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A novel and selective spectral method for the determination of trace chlorine in water basing on the resonance scattering effect of rhodamine B–I_3 association nanoparticles

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Abstract

In Na_2HPO_4–citric acid buffer solution, Cl_2 can oxidize I^- to form I_2 and then it reacts with excess I^- to form I_3^-. The I_3^- combines respectively with rhodamine dyes, including rhodamine B (RhB), butyl rhodamine B (b-RhB), rhodamine 6G (RhG) and rhodamine S (RhS), to form association particles which give stronger resonance scattering (RS) effect at 400 nm. The RS intensity of the RhB, b-RhB, RhG and RhS systems is proportional to chlorine concentrations in the range of 0.008–1.74, 0.019–1.33, 0.021–2.11 and 0.019–2.04 μg/mL Cl_2, respectively. The detection limits of the systems were 0.0020, 0.0048, 0.0063 and 0.0017 μg/mL, respectively. In them, the RhB system has good stability and high sensitivity, and has been applied to the analysis of chlorine in drinking water, with satisfactory results which is in agreement with that of the methyl orange (MO) spectrophotometry.

Keywords: Chlorine; Rhodamine B; KI; Association particles; Resonance scattering

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1. Introduction

Chlorine is a commonly used chemical disinfectant and bleacher, which is widely used in treatment of drinking water, industrial circle water and wastewater. Recent studies have shown that the process of chlorine reacting with organic matter in water leads to the formation of alkylhalide, a carcinogenic substance. Thus, it is very important to establish a new, simple and rapid, highly selective and sensitive method for determination of chlorine in drinking water. At present, there are several methods for Cl_2 determination, including iodiometry [1], spectrophotometry [2–6], atomic emission spectrometry (AES) [7], chemical sensor [8,9], ion chromatography [10], chemiluminescence method [11], etc. The iodometric method is often used for titration of chlorine standard solution [1], but its selectivity and sensitivity are poor for the determination of drinking water sample. Methyl orange (MO) is a preferable spectrophotometric reagent for the determination of 0.02–1.2 μg/mL Cl_2, with a detection limit of 0.01 μg/mL [2]. The *N*,*N*′-diethyl-*p*-phenlenediamine (DPD) is also a most frequently used spectrophotometric reagent [3]. The DPD has been also suggested as a reagent for the flow-injection spectrophotometric determination of 0.1–10 mg/L Cl_2 with a detection limit of 0.05 mg/L [4]. The flow and sequential injection spectrophotometric determination of 0.2–3.0 mg/L Cl_2 and 0.5–5.0 mg/L Cl_2 with *o*-tolidine in greywater has been described [5]. In this determinations employing MO and *o*-tolidine, the use is largely restricted because of its carcinogenic properties [6]. A simple method is described for the determination of low concentration of chlorine by atmospheric-pressure helium microwave-induced plasma atomic emission spectrometry (He MIP-AES) [7]. The detection limits for chlorine at 439.0, 479.4 and 481.0 nm were found to be 29.9, 6.8 and 12.3 ng/mL. However, the lowest

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concentration range was limited mostly by spectral background noise, for example, the linear range for 479.4 nm is about 0.05–50 mg/L. An optochemical sensor for determination of 0.05–5.0 mg/L chlorine has been developed by immobilizing *o*-tolidine in a silicone-polycarbonate copolymer membrane [8]. However, the sensor response was influenced by air humidity. A simple flow injection analysis system for 0.1–1.0 mg/L chlorine in tap water was described by using a Pb(II) ion-selective electrode (Pb ISE) detector [9]. The shortage is that it is affected by Cu(II) ion. An ion chromatographic method is developed for the determination of 0.01–24 mg/L Cl_2 [10]. A sensitive chemiluminescence method was described for the determination of free chlorine with Rhodamine 6G in aqueous solution [11]. A detection limit of 0.090 mg/L was obtained for free chlorine.

