Hach Method 8026

Spectrophotometric Measurement of Copper in Finished Drinking Water

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1.0 Scope and Application

1.1 This method is for the determination of copper (Cu) in finished drinking water.

1.2 The method is applicable in the range from 0.1 to 5.00 mg/L Cu. Higher Cu values can be determined by sample dilution.

1.3 This method is equally effective in performance and use to EPA 200.7 for the purposes of regulatory compliance reporting of Cu.

2.0 Summary of Method

2.1 The Hach Cu chemistry uses 2,2'-biquinoline-4,4'-dicarboxylic acid (bicinchoninic acid) for color development. Cuprous copper complexes with bicinchoninic acid to form a purple colored complex. The intensity of the color of this complex is proportional to the concentration of copper in the sample. Cupric copper is chemically reduced. Metal and hardness interferences are overcome through the addition of a chelating agent. Test results are measured at 560 nm.

3.0 Interferences

3.1 The items listed in the *Interfering substances* table have been identified as interferences for this chemistry. Sample treatments have been identified to overcome these interferences.

Interfering substance	Sample treatment
Acidity	For sample pH < 2, raise pH with 8 N KOH.
CN^-	Add 0.2 mL formaldehyde per 10 mL of sample to the sample prior to addition of powder reagent. Multiply the test results by 1.02 to correct for the formaldehyde addition.
Ag^+	Add 10 drops of saturated KCl solution to 75 mL of sample and filter to remove precipitate.
Al^{3+}	Complex with CuVer2 chemistry. Use 25 mL volume.
Hard Water	Complex with CuVer2 chemistry. Use 25 mL volume.
Fe^{3+}	Complex with CuVer2 chemistry. Use 25 mL volume.

4.0 Safety

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical should be treated as a potential health hazard. Exposure to these chemicals should be reduced to the lowest possible level. It is suggested that the laboratory perform personal hygiene monitoring of each analyst using this method and that the results of this monitoring be made available to the analyst.

4.2 Unknown samples may contain high concentrations of volatile toxic compounds. Sample containers should be opened in a hood and handled with gloves to prevent exposure.

4.3 This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of any chemicals specified in this method. A reference file of material safety data sheets (MSDSs) should be available to all personnel involved in these analyses. Additional information on laboratory safety can be found in Sections 16.3 and 16.4.

5.0 Equipment

Note: *Brand names, suppliers, and part numbers are for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using apparatus and materials other than those specified here, but demonstration of equivalent performance that meets the requirements of this method is the responsibility of the laboratory.*

5.1 Sampling equipment

5.1.1 Sample collection bottles – Collect samples in acid-cleaned glass or plastic bottles.

6.0 Equipment for sample analysis

6.1 Hach Company DR 6000, DR 3900, DR 1900 spectrophotometer, or equivalent

6.2 1 in square sample cells

6.3 Equipment for standard preparation

6.3.1 Volumetric flasks – Glass, 100 mL and 1000 mL.

6.3.2 Volumetric pipettes – Glass, 2.00 mL and 4.00 mL.

7.0 Reagents and Standards

7.1 Metal-free water – Water in which Cu concentration is below the detection limit of this method. Water prepared by passage of tap water through ion exchange and reverse osmosis has been shown to be an acceptable source of reagent water.

7.2 Hach Company CuVer Copper Reagent Powder Pillows, Cat. No. 2105869 and 2504025.

7.3 Hach Company Cu Standard Solution: 100 mg/L as Cu (Cat. No. 12842) or equivalent

7.4 Method detection limit (MDL) solution

7.4.1 If an MDL is required, prepare and measure 7 or more replicates of an MDL stock solution by diluting 2.0 mL of the 100 mg/L standard spiking solution (Section 7.3) to 1000 mL. Final concentration = 0.2 mg/L Cu.

7.5 Initial precision and recovery (IPR) solution

7.5.1 Prepare and measure 4 or more replicates of an IPR stock solution by diluting 2.0 mL of the 100 mg/L standard spiking solution (Section 7.3) to 100 mL. Final concentration = 2.0 mg/L Cu.

8.0 Sample Collection, Preservation and Storage

8.1 Samples should be collected in acid-cleaned glass or plastic bottles.

8.1.1 Rinse the sample bottle several times with sample. Fill the bottle completely full.

8.2 Preserve samples by acidifying to pH 2 or less with concentrated nitric acid. Preserved samples may be stored up to 6 months at room temperature prior to analysis.

9.0 Quality Control

9.1 Each laboratory that uses this method is expected to operate a formal quality assurance program (16.1). The minimum requirements of this program consist of an initial demonstration of laboratory capability and ongoing analyses of laboratory prepared water standards as a test of continued performance to assess accuracy and precision. Laboratory performance is compared to established performance criteria to determine if the results of analyses meet the performance characteristics of the method.

