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A new sensitive and selective fluorescence method for determination of chlorine dioxide in water using rhodamine S

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Abstract

A new simple, selective and sensitive method for the determination of trace chlorine dioxide in water has been developed, based on the oxidation by chlorine dioxide to reduction the fluorescence of rhodamine dyes in ammonia–ammonium chloride buffer solution. Four rhodamine dyes systems such as rhodamine S, rhodamine G, rhodamine B and butyl-rhodamine B were tested. The rhodamine S system is the best, with a linear range of 0.0060–0.450 μg mL^{-1} and a detection limit of 0.0030 μg mL^{-1} ClO_2. It was applied to the determination of chlorine dioxide in synthetic samples and real samples, with satisfactory results. This method has good selectivity, especially, other chlorine species such as chlorine, hypochlorite, chlorite and chlorate do not interfere the determination. The mechanism of fluorescence reduction was also considered.

Keywords: Chlorine dioxide; Rhodamine S; Fluorescence method

1. Introduction

It is widely known that chlorine is the most widely used chemical disinfectant for the treatment of drinking water. However, the chlorination of water often results the formation of carcinogenic trihalomethanes (THMs) [1,2]. In order to comply with the maximum contaminant level for total THM content, many countries are switching to alternative oxidants for water disinfections. Chlorine dioxide is the most attractive alternatives, because the formation of trihalomethanes hardly occurs during the disinfecting process when chlorine dioxide (ClO_2) is used [3,4]. The use of chlorine dioxide as an alternative disinfectant for drinking water has become increase in many countries, owing to its effectiveness and discarcinogenicity. However, a higher concentration of ClO_2 in drinking water is also harmful to human body [5]. Thus, it is very important to determine ClO_2 in drinking water, and a simple, sensitive and selective method for the determination is required.

At present, there are many methods for ClO_2 determination, including spectrophotometry, iodiometry, flow injection analysis (FIA), high-performance liquid chromatography (HLC), amperometric titrimetry, biochemical method, electrochemical method, fluorophotometry, etc. The *N*, *N*-diethyl-*p*-phenylenediamine (PDP) method [6] is based on the oxidation of I^- to I_2 by chlorine dioxide and the further reaction of I_2 with DPD to form a color compound. This method has high sensitivity. But the repeatability is poor because the stability of the color compounds can be expected to be light, and the selectivity is not satisfactory because the determination was interfered by other chlorine species. Furthermore, a PDP gives toxic consequences. The iodiometric method [7] is often used for titration of high concentration of chlorine dioxide standard solution. It is not suitable for the determination of low concentration of chlorine dioxide. Chen et al. [8] described a selective method for determination of 0–500 μg mL^{-1} chlorine dioxide in water by FIA, using chlorophenol red (CPR). Other chlorine species such as chlorite and chlorate do not interfere the determination. The detection limit of 20 μg mL^{-1} seem to be high. Watanabe [9] proposed a method for simultaneous

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determination of 1–20 μg mL^{-1} ClO_2 and 47–200 μg mL^{-1} ClO^- by HPLC with the detection limits of 0.2 μg mL^{-1} ClO_2 and 10 μg mL^{-1} ClO^-, respectively. Aieta et al. [10] suggested a amperotitrometric method for simultaneous determination of Cl_2, ClO_2, $ClO_2{}^-$ and $ClO_3{}^-$ using phenyl arsine oxide or sodiumhyposulfite as titrant. This method has a professional requirement for operators and the procedure was tedious. Based on the capacity of horseradish peroxidase to decolorize reactive yellow 17 in the presence of chlorine dioxide, Raunel et al. [11] proposed a biochemical method for determination of 0.2–4 μg mL^{-1} ClO_2 with a detection limit of 0.2 μg mL^{-1}. This method is faster and easier than the previous volumetric, amperometric and colorimetric methods; but chlorine has a serious interference with the determination. Quentel et al. [12] developed an electrochemical method to determine trace chlorine dioxide in water with a detect limit of 2 μg mL^{-1}. This method was based on the capacity of chlorine dioxide decolorize acidalizarin sulfoacid. Fluorescence method has good selectivity and sensitivity. However, there are very few fluorescence methods available for determination of chlorine dioxide. With high fluorescence efficiency and excellent stability, rhodamine dyes have been widely used in specotrophotometry, fluorescence, single sweep polarography and resonance scattering spectral [13–17]. In this paper, we developed a selective and sensitive fluorescence quenching method for determination of trace chlorine dioxide in drinking water using rhodamine S. In addition, the other rhodamine dyes, including rhodamine G, rhodamine B and butyl-rhodamine B, were tested and the mechanism of the fluorescence reduction was studied as well.

