Spectrophotometric Determination of Reducing Aldehyde Groups in Bleached Chemical Pulps

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Abstract: The objective of this study was to investigate the potential application of a simple spectrophotometric method for the determination of the reducing aldehyde groups present in pulps. Although the copper number measurement is the conventional way to determine the reducing aldehyde groups in pulps, it is a very complicated and time-consuming titration procedure. In the characterization of the absorption spectrum for the Cu²⁺ in solution, a distinct absorption band was observed in all the visible absorption range and its maximum peak was found at 700 nm. A strong linear relationship existed between the absorbance for Cu²⁺ at 700 nm and the reference copper number, indicating a good agreement between them. This spectroscopic method is a simple, fast, and accurate procedure for the determination of pulp copper numbers compared to the conventional method.

Keywords: copper number, pulp, reducing aldehyde groups, spectroscopy

Introduction

It is well established that hydrolyzed or oxidized groups present in cellulose are capable of reducing certain metallic ions to lower valence states. This type of reaction has been used to determine the amount of reducing groups and thereby estimate the damage to cellulose undergone during certain chemical reactions, such as bleaching. The copper number, commonly known as the number of grams of metallic copper (as Cu₂O) resulting from the reduction of CuSO₄ by 100 g of the pulp or paper fibers, has been widely used in the paper industry as an index to evaluate pulp fiber reducing properties. The Standard Testing Method [1] for copper number measurement, published by the American Technical Associate for Pulp and Paper Industry (TAPPI), was developed back in 1950s [2]. This method is based on the reaction between reducing groups, i.e., aldehyde groups, in pulp fibers and copper ions (Cu²⁺) in an alkaline solution; it can be expressed as,

\[ 2Cu^{2+} + RCHO + 5OH^- \rightarrow Cu_2O + RCOO^- + 3H_2O \] (1)

In the presence of an excess amount of Cu²⁺, it usually takes ca. 3 h at 100 °C for the reaction to be completed. The copper number of the pulp is determined by measuring cuprous oxide (Cu₂O), one of the products in the reaction (1). Cu₂O is an insoluble species in alkaline solution and tends to be strongly adsorbed on the pulp fibers. This property requires, therefore, the pulp sample to be thoroughly washed after the reaction to remove the residual chemicals (Cu²⁺ and alkali) from the pulp. Therefore, the pulp is added into the molybdophosphoric acid solution to release the Cu₂O precipitate from the pulp fibers. The pulp solution is then filtered to collect the filtrate, which can be titrated by a standard permanganate solution, i.e.,

\[ 5Cu^{2+} + MnO_4^- + 8H^+ \rightarrow 5Cu^{2+} + Mn^{2+} + 4H_2O \] (2)
Thus, the amount of Cu₂O determined in this manner is used as a copper number to quantify the amount of reducing aldehyde groups in the pulp samples. Clearly, the measurement can be considered a complicated and time-consuming procedure, including pulp washing, filtration, and titration processes. It also leads to low repeatability and reproducibility in the measurement due to the complicated experimental procedures involved. As reported, the repeatability in the conventional standard method is only 10% [1]. No other experimental methods to measure the reducing aldehyde groups in pulps have been reported previously. Therefore, it would be highly desirable to develop a novel testing method that can efficiently provide more accurate and reliable data in the pulp and paper industry. In our present study, we aimed to develop a novel method for pulp copper number determination using spectroscopy as a simplified experimental procedure with high test precision.

**Experimental**

**Apparatus**

A diode array spectrophotometer (UV-8453, Hewlett-Packard, CA, USA), equipped with a 10-mm silica cell, was used for the spectrophotometric measurements. A 5-mL plastic syringe and syringe filter (0.2 µm) were used for filtration of the resulting solutions.

**Materials**

All chemicals, including copper sulfate, sodium carbonate, and sodium bicarbonate, were obtained from commercial sources. Deionized water was used in solution preparation. A carbonate-bicarbonate solution was prepared by dissolving 129 g of Na₂CO₃ and 50 g of NaHCO₃ in 1000 mL of water. The Cu²⁺ standard solution was prepared by dissolving 10 g of CaSO₄ ⋅ 5H₂O in 100 mL of water, in which the exact Cu²⁺ concentration was determined by the complex titration method using 0.1 M EDTA standard solution as the titrant. The pulp samples were produced in a laboratory bleaching process.

