Study on key technologies of ammonia nitrogen on-line monitor based on distillation-conductivity method

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Abstract. The ammonia nitrogen on-line monitor based on distillation-neutralization titration (HJ 537-2009) is mainly suitable for the determination of ammonia nitrogen in domestic sewage and industrial wastewater. It has the advantages of wide measuring range, non-toxicity of reagents and waste liquor, etc. Focused on the water sample pretreatment system, conductance detection system and its key technologies to solve the problems including difficulty in precise sampling of water, difficulty in automatic addition of solid pH regulator, the low efficiency of distillation, the short stabilization time of mixing indicator, difficult to determine titration endpoints automatically and accurately (indicator discolouring point), long titration analysis time and so on. Meanwhile, a new ammonia nitrogen on-line monitor base on distillation-conductivity method was designed to measure some metering performance indexes, method detection limit (MDL) and limit of quantitation (LOQ). The results showed that the maximum absolute error of 0.02 mg/L on low concentration sample analysis (≤2 mg/L), the relative error reached -3.7 % on high concentration sample analysis (>2 mg/L). The method detection limit and limit of quantitation were 0.08 mg/L and 0.15 mg/L, respectively, which could satisfy the metering performance requirements in verification regulation of ammonia nitrogen automatic monitor.

1. Introduction

Ammonia nitrogen (NH₃-N) is an evaluation index of organic pollution in water and become an essential items for water quality monitoring [1]. With the rapid development of industries such as chemical, petroleum, metallurgy, paper, food and pharmaceutical industries and the continuous improvement of people's living standards, the total amount of industrial wastewater and urban domestic sewage and ammonia nitrogen content had risen sharply. More and more sources of ammonia nitrogen pollution and the increasing concentration of ammonia nitrogen emission led to environmental deterioration. Therefore, in the process of sewage treatment and discharge, on-line monitor, early warning and control of ammonia nitrogen had become the focus of compliance emissions, which also puts higher requirements on the online detection technology of ammonia nitrogen in sewage treatment.

Based on the different detection principles or analysis methods, there are different determining methods of ammonia nitrogen in water, such as the spectrophotometry, the electrode method, the distillation-neutralization titration method, the blow-off-conductometry, the ion chromatography method, the gas-phase molecular absorption spectrometry, the enzymic method, the fluorescence
method and so on [2]. At present, the ammonia nitrogen on-line monitors widely used in the market are developed by spectrophotometry [3,4], electrode method [5] and distillation – titration [6].

The ammonia nitrogen on-line monitor based on distillation-neutralization titration is mainly suitable for the determination of ammonia nitrogen in domestic sewage and industrial wastewater. It has the advantages of wide measuring range, non-toxicity of reagents and waste liquor, etc. Meanwhile, the measurement result will not be easily affected and interfered by the color, turbidity and suspended substance of the water after the water sample was pretreated by distillation. However, it has a large number of technology problems in the application including difficulty in precise sampling of water, difficulty in automatic addition of solid pH regulator (magnesium oxide), the low efficiency of distillation, the short stabilization time of mixing indicator, difficult to determine titration endpoints automatically and accurately (indicator discoloring point), long titration analysis time and so on. Therefore, this study will focus on the research and improvement of water sample pretreatment system according to the current situation of ammonia nitrogen on-line monitor based on distillation pretreatment at home and abroad. By researching the conductivity detection system, the conductivity method would be used instead of the neutralization titration method to solve the problems of difficult automatic determination of titration end point and long titration analysis time. The accuracy, stability, reliability and adaptability of the ammonia nitrogen on-line monitor would be improved to make it suitable for online monitoring of different concentrations of domestic sewage, industrial wastewater, tap water, rivers and lakes, etc.

2. Water sample pretreatment system

According to the basic principles and operation steps of the distillation-neutralization titration method stipulated in the national environmental protection standard (HJ 537-2009), all operation steps before analysis of water sample titration can be generally called as the water sample pretreatment system, mainly including collection, pretreatment, and the distillation of water sample. The main problems and technical difficulties consist of the difficulty to accurately collect the water sample, automatically add solid pH regulator (magnesium oxide), and the low distillation efficiency.

