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An On-line Determination of Chlorine Dioxide Using Chlorophenol Red by Gas Diffusion Flow-Injection Analysis

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ABSTRACT: An on-line determination of chlorine dioxide (ClO_2) in potable water using chlorophenol red (CPR) by gas diffusion flow-injection analysis (FIA) was investigated in the presence of various chlorinated species that can occur under normal water-treatment conditions. A gas diffusion membrane is used to separate the donor (sample) stream from the acceptor (detecting) stream (the donor stream transports the sample stream to the membrane separate device, and the acceptor stream collects all of the penetrated analytes and transports quantitatively to the detector) and makes it possible for this method to eliminate interference from metal ions, as well as other oxychlorinated compounds such as chlorite and chlorate. The system is more selective for chlorine dioxide than chlorine. The linear range of ClO_2 concentration is 0–0.5 mg·mL^{-1} with a detection limit of 0.02 μg·mL^{-1} ($S/N = 3$) and a sampling frequency of 50 h^{-1}. © 1999 John Wiley & Sons, Inc. Lab Robotics and Automation 11: 157–161, 1999

INTRODUCTION

As an alternative disinfectant to chlorine used in drinking-water treatment, chlorine dioxide has been increasingly considered [1–3]. In water treatment and subsequent distribution, chlorine dioxide can undergo a series of redox reactions, forming primarily chlorate, chlorite, hypochlorite, and chloride ions. Minimizing the oxychlorinated species residual in drinking water is important for health reasons; therefore, accurate methods for monitoring chlorine dioxide routinely in the presence of various chlorinated species are needed. Several different techniques for the determination of chlorine dioxide have been reported in the literature: flow-injection analysis [4], spectrophotometric [5–7, 11], iodometric [8], voltammetric [9], and amperometric [10] methods have been used. These methods have varying degrees of interference, with chlorine being the most common and largest in most cases. The *N′N-p-p*-phenylendiamine (DPD) method is recommended in standard procedures [12], which posses selectivity and necessary sensitivity, but it is not capable of on-line measurement of ClO_2 at low level.

This article describes a very selective spectrophotometric technique that makes use of the separation capabilities of gas diffusion FIA (GD-FIA). In this system, the microporous membrane was used to eliminate possible interferents from various oxido-reduction ions, that is, all nongaseous materials remain in the donor stream. In special, because chlorine dioxide differs from chlorine as to the selectivity of the microporous membrane, the excess chlorine

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can be tolerated without any masking reagents, which results in improving the selectivity of this method.

The discoloration reaction between chlorine dioxide and chlorophenal red (CPR) was developed by Wheeler and Loft [13]. The method was adapted by Harp et al. [14], using more precise buffering to cover the ranges 0–1.0 and 0–0.2 $mg \cdot L^{-1}$ ClO_2, and by Ian and Paul [15], using sodium cyclamate and thioacetamide to suppress the free chlorine interference at levels up to 20 $mg \cdot L^{-1}$. Coupling the CPR method with gas diffusion FIA, we developed a rapid, highly sensitive, and selective on-line determination of the low concentration of chlorine dioxide employed in potable water treatment.

EXPERIMENTAL

Standards

A stock solution of chlorine dioxide (ca. 600 $mg \cdot L^{-1}$) was prepared using a gas-generating and absorbing system [14] and stored at 4°C in a dark glass bottle. The solution was standardized prior to use by iodimetric titration [15]. Dilute standard solutions of chlorine dioxide were prepared daily from the stock solution.

Stock chlorine solution was prepared by bubbling chlorine gas through distilled water. The solution was stored in a dark glass bottle at 4°C and standardized by iodimetric titration prior to use.

Stock chlorophenol red solution (3×10^{-4} $mol \cdot L^{-1}$) was prepared by dissolving 0.1436 g of indicator-grade reagent in 100 mL of 0.01 $mol \cdot L^{-1}$ sodium hydroxide solution. The 3×10^{-5} $mol \cdot L^{-1}$ solution was obtained by a 10-fold dilution of the stock solution.

Phosphate buffer (pH = 7.0) containing 35.2 $g \cdot L^{-1}$ of potassium dihydrogen phosphate and 27.2 $g \cdot L^{-1}$ of disodium hydrogen phosphate was applied in this work.

All of the chemicals employed in the experiments were of analytical grade reagents; doubly distilled deionized water was used as reagent water.