9.1.1 The analyst shall make an initial demonstration of the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Sections 9.2 and 9.2. The laboratory shall, on an ongoing basis, demonstrate through analysis of the ongoing precision and recovery sample that the analysis system is in control.

9.1.2 Accompanying QC for the determination of Cu is required per analytical batch. An analytical batch is a set of samples processed during a contiguous 8-hour period. Each analytical batch must be accompanied by an ongoing precision and recovery sample (OPR), matrix spike sample (MS), and matrix spike duplicate sample (MSD) resulting in a minimum of four analyses (1 OPR, 1 sample, MS, and MSD).

9.2 Initial demonstration of laboratory capability.

9.2.1 To establish the ability to detect Cu the analyst shall determine the MDL using the apparatus, reagents, and standards that will be used in the practice of this method. An achieved MDL less than or equal to the MDL in Section 13.0 is recommended prior to the practice of this method.

9.2.2 Prepare and measure seven replicates of the MDL standard (Sect. 7.4) according to the procedure in Section 11

9.2.3 Using the results of the set of seven analyses, compute the MDL using the following equation:

$$MDL = \sqrt{\frac{\sum x^2 - \frac{\left(\sum x\right)^2}{n}}{n-1}} \times 3.14$$

where:

n = Number of samples (7)
x = measured concentration of each sample

9.3 Initial precision and recovery (IPR) - To establish the ability to generate acceptable precision and accuracy, the analyst shall perform the following operations:

9.3.1 Prepare and measure four samples of the IPR standard (Sect. 7.5) according to the procedure in Section 11.

9.3.2 Using the results of the set of four analyses, compute the average percent recovery (x) and the standard deviation of the percent recovery (s) for Cu. Use the following equation for calculation of the standard deviation of the percent recovery:

$$s = \sqrt{\frac{\sum x^2 - \frac{\left(\sum x\right)^2}{n}}{n-1}}$$

where:

n = Number of samples (4)
x = % recovery in each sample

9.3.2.1 Compare s and x with the corresponding limits for initial precision and recovery in Table 1 (Sect. 17). If s and x meet the acceptance criteria, system performance is acceptable and analysis of samples may begin. If, however, s exceeds the precision limit or x falls outside the range for recovery, system performance is unacceptable. In this event, correct the problem, and repeat the test.

9.4 Ongoing precision and recovery (OPR) - To demonstrate that the analysis system is in control, and acceptable precision and accuracy is being maintained with each analytical batch, the analyst shall perform the following operations:

9.4.1 Prepare a 2.0 mg/L recovery standard with each analytical batch as described in Sect. 7.5.1 and measure according to the procedure in Section 11. Calculate the percent recovery and compare this value with the limits for ongoing recovery in Table 2 (Sect. 17). If the percent recovery meets the acceptance criteria, system performance is acceptable. If the percent recovery falls outside the acceptance criteria, system performance is unacceptable. In this event, correct the problem, and repeat the test.

9.4.1.1 Measure a field sample. After measuring the background concentration, spike the sample with a known concentration of Cu. The spike concentration should be 1-5 times the background concentration, but still within the reporting range of the method. Prepare a duplicate of this spiked sample.

9.4.1.2 Measure the spike duplicates and calculate the spike recovery for each sample and the relative percent difference (RPD) between the two results.

Use the following equation to calculate the spike recovery:

$$Spike\ Recovery = \frac{[Conc] - [Bkgd]}{[Sp]} \times 100$$

where:

[Conc] = the measured concentration of the spiked sample
[Bkgd] = the measured concentration of the un-spiked sample
[Sp] = the concentration of the spike

$$RPD = \frac{|Conc_1 - Conc_2|}{\left(\frac{Conc_1 + Conc_2}{2}\right)} \times 100$$

where:

$Conc_1$ = the concentration of the first spiked sample
$Conc_2$ = the concentration of the second spiked sample

9.4.1.3 Compare the spike recoveries and RPD with the corresponding limits in Table 2 (Sect. 17). If recoveries and RPD meet the acceptance criteria, system performance is acceptable and analysis of samples may begin. If recoveries or RPD fall outside the limits, system performance is unacceptable. In this event, correct the problem, and repeat the test.

9.4.1.4 The laboratory should add results that pass to IPR and previous OPR data and update QC charts to form a graphic representation of continued laboratory performance. The laboratory should also develop a statement of laboratory data quality for each analyte by calculating the average percent recovery (R) and the standard deviation of the percent recovery (sr). Express the accuracy as a recovery interval from R - 2sr to R + 2sr. For example, if R = 95% and sr = 5%, the accuracy is 85% to 105%. Control charts are acceptable for evaluating process control, but under no circumstances can the control limits be widened beyond those established in the acceptance criteria defined in Section 13.

10.0 Calibration and Standardization

10.1 The Hach DR series spectrophotometers have a built-in calibration that is automatically initiated when the CuVer test is selected through the instrument interface. No further initial calibration is required. However, the instruments have the capability of developing a user-calibration. See manufacturer's manual for instructions.

