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**Effects of Monochloramine and Free Chlorine on Copper Dissolution  
in Drinking Water**

Submitted by

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Date Submitted: 23 March 2007

## Abstract

The effects of the disinfectants free chlorine and monochloramine have been studied on thin copper films using the electrochemical quartz crystal microbalance, scanning electron microscopy and x-ray diffraction. It has been found that after twenty four hours of immersion, the hypochlorite and the monochloramine both convert some of the copper into cuprous oxide. However, after immersion in monochloramine, tiny pinholes in the copper develop on the electrode and the gold substrate is visible underneath. This leads to suggest that while free chlorine may oxidize copper, monochloramine will oxidize copper and can cause pitting in the metal.

## Introduction

Many municipalities have recently switched from free chlorine to monochloramine as the chief disinfectant in their water treatment process. This was done to reduce the amount of carcinogenic trihalomethanes that are formed by the combination of free chlorine and organic material present in water. Shortly after this transition, the levels of dissolved lead in the drinking water had begun to skyrocket. The amount of lead in some samples of water taken after the switch contained 31-113  $\mu\text{g/l}$  of lead, which is much higher than the EPA action limit of 15  $\mu\text{g/l}$ . According to Edwards and Dudi (1), this can be attributed to the disinfectant monochloramine. Since monochloramine is structurally similar to ammonia, and ammonia and amine groups readily complex with copper ions (2), it is hypothesized that monochloramine will complex with copper used in plumbing lines and dissolve thus increasing the concentration of copper in potable drinking water. The electrochemical quartz crystal microbalance (EQCM) will be used to test whether or not a thin film of copper will experience mass loss when immersed in a solution of free chlorine and a solution of monochloramine. The EQCM will be used because it is a simple and accurate way to measure the small changes in mass of a thin film (3). The films will be analyzed using both x-ray diffraction analysis and scanning electron microscopy.

## Main Body

### **Experimental Section**

For this experiment, the Stanford Research Systems QCM200 electrochemical quartz crystal microbalance with a 5 MHz AT-cut gold plated quartz crystal was used to measure the change in mass of a copper film over a period of twenty four hours. Before each EQCM crystal was used, it was first washed with a 50 vol%  $\text{HNO}_3$  solution to remove any previously deposited copper and then rinsed with ethanol to remove any organic matter. The crystals were then allowed to dry before being used.

**Electrodeposition bath.** First, a copper electrodeposition solution had to be prepared to electrodeposit a film of copper onto the gold substrate of the EQCM. According to O'Keefe (4), a solution consisting of 50 g/l of  $\text{Cu}^{+2}$  and 180 g/l  $\text{H}_2\text{SO}_4$  makes an ideal electrodeposition solution when deposited at a current of 20  $\text{mA/cm}^2$ . Using this information, 49.11 g of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and 24.96 ml of concentrated  $\text{H}_2\text{SO}_4$  was dissolved in deionized water and then diluted to 250 ml in a volumetric flask. This is the standard electrodeposition solution that was used to electrodeposit all of the EQCMs.

**EQCM Electrodeposition.** Each EQCM in the experiment was electrodeposited under the same conditions and each EQCM was used immediately after electrodeposition. Each electrodeposition was run for sixty seconds. The electrodepositing solution was stirred with a magnetic stir bar at 250 rpm. A platinum wire was used in each electrodeposition as a counter electrode. The scale on the QCM200 was always set at 5 kHz/V and the current was set at -0.0274 A to allow for a depositing current of 20 mA/cm<sup>2</sup>. On each deposition, an average of 372 µg of elemental copper was deposited onto the electrode surface. The Sauerbrey equation was used to measure the change in mass of the quartz crystal due to the copper deposition as a function of the oscillation frequency of the quartz crystal.

The Sauerbrey equation:

$$\Delta m = (A \Delta f(\rho\mu)^{1/2})/(-2f_0^2)$$

Where  $\Delta m$  is the change in mass of the sample in grams,  $A$  is the area of the crystal (in this experiment, the area was 1.37 cm<sup>2</sup>),  $\Delta f$  is the change in frequency of the crystal,  $\rho$  is the density of quartz (2.648 g/cm<sup>3</sup>),  $\mu$  is the shear modulus of quartz (2.947 x 10<sup>11</sup> g cm<sup>-1</sup> s<sup>-2</sup>), and  $f_0$  is the original frequency of the quartz crystal before the experiment.