**Analysis Procedures**

The sample size used in the present method depends on the content of reducing aldehyde groups (or copper number) in the pulps. A small size should be taken for a sample with a high amount of the reducing groups. For the bleached pulp sample, ca. 0.30 ÷ 0.45 g of air-dried pulp with a known moisture content was accurately weighed and placed in a 20-mL vial, then 0.50 mL of the standard copper sulfate solution and 9.5 mL of the carbonate-bicarbonate solution were added [1]. The vial was sealed by a septum. Good mixing of the chemicals and pulps was performed by strong hand shaking. The vial was then heated to 100 °C and kept at this temperature for 3 h in a hot-water bath. After the reaction was complete, the sample vial was cooled to room temperature under tap water. The resulting solution was filtered and measured using a UV-Vis spectrophotometer, in which the spectral absorption data at 450 and 700 nm were recorded.

**Results and Discussion**

**Absorption Spectrum of Copper Sulfate**

We added a certain amount of pulp to a standard Cu²⁺ buffer solution containing carbonate and bicarbonate salts. After performing the reaction at 100 °C, the resulting solution was analyzed using a spectrophotometer. Distinct absorption bands for Cu²⁺ were observed in the visible wavelength range (500 ÷ 1100 nm), as indicated in Figure 1. A maximum peak was found at ca. 700 nm in both the sample solutions with or without pulp fibers. At the end of the reaction, a minimum amount of the absorbed Cu₂O on fibers was observed compared to that of the standard Cu²⁺ solution. When the absorbance of the solution was not very high, the absorption of Cu²⁺ at a given wavelength followed Beer’s Law, i.e.,

\[
A = εLC_{Cu^{2+}}
\]

where \(A\), \(ε\), and \(L\) are the absorbance, absorptivity, and optical path-length, respectively; \(C_{Cu^{2+}}\) is the molar concentration of the chemical species, i.e., Cu²⁺. Therefore, it could be possible to quantify the Cu²⁺ concentration in the solution using spectroscopy, in the absence of spectral interference. Figure 1 also clearly shows that the Cu²⁺ spectrum in an alkaline solution differs from that in water. The pH of the medium should be kept constant to obtain a high-accuracy absorption curve. The carbonate-bicarbonate buffer solution was used to ensure a constant pH of the reaction medium.

**Copper Number Determination**

Considering the Cu²⁺ concentrations in the reaction without (i.e., blank) pulp fibers, equation (3) can be rewritten as

\[
A_0 = εLC_{Cu^{2+},0}
\]

where \(A_0\) and \(C_{Cu^{2+},0}\) are the absorbance of the solution and the molar concentration of Cu²⁺ in the solution containing no pulp fiber, respectively. Because \(C_{Cu^{2+},0}\) is known (\(C_{Cu^{2+},0} = 0.05 \times C_{Cu^{2+}}\)), the Cu²⁺ concentration in the solution containing pulp fibers can be easily determined according to the relationship...
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Figure 1. Light absorption spectra for Cu$^{2+}$ in water and in carbonate-bicarbonate solution.

\[ C_{Cu^{2+}} = \frac{A}{A_0} \]  

(6)

Thus, the content of Cu$^{2+}$ ions consumed by the pulp during the reaction can be calculated as

\[ \frac{n}{V} = (C_{Cu^{2+},0} - C_{Cu^{2+}}) = C_{Cu^{2+},0} \left[ 1 - \frac{A}{A_0} \right] \]  

(7)

where \( n \) is the number of moles Cu$^{2+}$ consumed during the reaction and \( V \) is the volume of the reaction media. The copper numbers of the pulps \((Cu.N.)\) can, therefore, be expressed as

\[ Cu.N. = \frac{MC_{CuO}}{2w} \left[ \frac{1 - \frac{A}{A_0}}{A_0} \right] \times 100 = 3.575 \times \frac{C_{Cu^{2+}}}{w} \left[ \frac{1 - \frac{A}{A_0}}{A_0} \right] \]  

(8)

where \( MC_{CuO} \) is the molecular weight of cuprous dioxide and \( w \) is the oven-dry weight of pulp samples.

