

Development of an In-Situ Technique to Dynamically Monitor the Release of Copper from Copper Water Pipe

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ABSTRACT

The effect of long-term stagnation of water in copper pipe plumbing systems released various concentration of copper to the water. The analysis of stagnation time of water in copper pipe for the concentration of copper using ultrapure water, spring water and tap water were carryout in the laboratory using Atomic Absorption Spectroscopy. The analysis deals with water quality modification during its stagnation time in copper pipe cause electrochemical processes. Several variables were investigated, varying water composition in tap water, spring water, and ultrapure water from instrumentation laboratory for the stagnation time in the copper pipe for the different concentrations of copper metal released into the water, using different time of stagnation of 7 hours. For the experimental conditions used during stagnation time of water in the copper pipe in this work, the total concentration of copper released by the copper pipe into the water increases during the first four (4) hours of stagnation, which shows the oxidation of metallic copper which increase the concentration of the copper into the water when the release of copper is control by scale formation, the concentration of copper decreases steadily for the remaining hours in both the water sample been analyzed. The concentration of copper released from copper water pipe increases and decreases steadily due to the oxidation of cuprite (Cu₂O) and the solubility of malachite (CuCO₃Cu (OH)₂) in the tested water (spring water, ultrapure water and tap water), vary from 1 hour, 2 hours 3 hours, 4 hours and 7 hours respectively due to order of magnitude depending on the stagnation time. Indeed copper released into the drinking water by copper pipe became the major source of copper pollution into our system which contributes significantly to the dietary intake of copper through copper in drinking water. The acceptable limit of copper in drinking water is 2 mg/L (J. Dartmann et al., 2010) if drinking water exceeds this limit, the water can be treated.

Keywords: Stagnation, copper pipe, concentration, water, ultrapure.

INTRODUCTION

Copper is an essential element found with a variety of compound in different oxidation a state that is Cu⁺ and Cu²⁺ usually called cuprous and cupric compound. Copper is an essential element requiring for all higher organisms, but also toxic at higher concentration, the excess copper consumed from water can cause

manifestation of acute toxicity. (Magdalena A., et al 2001). The acceptable limit concerning the level of copper in drinking water as giving by U.S, EPA (U.S, EPA, 1991) is 1.3 mg/L after 6 hours of stagnation, and a provisional drinking water guideline of 2 mg/L by world Health Organization (WHO, 1993), Canadian drinking water guideline for copper is 1 mg/L (Agneta.

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O., and Leif. N., 1998). The accepted limit of copper in drinking should not exceeds 2 mg/L (J. Darmann., et al 2010), if above the water can be treated to allow the use of copper material for residential and hospital installations. In Europe the community Regulation as given in 1998 fixed a value of 2 mg/L, with different stagnation time by each country starting from 4 hours in Germany, to 12 hours in Denmark (M. Fabbicino., et al 2005). Water chemistry and copper corrosion result in the release of copper to the drinking water. Naturally copper occurs in the source of water supply systems for drinking. The major pollution of copper in water supply systems takes place in water delivery system, which occurs as a result of micro-corrosion of copper from copper pipes or fittings which are widely used in household plumbing. Copper has been used for decades as a material of choice for piping in various household for water distribution systems around the world. Indeed, due to the several reported cases of structural failures (I.T. Vargas et al, 2009) with unsafe copper concentrations in drinking water from copper pipes (Bruce, I.D, et al 2013 and Pehkonen et al, 2002) motivated several scientific studies, in order to understand the processes that initiate and control the copper release into the water through plumbing piping systems (I.T. Vargas et al, 2009). The properties of water vary depending on where the water comes

from; some water are naturally more corrosive than another depending on the place where the water comes from. There are several factors that causes the corrosion in copper pipe, which include low pH (less than 8.0), high temperature, low total dissolved solids (TDS) content and high amount of dissolved oxygen or carbon dioxide.(J. Dartmann et al, 2010). The copper corrosion starts as an electrochemical phenomenon involving two half-reactions, anodic and cathodic reaction. The anodic half-reaction is responsible for the release of copper ions into the water from the copper metal surface; the cathodic half-reaction usually involves an increase in pH, owing to the reduction of oxygen to the water. Copper is an important micronutrient which is required by the body in a very small quantity, excess copper release in drinking water can have other consequences on human body, which lead to stomach and intestinal distress such as nausea, abdominal pains, vomiting, stomach cramps, diarrhea, dizziness and headache. Long term exposure of copper over many months and years can cause liver damage and death (Bruce I. D., et al, 2013. and Fabbicino. M., et al, 2005). At low concentration of copper in drinking water may not cause any health symptoms but at high concentration of copper in drinking water determines a rapid deterioration of galvanized steel and aluminum utensils fittings. Moreover high copper concentration in

