Research Article

Determination of NH$_4^+$ in Environmental Water with Interfering Substances Using the Modified Nessler Method

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Nitrogen is an essential element in the environment. If excess nitrogen including NH$_4^+$ is present in water, however, it can result in algal blooming and eventually the destruction of the aquatic ecosystem. Therefore, the determination of NH$_4^+$ in streams, lakes, and effluents of the treatment facilities has long been carried out. The Nessler method is the most common spectrophotometric method to measure NH$_4^+$ in water. However, the result of the method becomes inaccurate if there are interfering substances such as Cl$_2$, Cl$^-$, hardness-causing compounds (e.g., Mg$^{2+}$), and Fe$^{2+}$ in target water samples. In this study, therefore, the traditional Nessler method has been modified to eliminate the effects of interfering substances; the so-called MS was added to water samples. In addition, the polyvinyl alcohol reagent as a dispersing agent was added to water samples to increase the sensitivity and reproducibility of the method. The modified method could successfully analyze NH$_4^+$ of water samples even with the interfering substance at high concentration.

1. Introduction

The nitrogen cycling in the environment is an important process because it is an essential element for the growth of all the lives; from a simple bacterium to a complex organism like a human [1, 2]. In general, nitrogen is present in natural water in the forms of organic nitrogen, ammonia, nitrate, and nitrite. In the case of raw wastewater, nitrogen is normally present in the organic nitrogen and NH$_4^+$ forms. Ammonia also can be naturally generated in the environment [3].

The presence of NH$_4^+$ at high concentrations in a stream or a lake can contribute to eutrophication, that is, massive algae blooming resulting in the depletion of dissolved oxygen in water and the subsequent devastation of aquatic life. Therefore, many countries regulate NH$_4^+$ concentration of surface water and wastewater. Some examples of the regulation on the NH$_4^+$ levels of different types of water are listed in Table 1 [4].

Since aqueous NH$_4^+$ is controlled by regulation, many authorities associated with water regularly collect water samples and analyze their NH$_4^+$ concentration. In general, the NH$_4^+$ concentration of a water sample can be determined by a titrimetric method [5], the method using an ammonia-selective electrode [6], or a colorimetric method [7–10].

In the titrimetric method, a color indicator is added to a water sample, which is subsequently titrated with 0.02 N H$_2$SO$_4$. At the end point of the titration, the color of the sample turns to a pale lavender color. The amount of sulfuric acid used for the color change is proportional to the amount of NH$_4^+$ in water [5].

The method using an NH$_3$-selective electrode is probably the easiest one; at pH 11, ammonia exists in the form of NH$_3$, which diffuses through a specially designed membrane at the tip of the electrode, resulting in the change of electrical potential which is measured to determine the NH$_4^+$ concentration [6].

There are two colorimetric methods available for the determination of NH$_4^+$ concentration. The first one is the Nessler method in which potassium, mercury, and iodine react with NH$_4^+$ to create a yellow-brownish colored compound; it is called the Nesslerization [8]. The second one is the phenate method in which phenol and HOCl react with NH$_4^+$ to create a blue-colored compound [9, 10]. In both methods,
the color intensity of the final compound is proportional to the \( \text{NH}_4^+ \) concentration of target samples.

In fact, the colorimetric methods are the most commonly used in practice [11]. Particularly, the Nessler method, since it was developed in 1856, has been the most widely applied for the analysis of \( \text{NH}_4^+ \) in water, especially at low concentrations (i.e., 0.4 mg L\(^{-1}\) to 1.0 mg L\(^{-1}\) \( \text{NH}_4^+ \)-N) [12].

When \( \text{NH}_4^+ \) in a water sample is analyzable, the Nesslerization is carried out. The product from the reaction between the Nessler reagent and aqueous \( \text{NH}_4^+ \) can absorb light over a wide wavelength range, that is, 400 nm–425 nm (= yellow brownish-colored light).

If the water sample is clean enough, the Nesslerization can be applied to it without any pretreatment. However, if a water sample contains other color or turbidity-causing substances (e.g., alkali ions such as Ca\(^{2+}\), Fe\(^{3+}\), Mg\(^{2+}\), and HS\(^-\)), the Nesslerization cannot be applied directly. The alkali ions and sulfide can form turbidity-causing substances or flocs when the water sample is treated with the Nessler reagent. In this case, the water sample should be pretreated with ZnSO\(_4\) ethylenediaminetetraacetic acid (EDTA), or Rochelle solution to remove the turbidity-causing substances. One of the disadvantages of using EDTA is that excess amount of the Nessler reagent should be provided to insure the reaction between the Nessler reagent and \( \text{NH}_4^+ \).

