

Copper Release from Copper Tableware

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Application of copper and its alloys in tableware in China can be dated back to the Bronze Age, ~3000 years ago. Even now, copper kettle, chafing dish, hollowware and cup are being used by some urban families in some rural areas. The use of copper tableware may cause health problems due to the release of copper corrosion by-products when copper tableware contacts chloride or natural organic materials. This is because copper develops pitting corrosion in the presence of chloride ions. Some recent studies have highlighted the importance of temperature, chlorine and natural organic matter in the release of corrosion by-product from copper pipe used to drinking water (Rehring and Edwards 1996; Korshin et al. 1996; Broo et al. 1998; Boulay and Edwards 2001). It has been reported that chlorine can either increase or decrease the corrosion of copper in drinking water pipes depending on the concentration of NaCl (Atlas et al. 1982; Stone et al. 1987; Singh and Mavinic 1991; Edwards and Ferguson, 1993; Edwards et al. 1999; Hong and Cauley 1998). However, few studies have focused on the release of copper from dietetic utensils. It is known that food and beverages contain abundant organic matter and sodium chloride that could affect copper corrosion by-products release. It is necessary to evaluate the systemic toxicity of using copper tableware in our daily life. This study has concentrated on the behaviors of copper release from copper hollowware and teapots under certain simulated circumstances.

MATERIALS AND METHODS

Copper release experiments were carried out using both tap water of Nanjing City in China and de-ionized water purchased from a local supermarket. Table 1 shows the main parameters of tap water used in the experiment. Copper hollowware and teapots were purchased from local junk shops. The Chinese tea used was local product (Lulang Tea Company in Nanjing, China). Prior to exposures, all copper dietetic utensils were rinsed in order with detergent, tap water, distilled water, ethanol and acetone to eliminate possible residual contamination and greases. Tap

Table 1. Main parameters of tap water of Nanjing City in China.

Parameter	Value
pH	7.84 ± 0.02
Alkalinity (as CaCO ₃) (mg/L)	186
Temperature (°C)	10~15
DOC range (mg/L)	0~7
DIC (mg/L)	44.7
TOC (mg/L)	4.6
Sulfate (mg/L)	27.73
Nitrate (mg/L)	9.48
Chloride (mg/L)	5.19

water used in the experiment was obtained by flushing tap water at a flow rate of ~15 L/min for 10 min.

Two sets of copper corrosion experiments were conducted in this study. In the first set of experiments, the copper hollowware items were exposed to both tap water and to de-ionized water containing different dosages of NaCl. The solutions of different dosages of sodium chloride were prepared by adding pure NaCl into tap water or de-ionized water, boiling it for 3 min in copper hollowware, and then letting them cool in glassware. The area of contact interface between salted water and the copper hollowware was controlled at about ~360cm².

The second set of experiments was to examine the copper release from a copper teapot when Chinese tea is served in the teapot. In this experiment, 500ml boiled water and the Chinese tea (1.5 or 3.0 g) was added to the copper teapot and infused for 10 min, which simulated the procedure of typical Chinese tea drinking. Then, the mixtures were transferred into glass cups to cool. Control tests were also designed to determine trace copper release from the Chinese tea. The contact area between the Chinese tea and copper teapot was controlled at ~300cm². The second infusion was performed using the above procedure after rinsing the teapot with distilled water three times.

Soluble copper and total copper were measured by an atomic absorption spectrometry spectrophotometer (AAS) with graphite furnace sampling system (Hitachi Z-8100). Commercial standard stock Cu solution was used for standardization. The experimental conditions of AAS were as follows: Dry temperature (80-140 °C within 30 seconds); Ash (600 °C for 30 seconds); Atomizing (2700°C for 7 seconds); Absorbation wavelength at 324.7 nm. The results for each sample were the averages of three readings, considered with the respective coefficients of variation or percentage of standard deviation.

Soluble copper was operationally defined using filtration through a 0.45µm pore size syringe filter according to standard methods (APHA, 1998). In preliminary experiments, copper was analyzed by an inductively coupled plasma emission

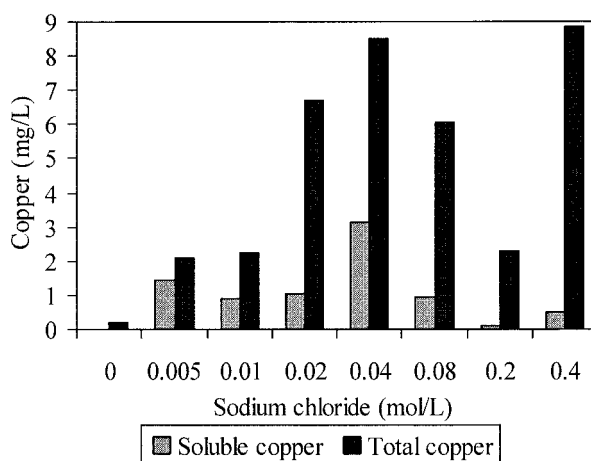


Figure 1. Sodium chloride doses versus the concentration of copper release from copper hollowware in de-ionized water.

spectrophotometer (ICP-ES) according to standard method 3120 or AAS 3111B(APHA, 1998). Results from the ICP-ES and AAS were compared and were not significantly different from one another.