2.1. Sampling

![Figure 1. Schematic diagram of the overflow tank.](image)

The sampling mainly aims to measure and transport the 250 ml of water samples to be determined. The online monitor of ammonia nitrogen of water quality generally adopted miniature ODM peristaltic pump to measure. However, sampling error did not satisfy the demand for accurate sampling because
of many influencing factors, including measurement frequency, hose properties, ambient temperature, number of rollers, and card compression force. The peristaltic pump was unsuitable for the on-line monitor given its high price and large volume, although it had high accuracy (±0.5%). The current study adopted an internal overflow sampling device designed for a constant volume overflow tank with two-port side overflow sampling [7]. Figure 1 shows the structure of the overflow tank. The water sample to be tested was inputted into the constant volume overflow tank from the liquid inlet pipe through the conventional peristaltic pump. The excess liquid flowed out of the side overflow pipe, and the water sample to be measured flowing out from the side outflow pipe after measurement. After sampling, the waste liquid was discharged from the outlet at the bottom. The material selected was polymethyl methacrylate given its characteristics of anti-vibration, anti-corrosion, antifouling, production of economy and convenience.

2.2. pH regulator
Ammonia nitrogen (NH$_3$-N) refers to the nitrogen in the form of free ammonia (NH$_3$) and ammonia ion (NH$_4^+$) in water. From equations (1) and (2), it can continuously escape from the water sample under high temperature and alkaline conditions.

$$\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3\text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$$  \hspace{1cm} (1)

$$\text{NH}_3\cdot\text{H}_2\text{O} \xrightarrow{\Delta} \text{H}_2\text{O} + \text{NH}_3 \uparrow$$  \hspace{1cm} (2)

With the gradual escape of ammonia gas, the pH value of water sample declines continuously, which slows down the escape of ammonia gas and eventually leads to incomplete ammonia nitrogen escape, and, ultimately affects the measurement results. Therefore, the light magnesia are added as pH regulator in manual operation, thus keeping the water sample always weakly alkaline in the distillation process, to ensure the escape of ammonia nitrogen completely. The equation (3) shows how light magnesium oxide reaches a solution equilibrium in water.

$$\text{MgO} + \text{H}_2\text{O} \rightleftharpoons \text{Mg(OH)}_2 \rightleftharpoons \text{Mg}^{2+} + 2\text{OH}^-$$  \hspace{1cm} (3)

However, light magnesium oxide as the solid powder is difficult to achieve addition automatically and solid MgO is easy to be adhered to the inner wall of the distillation device. As a consequence, the cleaning in the distillation process become more laborious. Besides, MgO absorb moisture and became extremely unstable in CO$_2$ and other acid gases. Which restrict the application of solid MgO in the application of on-line monitor of ammonia nitrogen.

To circumvent these problems, the research used a mixed buffer solution (Na$_2$HPO$_4$-NaOH) to replace solid MgO due to its difficulty to volatilize and decompose. The phosphate present a multistage dissociation equilibrium in water, and it can adjust the value of pH in the water sample. Meanwhile, the mixed buffer solution have the advantages of economy and easy to be cleaned and added automatically.

2.3. Distillation
Distillation is the most critical link in the water sample pretreatment system, which needed to reach evaporation and condensation of the water sample before measurement. Moreover, this stage also ensures that the ammonia nitrogen in the boiling water sample (about 100°C) entirely escape and completely absorbed by the boric acid absorption solution. Based on the challenges of high energy consumption, low heat utilization rate, and low evaporation condensation efficiency (time consumption), the current study designed an electric device to heat a small-volume and perform a rapid distillation. The main advantages are a simple structure, convenient operation, adjustable heating power, and controllable distillation rate [8]. The distillation device is shown in figure 2, which mainly includes an evaporation tank, condensing tank, a cooling pipe, and a controller.
In order to improve the heat transfer efficiency of the distillation unit and realize variable speed distillation, the electric heating device with adjustable power installed at the bottom of the tank was adopted for the heating of the evaporation tank. Meanwhile, a series of secondary condensation system was constructed with a jacket-type cylindrical condensing tank and straight cooling pipe to ensure that the evaporated water and ammonia nitrogen could be rapidly condensed and absorbed. Moreover, to minimize the retention of condensate, the top of the condensate tank was designed with butterfly shape, the bottom of the tank was designed as conical, and the condensate outlet pipe was designed as an arc. Additionally, to effectively prevent the influence of boiling liquid in the evaporator on the detection results of condensate and titration, the connecting pipe between the evaporator and the condensing tank was lengthened.

