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Removal of Dissolved Oxygen Interference in the Amperometric Detection of Monochloramine Using a pH Control Method

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***Abstract*—**Monochloramine amperometric determination was investigated using a pH control method to eliminate dissolved oxygen as an interferent. This method allowed local pH conditions to become more acidic, causing the production of dichloramine. This species showed an onset of electro-reduction at 450 mV, far outside of the oxygen reduction region. Monochloramine was calibrated using this method and showed good linearity (0.99) and a limit of detection of 0.03 ppm.

Keywords*—Monochloramine, Dual electrode sensors, pH, Water quality, In-line sensing, Generator-Collector, Dissolved oxygen*

I. Introduction

The disinfection step of the water treatment process is vital to remove the various bacteria, viruses and protozoa that contribute to water-borne disease transmission. Chlorine is the most widely used disinfectant in water systems, due mostly to the speed at which it can eliminate the contaminating species.[1] One issue with the use of chlorine disinfectants is the production of trihalomethanes (THM). These result from the reaction of chlorine with organic matter and are linked to various cancers and cause an increase in miscarriage rate in pregnant women.[2, 3] Monochloramine (MCA) is used as a complementary and in some cases alternative disinfectant to minimise the production of THM's. While dichloramine (DCA) and trichloramines exist they are not used in disinfection as they have a shorter lifetime and are more toxic than MCA.[4]

As with chlorine disinfection, adequate chloramine disinfection is monitored by measurement of residual MCA in the water system. Too low a residual may indicate inadequate disinfection, while too high a residual can potentially lead to nitrification of the water system and a variety of further issues associated with high concentrations of nitrate and nitrite.[5] MCA concentrations are typically measured by colorimetry[6] or spectrophotometry.[7] An electrochemical method to measure MCA would remove the need for an additional reagent and simplify in-line analysis. However one of the main issues with developing an electrochemical sensor is the interference due to the presence of dissolved oxygen. The electro-reduction of MCA occurs in the same potential window as the oxygen reduction reaction.[8-10] Due to the variability of dissolved oxygen concentration in water, calibration of a MCA sensor becomes difficult without first knowing how much oxygen is present.

In this work, a method is presented that eliminates oxygen as an interferent by applying pH control. The pH control method works by applying a high potential to one comb of electrodes in an interdigitated array which causes water splitting. The reaction mechanism for this is:[11]

$$\boldsymbol{Cathode}: 2H^+ + 2e^- \rightarrow H_2$$
$$\boldsymbol{Anode}: 2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$

The anode is the comb of electrodes being biased in the array. The sensing electrodes are spaced close by the anode so that a local pH change is observed, Fig 1. The cathode in this set up is the counter electrode, which is spaced far enough away from the array to not have an impact on pH control. This process allows for a local pH adjustment to more acidic conditions, wherein the MCA is converted to DCA by the reaction of MCA with acids, the mechanism for which is:[4, 12]

$$2NH_2Cl + H^+ \rightarrow NHCl_2 + NH_4^+$$

The onset of reduction associated with DCA has a potential outside of the window attributed to the oxygen reduction reaction.[13] Thus by using local pH control, oxygen can be removed as an interfering species as it has no impact on the DCA reduction.

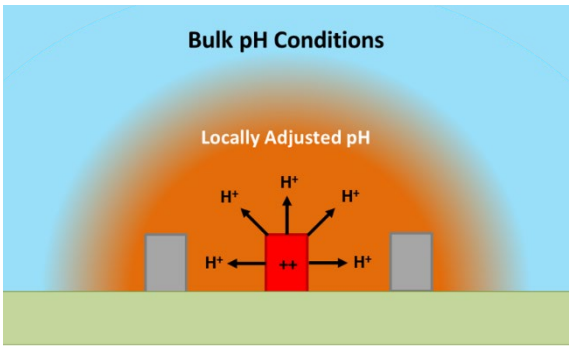


Fig. 1: A schematic representation of pH control wherein the anode or "protonator" (red) electrode causes a local pH change that can alter reactions and/or mechanisms at the sensing (grey) electrodes.

