

Determination of Carboxyl Groups in Pulp via Ultraviolet Spectrophotometry

Jin Long, Hao Gong, Dezhi Zhang, Mengru Liu, and Hailong Li *

A method was established for the determination of carboxyl groups in pulp by ultraviolet (UV) spectrophotometry. The method is based on the fact that the carboxylate pretreated with diluted hydrochloric acid was completely converted to carboxylic acid in pulp. In addition, content of carboxyl groups was measured with the capacity of copper ions exchanged with the hydrogen ions of carboxylic acid by UV spectrophotometry. The data showed that the pulp was suitable to react with 30% to 50% exchanged copper ions for 4 h at 45 °C. The results indicated that the method had excellent repeatability (RSD = 1.50%) and accuracy. Compared to traditional methods, the maximum relative error was less than 4%. The method is simple and accurate, such that it can be used for the efficient determination of carboxyl groups in pulp and other researches.

Keywords: Carboxyl groups; Copper ions; Ultraviolet spectrophotometry; Pulp

Contact information: State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou 510640, China; *Corresponding author: felhl@scut.edu.cn

INTRODUCTION

As essential functional groups, carboxyl groups are prone to substitution reaction and esterification reactions (Haslam 1980). Increases in the content of carboxyl groups in pulp would enlarge the application range of pulp and easily contribute to pulp modification with rich functions (Kitaoka *et al.* 1999). During pulping and bleaching processes, carboxyl groups can be formed in fibers. Especially in totally chlorine free bleaching processes, a lot of carboxyl groups are created on account of the usage of oxygen, ozone, and hydrogen peroxide (Lachenal *et al.* 2014). Pulp with more carboxyl groups is not only easier to undergo acid hydrolysis (Hirosawa *et al.* 2001), but also has a high water retention value and more recycling times and contributes to the bonding of fibers (Chen *et al.* 2013). Therefore, it is significant that the concentration of the carboxyl groups in pulp should be measured accurately and conveniently.

The methods for determination of the carboxyl groups in pulp include acid-base titration (Hiller and Pacsu 1946; Scott 1979; Bhardwaj *et al.* 2004), potentiometric titration (Barbosa *et al.* 2013), head-space gas chromatography (Chai *et al.* 2003; Zhu and Chai 2005), *etc.* As traditional methods, acid-base titrations with low sensitivity are vulnerable to artificial disturbances and squander time and vigor in the titration process (Fras *et al.* 2004). Although the head-space gas chromatograph has the characteristics of high reliability and high automation (Snow and Slack 2002), application is limited to the expense of the experimental instrument. In addition, due to the low strength of glass bottles, it is difficult to disperse the mixture of pulp and solution uniformly without considerable

oscillation, especially when the pulp has a high content of carboxyl groups.

In this paper, the content of carboxyl groups is indirectly measured with the exchanged copper ions by ultraviolet (UV) spectrophotometry and the reaction principle can be expressed as follows:



There is a unique characteristic absorption peak in the ultraviolet region when copper ions dissolve in a sodium carbonate (Na_2CO_3)-sodium bicarbonate (NaHCO_3) buffer (Chai *et al.* 2007); therefore, the exchanged capacity of copper ions can be calculated and the consistency of carboxyl groups is also ascertained. Through the investigation of optimum conditions, reliability and accuracy of the method in this paper, a convenient and precise method for quantification of the carboxyl groups in pulp is configured.

EXPERIMENTAL

Materials

The samples of bleaching chemical pulp with different contents of carboxyl groups were prepared through the TEMPO/ NaClO / NaBr oxidation system in the authors' laboratory. Copper chloride (CuCl_2 ; $\geq 99\%$), copper acetate ($[(\text{CH}_3\text{COO})_2\text{Cu}]$; $> 98\%$), hydrochloric acid (HCl ; 36% to 38%), sodium carbonate (Na_2CO_3 ; $\geq 99.8\%$), and sodium hydrogen carbonate (NaHCO_3 ; $\geq 99.5\%$) were obtained from Guangzhou Chemical Reagent Factory (Guangzhou, China). Deionized water was used for all experiments.

Methods

The different concentrations of CuCl_2 solutions were added to a volumetric flask and diluted with the Na_2CO_3 - NaHCO_3 buffer (129 g of Na_2CO_3 and 50 g of NaHCO_3 dissolved in 1000 mL of deionized water) (Chai *et al.* 2007).

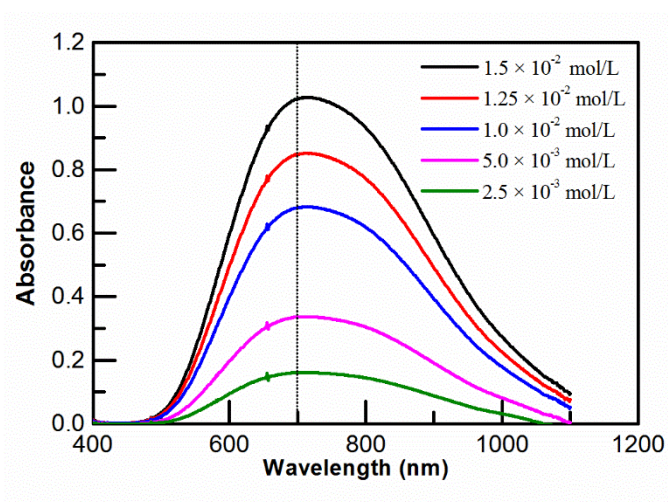


Fig. 1. The UV spectra of the solution with different concentrations of copper ions

The standard CuCl_2 solutions (2.5×10^{-3} mol/L, 5×10^{-3} mol/L, 1×10^{-2} mol/L, 1.25×10^{-2} mol/L, 1.5×10^{-2} mol/L) were prepared after shaking to evenly disperse the solution. The absorbance was identified by an Agilent 8453 (Agilent Technologies Co., Ltd., Beijing, China) UV spectrophotometer (Fig. 1), and the standard curve of the relationship between the absorbance and concentration of the copper ions was illustrated (Fig. 2).