**Disinfectant and buffer solutions.** The disinfectant solutions were all prepared fresh for each experimental run. Each solution was buffered to a specific pH and all tests were conducted with 250 ml solutions. A sodium hypochlorite solution with 10-13% available free chlorine was used as the source of HOCl/OCl<sup>-</sup>. The monochloramine was prepared by mixing free chlorine with a five molar excess of concentrated ammonia solution. This excess of ammonia was necessary to reduce the amount of dichloramine formed in the process. At higher pH the majority of excess ammonia exists as NH<sub>4</sub><sup>+</sup> (5). The concentrations of the disinfectants were chosen to be close to 1mM so that the concentration would remain relatively constant throughout the course of the experiment. The concentrations of all disinfectants in solution were measured spectrophotometrically using a CARY 5 UV-Vis-NIR spectrophotometer. The concentrations of the hypochlorite solutions were determined at 292 nm ( $\epsilon = 350 \text{ M}^{-1}\text{cm}^{-1}$ ). The concentrations of the monochloramine solutions were determined at 243 nm ( $\epsilon = 461 \text{ M}^{-1}\text{cm}^{-1}$ ) (5). To determine the concentration of hypochlorite in the stock solution, 500 µl of the stock solution was diluted to 250 ml with deionized water in a 250 ml volumetric flask. This solution was thoroughly shaken and then analyzed with the CARY 5. Using Beer's Law, the concentration of the solution was determined to be 2.60 mM. Then, using the equation  $M_1V_1 = M_2V_2$  where  $M$  is the molarity of the solution and  $V$  is the volume, the molarity of the stock solution was determined to be 1.30 M. Data was measured during all copper corrosion experiments while maintaining constant pH. The copper corrosion data were measured at pH 7 and 8.5. For each constant pH value, three runs were conducted: one in deionized water buffered to the pH of the group, one in a 0.628 mM hypochlorite solution, and one in a 0.893 mM monochloramine solution. For the pH 7 and 8.5 buffer solutions, data was taken from the CRC Handbook of Chemistry and Physics (6). Using this data, the pH 7 buffer solution was made by mixing 125 ml of 0.1 M aqueous tris(hydroxymethyl)aminomethane with 116.5 ml of 0.1 M HCl. This solution was diluted to 250 ml in a volumetric flask and then thoroughly mixed. The pH 8.5 solutions were prepared by mixing 125 ml of 0.025 M borax with 51.25 ml of 0.1 M HCl. The 0.025 M borax solution was

prepared by mixing 2.384 g of  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$  in deionized water and then diluting it to 250 ml in a volumetric flask. For the pH 9 runs, the pH of the solution was adjusted to pH 9 with a 0.60 M solution of  $\text{H}_3\text{BO}_3$  and 1.0 M NaOH. For a 0.628 mM solution of hypochlorite 200  $\mu\text{l}$  of the stock hypochlorite solution was added to the buffer precursors and then the solution was diluted to 250 ml. For a 0.893 mM monochloramine solution, 200  $\mu\text{l}$  of the stock hypochlorite solution was added to the buffer precursors. To this, 81  $\mu\text{l}$  of concentrated aqueous ammonia was added to the solution. Finally, the solution was diluted to 250 ml. The pH of all solutions was measured against a MeterLab EPM 220 pH meter that was calibrated every 24 hours.

