

Electrochemical Detection of Free Chlorine Using Anodic Current

Fumihiro KODERA, Shin-ya KISHIOKA, Minoru UMEDA and Akifumi YAMADA

Department of Chemistry, Faculty of Engineering, Nagaoka University of Technology, 1603-1 Kamitomioka, Nagaoka, Niigata 940-2188, Japan

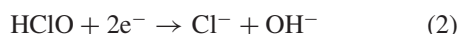
(Received April 1, 2004; accepted May 7, 2004; published June 18, 2004)

We have developed a new analysis method for high free-chlorine concentration using anodic current. The measurement was carried out using linear sweep voltammetry with a platinum disk electrode. An oxidation wave that was concentration dependent at about 1100 mV vs Ag/AgCl was observed, and a good linear relationship in the concentration range of 0.1–12.0 mmol·dm⁻³ (Cl) was obtained between the oxidation peak current and concentration. This method seemed to be very useful for the analysis of high free-chlorine concentration. [DOI: 10.1143/JJAP.43.L913]

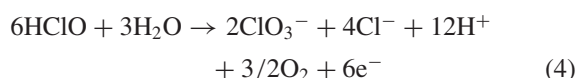
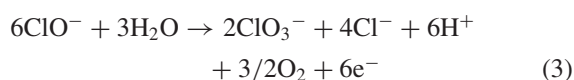
KEYWORDS: free chlorine, anodic current, electroanalytical method, linear sweep voltammetry, platinum disk electrode

Sodium hypochlorite is used worldwide as a water disinfectant and in bleaching agents.¹⁾ Sodium hypochlorite applied to water initially undergoes hydrolysis to form free chlorine consisting of hypochlorous acid (HClO) and hypochlorite ion (ClO⁻). Generally, the measurement method for free chlorine is colorimetric. However, the color reagent is not always safe. For example, the stabilized neutral *o*-tolidine method for practical uses was deleted from the 15th edition, *Standard Methods for the Examination of Water and Wastewater*,²⁾ because of its toxic nature. Instead of the *o*-tolidine, *N,N*-diethyl-*p*-phenylenediamine (DPD) whose toxicity is uncertain is being used at present.

For free-chlorine determination, an electroanalytical method is simple due to the electroactivity of free chlorine; it measures current and is free of most reagents.³⁾ Therefore, it is very safe and appears to be the most suitable technique for on-line monitoring. The electroanalytical method is usually based on the following reduction reactions.^{4–8)}



On the other hand, the oxidation current based on the anodic reaction is not used for quantitative analysis despite the electrochemical activity of free chlorine.^{9–11)}



In this study, the application of the anodic reaction to the electroanalytical method was examined using the potential sweep technique with the platinum disk electrode.

A free-chlorine standard solution was prepared by dilution of a sodium hypochlorite aqueous solution (Nacalai, Japan). The concentration of the standard solution was determined by iodometric titration.²⁾ The supporting electrolyte was sodium perchlorate (Merck). All reagents were of analytical grade and used as received. Water was obtained from a MILLI-Q purification system (Millipore).

The electrochemical measurements were carried out using a conventional three-electrode cell which contained a platinum disk working (1.6 mm diameter, BAS), platinum wire auxiliary and Ag/AgCl reference (3M NaCl, BAS) electrodes. A computer-controlled electrochemical system (BAS100B/W) was employed for the electrochemical measurements.

The surface of the working electrode was polished with lapping films (3, 2, 1, 0.5 and 0.3 μm grain size, 3M Co.), carefully sonicated in water, and then rinsed with water. A polished platinum electrode was pretreated in an aqueous solution containing a supporting electrolyte without free chlorine by a potential sweeping in the conventional manner.¹²⁾ After a background voltammogram was obtained in the solution, the free-chlorine solution was pipetted into the electrolytic solution. The determination of free chlorine was carried out by linear sweep voltammetry in the potential range from +600 mV to +1200 mV vs Ag/AgCl at room temperature.