Resonance scattering spectral (RSS) method has characteristics such as high sensitivity, good selectivity and simplicity and convenience [12–15]. It has been applied to analysis of trace NO_2^- [16], Se [17], and so on. Recently, inorganic nanoparticle, complex particle and association particle RS effect has been studied by our research group [18]. But up to now, there is no RSS method for determination of chlorine, based on the RS effect of association complex particles. Rhodamine dye (Rh) is a type of good analytical and stable reagent that have been used for the determination of ruthenium, phosphate, oxalic acid and chlorine dioxide with spectrophotometry, spectrofluorimetry, polarography and RSS method [19,20]. In this work, it has been found that, in Na_2HPO_4–citric acid buffer, I_3^- formed by the reaction of Cl_2 to excess I^- reacts with Rh^+ to form association particles which has strong RS effect. The chlorine concentration in certain range is linear to the RS intensities of the RhG, RhS, RhB and b-RhB systems, respectively. A novel RSS method has therefore been proposed for determination of chlorine using RhB. This method has some advantages such as simplicity, high sensitivity and good selectivity.

2. Experimental

2.1. Reagent and apparatus

Cl_2 standard solution: a stock solution containing about 300 μg/mL Cl_2 was prepared with a laboratory scale generator by the reaction between solid $KMnO_4$ and concentrated hydrochloric acid [1]. Chlorine concentration was standardized by iodimetry and was stored in icebox (4 °C). The working solution of 20.0 μg/mL Cl_2 was obtained by diluting the standard solution. A 0.02 mol/L KI solution and Na_2HPO_4–citric acid buffer solutions were prepared. A 1.00×10^{-4} mol/L rhodamine B (RhB), rhodamine 6G (RhG), rhodamine S (RhS) and 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. A model of Shimadzu RF-540 spectrofluorophotometer (Shimada, Japan) was used to record the intensity of RS, and RS spectrum that the excited wavelength λ_{ex} is equal to the emission wavelength λ_{em}. A model TU-1901 spectrophotometer (Beijing Puxi, China) was used to record absorption spectrum. A model JSM-6330 scanning electron microscope (SEM) (Electron Co., Japan) was used to record the SEM micro-photo.

2.2. Procedure

A 0.60 mL pH 4.0 Na_2HPO_4–citric acid buffer solution (or 0.80 mL pH 6.6, 1.0 mL pH 7.0, 1.0 mL pH 7.6), 0.8 mL 0.02 mol/L KI solution (or 0.8, 1.0 and 1.0 mL), and certain volume of chlorine solution were added successively to a 10-mL marked tube. The solution was mixed and left to stand for 5 min, then 2.0 mL 1.0×10^{-4} mol/L RhB (or 2.0 mL b-RhB, 1.5 mL RhS, 1.5 mL RhG)was added. The solution was diluted to 5 mL with doubly distilled water and mixed thoroughly. The RS spectra of the systems were obtained on the spectrofluorophotometer and the RS intensity I_{RS} of the RhG, RhS, RhB and b-RhB systems at 400 nm were measured, respectively.

3. Results and discussion

3.1. Principle

Under the conditions of the procedure, the I_3^- was formed by the reaction of chlorine with I^-. The Rh^+ and I_3^- combine with Rh–I_3 association complex molecule. These molecules aggregate spontaneously to association particles, owing to the strongly hydrophobic and intermolecular forces between the molecules. SEM shows that the means diameter of $(RhB–I_3)_n$ association particles is 66 ± 5 nm. The association particle gives strong RS effect, fluorescence quenching, and hypochromatic color effect [16]. Known concentration (C_p) of association particles is directly proportional to resonance scattering light intensity (I_{RS}) [16], namely $I_{RS} = k_{RS}C_p$, and the k_{RS} is a constant. According to the relationship between the Cl_2 concentration C_{Cl} and the association particles concentration is $C_{Cl} = nC_p$, namely,

$$I_{RS} = \left(\frac{k_{RS}}{n}\right) C_{Cl}$$

The above equation indicates that when other conditions hold constant, Cl_2 concentration is proportional to resonance scattering light intensity. According to it, a new resonance scattering spectral method can be established for the determination of Cl_2.

