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A novel, simple and sensitive resonance scattering spectral method for the determination of chlorite in water by means of rhodamine B

KANG Cai-yan[1,3], JIANG Zhi-liang[2,3,*], XI Dan-li[1,*], HE Xing-cun[3]

(1. College of Environmental Science and Engineering, Donghua University, Shanghai 200051, China; 2. Department of Material and Chemical Engineering, Guilin University of Technology, Guilin 541004, China; 3. School of Environmental Science and Resource, Guangxi Normal University, Guilin 541004, China. E-mail: zljiang@mailbox.gxnu.edu.cn; kcy621009@sina.com)

Abstract: A new resonance scattering method was proposed for the determination of chlorite, basing on the resonance scattering effect of rhodamine dye. In HCl-sodium acetate buffer solution, chlorite oxidizes I^- into I_2 and the reaction of I_2 and excess I^- results in I_3^-. It is respectively combined with rhodamine dyes, including rhodamine B (RhB), butyl rhodamine B (b-RhB), rhodamine G (RhG) and rhodamine S (RhS), to form association complex particles, which exhibit stronger resonance scattering (RS) effect at 400 nm. The chlorite concentration of ClO_2^- in the range of 0.00726—0.218 μg/ml, 0.0102—0.292 μg/ml, 0.00726—0.145 μg/ml and 0.0290—0.174 μg/ml is respectively linear to the RS intensity of association complex particle systems at 400 nm for the RhB, b-RhB, RhG and RhS. The detection limits of the four systems were respectively 0.00436, 0.00652, 0.00580 and 0.01450 μg/ml ClO_2^-. In the four systems, the RhB system possesses good stability and high sensitivity. It has been applied to the analysis of chlorite in wastewater with satisfactory results.

Keywords: chlorite; rhodamine dye; association complex particles; resonance scattering effect

Introduction

It is reported that chlorite may cause hemolytic anemia at a low level of exposure while higher levels of the exposure can result in an increase of methemoblobin (Drinking water and health, 1987). World Health Organization has published the guideline value of 0.02 mg/L for chlorite in drinking water (World Health Organization, 1996). Therefore, a simple and sensitive analytical method for the determination of chlorite in water is required. At present, several methods have been reported for the determination of chlorite, including spectrophotometry, amperometric titration, flow injection analysis, chromatography and electrochemical techniques. A spectrometric method based on the color change of indigo carmine had been used for the analysis of the chlorine species in water, with linear range of 0—0.51 mg/L and the detection limit of 0.036 mg/L ClO_2^- (Chriswell and Keller-Lehmann, 1993). The amperometric titration provided in the Standard Methods for the Examination of Water and Wastewater in America is a standard method for the determination of ClO_2^-, ClO_2, Cl_2 and ClO_3^- (Aieta *et al.*, 1984), the detection limit is 0.011 mg/L ClO_2^-. Themelis *et al.* (1989) determined the low concentration ClO_2^- and ClO_3^- using flow injection analysis, with the linear range of 0.1—10.1 mg/L ClO_2^- and 0.1—8.3 mg/L ClO_3^-. Chlorite can be also measured by on-line coupling of capillary isotachophoresis and capillary zone electrophoresis (Prous, 2004), with a detection limit of 0.012—0.017 mg/L. Denis *et al.* (1989) continuously monitored trace chlorite ion in water, based on anodic oxidation in pH 4.5 acetate buffer and the use of a gold electrode. The linear range is 0—1 mg/L ClO_2^- with a detection limit of 0.05 mg/L (Denis *et al.*, 1989). Nakareseison *et al.* (1988) determined chlorite using differential pulse polarography, with a linear range of 19 μg/L—19 mg/L and detection limit of 7 μg/L. However, many of the above methods can be labor intensive and suffer from limited sensitivity. The commonly recommended analytical method for the determination of chlorite in water is ion chromatography (IC) (Achminke and Seubert, 2000; Pfaff *et al.*, 1989, 1990). The detection limit for deioned water and drinking water was 700 ng/L and 3.5 μg/L, respectively (Achminke and Seubert, 2000). However, owing to its expensive cost and complex operation, it is difficult to be extensively spread and applied.

Resonance scattering spectral (RSS), with simple and sensitive characteristic (Pasternack *et al.*, 1995; Wang *et al.*, 2004; Huang *et al.*, 1996; Jia *et al.*, 2004), has been used to determine biological macromolecules, trace metal, nonmetal and organic substances (Pasternack *et al.*, 1993, 1995; Huang *et al.*, 1996; Liu *et al.*, 1999, 2000; Jiang *et al.*, 2005). However, up to now, it does not seem to have been used for determination of ClO_2^-. Rhodamine dyes is a type of major analytical reagent with stability, which has been used for the measurement of the trace Se, NO_2^- and chlorine dioxide using spectrofluorimetry, and RSS method (Liu *et al.*, 2000; Jiang *et al.*, 2002, 2005). In this paper, our studies suggest that ClO_2^- reacts with excess I^- to engender I_3^-, which combines

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*Corresponding author

Rhodamine' with form association complex particles with resonance scattering (RS) effect. The chlorite concentration, in a certain range, is respectively linear to the RS intensities of rhodamine B (RhB), rhodamine S (RhS), rhodamine G (RhG) and butyl rhodamine B (b-RhB) systems. In view of the above, a novel, simple, rapid, sensitive RSS method has been proposed for determination of chlorite in water using RhB.