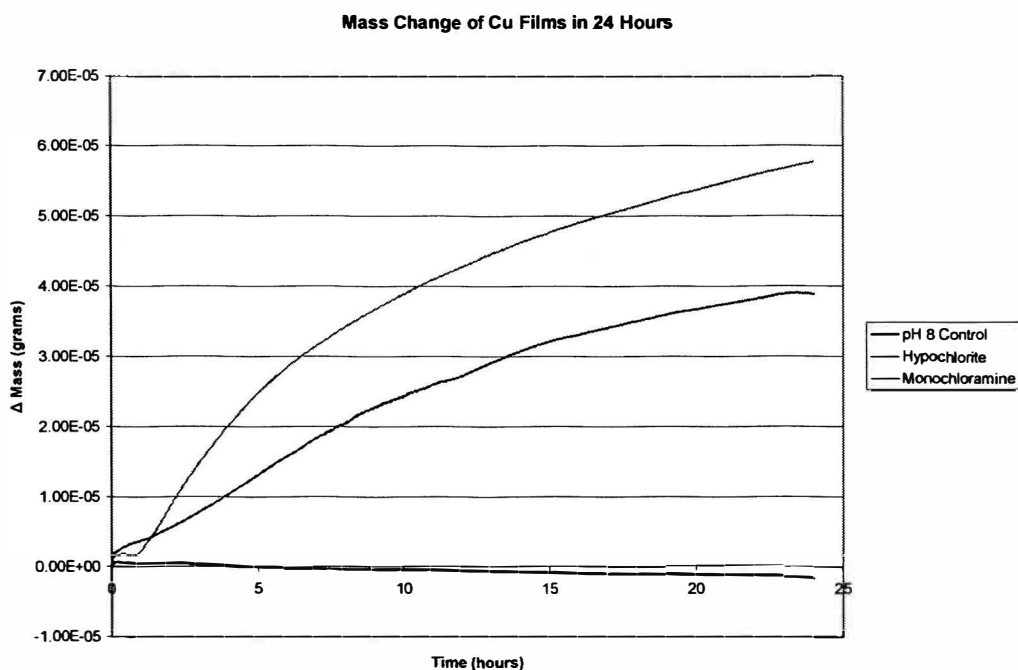
**SEM and XRD Instruments.** The scanning electron microscope (SEM) used for all EQCM surface photography is a Hitachi S4700 cold field emission scanning electron microscope. A Phillips X'Pert diffractometer was used for all glancing angle x-ray diffraction (XRD) patterns. The diffractometer uses  $\text{Cu K}\alpha$  source radiation with an x-ray mirror (PW3088/60) as the incident beam module and a  $0.18^\circ$  parallel collimator as the diffracted beam module. A fixed incident angle of  $1^\circ$  was maintained, and the instrument was operated in the continuous mode with a step size of  $0.03^\circ$  and a counting time of 10 seconds.

## Results and Discussion

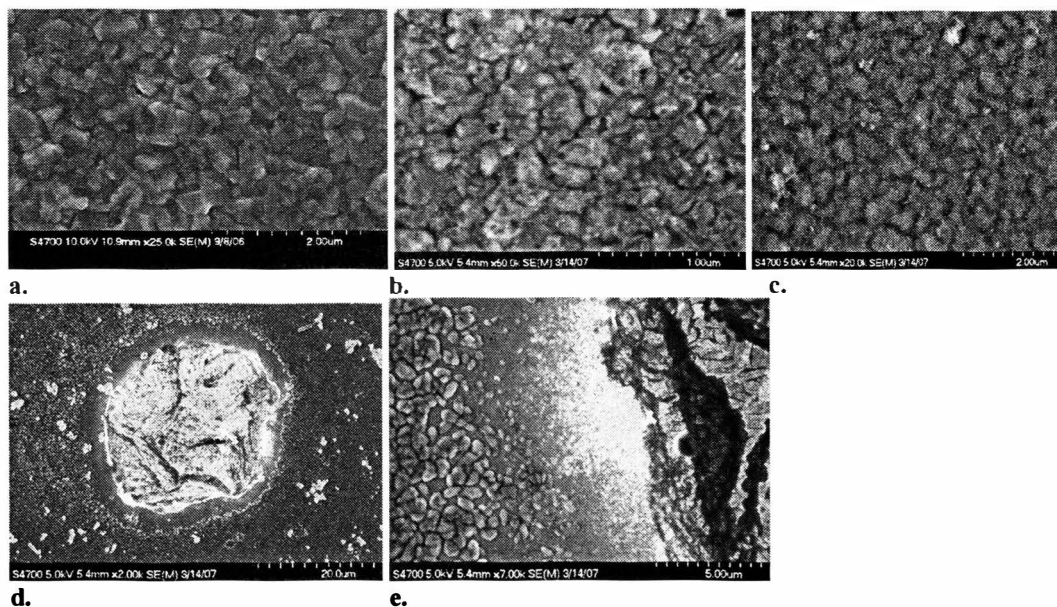
**EQCM Electrodes at pH 8.5.** For the pH 8.5 control electrode, figure 1 shows that roughly 1.5  $\mu\text{g}$  of mass had been lost from the surface of the electrode over the course of twenty four hours. At the start of the experiment, the pH of the buffer solution was 8.43. After the twenty four hour time period, the pH had been measured at 8.37. There was no visible change in the color and luster of the copper on the electrode surface. Upon viewing the SEM imagery in figure 2, there had been no visible change in the copper on the electrode as compared to a freshly electrodeposited film. According to figure 3, the EQCM electrode was still composed of elemental copper with a gold substrate indicating that no oxidations of the copper on the electrode had taken place.

