NON-MODIFIED Pt ELECTRODES ENABLING ACCURATE VOLTAMMETRIC QUANTIFICATION OF AMMONIA IN WATER SAMPLES

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Even though ammonia is a natural component of aquatic environments, elevated concentrations indicate pollution and environmental degradation. Consequently, efficient analytical methods for monitoring ammonia levels are crucial for preserving water quality. Voltammetry offers a sustainable approach for NH₃ quantification, combining good analytical performance with low sample and reagent consumption, minimizing waste generation. However, despite these advantages, the voltammetric determination of ammonia remains relatively unexplored. Therefore, this study investigated the electrochemical behavior of NH₃ in alkaline solutions using a non-modified Pt electrode and evaluated the performance of differential pulse voltammetry (DPV) and square wave voltammetry (SWV) for NH₃ determination. DPV provided superior performance, with limits of detection and quantification of 0.79 μ mol L⁻¹ (0.011 ppm_N) and 2.6 μ mol L⁻¹ (0.036 ppm_N), respectively, which comply with the maximum allowable ammonia concentration in natural waters according to Brazilian and European regulations. The voltammetric method successfully quantified ammonia in tap and river water samples, providing results concordant with the established Berthelot spectrophotometric method, at a 95% confidence level. Additionally, it is simple and fully accessible to non-electrochemist since no sophisticated procedures for electrode modification are needed. Finally, the high analytical performance of the proposed method makes it valuable for pollution monitoring in aquatic environments.

Keywords: aquatic chemistry; nitrogen cycle; water quality.

INTRODUCTION

Nitrogen, the predominant element in Earth's atmosphere, plays a crucial role in natural ecosystems through the nitrogen cycle, which transports nitrogen to natural waters. Ammonia, a natural component within this cycle in aquatic ecosystems, is essential for various biological processes.¹However, elevated concentrations of ammonia in water bodies often indicate pollution, originating from sources such as agricultural runoff, industrial effluents, or urban sewage.¹ High ammonia concentrations have detrimental effects on aquatic organisms and ecosystems as ammonia is toxic to fish and other aquatic organisms.^{2,3} Also, ammonia can be converted into nitrate which can lead to excessive algae growth, a phenomenon known as eutrophication. Eutrophication can deplete oxygen levels, leading to fish kills and ecosystem degradation.^{1,4} Therefore, monitoring and controlling ammonia levels in natural waters is crucial for assessing water quality, identifying pollution sources, mitigating risks to aquatic life, and ensuring the success of ecosystem restoration efforts.

Ammonia (NH₃) and its conjugated acid ammonium ion (NH₄⁺) are distributed in natural waters according to the pH. Below 8.75, ammonium predominates, whereas above 9.75, ammonia is the prevalent form.^{1,5} The primary quantitative parameter for assessing NH₃ concentration in natural water is ammoniacal nitrogen, commonly expressed as parts *per* million of nitrogen (ppm_N). This term refers to the total amount of nitrogen present in water in the form of both dissolved ammonia and ammonium ion, and it is widely used for monitoring water quality. According to the Brazilian legislation,⁶ the maximum allowable amount of ammoniacal nitrogen in fresh water varies depending on pH, ranging from 3.7 ppm_N at pH \leq 7.5 to 1.0 ppm_N for pH > 8.5. Therefore, to ensure compliance with Brazilian water quality standards, the analytical method used to quantify

ammonia must be capable of reliably determining concentrations as low as 1.0 ppm_N (equivalent to 71 µmol L⁻¹ of NH₃). European legislation⁵ is even more restrictive stating a maximum ammoniacal nitrogen content in drinking water at 0.5 ppm_N (equivalent to 36 µmol L⁻¹ of NH₃).⁵

The literature offers several established colorimetric methods for ammonia determination, primarily relying on the Nessler⁵ or Berthelot reactions.7 Despite their widespread application, these methods have significant drawbacks, including the utilization of toxic reagents such as mercury in the Nessler reaction and phenol in the Berthelot reaction. Moreover, despite being highly selective to ammonia, the Berthelot reaction suffers from issues concerning reproducibility, lack of sensitivity, and the generation of high and unstable blank signals.8 Despite significant advancements in the Berthelot reaction, such as reagent immobilization in colloidal polymeric hydrogels9 or porous paper matrices,¹⁰ its use for ammonia determination in water samples remains challenging. The colorimetric determination of ammonia, based on the color change of acid-base indicators induced by the presence of basic NH₃ vapor represents a simpler approach,^{11,12} however, it lacks selectivity. Additional approaches for ammonia determination include the use of spectrophotometry¹³ and fluorimetry¹⁴ coupled to gas-diffusion extraction, and ion-chromatography.¹⁵

