilong Scientific Co. Ltd. (Shantou, China). Other chemicals were purchased from Sinopharm Chemical Reagent (Shanghai, China). All reagents were of analytical grade and were used without further purification. The NH_3–N stock solution (1000 mg L^{-1}) was prepared by dissolving 0.3819 g of NH_4Cl (dried at 105 °C overnight) in 100 mL of deionized water. NH_3–N working solutions of lower concentrations were prepared daily by diluting the stock solution. An alkaline salicylic acid (SA) solution (20.0 mmol L^{-1}) was prepared by dissolving 2.76 g of SA in 1000 mL of a NaOH solution (10.0 g L^{-1}). A sodium dichloroisocyanurate (NaDTT) solution (10.0 mmol L^{-1}) was prepared by dissolving 2.1995 g of NaDTT in 1000 mL of deionized water. A sodium nitroprusside dihydrate (NP) solution (5.0 mmol L^{-1}) was prepared by dissolving 1.4898 g of NP in 1000 mL of deionized water. A buffer solution was prepared by dissolving 32.0 g of boric acid and 100.0 g of trisodium citrate dihydrate in 1000 mL of deionized water. The pH of the buffer solution was adjusted to 9.0 using a NaOH solution (5.0 mol L^{-1}). Finally, deionized water (≥18.2 MΩ cm) was produced using a Milli-Q water purification system (Millipore, Billerica, Massachusetts, USA).

2.2 Apparatus

Fig. 1 depicts the schematic diagram of the HFMC-FIA system. The fluidic propulsion and selection were managed using two four-channel peristaltic pumps (Shenchen Precision Pump, Baoding, Hebei, China) and two six-port valves. The pump tubing consisted of Tygon® rubber (Cole-Parmer Instrument, Vernon Hills, Illinois, USA) with an inner diameter of 0.89 mm and an outer diameter of 2.08 mm, while all other fluidic connections were made using PTFE tubing (0.70 mm i.d. × 1.59 mm o.d.; Yijia Technology Co., Ltd., Beijing, China). A physical image of the HFMC is shown in Fig. 1C. The construction of the HFMC followed a method described elsewhere.[16] Briefly, the HFMC comprised an ePTFE hollow-fiber membrane (1.00 mm i.d. × 1.50 mm o.d.; breakthrough pressure ≥ 4.0 bar, Sci-Nano Membrane Technology Co., Ltd., Hefei, Anhui, China) housed within a PTFE outer shell (2.175 mm i.d. × 3.175 mm o.d.; Nanjing Runze Fluid Co., Ltd., Nanjing, Jiangsu, China). The cross-sectional scanning electron microscope image of the ePTFE hollow-fiber membrane reveals its uniform pore structure with an average pore diameter of approximately 2.0 μm (Fig. 1D). Both ends of the module were fitted with PTFE tee connectors (3 mm i.d.; Hongshuang Electric Co., Ltd., Yueqing, Zhejing, China). A smart proportional-integral-derivative temperature controller (Yuyao Jingchuang Instrument Co., Ltd., Ningbo, Zhejiang, China) was attached to the HFMC module to maintain a constant operating temperature of 45 ± 0.5 °C. The chromogenic reaction module employed a 2.0 m PTFE coil (0.70 mm i.d. × 1.59 mm o.d.) as the reaction coil, also maintained at 45 ± 0.5 °C. The detection module comprised an optical unit and a signal acquisition unit. The optical unit was assembled by connecting an LS-1-LL tungsten halogen lamp (Ocean Optics, Dunedin, Florida, USA), a U-shaped flow-through cell (1.5 mm i.d., 2 cm optical path length, Jingke Optical Instrument, Yixing, Jiangsu, China), and a miniature STS-VIS spectrophotometer (Ocean Optics) in series *via* optical fibers. Absorbance was monitored at a fixed wavelength of 690 nm. The entire analytical process was automated and controlled using a custom software developed in the LabVIEW environment.

2.3 Analytical procedures

The operational sequence for NH_3–N determination using the HFMC-FIA system is summarized in Table 1. In step 1, the

