Rapid in situ determination of ClO$_2$ in drinking water by improved solid DPD spectrophotometry

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Abstract: This research aims to realize the rapid detection of ClO$_2$ content in drinking water by adopting improved solid DPD. This method is fast and convenient with low cost and less waste liquid. The results show that this method has good precision and sensitivity. The linear correlation coefficients of the cubic regression equation were all greater than 0.999. The detection limit of the method was 0.002mg/L ClO$_2$. The relative standard deviations (RSD) of seven parallel tests were between 1.37% and 8.87%, and the relative errors were small. The recovery rate was 96.67~110%. The method could be used for the direct determination of water samples with a mass concentration of 0.02mg/L~2.00mg/L in drinking water after ClO$_2$ disinfection.

1 Introduction

According to the statistics of the World Health Organization(WHO), 80% of human diseases are caused by drinking unclean water [1].In China, less than 11% of people drink water satisfying China's health standards, while up to 65% drink water which is muddy, bitter, polluted by industry or infectious diseases. The safety of drinking water quality is a major livelihood issue related to thousands of households, and disinfection technology is crucial to ensure the safety of drinking water microorganism [2, 3].The main disinfectants used in drinking water include chlorine dioxide (ClO$_2$), liquid chlorine, free chlorine preparation and ozone. ClO$_2$ disinfectant is listed as A1 safe disinfectant by WHO because of its non-carcinogenicity, non-teratogenicity and non-mutagenicity [4].At the same time, it also has advantages of strong oxidation and sterilization ability, a wide range of water quality and pH application. At present, ClO$_2$ disinfectant has been substituted by liquid chlorine gradually in China [5].Although ClO$_2$ does not produce halogenated disinfection by-products during the disinfecting of drinking water, it may produce chlorite, an inorganic by-product harmful to human body[6]. Therefore, it is clearly stipulated that the limit of ClO$_2$ in the factory water is 0.8mg /L in the GB5749-2006 "drinking water hygiene standards"[7].

The detection methods of ClO$_2$ mainly include iodine titration, current titration, spectrophotometry, fluorometric method, flow injection method, etc. [8, 9, 10, 11]. At present,N, N-diethyl-p-phenylenediamine (DPD) spectrophotometry and 3,3',5,5' -tetramethylbenzidine (TMB) colorimetry in the national standard detection methods are laboratory detection methods, which are not suitable for on-site detection. Although many manufacturers have designed portable spectrophotometer that can be used for the field measurement of residual chlorine and ClO$_2$ disinfectant according to the principle of DPD, research for domestic and drinking water detection is usually by adding liquid DPD reagent in the drinking water after the disinfection of ClO$_2$. On the other hand, the existing DPD spectrophotometry has disadvantages such as large consumption, inconvenient storage and transportation. Therefore, this study adopts the way of adding modified solid DPD to realize the rapid detection of ClO$_2$ content in drinking water on the spot.

2 Experimental

2.1 Experimental principle

ClO$_2$ in water reacts with DPD in red at pH 6.5(The equation is: $2ClO_2 + DPD \rightarrow 2ClO_2 + DPD^{2+}$(red)). The absorbance measured at 520 nm is linearly dependent on concentration. Glycine converts free chlorine in the water to chloroaminoacetic acid without interfering with the determination of ClO$_2$.

2.2 Reagents and Apparatus

Hand-held multi-parameter water quality detector, single wavelength colorimeter, 1/10,000th balance, ClO2 solution, glycine solution, modified solid DPD reagent.

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2.3 Analysis Operation Steps

2.3.1 Standard operating curve

Take 10 mL of each ClO_2 solution with concentrations of 0.00, 0.02, 0.10, 0.40, 0.80, 1.20 and 2.00mg/L. Add 2 drops of glycine solution respectively, shake well. Add a flat spoon of improved DPD solid reagent, shake well, and then stand for 30 seconds. Determine on the colorimeter of the instrument above.

2.3.2 Determination of the sample

(1) Take 10mL of pure water into a colorimetric bottle and use it as a blank sample. Put the blank sample into the colorimetric tank of the instrument for blank measurement.

(2) Take 10mL of water sample into the colorimetric bottle. Add 2 drops of glycine solution, shake well. Add a flat spoon of improved solid DPD reagent, shake well, and then stand for 30 seconds. Measure the mass concentration of ClO_2 (unit: mg/L) in the water sample on the colorimeter of the instrument.

