

Reducing copper toxicity by drinking coffee

H. Djati Utomo

UTM, Department of Environmental Engineering, Johor, Malaysia

Abstract

Copper contamination in drinking water is not a new issue in today's world. Various modern industries use copper for their raw materials and discharge copper by-products into the watercourse. Current water treatment technology is not a guarantee for providing safe drinking water required by humans. Although copper is one of the essential nutrients required by the human body for both physical and mental health, an excessive copper concentration in the human body becomes a toxic threat. Drinking coffee habitually may be helpful in reducing copper concentrations, which might lead to a reduction in copper toxicity. This experimental study, using copper-ion selective electrode (Cu-ISE), lowered copper concentrations due to the availability of copper binding ligands found in coffee solution. The copper electrodes were calibrated thoroughly using ethylenediamine (en) standard buffer solution before being used for determining free and bound copper ions in coffee solution.

Keywords: copper, Cu-ISE, coffee, copper binding ligands, en, toxicity.

1 Introduction

Water pollution due to toxic heavy metals contamination is a major issue for today's environment. Various trace metals such as lead, mercury, zinc, copper, nickel and cadmium are released to the environment as a result of human activities. Modern uses of these metals include the production of alloys, photography, paints and dyes, pesticides (e.g. copper oxychloride), textiles, electrical wiring and electroplating. Judd *et al.* [1] estimated that the production of printed wiring board (PWB) produced about 60% of the soluble metals disposed of into wastewaters. Copper is extremely toxic to aquatic biota exhibiting an adverse impact at concentrations as low as 15 to 30 nmol L⁻¹ (Davey *et al.* [2], Gillespie and Vaccaro [3]) Concerns about trace metals



primarily result from their potential toxicity, persistence and tendency to become concentrated in food chains (Brierley *et al.* [4], Holan *et al.* [5]).

Although some trace metals have a key role in the functioning of metallo-protein enzymes (Stumm and Morgan [6]), when a metal ion such as copper, exceeds its requirement by an organism there is the potential for toxic effects. Current US-Canadian Recommended Dietary Allowance (RDA) for copper is 9 mg/d for adults, with a tolerable upper intake level (UL) of 10 mg/d for adults (Institute of Medicine [7]). Chronic copper toxicity, as an effect of detrimental symptoms, can result in liver disease and severe neurological defects (Uriu-Adams and Keen [8], Davanzo *et al.* [9], Srivastava *et al.* [10], World Health Organization [11]). Acute copper toxicity can result in a number of pathologies and, in severe cases, death. It can result from the ingestion of copper contaminated beverages including water or the accidental or deliberate ingestion of high quantities of copper salts (Uriu-Adams and Keen [8]). Unfortunately the mechanism underlying the acute copper toxicity effects in humans is not well understood.

Drinking coffee not only gives much-needed lift in the morning but it can also reduce the copper concentration in the water used for preparing the coffee as an improvement of drinking water quality.

This paper deals with the health benefits of drinking coffee as a result of copper binding ligands released from soluble coffee. Tannin-containing materials such as coffee or tea contain metal-binding polyhydroxy-polyphenol functional groups (Bailey *et al.* [12]). Tannic acid is a phenolic material considered responsible for the tannin flavour of beverages such as tea or coffee. Tannic acid consists of a glucose core, which covalently links to 3–5 gallic acid residues through ester bonds. In addition, each gallic acid residue can covalently link to other gallic acid units as shown in Figure 1.

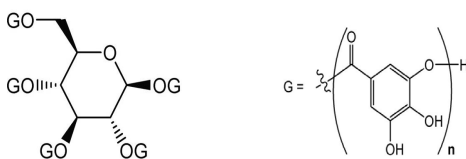


Figure 1: Molecular structure of tannic acid (Liu [26]).