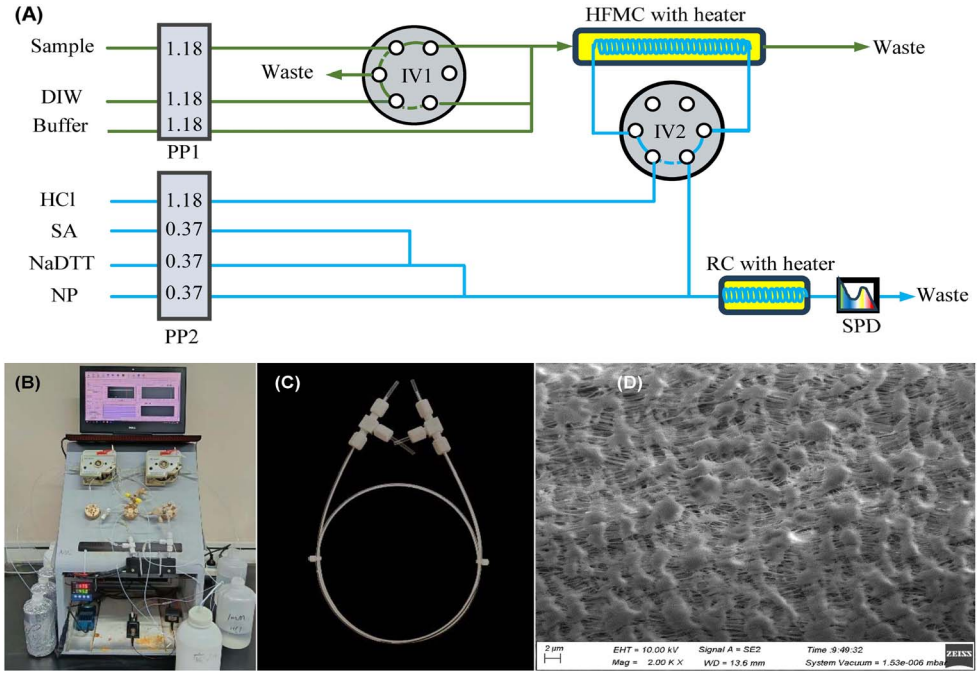

Fig. 1 Schematic and photographs of the developed HFMC-FIA system for NH_3–N determination. (A) Flow diagram of the analytical system. PP1 and PP2: peristaltic pumps; IV1 and IV2: six-port injection valves (solid lines represent the flow path in position A, dashed lines represent the flow path in position B); RC: reaction coil; and SPD: spectrophotometric detector. (B) Physical layout of the assembled HFMC-FIA system. (C) Photograph of the constructed HFMC. (D) Scanning electron microscope image of the hollow-fiber membrane.

Table 1 Operation program of the HFMC-FIA system

Step	IV1 position	IV2 position	Elapsed time	Description
1	B	A	30 s	Clean and load acceptor solution
2	A	B	45 s	NH_3 diffusion and preconcentration
3	B	A	180 s	Color development and detection

valves were switched to positions IV 1-B and IV 2-A, allowing the shell side of the HFMC to be rinsed with deionized water while the lumen was filled with an HCl acceptor solution. In step 2, the valves were switched to positions IV 1-A and IV 2-B, directing the sample mixed with buffer solution into the HFMC shell side while the HCl acceptor solution remained stagnant in the lumen. At 45 ± 0.5 °C, the NH_4^+ ions in the alkalized sample were converted into gaseous ammonia, which diffused across the hydrophobic ePTFE membrane and was trapped in the acidic acceptor solution. In step 3, the valves were returned to positions IV 1-B and IV 2-A, where the shell side was rinsed with deionized water while fresh HCl acceptor solution displaced the ammonium-enriched acceptor solution from the lumen. This eluate was then mixed sequentially with SA, NaDTT, and NP reagents in the reaction coil to form the indophenol blue dye, which was detected spectrophotometrically at 690 nm. Under continuous operation, the system achieved an analytical throughput of 14 samples per hour.

2.4 Method validation and application

The analytical performance of the developed HFMC-FIA system was evaluated through calibration, sensitivity, precision, and accuracy studies. The calibration curve was constructed by plotting an absorbance peak *versus* NH_3–N concentration. The limit of detection (LOD) and limit of quantification (LOQ) were determined according to the International Union of Pure and Applied Chemistry guidelines as 3SD/*S* and 10SD/*S*, respectively, where SD is the standard deviation of nine replicate analyses of a 0.8 mg L^{-1} NH_3–N sample, and *S* is the slope of the calibration curve.[17] Precision was assessed from seven replicate analyses of NH_3–N samples at 1.00, 10.0, and 25.0 mg L^{-1}.

For practical application, the developed method was applied to the determination of NH_3–N concentrations in real industrial wastewater samples. The industrial wastewater samples were collected from PetroChina (Changting) Catalyst (Longyan, Fujian, China). A ProDSS multi-parameter water quality sonde (YSI Inc., USA) measured the pH to be in the range of 9–10 and the salinity to be 13–18. The wastewater samples contained 4.5–31.6 mg L^{-1} of SiO_2, 6.4–144.3 mg L^{-1} of Ca^{2+}, and 0.68–10.8 mg L^{-1} of Al^{3+}. Prior to the analysis, the samples were filtered through a 0.45 μm pore-size polyethersulfone membrane filter (Pall Corporation, Port Washington, New York, USA) to remove suspended solids. For comparison, NH_3–N concentrations in the industrial wastewater were also measured

