

Reversed flow injection spectrophotometric determination of low residuals of chlorine dioxide in water using chlorophenol red

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Abstract: A novel, simple, rapid, sensitive and highly selective flow injection procedure for the spectrophotometric determination of chlorine dioxide in the presence of other chlorine species, viz. free chlorine, chlorite, chlorate and hypochlorite, is developed. The method is based on the discoloration reaction between chlorine dioxide and chlorophenol red and can overcome the shortcomings existed in direct spectrophotometric determination for chlorine dioxide owing to the serious interference of free and combined chlorine. The procedure gave a linear calibration graph over the range 0—0.71 mg/L of chlorine dioxide. With a detection limit of 0.024 mg/L and a sample throughput of 60 samples/h.

Keywords: chlorine dioxide; chlorophenol red; reversed flow injection; spectrophotometry

Introduction

Water treatment with free chlorine as the disinfectant has been the important subject of most waterworks the entire world in recent 100 years. However, the trihalomethanes produced by reaction of chlorine with organic compound in water during water treatment is harmful for living things and maybe lead to cancer. Thus, chlorine is gradually replaced by other disinfectants, such as chlorine dioxide, ozone, etc., and chlorine dioxide is the best one. The main products of reaction of chlorine dioxide with organic compounds are chlorite ion and chlorate ions. The low concentration of chlorite and chlorate ions have no harmfulness to living things, but the high level of chlorite and chlorate ions have potential health hazards (Kruijf, 1985). Therefore, it is necessary that the low level of chlorine dioxide is controlled and it is very important to study the determination method for low level of chlorine dioxide. Currently, many direct spectrophotometric methods have been described for the determination of chlorine dioxide (Chisivell, 1991; Masschelein, 1966; Hodgden, 1954; Marcel, 1960; Zhang, 1995). However, these methods do not possess either necessary selectivity or sensitivity. Only *n*'*n*-diethyl-*p*-phenylenediamine (DPD) reagent is recommended in standard procedures.

The discoloration reaction between chlorine dioxide and chlorophenol red has been investigated by Wheeler and Loft (Wheeler, 1978), who reported no interference in the determination of 0.5 mg/L of chlorine dioxide in the presence of 4.7 mg/L of chlorite, 4.9 mg/L of hypochlorous acid and 5.0 mg/L of chlorate. The method was adapted by Harp *et al.* (Harp, 1981) using more precise buffering to cover the ranges 0—1.0 and 0—2.0 mg/L. Afterwards, Lan J. Fletcher and Paul Hemings (Fletcher, 1985) reported on further investigations into the CPR method, in which other combined chlorine were suppressed by using sodium cyclamate. This method possesses both sensitivity and selectivity, but because it is handle operation, it has much insufficiency. Particularly, analytical speed is very slow and repeatability is not good, it cannot be applied to on-line analysis.

In this paper, we developed a rapid, highly sensitive and selective determinate method for chlorine dioxide with the reversed flow injection technical based on the discoloration reaction between chlorine dioxide and chlorophenol red without masks.

1 Experimental

1.1 Reagents

A 600 mg/L of stock chlorine dioxide solution was prepared as follows: in a gas-generating glass

bottle, a certain amount of sodium chlorite was dissolved in 500 ml of distilled water, hypochloric acid (36%) was added intermittently from a separating funnel. Chlorine dioxide liberated by reaction of hypochloric acid with sodium chlorite was absorbed with distilled water and stored at 4°C in a dark glass bottle. Some loss of chlorine dioxide occurred with time and the solution was standardized prior to use by iodimetric titration (Chen, 1996). Work solutions of chlorine dioxide were prepared daily from the stock solution. Under conditions above, the solutions were found to be stable for up to 5d. Prolonged exposure to light can result in a rapid loss of chlorine dioxide.