2 Cu-ISE as a method for determining copper binding organic ligands in coffee solution

A number of analytical approaches have been developed to measure metal speciation in natural waters. Metal ion-selective electrodes (ISE) are particularly useful for toxicity studies and for the determination of the complexation capacity of freshwater. ISEs have been used to directly measure ambient free metal concentrations in river or lake water, but they are in general limited by their sensitivity and selectivity (Sunda and Hanson [13], Camusson *et al.* [14], Xue

and Sunda [15]). The copper ion-selective electrode (Cu-ISE) has insufficient sensitivity for reliable measurement at the low ambient Cu concentrations in most natural waters. In addition, it cannot be used in seawater because of chloride interference (Westall [16]). Here the importance of calibration method can be the determinant factor before being used as a reliable method for characterising between free and bound copper ion (Chau and Chan [17], Ramamoorthy and Kushner [18]). The Cu-ISE has been applied to the determination of reaction stoichiometries and metal-ligand binding strengths (Rifkin *et al.* [19], Berminham-McDonogh *et al.* [20]).

The interaction between Cu^{2+} -binding organic compounds in coffee solutions and Cu^{2+} was examined by titrating a sample of solution with known additions of Cu^{2+} , measuring the free $[\text{Cu}^{2+}]$ using the Cu-ISE as used for titrations of Cu^{2+} in raw and treated potable waters (Luo [21], Sanders *et al.* [22]).

3 Experimental

3.1 Preparation of copper and coffee solutions

6.36 mL of Copper (II) Nitrate AAS Standards (APS Ajax Finechem, 1000 ppm in 0.5% HNO_3) were added to a 100 mL volumetric flask and made up with deionised water (Millipore Milli-Q System known as Milli-Q water) to make Cu^{2+} standard solution ($10^{-3} \text{ mol L}^{-1}$). Dilution method was used to prepare the remaining stock solutions ($10^{-4} \text{ mol L}^{-1}$, $10^{-5} \text{ mol L}^{-1}$, and $10^{-6} \text{ mol L}^{-1}$). All of these stock solutions were acidified to 0.1% v/v with HNO_3 to minimize adsorptive loss of Cu^{2+} and stored in polyethylene bottles. They were freshly prepared every 1–2 weeks.

Coffee solutions were prepared by soaking 10.0 g and 20.0 g of commercial coffee ground (Blue Mountain variety) in 1000 mL Milli-Q water overnight at room temperature. The solid phase was removed by filtering the coffee suspension through Whatman 114 filter paper before adding 10.1 g of KNO_3 to make a final ionic strength $I = 0.1 \text{ mol L}^{-1}$. After the KNO_3 was dissolved the solution was divided into 50 mL portions in beakers. Different concentrations of Cu^{2+} standard solution were then added to each solution aliquot to produce final concentrations of added Cu^{2+} ranging from $10^{-3} \text{ mol L}^{-1}$ to $0.5 \times 10^{-6} \text{ mol L}^{-1}$. The pH of each solution was adjusted (with either $0.1 \text{ mol L}^{-1} \text{ HCl}$ or $2 \text{ mol L}^{-1} \text{ NaOH}$) back to the pH of 5.03, which was observed before addition of Cu^{2+} before being equilibrated overnight.

3.2 Preparation of apparatus

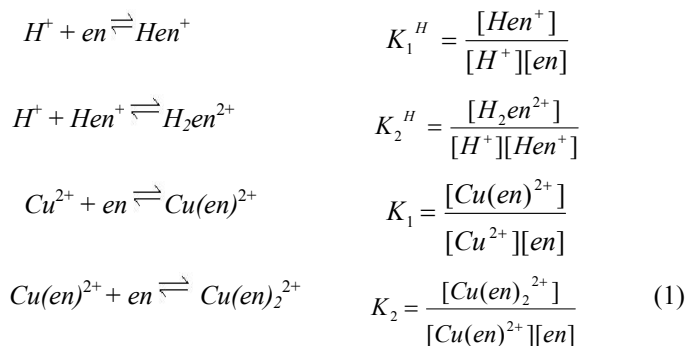
The 94298N Orion cupric electrode and 900200 Orion double junction reference electrode were stored in Milli-Q water while not in use. Before measurement, the shiny surface of the cupric electrode was buffed gently (30s) with Orion alumina polishing strips. The electrode was then rinsed vigorously with Milli-Q water and placed in $0.025 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ for 10 min, which served to clean the electrode (Blaedel and Dinwiddie [23]). Since the slope of the Nernst equation is temperature-dependent, temperature is a factor that can affect the potential



