Proposal Coversheet

Application Submitted

To:	Dr. Arlene Courtney
Program:	Ch 462 Experimental Chemistry
Title of Project:	Analyzing Copper Concentrations in Drinking Water and Removing Its Accompanying Blue-Green Stain
Suggested Timeline:	Two weeks after sample collection
Date Submitted:	January 24, 2009
Principle Investigator	Proposal #4
Applicant's Contact Information	

Abstract:

When copper is present in drinking water it produces a blue-green stain around plumbing fixtures. The concentration of copper in the water is regulated by the U.S. Environmental Protection Agency (EPA) to reduce toxicity to humans. The copper levels can be analyzed by following the EPA laboratory guidelines using atomic absorption spectroscopy (AAS). Since the presence of copper in the water is caused by pipe corrosion, proper plumbing maintenance is required to reduce its concentration. The unsightly blue-green stains resulting from the copper can be removed by converting the insoluble copper compounds into soluble complexes, using diluted acid.

Introduction:

The purpose of this proposal is to identify the cause of the blue-green stains in a bathroom shower, and to determine if the stains are a result of unsafe drinking water. Copper is a trace metal which can be found in aqueous solutions such as drinking water. Typically, a characteristic blue-green stain appears around surfaces where copper-contaminated water is present. These stains can be removed with an acidic cleaner. The amount of copper found in the drinking water can be analyzed to determine if the level is unsafe for human consumption.

The presence of copper in water is most readily identified by an unsightly blue or blue-green stain on sinks, baths and porcelain. When copper is present in moist air, it slowly oxidizes to form copper carbonate ($CuCO_3$) and cupric hydroxide ($Cu(OH)_2$).

$$2\,Cu\,(s) + H_2O + CO_2 + O_2 \rightarrow Cu(OH)_2 + CuCO_3\,(s)$$

Equation 1: The reaction between solid copper and water in air yields copper carbonate and cupric hydroxide.

These compounds form the stain and are insoluble in water, making them difficult to remove with household cleaners. Both cupric hydroxide and copper carbonate can be dissolved in diluted acids[1].

Copper exists in aqueous solutions in many forms. The potential for a copper complex to exist depends on the pH of the environment. In other words, by measuring the pH of the water sample, the analyst can identify the major copper species present in the water.

Copper seldom occurs naturally in the water supply. High levels of copper occur if corrosive water comes in contact with copper plumbing and/or copper-containing fixtures in the water distribution system. Corrosive water is alkaline and contains carbonates. The level of copper in drinking water increases with the corrosivity of the water and the length of time it remains in contact with the plumbing. The best way to remove copper from the drinking supply is to replace the corroded pipes. However, advanced water softener systems are also available to filter copper from the water before it exits the faucet[2].

Since the sample water comes from a well on property that was formerly used as a horse farm and cattle grazing, there is an alternative explanation for the presence of copper. The level of copper contamination can be increased around agricultural land[3]. Since copper is toxic to some insects, aglae and fungus, they are used to prevent animal and plant disease. Farmers have been known to supplement their water supply and fertilizers with copper as an insecticide or fungicide. A thorough analysis of the well water, as well as the soil, is the most useful way to determine the cause of the copper contamination.

Copper is not usually considered toxic to humans except in very large concentrations. The U.S. Environmental Protection Agency (EPA) has determined that the level of copper in drinking water should not exceed 1.3ppm or 1.3mg/L[4]. The most common health effects of excessive consumption of copper bearing water would be: nausea, vomiting, diarrhea, upset stomach and dizziness[5].

Justification

The stains in the bath tub are a result of copper carbonate and cupric hydroxide. Corrosive water contains carbonates and has an alkaline pH. These waters corrode copper pipes or joints causing copper to leach into the water. When the carbonates and copper exit the pipes and react with the air, they form stubborn copper complexes that are insoluble in water. These complexes form the blue-green stain. To eliminate the stains, the copper carbonate and cupric hydroxide must be converted into a water soluble complex. Copper sulfate is a soluble compound. Therefore, if the stains are cleaned with a strong, diluted acid, such as sodium bisulfate, the copper will react with the acid to form copper sulfate.

The copper concentration in drinking water can be analyzed using atomic absorption spectroscopy (AAS). In this procedure, a liquid sample is aspirated through a plastic tube into a flame that breaks the molecules apart. Radiation of the correct frequency is passed through the flame containing the atoms. The concentration of copper is measured by its absorption of radiation. The concentration of copper can be determined between 0.2 to 5ppm, offering a range of copper levels around the EPA recommendation.

Literature Review

While conducting a literature review for useful methods to analyze copper in drinking water, two procedures were considered. Typically, metal concentration in water is determined using atomic absorption spectrometry (AAS). A solid phase extraction technique is used to separate the sample ions by chelating[6]. The sample is diluted with nitric acid and analyzed using AAS. The optimal concentration of copper in the sample is approximately 0.2-5mg/L[7].

