ION SELECTIVE ELECTRODE VERSUS UV-VIS SPECTROSCOPY AFTER GAS STRIPPING FOR AMMONIUM MONITORING IN WATER

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ABSTRACT

Accurate measurement of ammonium (NH_4^+) is critical for assessing water quality in both environmental monitoring and industrial water management. Applications include controlling sour water stripping in petrochemical processes, regulating aeration in wastewater treatment plants and monitoring industrial effluents such as those from aquaculture or semiconductor manufacturing. Furthermore, ammonia is an efficient hydrogen carrier, making it essential to have reliable and various methods for its measurement in the context of hydrogen energy applications. Traditional methods often face challenges related to sensitivity, selectivity, or operational complexity. In this study, two analytical approaches for NH_4^+ quantification which are implemented as core technology in two instruments designed and manufactured by HORIBA: ion-selective electrode (ISE) and ultraviolet (UV) spectroscopy after gas stripping are compared. The ISE method offers rapid, real-time measurement capabilities, whereas UV spectroscopy after gas stripping can provide high sensitivity and minimize matrix interferences. Both techniques were evaluated using a range of aqueous samples, including standard solutions and industrial wastewater effluents. Key performance indicators such as analyser response, linearity and interference effects were assessed. Initial trends indicate that ISE tends to provide fast and simple measurements, while UV spectroscopy shows rapid and stable readings particularly in sample matrices with higher salt concentrations. A clear understanding of both technologies enables end-users to select the most suitable method according to specific monitoring requirements and enhances decision-making in environmental surveillance and process control applications.

INTRODUCTION

Ammonia, including its aqueous ammonium form, plays a crucial role in aquatic systems, industrial processes, and emerging energy technologies. In natural waters, wastewater, and industrial effluents, ammonium is a key indicator of organic pollution and biological activity. High concentrations of ammonium can lead to oxygen depletion, eutrophication, and toxicity to aquatic organisms[1], which has led to increasingly strict regulatory limits for its discharge into the environment. Beyond its environmental impact, ammonia has recently gained strong attention as a carbon-free energy carrier. Its high volumetric hydrogen density, low storage pressure and stability for long-term storage are among the beneficial characteristics of ammonia to be promising vectors for hydrogen storage, transport, and distribution[2]. Accordingly, accurate and robust ammonium measurements are needed not only to protect water resources but also to ensure safe and efficient operation of ammonia-based hydrogen systems.
Conventional methods for ammonium determination include spectrophotometric, fluorometric, and electrochemical techniques[3,4]. Although widely used, these techniques often suffer from significant drawbacks such as complex instrumentation, interference from other ions, the need for chemical reagents, or relatively long analysis times. These limitations become particularly critical when monitoring complex water matrices or when fast and reliable measurements are required for real-time or on-site applications.

Among the available analytical approaches, ion-selective electrodes (ISEs) and ultraviolet (UV) spectroscopic techniques represent two different routes for ammonium measurement. ISEs are a well-established technique widely used for their ability to provide continuous in-situ measurements, while UV-based systems coupled with gas stripping offer an alternative approach for online analysis based on optical detection. Both technologies are now implemented in water and wastewater treatment facilities for process supervision and environmental control.

The objective of this study is to compare ammonium measurement by ion-selective electrode and by UV spectroscopy after ammonia gas stripping. The two methods are evaluated in terms of sensitivity, precision, and applicability to real water samples. By addressing both environmental monitoring and emerging hydrogen-energy-related applications, this work aims to provide practical guidance for selecting the most appropriate analytical strategy for reliable ammonium measurement in aqueous systems.

1. ANALYTICAL PRINCIPLES

Two online instruments commercially available and manufactured by HORIBA were used for ammonium monitoring in this study: an ISE based system, the controller combined with ISE probe, which directly measures NH_4^+ in aqueous samples, and a UV-spectroscopy based water analyser, the UV analyser, which detects ammonia in the gas phase after converting ammonium to NH_3 via gas stripping. The following sections detail the scientific principles underlying each technique.

