Investigations on online monitoring of ammonia nitrogen based on distillation-potentiometric titration

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Abstract. Water sample pretreatment system and titration detection system were intensely studied based on National environmental protection standards HJ 537-2009 ‘Water quality-Determination of ammonia nitrogen-Distillation-neutralization titration’. These studies pointed out several problems and difficulties, such as an accurate sampling of water, automatically regulate pH, the low efficiency of distillation, short stabilization time of mixing indicator, and the challenge in determining titration endpoints. Some technical solutions exist, and a new on-line monitor of ammonia nitrogen base on distillation-potentiometric titration was designed to measure metering performance indexes, method detection limit (MDL), and limit of quantitation (LOQ). The results showed a maximum absolute error of 0.0398 mg/L on low concentration sample analysis (≤2 mg/L), the relative error reached 1.4% on high concentration sample analysis (>2 mg/L). The method detection limit and limit of quantitation were 0.025 mg/L and 0.17 mg/L, respectively, which could satisfy both A class and B class instruments of 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]. Nowadays, the environment pollution of water in China is worrisome, domestic water is especially threatened by ammonia nitrogen pollution, and a large number of rivers and lakes presents severe pollution and heavy eutrophication [2]. With the intensification of water pollution and the increasing environmental protection awareness, there is an increasing concern in monitoring water quality including remote online monitoring and forewarning control.

Based on the different detection principles and analysis methods, there are many methods to determine ammonia nitrogen in the water, such as spectrophotometry, ion chromatography, gas-phase molecular absorption spectrometry, enzymic method, distillation-titration method, blow-off-conductometry, fluorescence method, the electrode method, etc [3]. The online monitoring of ammonia nitrogen widely used in the market are developed by spectrophotometry [4,5], electrode method, and distillation-titration [6].

Distillation-neutralization titration was mainly applied for the determination of ammonia nitrogen in domestic and industrial wastewater. The advantage of this method is that the reagent used and the waste liquid produced are non-toxic and harmless, and the measuring range is wide. Meanwhile, the
measurement results were not easily affected and interfered by the color, turbidity, and suspended substance after the pretreatment of distilled water samples. However, the online monitor of ammonia nitrogen developed using the distillation-titration method showed a large number of technology problems in the application including difficulties in precise sampling of water and 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), among others. Therefore, the current research aimed to improve the total performance of the online monitor of ammonia nitrogen by increasing its accuracy, stability, reliability, and adaptability of measuring. Water sample pretreatment system, titration detection system and its key technologies could be used for online monitoring of surface water with different concentrations, such as domestic sewage, industrial water, tap water, rivers and lakes.

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 monitoring of ammonia nitrogen of water quality generally adopted miniature ODM peristaltic pump to realize. 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 online monitoring 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 organic glass given its characteristics of anti-vibration, anti-corrosion, antifouling, production of economy and convenience.

2.2. pH regulator

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

\[ NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \]  
\[ NH_3 \cdot H_2O \xrightarrow{\Delta} H_2O + NH_3 \uparrow \]

With the gradual escape of ammonia gas, the pH value of water sample declined continuously, which slowed down the escape of ammonia gas and eventually led to incomplete ammonia nitrogen escape, and, ultimately affected the measurement results. Therefore, we added light magnesia 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 reached a solution equilibrium in water.

\[ MgO + H_2O \rightleftharpoons Mg(OH)_2 \rightleftharpoons Mg^{2+} + 2OH^- \]

However, light magnesium oxide as the solid powder was difficult to achieve addition automatically and solid MgO was easy to adhere to the inner wall of the distillation device. As a consequence, the cleaning in the distillation process become more laborious. Besides, MgO absorbed moisture and became extremely unstable in CO$_2$ and other acid gases. Thus, the application of solid MgO in the online monitoring of ammonia nitrogen is limited.