3 Results and discussion

3.1 Draw and check the standard working curve

3.1.1 Standard working curve drawing

Three parallel tests were conducted on the samples in 1.3.2, and the results were listed in Table 1.

Table 1 shows the working curve of the method

1	The concentration of ClO_2 mg/L	0.000	0.020	0.100	0.400	0.800	1.200	1.600	2.000
	Absorbance	0.000	0.008	0.032	0.083	0.175	0.255	0.328	0.418
2	The concentration of ClO_2 mg/L	0.000	0.020	0.100	0.400	0.800	1.200	1.600	2.000
	Absorbance	0.000	0.007	0.031	0.085	0.185	0.268	0.349	0.443
3	The concentration of ClO_2 mg/L	0.00	0.02	0.10	0.40	0.80	1.20	1.60	2.00
	Absorbance	0.000	0.006	0.025	0.086	0.185	0.270	0.349	0.436

Linear regression was performed on the results in the above table in Microsoft Excel, and the regression curve was shown in Fig. 1.
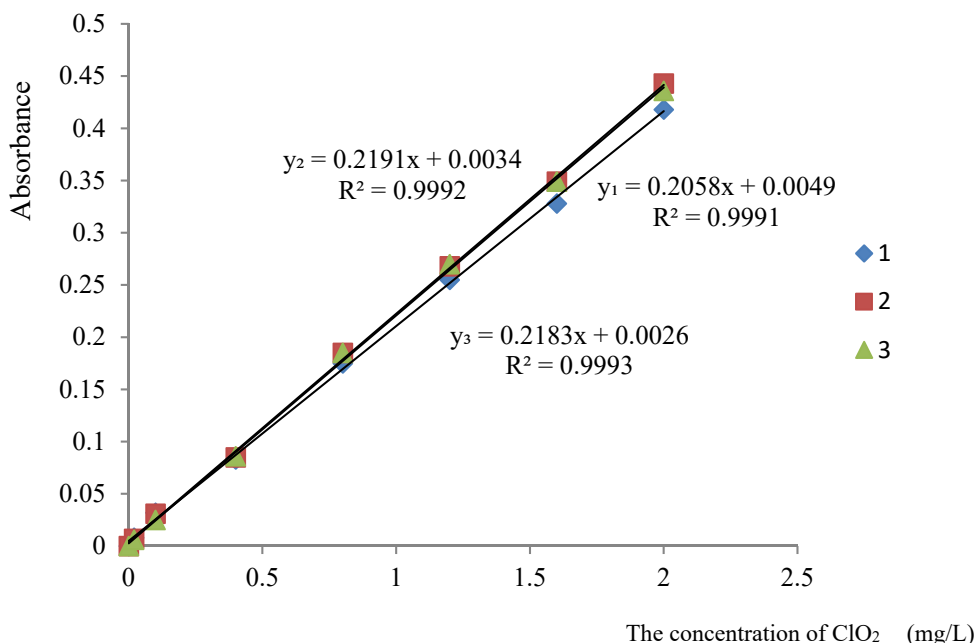

Fig. 1 Standard working curve

3.1.2 Linear test

The linear test is to check the precision of the calibration curve. In the concentration of 4 to 6 units, the measured value of the calibration curve was drawn, the related coefficient ｜r｜ is generally required as 0.9990 in spectrophotometry acuity, otherwise the reason and corrective must be found out, and the qualified calibration curve should be redrawn [12].

As can be seen from Fig.1, the linear correlation coefficients of the regression equation of the three tests were all greater than 0.999 after linear fitting of the test data, indicating that this method would have a good linear relationship and could be used for the direct

determination of water samples with a mass concentration of 0.02mg/L~2.00mg/L in drinking water after ClO_2 disinfection.

3.2 Methods to evaluate

3.2.1 Precision test

The precision of the method is the repeatability of the method, which refers to the degree of mutual agreement between the measured values if the same sample is repeatedly determined. The standard deviation (S) and the relative standard deviation (RSD) of the samples are the parameters to measure the dispersion degree of the repeated data, and precision is an important symbol to measure the reliability of the method.