reading in a test solution. Thus in the present study, a measurement cell having a water jacket through which water from a constant temperature water bath was pumped to keep the temperature of the sample as constant as possible through all the measurements. The temperature variation of the water bath was ± 0.2 °C. In addition, the size and rotation speed of the magnetic stirrer bar, and the distances of the electrodes from each other and the stirrer, were kept constant throughout all the experiments. Between two measurements, the electrodes, stirrer bar and inside of the cell were vigorously rinsed with $0.025 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ and soaked in Milli-Q water. Potentials were measured using an Orion Expandable Ion Analyzer EA920. A glass pH electrode was also inserted into the solution to measure solution pH. The EA920 has two electrode channels so it was possible to measure both pH and the potential of the Cu-ISE cell with a single instrument.

3.3 Calibration of copper electrodes and ethylenediamine (*en*) standard buffer solution

The calibration of the copper electrode could be conducted at very low copper concentration (as low as 10^{-19} mol/L) using copper ion buffer reagent following Avdeef's method (Avdeef *et al.* [24]). With the method the curves can possess > 99% ideal Nernstian slope (theoretically 29.58 mV / pCu at 25°C). The value of pCu in these solutions can be calculated by solving the equilibrium eqns (1) using a macro procedure written in Visual Basic (Djati Utomo [25]). The Cu^{2+}/en system involves the following reactions:



The equilibrium constants ($\log K_1 = 10.512$ and $K_2 = 9.034$) and protonation constants for *en* ($\log K_1^{\text{H}} = 10.063$ and $K_2^{\text{H}} = 7.204$) at an ionic strength $I = 0.1 \text{ mol L}^{-1}$ were reported by Avdeef *et al.* [24] and Djati Utomo [25] respectively. The new Avdeef's protonation constants for *en* were re-measured by Djati Utomo [25] to improve agreement between the Cu^{2+} -*en* buffers and Cu^{2+} solutions.

3.4 Measurement of pCu in coffee solutions using the Cu-ISE

Calibration of the ISE using $\text{Cu}(\text{NO}_3)_2$ and Cu^{2+} -*en* standard solutions of known free $[\text{Cu}^{2+}]$ was conducted before and after measuring the potential of the sample



of coffee solutions. Both the pH and potential of the Cu-ISE were measured for each coffee solution (after calibration of the Cu-ISE).

4 Results and discussion

4.1 Cu-ISE electrode calibration

The electrode calibration was carried out using the 10^{-6} to 10^{-3} mol L⁻¹ copper standard solutions, and the five Cu-en metal ion buffer solutions having nominal pH values of 5, 6, 7, 8 and 9 respectively. A typical calibration curve obtained by plotting the measured potential against pCu is shown in figure 2, with the corresponding data presented in table 1. It is seen that the electrode response follows the expected linear Nernst over the pCu range used for calibration. The slope of the calibration was -24.535 mV (the ideal Nernst value of -29.58 mV at 25 °C). It is important to note that the data points for Cu(NO₃)₂ standards lie on the same line, within experimental error, as those for the Cu²⁺-en metal ion buffers.

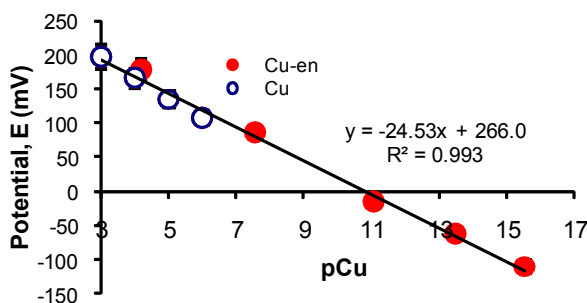


Figure 2: A typical Cu-ISE calibration used for coffee solution samples. The measured Cu-ISE potential is shown as a function of $pCu = -\log [Cu^{2+}]$, where $[Cu^{2+}]$ is the calculated concentration of free Cu^{2+} in the $Cu(NO_3)_2$ (open circles) and Cu^{2+} -en (solid circles) standard solutions.