3. Conductivity detection system
According to the problems existed in titration detection system of neutralization titration method, this section studied the application of conductivity analysis method instead of neutralization titration to achieve rapid detection and analysis of ammonia nitrogen content in the absorption liquid.

3.1. Principle of conductivity detection
The conductivity is a numerical representation of the ability of a solution to conduct current, and the conductivity of aqueous solution depends on the properties and concentration of ions, the temperature and viscosity of the solution, etc. Generally, the principle of determining solute concentration in solution by conductivity meter is that there is only one component concentration which causes the change of conductivity under the premise that the composition is known, so as to reflect the concentration of the component in solution [9].

The principle of conductivity detection of ammonia nitrogen concentration in this study is as follows. Under alkaline conditions, the water sample containing ammonia nitrogen is heated to boiling in a certain time. The ammonia nitrogen is distilled with steam, then condensed and absorbed by conductive absorption liquid. The change of conductivity of absorption liquid is proportional to the amount of ammonia nitrogen absorbed in a certain range [10]. According to this principle, several blank solutions and standard concentration ammonia-nitrogen solutions (standard samples) were
treated by distillation pretreatment in the same way as titration method, then the distillate was absorbed by absorbent solution with certain conductivity, and the conductivity of absorbent solution absorbed by blank experiment and standard experiment was measured separately, thus, the final conductivity (change of conductivity) corresponding to each standard sample can be expressed by formula (4):

$$E_{cf} = E_{cs} - E_{cb}$$  \( \text{(4)} \)

$E_{cf}$, $E_{cs}$, and $E_{cb}$ are the final conductivity of the standard sample, the conductivity measured in the standard sample experiment and the conductivity measured in the blank experiment respectively. Thus, the relationship between the change of conductivity and the concentration of ammonia-nitrogen could be found out by using the standard ammonia-nitrogen concentration $\rho_N$ corresponding to $E_{cf}$, then the curve between the concentration of ammonia-nitrogen and the change of conductivity was fitted. Finally, the ammonia-nitrogen concentration of the water sample to be measured could be calculated by this curve equation.

3.2. Design of conductivity detection device

Conductivity detection device is mainly composed of constant volume overflow tank, absorption detection tank and conductivity transmitter.

The constant volume overflow tank in conductivity analysis is mainly used for precise sampling of absorbent solution, and the design is similar to the constant volume overflow tank used for sampling the water sample to be tested, but the volume was appropriately reduced. In the absorption detection tank, the ammonia nitrogen in the distillate is absorbed by the absorbent solution, and the conductivity is detected by electrode inserted into the absorption detection tank. In addition, the inlet of distillate and the inlet of the absorbent solution connected with the outlet of the constant volume overflow tank were designed according to the size of the corresponding device.

In which, the conductivity transmitter adopts EC series water quality transmitter with accuracy of 1.5% (FS), range of 0~20/200/2000 μS/cm optional, and automatic temperature compensation. The electrode is a plastic platinum black electrode of 1.0 cm~1.

3.3. Selection of absorbent

Considering the economy, practicability and absorption performance of ammonia nitrogen, two commonly used solutions, sulfuric acid and boric acid, were selected as alternative absorbents.

In order to further explore the suitability of sulfuric acid and boric acid as absorbents for conductivity analysis, the following experiments were designed: seven groups of parallel blank experiments were performed with sulfuric acid (0.3 g/L) and boric acid (20 g/L) as absorbents respectively. Firstly, 125 ml non-ammonia water and 2 ml buffer solution were added into the small liquid distillation unit, then the 100 ml distillates evaporated by heating were absorbed by 50 ml absorption solution. Finally, the conductivity of the absorbed solution was measured by electrode. Results are shown in table 1.