To circumvent these problems, our 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 was the most critical link in the water sample pretreatment system, which not only needed to reach evaporation and condensation of the water sample before measurement. Moreover, this stage also ensures that the ammonia nitrogen in the water sample entirely escaped and was 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. The distillation device was 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. Titration detection system

According to the workflow of the online monitoring of ammonia nitrogen, the ammonia nitrogen
can be titrated and detected after treating the water sample via a distillation pretreatment
system. By the new national standard, the principle of neutralization titration method provides a
favorable condition for mixed indicator to judge the end of distillation with pH change that caused the
color change. Then, it is possible to calculate the volume of ammonia nitrogen at the end of titration
sample, which was consumed by the hydrochloric acid standard solution (known concentration) to
calculate the volume of ammonia nitrogen. The concentration of ammonia nitrogen was calculated by
following equation (4):

\[ \rho_N = \frac{V_i - V_b}{V} \times c \times 14.01 \times 1000 \]  

(4)

where, \( \rho_N \) is the mass concentration of ammonia nitrogen in water sample (mg/L), \( V \) is the volume of
water sample (ml), \( V_i \) is the volume that the standard solution of hydrochloric acid consumed by
titrating a water sample (ml), \( V_b \) is the volume that the standard solution of hydrochloric acid
consumed by blank experiment (ml), and \( C \), which is the molar concentration of the standard solution
of hydrochloric acid, is used for titration (mol/L).

However, the indicator had some problems, such as the short stability time of mixed indicator (one
month) and the difficulty in accurate automatic determination of titration endpoint.

3.1. Potentiometric titration

Ammonia, which escaped from distillation, was absorbed by a boric acid solution with standard
concentration, as specified in the equation (5):

\[ \text{NH}_3 + \text{H}_3\text{BO}_3 \rightarrow \text{NH}_4^+ + \text{H}_2\text{BO}_3^- \]  

(5)
The borate ions were neutralized with hydrochloric acid to form boric acid in the distillation, as described in equation (6):

\[ HCl + H_2BO_3^- \rightarrow H_3BO_3 + Cl^- \]  

Equations (5) and (6) revealed that the molar ratio of ammonia absorbed by the boric acid solution, borate ion formed and hydrochloric acid consumed by titration sample was 1:1:1 in the titration process. As the reaction progresses, the pH electrode potential of the distillate constantly changed with the concentration of hydrogen ions in the solution. According to the principle of electrochemistry, the concentration of hydrogen ion in the solution and the potential of electrode conformed to the Nernst Equation, as shown in equation (7):

\[ E = E^0 - 2.303RT \log[H^+] / F \]

where, E is the pH electrode potential of the solution at a specified absolute temperature and concentration (mV), E0 is the standard electrode potential (mV), R is the 8.314 J/(K•mol) as the gas constant, T is the absolute temperature (K), F is Faraday's constant. The equation (7) demonstrated that the change of hydrogen ion concentration changed the pH electrode potential of the solution. The electrode potential of the solution is controlled by adjusting the amount of hydrochloric acid added. Thus, the accurate determination of the titration endpoint requires potentiometric titration technology.

3.2. Judgment and correction of titration endpoint

At a certain temperature, the boric acid solution has an ionization equilibrium as shown in the equation (8):

\[ H_3BO_3 \rightleftharpoons H^+ + H_2BO_3^- \]  

The equation for calculating the ionization equilibrium constant of boric acid can be expressed in the equation (9):

\[ K_a = \frac{[H^+][H_2BO_3^-]}{[H_3BO_3]} \]

The pH was about 5.21 at the titration endpoint, as mostly borate ions combined with hydrogen ions converted to boric acid. Correction of the Nernst Equation under 25 °C as shown in the equation (10):

\[ \Delta E = 59.16 \times \Delta pH \]

where, \( \Delta E \) is the potential change (mV), \( \Delta pH \) is the change in the pH of the solution, and the constant (59.16) is the theoretical slope of the electrode under 25 °C.

According to the Equation, we noticed a linear relationship between the change of electric potential and the change of pH value. Assuming that as the PH of the solution was 7.00, the electrode potential was -14 mV (determined by the characteristics of the electrode). Consequently, \( \Delta E \) was approximately 106 mV and \( \Delta pH \) was 1.79 as the pH of the solution was 5.21. Therefore the theoretical titration endpoint of electric potential under 25 °C was 92 mV.

However, the following problems still exist, if the value of 92 mV was directly used as the actual titration endpoint of the potential titration method in practical applications. (1) The theoretical end point was the neutral point, which was difficult to control and titrate accurately. (2) With the change of distillation temperature, the ionization constant of boric acid and the acid-base value of theoretical end point changed accordingly. Meanwhile, the Nernst equation need to be revised so that the potential at the end of theoretical titration changed. (3) As time goes on, the aging and passivation of the electrode changed the characteristics of the electrode (e.g., as pH=7.00, the electrode potential was -14 mV), which led to the migration of titration endpoint in the process of using the pH composite electrode.

