

Experimental exploration for measurement of ammonia nitrogen in water by Nessler's reagent colorimetry

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Abstract

The basic principle of determining ammonia nitrogen by nessler's reagent colorimetry was expatiated, and the preparation method of nessler's reagent, blank control, curve drawing method, water sample treatment technology (preservation time, dilution method, absorption liquid type, outflow liquid volume), accuracy control, precision control and other influences on the determination results were discussed. The solutions are proposed according to the practical analysis and practice. It provides reference for analysis workers to carry out ammonia nitrogen detection in water.

Keywords Nessler's reagent colorimetry; Ammonia nitrogen; Experimental principle; Countermeasures for common problems

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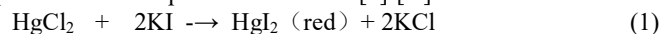
1. Introduction

Ammonia nitrogen is an important indicator in the monitoring of water and wastewater. The existing environmental Standards has established ammonia nitrogen as a project for the control of the quality of the water environment, such as: The Environmental Quality Standards for Surface Water(GB 3838-2002), Groundwater Quality Standards(GB 14848-93), Sanitation Standards for Drinking Water(GB 5749-2006) and Integrated Sewage Emission Standards(GB8978 -1996)^[1-2]. At the same time, ammonia nitrogen is also one of the binding targets for the reduction of four major pollutants (chemical oxygen demand, sulfur dioxide, ammonia nitrogen, and nitrogen oxides) during the "Twelfth Five-Year Plan" period. The determination methods of ammonia nitrogen in water include nahnese reagent spectrophotometry (HJ 535-2009), salicylic acid spectrophotometry(HJ 536-2009), distillation-neutralization titration(HJ 537-2009), mobile injection-salicylic acid spectrophotometry(HJ) 666-2013), gas phase molecular absorption spectrometry(HJ/T 195-2005) and so on. By comparison, nathan reagent spectrophotometry has the advantages of simplicity, rapidity and high sensitivity. It can be applied to the determination of ammonia nitrogen in surface water, groundwater, and domestic sewage, and is widely used in environmental monitoring and scientific research in China^[3-6].

2. Experimental principles

2.1 The principle of preparation of nessler's reagent

The preparation of nessler's reagent directly affects the sensitivity of the method. The nessler's reagent was invented by Nessler in 1856^[7]. There are two methods of formulation. The reaction process of HgCl₂ and KI is commonly used to prepare the reaction process as follows [1]-[4] :

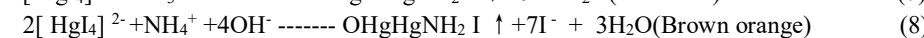
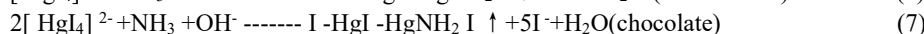
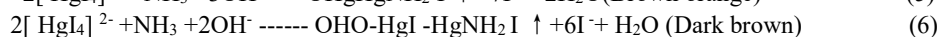
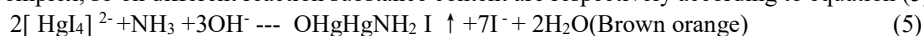


The chromophore group is [HgI₄]²⁻, and its formation is closely related to the concentration of I⁻. At the beginning, Hg²⁺ and I⁻ react (1) to form red precipitated HgI₂, and react (2) rapidly and excessively to form [HgI₄]²⁻ pale yellow chromogenic radical groups. When the red precipitation is no longer dissolved, it indicates that I⁻ is no longer excessive, and the addition of HgCl₂ should be stopped immediately, and the maximum number of chromogenic groups can be obtained. If HgCl₂ continues to be added, equation (3) and equation (4) of the reaction will be significantly carried out, which will promote the continuous decomposition of the chromogenic group and produce a large amount of HgI₂ red precipitation, thus resulting in the decrease of the sensitivity of nessler's reagent.

2.2 Principle of ammonia nitrogen reaction

Ammonia nitrogen, in the form of free ammonia or ammonium ions, reacts with nessler's reagent to form a reddish brown complex, the complex of the absorbance is proportional to the ammonia nitrogen content, measuring absorbance wavelengths of 420 nm, due to the reaction with ammonia nitrogen nessler's reagent is

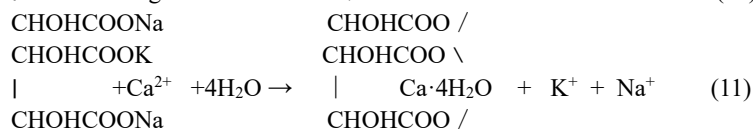
more complex, so on different reaction substance content are respectively according to equation (5) ~ (9) .