2. Experimental

2.1. Apparatus

A Shimadzu RF-540 spectrofluorophotometer (Kyoto, Japan) was used for recording the spectra and making fluorescence measurements. A 722S spectrophotometer (Shanghai, China) was used for the measurement of ClO_2 content. A model JP-2 single sweep oscillopolarograph (Chendu Instrument Factory, China), with a three-electrode system (dropping mercury electrode as working electrode, SCE as reference electrode and Pt wire as auxiliary electrode), was used for measuring the oxidation potential of Rh.

2.2. Reagents

ClO_2 standard solution: a stock solution containing about 40 μg mL^{-1} ClO_2 was prepared with a laboratory scale generator by the reaction between sodium chlorite and sulfuric acid [18]. Its concentration was standardized by iodimetry [7] and its molar absorptivity (1230 mol L^{-1} cm^{-1}) was calculated from its absorbance at 360 nm. The chlorine dioxide concentration was also calculated by its absorbance at 360 nm with the 1230 mol L^{-1} cm^{-1} absorptivity. The standard solution was stored in a cool dark place (4 °C). The working solution of 2.56 μg mL^{-1} ClO_2 was obtained by diluting the stock solution appropriately just before use. Ammonia–ammonium chloride buffer (Michelis buffer) solution was prepared by mixing 0.5 mol L^{-1} ammonia and 0.5 mol L^{-1}ammonium chloride solution appropriately. A 2.00×10^{-5} mol L^{-1} rhodamine 6G (RhG), 2.00×10^{-5} mol L^{-1} rhodamine S (RhS), 1.00×10^{-4} mol L^{-1} rhodamine B (RhB) and 2.00×10^{-5} mol L^{-1} butyl-rhodamine B (b-RhB) were prepared. All of the reagents were of analytical grade and all of the water used throughout was distilled doubly.

2.3. General procedure

In a 10 mL marked test tube, place certain volume of Michelis buffer and certain volume of rhlodamine dye orderly. The mixture was diluted to about 4 mL with doubly distilled water and mixed. To this solution, appropriate volume of standard ClO_2 solution was added and the solution was diluted to the mark of 5 mL with doubly distilled water and mixed thoroughly. The fluorescence intensity (F) was measured at maximum emission wavelength of each system against a reagent blank (F_0), the value of ΔF ($= F - F_0$) was calculated. For RhS, RhG, RhB and b-RhB system, the fluorescence intensities were measured at 546, 546, 576 and 576 nm, with excitations wavelength at 526, 558 and 558 nm, respectively.

3. Results and discussion

3.1. Excitation and fluorescence spectra

As in Figs. 1 and 2, the excitation and the fluorescence spectra for RhS system show that there are a max excitation peak at 526 nm and a fluorescence peak at 546 nm for different concentration of ClO_2. Therefore, the fluorescence intensity of RhS system was measured at 546 nm with excitation wavelength of 526 nm. For RhG, RhB and b-RhB, the fluorescence intensities were measured at 546, 576 and 576 nm, with excitation wavelength 526, 558 or 558 nm, respectively. With increasing of ClO_2 concentration, the fluorescence intensity of the four systems all decrease.

3.2. Optimum conditions for fluorescence quenching

3.2.1. Effect of pH value

The effect of pH value on ΔF was studied in the range of 7.5–11.2. When pH value is in the range of 8.0–10.0, the ΔF values of RhS and RhG system reach their maximum and keep relatively stable. Thus, the pH value 9.5 was chosen for the two systems. When pH value is 10, the ΔF of both RhB and of b-RhB systems reach their maximum. Therefore, the pH value 10 was selected for the two systems.