1.1 Ion-Selective Electrode (ISE) Principle

The ISE measures ammonium directly in water using a selective membrane containing an ammonium-specific ionophore. It is based on potentiometric analysis, where the

measurement signal is an electrical potential and is converted into an ion concentration reading. The electrode potential depends on the ammonium activity according to the Nernst equation:

$$E = E^0 + \frac{RT}{F} \ln [NH_4^+] \quad (1)$$

Where E = the measured potential (mV)
E^0 = the standard potential (mV)
R = Ideal gas constant (8.314 J mol^{-1} K^{-1})
T = Temperature in K
F = Faraday's constant (96 485 $C.mol^{-1}$)
$[NH_4^+]$ = Ion activity in solution

There is a linear dependence between the measured potential and the logarithm of the ammonium concentration, with a theoretical slope of approximately 59.2 mV per decade at 25 °C[5]. According to literature, this slope indicating ISE sensitivity can deviate from these theoretical values due to effects within the membrane ranging between 54 and 60 mV per decade for monovalent ions such as NH_4^+.

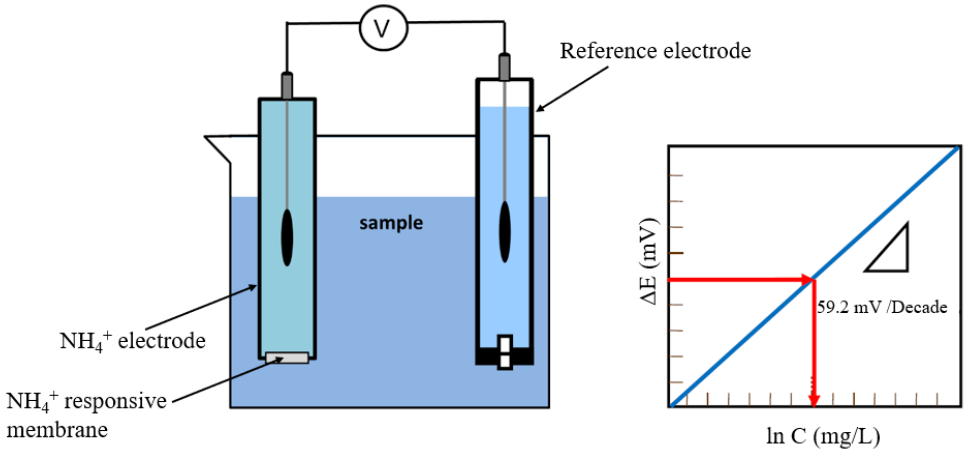

FIGURE 1: WORKING PRINCIPLE OF THE ISE

Figure 1 illustrates the main components of the ISE probe, including the selective membrane, reference electrode, and internal filling solution. Ammonium ions in the water sample interact with the membrane, generating a potential proportional to the ion activity in the sample. This potential is then measured and converted into ammonium concentration in real time. The integrated compensation electrode helps correct for potassium interference, ensuring accurate real-time ammonium measurements. Despite this compensation, the electrode response can still be

affected by changes in ionic strength and pH, which alter the activity coefficients of ammonium ions.

1.2 UV Spectroscopy After Gas Stripping

The UV analyser quantifies ammonium by combining chemical conversion, gas-phase stripping, and UV spectroscopy analysis in a continuous and automated operation. This method relies on the ammonium - ammonia equilibrium in aqueous solutions[3]:

$$NH_4^+ \rightleftharpoons NH_3 + H^+$$

This equilibrium is strongly pH-dependent: at low pH, ammonium predominates, whereas at high pH, ammonia becomes the dominant species (Figure 2). In the UV spectroscopic analyser, this is achieved by automatically adding small volumes of 10% NaOH to the water sample, ensuring the pH is sufficiently high (above 11) to drive quantitative conversion of NH_4^+ to NH_3.