Apparatus

A schematic of gas diffusion FIA is shown in Figure 1. The system consists of LZ-2000 Flow Injection apparatus (Shen Yang, China). The detector used was U-3400 Spectrophotometer (Hitachi, Japan) equipped with 10 mm path-length cell (18 μL), which was performed to measure absorbance at 575 nm. A digital pH-3C Meter with glass electrodes (Shang Hai, China) was used for the pH adjustments. A Model 501 super thermostatic bath (Shanghai, China) was used to keep the proper temperature. The gas diffusion cell consists of two pieces, each having curved grooves (245 × 5 × 0.2 mm), and the diffusion membranes were standard PTFE tape (thickness 0.08 mm, pore size of 0.45 μm). The flow system used 0.7 mm i.d. Teflon tubing throughout.

Procedure

The flow diagram for determination of ClO_2 is outlined in Figure 1. The flow rates of donor stream and acceptor stream are 1.5 mL min^{-1} and 1.0 mL min^{-1}, respectively. The coil length (100 cm) and temperature (30°C) were set within the flow system. The discoloration reaction between ClO_2 and reagent solution was carried out, and the absorbance of reaction product was determined at 575 nm. At least five injections per sample were made in all cases.

RESULTS AND DISCUSSION

Effect of Reagent Concentration

The effect of chlorophenol red (CPR) concentration on sensitivity is shown in Figure 2. When the concentration of CPR was changed from 1.0×10^{-5} $mol \cdot L^{-1}$ to 6.0×10^{-5} $mol \cdot L^{-1}$, the peak height of the reaction product reached a maximum at 3.0×10^{-5} $mol \cdot L^{-1}$ CPR for 0.7 $mg \cdot L^{-1}$ ClO_2, but with more than 3.0×10^{-5} $mol \cdot L^{-1}$, the baseline is not stable, and a low sensitivity is caused. So, this CPR concentration (3.0×10^{-5} $mol \cdot L^{-1}$) was applied to all subsequent studies.

Effect of pH on Sensitivity

Acidity is an important factor in decoloration reaction between the CPR and ClO_2. Figure 3 shows the relationship between pH and sensitivity, the highest sensitivity was obtained at the pH range 7.0–7.5. The pH was adjusted using buffer solution of potassium dihydrogen phosphate and disodium hydrogen phosphate (pH = 7.0). So, in this article, the buffer solution of KH_2PO_4-$NaHPO_4$ was selected to retain the solution acidity, and all subsequent studies were carried out at this pH.

Effect of Flow Rate

The flow rates of acceptor (P1) and donor stream (P2) were changed from 0.5 to 2.0 mL min^{-1} to determine the effect of flow rate on sensitivity (Figure 4.). High

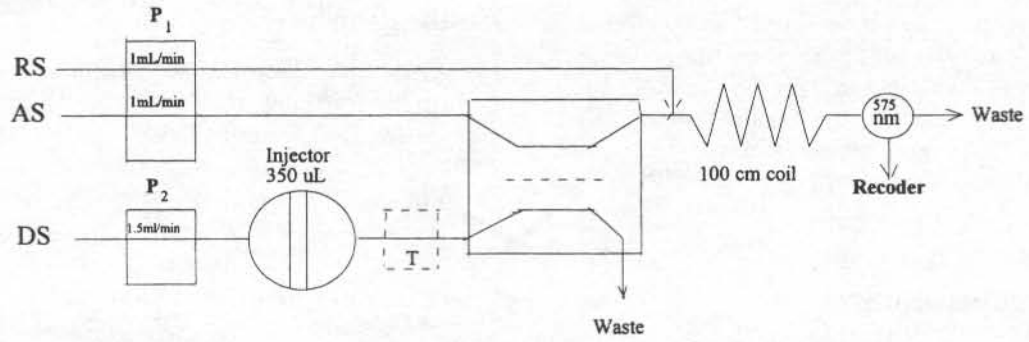

Figure 1. Schematic diagram of GD-FIA system used to determine ClO_2. AS, acceptor stream; DS, donor stream; RS, reagent stream (in buffer solution, pH 7.0); P, pump; T, super thermostatic bath.