1 Experimental

1.1 Reagent and apparatus

A model of Shimadzu RF-540 spectrofluorophotometer (Shimada, Japan) was used to record the intensity of RS, and RS spectrum that the excitation wavelength λ_{ex} is equal to the emission wavelength λ_{em}.

$NaClO_2$ standard stock solution: a sodium chlorite stock solution containing about 4 mg/ml ClO_2^- was prepared by dissolving 0.4 g $NaClO_2$ (A.R.) in distilled water and diluting quantitatively to 100 ml with distilled water. Chlorite concentration was standardized by 0.05 mol/L $Na_2S_2O_3$ standard solution and the solution was stored in icebox at 4℃. The working solution of 0.726 μg/ml ClO_2^- was prepared by appropriate diluting the standard solution before use. NaAc-HCl buffer solutions and 0.02 mol/L KI solution were prepared in distilled water. A 1.00×10^{-4} mol/L RhB, RhS, RhG and b-RhB solutions were prepared. All of the reagents were of analytical grade and all of the water used throughout was distilled doubly.

1.2 Procedure

In a 10-ml marked test tube, for RhB system, place 0.50 ml of pH 1.42 NaAc-HCl buffer solution (or 0.50 ml pH 1.85 for RhS system, 0.50 ml pH 1.42 for RhG, 0.50 ml pH 1.85 for b-RhB), 1.0 ml of 0.02 mol/L KI solution (or 1.00 ml, respectively, for RhS, RhG, b-RhB systems) and certain volume $NaClO_2$ solution orderly. The mixture was diluted to about 3 ml with doubly distilled water and mixed. The solution was left to stand for 5 min, then 1.5 ml 1.0×10^{-4} mol/L RhB (or 1.0 ml RhS, 1.5 ml RhG, 1.5 ml b-RhB) was added. The solution was diluted to 5 ml with doubly distilled water and mixed thoroughly. The RS spectra of the systems were obtained by spectrofluorophotometer and the RS intensity (I_{RS}) of the RhB, RhS, RhG and b-RhB systems at 400 nm were measured respectively.

2 Results and discussion

2.1 Resonance scattering spectrum

Fig.1a indicates that RhB-kI possesses a synchronous fluorescence peak at 580 nm. The synchronous scattering (SS; or Rayleigh scattering (RS)) of the RhB, RhB-I^- and ClO_2^--I^- systems are very weak. When ClO_2^- was added into the RhB-I^- system, owing to the formation of $(RhB\text{-}I_3)_n$ particles, the synchronous scattering signal is magnified. The synchronous emission spectra (Fig.1d) of the association-particle system indicate that there are four Rayleigh scattering peaks at 320, 400, 530 and 610 nm. Because of the influence of SS of the association complex particle, the synchronous fluorescence peak at 580 nm becomes stronger. It has been known that three factors causing SS peaks are light source of the apparatus, absorption of free molecule in the system and RS effect of particles (Jiang *et al.*, 2005). The strongest emission of the apparatus is at about 470 nm (Jiang *et al.*, 2002), while not at 320, 400, 530 and 610 nm. The absorption of the free molecule in the particle system causes SS signal to decrease. However, it can be seen from the synchronous emission spectra that the four SS peaks all become stronger, and there is no the four peaks without the particles. Therefore, the four SS peaks are RS peaks of $(RhB\text{-}I_3)_n$ association complex particles. The synchronous scattering spectrum can be called the resonance scattering spectrum. If the RS peaks at 400 and 530 nm were not stronger and did not cover the SS peak at 470 nm, a synchronous scattering peak at 470 nm would been observed. The SS signals at lower than 250 nm are very weak. The reason may be the weak incidence light intensity of the light source. Although RS peak at 610 nm is stronger, it is greatly affected by the synchronous fluorescence peak. So a wavelength of 400 nm was chosen for use in this work. Results show that the b-RhB association complex particle system exhibits three RS peaks at 320, 400, 605 nm and a strongest synchronous fluorescence peak at about 580 nm. The RhS association complex particle system has three RS peaks at 320, 400, 610 nm and a strongest synchronous fluorescence peak at about 550 nm. For the RhG association complex particle system, there are three RS peaks at 320, 400 and 600 nm and a strongest synchronous fluorescence peak at about 550 nm.