The stock chlorine and hypochlorite solutions (400—600 mg/L) were prepared according to the ref (Barry, 1993). A 4g amount of manganese (IV) oxide and 4g of potassium permanganate were mixed together in a mortar. The mixture was slowly treated in a conical flask with 30 ml of 36% hypochlorite acid. The chlorine liberated was passed into 400 ml of distilled water and 1 mol/L sodium hydroxide solution, respectively. The stock solution was stored in a light-proof bottle in a refrigerator. The concentrations of stock chlorine were determined by iodimetric titration. Low concentrations of chlorine and hypochlorite were obtained by subsequent dilution of the stock standard solution.

A chlorate stock standard solution was prepared by dissolving a certain amount of NaClO_3 in 500 ml of distilled water. Low concentrations of chlorate were obtained by properly diluting stock standard solution.

The chlorite solutions were freshly prepared prior to use and kept in black-painted calibrated flasks. Sodium chlorite (80%) used for preparing the chlorite solution was recrystallized thrice from water and standardized by iodimetric titration. More than 99% purity was obtained.

Stock chlorophenol red solution (3×10^{-4} mg/L) was prepared by dissolving 0.1436g of indicator-grade reagent in 100 ml of 0.005 mg/L sodium hydroxide solution and diluted to 1L with distilled water. The 3×10^{-5} mg/L work solution obtained from stock solution was used.

Phosphate buffer solution (pH = 7) containing 35.2 g/L of potassium dihydrogen phosphate and 27.2 g/L of disodium hydrogen phosphate was applied.

All chemicals used were analytical grade and distilled water was applied.

1.2 Apparatus

A schematic of reversed flow injection system is shown in Fig. 1. The reversed flow injection system consists of LZ-2000 Flow Injection Apparatus (Shenyang, China). The detector used was UV-3400 Spectrophotometer (Hitachi, Japan), equipped with 18 μl flow-cell. The absorbance was monitored at a wavelength of 571 nm. The flow rates of carrier stream and sample solution were 1.76 ml/min and 4.2 ml/min, respectively and 60 samples/h were analyzed. At least, five injections per sample were made in all cases. The flow system used 0.7 mm i.d. Teflon tubing throughout. pH measurement was took on a pHS-3C digital acidimeter (Zhejiang, China).

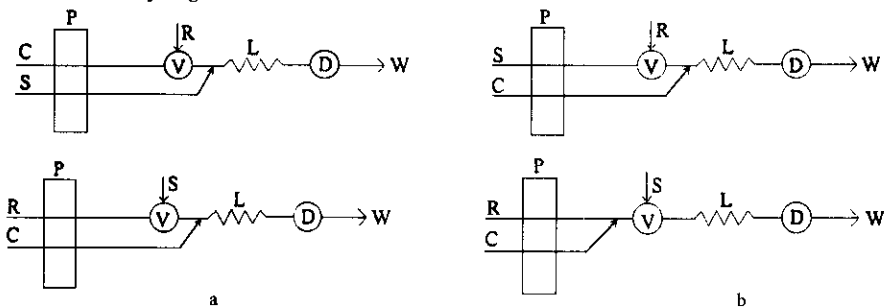


Fig.1 Flow injection manifolds

R: chlorophenol red (3×10 mg/L); C: carrier stream (phosphate buffer pH = 7); S: sample; L: reaction coil; P: pump; D: detector; W: waste water

1.3 Procedure

Linking flow system according to Fig.1a. Pump and detector are started in turn, carrier stream and distilled water are pumped into flow system. When baseline is steady, baseline data was recorded as A_0 . Then, chlorophenol red is pumped into the sample injection valve, sample and carrier stream are pumped into flow system, the absorbance value A was recorded, keeping the absorbance wavelength 571 nm.

2 Results and discussion

2.1 Measurement wavelength

Chlorophenol red is dark red in middle aqueous medium. The maximum absorption wavelength, 571 nm, was obtained and other materials existing with chlorophenol red have hardly absorption at this wavelength. In this study, 571 nm wavelength was used.

