Application Submitted

To:	Dr. Arlene Courtney
Program:	Ch 462 Experimental Chemistry
Title of Project:	[Determination of the Concentration of Copper in Potable Water Systems]
Suggested Timeline:	[One Week]
Date Submitted:	[26 January 2009]
Principle Investigator	Proposal #1
Applicant's Contact Information	

Signatures:

Abstract:

[The importance of the quality of drinking water is a large concern for agencies such as the EPA. Copper in water has been assigned an "action level" of 1.3 ppb which can create concerns for the level of copper in rural areas. Studies have shown significant leaching of metals like copper into residential drinking water systems, especially after long periods of stagnation.[1] The focus of our study is to analyze the concentration of copper from a home in southwestern Oklahoma. If copper is found, then further action can be perused in terms of quality of water and stain removal. Data from this experiment can be compared with water quality regulations to ensure the water is fit for human consumption.[2]]

[1] Wikipedia
[2] Environmental Protection Agency

Introduction:

Starting in the 1950s copper became a popular material used for tap water pipes. Studies have shown significant leaching of the metals into residential drinking water systems, particularly after long periods of low usage, i.e. sleeping hours, followed by periods of higher usage.[3] The leaching of metals into drinking water can pose serious problems to organisms that consume this water. Copper is an essential mineral, in small amounts, in the human diet, usually received from food or water supplies. However copper can lead to nausea, abdominal pain, diarrhea, etc. and chronic exposure can lead to the discoloration of skin and hair, damage that liver and kidneys, and/or cause chronic respiratory disease.[4] In 1991 the Environmental Protection Agency (EPA) created regulations concerning the concentration of copper in drinking waters by consumption of humans. [5] Copper in the aqueous form can be found as copper (I) or copper (II) forms. The EPA has set the action level for copper to 1,300 parts per billion.

There have been some blue stains noticed in the shower of a Ms. Becky Woodruff residing in southern Oklahoma, which leads us to believe there is a significant concentration of copper in the potable water. The objective of this experiment is to determine the concentration of copper in the water and to determine, by EPA standards, if it is safe for human consumption.

Justification

It is easy from an ethical point of view to see why this experiment is feasible. That is, for the protection of citizens across the world, there needs to be an efficient way

---

[3] Wikipedia
[4] Minnesota Department of Health
[5] United States Environmental Protection Agency

to determine accurate concentrations of copper being consumed, either in drinking water or foods. Economically this test can be done in a cost effective manner by UV-Visible spectophotmeter using highly functional chelating agents which trap the copper. Western Oregon University is fully equipped with the instrumentation necessary to run this experiment for the determination of copper. If the results are conclusive, there are steps in which the consumer can manage amounts of copper being leached from the pipes or they may be able to switch from copper pipes for their potable water to plastic pipes, eliminating the copper being leached altogether.[6] Other economic advantages include the removal of stains from affected areas, instead of replacement of the facilities, thus a method for removal will also be utilized.

Literature Review

In the study done by Townsend et al.[7] on the determination of copper in urine samples an Element High Resolution-Inductively Coupled Plasma- Mass Spectrometer was employed. High purity nitric acid was used for urine digestion and solution acidification. Prior to instrumentation analysis the samples were diluted and spiked with internal standard. Although this process is efficient and accurate, it cannot be employed based on cost efficiency because of the lack of instrument.

A method used by Thipyapong and Suksai[8] using spectrophotometric techniques to determine amounts of copper(II) using a diamine and dioxime derivative was performed using a Hewlett Packard 8453 and Jusco UV-VIS. This method entailed the preparation of 3, 6, 6, 9-tetramethyl-4, 8-diazaundecane-2, 10-dione dioxime, HMPAO,

---

[6] Pastn, Pablo A., et al. Enhanced Copper Release from Pipes by Alternating Stagnation and Flow Events.
[7] Townsend et al., The determination of copper, zinc, cadmium, and lead in urine by high resolution ICP-MS.
[8] Thipyapong and Suksai, Spectrophotometric Determination of Copper (II) Using Diamine-Dioxime Derivative.

consisting in a two step process from commercially available materials. We at Western Oregon University have access to a similar UV-VIS instrument with available quartz couvettes. Their experiment states the molar absorptivity of the chemical being analyzed, therefore beers law can be employed to determine the concentration of the copper (II) in water.

In Yunta et al.'s[9] experiment of free ligands and their chelates, Nuclear Magnetic Resonance was used to determine levels of heavier metals. This method was employed using soil samples but could also be readily available for the determination of copper in water. Again this method is not feasible do to the lack of instrumentation provided in the laboratory.