In general, nessler's reagent is mainly used for the determination of trace ammonia nitrogen. The reaction equations (5) and (8) and (9) indicate that NH_3 and NH_4^+ can be converted into each other in aqueous solution, which is mainly affected by the pH of the solution.

2.3 Potassium sodium tartrate masking principle

Common metal ions in the water are Ca^{2+} , Mg^{2+} , Fe^{2+} , Mn^{2+} , etc. If the content is high, it is easy to react with OH^- or I^- in the nessler's reagent to form precipitation or turbidity, which affects colorimetry. Therefore, sodium potassium tartrate should be added to cover these metal ions before adding natschner's reagent. The masking principle is as follows [9]-[10]:



3. Influencing factors and countermeasures of ammonia nitrogen experiment

3.1 Commercial reagent purity

The agent of the nessler's reagent method is the main one of the reagent is $\text{KNaC}_4\text{H}_6\text{O}_6 \cdot 4\text{H}_2\text{O}$, KI , HgCl_2 , KOH . It was found that some commercial analysis of pure reagent could not be required, so that the experiment could have a great influence, and according to our experiences, the agents which affect the experiment were mainly $\text{KNaC}_4\text{H}_6\text{O}_6 \cdot 4\text{H}_2\text{O}$ and HgCl_2 . It was found that potassium tartrate sodium tartrate could lead to a high level of blank space and a turbidity of actual wat. Not pure reagent is difficult to identify from the appearance, it is only through preliminary experiment test to determine whether conform to the requirements. HgCl_2 is a colorless crystal or white particle powder, and the modified HgCl_2 reagent is often mixed with red powder. According to experience, reagent contains a small amount of red powder reagent can also be used, but still want to avoid said take red powder preparation reaction reagent.

3.2 Sample pretreatment

3.2.1 Pretreatment by flocculation and precipitation

It is suggested that samples must be filtered or centrifuged after flocculation and precipitation. Since the filter paper contains a certain amount of soluble ammonium salt, and the content of quantitative filter paper is higher than that of qualitative filter paper, it is recommended to use qualitative filter paper to avoid flocculation when sampling. Before filtration, a small amount of ammonia free water should be used for repeated leaching (generally 100 mL). It is also possible to soak the filter paper with ammonia-free water for 30min in the preparation stage, and then leach it with ammonia-free water for a small amount of times when it is in use. In this way, the measurement error introduced by the filter paper can be reduced or avoided. In order to prevent the turbidity of the pretreated solution and the possible escape loss of ammonia nitrogen in the neutral solution, the water sample after flocculation precipitation filtration should be analyzed as soon as possible. It can be use for treating special wat samples, such as (after flocculation sedimentation, that cloud is obviously cloudy or not cloudy due to flocculation and turbid after coagulation of masking agent and developer), the flocculation precipitation method cannot remove all interference, and the pre-distillation method can be used to treat the water sample before the water sample.

3.2.2 Pretreatment by predistillation

In the distillation process, some organic compounds are likely to be distilled at the same time as ammonia, which may interfere with the determination. Some of these substances (such as formaldehyde) can be removed by boiling under acidic conditions ($\text{pH} < 1$). Because of the concentration of ammonia nitrogen from the distillery in the liquid phase, it occurs primarily in the pre-distillation period, especially in the high water sample

of ammonia nitrogen, the ammonia gas is flowing out of the liquid phase in the early stages of the water sample, and in order to absorb the efficiency, it can't be heated too fast, and it can be heated up slowly, or it can cause the ammonia to absorb not exactly. It was found in that clean of the distiller that the distil flask was added with 350 mL of water, the glass beads were added in several pieces, the instrument was placed, and the distillate was distilled to at least 100 mL of water, and the distillate and the residual liquid in the bottle were discarded.

3.3 Preparation of reaction reagents

3.3.1 Nessler's reagent preparation

There are two preparation methods for nessler's reagent. The first method uses KI, HgCl_2 and KOH for preparation, and the second method uses KI, HgI_2 and KOH for preparation. Both methods can produce chromogenic base groups $[\text{HgI}_4]^{2-}$, which is usually prepared by the first method. The key to this method is to grasp the amount of HgCl_2 added, which determines the amount of chromophore content, and thus affects the sensitivity of the method.