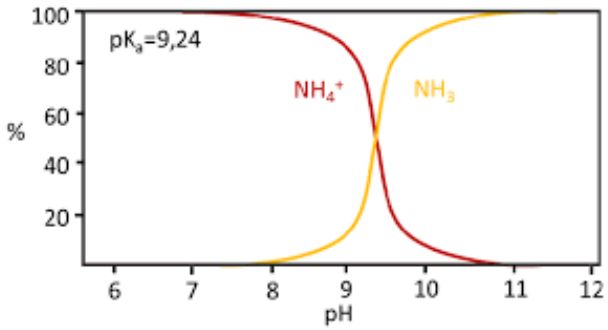

FIGURE 2: THE PH DEPENDENCE OF NH_3/NH_4^+ RATIO

Once formed, ammonia is transferred from the aqueous phase to the gas phase through a controlled airflow. The liquid-gas equilibrium of NH_3 follows Henry's Law which relates the concentration of ammonia in the aqueous phase to its concentration in the gas phase:

$$H = \frac{C_a}{C_g} \qquad (2)$$

Where Ca = Concentration of NH_3 in the dissolved phase
Cg = Concentration of NH_3 in the gas phase
H= Henry constant

The Henry constant depends on the temperature, the gas, and the liquid sample. By ensuring adequate stripping time, the UV analyser maximizes ammonia stripping efficiency, while minimizing losses and ensuring reproducible transfer from liquid to gas. The analyser has a preset temperature compensation option to address the variation of aqueous sample temperature.

The gaseous ammonia is then stripped out into a gas flow cell, where its absorption is measured by UV. The Beer–Lambert law relates absorbance to the ammonia concentration in the gas phase.

$$A = \varepsilon \, l \, C$$

Where A = Absorbance
ε = Molar absorption coefficient
l = Optical path length
C = NH_3 concentration in the gas phase

Unlike conventional absorbance measurements, the UV spectrum of ammonia exhibits a periodic pattern between 190 nm to 210 nm, which can be exploited for selective concentration determination. To achieve highly selective detection and minimize interferences, the UV spectroscopic analyser performs a mathematical treatment based on Fast Fourier Transform (FFT) on the measured spectrum. The characteristic frequency extracted from this analysis is directly correlated with ammonia concentration, enabling precise determination even in the presence of potential interferences from other compounds.

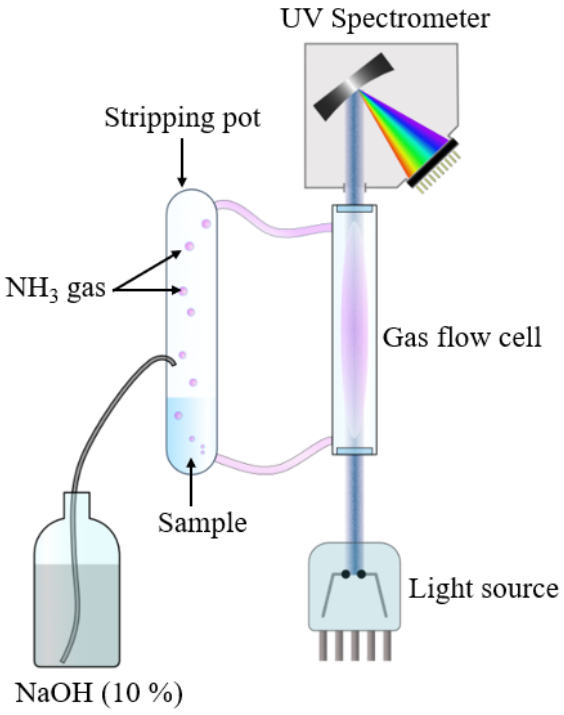

FIGURE 3: WORKING PRINCIPLE OF UV ANALYSER FOR NH_4^+ MEASUREMENT

Figure 3 shows the functional diagram of the UV analyser, illustrating sample alkalinization, ammonia stripping, and UV detection combined with FFT treatment. By integrating chemical conversion, gas-phase separation, and FFT-based UV detection, the UV analyser enables reliable, selective, and periodic online monitoring of ammonium while minimizing interference from salts, turbidity, color, or organic matter.

2. EXPERIMENTAL SETUP

2.1 Chemicals, Standard Solutions and Samples

Ammonium standard solutions were prepared by dissolving NH_4Cl (*Analytical grade*) powder weighed using a certified analytical balance in deionized water to prepare a stock solution. Dilution was then subsequently performed to obtain NH_4^+ concentrations in the range 0-100 ppm. This range was selected to cover typical concentrations encountered in wastewater and industrial process waters. To evaluate the influence of salinity, NaCl was added to selected ammonium standards at different concentrations representative of saline and sea water matrices. All solutions were prepared fresh prior to analysis.

