

# Differential Pulse Voltammetric Determination of Free Chlorine for Water Disinfection Process

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Received: May 21, 2010

Accepted: July 25, 2010

## Abstract

The electrochemical detection of free chlorine based on the reduction at a gold electrode has been studied. The differential pulse voltammetric curves exhibited well-defined cathodic peaks. Investigations with this system suggested that the active species in the cathodic reaction is HClO. Excellent reproducibility was demonstrated at pH 5. The peak height could be used for accurate and rapid determination of free chlorine in a sample water. A linear relationship ( $r^2=0.99$ ) was found for the concentration range of 1–5 mg Cl dm<sup>-3</sup> and the detection limit was estimated to be 0.04 mg Cl dm<sup>-3</sup>.

**Keywords:** Differential pulse voltammetry, Free chlorine, HClO reduction, Gold electrode, Drinking water

DOI: 10.1002/elan.201000322

Chlorine is a strong oxidizing agent and is the conventional chemical used for the disinfection of drinking water [1]. It was realized that aqueous chlorine solution is effective in preventing bacterial, viruses and protozoa infections [2,3] and then it has been widely used as a disinfectant since the early 1900's. The disinfection ability of chlorine depends on its concentration. The WHO drinking water standard states that 2 to 3 mg Cl dm<sup>-3</sup> give satisfactory disinfection and maximum residual concentration of free chlorine allowed is 5 mg Cl dm<sup>-3</sup> [4]. Therefore, easy-to-operate, accurate and sensitive method for the determination of residual free chlorine in water is a necessary requirement.

Sodium hypochlorite solutions were generally used for the source of free available chlorine as hypochlorous acid or hypochlorite ion equilibrate with chlorine [5–6]. NaClO is commercially available as an alkaline solution of approximate pH of 11, usually containing between 5 and 15% (w/v) in the form of ClO<sup>-</sup> ion.

There are several common analytical methods to detect free chlorine in aqueous media such as the colorimetric methods using *o*-toluidine and also *N,N*-diethyl-*p*-phenylenediamine (DPD), iodometric titration and amperometric titration [6–8]. The colorimetric method using *o*-toluidine has only poor accuracy. The DPD method is selective to distinguish free and combined chlorines, but the method suffers from the interference by co-existing iodide ion. The sensitivity of the iodometric titration is

not so high and then it requires a large volume of sample to titrate the sample of low chlorine concentration. In the case of amperometric titration, the presence of electroactive substances such as oxygen will arise systematic errors. Moreover, the potential applied in amperometric measurements is fixed at a given value and it is not allowed to estimate background current [9]. These difficulties in conventional chlorine determination methods make clearer that an accurate and rapid method for the determination of free chlorine must be established.

For the electrochemical determination of free chlorine, the methods combined with flow injection system have been reported so far [10–14]. It has also been reported the voltammetric methods for chlorine determination by using special electrode materials such as boron-doped diamond, edge-plane pyrolytic graphite and micromachined sensor chip [15–17]. However, there seems to be few reports on the simple batch electrochemical method for the determination of residual free chlorine available for the WHO standard level [1,9]. In this paper, we developed an easy-to-operate and highly sensitive batch electrochemical determination method for free chlorine in aqueous solution. The proposed method has been successfully applied to monitor the residual free chlorine in drinking water.

Figure 1 shows the differential pulse voltammograms (DPVs) obtained at the Au electrode in 0.01 mol dm<sup>-3</sup> KCl as a function of NaClO concentration from 0 to

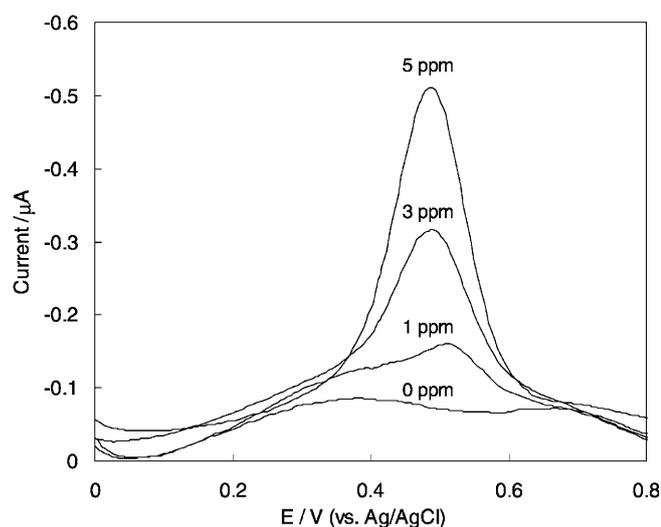
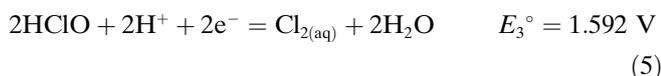
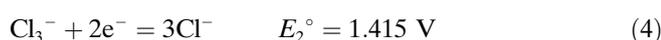
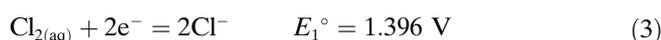
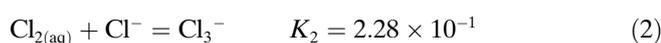
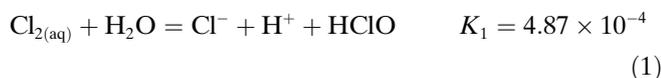