For the pH 8.5 electrode that had been immersed in the hypochlorite solution, there was roughly a 38.9  $\mu\text{g}$  gain in mass after 24 hours as can be seen in figure 1. At the start of the experiment the pH was 8.74 and the concentration of hypochlorite in the solution was measured to be 0.628 mM. After twenty four hours, the pH of the solution was 8.73 and the concentration of the hypochlorite was 0.608 mM. The coloration of the electrode had changed from the lustrous copper to a dull, slightly grayed copper color. SEM imaging resulted in an almost sponge-like surface on the copper film as seen in figure 2. Upon XRD analysis, the film was shown to consist of elemental copper as well as cuprous oxide. (See fig. 4). This conversion of elemental copper would account for the gain in mass of the EQCM electrode.

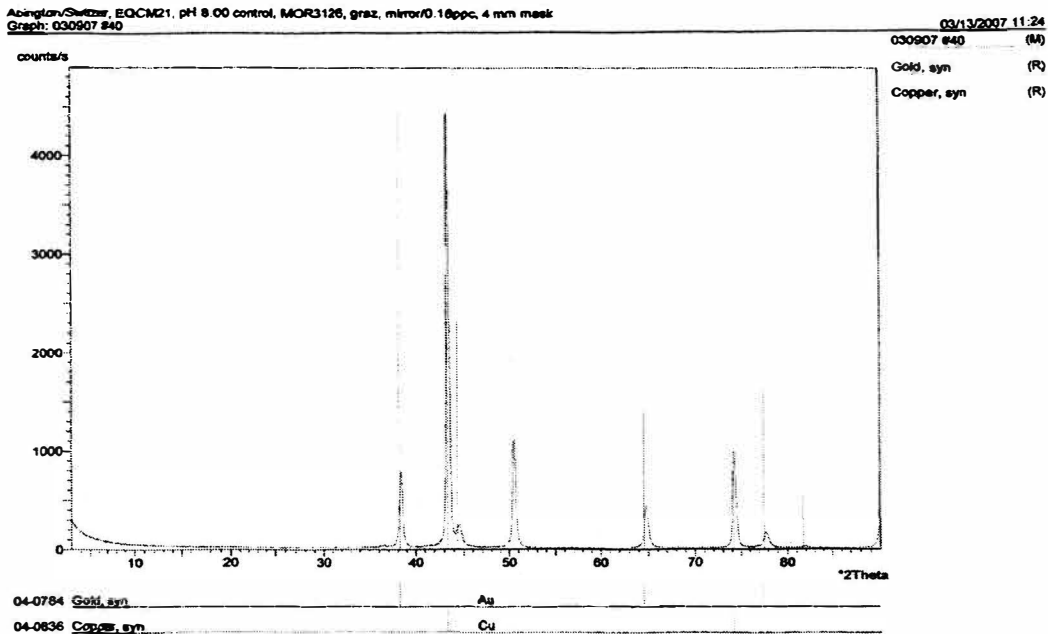
With the pH 8.5 electrode that had been immersed in monochloramine, there was roughly a 57.7  $\mu\text{g}$  gain in mass after twenty four hours as shown in figure 1. Over this time period, the pH had changed from 8.71 to 8.66. The surface of the electrode had been completely tarnished and lacked any luster. There were also tiny pinholes visible on the surface of the electrode. The SEM images in Fig. 1 show these pinholes where the copper has been stripped and the gold substrate is visible. The concentration of the monochloramine had decreased from 0.893 mM to 0.593 mM. The gain in mass of the EQCM electrode can be explained by some of the elemental copper being converted to cuprous oxide, which is shown in the XRD analysis in figure 5.