3.2. Resonance scattering spectrum

The synchronous fluorescence spectrum of Fig. 1a indicates that RhB has a synchronous fluorescence peak at

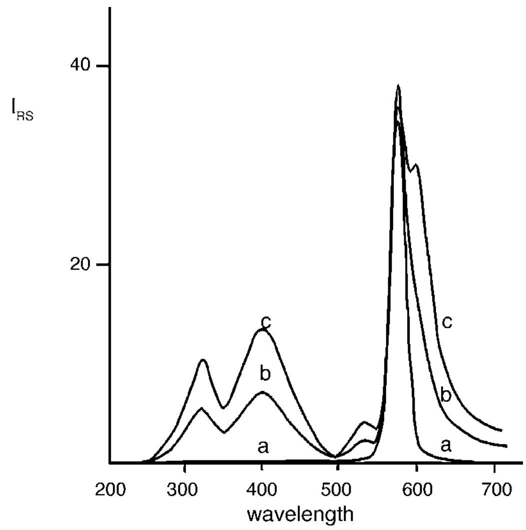

Fig. 1. Resonance scattering spectrum of the RhB system (a) pH 4.0: 4.0×10^{-3} mol/L KI–4.0×10^{-5} mol/L RhB; (b) a-0.342 μg/mL Cl_2; (c): a-0.684 μg/mL Cl_2.

575 nm. The synchronous scattering (SS) (or Rayleigh scattering) of the RhB, RhB–I^-, and ClO_2–I^- systems are very weak. After Cl_2 was added into the RhB–I^- system, the SS of the system (Fig. 1b and c) gives four SS peaks at 320, 400, 530 and 605 nm. Because of the influence of the SS of the association particle, the synchronous fluorescence peak at 575 nm becomes stronger. It is known that three factors including the light source of the apparatus, absorption of free molecule in the system and RS effect of particles cause SS peaks [16]. The strongest emission of the apparatus is at about 470 nm [21]. The absorption of the free molecule in the particle system causes the SS signal to decrease. However, the four SS peaks all become stronger, and there is no the four peaks if the particles is no existence. So that, the four SS peaks are RS peaks of $(RhB–I_3)_n$ association particles, and the SS spectrum including RS peak is called as RS spectrum. The RS peaks at 400 and 530 nm are stronger and cover the SS peak at 470 nm, so the SS peak at 470 nm cannot be observed in the system. The SS signals at lower than 250 nm are very weak. It may be owing to incidence light intensity of the light source being weak. Although the RS peak at 605 is stronger, the synchronous fluorescence peak greatly affects on it. So a wavelength of 400 nm was chosen for use in this work. Results show that the b-RhB association particle system has three RS peaks at 320, 400 and 605 nm and has a strongest synchronous fluorescence peak at 590 nm. The RhS association particle system has three RS peaks at 320, 400 and 550 nm and a strongest synchronous fluorescence peak at about 565 nm, and SS remarkably increase at more than 600 nm. For the RhG association particle system, there are two RS peaks at 320 and 400 nm and a strongest synchronous fluorescence peak at 560 nm and SS remarkably increase at more than 600 nm.

3.3. *Effect of pH value*

The effect of pH value on the ΔI ($=I_{RS} - I_B$, the I_B represents the blank value) was studied. The results indicate that, the effect of pH 2.0–8.0 on the ΔI value for the system of b-RhB, RhG and RhS, and the effect of pH 2.0–4.5 on the ΔI value for the RhB system are much small. It is owing to that the Cl_2 is a strong oxidant and I^- is a strong reductant in the pH range. The redox reaction does not affect by the pH. However, the pH value is in the range of 4.5–8.0, the ΔI value changes greatly, for the RhB system. This is related to the charges and hydrophobicity of RhB. A 0.60 mL pH 4.0, 0.80 mL pH 6.6, 1.0 mL pH 7.0 and 1.0 mL pH7.6 of the buffer solution were chosen for the RhB, b-RhB, RhG and RhS systems, respectively.