using a reference method.[9] Briefly, 250 mL of the wastewater sample was adjusted to a pH of 7.0 with 1 mol L^{-1} H_2SO_4, followed by the addition of two drops of a bromothymol blue indicator and 0.25 g of light magnesium oxide. After the solution turned blue, the sample was transferred into a 500 mL distillation flask, and several glass beads were added to prevent bumping. Distillation was carried out at approximately 10 mL min^{-1}, and the condensate was collected in a conical flask containing 50 mL of boric acid absorbent until 200 mL of the distillate was obtained. The distillate was then mixed with two drops of the methyl red-methylene blue mixed indicator and titrated with 0.02 mol L^{-1} HCl to the lavender endpoint. To evaluate the method accuracy and matrix effects, matrix-spiked recovery experiments were performed using the real industrial wastewater sample. Known amounts of the NH_3–N standard solution were spiked into the samples at three concentration levels (3.0, 6.0, and 9.0 mg L^{-1}). The matrix-spiked samples were then analyzed using the developed and reference methods.

3. Results and discussion

3.1 Optimization of method parameters

A single-factor experimental design was employed to optimize the key chemical and instrumental parameters for NH_3–N determination using the proposed method. The optimized chemical parameters included the concentrations of the SA, NaDTT, NP, and HCl solutions. The instrumental parameters optimized were sample injection time, HFMC membrane length, reaction coil length, and reaction temperature. The optimization results are presented in Fig. 2.

3.1.1 Chemical parameters. Salicylic acid serves as the key chromogenic reagent in the modified Berthelot (indophenol blue) reaction for ammonia detection.[18] Its concentration significantly affects the color development efficiency and overall sensitivity of the method. As shown in Fig. 2a, the absorbance signal increased markedly with increasing SA concentration over the range of 1.0–80 mmol L^{-1}. This enhancement occurs because higher SA concentrations promote more effective coupling with monochloramine to form the blue-green indophenol-like complex. However, SA has limited solubility in an aqueous solution. Achieving higher SA concentrations necessitates the addition of substantial amounts of alkali (typically NaOH) to ensure complete dissolution. The resulting excessively high pH in the reaction medium can suppress the formation of the indophenol chromophore, leading to reduced color development and lower absorbance. Taking these factors into consideration, a SA concentration of 20 mmol L^{-1} was selected as the optimal value. This concentration provides excellent sensitivity while maintaining good solubility and a suitable reaction pH for stable and reproducible color formation.

NaDTT serves as a stable oxidant that provides the necessary chlorine for the formation of monochloramine, the critical intermediate in the salicylate-based indophenol blue reaction.[19] As shown in Fig. 2b, the absorbance signal increased with an increase in the NaDTT concentration in the range of 2.0–6.0 mmol L^{-1} and then plateaued between 6.0 and 10.0 mmol L^{-1}. This trend indicates that sufficient available chlorine is required to ensure complete conversion of ammonia into monochloramine. However, further increases beyond 10.0 mmol L^{-1} resulted in a gradual decrease in absorbance, suggesting that excess oxidant can oxidize the indophenol blue chromophore or interfere with the coupling reaction between monochloramine and salicylic acid, thereby suppressing color development. To maintain a stable and sufficient supply of available chlorine while avoiding over-oxidation, a NaDTT