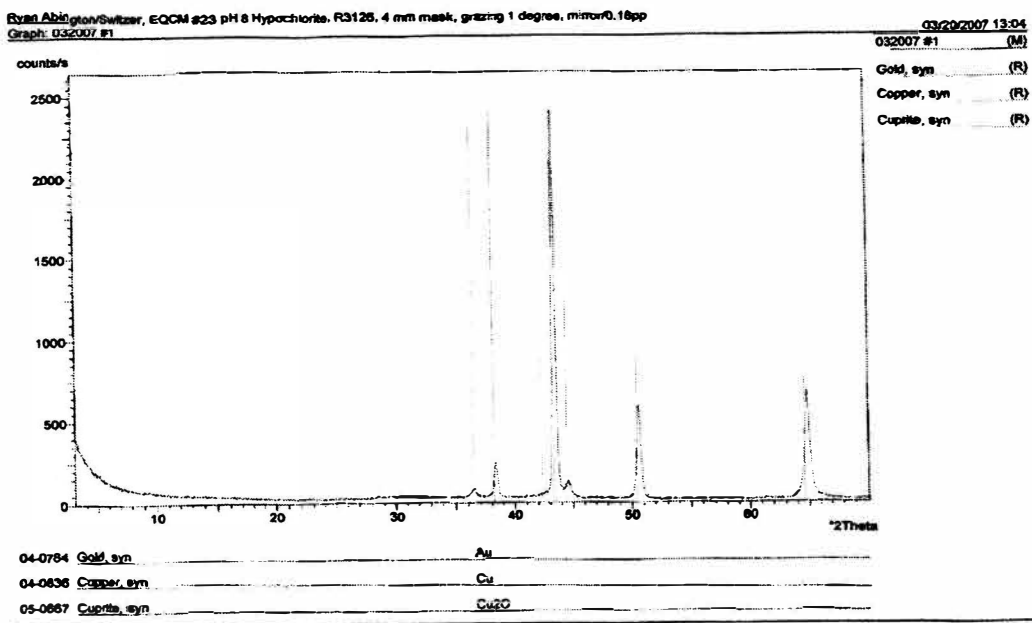
**Figure 1: Plot showing the change in mass of the three electrodes held at pH 8.5 over a 24 hour time interval.**



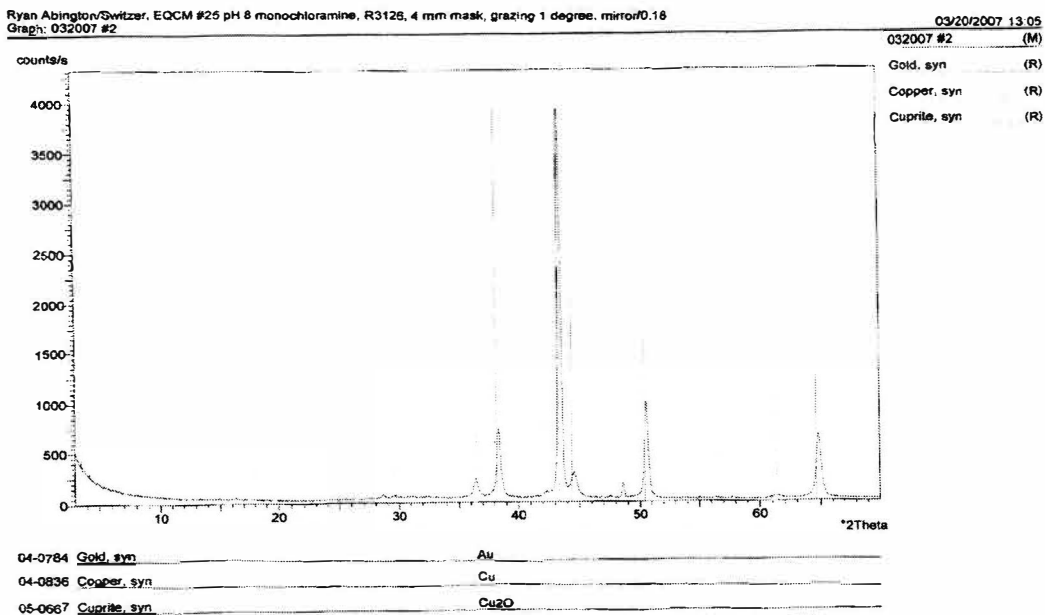
**Figure 2: (a.) EQCM crystal after electrodeposition. (b.) EQCM after immersion in pH 8.5 buffer for 24 hours. (c.) EQCM after immersion in pH 8.74 buffered hypochlorite for 24 hours. (d.) EQCM after immersion in pH 8.71 for 24 hours. Central object is one of the pinholes with the gold layer clearly visible underneath. (e.) Magnified view of the edge of one of the pinholes of the EQCM that had been immersed in monochloramine for 24 hours. Note the copper on the left hand side and the gold substrate on the right hand side.**



