Water Quality Determination by Electrically Controlled DPD Spectrophotometry Method Research

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Abstract. This article points out that free residual chlorine and monochloramine are important water quality indicators for measuring disinfection effects in various water industries. For the "Standard Inspection Method for Drinking Water Standard Test Method Disinfectant Index GB/T 5750.11-2006", the N,N-diethyl-p-phenylenediamine (DPD) spectrophotometric method for the determination of free residual chlorine and monochlorine in drinking water and its source water Amine for method validation. The results showed that: the correlation coefficient of the free residual chlorine determination standard song is 0.9994; the detection limit is 0.01mg/L, the lower limit of determination is 0.04 mg/L, and the detection limit meets the requirements of the method; the content levels are 0.73mg/L, 3.2mg/L, The free residual chlorine content of the L residual chlorine sample was measured in parallel for 6 times, the relative standard deviations were 3.5% and 2.9% respectively, and the precision met the method requirements; the free residual chlorine content level of the actual water sample was 0.05mg/L, 0.4mg/L, 1.0mg/L spiked experiment was measured 6 times, the average recovery rate of free residual chlorine: 104%, 103%, 97.1%, the accuracy meets the requirements of the method. For the content level 0.11mg/L and 1.2mg/L residual chlorine samples, the monochloramine content was measured in parallel for 6 times to determine the precision. The relative standard deviations are respectively: 0~5.6%, 0.34~4.0%, and the precision meets the requirements of the method. Therefore, it is confirmed that this method is applicable and feasible in this laboratory for the determination of free residual chlorine and monochloramine in water quality.

1. Introduction
In the field of water treatment, chlorine preparations (chloramines, hypochlorites, etc.) can destroy or inhibit pathogenic microorganisms in water [1], and can react with reducing substances in water, making it easy to use [2]. After the water body is disinfected by chlorination, the residual chlorine in the water is called residual chlorine. Therefore, chlorination disinfection is still the widely used water disinfection method [3]. However, in the disinfection process, excessive chlorine not only affects the taste and smell of the water, destroys the quality of the water, but also reacts with certain organic substances in the water to form a series of chlorine-containing organic compounds with a "three-in-one" effect, such as chloroform, Chlorinated hydrocarbons such as carbon tetrachloride and bromodichloromethane. Therefore, free residual chlorine is an important water quality indicator to
measure the disinfection effect of various water industries, and the frequency of testing is extremely high [4].

At present, the method widely used in my country to determine free residual chlorine and chloramine in water quality is the current standard GB/T 5750.11-2006 "Standard Test Method for Drinking Water Disinfectant Indicators", 1 Free residual chlorine 1.1 N, N-diethyl P-phenylenediamine (DPD) spectrophotometry and 3-chloramine 3.1 N, N-diethyl-p-phenylenediamine (DPD) spectrophotometry [5]. This method utilizes the reaction of N, N-diethyl-1,4-phenylenediamine (DPD) with free residual chlorine in water to produce red color under the condition of pH 6.2-6.5. Under the catalysis of iodide, monochloramine It can also react with DPD to develop color. In this experiment, potassium permanganate solution was used to prepare a permanent standard series, because the preparation of standard solutions with chlorinated water is cumbersome and unstable [6]. After testing, the amount of potassium permanganate in the standard solution is similar to the red color produced by DPD and the marked residual chlorine, so potassium permanganate solution is used to simulate the chlorine standard solution.

2. Experimental part

2.1. Instruments and reagents

UV spectrophotometer, one percent per day

2.2. Main reagents

Potassium Permanganate(Changzhou Xinghui Chemical Co., Ltd., analytical grade), N,N-Diethyl-p-phenylenediamine(Tianjin Damao Chemical Reagent Factory, Analytical Pure), Potassium iodide (Tianjin Komiou Chemical Reagent Co., Ltd., Analytical grade), Bleaching agent (Chengdu Kelong Chemical Co., Ltd., analytical grade), Disodium hydrogen phosphate anhydrous (Tianjin Komiou Chemical Reagent Co., Ltd. Analytical grade), Anhydrous potassium dihydrogen phosphate (Tianjin Komiou Chemical Reagent Co., Ltd., Analytical grade).

2.3. Test content

2.3.1. Standard curve drawing. draw 0, 0.1, 0.5, 2.0, 4.0, 8.0mL chlorine standard use solution (1μg/mL) into 6 10mL colorimetric tubes with stopper and dilute to the mark with water without chlorine. Add 0.5mL phosphate buffer solution (pH=6.5) and 0.5mL DPD solution (1g/L) to each, mix well, and measure the absorbance at a wavelength of 515nm, a 1cm cuvette, and pure water as a reference. Draw a standard curve with absorbance as the abscissa and the mass of residual chlorine (μg) as the ordinate.

2.3.2. Free residual chlorine Determination of absorbance. Take 10mL water sample and place it in a 10mL colorimetric tube, add 0.5mL phosphate buffer solution (pH=6.5), 0.5mL DPD solution (1g/L), mix well, and immediately perform colorimetry at 515nm wavelength, 1cm Use pure water as the reference to measure the absorbance and record the reading as A. At the same time, measure the blank value of the sample and deduct it from the reading. A is the absorbance of free residual chlorine.

