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Short communication

Simultaneous determination of chlorine dioxide and hypochlorite in water by high-performance liquid chromatography

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Abstract

The simultaneous determination of chlorine dioxide and hypochlorite by high-performance liquid chromatography was developed. The chromogenic substance formed by the oxidation–condensation reaction using 4-aminoantipyrine (4-AA) and phenol was determined at 503 nm by a post-column reaction system. Chlorine dioxide and hypochlorite were separated within 3 min by applying the elution solution (1.7 mM sodium carbonate–1.8 mM sodium carbonate) at 0.5 ml/min into a laboratory-prepared PTFE tube column (13 cm×1.0 mm I.D.×2 mm O.D.) packed with Waters Accell QMA as the anion-exchange material. A linear correlation between the peak height and concentration was obtained within the range of 1–20 $\mu\text{g/ml}$ for chlorine dioxide and 47–200 $\mu\text{g/ml}$ for hypochlorite, with good reproducibility (relative standard deviations of 4.0 and 2.2%, respectively, replicated determination). The limits of detection of chlorine dioxide and hypochlorite were approximately 0.2 and 10 $\mu\text{g/ml}$ ($S/N=3$), respectively. © 1998 Elsevier Science B.V.

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1. Introduction

It is widely known that the use of chlorine as a disinfectant for the treatment of drinking water causes the formation of carcinogenic trihalomethane [1]. Chlorine dioxide has been acknowledged as an alternative disinfectant with equivalent effectiveness in disinfection; the formation of trihalomethane hardly occurs during the disinfecting process when chlorine dioxide is used. Although chlorine dioxide has been in use for water treatment in Western countries [2,3], it is also known that chlorine dioxide undergoes disproportionations in aqueous environments, producing by-products such as hypochlorite,

chlorite and chlorate. Thus, a simple and selective analytical method for these oxidative chlorines is required and a number of analytical methods for the determination of chlorine dioxide have been reported in recent years [4–7]. However, all of the methods had the disadvantage of being prone to the influences of hypochlorite and metal ions. Iodometry [8], the *N,N*-diethyl-*p*-phenylenediamine (DPD) method [9] and ion chromatography (IC) [10,11] have also been reported as techniques for the separate determination of chlorine dioxide and other oxidative chlorines. However, iodometry and the DPD method are not able to determine chlorine dioxide and hypochlorite simultaneously and IC indirectly determines chlorine dioxide by analysis of chlorite. Hence, we attempted to establish a method for the simultaneous determi-

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nation of chlorine dioxide and hypochlorite, which was considered to be difficult to achieve until now, by high-performance liquid chromatography with post-column derivatization, where the separation of the two compounds was successfully achieved using a laboratory-prepared anion-exchange column.

2. Experimental

2.1. Reagents

4-Aminoantipyrine (4-AA) and phenol were of analytical reagent grade from Wako (Osaka, Japan). A sodium hypochlorite solution antiformalin (available chlorine >5%, w/v) was used. Sodium hydrogencarbonate and sodium carbonate, used for preparing buffer solutions, were of analytical grade and obtained from Wako.

2.2. Preparation of reagents

Chlorine dioxide gas, produced by the reaction between sodium chlorite (Wako) and hydrochloric acid, was trapped in ultra pure water at 0°C and stored in a cool dark place (5°C), followed by quantitation of this chloride dioxide solution using the integrated current-constant voltage polarographic current determination method [12] just before analysis and diluted to the various concentrations with ultra-pure water. Diluted sodium hypochlorite solution was kept in a cool dark place and its concentration was quantitatively measured by the integrated current-constant voltage polarographic current determination method [12] just before analysis and subsequently diluted to the various concentrations with ultra-pure water. Each 4-AA and phenol solution was dissolved in ultra-pure water and adjusted to a pH of 10.0 with a 1.7 mM NaHCO₃–1.8 mM Na₂CO₃ buffer solution and made up to final concentrations of 0.8 and 2.0 mM, respectively. The water used was purified by a Milli-Q-Reagent-Grade water system (ZD20) and had a resistivity of over 17 MΩ.

2.3. Quantitative procedure

Chromatography was carried out by applying a

mixture of chlorine dioxide and hypochlorite salt, at varying concentrations, into a separation system consisting of a laboratory-prepared PTFE tube column (13 cm×1.0 mm I.D.×2 mm O.D.) packed with Waters Accell QMA as the separation material. After chlorine dioxide and hypochlorite were separated on the separation column using an eluent concentration of 1.7 mM NaHCO₃–1.8 mM Na₂CO₃, a flow-rate of 0.5 ml/min and a column temperature of 30°C, the eluate was reacted with 0.8 mM 4-AA and 2.0 mM phenol and the absorptivity of the reaction product was measured at a maximum absorption wavelength of 503 nm. The concentration of each chlorine dioxide and hypochlorite was calculated from a linear regression line.