2.2 Choice of flow injection manifold

Four kinds of flow injection manifolds were devised (Fig.1). The sensitivity for different manifolds was investigated when other conditions were fixed except manifolds. The results showed that the manifold devised as Fig.1a has the highest sensitivity. The reason is the fact that reversed flow injection can improve sensitivity and save reagent, and meanwhile the sample in Fig.1a manifold is not diluted before flowing into detector while the sample in Fig.1b manifold is dispersed. Hence, Fig.1a manifold was chosen in this work.

2.3 Effects of reagent concentration

The effect of the concentration of reagent, chlorophenol red, on the difference (ΔA) of the absorbance of chlorophenol red in the presence and absence of chlorine dioxide is shown in Fig.2. The ΔA value increased with the reagent up to 3×10^{-5} mg/L. When the concentration is less than 3×10^{-5} mg/L, the determination system has a poor repeatability and sensitivity, but more than 3×10^{-5} mg/L, the baseline is not stable and a low sensitivity is caused. Thus, 3×10^{-5} mg/L reagent concentration was maintained in the study.

2.4 Choice of sampling loop volume

The results of the experiment indicated that the sensitivity increases with increasing injection volume, but the sampling loop volume in the LZ-2000 FIA processor is at 300 μ l maximum and cannot be expended conveniently. Hence, injection volume with 300 μ l is selected.

2.5 Choice of length of reaction coil

The effect of reaction coil length is studied. For a flow injection system, reactor and product of remain time is increased with the increase of reaction coil length. The longer remain time is, the completer reaction between chlorine dioxide and chlorophenol red is, thus the higher sensitivity is. But if reaction coil is too long, sample rate will decrease and disperse coefficient will increase. 1000 mm should be selected as appropriate.

2.6 Effect of rate of flow of carrier stream

The effect of rate of flow of carrier stream is studied. The results indicated that the bigger rate of flow of carrier stream is, the smaller ΔA is, but the larger sampling rate is. Giving consideration to sensitivity and sampling rate, 1.76 ml/min of rate of carrier stream was selected.

2.7 Effect of pH on sensitivity

Acidity is an important factor in decoloration reaction. This variable was studied in the pH range of 5 - 11 in the carrier stream (Fig.3), the highest sensitivity was obtained when the pH is 7, therefore a working pH of 7 was chosen. If the pH was adjusted using buffer solution of potassium dihydrogen phosphate and disodium hydrogen phosphate (pH = 7.0) instead of HCl and KOH, it caused no sensitivity change. Thus, in this study the buffer solution of KH_2PO_4 - Na_2HPO_4 was selected to retain the solution

acidity.

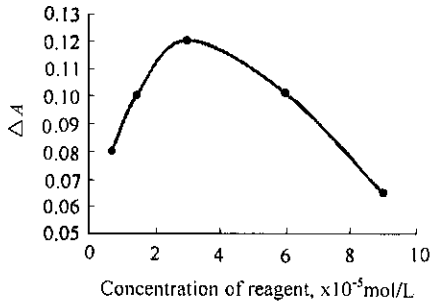


Fig.2 The effect of reagent concentration on sensitivity
 $[\text{ClO}_2] = 1.19 \text{ mg/L}$, $L = 1000 \text{ mm}$, $S_v = 300 \mu\text{l}$, rate of carrier stream = 1.76 ml/min

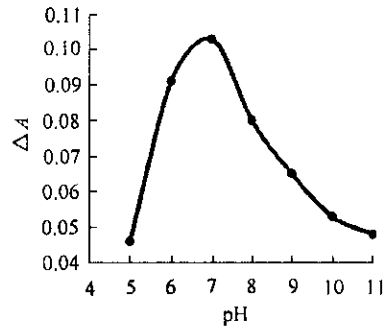


Fig.3 The effect of pH on sensitivity
 $[\text{ClO}_2] = 1.19 \text{ mg/L}$, $[\text{CPR}] = 3 \times 10^{-5} \text{ mg/L}$, $L = 1000 \text{ mm}$, $S_v = 300 \mu\text{l}$, rate of carrier stream = 1.76 ml/min

2.8 Calibration graph and response linear range

Using the optimized flow injection scheme. The useful working range was $0 - 0.71 \text{ mg/L}$ with a detection limit of 0.024 mg/L which is suitable for chlorine dioxide analysis (Fig. 4). The linear equation is $C = 2.10 - 12.05A$ (where C represents the concentration of chlorine dioxide (mg/L) and A stands for absorbance), with a correlation coefficient of $0.9993(R)$.