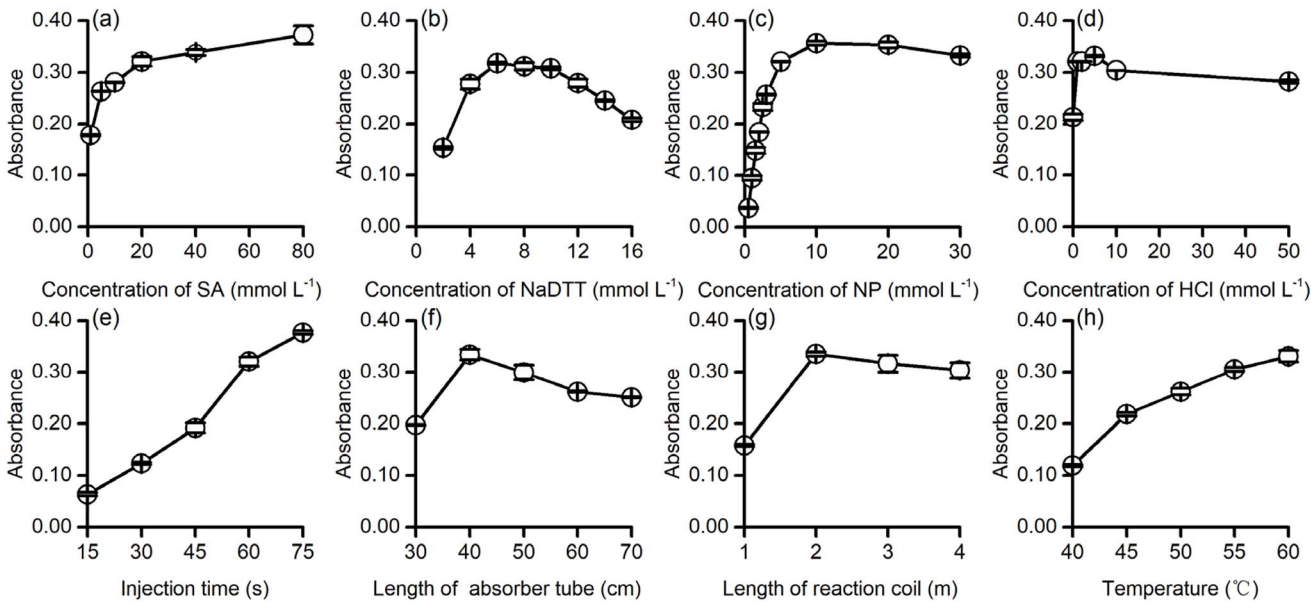

Fig. 2 Optimization of the chemical and instrumental parameters of the developed HFMC-FIA system. (a) Salicylic acid (SA) concentration; (b) NaDTT concentration; (c) sodium nitroprusside (NP) concentration; (d) HCl concentration; (e) injection time; (f) HFMC membrane length; (g) reaction coil length; and (h) HFMC temperature.

concentration of 10.0 mmol L^{-1} was selected as the optimal value. This concentration ensures the reproducible color formation of the reagent stream in the automated FIA system.

Sodium nitroprusside acts as an effective catalyst in the salicylate–hypochlorite reaction, significantly accelerating the coupling between monochloramine and SA.[20] Its concentration has a pronounced effect on the reaction rate and the final absorbance intensity. As shown in Fig. 2c, the absorbance increased steadily with increasing NP concentration over the range of 0.5–10.0 mmol L^{-1}, reaching a maximum at 10.0 mmol L^{-1}. This enhancement is attributed to the catalytic role of NP in promoting the formation of the blue-green indophenol-like chromophore. However, further increases in NP concentration beyond 10.0 mmol L^{-1} led to a gradual decrease in absorbance. This decline is likely caused by the intense intrinsic background color of NP itself, which interferes with the spectrophotometric measurement at the detection wavelength. In addition, excessively high NP concentrations tend to crystallize within the flow lines and tubing walls, increasing the risk of blockages and compromising the long-term stability and reliability of the automated FIA system. Taking these factors into account, an NP concentration of 5.0 mmol L^{-1} was selected as the optimal value. This concentration provides sufficient catalytic activity for rapid and sensitive color development while minimizing background interference and potential operational issues.

Hydrochloric acid serves as the acceptor solution in the HFMC system and plays a dual role in the determination of NH_3–N.[16] It not only facilitates the protonation and trapping of diffused ammonia gas as NH_4^+ in the acceptor stream, but also provides the appropriate acidic environment required for subsequent color development in the salicylate–hypochlorite reaction. As shown in Fig. 2d, the absorbance signal increased steadily with an increase in the HCl concentration over the range of 0–5.0 mmol L^{-1}, reaching a maximum at 5.0 mmol L^{-1}. This improvement is mainly attributed to enhanced preconcentration efficiency, as higher acidity in the acceptor solution promotes the complete trapping of the diffused ammonia. However, when the HCl concentration exceeded 5.0 mmol L^{-1}, the absorbance decreased significantly. The excessively low pH in the acceptor stream inhibits the formation of the indophenol blue chromophore in the subsequent reaction with SA and NADTT. Considering both the preconcentration efficiency and the requirements for optimal color development, a compromise concentration of 1.0 mmol L^{-1} HCl was selected as the optimal value. This concentration ensures efficient ammonia trapping while maintaining a suitable pH for sensitive and reproducible spectrophotometric detection.

3.1.2 Instrumental parameters. The injection time controls the volume of sample introduced into the HFMC and directly determines the amount of NH_3 enriched *via* gas diffusion. As shown in Fig. 2e, the absorbance signal increased steadily with an increase in the injection time in the range of 15–75 s. This occurs because a longer injection time allows a greater sample volume to pass through the shell side of the HFMC, resulting in the more efficient mass transfer of volatile NH_3 across the membrane and, thus, a stronger response from the spectrophotometric detection system. Considering that NH_3–N concentrations in complex industrial wastewater are often relatively high, an injection time of 45 s was selected as the optimum. This value provides sufficient sensitivity while preventing signal saturation and maintaining a suitable linear detection range and high sample throughput.

The length of the gas-diffusion membrane in the HFMC is a critical parameter that directly influences the separation and enrichment efficiency of ammonia. It controls both the effective contact area and the residence time available for NH_3 gas to diffuse from the alkaline donor (sample) stream across the hydrophobic microporous membrane into the acidic acceptor stream. As shown in Fig. 2f, the effect of membrane length on the absorbance signal was investigated over the range of 30–70 cm. The absorbance increased progressively as the membrane length was extended from 30 to 40 cm, reaching a maximum at 40 cm. This improvement results from the larger membrane surface area and longer contact time, which enhance the mass transfer and preconcentration of volatile ammonia. However, further extension of the membrane length beyond 40 cm led to a gradual decrease in absorbance. Excessively long membranes may cause a reduction in the concentration factor of NH_3 in the HFMC. Consequently, an optimal membrane length of 40 cm was selected as a compromise that provides high separation efficiency while maintaining sharp peak shapes, good sensitivity, and acceptable analytical frequency.