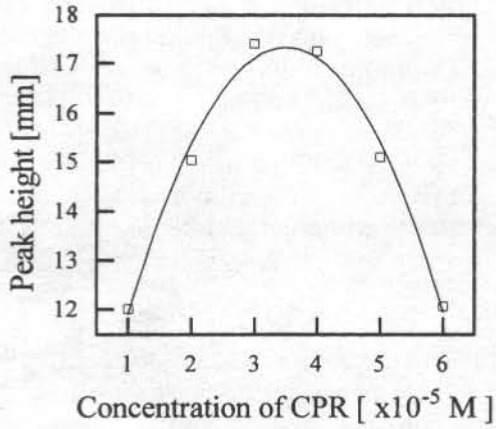

Figure 2. Effect of concentration of CPR on the sensitivity. The concentration of ClO_2 was 0.7 mg·L^{-1} at pH 7.0.

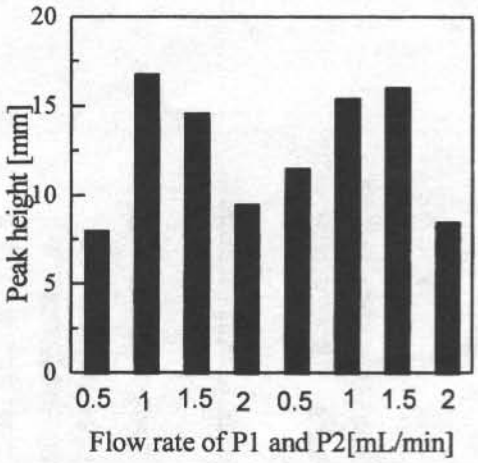

Figure 4. Effect of flow rate of P1 and P2 on sensitivity. P1 = flow rate of acceptor solution, and P2 = flow rate of donor solution.

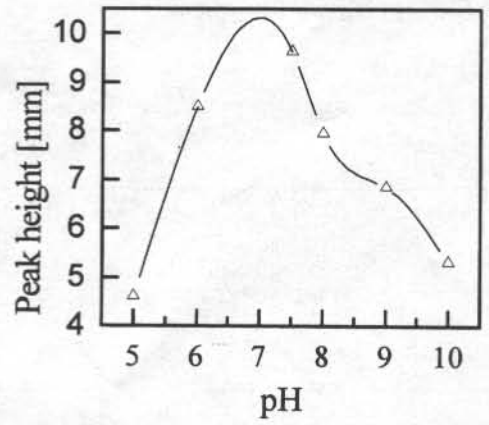

Figure 3. Effect of pH on the sensitivity. The concentration of ClO_2 was 0.7 mg·L^{-1} at pH 7.0.

sensitivity was obtained for those reaction conditions, in which the flow rates of P1 and P2 were set at 1.0 and 1.5 mL min^{-1}, respectively. Tryzell and Karlberg [16] found that, for gas diffusion manifolds, the peak height increases when the flow rates are decreased. But it is interesting to note that a change in the flow rate of reagent stream has only a minor effect on the peak height. Considering the transfer efficiency through the membrane of system, the flow rates were set at 1.0 and 1.5 mL min^{-1}. All subsequent studies were carried out at these flow rates.

Effect of Coil Length

The sensitivity for 0.7 mg·L^{-1} ClO_2 was examined by changing the coil length from 0.5 to 4.0 m, and the results are shown in Figure 5. As the discoloreaction

proceeds rapidly, it is preferable to make the coil length as short as possible. But, when the coil length was longer than 1.0 m, it was not easy to get the symmetric peak height nor was the baseline steady. Considering sensitivity and analysis time, 1.0 m coil length was chosen and applied for all subsequent studies.

Effect of Temperature

The sensitivity for 0.7 mg·L^{-1} ClO_2 was examined by changing the temperature from 20 to 70°C, and the results are shown in Figure 6. A substantial increase in peak height was observed when the temperature of the donor solution (just before entering the membrane device) was raised to 30°C, but the peak height decreased as the temperature increased. Therefore, the temperature was settled at 30°C, which was applied to all subsequent studies.

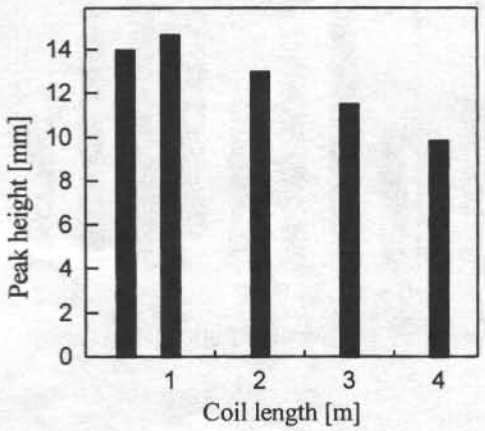

Figure 5. Effect of length of mixing coil on the sensitivity.