3.4. *Effect of KI volume*

The influences of KI concentration on ΔI were also studied. The results shown that the ΔI value of the systems gradually increase with the increasing of I^- concentration at first, and then when KI concentration is about 1.5×10^{-3} mol/L ΔI value reach their maximum and keep relatively stable with the increasing of I^- concentration. Hence, for RhB, b-RhB, RhG and RhS systems, a 3.0×10^{-3}, 3.0×10^{-3}, 4.0×10^{-3} and 4.0×10^{-3} mol/L KI were chosen, respectively.

3.5. *Effect of Rh concentration*

From Fig. 2, it can be found that the ΔI value gradually increases with the Rh concentration. When RhB, b-RhB, RhG and RhS concentration is about 1.0×10^{-5}, 3.0×10^{-5}, 1.0×10^{-5} and 3.0×10^{-5} mol/L, respectively, the ΔI value of the systems all reach their the maximum. Therefore, a concentration of 4.0×10^{-5} mol/L RhB, 4.0×10^{-5} mol/L b-RhB, 3.0×10^{-5} mol/L RhG and 3.0×10^{-5} mol/L RhS were selected, respectively.

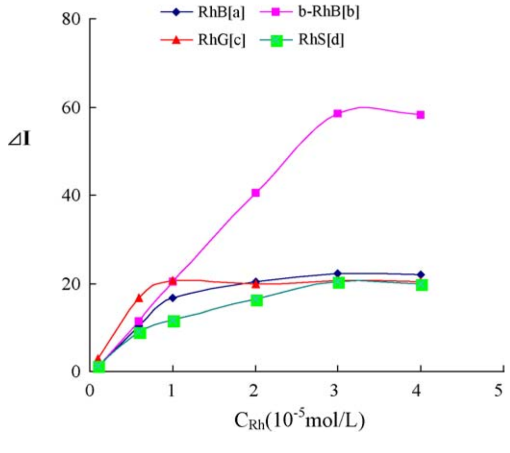

Fig. 2. Effect of Rh concentration (a) pH 4.0: 3.0×10^{-3} mol/L KI–0.78 μg/mL Cl_2, (b) pH 6.6: 3.0×10^{-3} mol/L KI–1.21 μg/mL Cl_2, (c) pH 7.0: 4.0×10^{-3} mol/L KI–0.578 μg/mL Cl_2, (d) pH 7.6: 4.0×10^{-3} mol/L KI–0.628 μg/mL Cl_2.

Table 1
Analytical features comparison of RS methods for Cl_2 with rhodamine dyes

System	Regress equation, C (μg/mL)	Linear range (μg/mL)	Correlation coefficient	Detection limit (3σ, μg/mL)
RhB	$\Delta I = 24.54C + 0.42$	0.008–1.74	0.9986	0.0020
b-RhB	$\Delta I = 53.74C - 0.50$	0.019–1.33	0.9990	0.0048
RhG	$\Delta I = 25.18C + 0.15$	0.021–2.11	0.9981	0.0063
RhS	$\Delta I = 24.89C - 0.13$	0.019–2.04	0.9989	0.0017

3.6. Stabilities of the four systems

According to the procedure, the effects of reaction times on ΔI value were examined. It was found that it reach the maxim ΔI value after about 3 min for the four systems. The ΔI value is stable at least 60 min for RhB. Whereas the stabile time of b-RhB, RhG and RhS systems were about 20 min and after the systems were stood for a period of time deposition easily occur. A 5 min was selected to record the I_{RS} value.