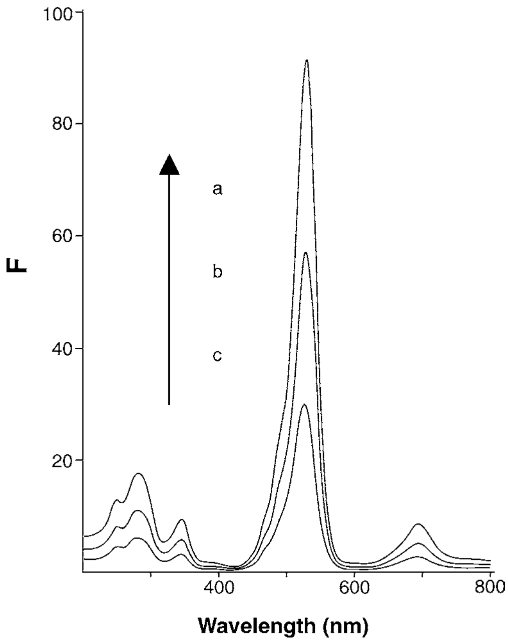

Fig. 1. Excitation spectra for RhS system: (a) pH 9.5–4.8 × 10^{-6} mol L^{-1} RhS, (b) 0.20 μg mL^{-1} ClO_2 and (c) 0.40 μg mL^{-} ClO_2. Low sensitivity, ordinate scale 5.

3.2.2. Effects of buffer volume

As ammonia–ammonium chloride buffer (Michelis buffer) is effective in eliminating free chlorine interference [19], it was also used to control pH at 9.5 or 10 in this work. The influence of Michelis buffer volume on ΔF was also tested. When the buffer volume is greater than 0.30 mL both for RhS and for RhG, 1.0 mL for RhB and 1.3 mL for b-RhB, all of their ΔFs reach its max and keep stable. Therefore, 1.0 mL buffer solution for RhS and RhG, 1.3 mL for RhB and 1.6 mL for b-RhB were used, respectively.

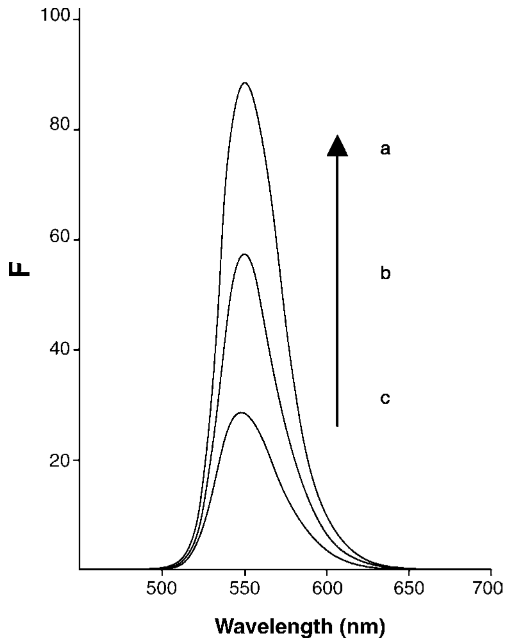

Fig. 2. Fluorescence spectra for RhS system. The conditions are same as that of Fig. 1.

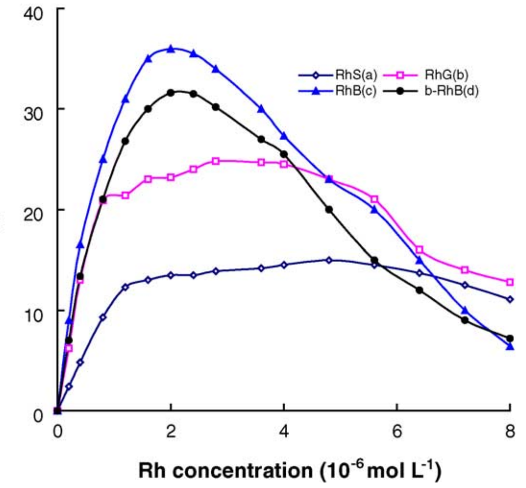

Fig. 3. Effects of Rh concentration: (a) 0.229 μg mL^{-1} ClO_2, pH = 9.5, ordinate scale 4; (b) 0.377 μg mL^{-1} ClO_2, pH = 9.5, ordinate scale 4; (c) 1.62 μg mL^{-1} ClO_2, pH = 10, ordinate scale 6; (d) 1.62 μg mL^{-1} ClO_2, pH = 10, ordinate scale 6. Low sensitivity.