Electrochemical techniques are promising analytical tools due to their simplicity, cost-effectiveness, and ability to provide rapid, sensitive, and user-friendly determination of multiple analytes ranging from ions to biomolecules.^{16,17} Conductometry and potentiometry are the prevalent electrochemical techniques used for ammonia determination.¹ Conductometry is frequently used as the detection mode in capillary electrophoresis and ion chromatography, while potentiometric methods typically utilize ion-selective electrodes coupled with permselective membranes or gas diffusion extraction.¹ Despite the efficacy of conductometry and potentiometry for ammonia determination, these techniques are frequently coupled with sophisticated and expensive instruments or time-consuming extraction procedures. Additionally, potentiometry may exhibit modest sensitivity and relatively high limits of detection (LOD).¹

Pulsed voltammetric techniques, such as differential pulse voltammetry (DPV) and square wave voltammetry (SWV), are recognized as high-performance analytical techniques, which also offer fast analysis and low consumption of chemicals and samples. Despite these advantages, the voltammetric determination of ammonia remains relatively unexplored, mainly due to the sluggish electron transfer kinetics associated with its electrooxidation.¹ Consequently, voltammetric responses for NH₃ are observed only on electrodes containing noble metals as electrocatalysts for ammonia oxidation, with Pt being recognized as the most effective electrocatalyst.¹⁸ The literature describes a few voltammetric methods for ammonia, all utilizing Pt-based chemically modified electrodes, including Ag-Pt electrodes,19 Pt-polyaniline electrodes,20 and Pt-Cu electrodes.21 Although these electrodes have demonstrated effectiveness for ammonia determination, the electrode modification process may be time-consuming and often requires expensive reagents or sophisticated procedures. Additionally, the modification step could potentially compromise the reproducibility of the analytical method.

In this study, we evaluate the voltammetric determination of ammonia using unmodified Pt electrodes. Despite their high initial cost, Pt electrodes are widely available commercially, durable and ready-to-use, making them still affordable for ammonia determination, particularly for non-electrochemical researchers. Our results demonstrated that unmodified Pt electrodes exhibit analytical performance comparable to the modified electrodes described in literature. We achieved LOD and limit of quantification (LOQ) fully compatible with the allowable concentrations of ammonia in natural water samples according to Brazilian⁶ and European legislation.⁵ Additionally, we observed that the voltammetric method provided results statistically equivalent to those from the Berthelot-spectrophotometric method, attesting the accuracy of the voltammetric method.

EXPERIMENTAL

Reagents and solutions

The reagents used in this study were of analytical grade and they were used as received. Aqueous solutions were prepared using ultrapure water obtained from a MegaPurity[®] (Billerica, MA, USA) system. The KOH, used as the supporting electrolyte, and NH₄Cl, used for calibration, were both from VETEC (Rio de Janeiro, Brazil). A stock solution of 0.1 mol L⁻¹ NH₄Cl was prepared by dissolving the salt in ultrapure water. This solution was stored in a refrigerator and used daily to prepare 1.0×10^{-3} mol L⁻¹ NH₄Cl solutions by dilution in the supporting electrolyte (KOH). Small aliquots of the 1.0×10^{-3} mol L⁻¹ NH₄Cl solution in KOH were transferred to the electrochemical cell according to the desired concentration.

Instrumentation and apparatus

Electrochemical measurements were conducted using a PGSTAT101 potentiostat/galvanostat (Metrohm Autolab, Utrecht, Netherlands) controlled by NOVA 2.1.6 software. A three-electrode electrochemical cell filled with 10.0 mL of solution was used for all experiments. The reference electrode was a miniaturized lab-made Ag/AgCl/KCl_{saturated} electrode,²² and the auxiliary electrode was a spiral platinized-Pt wire ($\Phi = 0.5$ mm). The working electrode was constructed from a 99.95% purity Pt rod ($\Phi = 2.0$ mm) from Sigma-Aldrich (Saint Louis, USA) embedded in polytetrafluoroethylene (PTFE). Prior to use, the working electrode

was polished with alumina suspension (particle size of 0.5 μ m) on a polishing pad affixed to a smooth ceramic surface, followed by thorough rinsing with ultrapure water. Subsequently, the electrode was conditioned through ten potential cycling in the supporting electrolyte, within the potential range from -1.0 to +0.5 V at 100 mV s⁻¹. Spectrophotometric measurements were conducted using a PerkinElmer Lambda 25 double-beam UV/Vis spectrophotometer (Shelton, USA) with 1.0 cm path length quartz cuvettes.