Figure 1 shows typical linear sweep voltammograms obtained in the electrolyte solution as a function of the free-chlorine concentration. A well-defined oxidation peak current is observed. The dashed line in Fig. 1 is the current-potential curve in the blank solution. A slightly large residual current in the blank was recognized from the beginning of the sweep potential at +600 mV although the oxidation peak did not appear. In the presence of the substrate, free chlorine, the background current was not significant. These results indicated that the current peaks in Fig. 1 are due to the oxidation of free chlorine at the Pt working electrode. The potential region near the oxidation peak in Fig. 1 is in good agreement with the area for the oxide film formation on the Pt surface. A current response below +800 mV where the oxidation of free chlorine begins

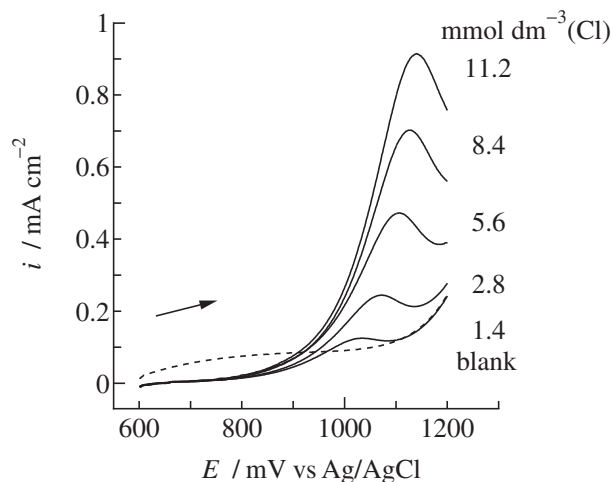


Fig. 1. Linear sweep voltammograms at Pt disk electrode in 0.1 mol·dm⁻³ NaClO₄ as a function of NaClO concentration. Sweep rate = 50 mV·s⁻¹.

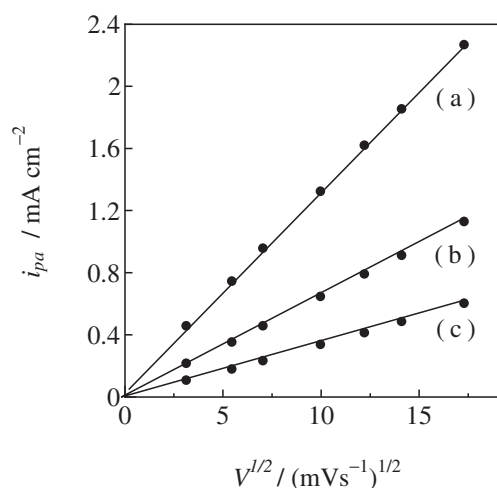


Fig. 2. Anodic peak current versus square root of sweep rate for oxidation at varying concentrations: (a) 11.2, (b) 5.6, and (c) 2.8 mmol-dm⁻³ (Cl).

does not seem to form any oxide. It is speculated that the presence of free chlorine inhibits the oxide layer formation, and the free chlorine itself is oxidized at the bare Pt electrode surface.

Figure 2 shows the relationship between the peak current and the square root of the sweep rate, indicating that the primary electron transfer takes place by a diffusion-controlled process. Djordjević *et al.* reported that during the initial step, a neutral radical, ClO•, is formed by the one-electron oxidation of the free-chlorine anion which then causes complicated reactions.⁹⁾ From the process, an excellent reproducibility is observed in the linear sweep voltammograms without any treatment of the electrode.

Figure 3 shows a plot of the oxidation peak current value versus the concentration of free chlorine. Figure 3(a) is the plot in the high-concentration region, and Fig. 3(b) is that in the low-concentration region. A linear calibration curve was obtained in the concentration range of 0.1 to 12.0

mmol-dm⁻³ (Cl). For lower free-chlorine concentrations, a considerable amount of work has been carried out using a cathodic current.⁴⁻⁸⁾ These methods have, however, a weak point; the electrochemical reduction current of free chlorine suffers from the reduction of dissolved oxygen. To remove the dissolved oxygen, the test solutions were deaerated with an inert gas such as nitrogen. However, deaeration might vaporize the free chlorine thus lowering its concentration. Furthermore, the existence of some metal ions might affect the reduction of the free chlorine during the cathodic process. Because the presence of dissolved oxygen is unavoidable under practical conditions, the electrooxidative determination in this study is the favored technique for practical analyses. Alternative electrode materials and their treatments might enable us to extend the lower limit of the detection with electrooxidation.