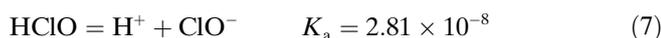
Fig. 1. DP voltammograms of solutions containing different concentrations of NaClO and  $0.01 \text{ mol dm}^{-3}$  KCl at pH 5.0. Working electrode was Au disk (1.6 mm diameter), the pulse amplitude was 25 mV and scan rate was  $20 \text{ mV s}^{-1}$ .

$5 \text{ mg Cl dm}^{-3}$ . When the potential was swept from  $+0.825$  to  $-0.275 \text{ V}$  (vs. Ag/AgCl), a cathodic peak was observed at about  $+0.5 \text{ V}$  proportional to the NaClO concentration.

For the aqueous acidic solution initially containing HClO and  $\text{Cl}^-$ , the following reactions in Equations 1 and 2 should be considered to specify the predominant redox species in solution because of their similar standard potentials as shown in Equations 3 to 6 [16, 19].



The reaction of  $\text{ClO}^-$  ion can be ignored in acidic solution because of the high  $\text{p}K_a$  value of the following acid dissociation reaction.



Then the equilibrium concentration of each Cl species was simulated using the mass balance Equation 8 and charge balance Equation 9,

$$C_{(\text{Cl})} = [\text{HClO}] + [\text{Cl}^-] + 2[\text{Cl}_2] + 3[\text{Cl}_3^-] \quad (8)$$

$$[\text{K}^+] + [\text{H}^+] = [\text{Cl}^-] + [\text{Cl}_3^-] + [\text{A}^-] \quad (9)$$

where  $C_{(\text{Cl})}$  is the total concentration of Cl species and  $\text{A}^-$  is the conjugate base of weak acid HA added for pH adjustment.

Figure 2 shows the simulated equilibrium concentration of each species for the initial HClO concentration of  $1.5 \times 10^{-4} \text{ mol dm}^{-3}$  at pH 5.0. Although the equilibrium concentration of each species changes depending on the ini-

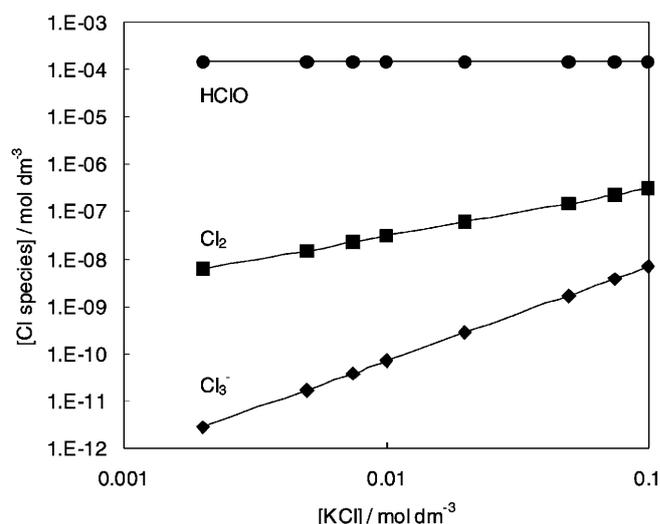


Fig. 2. Simulated dependence of the each concentration of Cl species on KCl concentration at pH 5.0.

tial  $\text{Cl}^-$  concentration, the predominant electroactive species was confirmed to be HClO and then the contributions of  $\text{Cl}_{2(\text{aq})}$  and  $\text{Cl}_3^-$  on the DPV peak can be negligible under the experimental condition of the present study. As for the electrochemical reaction of HClO, two possible reaction mechanisms in Equations 5 and 6 should be considered. At the standard state, that is at pH 0, the Reaction 5 is the more preferential reaction than Reaction 6 because of its higher standard potential, however at pH 5.0, the Reaction 6 is the more preferential reaction than Reaction 5 as expected from the Nernst equations of these reactions. The DPV peak observed in the present study can then be ascribed to the Reaction 6, the reduction of HClO to form  $\text{Cl}^-$  ion.