II. Materials and Methods

A. Device Fabrication

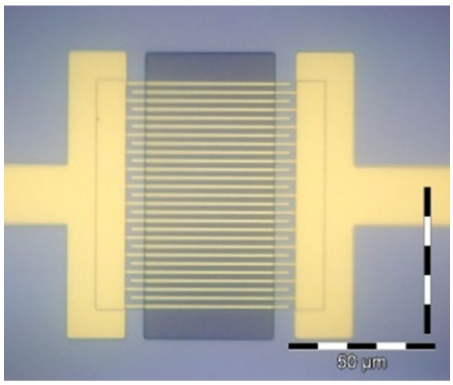


Fig. 2: Optical image of the fabricated electrode array. The electrode combs are separated by a 2 µm gap.

All devices were fabricated following the process shown in previous work within this group.[14-16] This process was used to fabricated interdigitated gold ultramicrobands, wherein the combs were 2 µm bands separated by a 2 µm gap. The fabricated device is shown in Fig. 2.

B. Device Characterisation

Electrochemical characterisation was performed in a solution of 1 mM Ferrocene Carboxylic Acid (FCA) (Sigma) in 10 mM Phosphate Buffered Saline (Sigma). Scans were performed in dual electrode mode wherein one comb of electrodes was swept from 0 V to 0.6 V at 50 mV/s while the other comb were biased at 0 V. All measurements were performed using an Autolab Bipotentiostat (Metrohm) using the on-chip counter and an external saturated calomel electrode.

C. pH Control in Deionised Water

The pH dependence of the oxide reduction reaction was used as a probe for pH control. Neutral, acidic and basic solutions were investigated to show how the oxide reduction potential changes with pH. Deionised water was acidified using 0.1 M HCl (Sigma) and basified with 0.1 M NaOH (Sigma). Scans were performed in each pH sample by sweeping from 0 V to 1.2 V at 50 mV/s to generate the oxide and back to 0 V to subsequently reduce the formed oxide.

When carrying out pH control experiments, it was determined that applying a potential of 1.65 V at the protonator electrode was sufficient to change the solution around the electrodes from the bulk pH of 8 to 3.

D. pH Control in Monochloramine samples

MCA stock solutions were made by mixing equal volumes of an 8 mM ammonium chloride solution with an 8 mM sodium hypochlorite solution. The ammonium chloride solution was made by dissolving 0.1 g of salt in 250 mls of deionised water and adjusted to pH 8.5 with 1 M NaOH. The sodium hypochlorite solution was made by diluting 7 mls. of commercial bleach with 250 mls. deionised water and adjusting to pH 8.5 with 1 M HCl. This yielded a 150 ppm stock of MCA, which was diluted with deionised water as required.

III. Results and Discussions

A. Scans in FCA

Fig. 3 shows a typical generator collector type FCA scan done using the interdigitated electrode arrays. The collector electrode is held at a constant potential of 0 V and reduces the oxidised FCA produced by the generator electrode. The current measured at both combs of electrodes is typical behaviour expected from a fully working sensor array.

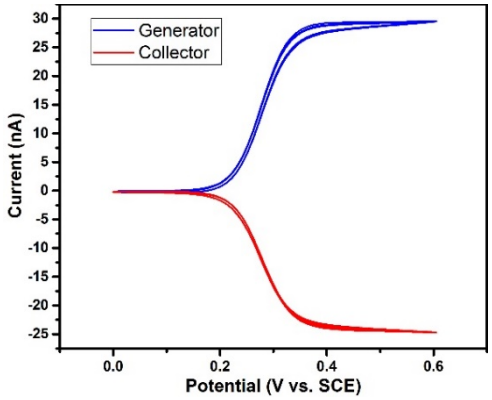


Fig. 3: Generator collector CV in 1 mM FCA. The generator electrodes (blue) are cycled from 0 V to 0.6 V vs. SCE at 50 mV/s. The collector electrodes (red) are held at 0V.

B. pH Control in Deionised Water

The variability of the oxide reduction potential is shown in Fig. 4 where it moves in response to the solution pH. In basic solutions, the oxide reduction occurs at approximately 250 mV vs. SCE. As the solution becomes more acidic, the oxide reduction moves to more positive potentials. This was used to establish parameters for pH control. As the desired pH for DCA production is 3, different protonator potentials were tested to see at which imposed potential the oxide reduction peak moved into the desired region. Biasing the protonator electrode at 1.65 V resulted in the sensing electrode showing an oxide reduction at 750 mV (Fig. 5) which was indicative of pH 3.

