

Detection of Hypochlorous Acid Using Reduction Wave During Anodic Cyclic Voltammetry

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A novel analysis method for detecting low free-chlorine concentrations using a reduction wave based on anodic cyclic voltammetry has been developed. The reduction wave has been observed at approximately 600 mV vs Ag/AgCl, which is dependent on the free-chlorine concentration and switching potential. The wave peak showed a maximum value for the switching potential at approximately 1350 mV vs Ag/AgCl, and a good linear relationship between the peak current and the concentrations in the range of 0.2–6.0 mg dm⁻³. The relative standard deviation (RSD) at each concentration was less than 2%. This method seems to be useful for the analysis of low free-chlorine concentrations. [DOI: 10.1143/JJAP.44.L718]

KEYWORDS: electrochemical method, anodic cyclic voltammetry, reduction wave, hypochlorous acid, free chlorine, platinum electrode, switching potential

The chlorination of water is widely used for disinfection, usually at a concentration lower than 1 mg dm⁻³.¹⁾ It is recognized that chlorine is highly toxic, and provides a strong and persistent odor even at low concentrations. Chlorine applied to water in its molecular or hypochlorite form initially undergoes hydrolysis to form free chlorine consisting of aqueous molecular chlorine, hypochlorous acid (HClO), and hypochlorite ions (ClO⁻). At the pH of most types of water, 4–9, HClO and ClO⁻ predominate.²⁾ Various techniques are used to monitor free chlorine, however, portable techniques suitable for trace levels are often required for environmental monitoring.³⁾ In recent years, electrochemical methods have been becoming very attractive because they are free of any reagent, provide sufficient sensitivity, and allow the possibility of miniaturization.⁴⁾ We have previously developed an electrochemical method using the oxidation wave of anodic voltammetry.⁵⁾ However, the determination of the low free-chlorine concentrations was not sufficient, because the detection limit of the oxidation wave was approximately 4.0 mg dm⁻³. On the other hand, a reduction wave, at approximately 600 mV vs Ag/AgCl, is observed during the cathodic potential sweep of anodic cyclic voltammetry. In the voltammogram, we found that the reduction wave was dependent on free-chlorine concentration and switching potential. In this letter, we examined the utility of this reduction wave for the determination of low free-chlorine concentrations. The results indicate that the reduction wave provides a more enhanced analytical sensitivity for the determination of low concentrations (< 6 mg dm⁻³).

A standard free-chlorine solution was prepared from an 8.5–13.5% sodium hypochlorite aqueous solution (Nakarai, Japan). The concentration of the solution was determined by iodometric titration.²⁾ During a series of analyses, this solution was stored in a brown glass, stoppered bottle. 0.1 M NaClO₄ (Merk) was used as the supporting electrolyte.⁶⁾ All reagents were of analytical grade and were used as received. All solutions were prepared using Milli-Q water. The pH was measured with a conventional glass electrode system (HORIBA, F-12). The electrochemical measurements were carried out in a conventional three-electrode cell using a computer-controlled electrochemical system (BAS100B/W or ALS600A). A platinum disk (1.6 mm diameter, BAS) was used as the working electrode, a platinum wire was used as

the counter-electrode, and an Ag/AgCl electrode (3M NaCl, BAS) was used as the reference electrode. The surface of the working electrode was polished with lapping films (in the sequence of 3, 2, 1, 0.5 and 0.3 μm grain sizes, 3M Co.), carefully sonicated in distilled water, and then rinsed with Milli-Q water. Furthermore, the polished electrode was pretreated in an electrolytic solution by a potential sweep in the conventional manner.⁷⁾ The determination of free chlorine was carried out by anodic cyclic voltammetry at 50 mV s⁻¹. First, a background voltammogram was measured in the electrolytic aqueous solution, then each amount of the free-chlorine solution was pipetted into the solution. The measurement was carried out 1 h after the addition of the free-chlorine solution to prevent the decomposition of the free chlorine. All experiments were performed under a nondeaerated condition at 25 ± 1°C.

Figure 1 shows the anodic cyclic voltammogram of 100 mg dm⁻³ free chlorine in 0.1 M NaClO₄ at a sweep rate of 50 mV s⁻¹ at pH 7.9. The dashed line represents the blank (0.1 M NaClO₄) solution. When the potential was swept from 600 to approximately 1200 mV vs Ag/AgCl, an oxidation wave based on the free chlorine appeared at approximately 1000 mV vs Ag/AgCl. These results were shown detail in previous research.^{8,9)} In the reverse sweep from switching potential, a well-defined reduction wave was detected at approximately 600 mV vs Ag/AgCl. This reduction wave is dependent on the free-chlorine concentration as well as the oxidation wave, and also dependent on

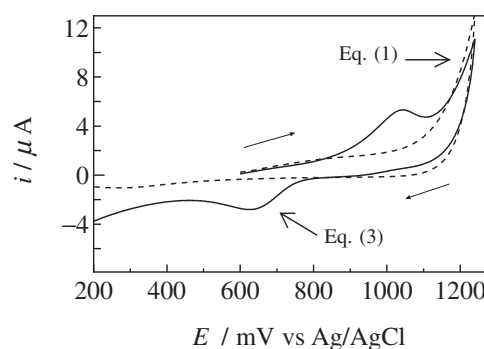


Fig. 1. Cyclic voltammogram of 100 mg dm⁻³ free chlorine in 0.1 M NaClO₄ at sweep rate of 50 mV s⁻¹ at pH 7.9. Short dashed line: blank (0.1 M NaClO₄) solution.