Water sample analyses

Four water samples were analyzed. The first sample was tap water collected directly from the laboratory where this study was conducted (Ituiutaba-MG, 19°00'22.8"S, 49°27'25.5"W). The remaining three samples were collected from different points along the Paranafba River in Cachoeira Dourada-MG. These samples were selected to represent a variety of water conditions: one sample exhibited crystalline water characteristics (18°29'34.3"S, 49°30'46.7"W), another sample showed signs of eutrophication (18°31'00.7"S, 49°29'50.9"W), and the final sample was obtained from an area designated for fish farming (18°33'52.3"S, 49°29'24.7"W).

The samples were collected in plastic bottles, stored in a refrigerator, and filtrated using qualitative paper prior to analysis. The KOH used as the supporting electrolyte was directly dissolved in the sample to minimize sample dilution. This procedure was performed while the samples were still cold to avoid an abrupt increase in temperature, which could lead to the loss of ammonia through volatilization. Ammonia was not detected in the tap water sample, so it was spiked with 0.14 ppm_N of ammoniacal N, equivalent to 10 μ mol L⁻¹ of ammonia, and addition-recover experiments were performed. All samples were analyzed in triplicate.

Spectrophotometric comparative method

The Berthelot reaction, also known as the indophenol reaction, was utilized as the basis for a comparative spectrophotometric method. This reaction results in the formation of an indophenol dye, which absorbs light between 630 and 720 nm.⁷ While the mechanism of this reaction is complex and not fully understood, the reaction sequence presented in Figure 1S (Supplementary Material) is widely accepted.^{7,8}

The reagents necessary for the Berthelot reaction were sourced from a kit (Alcon[®], Camboriú, Brazil) designed for the semiquantitative determination of the ammonia in aquarium water. This kit comprises two solutions: Solution 1 containing phenol, sodium nitroprusside, isopropyl alcohol, and distilled water, and Solution 2 containing sodium hydroxide, sodium hypochlorite, and distilled water. The procedure involved transferring 4.0 mL of the sample or ammonia standard to a 5.00 mL volumetric flask. Subsequently, 400 μ L of Solution 1 and 400 μ L of Solution 2 were added. The volume was then completed with ultrapure water, and the mixture was homogenized. Absorption spectra were recorded from 400 to 800 nm after a reaction time of 10 min. The absorption at 680 nm was used as the analytical signal.

RESULTS AND DISCUSSION

Cyclic voltammetry of NH₃ in alkaline solutions

Ammonia electrooxidation on Pt electrodes requires alkaline media, with KOH solutions being the most commonly used.¹⁹⁻²¹ Therefore, for this study, we selected KOH as the supporting electrolyte. Figure 1a displays the cyclic voltammograms recorded

with a Pt electrode in a 0.5 mol L⁻¹ KOH solution, both in the presence and absence of NH₃. In the absence of NH₃ (black curve), the typical voltammetric behavior of Pt in alkaline solutions was observed. The processes of hydrogen adsorption/desorption gave rise to anodic and cathodic peaks between -1.0 and -0.5 V, while the multiple peaks ranging from -0.4 to 0.2 V are associated with the formation of PtO and its reduction during the reverse scan.^{21,23} The addition of 5.0 mmol L⁻¹ NH₃ (Figure 1a, red curve) produced an anodic peak at approximately -0.3 V (peak I_a) and a pair of peaks between -0.8and -0.7 V (peaks II_a and II_a).