Two types of real wastewater matrices were investigated in this study: grab samples analysed under controlled laboratory conditions and wastewater effluents monitored online.

A grab sample was collected at the outlet of a dairy wastewater treatment plant (WWTP) and used for comparative measurements with ISE and UV analyser. The sample was stored at 4 °C and analyzed within 24 h.

In addition, online monitoring data from wastewater treatment plants were used to illustrate instrument performance under real operating conditions. The ISE was installed at a municipal WWTP treating domestic wastewater in Japan, while the UV-gas stripping analyser was operated at a different municipal WWTP in Turkey receiving a mixture of domestic and industrial wastewater. These sites provided representative and contrasting water matrices for evaluating the robustness and suitability of both monitoring technologies.

2.2 Instrumentation

FIGURE 4: PICTURE OF ION SELECTIVE ELECTRODE

The ISE probe is equipped with an ammonium ion chip, a reference chip and a potassium-selective chip. The probe is connected to a dedicated controller that continuously displays NH_4^+ concentrations, records measurements over time, and allows rapid and real-time monitoring. The electrode system is designed for minimal sample handling and easy installation in aeration tank of wastewater plants.

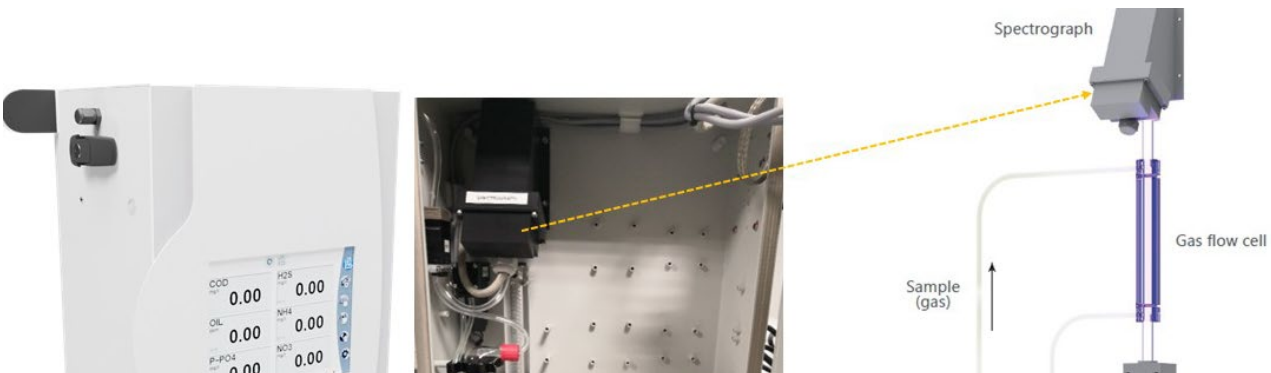

FIGURE 5: UV-GAS STRIPPING ANALYSER (PHOTO OF THE INSTRUMENT SHOWING SAMPLE INLET, GAS STRIPPING UNIT, AND UV DETECTION SYSTEM)

The UV analyser is equipped with a xenon flash lamp serving as the light source and a full UV-Vis spectrograph functioning as the photodetector. The sample is injected through a three-way solenoid valve into the stripping pot, where NaOH solution is automatically added using a pump to convert NH_4^+ to NH_3. Filtered air is then injected into the stripping pot by an air pump in a closed loop to transfer the NH_3 gas into the gas flow cell for measurement. The optical path length of the flow cell is 200 mm, and the UV spectrum is collected over the 190 210 nm range. The UV analyser operates in a periodic measurement mode, with an NH_4^+ measurement cycle of approximately 3 minutes.