2.4. Instrumentation

The HPLC system consisted of a Shimadzu (Kyoto, Japan) LC-10AD pump for the delivery of mobile phase and reagents, a Shimadzu SPD-10AV UV-Vis detector and a Rheodyne (Cotati, CA, USA) Model 7125 loop injector for sample injection. The anion-exchange column used was prepared in the laboratory by packing a PTFE tube column (13 cm×1.0 mm I.D.×2 mm O.D.) with Waters Accell QMA. A stainless-steel tube (0.5 mm I.D.) and the reaction coil (0.3 m) were used for the flow system.

3. Results and discussion

As this post-column reaction, based on an oxidation–condensation reaction using 4-AA and phenol, proceeds rapidly under alkaline conditions, it is preferable to make the coil length as short as possible. The minimum coil length that can be used is 0.3 m, because of the configuration of the device. When the effect of pH (8.0–10.5) on the peak height of chlorine dioxide was examined, the maximum peak height was at pH 10.0. Therefore, a NaHCO₃–Na₂CO₃ buffer (pH 10.0) was used as the eluent. The experiment was carried out using various anion-exchange resins, such as Dowex 1-X8, Dowex 1-X4, Waters Accell QMA, Waters Accell QMA plus and Shimpac IC-AI, and various column sizes were also tested to study the change in resolution of chlorine dioxide and hypochlorite. Upon comparing various

types of anion-exchange resin with regard to ion-exchange composition, ion-exchange capacity and particle size, Waters Accell QMA (exchange capacity, 0.22 mequiv./ml; particle size, 35–55 μm) was the best at separating chlorine dioxide and hypochlorite. However, for conventional columns, e.g., 10 cm \times 4.0 mm I.D. or 15 cm \times 4.0 mm I.D., it takes a long time to perform the separation and no reproducibility is obtained, leading to the assumption that chlorine dioxide can undergo reduction and disproportionation to form chlorite, chlorate and hypochlorite during the separation process. The effectiveness of the separation was examined by packing the ion-exchange resin into various sizes of column. On adjusting the conditions for optimum separation by varying the analytical parameters, such as flow-rate, eluent concentration and temperature, using three different sizes of commercially available columns, 1 cm \times 4.5 mm I.D., 2 cm \times 4.5 mm I.D. and 2.5 cm \times 4.0 mm I.D., packed with Waters Accell QMA, resulted in resolutions (calculated under the optimum conditions) of 0.6, 0.8 and 0.8, respectively. Thus, the complete separation of chlorine dioxide and hypochlorite peaks was not possible with these columns. On varying the amount of ion-exchange resin and changing the length and diameter of the column, it was possible to completely separate chlorine dioxide and hypochlorite (resolution=1.7) using a laboratory-prepared PTFE tube column, 13 cm \times 1.0 mm I.D. Therefore, a 13 cm \times 1 mm I.D. column was chosen for analysis.

Table 1 shows the effect of a NaHCO_3 – Na_2CO_3 buffer (pH 10.0) on resolution and peak shapes for 10 $\mu\text{g}/\text{ml}$ chlorine dioxide and 50 $\mu\text{g}/\text{ml}$ hypochlorite.

Table 1
Effect of buffer concentration on the resolution and peak height of chlorine dioxide and hypochlorite

Buffer concentration (mM) (pH 10.0)		Resolution	Peak height (mm)	
NaHCO_3	Na_2CO_3		ClO_2	NaClO
0.9	0.9	1.9	31.4	9.5
1.7	1.8	1.7	59.0	16.0
3.4	3.6	1.4	100.8	28.6
7.2	6.8	1.3	114.2	31.4

The concentrations of chlorine dioxide and hypochlorite were 10 and 50 $\mu\text{g}/\text{ml}$ at pH 10.0, respectively.

rite. By varying the concentrations of NaHCO_3 and Na_2CO_3 between 0.9–7.2 and 0.9–6.8 mM, respectively, it was found that as the concentration increased, resolution decreased, but the intensity of the peak heights increased for both chlorine dioxide and hypochlorite.