According to the literature, the voltammetric peak I_a is attributed to the electrooxidation of ammonia, represented by the overall anodic semi-reaction shown in Equation 1.¹⁸

$$2NH_{3(aq)} + 6OH_{(aq)}^{-} \rightarrow N_{2(g)} + 6H_2O_{(1)} + 6e^{-}$$
(1)

The overall semi-reaction shown in Equation 1 is a complex process and two mechanisms have been suggested: the Oswin-Salomon mechanism²⁴ (Figure 2Sa, Supplementary Material), and the Gerischer-Mauerer mechanism²⁵ (Figure 2Sb, Supplementary Material). Both mechanisms suggest the formation of $NH_{x(ads)}$ intermediates, whose oxidation and reduction are responsible for the voltammetric peaks II_a and II_c .¹⁹ Essentially, the main difference between these mechanisms lies in N₂ formation. While the Oswin-Salomon mechanism considers that two adsorbed N atoms combine to form the N2 molecule, the Gerischer-Mauerer mechanism proposes that the N₂ molecule is formed from the combination of partially dehydrogenated intermediates (Figure 2S). A more subtle difference is that the Gerischer-Mauerer mechanism suggests that ammonia oxidation starts from adsorbed NH₃ while according to the Oswin-Salomon mechanism, NH3 diffuses to the electrode surface where it loses one proton, forming the adsorbed NH₂ intermediate.

Figure 1b displays the cyclic voltammograms recorded in the presence of NH_3 at increasing scan rates. Linear relationships were observed for both the i_n (peak current) *vs.* v^{1/2} (scan rate) and $\log i_n vs. \log v$

plots (Figure 3S, Supplementary Material), described by the equations: $i_p(\mu A) = 136 v^{1/2} (mV s^{-1})^{1/2}$, R² (coefficient of determination) = 0.99846, and log $i_p = 2.1 + 0.47 \log v$, R² = 0.99461, respectively. The *t*-test showed that the slope from the log $i_p vs$. log v plot was statistically equivalent to 0.5 at a 95% confidence level since its standard deviation (sd) was 0.03 (n = 3). These results demonstrated that, under our experimental conditions, the kinetics of ammonia oxidation is controlled by its diffusion to the electrode surface.²⁶ This is in accordance with the Oswin-Salomon mechanism which predicts that ammonia must diffuse to electrode surface before undergoing electrooxidation. Similarly, Wang *et al.*²¹ observed diffusion-controlled ammonia electrooxidation on PtCu alloy electrodes in a 1.0 mol L⁻¹ KOH solution.

The influence of KOH concentration, ranging from 0.1 to 1.0 mol L⁻¹, on the voltammetric behavior of NH₃ was investigated. Analytical curves were constructed for NH₃ between 0.1 to 1.0 mmol L⁻¹ for each KOH concentration, aiming to evaluate the effect of this parameter on the sensitivity for NH₃. As shown in Figure 1c, increasing the KOH concentration shifted the NH₃ peak towards less positive potentials. Slightly higher values for i_p and sensitivity achieved with 0.1 mol L⁻¹ KOH (Figure 1d). However, the sensitivity achieved with 0.1 mol L⁻¹ KOH was nearly equivalent to that observed with 1.0 mol L⁻¹ KOH. Consequently, the lower KOH concentration was selected for the analytical studies due to its economic and environmental advantages. Lower KOH concentration reduces reagent consumption and generates less alkaline waste, which is more favorable for disposal and treatment.

Comparing the analytical performance of DPV and SWV for $\rm NH_3$ determination

Before constructing analytical curves for NH₃, the operational parameters of DPV and SWV were univariably optimized. Optimization studies were conducted in a 0.1 mol L⁻¹ KOH solution containing 100 μ mol L⁻¹ NH₃. For DPV, pulse amplitude (Δ E), pulse width, and



Figure 1. (a) Cyclic voltammograms recorded with a Pt electrode ($\Phi = 2.0 \text{ mm}$) in 0.5 mol L^{-1} KOH solution in the absence (—) and presence of 5.0 mmol L^{-1} NH₃(—), $v = 100 \text{ mV s}^{-1}$; I_a and II_a are anodic peaks, and II_c is the cathodic peak; (b) cyclic voltammograms recorded as in (a) but at difference scan rates: (—) 25; (—) 50; (—) 75; (—) 100; (—) 150; (—) 200; (—) 250 and (—) 300 mV s^{-1}; (c) cyclic voltammograms recorded in the presence of 5.0 mmol L^{-1} NH₃ at different concentrations of KOH: (—) 0.1; (—) 0.25; (—) 0.5; and (—) 1.0 mol L^{-1} , $v = 100 \text{ mV s}^{-1}$; (d) sensitivity for NH₃ achieved with different KOH concentrations