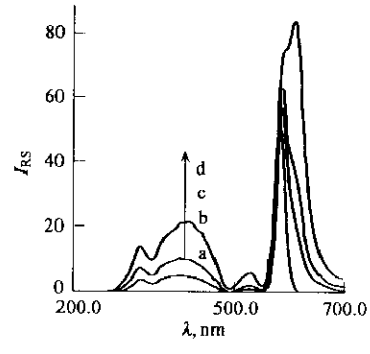

Fig.1 Synchronous emission scattering spectra of the RhB system
a. pH 1.42, 4.0×10^{-5} mol/L KI to 3.0×10^{-5} mol/L RhB; b. 0.0145μg/ml ClO_2^-; c. 0.0436 μg/ml ClO_2^-; d. 0.0726 μg/ml ClO_2^- (OR=5, S-2)

2.2 Effect of pH

The effect of pH value on the ΔI ($\Delta I = I_{RS} - I_B$, where, I_{RS} represents RS intensity, I_B represents blank value) shows that when pH is in the range of 0.65—3.29, 0.65—4.76, 0.65—3.61 and 0.65—2.72, for RhB, b-RhB, RhG and RhS systems, respectively, ΔI value is bigger. This is because that the chlorite form easily chlorine dioxide in acid solution, and the oxidation ability of chlorite is stronger. Therefore, pH 1.42, 1.85, 1.42 and 1.85 of the buffer solution were chosen for the RhB, b-RhB, RhG and RhS systems. The volume of the buffer solutions is all 0.50 ml.

2.3 Effect of KI volume

The ΔI value of the systems gradually increase with I^- concentration (Fig.2), and when KI concentration is about 2.0×10^{-3}, 1.2×10^{-3}, 1.2×10^{-3} and 3.2×10^{-3} mol/L for RhB, b-RhB, RhG and RhS systems, respectively, the ΔI value of the systems reached their maximum, and kept relatively stable when KI concentration increased. This suggests that reactions of I^- and ClO_2^- tend towards completion after KI concentration reach about 2.0×10^{-3}, 1.2×10^{-3}, 1.2×10^{-3} and 3.2×10^{-3} mol/L for RhB, b-RhB, RhG and RhS systems, respectively. Hence, for RhB, b-RhB, RhG and RhS systems, the KI concentration all was chosen to be 4.0×10^{-3} mol/L.

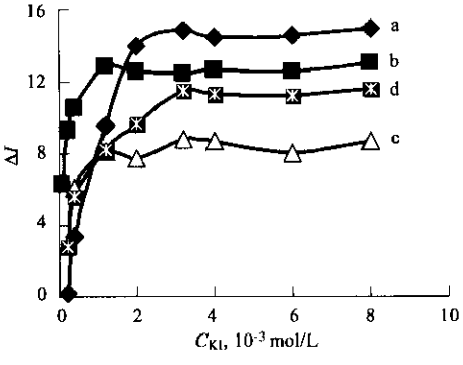

Fig.2 Effect of KI concentration
a. pH=1.42, 0.0726 μg/ml ClO_2^-, 2.0×10^{-5} mol/L RhB (OR=5, S=2); b. pH=1.85, 0.102 μg/ml ClO_2^-, 2.0×10^{-5} mol/L b-RhB (OR=4, S=2); c. pH=1.42, 0.102 μg/ml ClO_2^-, 3.0×10^{-5} mol/L RhG (OR=4, S=2); d. pH=1.42, 0.102 μg/ml ClO_2^-, 2.0×10^{-5} mol/L RhS (OR=4, S=2)

2.4 Effect of Rh concentration

From Fig.3, it can be found that ΔI value gradually increases with the Rhodamine concentration. It is owing to more particles forming. When RhB, b-RhB, RhG and RhS concentration is about 2.4×10^{-5}, 6.0×10^{-6}, 1.4×10^{-5} and 1.6×10^{-5} mol/L, respectively, ΔI value of the systems all reached their maximum and were relatively stable. This indicates that the reactions of Rh dyes and I_3^- reached completion at this moment. Therefore, a concentration of 3.0×10^{-5} mol/L RhB, 2.0×10^{-5} mol/L b-RhB, 3.0×10^{-5} mol/L RhG and 2.0×10^{-5} mol/L RhS was selected, respectively.