2.3 Measurement Protocols

Both instruments were first calibrated using 100 ppm standard ammonium solutions**.** All samples, including grab samples and representative online datasets, were analysed as follows:

- **ISE:** The probe was immersed directly in the sample. NH_4^+ concentration was recorded once a stable reading was reached.
- **UV spectroscopic analyser:** Each sample was processed according to the NH_4^+ measurement cycle, which has a duration of 3 minutes.

All measurements were performed in triplicate to assess repeatability. Additional experiments were conducted to evaluate the effect of NaCl concentrations (0, 1, 2, 3.5, and 5%) on the response of each instrument.

3. RESULTS

3.1 Response to Ammonium Standard Solutions

Both the ISE and the UV spectroscopic analyser depicted a clear and reproducible response to ammonium standards over the concentration range 0 -100 ppm NH_4^+.

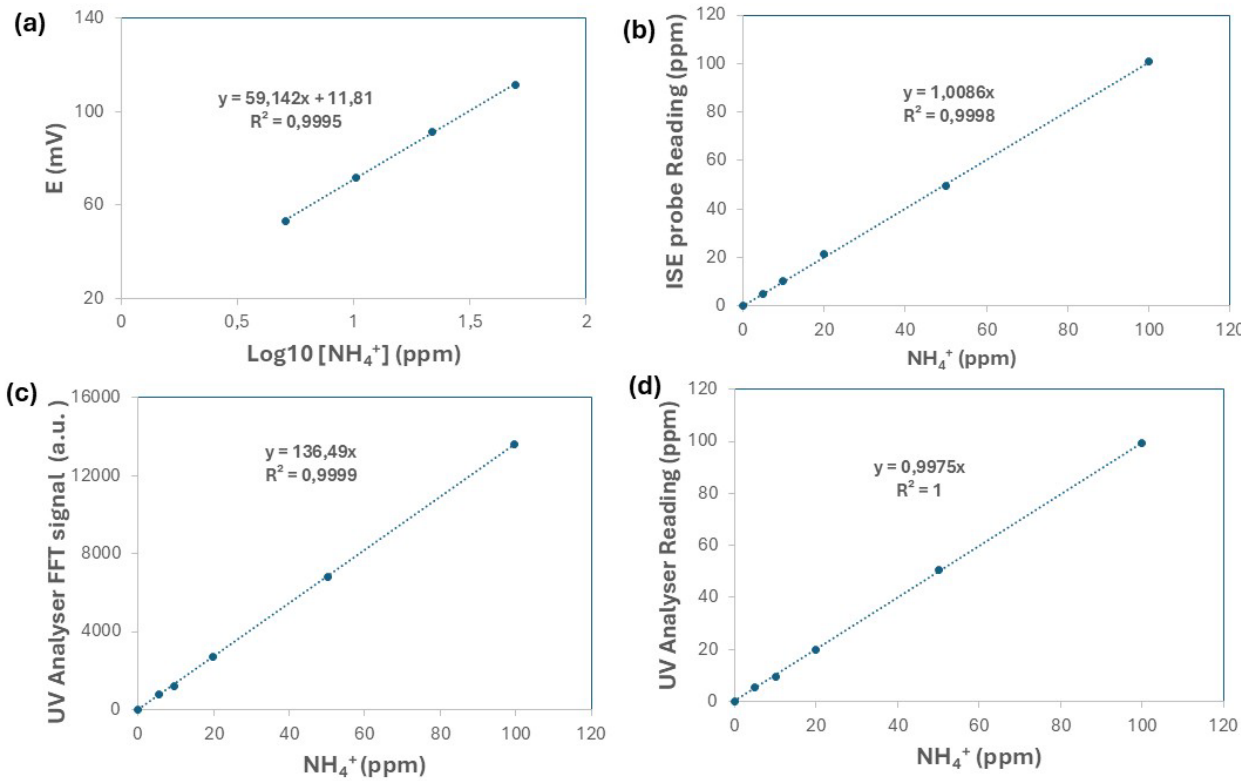

FIGURE 6: (a, b) ISE PROBE RESPONSE: ELECTRODE POTENTIAL AND CONCENTRATION OUTPUT AS A FUNCTION OF [NH_4^+] (c) UV analyser FFT-DERIVED SIGNAL AS A FUNCTION OF [NH_4^+]. (d) UV ANALYSER READINGS VERSUS STANDARD SOLUTIONS.