3.2.3. Effect of rhodamine

The influences of Rh concentration on ΔF were also studied. From the results showed in Fig. 3, it can be seen that, for RhB and b-RhB system, when the Rh concentration is 2.0 × 10^{-6} mol L^{-1}, the ΔF values both of the two systems reach their maximum. Hence, 2.0 × 10^{-6} mol L^{-1} RhB and 2.0 × 10^{-6} mol L^{-1} b-RhB are chosen. For RhS and RhG system, when the Rh concentrations are 1.6 × 10^{-6} to 3.6 × 10^{-6} mol L^{-1} RhG and 1.6 × 10^{-6} to 5.6 × 10^{-6} mol L^{-1} RhS, their ΔF is relatively constant. Therefore, a concentration of 2.8 × 10^{-6} mol L^{-1} RhG and 4.8 × 10^{-6} mol L^{-1} RhS were selected, which give wider linear range.

3.3. Stabilities

The effects of reaction times on ΔF value were tested. It was found that it needed less time to reach the maximal ΔF for RhS and RhG systems than that for RhB and b-RhB. In other words, reactions between RhS or RhG and chlorine dioxide is rapider than that between RhB or b-RhB and chlorine dioxide, which may be interpreted by the molecular structure differences between the four dyes. The fluorescence intensities were measured at about 5 min for RhS and RhG system or 15 min for RhB and b-RhB system later. After reaching their maximum, the ΔF values were stable to at least 50 min.

3.4. Calibration graphs

The calibration graphs for the determination of chlorine dioxide were constructed under the optimum conditions (Fig. 4). The results are listed in Table 1. From Table 1, it can

Table 1
Comparison of the four systems for determination of ClO_2

Systems	Wavelength (nm)	Linear regression equation (C: μg mL^{-1})	Linear range (μg mL^{-1})	Correlation coefficient, r	Detection limit (μg mL^{-1})
RhS	546	$\Delta F = 157.10 \times C + 0.4$	0.0060–0. 450	0.9996	0.003
RhG	546	$\Delta F = 65.96 \times C - 0.4$	0.0373–0.996	0.9998	0.027
RhB	576	$\Delta F = 20.32 \times C + 0.4$	0.0830–3.06	0.9998	0.064
b-RhB	576	$\Delta F = 14.62 \times C + 0.2$	0.139–2.50	0.9990	0.123

Table 2
Selectivity of the method ($ClO_2 = 0.288$ μg mL^{-1})

Coexistent substance	Content (μg mL^{-1})	Relative error (%)	Coexistent substance	Concent (μg mL^{-1})	Relative error (%)
Na^+, Cl^-	9200	+0.7	$SO_4{}^{2-}$, Na^+	19200	+7.3
K^+, Cl^-	15600	+0.6	$NO_3{}^-$, Na^+	18600	+0.6
Ca^{2+}, Cl^-	240	+9.3	Ac^-, Na^+	3540	+7.3
Mg^{2+}, Cl^-	192	+4.7	$SO_3{}^{2-}$, Na^+	2400	+3.6
Zn^{2+}, $SO_4{}^{2-}$	26	+7.0	$PO_4{}^{3-}$, Na^+	190	+6.2
Cu^{2+}, $SO_4{}^{2-}$	6	+4.2	NaC_2O_4	500	+8.7
Ba^{2+}, Cl^-	680	+7.2	$CO_3{}^{2-}$, Na^+	120	+1.3
Al^{3+}, $SO_4{}^2$	80	+3.3	$ClO_3{}^-$, Na^+	750	+9.5
Ni^{2+}, $SO_4{}^2$	10	+8.4	Cl_2	27	+2.3
Fe^{3+}, Cl^-	5	+6.2	ClO^-, Na^+	18	+4.6
F^-, Na^+	380	+4.8	$ClO_2{}^-$, Na^+	81	+3.1

