Copper

For water, wastewater and seawater

Bicinchoninate, Porphyrin and Bathocuproine Methods

Introduction

Although copper comprises only 0.007% of the earth's crust, it is a very important element. Copper occurs in both free and combined forms throughout nature in many minerals. Copper may occur in natural waters, wastewaters, and industrial waste streams as soluble copper salts or as copper compounds precipitated on suspended solids. Forms of copper in water can be classified as *insoluble*, *dissolved* (free and complexed), and *total recoverable*. Insoluble copper includes precipitates such as copper sulfides and hydroxides. All copper in solution is known as dissolved copper, including Cu^{1+} (cuprous) and Cu^{2+} (cupric) ions and copper chelates such as CuEDTA.

Copper concentrations in potable water are usually very low. Copper is not considered a health hazard to humans although more than 1 mg/L can impart a bitter taste to water and large oral doses can cause vomiting and may eventually cause liver damage. Copper salts, such as copper sulfate ($CuSO_4$), may be used to control algae; however, they may also be toxic to fish and wildlife. Hach's simplified test procedures for copper use a variety of reagents to satisfy the desired range of detection and the form of copper to be measured. Hach procedures use primarily the Bicinchoninate and the Porphyrin Methods.

The *Copper reagents and applications* table lists proprietary reagents and applications.

Table 1 Copper reagents and applications

Reagent	Form measured		Application
	Without pretreatment	With digestion	
CuVer 1™[1]	Free	Total recoverable	water, wastewater
CuVer 2™	Total dissolved copper	Total recoverable	
Free copper reagent	Free	Total recoverable	hard water, wastewater, seawater
Porphyrin reagents	Free	Total recoverable	extremely low levels in water, wastewater and seawater

[1] CuVer is a trademark of Hach Company.

Chemical reactions

Bicinchoninate method

Copper can be determined by the reaction of copper with 2, 2'-biquinoline-4,4'-dicarboxylic acid (bicinchoninic acid). Bicinchoninate reacts with Cu^{1+} to produce a purple-colored complex.

Bicinchoninate does not react readily with Cu^{2+}. Determination of Cu^{2+} begins by reducing it to Cu^{1+}. The CuVer 1 Reagent combines the bicinchoninate reagent with a buffer and reducing agent, allowing determination of Cu^{1+} and Cu^{2+}. Total recoverable copper can be determined with this method if the sample is first digested to convert all of the copper present (including insoluble forms and complexed forms) to free copper.

Complexed copper forms such as CuEDTA react directly with CuVer 2™. Digestion is not necessary, and high levels of hardness do not interfere. The results will be in terms of total dissolved copper (free and complexed). When using CuVer 1, digestion is necessary and high levels of hardness interfere.

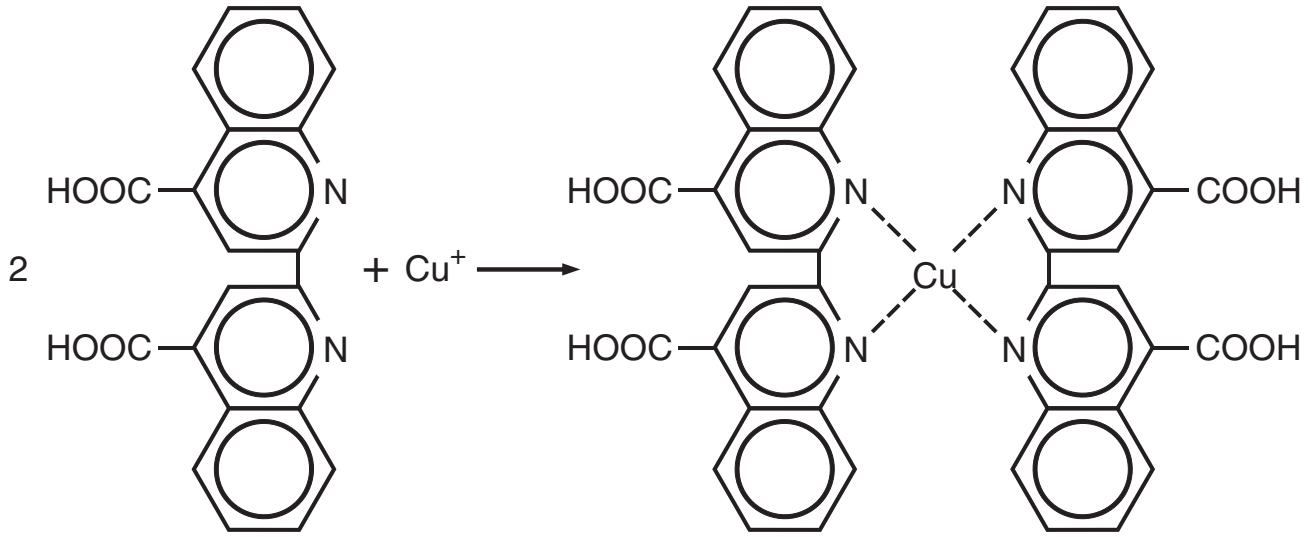

Figure 1 Reaction of Cu^{1+} and bicinchoninic acid

Use Free Copper Reagent Powder Pillows to determine free copper separately from complexed copper. The powder pillows contain bicinchoninate, a reducing agent and an inhibitor to eliminate calcium and magnesium interference. The results will be in terms of free copper. Complexed copper may then be determined by adding Hydrosulfite Reagent, repeating the analysis and subtracting the results of the two analyses.