Based on the above problems and difficulties, this study corrected the titration endpoint to improve
the accuracy of ammonia nitrogen quantification. The specific correction methods were as follows. (1) The potentiometric titration method avoids judging the end point of titration according to the change of indicator color. Therefore the titration endpoint could be changed to a "flat area" far away from "abrupt jump area" of the pH value in order to facilitate the control of the titration endpoint. The value of pH was approximately 4.57, as the titration endpoint of electrode potential was 130 mV under 25 °C. (2) The temperature correction was carried out by the relationship curve using between different temperatures and pH value of titration endpoint or electric potential. (3) The characteristics of composite electrodes were basically stable within half a year, and only periodic detection was needed.

3.3. Control of potentiometric titration
According to equation (4), the volume of the standard solution of hydrochloric acid consumed by titration directly affected the detection results. So industrial syringe pump, composite pH electrode, and intelligent industrial transmitter were used as the actuator, measuring element and transmitter respectively in the potentiometric titration control system. Through the self-defined communication protocol, the injection pump communicated with PLC using RS485 interface. PLC sent titration instructions to which the injection pump received and responded to instructions.

The potentiometric titration control system had a specific particularity that does not allow the potential of the controlled variable to overshoot in the titration process. Otherwise, it would lead to excessive titration and result in too large values. Traditional PID control strategy had no self-adaptability and was prone to overshoot. Through simulation and comparison with the effect of variable gain PID control, expert control strategy was selected and implemented [9].

Meantime, it was considered that the lag time of pH electrode detection was about 3 s, the injection time of syringe pump was a certain range (1~5 s) and it took a certain time (6-12 s) for the solution to mix well. Therefore, the control cycle (T) of the potential titration control system set the time between 10 s and 20 s depending on the deviation, to reduce the operating frequency of the syringe pump and extend the device life.

4. Results and discussion

4.1. Overflow sampling
The double-port side overflow constant-volume overflow tank was used for 7 consecutive parallel sampling experiments, and table 1 showed the sampling results for three consecutive days.

| Time          | Sampling results (ml) | Maximum deviation (%) |
|---------------|-----------------------|-----------------------|
| First day     | 249.91 249.91 249.84 | 250.10 250.07 249.93 | 249.92 0.096                     |
| Second day    | 250.16 250.06 250.27 | 249.73 249.87 250.01 | 249.90 0.108                     |
| Third day     | 250.21 249.91 249.69 | 250.01 249.79 250.19 | 250.19 0.124                     |

According to experiment dates, the design of constant volume overflow sampling device ensured that the sampling error did not exceed values(±0.15%) and satisfy with high accurate demand of the online monitor. Thus, the design had the advantages of high measurement accuracy, simple structure, economy and practicability.

4.2. Effectivity of buffer solution
The samples with concentrations of 4, 8, 16, 24 and 32 mg/L were distilled in the ammonia-nitrogen standard solution (1 g/L) with two kinds of buffer solution (2 ml NaHPO₄ (1 mol/L); the mixed solution with volume of 2 ml consists of NaHPO₄ solution (1 mol/L) and NaOH solution (1 mol/L) with volume ratio of 25:2.). Titration was done three times according to the standard method. The average value was taken as the test result. Figure 3 showed the results under two different buffers.
The results revealed a negative deviation in the detection result (figure 3), since the high concentration of ammonia nitrogen carried by air in the distillation tank that diffused and escaped with vast steam quickly, and it led to ammonia nitrogen could not be absorbed absolutely as the water sampling began to boil. Under the formula (1), the result of a low concentration of ammonia nitrogen presented small deviations, whereas the high concentration resulted in large deviations, mainly as the pH value of Na$_2$HPO$_4$ (about 9) was low.

With the distillation proceeding, the high concentration of ammonia nitrogen did not escape completely, which resulted in the pH value that gradually reduced in the system. However, under the formula (2), the negative bias of the total concentration range was large, since the mixed solution of Na$_2$HPO$_4$-NaOH had a large pH value (about 11), and ammonia nitrogen escaped so fast that it could not be entirely absorbed in the early stage of boiling. In order to reduce the negative deviation of test results, it was consider that the formula (2) to compound buffer solution and designed a segmented heating scheme for distillation operation.