Table 1. Blank experiment data table of sulfuric acid and boric acid.

| Absorbent solution | Initial conductivity (μS/cm) | Average value of blank conductivity (μS/cm) | Maximum difference between groups (μS/cm) | Standard deviation between groups (μS/cm) |
|--------------------|----------------------------|---------------------------------|-----------------------------------------|---------------------------------------|
| sulfuric acid      | 1982.144                   | 837.506                        | 120.00                                  | 42.564                                |
| boric acid         | 28.750                     | 14.607                         | 3.50                                    | 1.099                                 |

Table 1 shows that the initial conductivity, average blank conductivity, maximum difference between groups and standard deviation of sulfuric acid absorption solution are much larger than those of boric acid absorption solution. As we know, sulfuric acid is a strong electrolyte, which is completely ionized into hydrogen ion and sulfate ion in water, and the ion concentration is much
higher than the partially ionized weak electrolyte boric acid. If sulfuric acid was chosen as the absorbent, the final blank conductivity would have large fluctuations and errors when the amount of sulfuric acid or diluted non-ammonia water was inaccurately measured, the sampling accuracy of the prepared sulfuric acid absorbent was low, and the amount of distillate was controlled inaccurately during the preparation of low-concentration sulfuric acid absorbent. However, the partial ionization of boric acid make it have a certain buffer capability. The inaccurate measurement of boric acid sampling or the inaccurate control of distillate volume will not lead to a large fluctuation of blank conductivity during the preparation process. Certainly, low initial conductivity of boric acid and no obvious change in conductivity will also affect the sensitivity of conductivity analysis method. When measuring low concentration of ammonia nitrogen, the error would be larger relatively, and the limit of quantitation would also be higher accordingly. By comprehensive consideration, boric acid was chosen as the absorbent in this study.

3.4. Optimization of absorbent
In order to solve the problem that small change of conductivity leads to detect trace ammonia nitrogen inaccurately, two schemes were designed and compared in this study. In the scheme 1, the 100 ml distillation from 125 ml water sample was absorbed by 50 ml boric acid. In the scheme 2, the 75 ml distillation from 100 ml water sample was absorbed by 25 ml boric acid. Then three groups of blank experiments and standard samples (2 mg/L) experiments were carried out respectively, in which, the average value of the three groups was used as the final conductivity, and the difference of conductivity between the standard sample experiment and the blank experiment was obtained. Results are shown in table 2.

| Table 2. Table of experimental results with different ratios. |
|---------------------------------------------------------------|
| Blank conductivity (μS/cm) | Standard samples conductivity (μS/cm) | Difference of conductivity (μS/cm) |
| Scheme 1 | 14.607 | 20.714 | 6.107 |
| Scheme 2 | 12.625 | 26.875 | 14.250 |

Table 2 shows that the difference of conductivity under different schemes is quite large, it means that the sensitivity of conductivity analysis method for ammonia nitrogen detection can be improved by changing the amount of distillate and absorbent liquid.

Now, assumed that \( V_S \), \( V_D \) and \( V_A \) (ml) are the volume of standard water sample, distillate and absorbent liquid respectively, and the initial concentration of boric acid solution is \( C_B \) (mol/L), its ionization constant is \( K \) at experimental temperature. For blank experiment, after absorbing the distillate of blank water sample, the diluted concentration of boric acid solution was \( C'_B = C_B V_A / (V_D + V_A) \), and its positive ion was only \( H^+ \) in the absorption tank. According to the ionization balance of boric acid, both of the concentration of hydrogen ions and borate ions are approximately \( (K C'_B)^{1/2} \). For the standard sample experiment, assumed that the concentration of ammonia nitrogen in the standard sample is \( \rho_N \) (mg/L). After distillation and absorption, the concentration of ammonia in the absorption solution is \( C_N = \rho_N V_S / 14000(V_D + V_A) \). Since ammonia and boric acid reacted in the same molar to produce the same amount of ammonium ion and borate ion, the concentration of ammonium ion in the absorption detection tank is \( C_N \), the concentration of boric acid is \( C'_B - C_N \approx C'_B \), and the concentration of borate ion is \( (K C'_B)^{1/2} + C_N \). Meanwhile, according to the ionization equilibrium of boric acid, the concentration of \( H^+ \) change to \( K [(C'_B - C_N) / (K C'_B)^{1/2} + C_N] \).

