Measurement of Chlorine Dioxide in Water by DPD Colorimetric Method

Min Songa, Panping Yanb, Jun Yaoc
Zhejiang University Kunshan Innovation Institute, Suzhou, 215300, China

asong2015@163.com, b2973473175@qq.com, cxyz_rgb@126.com

Abstract. In order to solve the problems of chlorine dioxide in water by DPD colorimetric method, this paper discusses the effects of the formulation, temperature, color development time and amount of color reagent on the measurement process, improving the on-line instrument for domestic and drinking water in chlorine dioxide measurement precision and accuracy.

1. Introduction
At present, chlorine dioxide is a disinfectant, and strong oxidizer, broad-spectrum sterilization, as a kind of efficient, spectral drinking water disinfectant, has been widely used in drinking water, food safety control, and other fields.

Chlorine dioxide has a strong reactivity and volatile properties, easy to dissolve in water. To achieve the best disinfection effect, and the water pipe network residual chlorine dioxide in accordance with GB/T 5750.11 2006 national standard of the People's Republic of China-life drinking water standard test methods - disinfectant indicators, to ensure the accuracy of the test. The above requirements shall be as fast as possible, as well as sensitive and real-time on-line monitoring [1].

This research adopts DPD colorimetric method of online instrument under different concentration of chlorine dioxide standard solution is measured, and the confecting of from indicator, temperature, color rendering time and chromogenic agent dosage on the influence of the measurement process, further verify the online analytical instrument accuracy and reliability of the test results, and analyze the above situation, the better the on-line instrument used in measuring the concentration of chlorine dioxide in water.

2. Principle
In the acid medium, chlorine dioxide and N, n-diethyl-1, 4-phenylenediamine hydrochloride react to generate the fuchsia compounds, and the colorimetric measurement is performed using the on-line chlorine dioxide analyzer.

3. Materials And Methods[2,3,4]

3.1. Major Instruments and Reagents

3.1.1. On-line chlorine dioxide analyser. On-line chlorine dioxide analyzer (ATF-CLO2-2A, SuZhou optfull environmental science and technology co., Ltd), agitator (Rex).
3.1.2. Buffer solution (pH 7.8). According to scale 130:58:18:3:1, it is called potassium dihydrogen phosphate, disodium hydrogen phosphate, and sodium sulfate, thioacetamide and barium chloride. After drying, respectively dissolve in 300mL chlorine-free ultra-pure water.

3.1.3. Indicator. N, N - diethyl 1, 4 - phenylenediamine hydrochloride and ethylenediamine tetraacetic acid disodium after drying in accordance with the ratio 3:1 respectively dissolved in 300 ml without chlorine ultrapure water, and in proportion to add 8 volume of 1 + 3 sulfuric acid solution, 2 volume of anhydrous ethanol blending, storage in brown glass bottle, placed a refrigerator.

3.1.4. No chlorine water. Add a small amount of bleaching powder to the ultra pure water, so that the total chlorine dioxide concentration in the water is about 0.5 mg/L, and the chlorine dioxide can be boiled and removed.

3.1.5. Chlorine dioxide standard solution. The chlorine dioxide (GF6054) is diluted with chlorine free water to 1, 2, 3 mg/L.

3.2. Experiment Method
The configured phosphate buffer and DPD indicator solution are in two 500ml reagent bottles, and the diluted concentration of chlorine dioxide standard solution is stored in 50mL colorimetric tubes. According to the requirements of the above reagents connected to the ATF-CLO2-2A on-line chlorine dioxide analyzer, reagents and samples according to the ratio of 1: 1: 1 injection colorimetric, the data that is read is free chlorine dioxide.

This experiment respectively in different temperature, reaction time and dosage of agent under the testing standards of different concentration of chlorine dioxide solution, respectively, to explore the effects of influence factors on the accuracy of determination results.

4. Results And Discussion
4.1. The Preparation of Indicator Solution
According to the standard requirements, N, N - diethyl-1, 4-phenylenediamine salt in the indicator solution is easy to be decomposed, discolored, and not resistant to storage. In the process of preparation of the reagent of N, N - diethyl 1, 4 - phenylenediamine hydrochloride and ethylenediamine tetraacetic acid disodium after 100 °C drying 30 min, dissolved, and join the anhydrous ethanol, blending, not easy to change color, storage time can be a standard in the formula and preparation method of long at least six months.