In the case of Reaction 6, the peak potential of DPV is expected to be affected by the  $\text{Cl}^-$  concentration. Figure 3 shows the effect of KCl concentration on the DPV profiles which were observed with the blank solutions containing 0.01 and  $0.1 \text{ mol dm}^{-3}$  KCl as the supporting electrolyte. As expected from the Nernst Equation 10 for the Reaction 6, the peak potential was shifted by  $-30 \text{ mV}$  with the increase of KCl concentration from 0.01 to  $0.1 \text{ mol dm}^{-3}$ , however, it was also confirmed that the peak current and peak shape were not changed by

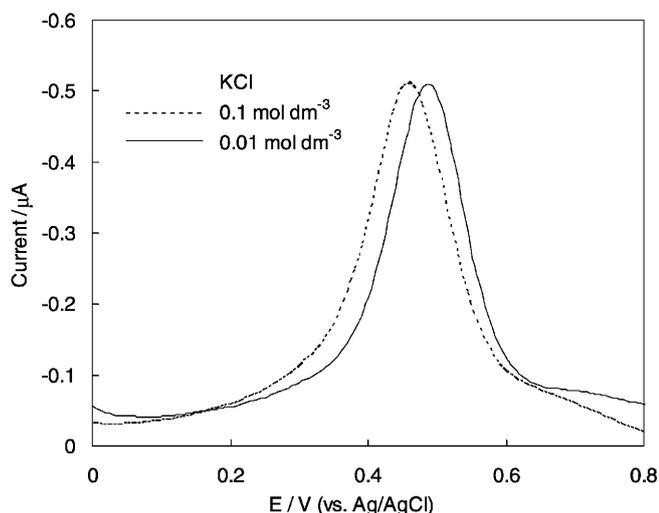


Fig. 3. DP voltammograms for the solution of  $0.01 \text{ mol dm}^{-3}$  and  $0.1 \text{ mol dm}^{-3}$  of KCl at pH 5.0. NaClO was  $5 \text{ mg Cl dm}^{-3}$ , pulse amplitude was  $25 \text{ mV}$  and scan rate was  $20 \text{ mV s}^{-1}$

the KCl concentration which is a favorable property for analytical purpose.

$$E_4 = E_4^\circ - \frac{RT}{2F} \ln \frac{[\text{Cl}^-]}{[\text{HClO}][\text{H}^+]} \quad (10)$$

Figure 4a shows the calibration curve made from the DPV peaks of HClO solutions at pH 5.0. A good linearity ( $r^2 = 0.99$ ) was obtained between 0 to  $5 \text{ mg Cl dm}^{-3}$  for 5 times measurements of each concentration. The limit of detection ( $LOD$ ) was estimated using the  $3s_B/m$  IUPAC criteria [18], where  $m$  is the slope of the linear calibration plot and the  $s_B$  corresponds to the standard deviation of the sensor response in the absence of chlorine (blank). The detection limit of the proposed method was  $0.04 \text{ mg Cl dm}^{-3}$  which covers the WHO drinking water regulation range. The  $LOD$  of this method is better than

that achieved by previous works employing the hypochlorite oxidation,  $1.0 \text{ mg Cl dm}^{-3}$  [1], and is similar to the flow injection analysis (FIA) method which used hypochlorite reduction,  $0.05 \text{ mg Cl dm}^{-3}$  [10].

The proposed method was applied to the determination of free chlorine in tap water collected at the Hakozaki Campus, Kyushu University, Japan. By using the standard addition method shown in Figure 4a, the concentration of free chlorine was estimated to be  $0.18 \pm 0.01 \text{ mg Cl dm}^{-3}$  ( $n=5$ ) with a recovery of 94–98%. The relative standard deviation for five measurements was 6.5%. The analytical result for the tap water sample was compared with that obtained by iodometric titration method (Figure 4b) [1,8]. The result obtained by the present method was in good agreement with that by the iodometric titration,  $0.21 \pm 0.02 \text{ mg Cl dm}^{-3}$ .

As reported by Jin et al. [10], a gold electrode provides the reactive electrode surface for chlorine reaction in comparison with platinum and glassy carbon electrodes in the pH range of 4 to 8. Moreover, the gold electrode is less influenced by the dissolved oxygen [9]. In the present method, the reduction peak of oxygen was observed at around  $-0.1 \text{ V}$  and therefore it did not affect the reduction peak of HClO at  $+0.5 \text{ V}$ .

Although FIA method has the advantage for the continuous routine monitoring of the residual chlorine in water samples, it requires expensive set-up cost and continuous maintenance to keep constant performance. The present batch method is easy to set-up and simple in operation. In this measurement, we found that it is not necessary to polish the electrode surface for each DPV measurement by using the Au electrode as the working electrode, which contributes to the improvement of the reproducibility of DPV signal. Moreover, we also found that it does not necessary to deaerate the solution before the DPV measurement. These features of the proposed method gives the advantage in on-site operation.