### 4.3. General performance index

According to the metering performance requirements of automatic monitor of ammonia nitrogen of national metrological verification regulations (JJG 631-2013), standard solutions with ammonia nitrogen concentration of 0 (blank), 0.5, 1.0, 2.0 and 16.0 mg/L were prepared and determined on the sample device. Each concentration was tested in parallel via multi-group experiments (Each concentration was tested three times in the error process of calculations, and the 2 mg/L concentration was tested seven and four times in the repeatability and stability process of calculations, respectively). Lastly, the performance indexes were calculated such as the error, repeatability, and stability of indication.

#### Table 2. Table of blank test results under potentiometric titration analysis.

| Number | Absorption pH | Distillation liquid pH | Temperature ℃ | Endpoint of titration mV | Endpoint pH | Volume of hydrochloric acid consumed ml |
|--------|---------------|------------------------|---------------|--------------------------|-------------|----------------------------------------|
| 1      | 4.46          | 5.20                   | 25            | 130                      | 4.57        | 0.352                                  |
| 2      | 4.49          | 5.15                   | 27            | 131                      | 4.56        | 0.304                                  |
| 3      | 4.47          | 5.18                   | 25.5          | 130                      | 4.57        | 0.300                                  |
| 4      | 4.49          | 5.18                   | 27.5          | 131                      | 4.56        | 0.326                                  |
| 5      | 4.47          | 5.20                   | 24            | 130                      | 4.57        | 0.385                                  |
| 6      | 4.47          | 5.11                   | 22.5          | 129                      | 4.56        | 0.310                                  |
| 7      | 4.46          | 5.17                   | 26            | 130                      | 4.57        | 0.305                                  |
| Average: |              |                        |               |                          |             | 0.326                                  |

Hydrochloric acid concentration: 0.0204 mol/L  
Blank value: 0.326×0.0204×14.01×4=0.373 mg/L
The experimental results were shown in tables 2 and 3. Table 2 presents the blank experimental data and processing results, whereas table 3 corresponds to the detection results of four different concentration of standard solutions.

### Table 3. Table of standard test results under potentiometric titration analysis.

| Normal concentration mg/L | Measured concentration mg/L | Absolute error mg/L | Relative error % | Repeatability % | Stability % |
|---------------------------|-----------------------------|---------------------|------------------|-----------------|------------|
| 0.5                       | 0.5398                      | 0.0398              | 7.96             |                 |            |
| 1.0                       | 1.0067                      | 0.0067              | 0.67             | 2.29            | 1.45       |
| 2.0                       | 2.0281                      | 0.0281              | 1.40             |                 |            |
| 16.0                      | 16.1160                     | 0.1160              | 0.73             |                 |            |

According to the data in table 3, the maximum indication error of potentiometric titration method used in this study was 0.0398 mg/L as detecting low concentration (≤2 mg/L) ammonia nitrogen, which was much lower than the value stipulated (±0.2 mg/L) by the metrological verification rules for class A automatic monitor. Within the range of high concentration (>2 mg/L), the indication error was only 1.40%, which was much less than (±10%) stipulated in the verification rules. Repeatability (2.29%) and stability (1.45%) also respectively meet the requirements of the verification regulations that repeatability did not less than 3% and stability within 4 hours does not exceed ±10%.

### 4.4. Method detection limit

The method widely used in calculating the detection limits in China consists 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 standard solution concentration (C). The average signal (X) and the standard deviation of the measured signal (S) were obtained by the blank value of standard solution concentration (C) that was measured more than 20 times. So the method detection limit follows the equation (11):

\[
MDL = \frac{3S \times C}{X}
\]

(11)

The standard solution concentration (C) near the blank in the equation was 1~3 times of the expected detection limit. Based on the national environmental protection standard [10], the method detection limit was 0.05 mg/L for the volume of water sample of 250 ml. Therefore, NH₄Cl standard solution (0.1 mg/L) was used as near standard blank solution. The detection results were shown as table 4.