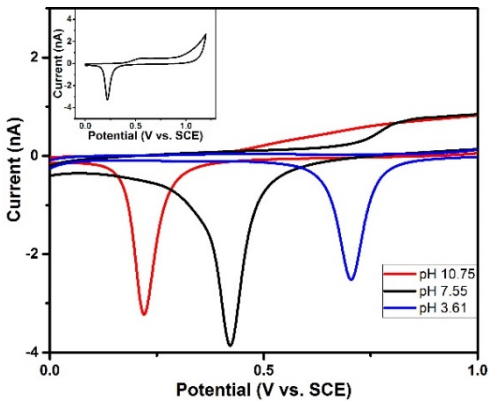


Fig. 4: Gold oxide reduction in various basic (red), neutral (black) and acidic (blue) water samples. CV's were swept from 0 V to 1.2 V at 50 mV/s (inset).

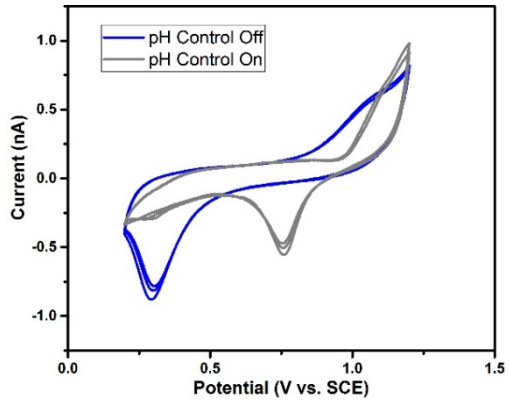


Fig. 5: Preliminary pH control experiments done in deionised water. The CV's were swept from 1.2 V to 0.2 V at 50 mV/s with the protonator off (blue) and biased at 1.65 V (grey).

C. *Monochloramine Calibration Using pH Control*

The pH control method that was established using deionised water was then applied to water samples containing various concentrations of MCA. In Fig. 6 the reduction of dichloramine is shown to have an onset at approximately 450 mV. The current increases with increasing concentration of MCA, which indicates that the MCA is converted to DCA within the timeframe of the experiment. The potential window wherein an accurate measurement of monochloramine concentration can be determined is now significantly outside the window where oxygen reduction causes an interference. The blank sample shows very little activity and was found to be constant in varying oxygen concentrations so it does not indicate any other interference for this analysis method.

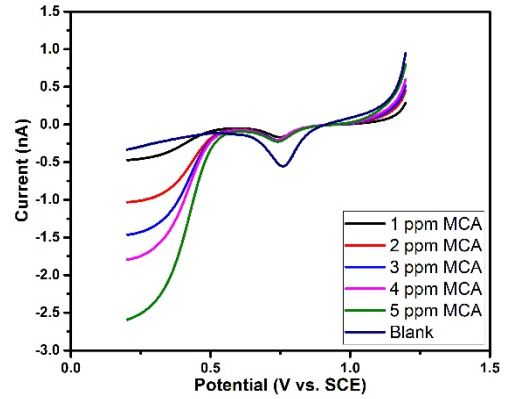


Fig. 6: LSV's in various concentrations of monochloramine using the pH control method. The sensing electrode was scanned from 1.2 V to 0.2 V at 50 mV/s with the protonator electrode biased at 1.65 V.

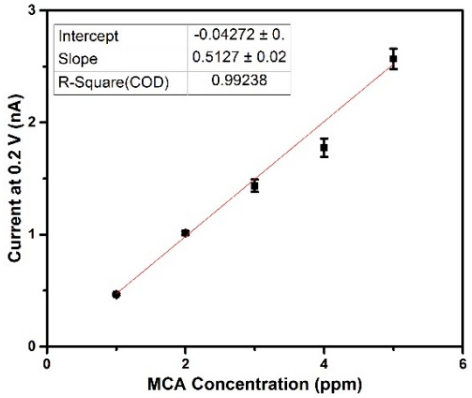


Fig. 7: Calibration plot for the monochloramine sensing with pH control applied. Graph shows a linearity of 0.99 with minimal error.

The calibration plot for this (Fig. 7) shows that the current measured is directly proportional to the amount of monochloramine present. The calibration plot indicates that a current of approximately 0.5 nA is achieved for each part per million of MCA. An estimated limit of detection was calculated to be 0.03 ppm. This value was obtained by tripling the standard deviation of seven measurements in 0.5 ppm MCA samples.

IV. Conclusions and Future Work

This work shows that a MCA sensor can be developed using a pH control method to eliminate the interference due to dissolved oxygen. Furthermore this work shows the viability of a pH control method for use in sensor systems. Analysis of real world samples will be assessed to further validate the method.

V. Acknowledgements

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