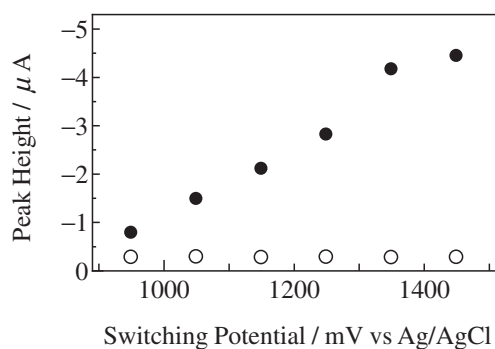
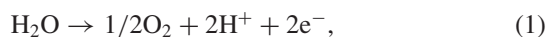


Fig. 2. Relationship between peak height of reduction wave and switching potential. These plots correspond to the measurement conditions listed in Fig. 1. ○: background current.

Table I. Reproducibility test at different free-chlorine concentration levels ($n = 5$).

C (mg dm^{-3})	Mean I_p (μA)	RSD (%)
6.0	-0.306	1.98
1.0	-0.054	1.65
0.6	-0.034	1.89

the switching potential. Chao reported that HClO is reduced at approximately 600 mV vs Ag/AgCl.¹⁰ For this mechanism, we consider the following: First, by the electrolysis of water, the pH of the electrode interface becomes acidic from eq. (1). As a result, the equilibrium of HClO/ ClO^- progresses toward the left in eq. (2).¹¹ Finally, the formed HClO is reduced at approximately 600 mV vs Ag/AgCl in eq. (3).



$$K = 2.9 \times 10^{-8} \text{ mol dm}^{-3} \text{ at } 25^\circ\text{C}$$

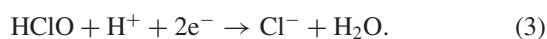


Figure 2 shows the relationship between the peak height of the reduction wave and switching potential. Open circles represent the background current in each switching potential. From Fig. 2, peak height increases with increasing switching potential. At nearly 1350 mV vs Ag/AgCl, the peak height almost saturates.

Table I lists the results of a reproducibility test for the reduction peak current at different free-chlorine concentrations. In the measurement, the switching potential was 1350 mV vs Ag/AgCl because the sensitivity was the highest in Fig. 2, and the effect of the background was not observed. From Table I, the RSD was less than 2% ($n = 5$).

Figure 3(a) shows an enlarged view of the reverse sweep on anodic cyclic voltammograms as a function of free-chlorine concentration in 0.1 M NaClO₄ at a sweep rate of

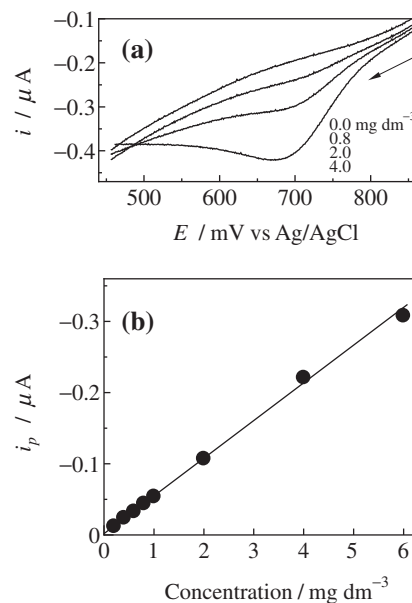


Fig. 3. (a) Enlarged view of reverse sweep on anodic cyclic voltammograms as function of free-chlorine concentration in 0.1 M NaClO₄ at sweep rate of 50 mV s⁻¹ and switching potential of 1300 mV vs Ag/AgCl. (b) Relationship between peak current of reduction wave and low free-chlorine concentration. This plot corresponds to the measurement conditions listed for (a).

50 mV s⁻¹ and a switching potential of 1300 mV vs Ag/AgCl. In this figure, the reduction wave, even at concentrations as low as the chlorination of water, was observed. Figure 3(b) shows a plot of the reduction peak current vs the free-chlorine concentration. This plot represents the data after being background-corrected. From this figure, a good linear relationship was obtained in the concentration range of 0.2 to 6.0 mg dm⁻³, and the linear regression coefficient (R-squared) is greater than 0.998. These results indicate that the reduction wave provides a better analytical sensitivity for the determination of low free-chlorine concentrations.

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