In this study, an MS (MS) was proposed to suppress the interference from the residual \( \text{Cl}_2\), \( \text{Cl}^-\), \( \text{Mg}^{2+}\) (as a hardness-causing compound), and Fe\(^{3+}\) in the determination of water \( \text{NH}_4^+ \) using the Nessler method. In fact, Boopathy [13] applied the stabilizer to remove hardness from the samples, when he analyzed \( \text{NH}_4^+ \) in the samples collected from an anaerobic soil slurry system. In addition, the polyvinyl alcohol (PVA) reagent was added to increase the light absorbance of a water sample and the sensitivity of the Nessler method [14, 15]. We believe that the addition of the MS and the PVA reagents will increase the usability of the Nessler method in water chemistry researches involving \( \text{NH}_4^+ \) measurement.

2. Materials and Methods

2.1. Preparation of MS and PVA Dispersing Agent. Unless stated otherwise, all the chemicals used in this study were purchased from Sigma-Aldrich (St. Louis, MO, USA). In addition, all the reagents used in experiments were prepared with ammonia-free water.

First, the MS was formulated to suppress the interference from various ions and hardness of water samples to the \( \text{NH}_4^+ \) determination via the Nessler method. It was synthesized by carefully dissolving 250 g of sodium citrate and 300 g of NaK\(_2\)C\(_6\)H\(_6\)O\(_6\) in 1 L deionized water.

Second, the PVA as a dispersing agent, which was used to help the yellow color to well develop in the reaction with the Nessler reagent and \( \text{NH}_4^+ \) in a water sample, was formulated by dissolving PVA of 1.35 g in 1 L deionized water.

Sodium citrate (purity = 99.8%) and PVA (purity = 75% hydrolyzed, approx. M.W.: 2000) was obtained from Acros Organics (Geel, Belgium), and NaK\(_2\)C\(_6\)H\(_6\)O\(_6\) (purity = 99.0%) were obtained from Samchun Pure Chemical Inc. (Pyeongtaek, Korea).

The Nessler reagent for color development was prepared following the Standard Method [16].

2.2. Preparation of Standard \( \text{NH}_4^+ \) and Interfering Chemical Solutions. In order to evaluate the feasibility of the developed interference suppressor and the color development aid in the Nessler method, they were applied to the quantitation of \( \text{NH}_4^+ \) in synthesized solutions with different interfering chemicals, that is, residual \( \text{Cl}_2\), \( \text{Cl}^-\), hardness (or \( \text{Mg}^{2+}\)), or Fe\(^{3+}\).

Standard solutions of \( \text{NH}_4^+ \) and the interfering chemicals were prepared by diluting premade stock solution for each of the chemicals with deionized water. A \( \text{NH}_4^+ \) stock solution for the experiment was made by dissolving 3.819 g anhydrous \( \text{NH}_4\)Cl which was previously dried at 103°C for 3 h in 1 L water. If 1 mL stock solution is added to 1 L deionized water, the \( \text{NH}_4^+ \) concentration of the final solution is 1 mg N L\(^{-1}\).

In the same or similar ways, the standard solutions for each of four interfering chemicals were prepared. First, standard chloride solutions were prepared by diluting appropriate amount of 50–75 mg \( \text{Cl}^-\) certified standard solution (2 mL PourRite Ampules; HACH, USA) in deionized water.

Standard \( \text{Cl}^-\) solution was prepared by appropriately diluting the premade 2000 mg L\(^{-1}\) \( \text{Cl}^-\) stock solution (1.75 g anhydrous NaCl in 50 mL water) with deionized water. Standard hardness (or \( \text{Mg}^{2+}\) ) solution was prepared by diluting premade 500 mg L\(^{-1}\) \( \text{Mg}^{2+}\) stock solution (0.123 g MgSO\(_4\) \( \cdot \)7H\(_2\)O in 100 mL water) with deionized water. Lastly, to prepare standard Fe\(^{3+}\) solutions, a 100 mg L\(^{-1}\) Fe\(^{3+}\) stock solution was made by dissolving 0.0702 g NH\(_4\)Fe(SO\(_4\))\(_2\)\( \cdot \)hexahydrate in 100 mL.

2.3. Experimental Procedure. Two sets of experiments were carried out. In the first set of the experiments, the effects of the developed MS and the PVA on the light absorbance of \( \text{NH}_4^+ \) standard solutions of 0.5, 1.0, and 1.5 mg N L\(^{-1}\) were evaluated. In the second set, the effects of the presence of \( \text{Cl}_2\), \( \text{Cl}^-\), \( \text{Mg}^{2+}\) (as a hardness-causing chemical), or Fe\(^{3+}\) on the determination of \( \text{NH}_4^+ \) using the Nessler method were evaluated.