3.7. Calibration graph

Under the optimum conditions of the procedure, the analytical features of the four systems were examined as in Table 1. It can be seen from Table 1 that the detection limit of the RhB system is lower and the stability is better than that of the RhG, RhS and b-RhB system. Hence the RhB system is chosen for the measurement of chlorine content in water samples. Compared with the sensitivity and the selectivity of the reported analytical methods for chlorine [2,4,7–10], this RhB RSS method has high sensitivity and good selectivity and is one of best analytical methods for chlorine at present.

3.8. Effects of coexistence substances

According to the procedure, the effects of foreign substances on the RhB system were examined at a concentration of 0.142 μg/mL Cl_2. The tolerance limit is defined as the content of substance that gives a relative error not more than ±5%. The results are summarized in Table 2. It can be seen that most of the ions normally present in water do not interfere with the determination, and the tolerance of other chlorine species such as hypochlorite ions, chlorite ions and chlorate ions is comparatively higher, which demonstrate the method has good selectivity.

3.9. Analytical application

A suitable volume of sample solution was added to a 10-mL tube. The Cl_2 content in samples was determined as the RhB RSS procedure and the MO spectrophotometry, respectively. The results were given in Table 3. Student's *t*-test shows that the results of the proposed RSS method and the spectrophotometry are equal within 95% confidence level.

Table 2
Effects of coexistence substances (0.142 μg/mL Cl_2)

Coexistent substance	Tolerance limit (μg/mL)	Relative error (%)	Coexistent substance	Tolerance limit (μg/mL)	Relative error (%)
Ca^{2+}	800	+4.0	$SO_4{}^{2-}$	400	+5.0
Mg^{2+}	280	+2.5	F^-	500	+4.2
Zn^{2+}	120	+4.8	$NO_3{}^-$	340	+5.0
Cu^{2+}	20	+4.3	Ac^-	280	−4.6
Ni^{2+}	10	+5.0	$C_2O_4{}^{2-}$	1080	−4.3
Co^{2+}	8	+3.0	Urea	710	+2.9
Al^{3+}	500	+4.7	Tartrate	900	−4.4
Fe^{3+}	20	+4.3	$ClO_3{}^-$	2300	+4.9
Ba^{2+}	4500	+5.0	ClO_2	6	+2.3
Hg^{2+}	5	+4.2	ClO^-	1.8	+4.6
Mn^{2+}	80	+3.3	$ClO_2{}^-$	80	+3.1
$NH_4{}^+$	60	−4.3	Chloramine	2	+3.3

Table 3
Analytical results of Cl_2 in water samples

Samples	Single determination value (μg/mL)	Average value (μg/mL)	R.S.D. (%)	MO spectrophotometry (μg/mL, $n = 5$)
$1^{\#}$	0.152, 0.153, 0.152, 0.148, 0.151	0.151 ± 0.002	1.5	0.150 ± 0.003
$2^{\#}$	0.250, 0.258, 0.254, 0.254, 0.252	0.254 ± 0.002	0.77	0.255 ± 0.006
$3^{\#}$	0.477, 0.500, 0.480, 0.460, 0.470	0.477 ± 0.018	3.8	0.490 ± 0.009
$4^{\#}$	0.060, 0.066, 0.068, 0.068, 0.070	0.066 ± 0.003	5.3	0.067 ± 0.009
$5^{\#}$	0.082, 0.082 0.088, 0.089, 0.089	0.086 ± 0.004	4.3	0.088 ± 0.007

4. Conclusion

Based on the oxidation of I^- by chlorine in presence of Rh, four rhodamine dye association complex particle systems were considered. A new RhB RSS method was developed to determination of chlorine in the ranges of 0.008–1.74 μg/mL. The detection limits is 0.0020 μg/mL. The determination is not much affected by normal ions present in water and other chlorine species, such as hypochlorite, chlorite and chlorate. The sensitive RhB RSS method has been applied to the determination of chlorine in real samples, with satisfactory results.

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