Inorganic carbon (IC) and total carbon (TC) were quantified using a SHIMADZU TOC-500. Hydrochloric acid (made by SHIMADZU Corporation) was used to take out carbon dioxide dissolved in the samples. Total organic carbon (TOC) is the difference between TC and IC. Measurement of pH was carried out with a pH meter (Microcomputer pH/mv/TEMP Meter 6171, made in China for JENCO U.S.A.).

RESULTS AND DISCUSSION

Figure 1 shows the influence of sodium chloride doses on copper release from the copper hollowware in the de-ionized water. The results indicate that when sodium chloride content is less than 0.04mol/L the copper release increases significantly with increasing the level of chloride ions in the de-ionized water. When sodium chloride level is more than 0.04mol/L, however, the copper release decreases with sodium chloride addition up to 0.2mol/L. Further increasing sodium chloride to 0.4mol/L increases the copper release again. Compared to the dose of chloride ions at 0.04mol/L, high sodium chloride concentration (0.4mol/L) results in a similar quantity of copper release from the copper hollowware. These experimental results are consistent with the previous studies that copper corroded faster at increasing chloride concentrations (Braun and Nobe 1979; Nishikata et al 1990; Drogowska et al. 1987). However, under some circumstances high concentrations of chloride could inhibit continuous corrosion due to the formation of a surface protective film when chloride came in contact with copper (Edwards

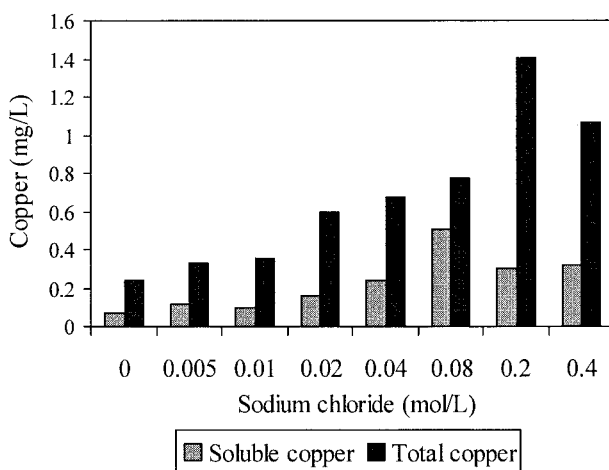


Figure 2. Sodium chloride dose versus the concentration of copper release from copper hollowware in tap water of Nanjing.

et al. 1994 B).

Figure 2 shows the influence of sodium chloride dose on copper release from copper hollowware using the tap water of Nanjing City. Compared to the de-ionized water, tap water shows much less influence of chloride ions on the copper release from copper hollowware. For a given content of sodium chloride, the amount of copper release in tap water is about one order of magnitude less than that in the de-ionized water. In addition, the copper release from copper hollowware continuously increases with sodium chloride content up to 0.2mol/L, which is about 5 times higher than that (0.04mol/L) in the de-ionized water, and then decreases afterwards. This can be attributed to the fact that copper surfaces are passivated in the presence of chloride at pH >7.0 (Edwards et al. 1994 A). It may also be due to the difference of water properties that affect copper corrosion by-product release. Compared to the de-ionized water, the tap water of Nanjing City contains much more inorganic carbon, which might play an important role in soluble copper release. Average concentration of TC in tap water of Nanjing City was 49.3mg/L, but IC (44.7mg/L) was much more than TOC (4.6mg/L). The effects of carbonates and bicarbonates had been extensively studied in relation to the corrosion of copper (Edwards et al. 1994 A; Cruse and Pomeroy 1974; Cohen and Lyman 1972; Campbell 1971). The apparent formation of a surface film, for instance, calcium carbonate and malachite, is one of the possible reasons for the corrosion inhibition. Edwards, Meyer and Rehling also found that the aggressiveness of anions was $\text{HCO}_3^- > \text{SO}_4^{2-} > \text{NO}_3^- > \text{ClO}_4^- > \text{Cl}^-$ at pH 7.0 and the aggressiveness strength changed to $\text{SO}_4^{2-} > \text{ClO}_4^- > \text{NO}_3^- > \text{HCO}_3^- > \text{Cl}^-$ at pH 8.5 (Shalaby et al. 1990). Research is still needed to further understand the mechanisms of the corrosion of copper in natural water in the presence of Cl^- and HCO_3^- .