drinking water may cause symptoms easily mistaken as flu, cause a bitter metallic taste in water and result in blue-green stains on plumbing fixtures (Bruce I. D., *et al*, 2013). Corrosion of copper pipes and copper release in drinking water distribution systems have a serious problem, not only because it causes water losses, but also it can be responsible for health problems related to heavy metal absorption into the body system (d Antonio, L., *et al*. 2008). The major source of copper exposure is the drinking water, due to the widespread use of copper pipes in household plumbing systems (D. James, Fitzgerald. 1998). The toxicity of copper when exposed increases the intercellular production and promotes the release of cytokine and also increases the expression of apoptotic protein that brings about irreversible changes in nucleotides of DNA which lead to the damage of DNA. (Manju. B.G., *et al*, 2015). When water is motionless and in contact with copper pipes, the water will continue to dissolve copper from the copper pipe, which makes the highest concentration of copper in drinking water which results from water that sits stagnant in plumbing systems in contact with copper-containing components for a long period of time. High levels of copper in drinking water will give a major contribution to the intake of copper in

humans. (D.J. Horton, *et al*, 2015; Caroline N., *et al*, 2012) High copper concentration by the release of copper from the copper pipe to the water and subsequently to waste-water sludge limits the use of the sludge for agricultural purposes (Agneta, O., and Leif. N., 1998). The stagnation of water in copper pipes causes corrosion processes in residential copper plumbing installations through pitting, which will also increase the copper metal released into the drinking water. The acceptable limit of copper in drinking water is 2 mg/L (J. Dartmann *et al*, 2010) if drinking water exceeds this limit, the water can be treated using central treatment steps like pH-adjustment, phosphate-based or softening/decarbonisation inhibitors. Dosages will be measures that can be applied to reduce the copper release into the water. In order to investigate the release of copper over a period of time into water from copper plumbing pipes used in hospital and some residential houses, due to the conversion of copper metal to copper 1+ and copper 2+ by oxygen in the tap water, various drinking waters were tested using copper pipes in different stagnation times. The techniques used for this analysis are atomic absorption spectroscopy (AAS) and ultra-violet – visible spectroscopy (UV-Vis). All the measurements are made in-situ by the visible spectroscopy.

Copper Pipes

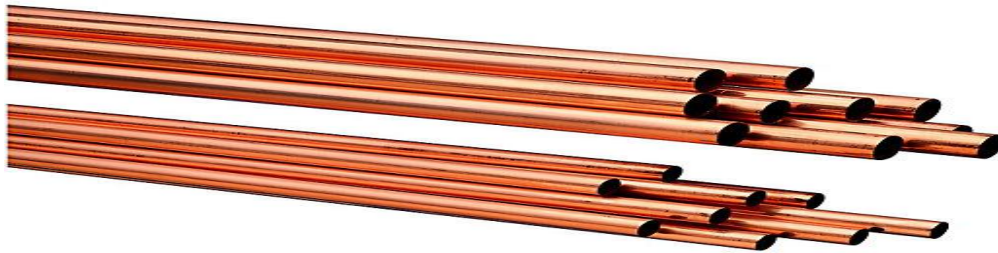


Figure 1. shows the copper pipes (Wickers, 2015)

Copper pipes are rigid but can easily be bend or cut into various length and is available in a variety of sizes and length. The sizes ranging from the inner diameter of 4 mm copper pipe to the inner diameter of 108 mm copper pipes. (Wickers. 2015). That is the inner diameter ranges from 4 mm, 5 mm, 6 mm, 8 mm, 10 mm, 12 mm, 15 mm, 22 mm, 28 mm, 35 mm, 42 mm, 76 mm and 108 mm copper pipes. The copper pipe used for this project has the inner diameter of 15 mm copper pipe × 1000 mm copper pipe.

Analysis of copper

The analytical methods used for this research are UV-Visible spectrophotometer and Atomic Absorption Spectrophotometer, Agilent technology.

UV- visible Spectrophotometer

The ultraviolet – visible reflectance or ultraviolet – visible spectroscopy (UV – Vis or UV/vis) refers to absorption spectroscopy or reflectance spectroscopy in the ultraviolet – visible spectra region. Which means it uses light in the visible and adjacent ranges.