The ISE probe exhibited a linear Nernstian-type response over the 0-100 ppm range. A linear regression of electrode potential versus $\log_{10}[NH_4^+]$ yielded a slope of 59.1 mV per decade with an excellent correlation coefficient (R^2 = 0.999), confirming the logarithmic dependence predicted by the Nernst equation (Figure 6a). This confirms the proper functioning of the ammonium-selective membrane and reference electrode. Moreover, linear regression between measured and standard concentrations gave a

slope of 1.004 (R^2 = 0.9997), indicating high analytical precision of the sensor (Figure 6b).

Both the UV analyser concentration readings and the corresponding FFT signal extracted from the UV spectra exhibited a strong linear relationship with the ammonium standards over the investigated range, confirming that the gas-phase UV-FFT detection provides a stable and quantitative analytical response (see figure 6c and 6d).

3.2 Influence of Salinity (NaCl)

To assess the effect of salinity or ionic strength on ammonium measurement, standard solutions with fixed NH_4^+ concentration (~100 ppm) were prepared at NaCl 0.0 % and 3.5 %, and measurements were recorded every 5 minutes over 55 minutes for both ISE and UV analyser.

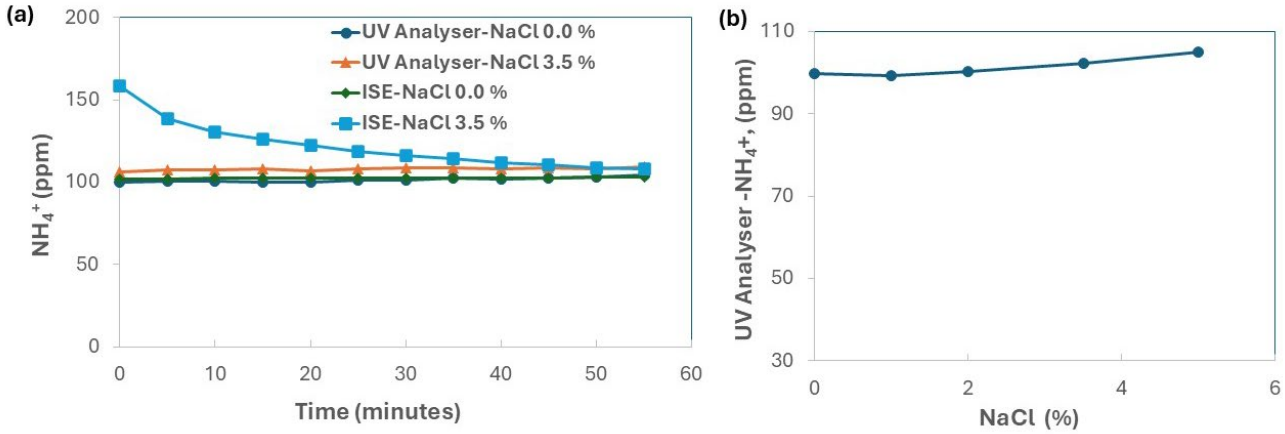

FIGURE 7: (a) MEASURED NH_4^+ 100 PPM OVER TIME FOR UV ANALYSER AND ISE AT NaCl 0.0 % AND 3.5 %. (b) EFFECT OF NaCl CONCENTRATION ON UV ANALYSER AMMONIUM MEASUREMENT AT 100 PPM NH_4^+

Figure 7a shows that the UV analyser provides stable measurements within 5 minutes under both low and high salinity conditions, whereas approximately 5 % higher measurement value was observed. On the other hand, the ISE probe shows approximately 150 % higher reading value then gradually drifted close to 100 ppm after 50 minutes. This behavior suggests limitations of ISEs under high ionic strength. The ISE sensor requires a longer stabilization time of around 50 minutes, which is usually not acceptable level for real time or punctual measurement. In contrast, UV analyser maintains stable readings, confirming its robustness for ammonium monitoring in saline wastewater. As shown in Figure 7b, the UV analyser readings remain close within prepared ammonium concentration (~100 ppm) over the NaCl range from 0 to 5%. This is most likely due to changes in the gas-liquid equilibrium during the ammonia stripping step. Even at 5% NaCl, UV analyser can provide a

reliable value within 5 minutes, this is one of the advantages of gas-stripping UV spectrum measurement.