4.2 Copper binding ligands in coffee solutions

Two different concentrations of coffee soluble sourced from 10 and 20 g L⁻¹ of coffee grounds leached in Milli-Q water are presented in figure 3. The measured concentrations of free Cu^{2+} fall well below the 1:1 line as a result of Cu^{2+} binding by soluble ligands in the solution. In addition, the decrease in $[Cu^{2+}]$ is greater for the 20 g L⁻¹ solution than for the ones containing only 10 g L⁻¹ in agreement with an expected higher concentration of soluble material in the former case. In figure 3 the curvature of the plot is changing in two different regions, i.e. near $\log [Cu^{2+}] \approx 3$ and 5. This might be explained from the complexity of organic

materials in coffee soluble. It was very unlikely that there is a single functional group responsible for Cu^{2+} binding. It is probable that the observed behaviour is due to many functional groups whose Cu^{2+} -binding properties differ slightly from each other. However, it is difficult to be certain about this because of the lack of data points. It was difficult to predict in advance which values of $[\text{Cu}^{2+}]_T$ to choose in constructing the curves due to the drift of Cu-ISE (each sample reading took 30-45 min).

Table 1: pH and pCu of Cu^{2+} standard solutions and typical measured potential for Cu-ISE calibration at $25 \pm 0.1^\circ\text{C}$.

Calibration standards	pH	pCu	Potential / mV
$10^{-3} \text{ mol L}^{-1} \text{ Cu}^{2+}$ solution	2.00	3.00	196.5
$10^{-4} \text{ mol L}^{-1} \text{ Cu}^{2+}$ solution	2.07	4.00	165.5
$10^{-5} \text{ mol L}^{-1} \text{ Cu}^{2+}$ solution	2.02	5.00	134.6
$10^{-6} \text{ mol L}^{-1} \text{ Cu}^{2+}$ solution	2.03	6.00	107.5
Standard solution A	5.20	4.18	178.6
Standard solution B	6.21	7.56	86.3
Standard solution C	7.21	11.05	-15.0
Standard solution D	8.19	13.49	-62.0
Standard solution E	9.22	15.53	-110.2

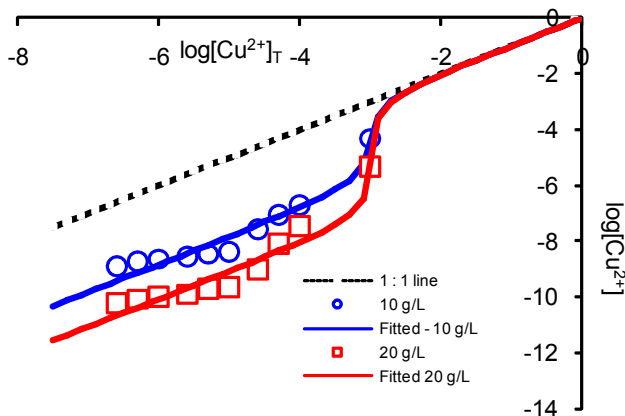


Figure 3: Results of Cu-ISE titration of coffee solution samples containing 10 g L^{-1} (upper, circles) and 20 g L^{-1} (lower, squares) of solid. The free Cu^{2+} concentrations calculated from the ISE calibration parameters are shown as a function of the total concentration of Cu^{2+} added to each sample aliquot. The dotted line shows the 1:1 relationship and the solid lines show the fitted results as described in the text.

5 Conclusions

Organic materials that leached in coffee solution contain copper binding ligands. With a proper calibration the results from the experimental study using Cu-ISE showed the existence of the copper binding ligands in coffee solution. The higher pCu (as indicated by a lower potential reading in copper electrode of Cu-ISE) means less free $[\text{Cu}^{2+}]$ in coffee solution due to the binding mechanism to soluble organic ligands.

The habit of drinking coffee may be helpful in reducing free excessive copper concentration found in the drinking water and may benefit to human health.

The Cu-ISE experiments were very time-consuming because of the slow equilibration, making it possible for changes to occur with time. Advanced electrochemical techniques such as anodic stripping voltammetry (ASV) and competitive ligand equilibration cathodic stripping voltammetry (CLE-CSV) might be very useful for furthering a fundamental study of complexing of metal ions by soluble coffee organic materials.

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