Table 1: Examples of regulation on maximum allowable \( \text{NH}_4^+ \) concentrations for different waters.

<table>
<thead>
<tr>
<th>Type of sample</th>
<th>WHO</th>
<th>Korean legislation</th>
<th>EPA</th>
<th>European legislation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drinking water</td>
<td>—</td>
<td>0.5 mg L(^{-1})</td>
<td>—</td>
<td>0.5 mg L(^{-1})</td>
</tr>
<tr>
<td>Surface water</td>
<td>&lt;0.2 mg L(^{-1}) (up to 0.3 mg L(^{-1}) in anaerobic waters)</td>
<td>—</td>
<td>0.02 mg L(^{-1})</td>
<td>1.5 mg L(^{-1})</td>
</tr>
<tr>
<td>Wastewater</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>20 mg L(^{-1}) (expressed as N total)</td>
</tr>
</tbody>
</table>
The recovery efficiency of the proposed method was also evaluated with stream water and domestic sewage. On collection, the stream and sewage samples were filtered with 0.4 μm glass fiber filters. NH$_4^+$-N of 1 mg L$^{-1}$ was then spiked into water samples. For each water matrix, a total of seven replicates were prepared.

All the experiments were carried out as follows. First, a 25 mL water sample was filled into a 100 mL graduated cylinder. Then, three drops of the MS were added to the cylinder, which was subsequently put a cover on and shaken to mix its solution inside. After the solution was mixed, three drops of the PVA reagent were also added to the solution. Then, the solution was again covered and mixed.

Lastly, 1.0 mL of the Nessler reagent was added into the cylinder with mixture. Once the final solution was prepared, its portion was transferred into a spectrophotometer (CMAC QVIS 3000 Spectrophotometer, Daejeon, Korea) cell and the UV light absorbance was measured. The wavelength for the light used in the measurement was set at 425 nm.

Prior to the measurement of each water sample, a blank solution was prepared for reference. When only the MS was added to the blank solution with the Nessler reagent and without NH$_4^+$, the absorbance did not increase (Figure 1). However, when the PVA was alone added to the NH$_4^+$ blank solution, a slight increase in the absorbance could be observed, since the PVA is a color-dispersing agent. The same level of absorbance increase could be observed when both the PVA and the MS were added to the NH$_4^+$ blank solution. Therefore, when NH$_4^+$ in water samples is quantitated using the proposed method, zero point of the spectrometer should be adjusted accordingly.

3. Results and Discussion

3.1. Effects of PVA and/or MS on NH$_4^+$ Analysis Using Nessler Method. First, the effects of the MS or the PVA reagent on the determination of NH$_4^+$ in water by the Nessler method were evaluated as follows. For each test, samples with three different NH$_4^+$ concentrations, that is, 0.5, 1.0, and 1.5 mg N L$^{-1}$ were prepared. Before the NH$_4^+$ concentration of each sample was quantitated by the Nessler method, the sample was pretreated as follows. The first one was added with three drops of the MS. The second one was added with three drops of the PVA reagent. In the case of the third sample, both MS and PVA reagent were added. Lastly, the fourth one was not pretreated as a control. Therefore, a total of four test samples for each NH$_4^+$ concentration level were prepared.

Once the samples were prepared, the light absorbance of each sample was monitored over 20 min using the spectrophotometer. The result from the measurement of the four samples is provided in Figure 2. Apparently, it was evident that the addition of PVA increased the light absorbance of water samples with NH$_4^+$; the UV absorbance increase of 33–53% could be obtained for all the NH$_4^+$ concentration levels (Figure 2). The result indicates that the Nessler method with the PVA addition would be more sensitive than the one without; lower NH$_4^+$ concentration can be determined. In addition, the absorbance of the sample with the PVA added did not change over 20 min (c.v. = 0.38–3.90%); the absorbance of the sample with the PVA reached its maximum instantaneously. Therefore, it was confirmed that the PVA would help the color development of the samples analyzed with the Nessler method. In fact, only a slight change in the light absorbance of the sample without any treatment (i.e., control) also could be observed.

In the case of the MS, it did not have an effect on the result of the NH$_4^+$ measurement using the Nessler method; the sample with the MS only showed the same absorbance with the one without any pretreatment for all the NH$_4^+$ concentration levels. However, the water sample with both the MS and the PVA reagents added showed lower or higher light absorbance than the one with the PVA only (Figure 2). Probably an interaction between the MS and the PVA occurred and affected the sample absorbance.