The length of the reaction coil determines the residence time of the reaction mixture in the flow system and directly affects the completeness of the indophenol blue chromogenic reaction.[21] As shown in Fig. 2g, the absorbance signal increased significantly when the reaction coil length was extended from 1 to 2 m. This improvement is attributed to the longer residence time, which allows sufficient opportunity for monochloramine to react with salicylic acid in the presence of the catalyst, resulting in the complete formation of the blue-green indophenol-like complex. However, further extension of the coil length to 4 m led to a noticeable decline in the response signal. Excessive coil length causes the increased dispersion and broadening of the sample zone, which dilutes the concentrated analyte and reduces the peak height. In addition, longer coils decrease the overall sample throughput of the proposed system. Therefore, a reaction coil length of 2 m was selected as the optimal value.

Temperature plays a dual role in the gas diffusion membrane separation-flow injection analysis system for NH_3–N determination. It not only accelerates the conversion of NH_4^+ into volatile NH_3 gas in the alkaline donor stream but also enhances the mass transfer rate of NH_3 across the hydrophobic microporous membrane into the acceptor stream.[22] As shown in Fig. 2h, the effect of the HFMC temperature on the absorbance signal was investigated over the range of 40–60 °C. The absorbance increased gradually with a rise in temperature, reflecting the improved volatilization of ammonia and faster diffusion kinetics. However, at temperatures above 50 °C, bubble formation was observed in the flow tubing due to decreased gas solubility and increased vapor pressure. These bubbles caused flow instability, baseline noise, and distortion of the signal

peaks, which compromised measurement precision and system reliability. Therefore, a HFMC temperature of 45 °C was selected as the optimal value.

3.2 Evaluation of interference factors

High-salinity matrices, complex ionic compositions, and organic nitrogen compounds are common interfering factors in the determination of ammonium in industrial wastewater. In this study, the potential effects of these interferences on the proposed method were systematically evaluated, and the results are presented in Fig. 3.

3.2.1 Effect of co-existing ions. Complex industrial wastewater often contains high concentrations of various co-existing ions that can interfere with conventional spectrophotometric methods for NH_3–N determination. To evaluate the anti-interference capability of the developed online gas diffusion HFMC-FIA method, the effects of six common ions (Ca^{2+}, Cl^-, Mn^{2+}, Mg^{2+}, Fe^{2+}, and Fe^{3+}) were systematically investigated. These ions were selected based on their known potential to interfere with the SA method, as reported in the Chinese national standard.[10] A 10.0 mg L^{-1} NH_3–N standard solution was spiked with each ion at concentrations significantly higher than their typical tolerance limits in environmental samples. The tested concentrations were 500 mg L^{-1} for Ca^{2+}, 20 000 mg L^{-1} for Cl^-, 20 mg L^{-1} for Mn^{2+}, 500 mg L^{-1} for Mg^{2+}, 500 mg L^{-1} for Fe^{2+}, and 500 mg L^{-1} for Fe^{3+}. The recoveries were calculated against the working calibration curve prepared in deionized water. As shown in Fig. 3B, the spiked recoveries for all tested ions ranged from 98% to 103%, with RSDs below 3%. These excellent recoveries indicate that the proposed method exhibits strong tolerance to these co-existing ions. The high selectivity is primarily attributed to the gas diffusion membrane separation step, which allows only volatile NH_3 to pass through the hydrophobic microporous membrane while effectively excluding non-volatile ionic species from the acceptor stream. This online matrix isolation effectively eliminates potential interferences from metal ions and high salinity before color development, making the method particularly suitable for complex industrial wastewater matrices.

3.2.2 Effect of organic nitrogen compounds. Organic nitrogen compounds are commonly present in industrial wastewater and can potentially interfere with NH_3–N determination through two main pathways. First, under alkaline and heated conditions, some organic nitrogen species may undergo hydrolysis, releasing additional ammonia and leading to positive bias. Second, certain volatile organic amines possess functional groups similar to ammonia and may compete with NH_3 in the chromogenic reaction, thereby affecting color