The absorption in the visible range directly affects the perceived color of the chemical involved. In this region the electromagnetic spectrum molecules undergo electronic transition and the absorption measures the transition from ground state to the excited state (skoog.D. A., et al 2007) The UV-Visible Spectrophotometer is used to determine the concentration of an analyte in solution. The techniques exploit Beer lamberts law which predicts a linear relationship between the absorbance and concentration of the analyte. It involves the use of spectrophotometer for the measurement of transmittance of solution, transparent or opaque solids, such as polished glass or gases (Blauch. 2014)

Atomic Absorption Spectrophotometer

The Atomic Absorption Spectrophotometer simply converts complex samples into elemental form for identification and determining concentration of various samples. A multiple sample can be loaded into the AAS auto – injection carousel. Each sample will be drawn or aspirated into

the nebulizer chamber where it is mixed with acetylene and air which is reduced in the ignited air to elemental form. (Concoa, 2012).

MATERIALS

Copper sulfate pentahydrate ($\text{Cu}(\text{SO}_4)_5\text{H}_2\text{O}$, MW: 249.61 g/mol, CAS: 7758-99-8, Assay: 98 %), Copper Nitrate ($\text{Cu}(\text{NO}_3)_2$, MW: 187.55 g/mol, CAS: 10031-43-3, Assay: 99 %), Copper (Cu , MW: 63.55 g/mol, CAS: 7440-50-8, Assay: 99.9 %), Nitric Acid (HNO_3 ,

MW: 63.01 g/mol, CAS: 7697-37-2, Assay: 68 – 70 %). The copper pipe is of 15 mm × 1000 mm, which was cut into 15 mm × 105 mm. One hundred and twenty pieces of 15 mm × 105 mm were used for the analysis. The B & Q, Tube Cutter 3 – 30 mm (1/8 to 11/8) cutting range was used for the cutting of the copper pipes into One hundred and twenty pieces of 15 mm × 105 mm. B & Q Tube cutter is suitable for cutting copper, brass, aluminum and thin walled stainless steel.

RESULTS

The UV – Vis spectroscopy of standard copper solution with different concentrations.

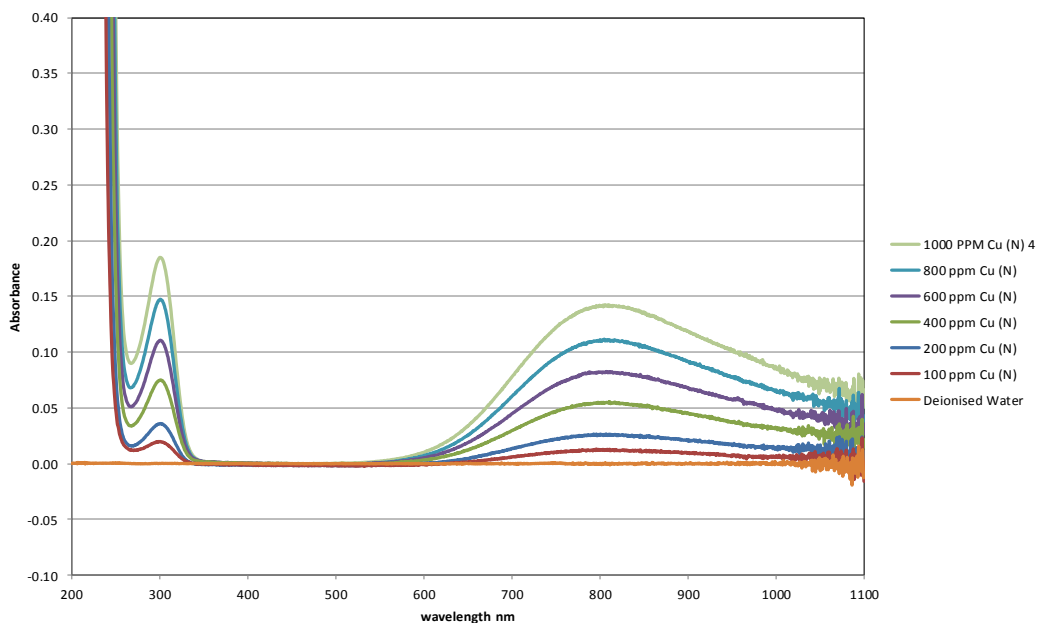


Figure 2; The UV-Vis spectra of copper in copper nitrate ($\text{Cu}(\text{NO}_3)_2$) with 100 ppm, 200 ppm, 400 ppm, 600 ppm, 800 ppm, 1000 ppm and deionized water respectively.