A new technique for determining the amount of copper in drinking water is by reverse-phase high-performance liquid chromatography (RP-HPLC)[8]. The sample is reacted with a chelating reagent necessary to concentrate the copper ions. The ions are separated using solid-phase extraction, and then eluted through the instrument's capillary column. The preparation for the reagent is time intensive and expensive, making the RP-HPCL method unsuitable for this analysis.

There are no published procedures for the removal of copper stains from bathroom fixtures, besides product advertisements. Instead, research was conducted on the physical and chemical properties of copper compounds in solution. According to Pourbaix, copper carbonate is the least soluble complex in water; however, it can dissolve in dilute strong acids, such as sodium bisulfate[1].

Method

This procedure is used for determining the copper concentration in drinking water[9]. The following conditions are for an AAS instrument equipped with a copper hollow cathode lamp and acetylene fuel. The wavelength is 324.7nm. The optimum copper concentration range is 0.2-5 mg/L with a 0.02 mg/L limit of detection

The preparation of a stock solution is used to establish a calibration curve. Prepare 1L of stock solution by dissolving 1.0g of electrolyte copper (analytical reagent grade) in 5mL of redistilled HNO_3 and diluting with distilled water[7]. Prepare various stock dilutions for calibration curve.

A sample solution is prepared to compare to the calibration curve for determining the copper concentration. Combine the sample with 1:1 redistilled HNO_3 to a pH of less than 2. Usually 3mL of acid is sufficient. The sample is not filtered before processing. Adjust the volume with distilled water based on expected copper concentration levels[10].

Run sequential stock dilutions and construct a calibration curve by plotting the concentrations of the standards against the absorbance. Aspirate the sample and determine the concentration of copper from the calibration curve[9].

This procedure is used to eliminate copper stains from bathroom tiles and fixtures. Using a household scrub brush, wash the blue-green stains with Sani-Flush, a toilet bowl cleaner containing sodium bisulfate. Rinse with water and continue scrubbing with the toilet bowl cleaner until the stain is gone. WARNING: Sani-Flush contains toxic ingredients. Always wear protective gloves. Adequate ventilation is required.

Conclusion

The blue discoloration found on the bathroom tile and fixtures is a result of copper in the water. In a moist environment, copper oxidizes into its characteristic blue-green color, better known as patina. The presence of copper in the water is most likely caused by pipe corrosion, and can be corrected with a water softener or pipe repair. Since drinking water containing copper can cause mild to moderate health concerns, it is important to analyze the amount of copper in the water to determine if it meets EPA guidelines. In addition, the unsightly stains caused by insoluble copper complexes can be removed with an acidic solution such as sodium bisulfate found in toilet bowl cleaners.

Budget and Timeline

The instrument, reagents, and materials will be provided by Western Oregon University (WOU) Chemistry Department since this procedure will be used as an instructional aide. All the materials are affordable and readily available to the laboratory. An additional fee for mailing the samples to WOU is estimated at $20. The toilet bowl cleaner needed to remove the stains and gloves is estimated at $10.

According to proper sample preservation methods, the copper concentration analysis will be completed within two weeks of sample collection[9].

References

[1]Pourbaix, M.: *Atlas of Electrochemical Equilibria in Aqueous Solutions;* National Association of Corrosion Engineers: Texas, 1974; pp 384-392.

[2]Water Systems Home Page. http://www.watersystems.co.nz/learn/stains/htm (accessed Jan 20,2009).

[3]Steinhauer, T.; In *Copper Analysis,* Proceedings of the SDWF Advanced Aboriginal Water Treatment Team, Ontario, Canada, Sept 13-20,2008; via webinar at www.safewater.org.

[4]*Economic and Supporting Analysis: Short Term Regulartory Changes to the Lead and Copper Rule;* U.S. Environmental Protection Agency, EPA-815-RO-7022: 2007.

[5]Prasad, R.; *Copper in Drinking-water;* Background Document for the Development of WHO Guidelines for Drinking Water, WHO: 2004.

[6]Mustafa, T.; A Preconcentration System for Determination of Copper and Nickel in Water and Food Samples Employing Atomic Absorption Spectrometry. *Journal Of Hazardous Materials.* **2009,** 162, 1041-1045.

[7]*Method 220.1 Direct Aspiration Atomic Absorption Spectroscopy;* U.S. Environmental Protection Agency: 2004.

[8]Qiufen, H.; Study on Determination of Iron, Cobalt, Nickel, Copper, Zinc and Manganese in Drinking Water by Solid-Phase Extraction and RP-HPLC with 2-(2-quinolinylazo)-5-diethylaminophenol as Precolumn Derivatizing Reagent. *J. Environ. Monit.* **2002,** 4, 956-959.

[9]*Methods for the Determination of Metals in Environmental Samples, Supplement 1;* U.S. Environmental Protection Agency, EPA/600/R-94/111: 2003.

[10]*Methods for Chemical Analysis of Water & Wastes;* U.S. Environmental Protection Agency, EPA-600/4-79-020: 1993.