Nonetheless, it was concluded that the addition of the MS would not have any effect on the analysis of NH$_4^+$ in water samples using the Nessler method. Particularly, it was concluded that the PVA addition would increase the sensitivity of the Nessler method for the NH$_4^+$ analysis.

3.2. Effects of PVA and/or MS on NH$_4^+$ Analysis Using Nessler Method for Water with Interfering Substances. As stated in Section 1, residual Cl$^-$, Cl$^-$, hardness, and iron salts in water are known common interfering substances in the NH$_4^+$ analysis using the Nessler method. In this section, therefore, the effects of the addition of the PVA and the MS on the result of the Nessler method application for the quantitation of NH$_4^+$ in water samples with residual Cl$^-$, Cl$^-$, Mg$^{2+}$ for hardness, or Fe$^{3+}$ as an interfering substance were evaluated.

3.2.1. Effect of PVA and MS Addition on NH$_4^+$ Analysis of Water with Residual Chlorine. Water samples with the residual Cl$^-$ of 0.0, 0.1, or 0.5 mg L$^{-1}$ were analyzed with the modified Nessler method in which the MS and the PVA reagents had been added into the samples before the
Nessler reagent was added. The result was compared with the one from the measurement with the original Nessler method (Figure 3). The effect of residual chlorine on both the modified and the original Nessler methods was evaluated with the samples of three different NH$_4^+$ concentrations, that is, 0.5, 1.0, and 1.5 mg N L$^{-1}$.

Again, the modified Nessler method showed higher UV absorbance than the original one for all the NH$_4^+$ concentration levels. However, the light absorbance was slightly affected by the presence of residual chlorine when NH$_4^+$ concentration was 1.5 mg N L$^{-1}$; absorbance difference of 12% was observed. In fact, the original method also showed similar difference in the UV absorbance for the water sample with NH$_4^+$ concentration of 1.5 mg N L$^{-1}$, when the samples contained residual Cl$_2$. Unlike the modified Nessler method, the original method's UV absorbance was also unstable when NH$_4^+$ concentration was low, that is, 0.5 mg N L$^{-1}$.

However, it should be stated that in practice it would take a while until a water sample would be analyzed after its collection. If residual Cl$_2$ is present in water samples, it can react with NH$_4^+$ in water to form chloramines [17], resulting in the underestimation of NH$_4^+$ concentration. Therefore, it would be a good practice to remove residual Cl$_2$ by adding NaHSO$_3$ right after sample collection, if the presence of chlorine in water is suspected.

3.2.2. Effect of PVA and MS Addition on NH$_4^+$ Analysis of Water with Cl$^-$

For water samples with 1.5 mg NH$_4^+$-N and 10000 mg L$^{-1}$ Cl$^-$, the UV absorbance values measured by both the modified and the original Nessler methods were higher than the one for water samples with the same NH$_4^+$ concentration but with lower Cl$^-$ (Figure 4); 12% higher UV absorbance was observed for the sample with 10000 mg L$^{-1}$ Cl$^-$, compared to the one with those lower Cl$^-$ concentrations.

However, the modified Nessler method showed almost the same absorbance for the samples with lower NH$_4^+$ concentrations regardless of Cl$^-$ concentration levels. On the other hand, the original method still shows significantly different absorbance for the water samples even of lower NH$_4^+$ concentrations, if Cl$^-$ concentration was high (Figure 4).

In fact, 1000–3000 mg L$^{-1}$ Cl$^-$ is not uncommon to water samples collected from industrial wastewater plants. Therefore, the modified Nessler method can be beneficial in the analysis of NH$_4^+$ in industrial wastewater.

3.2.3. Effect of PVA and MS Addition on NH$_4^+$ Analysis of Water with Hardness.

Water samples with Mg$^{2+}$ (as a hardness-causing substance) of 0.0, 500, 750, or 10000 mg L$^{-1}$ as CaCO$_3$ were analyzed with the modified Nessler method in which the MS and PVA reagents had been added into the samples before the Nessler reagent was added. The result was compared with the one from the measurement with
the original Nessler method (Figure 5). The effect of Mg$^{2+}$ on both the modified Nessler method and the original Nessler one was evaluated with samples of three different NH$_4^+$ concentrations, that is, 0.5, 1.0, and 1.5 mg L$^{-1}$.