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Table1. The data using experimental method, each result was taken from a different copper pipe. The table shows the time in (hours), the concentration in

(mg/L), the mean concentration in (mg/L), and the standard deviation of the mean concentration in (mg/L) of ultrapure water used for the analysis

Measurement	Concentration of Copper (Cu) mg/L, at different times, in ultrapure water						
	t=1hr	t=2hrs	t=3hrs	t=4hrs	t=5hrs	t=6hrs	t=7hrs
1	1.10	2.80	0.80	3.80	2.00	0.50	0.90
2	3.20	0.90	3.50	3.60	4.00	2.00	1.10
3	3.80	1.60	2.40	0.90	2.20	1.20	0.90
4	1.10	1.50	2.00	1.20	2.50	1.20	1.30
5	0.40	0.30	2.10	2.00	2.10	1.10	0.50
6	1.80	1.10	2.80	2.50	1.90	1.50	2.10
Range of concentration (mg/L)	0.40 – 3.80	0.30 – 2.80	0.8 – 3.50	0.90 – 3.80	0.79 – 4.00	0.50 – 2.00	0.50 – 2.10
Mean of the concentration (mg/L)	1.90	1.37	2.27	2.33	2.45	1.25	1.50
Standard deviation of mean the mean(mg/L)	1.33	0.84	0.90	1.20	0.79	0.50	0.54

Table 2: The data using experimental method, each result was taken from the same copper pipe. The table shows the time in (hours), the concentration in

(mg/L), the mean concentration in (mg/L), and the standard deviation of the mean concentration in (mg/L) of spring water used for the analysis

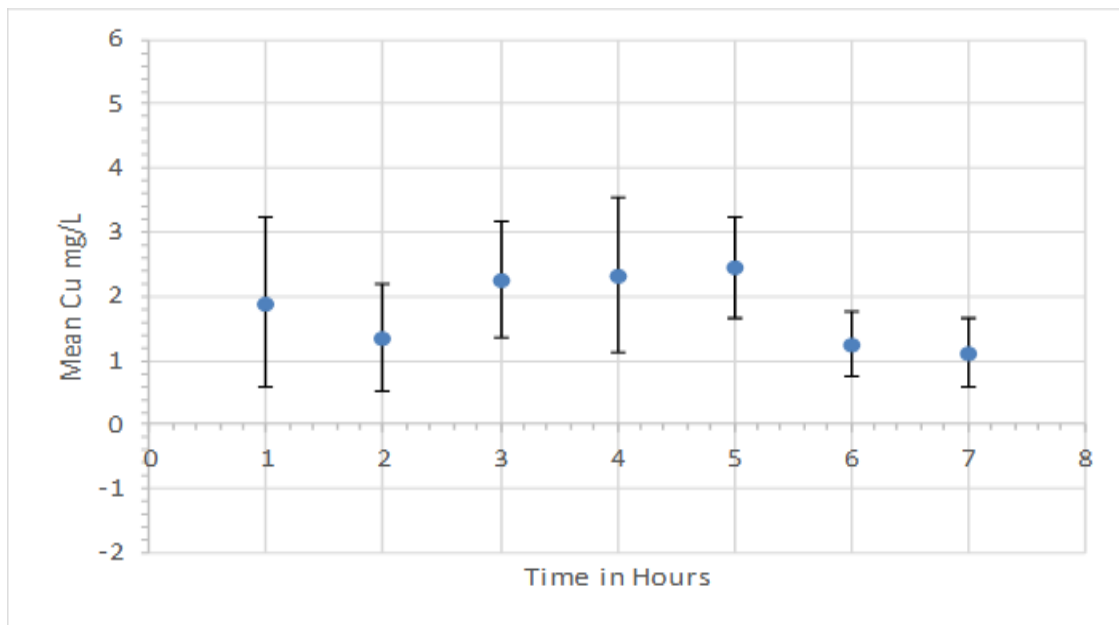
measurement	Concentration of Copper (Cu) mg/L, at different times, in spring water						
	t = 1hr	t = 2hrs	t = 3hrs	t = 4hrs	t = 5hrs	t = 6hrs	t = 7hrs
1	1.90	1.20	5.60	4.50	4.80	3.20	3.80
2	8.90	4.00	5.40	3.00	4.50	1.20	3.90
3	0.20	-0.20	1.10	1.00	0.90	2.40	-0.40
4	0.10	0.70	0.60	1.80	1.00	0.40	0.80
5	0.20	0.10	2.00	0.30	0.80	0.40	1.40
6	0.20	0.01	0.20	1.20	1.30	0.50	0.30
Range of concentration (mg/L)	0.10 – 8.90	-0.20 – 4.00	0.20 – 5.60	1.00 – 4.50	0.80 – 4.80	0.40 – 3.20	-0.40 – 3.80
Mean of the concentration (mg/L)	1.92	0.97	2.48	1.97	2.22	1.35	1.63
Standard deviation of the mean (mg/L)	3.49	1.57	2.41	1.54	1.1.89	1.19	1.82