Porphyrin method

The porphyrin method for determining copper is a very sensitive test, capable of detecting free copper (Cu^{1+} and Cu^{2+}) and total recoverable copper (with digestion) in the range of 0–150 µg/L.

Because of the sensitivity of the method, it is difficult to obtain water of high enough quality to establish a blank value. The porphyrin method uses a split sample. One half of the split sample is treated with a masking agent to complex the free copper forms; then, porphyrin reagent, a buffer, and a reducing agent is added. This forms a “zero blank” without the need for special copper-free water. Porphyrin reagent is added to the second half of the split sample, where it reacts with the free copper.

Interference caused by the reaction of porphyrin with other metals is minimized by using the split sample because interferences are compensated for in the blank. Porphyrin reacts slowly with Cu^{2+}, but a special formulation of the porphyrin and addition of a buffer allow the reaction with free copper to be completed within seconds. A reducing agent is also added in order to destroy unreacted porphyrin (which would otherwise interfere). An intense absorbance at 425 nm makes this method very sensitive when using a colorimeter or spectrophotometer. However, strong visual color development does not occur.

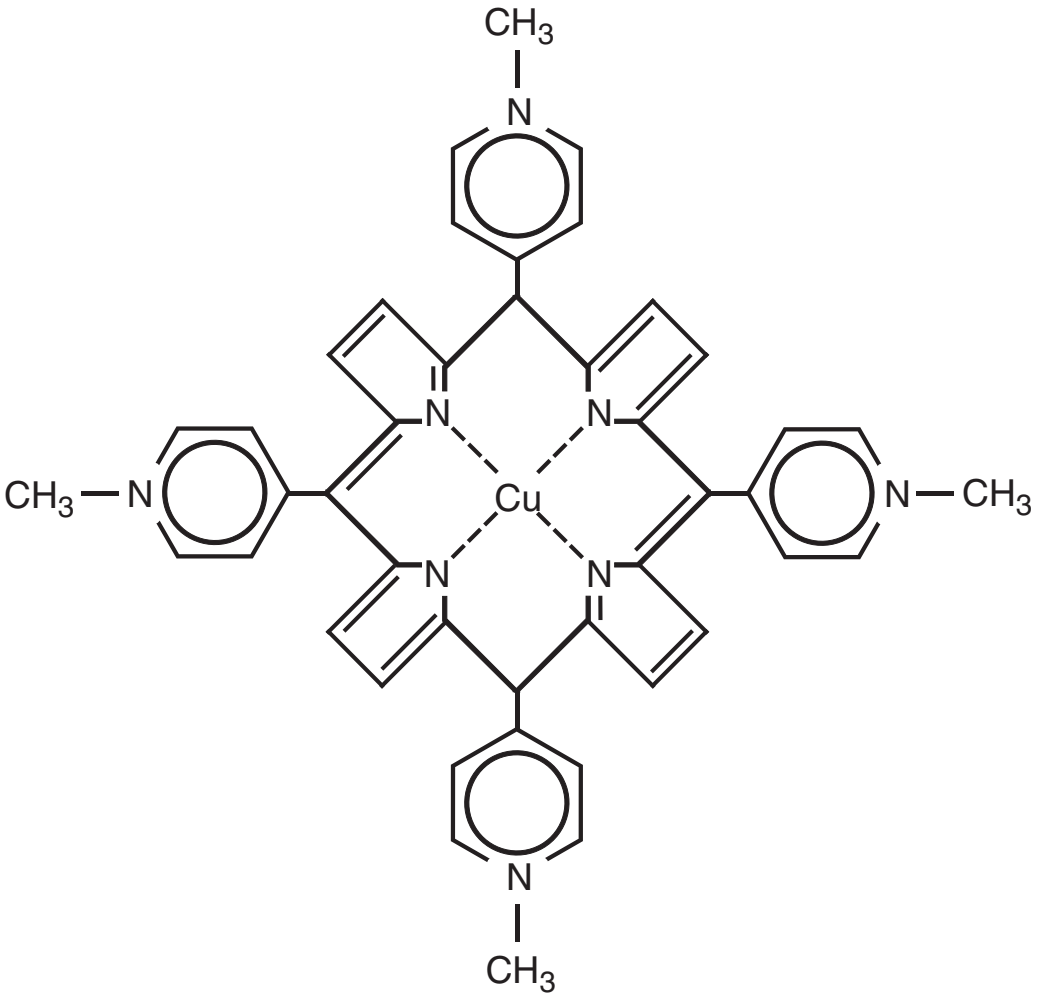

Figure 2 Final structure from the porphyrin method