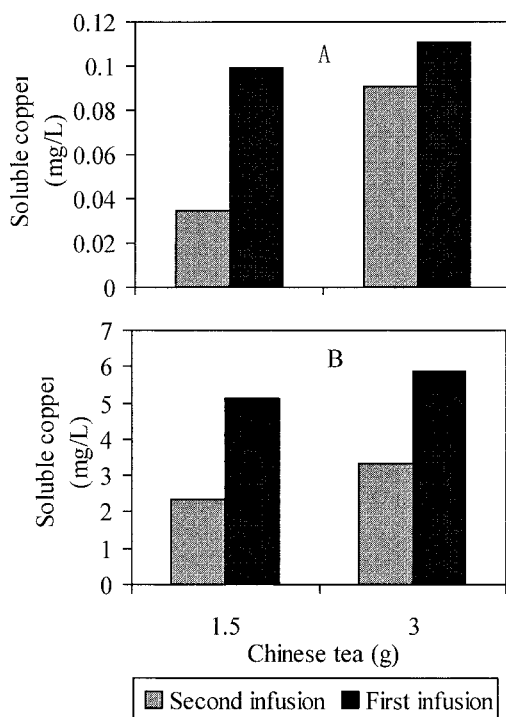


Figure 3. Influence of the Chinese tea dose on soluble copper release from copper teapots in (A) tap water of Nanjing at pH 7.84 and (B) de-ionized water at pH 6.34.

Figure 3 shows the influence of the Chinese tea dosage on the soluble copper release from a copper teapot in two kinds of boiled water. The amount of soluble copper released from the copper teapot in the tap water is at least one order of magnitude lower than that in the de-ionized water. For given water conditions, increasing concentration of the Chinese tea increases the amount of soluble copper released from the copper teapot, indicating that organic materials released from the Chinese tea play an important role in soluble copper release. Similar results were observed in the experiment in which twice as much tea was infused. The soluble copper released in the first infusion of the Chinese tea is much higher, due to the higher quantity of organic matter released from the tea, than that in the second infusion. Previous studies indicated that the adverse effects of organic matter on copper corrosion by-product release to drinking water resulted from soluble complex formation, colloid mobilization/ dispersion, and interference with aging processes that tend to decrease scale solubility (Edwards et al. 1996). In this work, the soluble copper release from the first infusion was significantly higher than that from the second infusion in both tap water and the de-ionized water. The results are in good agreement with the published findings (Broo et al. 1998). The predictions of copper corrosion by-product release in low alkalinity water were significantly improved by explicitly considering possible complexation of copper

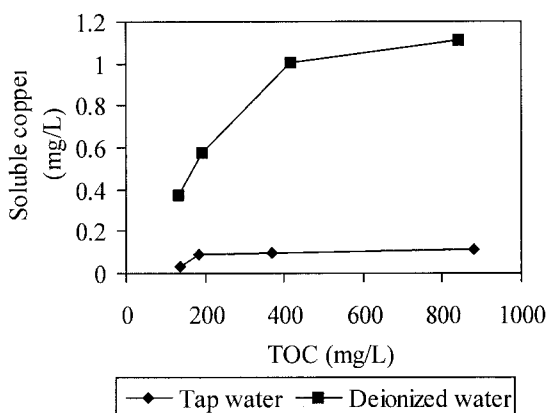


Figure 4. TOCs versus soluble copper release from copper teapots in two types of water.

by natural organic matter. For a given concentration of the Chinese tea, the difference in copper release between the tap water and the de-ionized water is attributed to the variation of water constituents, which lead to the change of organic matter content in water.

The impact of TOC on soluble copper release from copper teapots in two types of water is shown in Fig.4. In the de-ionized water, soluble copper release dramatically increased with levels of TOC ranging from 133.3 mg/L to 416.5 mg/L. However, further increases in TOC concentration produced only a slight additional increase in the soluble copper concentration. In tap water, the influence of TOC on the amount of soluble copper release is much less than that in the de-ionized water. A very slight increase of soluble copper release can be seen in the range of TOC from 136.9 mg/L to 185.7 mg/L. It is also noted that the IC content in the water decreased from 44.7mg/L to 20.8mg/L when the tap water was blended with the Chinese tea and boiled for three minutes in the copper teapot. Possible formation of a surface film, for instance, calcium carbonate, which inhibited corrosion by-product release, was one of the reasons for the reduction of the concentration of inorganic carbon. Compared to the WHO's action level for copper (2mg/L), the soluble copper level in the Chinese tea drinking is still low even though a copper teapot is used. Considering the abundant tea polyphenols in Chinese tea, the bioavailable copper level is even lower because polyphenols are easy to complex to copper and change the formation of copper in water (Suresh and Subramanyam 1998).

In conclusion, sodium chloride and Chinese tea tend to cause relatively high copper release from copper tableware in both the de-ionized water and tap water. Adding a small amount of chloride ions (0.005~0.04mol/L) in the de-ionized water dramatically increases copper corrosion by-product release from copper hollowware. Different infusion frequencies and Chinese tea doses (1.5g and 3g

Chinese tea/500ml water) have significant effects on the concentration of organic matters released from the Chinese tea and thus the soluble copper release from copper teapots. Compared to the de-ionized water, the tap water of Nanjing city shows much less influence of sodium chloride or Chinese tea on the copper release from the copper tableware. According to the experiment results in this work, the soluble copper level is lower than the WHO's drinking water action level (2 mg/L) when the copper tableware is used in contact with sodium chloride or Chinese tea in tap water.

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