10.2 Calibration Verification

10.2.1 To verify that the instrument is measuring Cu properly, analyze 2.0 mg/L (Sect. 7.5) and 0.2 mg/L (Sect. 7.4) Cu standards. Results should be within 15 percent of the actual value. Perform this calibration verification daily while instrument is in use. If the calibration verification standard result is outside the limit, it is unacceptable. In this event, correct the problem, and repeat the test.

11.0 Procedure

11.1 Instrument Setup – follow the instrument manufacturer's instructions for instrument setup.

11.2 Determine if the sample contain interferences as described in Section 3.1. If the sample is interferent free, proceed to Section 11.2.1. If the sample contains interferences or the interferences are unknown, proceed to Section 11.2.2.

11.2.1 Interference-free sample (CuVer1) Pipet 10.0 mL of sample into the sample cell. Use this preparation for samples which do not contain aluminum, iron, or hardness as listed in section 3.1.

11.2.2 Challenging matrix (CuVer2): Pipet 25.0 mL of sample into the sample cell. Use this preparation for samples containing aluminum, iron, or hardness as listed in section 3.1.

11.3 Add the contents of the appropriate CuVer powder pillow to the sample cell, and swirl to mix.

11.4 Allow to react for 2 min.

11.5 Fill a second sample cell to the appropriate volume with sample for use as a blank.

11.5.1 Insert the blank into the spectrophotometer cell compartment.

11.5.2 Zero the instrument on the blank.

11.6 Sample Analysis

11.6.1 Insert the sample cell into the spectrophotometer cell compartment.

11.6.2 Read the sample results. Sample results are reported in mg/L Cu.

12.0 Data Analysis and Calculations

12.1 Cu concentration is calculated automatically against internal instrument calibration.

13.0 Method Performance

Performance of the method was demonstrated in multi-lab studies comparing the method against EPA Reference Method EPA 200.7. The method was evaluated in a low ionic strength reference matrix as well as multiple geographically diverse finished drinking water samples obtained from both surface water and ground water sources.

Validation Results	Section	Limit
Method Detection Limit	9.2	0.03 mg/L Cu
Initial Recovery	9.3	101%
Initial Recovery Range	9.3	84.9% - 117%
Initial Precision 95%	9.3	0.02

Matrix Recovery	9.4	94.7%
Matrix Recovery Range	9.4	79.5% – 110%
Matrix Recovery RPD_{max}	9.4	0.15

14.0 Pollution Prevention

14.1 Follow guidelines in Section 15.

15.0 Waste Management

15.1 It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect air, water, and land by minimizing and control all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is also required.

15.2 For further information on waste management, consult "The Waste Management manual for Laboratory Personnel", and "Less is Better: Laboratory Chemical Management for Waste Reduction", both available from the American Society's Department of Government Relations and Science Policy, 1155 16th Street N.W., Washington, D.C. 20036.

16.0 References

16.1 "Protocol for the Evaluation of Alternate Test Procedures for Organic and Inorganic Analytes in Drinking Water," USEPA, EPA-815-R-15-007, February 2015.

16.2 40 CFR 136, Appendix B.

16.3 "OSHA Safety and Health Standards, General Industry," (29 CFR 1910), Occupational Safety and Health Administration, OSHA 2206 (Revised, January 1976)

16.4 "Safety in Academic Chemistry Laboratories," American Chemical Society, Committee on Chemical Safety, 3rd Edition, 1979.

16.5 "Water Analysis Handbook," Hach Company, 8th Edition, 2013.

17.0 Tables

17.1 Acceptance Criteria for Performance tests – The QC performance criteria for this method were performed with a Hach Company DR3900 Spectrophotometer and CuVer2 reagents.

Table 1. Initial Precision and Recovery Acceptance Criteria

Parameter	Acceptance Criteria
Relative Standard Deviation	≤ 10%
Percent Recovery Range	90 – 100%

Table 2. Ongoing Precision and Recovery Acceptance Criteria

Parameter	Initial Criteria
Lab Fortified Blank Recovery Range	84.9-117%
Sample Matrix Spike Recovery	70% - 130%
Sample Matrix Spike RPD	≤ 10%

18.0 Glossary of Definitions and Purposes

The definitions and purposes are specified to this method but have been conformed to common usage as much as possible.

18.1 Units of weight and measure and their abbreviations

18.1.1 Symbols
°C: degrees Celsius

18.1.2 Alphabetical characters
mg/L: milligram per liter

18.2 Definitions, acronyms, and abbreviations

18.2.1 MDL: Method detection limit

18.2.2 IPR: Initial precision and recovery

18.2.3 OPR: On-going precision and recovery

18.2.4 MS: Matrix spike

18.2.5 MSD: Matrix spike duplicate

18.2.6 LIS: Low ionic strength, deionized water