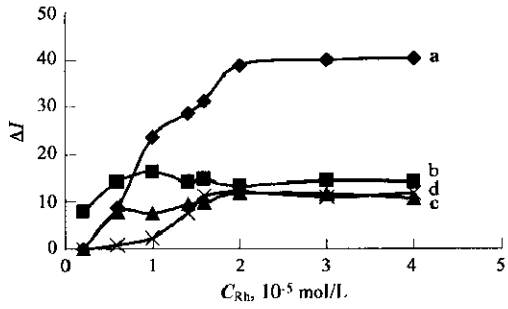

Fig.3 Effect of Rh concentration
a. RhB, 4.0×10^{-3} mol/L KI, 0.102 μg/ml ClO_2^-, pH=1.42 (OR=5, S=2); b. b-RhB, 4.0×10^{-3} mol/L KI, 0.145 μg/ml ClO_2^-, pH=1.85 (OR=4, S=2); c. RhG, 4.0×10^{-3} mol/L KI, 0.102 μg/ml ClO_2^-, pH=1.42 (OR=4, S=2); d. RhS, 4.0×10^{-3} mol/L KI, 0.102 μg/ml ClO_2^-, pH=1.85 (OR=4, S=2)

2.5 System stabilities

The effects of reaction times on ΔI value were examined. The results show that ΔI value of the systems quickly reach the maxim value. ΔI value is stable at least 90 min for RhB, whereas for b-RhB, RhG and RhS systems, about 20, 15 and 25 min, respectively.

2.6 Calibration graph

Under optimum conditions of the procedure, the analytical features of the four systems were investigated (Table 1). The results indicate that the detection limit of RhB system is lower and the stability is better than that of the other systems. Hence RhB system is chosen for the measurement of chlorite content in water samples.

Table 1 Analytical feature of Rhodamine RS methods for ClO_2^-

System	Regression equation (C, μg/ml)	Linear range, μg/ml	Correlation coefficient	Detection limit, μg/ml
RhB	ΔI=178.2C+0.92	0.00726—0.218	0.9955	0.00436
b-RhB	ΔI=53.74C−0.50	0.0102—0.292	0.9905	0.00652
RhG	ΔI=25.18C+0.15	0.00726—0.145	0.9955	0.00580
RhS	ΔI=24.89C−0.13	0.0290—0.174	0.9984	0.01450

Note: * Concentration of ClO_2^-

2.7 Effects of coexistence substances

According to the procedure, the effects of foreign substances on the determination of 0.102 μg/ml ClO_2^- were examined. 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. There is no interference for most ions. Only ClO_2 interfered the determination.

2.8 Sample analysis

The proposed method was applied to determine chlorite in waste water. The results of the proposed method and the indigo carmine (IC) spectrophotometric method are presented in Table 3. Student's test shows that the results of the proposed method and

the spectrophotometry are equal within 95% confidence level.

Table 2 Effects of coexistence substances

Coexistent substance	Tolerance, μg/ml	Relative error, %	Coexistent substance	Tolerance, μg/ml	Relative error, %
K^+	7000	+4.0	SO_4^{2-}	2500	-5.1
NH_4^+	5000	-5.1	NO_3^-	1000	+4.5
Ca^{2+}	7000	-2.0	F^-	250	-5.5
Mg^{2+}	1500	+4.6	$C_2O_4^{2-}$	2000	+1.5
Ba^{2+}	9000	-5.1	Urea	2000	-5.2
Co^{2+}	150	-5.0	Tartaric acid	150	-3.2
Ni^{2+}	180	+3.1	Mathanol	10000	+5.0
Al^{3+}	13000	-2.1	$Cr_2O_7^{2-}$	45	+5.0
Zn^{2+}	100	-4.4	BrO_3^-	15	+5.1
Fe^{3+}	13	+2.9	ClO_3^-	600	+3.5
Mn^{2+}	100	+4.3	Cl_2	80*	+4.8
Pb^{2+}	130	-3.2	ClO_2	0.1	+7.5

Note: * 0.02 mol/L dimethylsulfoxide masking

Table 3 Analytical results of ClO_2^- in wastewater

Sample	Single determination value, μg/ml	Average value, μg/ml	RSD, %	IC spectrophotometry, μg/ml (n=5)
1#	0.0445, 0.0487, 0.0423, 0.0460, 0.0448	0.0453±0.0007	1.7	0.0463±0.0006
2#	0.0686, 0.0653, 0.0645, 0.0678, 0.0620	0.0656±0.0022	3.4	0.0649±0.0010
3#	0.0866, 0.0838, 0.0847, 0.0889, 0.0865	0.0861±0.0002	0.2	0.0845±0.0004
4#	0.104, 0.110, 0.116, 0.098, 0.109	0.107±0.005	4.7	0.110±0.007

3 Conclusions

Under the acidic conditions, based on the oxidation of I^- by chlorite in presence of Rh, the resonance scattering spectrum of four rhodamine dyes association complex particle systems were studied. A new RhB RSS method was developed for the determination of chlorite in the range of 0.00726—0.218 μg/ml ClO_2^-, with a detection limit of 0.00436 μg/ml ClO_2^-. The method has been applied to the determination of ClO_2^- in water samples, with satisfactory results.

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