Method

This method is based on the formation of a stable 1:1 red-pink complex between copper (II) and meso-HMPAO in aqueous solution. Absorption methods will be carried out at 497 nm, with a molar absorptivity value of 338 L mol^{-1} cm^{-1}. Materials needed for this experiment include, UV-Vis spectrophometer, a quartz cell of 10 mm path length, beakers, stirring bars, refrigerator set at 4°C, a nitrogen glove box, a filter and a heating station. The reagents needed include: 2, 3-butanedione monooxime, p-toluene sulfonic acid monohydrate, benzene, 2, 2-dimethyl-1, 3-propanediamine, and acetronitrile. Water samples have already been sent to the laboratory form the test site in southwestern Oklahoma. The purpose of this lab is to test the sampled water for copper concentration.

---

[9] Yunta et al., Chelating Agents Related to Ethylenediamine Bis(2-hydroxyphenol)acetic Acid (EDDHA): Synthesis, Characterization, and Equilibrium Studies of the Free Ligands and Their Mg, Ca, Cu, and Fe Chelates.

Most materials needed for this experiment have already been obtained and are adequate for these procedures.

The preparation of the ligand involves taking bisimine, 3, 6, 6, 9-tetramethyl-4, 8-diazaundecane-3, 8-diene-2; 10-dione dioxime was prepared by refluxing a mixture of 2, 3-butanedione monooxime (0.50mol, 50.55 g) and *p*-toluene sulfonic acid monohydrate (0.15 g) in benzene under nitrogen atmosphere. To this mixture was slowly added a solution of 2, 2-dimethyl-1, 3-propanediamine (0.31 mol, 31.7 g) in benzene (75 mL) over a period of one hour. Heating of the resulting mixture was continued at refluxed for 16 hours and stirred at room temperature for 12 hours. The white powder was obtained by chilling the mixture at 4°C for 16 hours. Then the solid was filtered and washed with cold benzene. The crude product was recrystallized in acetronitrile and dried under reduced pressure. The Determination of copper will be done by transferring the water sample into a 25 mL volumetric flask, 5 mL of 0.036 M ligand solution will be added after addition of 2 mL buffer solution. The absorbance was measured after 5 min at the wavelength of maximum absorbance. Concentration will be calculated using beer's law with the measurements having a 0.5 $\mu g\ mL^{-1}$ limit of detection.[10] If a copper solution is not found then determination of alternative characterizations will have to be applied, most likely of the origin of transition metals.

Budget and Timeline

The main expense for this experiment is going to be any reagent not readily available in the stock room. The experiment should take no longer than a couple days to be complete. The UV-Vis is properly equipped for this experiment and the other equipment is present in the lab.

---

[10] Thipyapong and Suksai,

References

1. Wikipedia.

   http://en.wikipedia.org/wiki/Tap_water

2. United States Environmental Protection Agency.

   http://www.epa.gov/safewater/lcrmr/index.html

3. Minnesota Department of Health.

   http://www.health.state.mn.us/divs/eh/water/com/fs/copper.htmll

4. Townsend, Ashley.;Miller, K.A.; McLean, S.; Aldous, S. The Determination of Copper, Zinc, Cadmium, and Lead in Urine by High Resolution ICP-MS. Journal of Analytical Atomic Spectrometry, September 1998, 13, pp. 1213-1219.

5. Thipyapong, Khajadpai; Suksai, Chomchai. Spectrophotometric Determination of Copper (II) Using Diamine-Dioxime Derivative. Bull. Korean Chem. Soc. 2003 Vol. 24, No. 12 pp. 1767-1770.

6. Yunta, Felipe; Garca-Marco, Sonia; Lecena, Juan J.; Gmez-Gallego, Mar; Alczar, Roberto; Sierra, Miguel A. Chelating Agents Related to Ethylenediamine Bis(2-hydroxyphenol)acetic Acid (EDDHA): Synthesis, Characterization, and Equilibrium Studies of the Free Ligands and Their Mg, Ca, Cu, and Fe Chelates. Inorg. Chem., 2003, 42 (17), 5412-5421.

7. Calle, Gustavo R.; Vargas, Ignacio T.; Alsina, Marco A.; Pastn, Pablo A.; Pizarro, Gonzalo E. Enhanced Copper Release from Pipes by Alternating Stagnation and Flow Events. Eviron. Sci. Technol., 2007, 41 (21), 7430-7436.