Table 3; the data using experimental method, each result was taken from the same copper pipe. The table shows the time in (hours), the concentration in

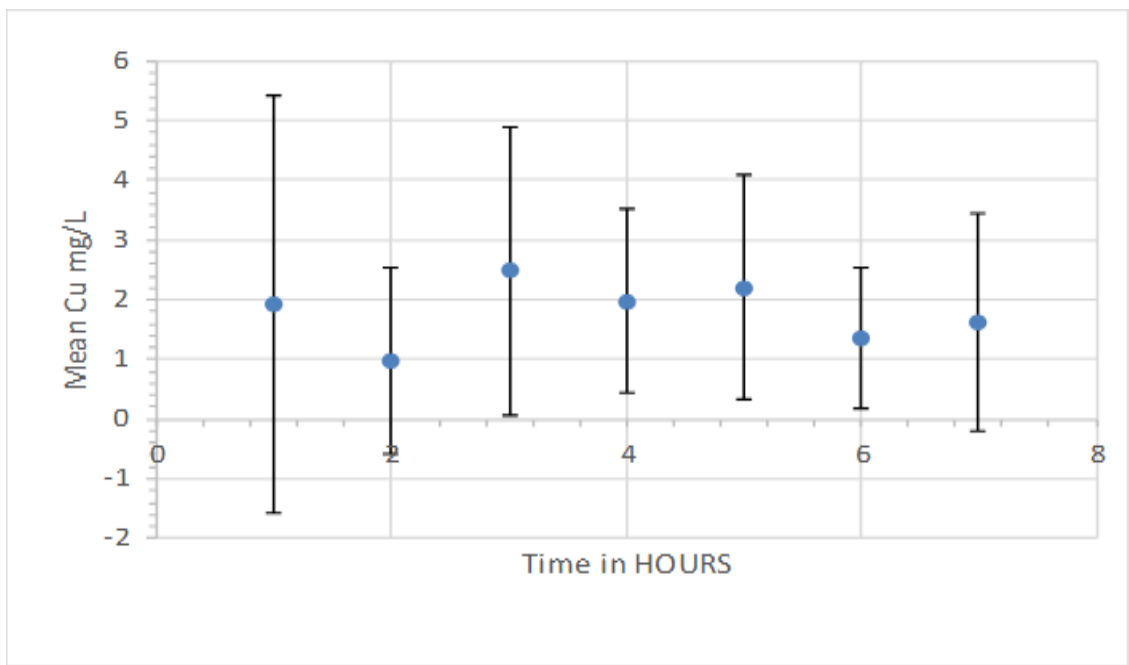
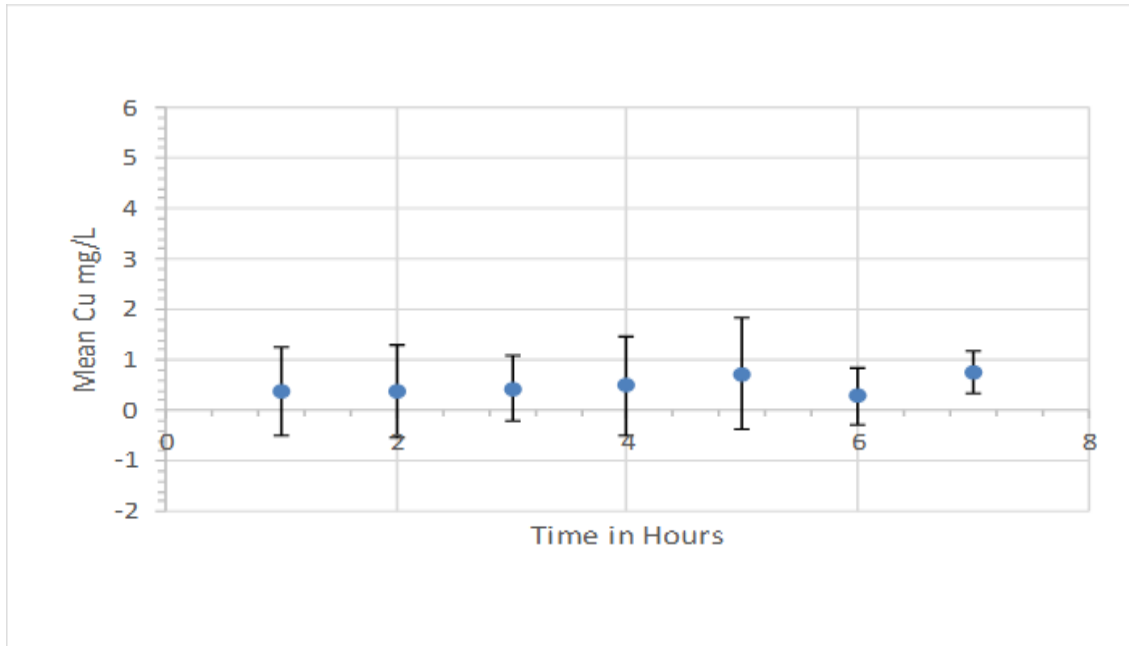
(mg/L), the mean concentration in (mg/L), and the standard deviation of the mean concentration in (mg/L) of the tap water used for the analysis