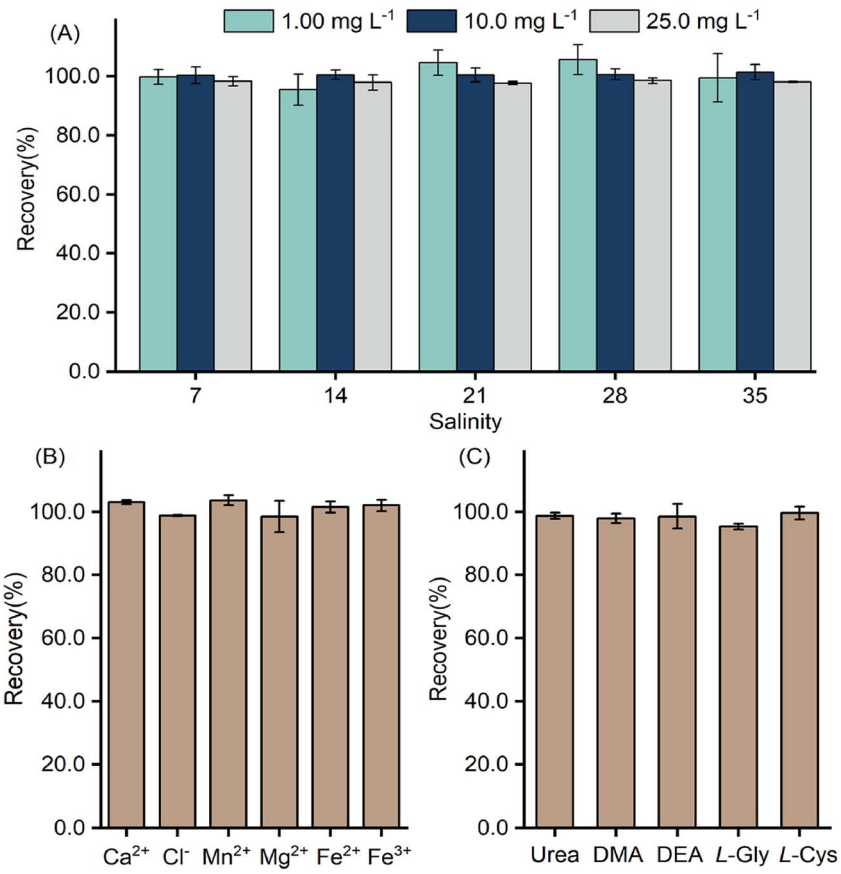

Fig. 3 Anti-interference performance of the developed method. (A) Effect of salinity on NH_3–N analysis. (B) Effect of co-existing common ions on NH_3–N analysis at a concentration of 2.0 mg L^{-1}. (C) Effect of organic nitrogen on NH_3–N analysis at a concentration of 2.0 mg L^{-1}. DMA: dimethylamine, DEA: diethylamine, L-Gly: L-glycine, and L-Cys: L-cysteine.

development and analytical accuracy.[23] To assess the selectivity of the developed online gas diffusion HFMC-FIA method, a 2.0 mg L^{-1} NH_3–N standard solution was spiked with urea, dimethylamine (DMA), diethylamine (DEA), L-glycine (L-Gly), and L-cysteine (L-Cys) at equivalent nitrogen concentrations (2.0 mg L^{-1} as N). The spiked recoveries were then calculated using the working calibration curve. As shown in Fig. 3C, the recoveries for all tested organic nitrogen compounds ranged from 95.3% to 100.2%. These high and consistent recoveries demonstrate that the proposed method possesses excellent selectivity toward inorganic ammonium. The superior anti-interference performance is mainly due to the gas diffusion membrane separation process, which selectively allows only volatile NH_3 to permeate the hydrophobic membrane while effectively retaining non-volatile or less volatile organic nitrogen species in the donor stream. This online separation step effectively minimizes competitive reactions and hydrolysis interferences before spectrophotometric detection.

3.2.3 Effect of salinity. High-salinity matrices are known to affect the determination of ammonium in water samples.[24] The salinity effect on the developed method manifests primarily in two aspects: (1) a refractive index mismatch between the carrier stream and trace amounts of high-salinity sample permeating the membrane can cause light deflection upon passing through the detection cell, generating a "false peak" or baseline fluctuation unrelated to the chemical reaction, which severely interferes with the identification and integration of the true analyte peak; and (2) high salinity may reduce the solubility of the target analyte through a salting-out effect, thereby compromising the sensitivity and accuracy of the ammonium analysis.[25,26] To evaluate the influence of salinity on ammonium determination, a series of water samples with salinities ranging from 0 to 35 were prepared by mixing deionized water with artificial seawater (salinity = 35) in varying proportions. Ammonium standard solutions at different concentrations (1.0, 10, and 25 mg L^{-1}) were spiked into these samples for recovery tests. As shown in Fig. 3A, the recoveries of all spiked samples ranged from 95.5% to 105.7%, indicating that salinity only had a negligible effect on the NH_3–N measurement.