In the case of the original Nessler method, an accurate analysis of NH$_4^+$ content could not be possible when Mg$^{2+}$ was present in water samples. Even at the lowest concentration (i.e., 500 mg L$^{-1}$), Mg$^{2+}$ increased the absorbance more than double, resulting in large overestimation for all the NH$_4^+$ concentrations levels. In fact, the absorbance of water samples was very proportional to the Mg$^{2+}$ concentration; higher absorbance could be observed at higher Mg$^{2+}$ concentration. Interestingly, the exaggerated UV absorbance rapidly dropped below that of the control (Figure 5). Probably, the Mg$^{2+}$ precipitates formed from the Nessler reaction settled down over time and turned the turbid water samples to clearer ones [18].

On the other hand, the water samples analyzed with the modified Nessler method showed relatively smaller difference in the UV absorbance if the Mg$^{2+}$ concentration of the water samples was less than 750 mg L$^{-1}$ as CaCO$_3$ (Figure 5). Nonetheless, in the presence of a hardness-causing chemical
like Mg\(^{2+}\), the accurate measurement might be to some degree difficult. Therefore, it is necessary to remove it from a sample before \(NH_4^+\) analysis is carried out, if higher hardness is suspected for the sample.

3.2.4. Effect of PVA and MS Addition on \(NH_4^+\) Analysis of Water with \(Fe^{2+}\). Water samples with \(Fe^{2+}\) of 0.0, 0.5, 1.0, or 2.0 mg L\(^{-1}\) were analyzed with the modified Nessler method in which the MS and PVA reagents had been added into the samples before the Nessler reagent was added. The result was compared with the one from the measurement by the original Nessler method (Figure 6). The effect of \(Fe^{2+}\) on both the modified Nessler method and the original Nessler one was evaluated with samples of three different \(NH_4^+\) concentrations, that is, 0.5, 1.0, and 1.5 mg N L\(^{-1}\).

In the case of the original Nessler method, an accurate analysis of \(NH_4^+\) content could not be possible when \(Fe^{2+}\) content of water samples was more than 1.0 mg L\(^{-1}\). In fact, \(Fe^{2+}\) in water is known to form a complex with salts in the Nessler reagent, and increases turbidity and the absorbance.

The modified Nessler method also could not accurately quantitate \(NH_4^+\) in water samples with \(Fe^{2+}\). For any \(NH_4^+\) concentration, the water sample even with 0.5 mg L\(^{-1}\) \(Fe^{2+}\) showed significantly higher UV absorbance than that of the
without Fe$^{2+}$ (Figure 6). Therefore, it was concluded that both the original and the modified Nessler methods for NH$_4^+$ quantitation cannot be applied to water samples with Fe$^{2+}$. Like the case of Mg$^{2+}$ as an interfering substance, it is necessary to remove Fe$^{2+}$ from a sample before NH$_4^+$ analysis is carried out, if the sample is suspected to have Fe$^{2+}$.

### 3.3. Recovery Efficiency of the Proposed NH$_4^+$ Analysis Method

Recovery efficiency of the modified Nessler method was performed with sewage and fresh water samples which were collected from a local sewage treatment plant and a nearby river. Upon delivery to the laboratory, the water samples were filtered and analyzed for their NH$_4^+$ contents. The sewage contained NH$_4^+$-N of 12.4 mg L$^{-1}$, while the surface water did contain 0.8 mg L$^{-1}$ NH$_4^+$-N. In fact, the sewage sample was ten times diluted before being used for the recovery test. Then, the sewage and stream water samples of 100 mL each were spiked with NH$_4^+$ stock solution to increase their NH$_4^+$ concentration as much as 1 mg L$^{-1}$. Then, the samples analyzed for NH$_4^+$ concentration using the modified method.
The traditional Nessler method for the analysis of water $\text{NH}_4^+$ was modified by introducing the additional reagents, that is, the MS and the PAV. With the help of the PVA, the light absorbance of the water samples under analysis could be increased significantly; so the sensitivity of the Nessler method increased. In addition, the maximum absorbance could be rapidly achieved and did not change over time. Therefore, the sensitivity and stability of the original Nessler method could be improved decently.

Due to the addition of the MS, the modified method could accurately analyze $\text{NH}_4^+$ in water samples with residual $\text{Cl}_2^-$, $\text{Cl}^-$, or $\text{Mg}^{2+}$, each of which is a well-known substance causing interference to the accurate determination of the $\text{NH}_4^+$ concentration. However, both the traditional and modified Nessler methods could not accurately determine $\text{NH}_4^+$ of a water sample with $\text{Fe}^{3+}$. Nonetheless, we believe that the proposed method will be beneficial to researchers who regularly analyze $\text{NH}_4^+$ in water samples.
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