measurement	Concentration of Copper (Cu) mg/ L, at different times in tap water						
	t = 1hr	t = 2hrs	t = 3hrs	t = 4hrs	t = 5hrs	t = 6hrs	t = 7hrs
1	2.00	-0.10	0.10	2.10	2.80	0.10	1.20
2	0.80	2.00	1.10	1.00	0.90	1.20	1.00
3	-0.40	-0.40	-0.30	-0.30	0.10	0.50	0.10
4	0.02	0.30	0.10	0.60	0.40	0.30	0.60
5	0.06	0.20	0.23	0.14	0.50	0.05	0.60
6	-0.22	-0.50	1.40	-0.60	-0.30	-0.50	1.10
Range of concentration (mg/L)	-0.22 – 2.00	-0.10 – 2.00	-0.30 – 1.40	-0.30 – 2.10	-0.30 – 2.80	-0.50 – 1.20	1.00 – 1.20
Mean of the concentration (mg/L)	0.38	0.25	0.44	0.49	0.73	0.28	0.77
Standard deviation of the mean (mg/L)	0.89	0.91	0.66	0.98	1.09	0.56	0.41

(Miller, Miller. 2010)



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Graphs of the mean concentration (mg/L) verses time in (hours) of copper in copper pipe using A. ultrapure water for seven hours stagnation period. Using a new copper pipe for the sample collection in each step of the analysis. B. spring water for seven hours stagnation period. Using a new copper pipe for the sample collection in each step of the analysis, C. tap water for seven hours stagnation period. Using a new copper pipe for the sample collection in each step for the analysis.

CONCLUSION

The analysis shows that for using UV-Vis spectroscopy, the lowest concentration observed is at 100 ppm for copper. But for copper in water the lowest concentration was observed at 0.5 mg/L, so there is need for the improved path length in order to enhance sensitivity of the UV-Vis spectroscopy, because sensitivity in absorption spectroscopy is proportional to the sample molar concentration, absorption and path length. The long-term stagnation analysis of water in copper pipe to dynamically monitor and investigate the rate of copper concentration released into the water, using spring water, tap water and ultrapure water shows significantly the different result base on the different stagnation time and the type of water been used in the copper pipe for the analysis. As a result of stagnation time of water for copper release in seven hours, the maximum stagnation time for total copper concentration is around 1 to 4 hour, from there copper release is limited by the amount of dissolve oxygen in the water. That show the oxidation of the metallic copper and the mass of hydrogen ions controls the released of copper into the water. The result shows that the water compositions affect the release of copper; the insoluble compounds formed by copper ions in reacting with water will precipitate on metal surface and reduced the rate of copper released into the water. However, The presence

of these basic cupric carbonate $\text{Cu}_2\text{CO}_3(\text{OH})_2$ (malachite), cupric hydroxide $\text{Cu}(\text{OH})_2$, and cupric oxide CuO in the water will increase the rate of corrosion process in the copper pipe and increase in corrosion will leads to the increase of high copper concentration into the water.

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