3.3.2 Preparation of nessler's reagent

In order to guarantee good color rendering ability, nessler's reagent preparation is important to the control of HgCl_2 addition amount, to trace HgI_2 red precipitate dissolve no longer. The ratio of HgCl_2 to KI required for the preparation of 100 mL of nessler's reagent is about 2.3:5. In order to speed up the reaction speed and save the preparation time, low-temperature heating can be used to prevent the red precipitation of HgCl_2 in advance.

The process of the configuration of the two nines is a big influence on the blank absorbance, and the process of the process is that the mercury salt solution needs to be stirred, so it can be dissolved in as much as possible, and then it's dissoluble, and it's sealed in the case of static, and it prevents the ammonia in the air from rising up in the air; Sodium hydroxide (potassium) solution must be dissolved at room temperature and then mixed with mercury salt solution; It is necessary to slowly mix that solution of mercury salt with the alkali solution and stir to ensure that the resultant precipitate dissolve in time.

The exposure time in air should be reduced as much as possible during the use of nessler's reagent, and the reagent should be sealed during storage to prevent the dissolution of ammonia in the air from increasing the blank.

The nessler's reagent can be stored for longer time, but the shelf life of the nessler's reagent may be prolonged, and the absorbance may be increased or the slope of the blank test may be smaller. If the test or slope of the test blank does not meet the requirement, reconfigure it.

3.3.3 Preparation of potassium sodium tartrate solution

It is simple in preparation method of potassium tartrate, but for non-conforming reagent, because that amount of ammonium salt is great, it can only be heated and boil and cannot be completely removed, the following two methods can be adopted: (1) adding 5 ml of the sodium tartrate solution into potassium sodium tartrate sodium solution after precipitating, precipitating, and removing the supernatant. (2) add a small amount of alkali to potassium and sodium tartrate solution, boil and evaporate 20% ~ 30% of the solution volume, and dilute to the original volume with ammonia-free water after cooling. We believe that the second method is superior to the first method. Even potassium and sodium tartrate with high ammonium salt content can meet the experimental requirements after treatment with blank value. At the same time, the solution should be sealed to prevent contamination and lead to blank rise.

3.4 High blank experimental value

The blank test value can reflect the comprehensive influence of various factors on material analysis in the process of experiment. The high blank value will affect the precision and accuracy of the experiment, so each experiment has certain requirements on the blank value. The blank value of ammonia nitrogen experiment generally requires absorbance A less than or equal to 0.030. However, sometimes the blank value is much higher than this, and the main influencing factors include high blank reagent, high ammonia content in experimental water and certain ammonium salt in filter paper.

3.4.1 Influence of reagents on experimental blank values

The results show that the absorbance of the blank test of narrating reagent prepared by the second method in 3.3.1 is generally more than twice as high as that of the blank test of narrating reagent prepared by the first

method, and is greater than 0.030. Although the first method is more difficult to prepare nanoscale reagent, it becomes the preferred method because of the low blank value. The commercial analysis pure tartrate potassium sodium, sometimes ammonium salt content is high, direct heating boiling preparation, often resulting in high blank test value. Therefore, to reduce the blank value, potassium and sodium tartrate solution can be prepared according to the method in 3.3.3, and the effect is very good.

3.4.2 Influence of experimental water use on blank values

The water for ammonia nitrogen experiment is required to be ammonia-free. If ammonia dissolves in water in the air or ammonium salt enters the water for experiment through other channels, and the content reaches the detection limit of the method, the experimental blank value will be high, so the ammonia-free water should be sealed and stored after each use. Some experimental studies have used fresh distilled water instead of ammonia-free water to measure ammonia nitrogen, and the blank value and standard curve of the experiment are not significantly different from the method of ammonia-free water, and have a high precision and accuracy. It can be seen that as long as that experimental water is free from ammonia or very low ammonia content, whether or not distilled water is distilled, can be used.

3.4.3 Influence of filter paper on blank value

In the experiment of ammonia nitrogen, the water sample should be filtered and determined. Therefore, blank control experiment of filtration should be conducted to deduct the influence of filter paper. Since the filter paper generally contains ammonium salt, the filter blank value can be increased. Experiments have shown that the ammonium content of different filter paper or the same filter paper with different sheets varies greatly, and some filter paper with higher content cannot meet the experimental requirements despite repeated washing with water. Therefore, each batch of filter paper should be sampled before use. We choose to filter water samples with thin HCl soaked and cleaned 0.45 microns ethyl acetate fiber filter membrane to solve the problem of high blank caused by filter paper filtration. Not only is the blank value of filtration low, but also the repeatability is good, so it is recommended to use membrane filtration.