Therefore, the difference of the final ion concentration between the standard sample experiment and the blank experiment could be expressed by formula (5):
\[
\Delta C = C_N + K(C_B - C_N)/[\sqrt{(K C_B')^2} + C_N] + (K C_B') \sqrt{C_N} - 2 (K C_B') \sqrt{C_N}
\]
\[
= 2C_N + K(C_B - C_N)/[\sqrt{(K C_B')^2} + C_N] - (K C_B') \sqrt{C_N}
\]
\[
\approx 2C_N + KC_B/C_N - (K C_B') \sqrt{C_N}
\]
\[
\approx 2C_N = 2 \rho_a \times V_d/14000(V_d + V_a)
\]

In order to further improve the distillation efficiency (reduce sampling and evaporation) and shorten the pretreatment time of water sample, \( V_s \) was selected as 150 ml, which was also limited by the size of quick distillation device. At the same time, in order to ensure that ammonia nitrogen in water sample can be fully distilled out, 80% of the distillate was also distilled off by distillation according to distillation titration method, so the \( V_d \) is 120 ml. Formula (5) shows that the difference of conductivity is inversely proportional to the amount of absorbent liquid, and the smaller \( V_a \), the higher \( \Delta C \), the higher the sensitivity of ammonia nitrogen detection. However, the minimum amount of absorbent liquid used in this study is also limited by the size of the absorbent detection tank. It is necessary to ensure that the absorbent liquid have a certain level height and sufficient absorption capacity in the absorbent detection tank. Ultimately, the dosage of absorbent liquid was determined as 15 ml, concentration of 5 g/L, and the conductivity detection electrode with the measurement range of 0-200 μS/cm was selected.

4. Performance verification

4.1. General performance indexes

According to the requirement of measurement performance of national ammonia nitrogen automatic monitor (JJG 631-2013) [11], standard ammonia nitrogen concentration of 0 (blank), 0.5, 1.0, 2.0, 5.0, 10.0 and 16.0 mg/L were prepared respectively, and seven groups of parallel experiments were carried out for each concentration.

Table 3. Table of blank test results under conductivity analysis.

|       | Initial signal value (mA) | Initial conductivity value (μS/cm) | Signal value after distillation (mA) | Conductivity value of blank experiment (μS/cm) |
|-------|---------------------------|-----------------------------------|-----------------------------------|---------------------------------------------|
| 1     | 4.643                     | 8.038                             | 4.270                             | 3.375                                       |
| 2     | 4.619                     | 7.738                             | 4.276                             | 3.450                                       |
| 3     | 4.619                     | 7.738                             | 4.305                             | 3.813                                       |
| 4     | 4.540                     | 6.750                             | 4.286                             | 3.575                                       |
| 5     | 4.635                     | 7.938                             | 4.319                             | 3.988                                       |
| 6     | 4.616                     | 7.700                             | 4.287                             | 3.588                                       |
| 7     | 4.620                     | 7.750                             | 4.248                             | 3.100                                       |
| Average | 4.613                     | 7.664                             | 4.284                             | 3.555                                       |

Table 4. Table of standard test results under conductivity analysis.

| Standard ammonia nitrogen concentration (mg/L) | Signal value at end of distillation (mA) | Conductivity values measured (μS/cm) | Final conductivity values of standard samples (μS/cm) |
|-----------------------------------------------|-------------------------------------------|-------------------------------------|------------------------------------------------------|
| 0.5                                          | 4.522                                     | 6.525                               | 2.970                                                |
| 1.0                                          | 4.819                                     | 10.243                              | 6.688                                                |
| 2.0                                          | 5.441                                     | 18.014                              | 14.459                                               |
| 5.0                                          | 6.657                                     | 33.211                              | 29.655                                               |
| 10.0                                         | 8.949                                     | 61.859                              | 58.304                                               |
| 16.0                                         | 11.763                                    | 97.036                              | 93.480                                               |

In which, the average value of seven groups of experiments was used as the conductivity value of...
each concentration, and the final conductivity values of standard samples are the difference between the conductivity values measured and conductivity value of blank experiment. Experimental results are shown in tables 3 and 4. Table 3 is the experimental results of seven groups of blank solutions and table 4 is the final experimental results of standard solutions of different concentrations of ammonia nitrogen.