Hence, the optimum concentration of eluent was determined to be 1.7 mM NaHCO_3 –1.8 mM Na_2CO_3 , where the two compounds can still be separated. Also, the change in resolution and peak shape of 10 $\mu\text{g}/\text{ml}$ chlorine dioxide and 50 $\mu\text{g}/\text{ml}$ hypochlorite at various flow-rates in a 1.7 mM NaHCO_3 –1.8 mM Na_2CO_3 buffer solution (P_2) is shown in Fig. 1. As the flow-rate of P_2 changed from 0.1 to 0.7 ml/min, while maintaining the flow-rate of the reaction reagent (P_1) at 0.5 ml/min, the resolution decreased with increasing flow-rate, but the intensity of the peak heights for both chlorine dioxide and hypochlorite increased. Considering the peak heights and resolution of compounds, the flow-rate was set at $P_2=0.5$ ml/min. The flow-rate of P_1 was set at 0.5 ml/min, since the results of further study revealed that the best peak shape was obtained when P_1 and P_2 are equal. Also, the column's temperature had hardly any effect on resolution. A typical chromatogram of chlorine dioxide (10 $\mu\text{g}/\text{ml}$) and hypochlorite (50 $\mu\text{g}/\text{ml}$), under optimum conditions, is shown in Fig. 2. The value of t_0 is 0.8 min. Quantitative evaluation indicated that there was excellent correlation between peak height and concentration, in the ranges of 1–20 $\mu\text{g}/\text{ml}$ for chlorine dioxide and 47–200 $\mu\text{g}/\text{ml}$ for hypochlorite. Moreover, good reproducibility with relative standard

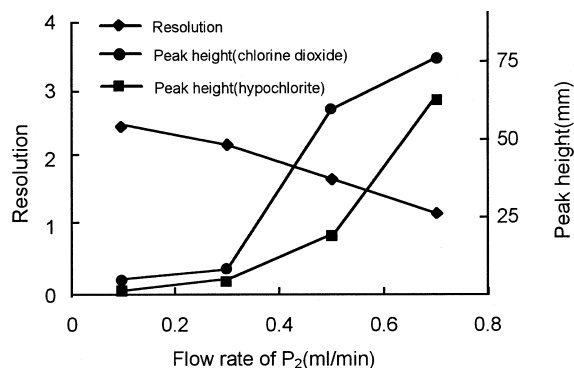


Fig. 1. Effect of flow-rate on the resolution of chlorine dioxide (10 $\mu\text{g}/\text{ml}$) and hypochlorite (50 $\mu\text{g}/\text{ml}$) at pH 10.0.

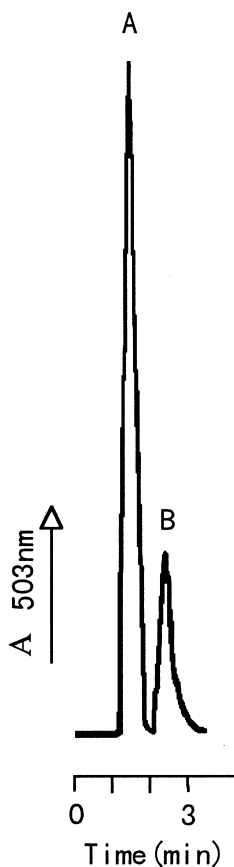


Fig. 2. Typical chromatogram of chlorine dioxide and hypochlorite. Peaks: A=chlorine dioxide (10 $\mu\text{g}/\text{ml}$); B=hypochlorite (50 $\mu\text{g}/\text{ml}$).

deviations of 4.0 and 2.2% were obtained for 10 $\mu\text{g}/\text{ml}$ chlorine dioxide and 50 $\mu\text{g}/\text{ml}$ hypochlorite, respectively, based on five replicate determinations. The recoveries of chlorine dioxide and hypochlorite from tap water were assessed by using a spiked real sample at 10 $\mu\text{g}/\text{ml}$ chlorine dioxide and 50 $\mu\text{g}/\text{ml}$ hypochlorite. The mean recoveries of chlorine dioxide and hypochlorite from tap water were 98.4 and 99.0%, respectively. The limits of detection of

chlorine dioxide and hypochlorite were approximately 0.2 and 10 $\mu\text{g}/\text{ml}$ ($S/N=3$), respectively.

4. Conclusions

The newly developed separation system for the simultaneous direct determination of chlorine dioxide and hypochlorite, which has been considered difficult to achieve until now, was established by using a laboratory-prepared PTFE tube column packed with Waters Accell QMA as the anion-exchange resin. The HPLC method described in this paper provides for the highly effective, quantitative separation of chlorine dioxide and hypochlorite within 3 min. The limits of detection of chlorine dioxide and hypochlorite were approximately 0.2 and 10 $\mu\text{g}/\text{ml}$ ($S/N=3$), respectively. This method is suitable for routine laboratory analysis.

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