v were optimized. For SWV, optimization focused on ΔE , frequency (f) and step potential (ΔE_s). Table 1S (Supplementary Material) summarizes the evaluated ranges for each parameter, along with their corresponding optimized values. Figure 4Sa (Supplementary Material) compares differential pulse voltammograms before and after parameter optimization. For DPV, optimization increased both the intensity of the voltammetric signal for NH₃ and the background current. In contrast, optimizing SWV parameters decreased the NH₃ signal, but significantly lowered background currents and improved separation between the NH₃ and PtO formation peaks (Figure 4Sb, Supplementary Material). The optimized conditions for both techniques demonstrated satisfactory repeatability. For DPV, the average in for 50 µmol L⁻¹ NH₃ was $19.8 \pm 0.1 \,\mu\text{A}$ (n = 5), with a relative standard deviation (RSD) of 0.5% (Figure 5S, Supplementary Material). For SWV, the optimized conditions exhibited slightly lower repeatability, with an average in of $17.8 \pm 0.9 \ \mu\text{A}$ (n = 5) and RSD of 5.0% (Figure 6S, Supplementary Material).

Figures 2a and 2c depict, respectively, the differential pulse and square wave voltammograms obtained under the optimized conditions at increasing NH₃ concentrations. These figures show expanded regions of the original voltammograms which were always recorded from -1.0 to +0.5 V. While these expanded views provide a better visualization of the NH₃ peak, it is important to note that they do not represent the entire voltammograms. This clarification is crucial since the scanned potential range significantly affected the intensity of NH₃ peaks, with initial potentials less negative than -1.0 V leading to lower in values. For square wave voltammograms, the scale for the expanded view reveals that the ΔE_s of 3 mV provides a relatively poor resolution, leading to squared peaks. This is not an issue when the entire voltammogram is shown, as demonstrated in Figure 4Sb. As relatively high background currents were obtained even after parameter optimization, the voltammograms were baseline-corrected. Baseline correction was performed using NOVA 2.1.6 software and the moving average mode with window size of 2.

The analytical curves for NH₃ obtained with DPV and SWV

are presented in Figures 2b and 2d, respectively. It was observed that using the area under the voltammetric peak as the analytical signal, rather than i_p , significantly improved linearity (higher R^2) and repeatability. Additionally, a voltammetric peak, attributed to PtO formation, was observed in the blank response. To address this interference on the voltammetric response for NH₃, the area of this peak was subtracted from the areas obtained in the presence of ammonia before constructing the analytical curves.

The analytical curve with DPV was linear from 2.5 to 20 μ mol L⁻¹ (0.035 to 0.28 ppm_N), according to the Equation 2:

Area
$$(\times 10^7) = 0.34 + 0.53C_{NH3} (\mu mol L^{-1}), R^2 = 0.99841$$
 (2)

LOD and LOQ were calculated from the Equations 3 and 4:

$$LOD = \frac{3 \times sd_{\rm B}}{S}$$
(3)

$$LOQ = \frac{10 \times sd_{\rm B}}{S}$$
(4)

where S is the slope of the analytical curve and sd_B is the standard deviation for the blank signal. The sd_B was estimated from the standard deviation of the intercept from the analytical curve.^{27,28} The LOD and LOQ achieved with DPV were 0.79 µmol L⁻¹ (0.011 ppm_N) and 2.6 µmol L⁻¹ (0.036 ppm_N), respectively. Using SWV, a linear range from 5.0 to 75 µmol L⁻¹ (0.070 to 1.05 ppm_N) was observed, with the Equation 5:

Area
$$(\times 10^7) = -0.34 + 0.24 C_{NH3} (\mu mol L^{-1}), R^2 = 0.98784$$
 (5)

LOD and LOQ were 2.2 μ mol L⁻¹ (0.031 ppm_N) and 7.3 μ mol L⁻¹ (0.103 ppm_N), respectively. Therefore, DPV exhibited significantly superior analytical performance compared to SWV, and it was selected to continue this study.