**Figure 3: XRD of pH 8.5 control electrode after 24 hours immersion in borax/HCl buffer. This XRD indicates that the composition of the deposited material on the EQCM is still elemental copper on a gold substrate.**

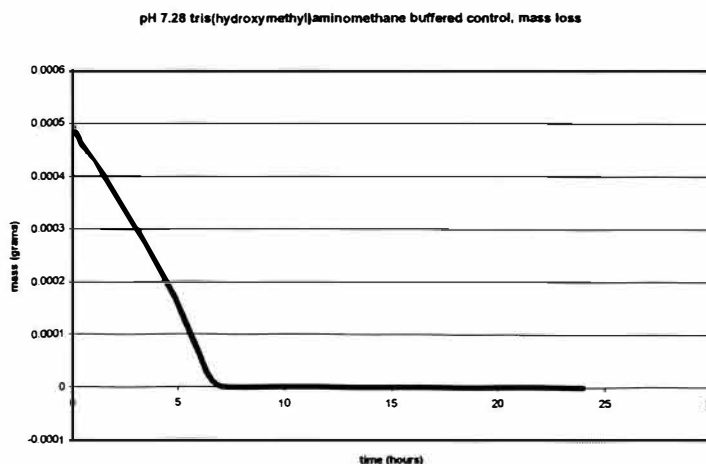


**Figure 4: XRD of EQCM immersed in 0.628 mM hypochlorite solution for 24 hours. Indicates that some of the copper has been converted to Cu<sub>2</sub>O.**



**Figure 5: XRD of EQCM that had been immersed in 0.893 mM monochloramine for 24 hours. Indicates that some elemental copper has been converted to  $\text{Cu}_2\text{O}$ .**

**EQCM Electrodes at pH 7.0.** As can be seen in figure 6 the EQCM that was dipped in the tris(hydroxymethyl)aminomethane/HCl buffer, had been stripped of the deposited copper in just over eight hours. The pH of the solution did change from 7.28 to 7.33 in that time frame. There was no visible copper on the electrode. Since there is a prominent amine group in tris(hydroxymethyl)aminomethane and amine groups readily complex with  $\text{Cu}^{+2}$  (2), this mass loss is most likely attributed to that amine group and is the cause for dissolution. Since this buffer solution causes dissolution of the copper films that are immersed in it, it would have been a futile effort to run a test at pH 7 with hypochlorite and monochloramine. Therefore, no further experiments were run.



**Figure 6: Mass loss of pH 7.0 buffered control electrode over a 24 hour period.**



**Conclusions.** The results of these experiments suggest that the switch of disinfectants from free chlorine to monochloramine might have a slight effect on copper piping. At pH 8.5 some of the copper on the EQCM electrodes that have been immersed in hypochlorite and in monochloramine got converted into  $\text{Cu}_2\text{O}$ . On the monochloramine electrode, tiny pinholes were noticeable to the naked eye with the gold substrate visible underneath. Areas for further research in this topic include: looking for buffer solutions for pH 7 that do not interact with the copper substrate on the EQCM electrode, determining the change in the concentration of copper in the solution over time as a result of the disinfectant, and the effects of temperature on the concentration of disinfectant in solution. Another topic of interest would be to conduct the experiments at pH lower than 7 to see if the disinfectants produce the same results that they do at pH 8.5.

### **Acknowledgments**

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