2.3.3. Monochloramine Determination of absorbance. Continue to add a small solid potassium iodide (about 0.1 mg) to the above test tube. After mixing, measure the absorbance again and record the reading as B. B-A is the absorbance of monochloramine.
2.3.4. Free residual chlorine and monochloramine are calculated under the following conditions:

| Table 1. Determination of the absorbance of residual chlorine |
|-------------------------------------------------------------|
| AbsorbanceReading | water sample without trichloramine |
| A | Free residual chlorine |
| B-A | monochloramine |

3. Results and discussion

3.1. Linear range

Draw a standard curve with absorbance as the abscissa and the mass of residual chlorine (μg) as the ordinate. The N, N-diethyl-p-phenylenediamine (DPD) spectrophotometric method is used to determine the free residual chlorine and monochloramine content in drinking water and its source water. The chlorine content in the standard series is 0.0, 0.1, 0.5, 2.0, 4.0, 8.0μg, the linear equation is y=50.057x+0.1046, and the correlation coefficient is 0.9994. Meet the requirements of 5.2 (correlation coefficient of calibration curve regression equation γ≥0.999) of "Standard Inspection Methods for Drinking Water Quality Control of Water Quality Analysis GB/T5750.3-2006".

3.2. Determination of method detection limit and lower limit of determination

The "Technical Guidelines for the Establishment and Revision of Environmental Monitoring and Analysis Methods Standards" (HJ 168-2010) clearly stipulates the determination method of the detection limit. That is, sampling, pre-processing, color development, and computer operation are carried out according to the entire process of residual chlorine sample analysis, and the concentration content is 2-5 times the detection limit of the estimated method for 7 parallel determinations, and 7 parallel determinations are calculated during the determination process. The standard deviation of, according to the detection limit of MDL=3.143×S calculation method. The data summary table is shown in Table 4.

| Table 2. Test data table of the detection limit and lower limit of the residual chlorine method |
|-----------------------------------------------------------------------------------------------|
| Parallel sample number | Detection limit sample |
|------------------------|------------------------|
| 1                      | 0.036                  |
| 2                      | 0.035                  |
| 3                      | 0.036                  |
| 4                      | 0.036                  |
| 5                      | 0.031                  |
| 6                      | 0.036                  |
| 7                      | 0.035                  |
| The measurement results(mg/L) |                        |
| average value x(mg/L) | 0.035                  |
| standard deviation s(mg/L) | 0.002                |
| t value                | 3.143                  |
| The detection limit(mg/L) | 0.01                 |
| Lower limit of determination(mg/L) | 0.04              |
| Detection limit(mg/L)  | 0.01                   |
| Whether it meets the method requirements | YES                   |

3.3. Determination of precision

Perform precision experiments on residual chlorine samples with content levels of 0.73mg/L and 3.23mg/L. Follow all steps of sample analysis to determine free residual chlorine and monochloramine. Each sample is measured in parallel 6 times, paying attention to color development Perform the test
immediately after completion. The color development stability time is short, and the test results will lose accuracy if placed for too long; see Table 5 and Table 6 for the data summary table. Calculate the average value, standard deviation, relative standard deviation and other parameters of different samples. The standard deviation (SD) is calculated using Bessel's formula.

Table 3. Free residual chlorine precision test data

| Parallel number | Sample 1 (mg/L) | Sample 2 (mg/L) |
|-----------------|-----------------|-----------------|
| 1               | 0.72            | 3.36            |
| 2               | 0.70            | 3.14            |
| 3               | 0.74            | 3.33            |
| 4               | 0.71            | 3.15            |
| 5               | 0.76            | 3.24            |
| 6               | 0.77            | 3.18            |

average value \( \bar{x} \) (mg/L): 0.73, 3.23

standard deviation \( s \) (mg/L): 0.026, 0.094

relative standard deviation RSD (mg/L): 3.5, 2.9

Requires relative standard deviation(%) 2.5~16.9, 1~8.5

Whether it meets the method requirements YES YES

For samples with content levels of 0.73 mg/L and 3.2 mg/L of residual chlorine, the free residual chlorine content was measured in parallel for 6 times, and the relative standard deviations were 3.5% and 2.9%, respectively. It shows that the dispersion of free residual chlorine content of water quality repeated by spectrophotometric method is small and the precision is good. Comply with "Standard Test Method for Drinking Water Standard Test Method Disinfectant Index GB/T 5750.11-2006" 1.1 N, N-diethyl-p-phenylenediamine (DPD) spectrophotometric method to determine the precision of free residual chlorine in drinking water and its source water (The relative standard deviation is 2.5~16.9%, 1~8.5%).