Table 3
Results for the determination of ClO_2 in synthetic samples

Samples	Content (μg mL^{-1})	Found (μg mL^{-1})	Recovery (%)	R.S.D. ($n = 5$) (%)
1	ClO_2 0.117, $ClO_3{}^-$ 2.3, $ClO_2{}^-$ 1.2, Cl_2 2.6, Na^+ 220, K^+ 340, Ca^{2+} 20, Mg^{2+} 19, $NO_3{}^-$ 570	0.112 ± 0.003	95.7	2.6
2	ClO_2 0.236, $ClO_3{}^-$ 3.5, ClO^- 1.8, Na^+ 220, K^+ 420, Zn^{2+} 4, Mg^{2+} 19, $NO_3{}^-$ 600, $SO_4{}^{2-}$ 480, $PO_4{}^{3-}$ 20	0.240 ± 0.005	101.7	2.1
3	ClO_2 0.368, $ClO_3{}^-$ 4.6, $ClO_2{}^-$ 1.2, ClO^- 2.7, Cl_2 2.6, Na^+ 360, K^+ 580, $NO_3{}^-$ 900, $CO_3{}^{2-}$ 12, $PO_4{}^{3-}$ 20	0.379 ± 0.006	103.0	1.6

be seen that the RhS method is the most sensitive. Its detection limit even reaches 0.0030 μg mL^{-1} ClO_2. The relative standard deviation for 0.15 and 0.30 μg mL^{-1} ClO_2 was 2.1 and 1.7%, respectively (10 replicates). The RhS method was used for the determination of chlorine dioxide in this work.

3.5. Selectivity of the method

In order to examine the effect of foreign ions on the determination of chlorine dioxide, the influence of a number of ions was investigated according to the recommended procedure at a concentration of 0.288 μg mL^{-1} ClO_2. The tolerance limit is defined as the content of substance that gives a relative error not more than ±10%. The results are summarized in Table 2. It can be seen that most of the ions normally present in water and other chlorine species such as free chlorine, hypochlorite ions, chlorite ions and chlorate ions do not interfere with the determination, which demonstrate the method has high selectivity.

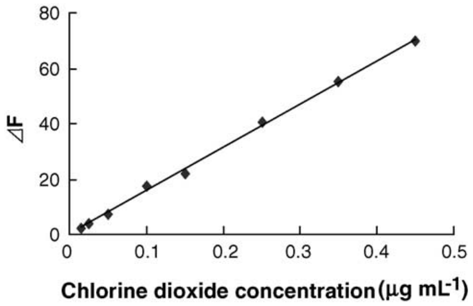

Fig. 4. Calibration graph for RhS system: 4.8×10^{-6} mol L^{-1} RhS, pH = 9.5, ordinate scale 4. Low sensitivity.

3.6. Sample analysis

The method developed was applied to determination of chlorine dioxide in synthetic samples, which contain some inorganic ions and some other chlorine species, such as chlorine, hypochlorite, chlorite or chlorate ions, etc. The results were given in Table 3. The recovery is 95.7–103.0% and the R.S.D. is 1.6–2.6%. This method was used to the determination of chlorine dioxide in water samples, as well. The results of the proposed method and the spectrophotometric method [18] were presented in Table 4. Student's t-test shows that the results of the proposed and the spectrophotometry are equal within 95% confidence level. It can be seen that the

Table 4
Results for the determination of ClO_2 in water

Samples	Found ($\mu g\,mL^{-1}$)	Average ($\mu g\,mL^{-1}$)	R.S.D. ($n = 5$) (%)	Spectrophotometry ($\mu g\,mL^{-1}$)
1	0.932, 0.10, 0.917, 0.901, 0.958	0.924 ± 0.022	2.4	0.952
2	1.74, 1.72, 1.76, 1.71, 1.67	1.70 ± 0.026	1.5	1.75
3	3.78, 3.72, 3.74, 3.76, 3.83	3.77 ± 0.041	1.1	3.86