Figure 2. Baseline corrected differential pulse (a) and square wave (c) voltammograms recorded in 0.1 mol L^{-1} KOH at increasing NH₃ concentrations. Corresponding analytical curves for NH₃ using DPV (b) and SWV (d). Voltammetric conditions for DPV: $\Delta E = 50$ mV, pulse width = 10 ms, and v = 15 mV s⁻¹. Voltammetric conditions for SWV: $\Delta E = 50$ mV, f = 25 Hz, and $\Delta E_s = 3$ mV. Figures 2a and 2c present expanded views of voltammograms recorded from -1.0 to +0.5 V. The baselines were corrected using the moving average mode with window size of 2

The LOD and LOQ achieved with DPV are in full compliance with Brazilian⁶ and European legislation⁵ regarding the maximum allowed concentration of ammoniacal nitrogen in both drinking and tap water.^{5,6} Furthermore, the analytical performance achieved in this study was, on average, similar to that from other voltammetric and amperometric methods proposed for ammonia determination (Table 1). The main advantage of the proposed method is the use of non-modified Pt electrode, which is not the most cost-effective option, but offers the benefits of wide commercial availability, durability, and its ready-to-use nature. Moreover, the approach described herein does not require toxic or expensive chemicals in electrode preparation.

Finally, DPV provided intra- and inter-day RSD for the voltammetric signal of 10 µmol L⁻¹ NH₃ of 0.5 and 4.6% (n = 3), respectively, indicating satisfactory repeatability. Ammonia volatilization is a concern in alkaline solutions. However, within the concentration range used for calibration, this issue is minimized. This was confirmed by observing that 96.5% of the voltammetric signal for 20 µmol L⁻¹ NH₃ is retained, even when this solution is left undisturbed for 4-h at 24 ± 1 °C (Figure 7S, Supplementary Material).

Selectivity towards ammonia and sample analysis

To assess possible interfering effects from some ions commonly found in water samples, analytical curves for NH_3 were constructed in a solution containing 250 ppm sulfate, 250 ppm chloride, 10 ppm_N nitrate, and 1.0 ppm_N nitrite dissolved in ultrapure water, which was named "simulated natural water" sample. These ion concentrations were set at the maximum allowed levels in CONAMA resolution 357/2005.⁶ The matrix effects of a tap water sample and a river water sample exhibiting signs of eutrophication were evaluated by directly constructing analytical curves for NH_3 in these samples. NH_3 was initially detected in the river water sample and subsequently removed before constructing analytical curves. To eliminate NH_3 , 0.1 mol L⁻¹ KOH was added, followed by bubbling argon through the sample until NH_3 was no longer detectable. The analytical curves for NH_3 constructed in these solutions/samples, along with their respective slopes, are shown in Figure 3 while Figure 8S (Supplementary Material) shows the differential pulse voltammograms recorded in each sample.

Regardless of the water sample used to construct the analytical curve, R² values exceeding 0.99 were obtained (Figure 3a). This indicates a robust linear correlation between the voltammetric area and ammonia concentration, which is unaffected by the composition of the water sample. Additionally, the slopes of the analytical curves did not significantly differ from the slope obtained in ultrapure water at a 95% confidence level (Figure 3b). These results are a strong indication of good selectivity for ammonia since they demonstrate that matrix effects of these water samples are not significant. Consequently, external calibration using an analytical curve prepared in ultrapure water is feasible.

To evaluate the ability of the proposed method in quantifying ammonia in real samples, four water samples were analyzed (Table 2). The results obtained via voltammetric method were compared with those obtained using the spectrophotometric Berthelot method. Figure 9S (Supplementary Material) displays the visible absorption spectra recorded at increasing ammonia concentrations, along with the corresponding analytical curve used for calibration of the spectrophotometric method. The external calibration was used in both methods.

Table 1. Analytical performance of some amperometric and voltammetric methods for ammonia determination

Electrode	Technique	Linear range / (µmol L ⁻¹)	LOD / (μ mol L ⁻¹)	LOQ / (µmol L ⁻¹)	Reference
ITO/PtAg	CV	nonlinear correlation	3.946	13.14	19
Pt-PANI	DPV	0.5-550	0.0772	0.2571	20
PtCu alloy	DPV	0.5-40	0.0086	0.0286	21
Ag-CNT/eCE	DPV	NI	1.0	3.33	29
CuO-ZnO	LSV	77-770000	8.9	29.6	30
Pt-Ni(OH) ₂	CV	5-9424	0.42	1.40	31
Ir-Gr/nanospheres	amperometry	15-750	6.5	21.64	32
CuNP	amperometry	5-1000	1.25	4.16	33
Pt	DPV	2.5-20	0.79	2.64	this study

LOD: limit of detection; LOQ: limit of quantification; ITO: indium tin oxide; PANI: polyaniline; CNT: carbon nanotubes; eCE: epoxy composite; Gr: graphene; NP: nanoparticles; CV: cyclic voltammetry; DPV: differential pulse voltammetry; LSV: linear sweep voltammetry; NI: not informed.