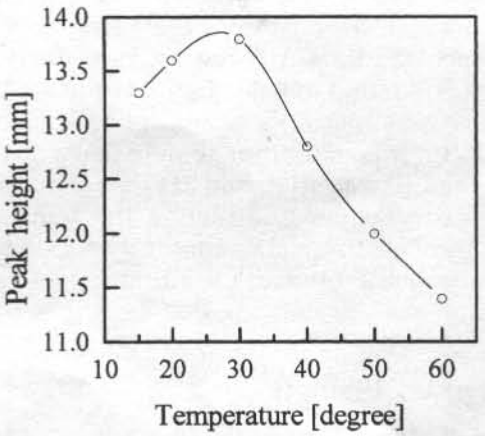

Figure 6. Effect of temperature on the sensitivity.

Calibration

Using the optimized flow-injection scheme, the procedure exhibited a linear response in the concentration range 0–0.5 mg·L^{-1} with a detection limit of (0.02 μg·mL^{-1}), which is suitable for determination of chlorine dioxide at low level. The linear equation is $H = 3.996 - 8.042 \times C$ [where C represents the concentration of ClO_2 (mg·L^{-1}) and H stands for peak height (mm)], with a correlation coefficient of 0.9994 ($N = 5$).

Interferences

Free chlorine, oxychlorine species, and other oxidizing agents were tested for possible reaction with CPR. Chlorite and chlorate, both decomposition products of chlorine dioxide in aqueous solution, were not found to react with CPR at concentration up to 245 mg·L^{-1} without any masking reagents. Other oxidizing agents were not found to interfere with the determination of ClO_2. The results of these assays are shown in Table 1. As can be expected, this method shows excellent selectivity for chlorine dioxide over chlorine, as well as other oxychlorinated compounds such as chlorite and chlorate ions.

Application

To determine the recovery of chlorine dioxide contained in water matrix and also to check the accuracy of this method, the synthetic samples were prepared containing known amounts of chlorine dioxide and with very high levels of chlorine. The results of these assays are shown in Table 2. As can be expected, the recovery of ClO_2 is 95–104%. It is shown that the determination of chlorine dioxide with the gas diffusion FIA based on the decoloration of chlorophenol red has good accuracy. A comparison of this method and the DPD method [12] indicates that the CPR gas

TABLE 1. Determination of ClO_2 in Presence of Oxidizing Agents and Other Oxychlorinated Compound

ClO_2 Taken (mg L^{-1})	Cl_2 Taken (mg L^{-1})	Interferences	ClO_2 Found (mg L^{-1})	RSD (%) ($N = 5$)
0.50	140	α	0.46	2.16
0.70	140	α	0.74	2.43
1.50	245	α	1.55	2.86

α: Na_2CrO_4: 40 mg·L^{-1} as CrO_4^{2-}; $Fe(No_3)_3$: 40 mg·L^{-1} as Fe^{3+}; $KMnO_4$; 10 mg·L^{-1} as MnO_4^-; $NaClO_2$: 12 mg·L^{-1} as ClO_2^-; HOCl: 100 mg·L^{-1} as OCl^-; $KClO_3$: 100 mg·L^{-1} as IO_3^-.

TABLE 2. The Result of Sample Determination ($mg \cdot L^{-1}$)

Sample	ClO_2 Added	ClO_2 Found DPD	ClO_2 Found (GD-FIA)	Recovery (%)
1	0.50	0.52	0.47	94.6
2	0.70	0.63	0.73	104
3	1.25	1.22	1.20	97.6

diffusion FIA is applicable over a wider range and shows a lower deviation.

CONCLUSION

A sensitive and highly selective method for the determination of aqueous chlorine dioxide has been developed through the successful coupling of gas diffusion FIA and spectrophotometer detection. Interferences from transition metals ionic, oxychlorinated species, chloramines, and chlorine have been significantly reduced or entirely eliminated. Although, in some cases, other methods have demonstrated superior detection limits for individual species, the excellent selectivity of this method makes it a viable technique for on-line determination of aqueous ClO_2 in drinking water treatment.

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