Thus, the standard curve of ammonia nitrogen concentration-conductivity relationship was fitted by the corresponding relationship between the standard ammonia nitrogen concentration and the final conductivity of the standard sample. Since the verification regulation of ammonia nitrogen automatic monitor has different requirements for the indication error of different concentrations of ammonia nitrogen, this study used the ammonia nitrogen concentration of 2 mg/L as the boundary and linearly fitted by the least squares method. The results are shown in figure 3.

![Figure 3. Diagram of relationship between ammonia nitrogen concentration and conductivity.](image)

According to the fitting results, the relationship between ammonia nitrogen concentration ($\rho_N$) and the conductivity ($E_c$) in the low concentration range (< 2 mg/L) is expressed by formula (6).

$$E_c = 7.6753\rho_N - 0.9155(R_f = 0.9999)$$

(6)

The relationship between ammonia nitrogen concentration ($\rho_N$) and the conductivity ($E_c$) in the high concentration range (> 2 mg/L) is expressed by formula (7).

$$E_c = 5.6741\rho_N + 2.1632(R_f = 0.9997)$$

(7)

From the correlation coefficients ($R_f$) of formula (6) and formula (7), it indicates that there is a good linear relationship between ammonia nitrogen concentration and conductivity in the whole measurement range.

In order to verify the conventional performance indicators, seven groups of parallel experiments were respectively carried out with the standard solution of 0.5, 1.0, 2.0, 5.0, 10.0 and 16.0 mg/L ammonia nitrogen concentration. After obtaining the final conductivity of the standard sample, the formula (6) and the formula (7) were used to calculate the measured ammonia nitrogen concentration. Finally, the indication error, repeatability and stability were calculated according to the requirements of metrological verification regulation. The results are shown in table 5.

Table 5 shows that the maximum indication error of conductivity analysis method is 0.018 mg/L as detecting low concentration (<2 mg/L) ammonia nitrogen, which is much lower than the value stipulated (±0.2 mg/L) by the national metrological verification regulations for class A of automatic
Within the range of high concentration (>2 mg/L), the indication error is only -3.70%, which is much less than (±10%) stipulated in the verification regulations. Repeatability (2.878%) and stability (5.229%) also respectively meet the requirements of the verification regulations that repeatability does not less than 3% and stability within 4 hours does not exceed ±10%.

### Table 5. Table of standard test results under conductivity analysis.

| Standard concentration (mg/L) | Final conductivity (μS/cm) | Measured concentration (mg/L) | Absolute error (mg/L) | Relative error (%) | Repeatability (%) | Stability (%) |
|-------------------------------|---------------------------|-------------------------------|----------------------|-------------------|------------------|---------------|
| 0.5                           | 3.057                     | 0.518                         | 0.018                | 3.60              |                  |               |
| 1.0                           | 6.707                     | 0.993                         | -0.007               | -0.70             |                  |               |
| 2.0                           | 14.545                    | 2.014                         | 0.014                | 0.70              | 2.878            | 5.229         |
| 5.0                           | 29.482                    | 4.815                         | -0.185               | -3.70             |                  |               |
| 10.0                          | 58.570                    | 9.941                         | 0.059                | 0.59              |                  |               |
| 16.0                          | 93.495                    | 16.096                        | 0.096                | 0.60              |                  |               |

4.2. Method detection limit

The methods widely used in calculating the detection limit in China consist of the approach recommended in IUPAC and the Guidelines for Water Monitoring Operations of Global Environmental Monitoring System. The method recommended in IUPAC allows preparing a standard solution with a concentration close to the blank value of C. The average signal (X) and the standard deviation (S) of the measured signal were obtained by the blank value of C that was measured more than 20 times. So the method detection limit follows the formula (8).

$$\text{MDL} = \frac{3S \times C}{X}$$  \hspace{1cm} (8)

Where, the standard solution concentration (C) near the blank in the formula is 1~3 times of the expected detection limit. When the volume of water sample is 150 ml, the detection limit of conductivity analysis is about 0.1 mg/L [11]. Therefore, NH₄Cl standard solution of 0.1 mg/L ammonia nitrogen was used as near standard blank solution. The experimental results are shown in table 6.