Figure 3. (a) Analytical curves for ammonia obtained with DPV in ultrapure (\blacksquare), simulated (\bullet), tap (\blacktriangle), and river (\bigtriangledown) water; (b) corresponding slopes of the analytical curves. The dashed red lines represent the confidence interval for the average of the slope obtained in ultrapure water at a 95% confidence level and two degrees of freedom. The supporting electrolyte was 0.1 mol L⁻¹ KOH dissolved directly in each water sample. DPV voltammetric conditions: $\Delta E = 50 \text{ mV}$, pulse width = 10 ms, and v = 15 mV s⁻¹

Table 2. NH₃ determination in water samples using the proposed voltammetric method and the Berthelot spectrophotometric method

Sample	Voltammetric ^a / ppm _N	Berthelot ^a / ppm _N	F^{b}	t ^c
Tap water (pH = 7.45)	ND	ND	_	_
River water 1 $(pH = 7.36)^d$	$0.13_2 \pm 0.01_1$	0.144 ± 0.004	8	1.78
River water 2 $(pH = 7.38)^{e}$	$0.09_5 \pm 0.02_8$	$0.089_5 \pm 0.01_0$	8	0.35
River water 3 $(pH = 7.10)^{f}$	0.125 ± 0.004	0.131 ± 0.002	4	2.32

^aExpressed as mean value ± standard deviation (n = 3); ${}^{b}F_{2/2 critical} = 19.00; {}^{34} {}^{c}t_{critical} = 2.78$ (P = 0.05, 4 degrees of freedom); ${}^{34} {}^{d}signs of eutrophication; {}^{e}used for fish farming; {}^{f}crystalline water. ND: not detected.$

Table 2 indicates that for all analyzed samples, neither *F*- nor *t*-values exceeded their critical values. These results demonstrate that both the precision and NH₃ concentrations obtained with the voltammetric, and the spectrophotometric methods are statistically equivalent at a 95% confidence level. As ammonia was not detected in the tap water sample, it was spiked with 0.140 ppm_N and addition-recovery studies were conducted. The recovered ammonia concentration in this sample was $0.133 \pm 0.01_7$ ppm_N (n = 3), corresponding to a recovery percentage of 95 ± 12%. Therefore, the results from real samples analysis demonstrated the good accuracy and suitability of the voltammetric method with a Pt working electrode for ammonia determination in water samples. Furthermore, Table 2 reveals that all analyzed samples comply with the ammonia concentration limit of 3.7 ppm_N for natural water with pH ≤ 7.5, as established by CONAMA resolution 357/2005.⁶

CONCLUSIONS

This study demonstrated that the electrooxidation of NH₃ in alkaline media on Pt working electrodes provides an effective approach for its quantification in water samples. After optimizing the voltammetric parameters of DPV and SWV, we observed that DPV provided superior analytical performance, when using 0.1 mol L⁻¹ KOH as the supporting electrolyte. The LOD and LOQ achieved with DPV comply with the maximum allowable concentration of ammonia in natural water samples according to Brazilian and European legislations. Additionally, the analytical performance obtained using DPV was comparable to those reported for other voltammetric and amperometric methods reported in the literature. The proposed voltammetric method was successfully applied to quantify ammonia in tap and river water samples, and the results were compared with those from the established Berthelot spectrophotometric method. Both methods provided concordant results at a 95% confidence level, demonstrating the accuracy of the voltammetric method.

Therefore, this study shows that despite its high initial cost, utilizing a non-modified Pt electrode offers an affordable and environmentally sustainable approach for NH_3 determination in water samples. The use of a non-modified electrode eliminates the need for toxic or expensive chemicals and time-consuming procedures typically required for electrode modification. Furthermore, the widespread availability, durability, and ready-to-use nature of commercially available Pt electrodes enhance the accessibility of the proposed method, particularly for non-electrochemists unfamiliar with electrode modification procedures. Despite its simplicity, the proposed method offers excellent analytical performance making it a valuable tool for quality control and pollution monitoring in aquatic environments.

SUPPLEMENTARY MATERIAL

A schematic representation of the Berthelot reaction, the main proposed mechanisms for ammonia electrooxidation, data related to the optimization of voltammetric techniques, and calibration of the spectrophotometric method are available free of charge at http://quimicanova.sbq.org.br, as a PDF file.

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