The present work was supported by a Grant-in-Aid for Scientific Research (B) (No. 14350450) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

- 1) World Health Organization: *Guidelines for Drinking-Water Quality* (WHO, Geneva, 1993) 2nd ed., Vol. 1—Recommendations.
- 2) APHA, AWWA, WCCF: *Standard Methods for the Examination of Water and Wastewater* (APHA, Washington, 1992) 18th ed., p. 4–36.
- 3) K. Heller and E. N. Jenkins: *Nature* **158** (1946) 706.
- 4) A. N. Tsaousis and C. O. Huber: *Anal. Chim. Acta* **178** (1985) 319.
- 5) S. Uchiyama, O. Hamamoto and S. Suzuki: *Electroanalysis* **1** (1989) 323.
- 6) A. van den Berg, M. Koudelka-Hep, B. H. van der Schoot, N. F. de Rooij, E. Verney-Norberg and A. Grisel: *Anal. Chim. Acta* **269** (1992) 75.
- 7) A. Okumura, A. Hirabayashi, Y. Sasaki and R. Miyake: *Anal. Sci.* **17** (2001) 1113.
- 8) K. Nagashima, H. Furui, M. Ejiri and N. Nakano: *Bunseki Kagaku* **51** (2002) 1175 [in Japanese].
- 9) A. B. Djordjević, B. Z. Nikolić, I. V. Kadija, A. R. Despić and M. M. Jaksić: *Electrochim. Acta* **18** (1973) 456.
- 10) A. Tasaka and T. Tojo: *J. Electrochem. Soc.* **132** (1985) 1855.
- 11) L. Czarnetzki and L. J. J. Janssen: *Electrochim. Acta* **33** (1988) 561.
- 12) A. J. Bard and L. R. Faulkner: *Electrochemical Methods* (John Wiley & Sons, New York, 2001) 2nd ed.

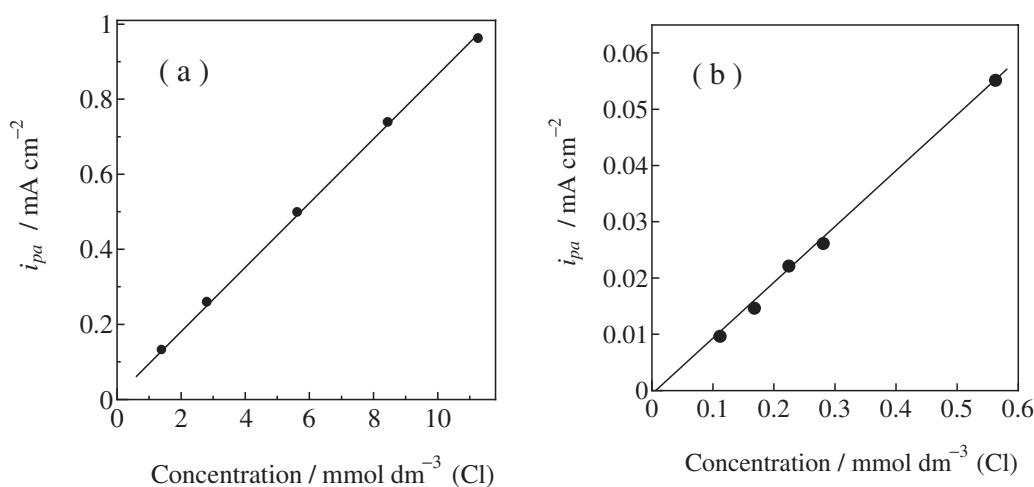


Fig. 3. Relationship between oxidation peak current and free-chlorine concentration: (a) high-concentration region and (b) low-concentration region. These plots correspond to the measurement condition described in Fig. 1.