### Table 6. Table of method detection limit test results for conductivity analysis.

| Final conductivity (μS/cm) | Measured standard concentration (mg/L) | Final conductivity (μS/cm) | Measured standard concentration (mg/L) |
|---------------------------|---------------------------------------|---------------------------|---------------------------------------|
| 1                         | 0.377                                 | 11                        | -0.311                                | 0.079                                |
| 2                         | 0.189                                 | 12                        | -0.286                                | 0.082                                |
| 3                         | 0.389                                 | 13                        | -0.123                                | 0.103                                |
| 4                         | 0.377                                 | 14                        | 0.040                                 | 0.124                                |
| 5                         | 0.365                                 | 15                        | 0.240                                 | 0.150                                |
| 6                         | 0.540                                 | 16                        | -0.035                                | 0.115                                |
| 7                         | 0.352                                 | 17                        | 0.265                                 | 0.154                                |
| 8                         | -0.086                                | 18                        | -0.273                                | 0.084                                |
| 9                         | 0.114                                 | 19                        | 0.352                                 | 0.165                                |
| 10                        | -0.273                                | 20                        | 0.265                                 | 0.154                                |

The average (X) and the standard deviation (S) are respectively 0.135 mg/L and 0.0353581 mg/L by the data calculated in table 6. By substituting X and S into formula (8), method detection limit MDL results in 0.07857 mg/L by distillation-conductivity method could be obtained. The final method detection limit after revision is MDL=0.08 mg/L [12].
4.3. Limit of quantitation

According to the IUPAC recommended method, non-ammonia water was used as a blank solution to conduct measurement experiments of not less than 20 sets of ammonia nitrogen concentration by conductivity analysis method. Ten times of the standard deviation was used as the limit of quantitation for the distillation-conductivity method in this study. Experimental results are shown in table 7, and the limit of quantitation of distillation-conductivity method is 0.15 mg/L.

| Final conductivity (µS/cm) | Blank value (mg/L) | Final conductivity (µS/cm) | Blank value (mg/L) |
|--------------------------|-------------------|--------------------------|-------------------|
| 1                        | 2.038             | 11                       | 2.125             |
|                          | 0.385             |                          | 0.396             |
| 2                        | 2.212             | 12                       | 1.912             |
|                          | 0.408             |                          | 0.368             |
| 3                        | 2.200             | 13                       | 2.063             |
|                          | 0.406             |                          | 0.388             |
| 4                        | 2.188             | 14                       | 2.038             |
|                          | 0.404             |                          | 0.385             |
| 5                        | 2.063             | 15                       | 2.063             |
|                          | 0.388             |                          | 0.388             |
| 6                        | 2.188             | 16                       | 2.088             |
|                          | 0.404             |                          | 0.391             |
| 7                        | 1.988             | 17                       | 2.075             |
|                          | 0.378             |                          | 0.390             |
| 8                        | 1.925             | 18                       | 2.263             |
|                          | 0.370             |                          | 0.414             |
| 9                        | 1.900             | 19                       | 2.225             |
|                          | 0.367             |                          | 0.409             |
| 10                       | 2.188             | 20                       | 2.225             |
|                          | 0.404             |                          | 0.409             |

5. Conclusions

In order to improve the total performance of the on-line monitor of ammonia nitrogen and make it suitable for on-line monitor of surface water with different concentrations, such as domestic sewage, industrial wastewater, tap water, rivers and lakes, this study focused on the research and development of water sample pretreatment system, conductivity detection system and its key technologies. Through the comprehensive application of key technologies, not only the detection and analysis time was shortened, but also the technical performance indicators of the system were improved. As detecting low concentration (≤2 mg/L) ammonia nitrogen, the maximum indication error was 0.018 mg/L, which was much lower than the value (±0.2 mg/L) stipulated by the national metrological verification regulations for class A of automatic monitor. Within the range of high concentration (>2 mg/L), the indication error was -3.7%, which also less than the value (±10%) stipulated in the verification regulation; the repeatability (2.88%) and stability (5.23%) also meet the requirements (repeatability no more than 3% and stability does not exceed ±10% within 4 hours). The method detection limit and limit of quantitation were 0.08 mg/L and 0.15 mg/L, respectively, which could satisfy the metering performance requirements in verification regulation of ammonia nitrogen automatic monitor.

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