Figure 2 shows that a linear relationship existed between the absorbance of Cu$^{2+}$ in the solutions measured at 700 nm and the pulp copper numbers measured by the conventional method [1]. This result strongly suggests that the copper number of pulps can be easily determined through spectrophotometric measurement at high accuracy.

**Interference and Errors**

In alkaline media, Cu$^{2+}$ ions react with the reducing groups in cellulosic pulps to produce Cu$_2$O as a precipitate, which has a strong affinity to pulp fibers. Thus, there is always a certain amount of Cu$_2$O precipitate present in the resulting solution. To eliminate the light scattering error caused mainly by the cuprous oxide particles, the solution must be filtered carefully. Because the particle size of the Cu$_2$O precipitate is extremely small, it is strongly recommended that the filter should have a pore diameter smaller than 0.2 µm.

In the UV spectra, baseline shifting is another common problem that causes experimental error; this effect can be simply corrected, however, by using a dual-wavelength spectral measurement technique. In this work, we used a reference wavelength of 450 nm to correct the error caused by baseline shifting during the spectroscopic measurement. Thus, we used the following equation to calculate the copper number:

\[ Cu.N. = 3.575 \times \frac{C_{Cu^{2+}}}{w} \left[ \frac{1 - \frac{A}{A_{450}}}{A_0 - A_{450}} \right] \]  

(9)

where \( A_{450} \) is the light absorbance at 450 nm.

**Measurement Sensitivity**

In the present work, the reaction conditions were basically the same as those described in the standard method, which ensures a complete reaction between pulp and Cu$^{2+}$ for copper numbers in the sample up to 6, as stated in reference [1]. If the sample has a higher copper number (greater than 6), a reduced size of pulp sample should be employed. Because the typical bleached pulp samples usually have very low copper numbers, e.g., less than 1, this requirement may not be a problem in the conventional standard method [1]. The spectroscopic method, however, could have some detrimental effects, causing a relatively low measurement sensitivity, as shown in Figure 2. In an attempt to improve the test sensitivity, we used a reduced Cu$^{2+}$ concentration (1/5 of the previous concentration) for the reaction. Even though a faster reaction was observed at the beginning of this first trial, a complete reaction could not be achieved within 3 hours, as shown in Figure 3. This situation also led to under-estimation of the real copper number of the pulp sample, which was only ca. 2/3 of that obtained under the standard test conditions.
In the second trial, however, we found that the measurement sensitivity was improved by increasing the pulp consistency (i.e., pulp content in the reaction solution), for example, when increasing sample size to 3 % or higher from the original 1.5 %. Using this method, the measurement sensitivity (i.e., the slope in Figure 2) could be improved without lowering the reaction rate.

**Precision Evaluation**

The repeatability for the spectroscopic method was evaluated using a bleached pulp sample for which the copper number was 0.53. The result showed that the average relative standard deviation (RSD) from five measurements was less than 6 %, that is, lower than 10 %, as reported in the standard conventional method [1]. The copper numbers obtained from the spectroscopic method were plotted as a function of conventional copper number data, as shown in Figure 4. There is a good agreement between the copper number measurements obtained through the spectroscopic and reference methods, indicating that the conventional method can be replaced by the simple spectroscopic measurement.

### Conclusions

The present study was conducted to develop a novel method for pulp copper number determination using spectroscopy to provide a simplified test procedure with high precision. The spectrophotometric absorption for \( \text{Cu}^{2+} \) in solution was characterized in solutions with and without pulp fibers. Distinct absorption bands for \( \text{Cu}^{2+} \) were observed in the visible wavelength range and maximum peaks were found at ca. 700 nm in both sample solutions with and without pulp fibers. A strong linear relationship existed between the absorbance for \( \text{Cu}^{2+} \) in the solutions measured at 700 nm and the reference copper numbers. High sensitivity for measurement was achieved using samples with an increased consistency of pulp solution greater than 3 %. A good agreement existed between the copper numbers measured using the spectroscopic and reference methods. From the results obtained from this study, it could be concluded that the spectroscopic method is a simple, fast, and accurate procedure for the determination of pulp pulp reducing aldehyde groups when compared with the conventional titration method.

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### References