4.2. Influence of Temperature
Take more than two sets of the concentration of chlorine dioxide standard solution were tested respectively, respectively in four,10,20,30,40,50,60,70,80,85 °C temperature test. At room temperature 25 °C as the reference standard, when the temperature above 60 °C, the measured results of chlorine dioxide standard solution was obviously higher than that of the result of room temperature, abnormal situation. The temperature is below 60 °C, the measurement results of free chlorine dioxide are shown in table 1.
Table 1. Effect of Temperature on Measurement Results

| Sample                                | Temperature/℃ |
|---------------------------------------|---------------|
|                                       | 4 10 20 30 40 50 60 |
| Chlorine dioxide standard solution:  |
| (25℃, 1.00mg/L)                       | 0.94 0.96 1.00 1.00 1.01 1.03 1.04 |
| Chlorine dioxide standard solution:  |
| (25℃, 2.00mg/L)                       | 1.92 1.95 2.00 2.00 2.00 2.02 2.03 |
| Chlorine dioxide standard solution:  |
| (25℃, 3.00mg/L)                       | 2.91 2.93 2.99 3.00 3.00 3.04 3.05 |

It can be seen from Table 1, the temperature is below 10 ℃, low concentration of chlorine dioxide have been measured, when the temperature at room temperature to 60 ℃, the concentration of chlorine dioxide have small amplitude increases, but within the error range, so general optional at room temperature, the measurement of chlorine dioxide.

4.3. Influence of Reaction Time
The chlorine dioxide standard solution of the two groups was measured at 0.5, 1, 2, 3, 4, 5, 6, and for min. The measurement value of chlorine dioxide after the sample and reagent in the national standard is the reference standard, and the results are shown in table 2.

Table 2. Effect of Reaction Time on Measurement Results

| Sample                                | Time/min |
|---------------------------------------|----------|
|                                       | 0.5 1 2 3 4 5 6 |
| Chlorine dioxide standard solution:  |
| (0min, 1.00mg/L)                      | 1.00 1.00 1.02 1.09 1.20 1.20 1.30 |
| Chlorine dioxide standard solution:  |
| (0min, 2.00mg/L)                      | 2.00 2.00 2.01 2.10 2.10 2.20 2.20 |
| Chlorine dioxide standard solution:  |
| (0min, 3.00mg/L)                      | 3.00 3.01 3.01 3.10 3.15 3.15 3.20 |

Table 2 shows that different reaction times have a certain effect on the measurement results. Color development time within 2min measurement, the results vary little.

4.4. Influence of The Dosage of The Colorant
Take more than two sets of the concentration of chlorine dioxide standard solution were tested respectively. Samples with chromogenic agent respectively according to 0.5:1,1:1.5,1:2,1:4,1:6,1:8 on-line colorimetric determination of proportion, the ratio of 2.2 is the reference standard and the measurement results are shown in table 3.

Table 3. Effect of Amount of Color Reagent on Measurement Results

| Sample                                | Sample volume/Color rendering agent |
|---------------------------------------|-------------------------------------|
|                                       | 1: 0.5 1:1.5 1:2 1:4 1:6 1:8        |
| Chlorine dioxide standard solution:  |
| (1:1, 1.00mg/L)                       | 0.65 1.00 1.02 1.50 1.50 1.50        |
| Chlorine dioxide standard solution:  |
| (1:1, 2.00mg/L)                       | 1.59 2.00 2.05 2.55 2.55 2.55        |
| Chlorine dioxide standard solution:  |
| (1:1, 3.00mg/L)                       | 2.45 3.00 3.03 3.48 3.48 3.8          |
As shown in table 3, sample size: between 1:1 and 1:2, the measured results are relatively constant; Below 1:1, the dosage of the colorant is not sufficient and cannot be fully responded; Higher than 1:2, the concentration of chlorine dioxide is constant, and it no longer changes with the amount of chroma. Therefore, the ratio is 1:1, which does not waste the colorant, and the reaction is complete.

5. Conclusion
The above experiments show that the DPD colorimetry method is used for on-line measurement of chlorine dioxide in general living drinking water, and the sensitivity is high.

References
[1] J. Y. Zhou, W. J. Liu, A. P. Li, et al. Comparative study on determining methods of chlorine dioxide concentration in water (Chinese Jounal of Disinfection, Beijing, 2010), pp.576.
[2] GB 5009.244-2016, National food safety standard determination of chlorine dioxide in food, (The health and family planning commission of the People's Republic of China, Beijing, 2016), pp.1-6.
[3] H. Qin, J. H. Deng, F. F. Li, et al. Application of several new products for on-site rapid determination of chlorine dioxide (Modern Scientific Instruments, Beijing, 2016), pp.131.
[4] HJ 551-2009, Water quality-Determination of chlorine dioxide and chlorite continuous iodometric method, (Ministry of environmental protection, Beijing, 2010), pp.1-7.