3.3 Performance in real wastewater matrices

3.3.1 Dairy Industry WWTP Effluent (Grab Sample)

A grab sample collected at the outlet of a dairy industry wastewater treatment plant was analyzed using both the ISE probe and the UV analyser. Due to the limited sample volume and the exploratory nature of this test, a restricted number of measurements were performed.

TABLE I. NH_4^+ MEASURED IN A DAIRY WWTP EFFLUENT USING ISE AND UV ANALYSER.

Measurement number	ISE (NH_4^+, ppm)	UV Analyser (NH_4^+, ppm)
1	59.98	58.08
2	61.00	56.00
3	62.53	/
4	63.55	/
5	65.02	/

Table I summarizes the results of this experiment. ISE probe readings ranged from 59.98 to 65.02 ppm, while UV analyser measurements varied between 56.00 and 58.08 ppm. Although both instruments reported ammonium concentrations within the same order of magnitude, ISE systematically yielded slightly higher values compared to UV analyser. The sample shows a measured conductivity of approximately 2754 µS/cm, corresponding to an estimated NaCl equivalent of about 0.14 %, and a turbidity of around 400 NTU. These values fall within the operational ranges of both instruments.

3.3.2 Online Monitoring of Water

Figure 8 presents the evaluation of both instruments under real operational conditions, with each instrument deployed at a different wastewater treatment plant. In addition, UV analyser was evaluated at a fish farm, where a recirculating aquaculture system supplied with seawater was continuously monitored. For each installation, routine laboratory analyses using a colorimetric method were conducted in parallel to provide reference ammonium concentrations for comparison.