3.3 Analytical performances

Under the optimized experimental conditions, the analytical performance of the developed online gas diffusion HFMC-FIA method was systematically evaluated, including the linear range, LOD, LOQ, and precision. As shown in Fig. 4A, a series of NH_3–N standard solutions prepared in deionized water was analyzed. The typical signal outputs and the corresponding calibration curve are presented. The inset in Fig. 4A reveals an excellent linear relationship between the absorbance and NH_3–N concentration over the range of 1.0–50.0 mg L^{-1}. The calibration curve was fitted with the regression equation: $A = 0.0117C + 0.00006$ ($R^2 = 0.9997$, $n = 3$), where A is the absorbance, and C is the NH_3–N concentration in mg L^{-1}. According to the International Union of Pure and Applied Chemistry guidelines, the LOD and LOQ were calculated as 3SD/S and 10SD/S, respectively, where SD is the standard deviation of the blank signal, and S is the slope of the calibration curve.[17] The obtained LOD and LOQ were 0.22 and 0.72 mg L^{-1}, respectively. These results indicate that the method is sufficiently sensitive for the determination of NH_3–N in most industrial wastewater samples, which normally contain several to several thousand mg L^{-1} of NH_3–N.[3] Precision was assessed by repeatedly measuring NH_3–N standard solutions at three concentration levels (1.0, 10.0, and 25.0 mg L^{-1}). As shown in Fig. 4B, the RSDs ($n = 7$) were 3.0%, 1.6%, and 1.3%, respectively. These low RSD values demonstrate the excellent repeatability and good precision of the proposed automated system.

The stability of the membrane strongly influenced the analytical performance of the developed system. The developed system was operated continuously for the analysis of 1000 industrial wastewater samples, which contained 4.5–31.6 mg L^{-1} of SiO_2, 6.4–144.3 mg L^{-1} of Ca^{2+}, and 0.68–10.8 mg L^{-1} of Al^{3+}. After every 100 samples, a 2.0 mg L^{-1} NH_3–N standard solution was measured to evaluate recovery performance. The results showed no significant difference in recovery for the first 800 samples compared with the measurement obtained before analyzing real wastewater samples, whereas a significant decrease was observed after 900 samples (Fig. 5A). Scanning electron microscopy revealed that the hollow-fiber

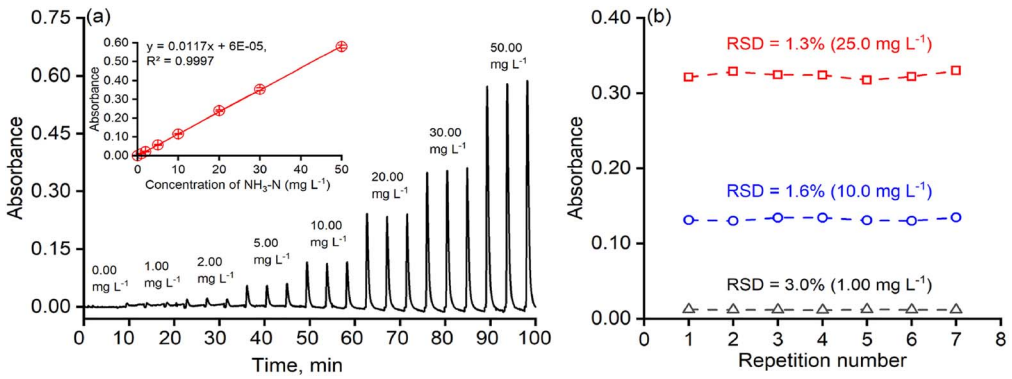

Fig. 4 Analytical performance of the developed method. (a) Typical signal output profiles for NH_3–N standard solutions in the range of 0–50 mg L^{-1}. The inset shows the corresponding calibration curve. (b) Precision values of seven repetitive analyses for 1.0, 10.0, and 25.0 mg L^{-1} NH_3–N standard solutions.

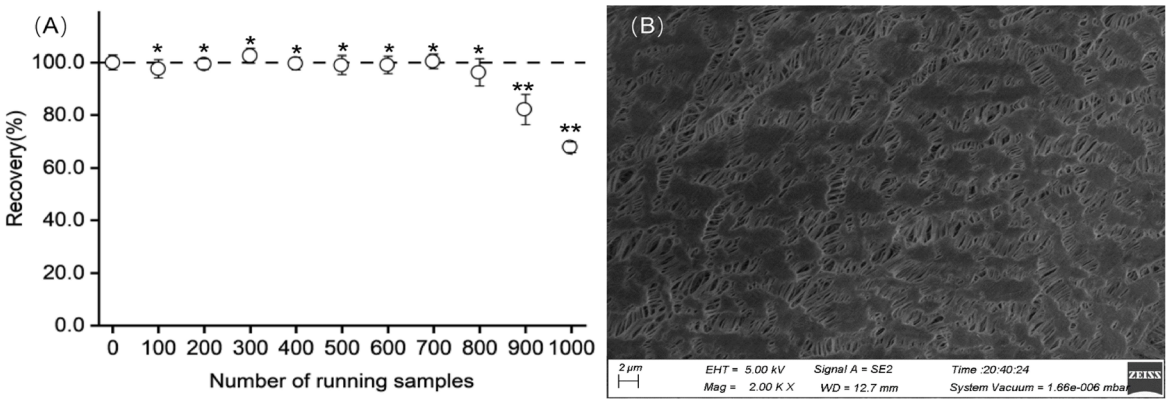

Fig. 5 Membrane antifouling performance. (A) Stability of the analytical method. The developed system was operated continuously to analyze 1000 industrial wastewater samples. A 2.0 mg L^{-1} NH_3–N standard solution was analyzed after every 100 samples to evaluate recovery performance. Error bars represent the standard deviations of seven replicate measurements. Symbol * indicates no significant difference compared with the measurement obtained before the analysis of the real industrial wastewater samples, while symbol ** indicates a significant difference. (B) Scanning electron microscope image of the hollow-fiber membrane after the analysis of 1000 real industrial wastewater samples.