### Table 4. Table of method detection limit test results for potentiometric titration analysis.

| Number | Dosage of hydrochloric acid mol | Measured concentration mg/L | Number | Dosage of hydrochloric acid mol | Measured concentration mg/L |
|--------|---------------------------------|-----------------------------|--------|---------------------------------|-----------------------------|
| 1      | 0.0015933                       | 0.0893                      | 11     | 0.0016946                       | 0.0950                      |
| 2      | 0.0016946                       | 0.0950                      | 12     | 0.0015933                       | 0.0893                      |
| 3      | 0.0016946                       | 0.0950                      | 13     | 0.0016946                       | 0.0950                      |
| 4      | 0.0017352                       | 0.0972                      | 14     | 0.0021000                       | 0.1177                      |
| 5      | 0.0018365                       | 0.1029                      | 15     | 0.0020189                       | 0.1131                      |
| 6      | 0.0017554                       | 0.0984                      | 16     | 0.0021406                       | 0.1200                      |
| 7      | 0.0017352                       | 0.0972                      | 17     | 0.0019987                       | 0.1120                      |
| 8      | 0.0017757                       | 0.0995                      | 18     | 0.0019987                       | 0.1120                      |
| 9      | 0.0016541                       | 0.0927                      | 19     | 0.0020595                       | 0.1154                      |
| 10     | 0.0019987                       | 0.1120                      | 20     | 0.0017352                       | 0.0972                      |

Average (X)=0.1023 Standard deviation (S)=0.00827
The average (X) and the standard deviation (S) were respectively 0.1023 mg/L and 0.0082 by the data calculated in table 4. By substituting X and S into equation (12), method detection limit MDL results in 0.02425 mg/L by potentiometric titration analysis could be obtained. The final method detection limit after revision was MDL=0.025 mg/L.

4.5. The lower limit of quantitation
According to IUPAC recommended method, the experimental results were shown in table 5. The lower limit of quantitation for potentiometric titration was 0.17 mg/L.

Table 5. Table of test results for potentiometric titration analysis.

| Number | Dosage of hydrochloric acid mol | Blank value mg/L | Number | Dosage of hydrochloric acid mol | Blank value mg/L |
|--------|-------------------------------|-----------------|--------|-------------------------------|-----------------|
| 1      | 0.0071456                     | 0.4004          | 15     | 0.0075313                     | 0.4221          |
| 2      | 0.0075516                     | 0.4232          | 16     | 0.0074095                     | 0.4152          |
| 3      | 0.0073080                     | 0.4095          | 17     | 0.0078155                     | 0.4380          |
| 4      | 0.0076328                     | 0.4277          | 18     | 0.0077140                     | 0.4322          |
| 5      | 0.0073425                     | 0.4115          | 19     | 0.0079373                     | 0.4448          |
| 6      | 0.0079170                     | 0.4436          | 20     | 0.0074704                     | 0.4186          |
| 7      | 0.0077140                     | 0.4322          | 21     | 0.0078155                     | 0.4380          |
| 8      | 0.0072065                     | 0.4038          | 22     | 0.0075313                     | 0.4221          |
| 9      | 0.0069020                     | 0.3868          | 23     | 0.0078155                     | 0.4380          |
| 10     | 0.0075110                     | 0.4209          | 24     | 0.0075313                     | 0.4221          |
| 11     | 0.0075110                     | 0.4209          | 25     | 0.0073080                     | 0.4095          |
| 12     | 0.0077140                     | 0.4322          | 26     | 0.0079373                     | 0.4437          |
| 13     | 0.0066990                     | 0.3754          | 27     | 0.0079373                     | 0.4437          |
| 14     | 0.0074095                     | 0.4152          | 28     | 0.0075110                     | 0.4209          |

The average of blank value: 0.4219 standard deviation (S): 0.01697

5. Conclusions
In order to develop a new online monitoring of ammonia nitrogen based on the new national environmental production standard HJ 537-2009 ‘Water quality-determination of ammonia nitrogen-Distillation-neutralization titration’, this study focused on the research and development of water sample pretreatment system, titration detection system and its key technologies. The comprehensive application of key technologies allowed to improve system performance and technical performance indicators. As detecting low concentration (≤2 mg/L) ammonia nitrogen, the maximum indication error was 0.0398 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 only 1.40%, which was much less than the value (±10%) stipulated in the verification regulation; the repeatability (2.29%) and stability (1.45%) also meet the requirements (repeatability no more than 3% and stability did not exceed ±10% within 4 hours). The method detection limit (MDL=0.025 mg/L) and limit of quantitation (LOQ=0.17 mg/L) of potentiometric titration method were lower than those of the corresponding national standard method (MDL=0.05 mg/L and LOQ=0.2 mg/L).

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