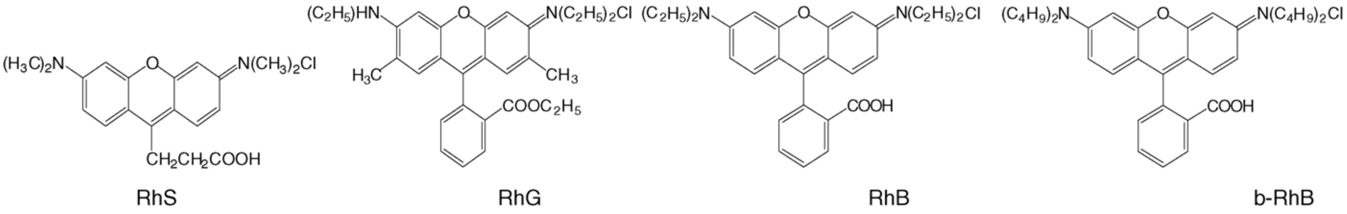

Fig. 5. Molecular structures of the four rhodamine dyes.

results were in good agreement with that obtained by the spectrophotometry, indicating that this method has the potential for practical application to the determination of ClO_2 in water.

3.7. Mechanism of the fluorescence reduction

Rhodamine dyes are triphenlymethene dyes, which have rigidity planes with quinoid structure and emit very strong fluorescence. As oxidized by such strong oxidizer as chlorine dioxide, its molecular structure is destroyed and the fluorescence disappears [20,21]. It is clear that the reaction between Rh and chlorine dioxide in solution is redox reactions. There are some differences between the four dyes. As a result, the sensitivities of the four systems are various in Table 1, from which, it can be seen that RhS system is the most sensitive in the four systems, and RhG system is more sensitive than both RhB and b-RhB systems, which may be explained by the differences between their molecular structures (Fig. 5). The results were also approved by electrochemical experiment, which show the polarographic peak potentials for RhS, RhG, b-RhB and RhB are −0.95, −0.78, −0.64 and −0.55 V [22,23], respectively, in 0.05 mol L^{-1} sulfuric acid (pH = 1.0).

All of the four dyes have conjugated plain structures. RhS has a propionyloxy connected to ‘7’ position. Propionyloxy is electron-donating group, which augments the charge density of the conjugated system. Unlike RhS, there is a more benzoic acid (on ‘7’ position) for the molecular structures of RhG, RhB or b-RhB. As a result, a larger conjugated is formed. Because phenyl group is electron-defect group, the charge densities of the conjugated systems of RhG, RhB or b-RhB were reduced. Therefore, the charge density of conjugated system of RhS molecule is higher than that of RhG, RhB or b-RhB. As a result, it is easier to be oxidized by chlorine dioxide for RhS than for RhG, RhB or b-RhB. Compared with the conjugated system structure of RhB or b-RhB, there are two more methyl connected to that of RhG (4 and 10 position). Methyl is electron-donating group, which augment the charge density of the conjugated system of RhG. As a result, the charge density of the conjugated system of RhG molecule is higher than that of RhG, RhB or b-RhB, and RhG can be oxidized more easily by chlorine dioxide than RhB or b-RhB. Thus, the RhG system is more sensitive than RhB or b-RhB.

4. Conclusions

Based on the oxidation of rhodamine dyes by chlorine dioxide in Michelis buffer solution, a new fluorescence quenching method was developed to the determination of chlorine dioxide. Four rhodamine dyes were considered. For RhS, RhG, RhB and b-RhB systems, the linear ranges are 0.0060–0.450, 0.0373–0.996, 0.0830–3.06 and 0.139–2.50 $\mu g\,mL^{-1}$ ClO_2 and the detection limits are 0.0030, 0.027, 0.064 and 0.123 $\mu g\,mL^{-1}$, respectively. The determination is not much affected by normal ions present in water and other chlorine species, such as chlorine, hypochlorite, chlorite and chlorate. The sensitive RhS fluorescence method has been applied to the determination of chlorine dioxide in synthetic samples and real samples. The mechanism of the fluorescence quenching was discussed.

Acknowledgements

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