The precision is calculated by the following formula:

Arithmetic mean:
$$\bar{x}=\frac{1}{n}\sum_{i=1}^{n}x_i \qquad (1)$$

Standard deviation:
$$S=\sqrt{\frac{1}{n}\sum_{i=1}^{n}(x_i-\bar{x})^2} \qquad (2)$$

Relative standard deviation:
$$RSD=\frac{S}{\bar{x}} \qquad (3)$$

Seven parallel tests were carried out on ClO_2 solutions with concentrations of 0.10, 1.00 and 1.50mg/L, respectively. The determination results were shown in Table 2, and the precision was evaluated. The RSD of the three ClO_2 solution concentrations were all controlled in the range of 1.37%~8.87%, which indicated that the precision of the method was good.

Table 2 ClO_2 precision test

Parallel number		Sample		
		0.10mg/L	1.00mg/L	1.50mg/L
	1	0.11	0.97	1.52
	2	0.10	0.97	1.53
Determination results (mg/L)	3	0.10	0.96	1.5
	4	0.11	0.96	1.52
	5	0.09	0.96	1.51
	6	0.09	0.99	1.49
	7	0.11	1.01	1.47

3.2.2 Standard recovery test

ClO_2 was added to tap water and the standard recovery experiment was carried out according to the procedure of sample determination in 1.3.2. Scalar add 0.1ml, 0.4ml and 0.1ml of 20mg/L ClO_2 solution to 10ml tap water disinfected with ClO_2 as a standard sample, and measure each scalar by 3 times. The test results are shown in Table 3. The recovery rates were between 96.67~110% and the accuracy was high.

Table 3 Recovery rate experiment of spiked standard

Parallel number		Actual sample					
		Sample 1/mg/L		Sample 2/mg/L		Sample 3/mg/L	
		Sample	Add the sample	Sample	Add the sample	Sample	Add the sample
	1	0.12	0.33	0.90	1.69	0.22	0.43
Determination results (mg/L)	2	0.13	0.34	0.92	1.70	0.21	0.43
	3	0.13	0.33	0.93	1.68	0.22	0.45

3.2.3 The detection limit of the method

The detection limit of a method is the minimum detection concentration, which is defined as the minimum content or concentration of the component required only one analytical signal to confirm the presence of the component under test in the sample. The general meaning of "confirmation" in statistics refers to confirming the detection component in the sample under

a certain confidence probability (generally 95% or 90%). Detection limit and sensitivity are two indicators indicating the sensitivity of the detector to the measured substance from different perspectives. The lower the former is, and the higher the latter is, indicating the better performance of the detector.

According to the technical guidelines for the revision of the HJ168-2010 standard for analysis of environmental testing methods, n ($\geq$7) blank tests were repeated following all steps of sample analysis. The test

results are shown in Table 2-1. The detection limit of the method is calculated according to the following formula.

$$MDL= t (n-1,0.99) \times S \qquad (4)$$

Type:

MDL: method detection limit;

n: number of parallel measurement of the sample;

t: T distribution (unilateral) when the degree of freedom is n-1 and the confidence is 99%;

S: standard deviation of n measurements.

As can be seen from the test results in Table 4, the lower limit of detection for the results of seven parallel tests was 0.007mg /L. The detection limit of this spectrophotometric method for the determination of ClO_2 solution concentration was 0.002mg/L, which shows that the sensitivity of this method is very high. Substitute the detected lower limit absorbance value of 0.007 into the three linear equations in Figure 1 to calculate the lower limit of determination as 0.01mg/L, 0.02mg/L and 0.02mg/L respectively, and select 0.02mg/L as the lower limit of determination of this method.

Table 4 Method detection limit test

Parallel sample number	1	2	3	4	5	6	7
Determination results	0.008	0.007	0.008	0.007	0.007	0.008	0.007

4 Conclusions

(1) This method can realize the rapid on-site detection of ClO_2 content in drinking water by adding improved solid DPD. It has characteristics of fast and convenience, and is expected to be popularized. It can be used for the direct determination of water samples with a mass concentration of 0.02mg/L~2.00mg/L in drinking water after ClO_2 disinfection.

(2) The method was evaluated by linear relation, precision and detection limit tests. The results show that this method has good precision and sensitivity. The linear correlation coefficients of the cubic regression equation were all greater than 0.999. The detection limit of this method was 0.002mg/L ClO_2. The RSD of seven parallel tests was controlled from 1.37% to 8.87%. The recoveries were 96.67~110%, and the accuracy was high.

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