Table 4. Monochloramine precision test data

| Parallel number | Sample 1 (mg/L) | Sample 2 (mg/L) |
|-----------------|-----------------|-----------------|
| 1               | 0.11            | 1.11            |
| 2               | 0.13            | 1.22            |
| 3               | 0.11            | 1.13            |
| 4               | 0.11            | 1.27            |
| 5               | 0.11            | 1.29            |
| 6               | 0.10            | 1.31            |

average value \( \bar{x} \) (mg/L): 0.11, 1.2

standard deviation \( s \) (mg/L): 0.011, 0.083

relative standard deviation RSD (mg/L): 9.7, 6.8

Allowable value of relative deviation of parallel double sample (%) 0~6.6, 0.34~4.0

The method requires the allowable value of relative deviation (%) 5~10, 2.5~5

Whether it meets the method requirements YES YES

For the content of 0.11mg/L and 1.2mg/L residual chlorine samples, the monochloramine content was measured in parallel for 6 times, and the relative standard deviations were 0~5.6% and 0.34~4.0%
respectively. It shows that the dispersion of free residual chlorine content of water quality repeated by spectrophotometric method is small and the precision is good. Comply with "Quality Control of Water Quality Analysis of Drinking Water Standard Inspection Methods GB/T 5750.3-2006" 7.2 (when the mass concentration levels are 0.1~1mg/L and 1~10 mg/L, the allowable value of relative deviation of parallel double sample analysis is 5~10%, 2.5~5%) requirements.

3.4. Determination of accuracy

The laboratory verifies the accuracy of the method through a standard addition experiment. The actual water samples are spiked, because the residual chlorine is very unstable in the water, especially when it contains organic matter or other reducing inorganic substances, it is easier to decompose and disappear. Therefore, it is necessary to quickly prepare spiked samples during the experiment to make the results more accurate. Perform the measurement according to all the steps of the sample analysis, and perform the measurement 6 times in parallel. The data summary table is shown in Table 5. Calculate the average value of free residual chlorine spiked experiment content, spiked concentration, spiked recovery rate and other parameters.

| Parallel number | Actual spiked samples | The measurement results(mg/L) | Background value(mg/L) | Spiked concentration(mg/L) | Standard recovery rate(%) |
|-----------------|-----------------------|-------------------------------|------------------------|---------------------------|--------------------------|
|                 | content 1 | content 2 | content 3 | 0.046 | 0.411 | 0.961 | 0.054 | 0.409 | 0.961 | 0.053 | 0.403 | 0.911 | 0.055 | 0.415 | 0.991 | 0.054 | 0.404 | 1.046 | 0.053 | 0.418 | 0.961 | average value(mg/L) | 0.052 | 0.410 | 0.971 | Background value(mg/L) | 0.000 | 0.000 | 0.000 | Spiked concentration(mg/L) | 0.05 | 0.4 | 1.0 | Standard recovery rate(%) | 104 | 103 | 97.1 | Method requires average recovery(%) | 97.0~108 | 90.0~103 | 94.0~106 | Whether it meets the method requirements | YES | YES | YES |

For the actual water samples, the free residual chlorine content levels were 0.05 mg/L, 0.4mg/L, and 1.0 mg/L spiked experiments to determine 6 times respectively. The average recovery rate of free residual chlorine: 104%, 103%, 97.1%. It shows that the determination result is close to the real standard addition, and the N, N-diethyl-p-phenylenediamine (DPD) spectrophotometric method is more accurate in determining the free residual chlorine content of water quality. It also meets the standard test method for drinking water and disinfectant indicators GB/T 5750.11-2006 1.1 in the N, N-diethyl-p-phenylenediamine (DPD) spectrophotometric method for the determination of free residual chlorine in drinking water and its source water. Accurate Degree (average recovery rate of 97.0~108%, 90.0~103%, 94.0~106%).

4. Conclusion

The laboratory has verified the method for the determination of free residual chlorine and monochloramine in drinking water and its source water by N,N-diethyl-p-phenylenediamine (DPD) spectrophotometry, and the results show that the determination of free residual chlorine is relevant to the standard song The coefficient is 0.9994; the detection limit is 0.01 mg/L, and the lower limit of determination is 0.04 mg/L; the content levels are 0.73 mg/L and 3.2 mg/L residual chlorine samples in parallel determination of free residual chlorine content 6 times, the relative standard deviations are respectively 3.5%, 2.9%; free residual chlorine content levels of 0.05mg/L, 0.4mg/L, 1.0mg/L spiked.
experiments were carried out for the actual water samples to determine 6 times respectively, the average recovery rate of free residual chlorine: 104%, 103%, 97.1%. For the content of 0.11mg/L and 1.2mg/L residual chlorine samples, the monochloramine content was measured in parallel for 6 times to determine the precision. The relative standard deviations were 0~5.6% and 0.34~4.0%, respectively. The linear relationship, detection limit, precision and accuracy meet the requirements of 1.1, 3.1 of the Standard Inspection Method for Drinking Water Standard Inspection Method Disinfectant Index GB/T 5750.11-2006 1.1 and 3.1 and the Standard Inspection Method for Drinking Water Quality Control of Water Quality Analysis GB/T 5750. 3-2006" 7.2 requirements. Therefore, this method is suitable for the determination of free residual chlorine and monochloramine in water quality in our laboratory.

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