3.5 Standard curve drawing

According to the actual sample concentration range, the standard range can be adjusted appropriately, including at least 6 points of 0 mg/L, the slope range of the standard curve is 0.0060-0.0078, and the slant distance is less than or equal to 0.005.

3.6 Material disturbance in water

The actual water sample contains not only the components to be tested, but also other components. Especially for the waste water sample, the substances contained are more complex, so there are interfering substances in the water sample to varying degrees, which affect the colorimetric determination of ammonia nitrogen. For general surface water, interfering substances are mainly Ca^{2+} , Mg^{2+} and other metal ions, which can be eliminated by filtering and masking agent potassium and sodium tartrate. However, we have found that turbidity occurred when potassium and sodium tartrate was added to the filtered water sample, but the turbidity did not occur in the standard curve group, so that the water sample could not be determined colorimetric. This is related to the unqualified potassium and sodium tartrate reagent, non-aqueous sample interference problem. When the sodium hydrochloride reagent contains more Ca^{2+} , Mg^{2+} impurities, it's a reaction to Ca^{2+} , Mg^{2+} , in the actual water sample, to produce a lot of calcium tartrate or magnesium, which makes the filtration water cloudy and cloudy; Because of trace amounts of Ca^{2+} and Mg^{2+} in distilled water, turbidity did not occur. In this case, the sodium tartrate agent shall be replaced and retested.

3.7 Determination of samples

In the acidic conditions, the water sample is treated with a certain amount of sodium hydroxide, and the analysis of the water sample to neutral. It is found that that pH of the absorb boric acid solution can be adjusted to be neutral to weakly alkaline by mean of dilute NaOH, such as 7-9 (alkaline is not too large, or the ammonia nitrogen to be measured can be converted to ammonia gas) and then added with the masking agent and the nonix reagent, if the red precipitate appear, the acid alkaline of the water sample is not adjusted well.

3.8 quality assurance and quality control

3.8.1 Blank laboratory

The absorbance of the laboratory blank should not exceed 0.060.

3.8.2 Precision control

For each batch of samples (less than or equal to 20 samples), at least 10% of the parallel double-samples should be determined. For samples with less than 10 samples, one parallel double-sample should be determined. For samples with less than or equal to 1.0mg/L, the relative deviation of the result of the parallel double-sample determination should be less than or equal to 20%. When the sample content is >1.0mg/L, the relative deviation of the parallel double-sample measurement results should be less than 15%.

3.8.3 Accuracy control

For each batch of samples (no more than 20 samples), at least one certified standard sample or matrix labeled recovery sample shall be determined, and the determination value of certified standard sample shall be within the allowed range. When the sample content is less than or equal to 1.0mg/L, the standard recovery is 70-130%. When the sample content was >1.0mg/L, the standard recovery was 80-120%.

3.9 Sample dilution

When the concentration of ammonia nitrogen in the water sample is greater than 2.0mg/L, the water sample shall be diluted for determination, which is called "pre-dilution". This dilution method is relatively accurate, but it is difficult to predict before determination, which is not conducive to timely analysis of large quantities of samples. Another dilution method is to directly dilute the coloration of the samples after the dilution colorimetry, known as "post-dilution". There is a study that shows that, in the case of an unpredictable amount of concentration of ammonia nitrogen waste in a linear range of concentration, the results of two dilution methods, the relative error meets the environmental monitoring requirements. The results also show that the negative error is the most in the post-diluting process when ammonia free water is used as the diluting solvent, but some negative error can be offset by the preparation of a certain amount of blank solution as the diluting solvent.

4. Summary

It can be seen from the experiment and discussion that six common problems should be paid attention to and solved in the determination of ammonia nitrogen by narrating reagent spectrophotometry : (1) Main reagent properties should be paid attention to and qualified reagents should be selected. (2) The correct preparation of the reagent determines the sensitivity of the method. Special attention should be paid to the understanding of the principle of the preparation of nessler's reagent and the correct grasp of the key points of the preparation of nessler's reagent. (3) Reducing the blank test value can improve the precision of the experiment, and the test water, reagent blank and filter paper should be checked carefully. (4) The test meets the requirements of accuracy and precision. (5) Dissolved inorganic or organic matter and insoluble suspended matter in water have interference with the spectrophotometric determination of ammonia nitrogen by nessler's reagent. Different methods should be selected according to different situations to eliminate the interference. In particular, potassium and sodium tartrate masking failure should be paid attention to. (6) For the dilution determination of water samples exceeding the detection upper limit, because the relative errors of the two methods meet the analysis requirements, the post-dilution measurement can be adopted for mass determination.

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