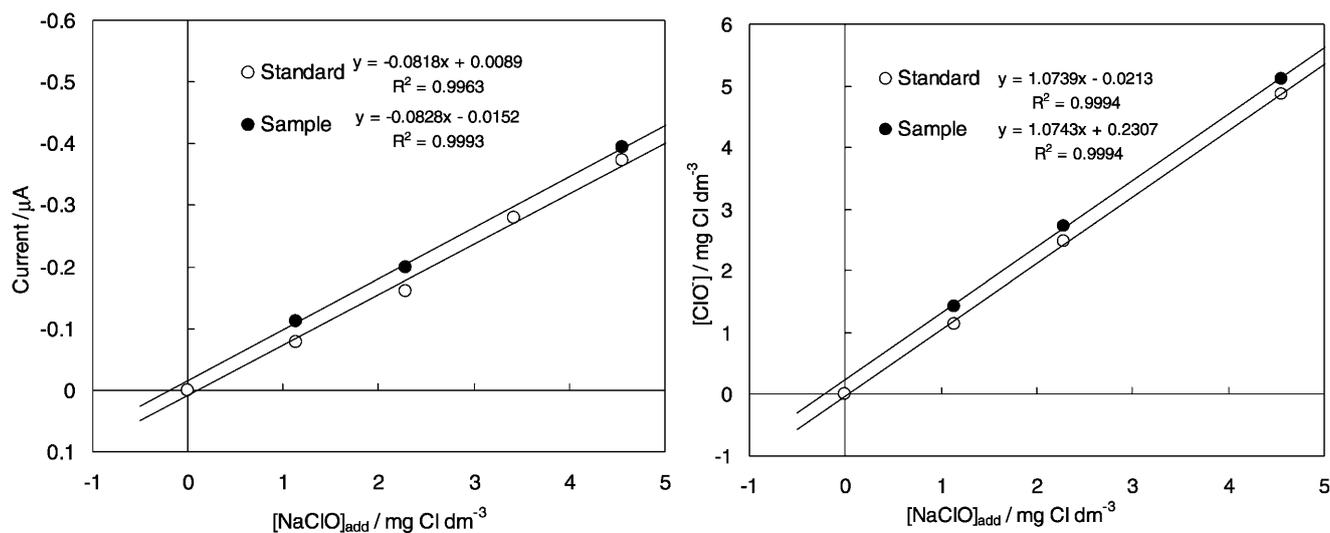


Fig. 4. Calibration curves of (a) the DPV peak height versus the concentration of NaClO and (b) the iodometric titration of NaClO using standard addition method applied for tap water and purified water.

In conclusion, we developed the easy-to-operate and high sensitive free chlorine determination method by using differential pulse voltammetry with an Au working electrode. It was demonstrated that the proposed method can be applied to monitor the residual free chlorine concentration of drinking water.

### Experimental

A standard free chlorine solution was prepared by diluting a NaClO aqueous solution (antiformine) with available chlorine of 5% (Wako, Japan). The initial concentration of free available chlorine in solution was determined by iodometric titration.

The electrochemical measurements were carried out with a single compartment cell. An Au disk (1.6 mm diameter), Ag/AgCl (saturated KCl) and Pt wire were used as the working, reference and counter electrodes, respectively. For pretreatment of the Au working electrode, the surface of the electrode was polished with aluminum oxide suspension, carefully sonicated in water, and then rinsed with highly purified water. A 0.1 mol dm<sup>-3</sup> potassium chloride was used as the supporting electrolyte. The pH solution for the DPV measurements was adjusted to 5 using acetate buffer solution.

DPV measurements were performed using a BD-101 electrochemical analyzer (Satoda Science, Japan) with a C-1B cell stand (BAS, USA). The scan rate of the DPV measurements was 20 mV s<sup>-1</sup> and the pulse amplitude was set at 25 mV. To a 20 cm<sup>3</sup> water sample, potassium chloride was added until the final concentration was 0.01 mol dm<sup>-3</sup>. All measurements were carried out at room temperature thermostated at about 25 °C. In order to obtain the analytical values for ClO<sup>-</sup>, we applied the standard addition method by plotting the DPV current peak in against the added concentration of NaClO. From the regression analysis of the plot of current peak versus concentration of the added NaClO, the concentration of the ClO<sup>-</sup> in the tap water sample was obtained as the X-axis intercept of the plot. The calibration curve was also made by using water and with adding the known quantities of NaClO. To obtain the peak current of DPV signal plotted in Figure 4a, the base current of the blank solution was subtracted from each peak current. All DPV measurements were performed without deaerating the solution unless otherwise stated.

### Acknowledgements

This work was partially supported by the JSPS Ronpaku Program (DGHE-10715) for S. S. (2009), by Grant-in-Aids for Scientific Research (B), No. 19310011 for K. Y., from the Ministry of Education, Science, Sports and Culture, Japan, and by Takaoka Chemical Company.

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