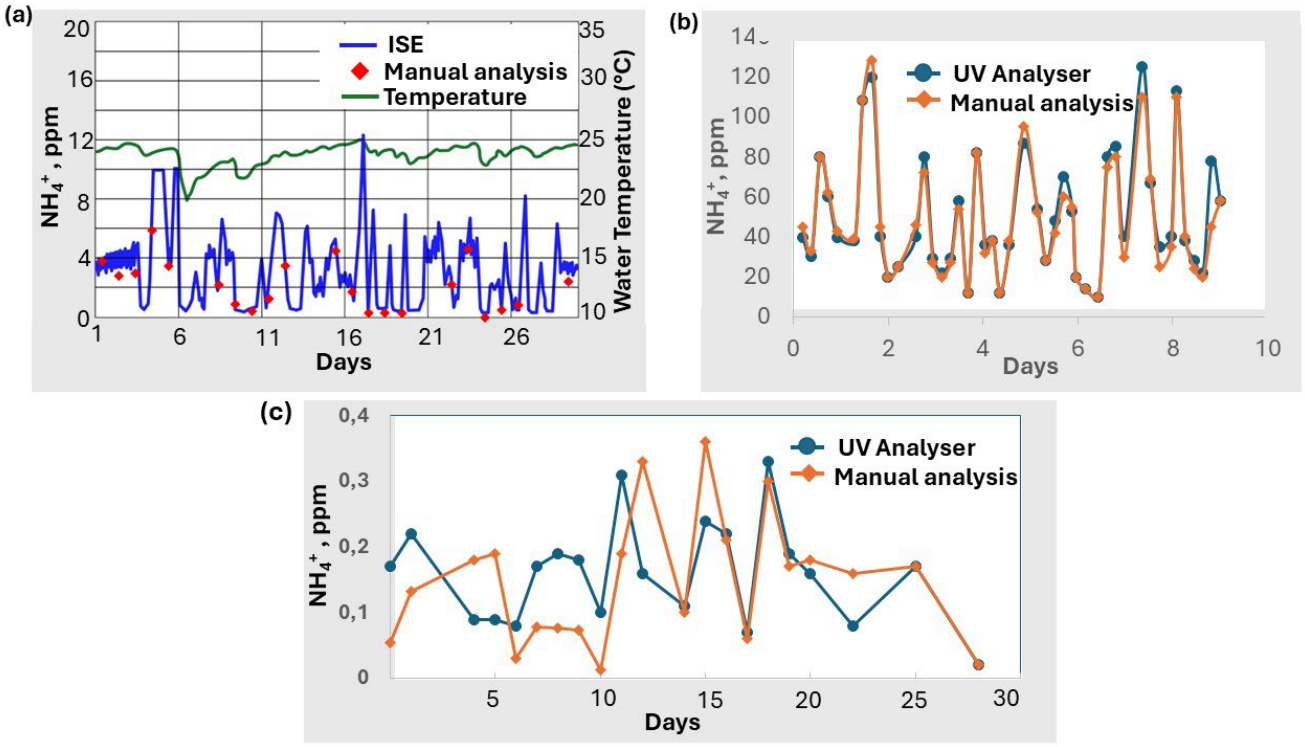

FIGURE 8: LONG-TERM MONITORING OF AMMONIUM IN WASTEWATER: (A) ISE PROBE IN A MUNICIPAL WWTP AERATION TANK IN JAPAN (B) UV SPECTROSCOPIC ANALYSER ANALYSER IN A MIXED MUNICIPAL–INDUSTRIAL WASTEWATER STREAM IN TURKEY (C) UV ANALYSER MONITORING IN A SEAWATER-FED RECIRCULATING AQUACULTURE SYSTEM

The results of a 25-days evaluation of the ammonium probe installed in the aeration tank of a wastewater treatment plant in Japan are shown in Figure 8a. A consistent correlation was observed between laboratory analyses and the sensor measurements, indicating that the ISE sensor is well suited for controlling aeration blower operation.

Similarly, the UV analyser deployed on a mixed municipal-industrial wastewater stream in Turkey, demonstrated comparable stability and strong agreement with laboratory reference values, providing reliable ammonium measurements throughout the 9 days monitoring period, see figure 8b.

For water from the fish farm system (Figure 8c), UV analyser follows the same variation pattern as the laboratory results, demonstrating its ability to track concentration dynamics in saline water. The differences observed between the laboratory and analyser concentrations are likely related to measurements being close to the NH_4^+ detection limit of the analyser.

CONCLUSION

This study compared two online instruments for ammonium monitoring in water: the ion-selective electrode and the analyser based on UV spectroscopy after gas stripping. Both instruments demonstrated linear response and consistent performance across the range of standards solutions tested, indicating their suitability for quantitative measurements. The influence of salinity on ammonium measurements was also assessed. UV analyser exhibited rapid and stable readings, with deviations below 5% even at 5% salinity, whereas the ISE showed slower stabilization and greater sensitivity to ionic strength, highlighting the advantages of gas-phase detection for salty samples.

Analysis of real wastewater from a dairy industry treatment plant showed that both instruments provided comparable ammonium concentrations. Long-term online monitoring demonstrated that the ISE provides continuous real-time measurements and maintained good performance in municipal wastewater. In parallel, the UV spectroscopic analyser provided reliable measurements in mixed municipal-industrial streams and saline water from a fish farm, reproducing laboratory trends and enabling periodic monitoring of samples over several days across different water matrices.

To support method selection for different applications, Table II summarizes the key technical characteristics of both ammonium measurement technologies, including range, repeatability, salt interference. Both methods are suitable for ammonium determination; however, the choice of the appropriate method should take into account the intended measurement purpose and any interfering substances present in the sample.

TABLE II. TECHNICAL COMPARISON OF THE TWO AMMONIUM MEASUREMENT METHODS

	ISE	UV ANALYSER
Measurement range	0-100 ppm 0-1000 ppm	0-100 ppm 0-1000 ppm
Repeatability	± 3 %	± 5 %
Salt interference	Higher	Lower
Measuring mode	Continuous	Periodic (> 5 minutes)
Recommended Application	✓ Aeration tank of WWTP* ✓ Real time monitoring	✓ Process control ✓ Complex sample matrix (particularly up to 5 % salt concentration) ✓ Environmental monitoring

* Waste water Treatment Plant

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