membrane was covered with fouling material after analyzing 1000 samples (Fig. 5B), which could compromise its separation efficiency. This fouling is likely caused by the precipitation of SiO_2, $Ca(OH)_2$, and $Al(OH)_3$ on the membrane under alkaline conditions. Therefore, it is recommended to include a standard solution (*e.g.*, 2.0 mg L^{-1} NH_3–N) periodically within the sample sequence to monitor method performance. We suggest replacing the HFMC with a new one if the recovery of the standard solution drops below 85%.

3.4 Application to real wastewater determination

To evaluate the practical applicability and reliability of the developed online gas diffusion HFMC-FIA method, the system was applied to the determination of NH_3–N in real industrial wastewater samples collected from the effluent of an ammonia-stripping process at a chemical plant. The results were compared with those obtained using the standard reference salicylate spectrophotometry method.[9]

Table 2 Comparison of analytical results for real industrial wastewater samples determined by the developed method and the reference salicylic acid spectrophotometry method[9]

		Developed method		Reference method	
Sample	Spiked (mg L^{-1})	Found (mg L^{-1})	Recovery (%)	Found (mg L^{-1})	Recovery (%)
1	0	2.07	—	2.60	—
	3.00	4.83	92.0	4.49	63.0
	6.00	7.81	95.7	6.67	67.8
	9.00	10.64	95.2	8.24	62.7
2	0	3.23	—	2.97	—
	3.00	6.13	96.7	4.76	59.7
	6.00	8.70	91.2	6.72	62.5
	9.00	11.84	95.7	8.29	59.1
3	0	5.28	—	6.05	—
	3.00	7.86	86.0	7.98	64.3
	6.00	10.69	90.2	10.04	66.5
	9.00	13.32	89.3	12.18	68.1

The analytical results are summarized in Table 2. Overall, the NH_3–N concentrations determined using the developed method were in good agreement with those measured using the reference method. More importantly, the developed online method demonstrated significantly better matrix tolerance. Spike recoveries for the real wastewater samples ranged from 86.0% to 96.7% using the proposed method, which were markedly higher than those obtained using the reference method (59.1–68.1%). These results indicate that the conventional reference procedure suffers from serious matrix interferences in complex industrial effluents, whereas the gas diffusion membrane separation step in the proposed system effectively eliminates non-volatile interferences, leading to more accurate and reliable measurements.

In addition, the reference method is relatively time-consuming and labor-intensive. It typically requires approximately 30 min for distillation, followed by cooling and spectrophotometric measurement, resulting in a total analysis time of about 60 min per sample. In contrast, the developed automated HFMC-FIA system can complete the analysis of a single sample in less than 5 min, offering significantly higher sample throughput and reduced manual operation. These advantages make the proposed method particularly suitable for high-frequency monitoring and process control in industrial wastewater treatment.

4. Conclusions

In this study, an automated online gas diffusion membrane separation-flow injection analysis system coupled with salicylate spectrophotometric detection was successfully developed for the rapid and reliable determination of NH_3–N in complex industrial wastewater. The method effectively overcomes matrix interferences through selective gas diffusion separation while employing the environmentally friendly salicylate reagent. Under optimized conditions, the method showed a linear range of 1.0–50.0 mg L^{-1} ($R^2 = 0.9997$), with an LOD and LOQ of 0.22 and 0.72 mg L^{-1}, respectively. The precision was excellent, with

RSDs below 3.0%. Interference studies confirmed high tolerance to salinity (up to 35), common ions, and organic nitrogen compounds. The application to real wastewater samples from an ammonia-stripping process demonstrated good agreement with the reference method. With a sample throughput of 14 samples per hour, the system offers clear advantages in speed and automation over traditional manual procedures. The proposed system offers a rapid, accurate, automated, and practical solution for the high-frequency monitoring of NH_3–N in complex industrial effluents, supporting better process control and regulatory compliance.

Author contributions

Jun Hu: methodology, investigation, formal analysis, writing – original draft; Rui Huang: field application; Peng Li: methodology; Yanli Hua: field application; and Kunde Lin: project administration, writing – review & editing.

Conflicts of interest

The authors declare no competing interests.

Data availability

The authors state that the data supporting the findings of this study are available within the article.

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