2.9 Effect of diverse ions

The effects of chlorine species on ΔA of determining system were investigated under the optimum experimental conditions. With 0.5 mg/L of chlorine dioxide solution, 2000 fold concentration of ClO_3^- , 2500 fold concentration ClO_2^- , 260 fold concentration of ClO^- , and 210 fold concentration of Cl_2 did not interfere the determination. The relative standard deviation is within $\pm 5\%$.

2.10 Determination of recovery

Table 1 gives analytical results of the determination of recovery for chlorine dioxide contained in water matrix. The results of recovery, $97\% - 104\%$, showed that the determination of chlorine dioxide with the reversed flow injection method based on the decoloration of chlorophenol red has a good repeatability. In three sample, $[\text{ClO}_2^-] = 80 \text{ mg/L}$, $[\text{ClO}_3^-] = 84 \text{ mg/L}$, $[\text{ClO}^-] = 10 \text{ mg/L}$.

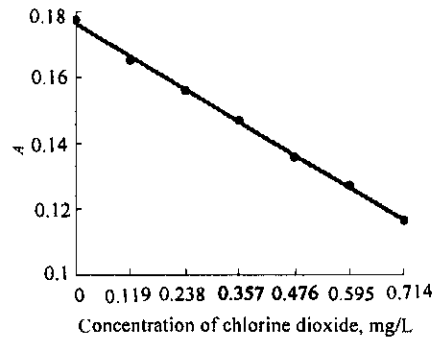


Fig.4 Calibration graph for the determination of chlorine dioxide in the range of $0 - 0.71 \text{ mg/L}$.

Table 1 The result of sample determination

Sample	Chlorine dioxide added, mg/L	Found, mg/L	Average, mg/L	Recovery, %	RSD, %
1	0.369	0.346, 0.347, 0.390, 0.329, 0.315, 0.412	0.357	97	3.7
2	0.554	0.584, 0.567, 0.578, 0.543, 0.580, 0.598	0.575	104	1.9
3	0.714	0.680, 0.738, 0.739, 0.660, 0.721, 0.752	0.715	100	3.7

2.11 Sample analysis

Placing accurately requisite volume of aqueous chlorine dioxide solution into two 100 ml calibration flasks, and then, dilute them to marks with tap water and make their concentrations be 0.74 mg/L and 1.11 mg/L, respectively. The samples were placed 2.5h for 0.74 mg/L solution and 4.0h for 1.11 mg/L solution. Under the optimum experimental conditions mentioned above, the residuals of chlorine dioxide were determined and the results are shown in Table 2.

Table 2 The results of sample analysis

Sample	Added chlorine dioxide	Placed time, h	Chlorine dioxide residuals	Average, %	RSD, %
1	0.74	2.5	0.50, 0.52, 0.53, 0.53, 0.51 0.50, 0.49, 0.50, 0.49	0.52	1.5
2	1.11	4	0.50, 0.49, 0.52, 0.50, 0.54, 0.51, 0.52, 0.52, 0.50	0.51	1.5

3 Conclusion

This paper has reported a new method of determining chlorine dioxide. The proposed method is based on decolorization reaction with *r*-FIA. As compared with previous works, the method is simple, rapid, sensitive and highly selective for determination of chlorine dioxide and can save reagent as well as has a good replication. The results for the determination of residuals chlorine dioxide in running water treatment are satisfactory.

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