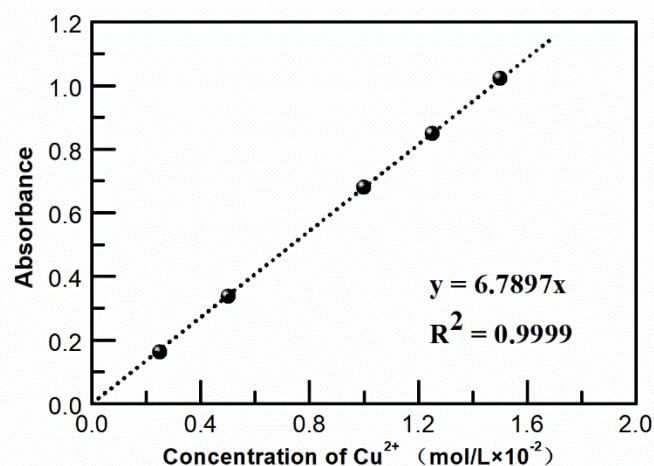


Fig. 2. Standard curve of copper ions at 700nm

The pulp was pretreated with 0.1 mol/L HCl and magnetically stirred at room temperature for 1 h so that the carboxylate completely transformed into carboxylic acid. The pulp consistency was 1% (w/v) for the whole process. The pulp was washed with deionized water to neutralize and was conserved after air-drying.

At the beginning of the analysis, two samples of oven-dried (OD) pulp (approximately 0.1 g to 0.3 g) were placed in two plastic bottles that separately contained 5 mL of 0.025 mol/L copper chloride or copper acetate. The dispersed pulp was processed at different temperatures and times to reach an equilibrium of ions. The absorbance at 700 nm was measured by UV spectrophotometer when the 2 mL of reaction liquor (treated with 0.25 μm filter) was added into 3 mL of Na_2CO_3 - NaHCO_3 buffer. It should be noted that the weight of the pulp was dependent upon the exchanged capacity of copper ions (approximately 30% to 50% copper ions); the concentration of copper ions can be tuned if the exchanged copper ions disagree with the mass of pulp.

Results Processing

The exchanged capacity of copper ions was calculated with the standard curves of copper ions and the concentration of carboxyl groups was calculated with Eq. 2,

$$C_{\text{COOH}} = \frac{25(A_2 - A_1)}{\xi m} \quad (\text{mmol/g}) \quad (2)$$

where A_1 is the absorbance at 700 nm in ultraviolet when the reaction with copper acetate is finished, A_2 is the absorbance at 700 nm in ultraviolet when the reaction with copper chloride is finished, ξ is the molar absorptivity of copper ions at 700 nm, m is the mass of OD pulp (g), and C_{COOH} is the content of carboxyl groups (mmol/g).

RESULTS AND DISCUSSION

Sample Analysis

The exchanged capacity of copper ions in the mixture is dependent on the content of carboxyl groups in pulp. For the same pulp, the effect of the sample mass on exchanged copper ions was obvious. The relationship between the calculated carboxyl groups in pulp and the exchanged copper ions is shown in Fig. 3. The measurement was higher than the actual value when the exchanged copper ions were lower than 30% copper ions. This indicated that the measured value was influenced by the low content of exchanged copper ions and the measurement was higher while the exchanged copper ions were lower. In contrast, the test value was lower than the actual value when the exchanged copper ions were higher than 50% copper ions. This illustrated that the hydrogen ion of carboxyl groups in pulp was hard to exchange with copper ions absolutely with the increase of exchanged copper ions due to the existence of a saturation point. Therefore, what is of importance is that the mass of the employed pulp should react with 30% to 50% exchanged copper ions in the process of quantifying carboxyl groups.

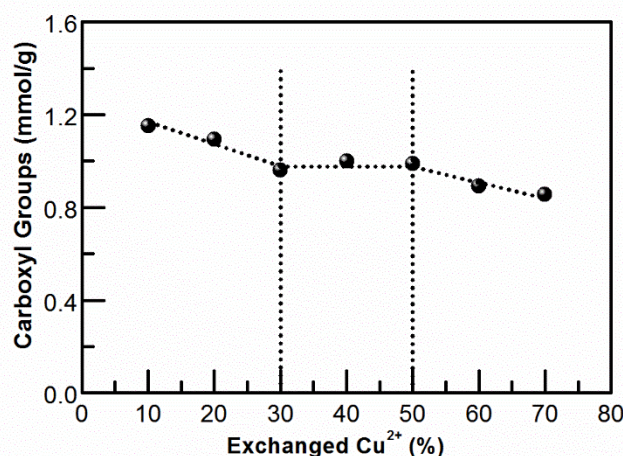


Fig. 3. The relationship between the calculated carboxyl groups in pulp and the exchanged copper ions

Reaction Temperature and Reaction Time

The effect of reaction temperature and reaction time on the quantification of the carboxyl groups in pulp is shown in Fig. 4. The exchanged copper ions gradually increased to a maximum and ultimately approached a state of equilibrium with increased reaction time. It is worth noting that the hydrogen ions of carboxyl groups in pulp exchanged with copper ions totally. At the same time, Fig. 4 illustrates that the reaction time would evidently reduce if the reaction temperature increased from 25 °C to 45 °C. The total reaction time was 8 h at 25 °C, but rapidly decreased to 4 h at 45 °C. According to the above results, 45 °C for 4 h is commendably suitable as the reaction temperature and reaction time, respectively.

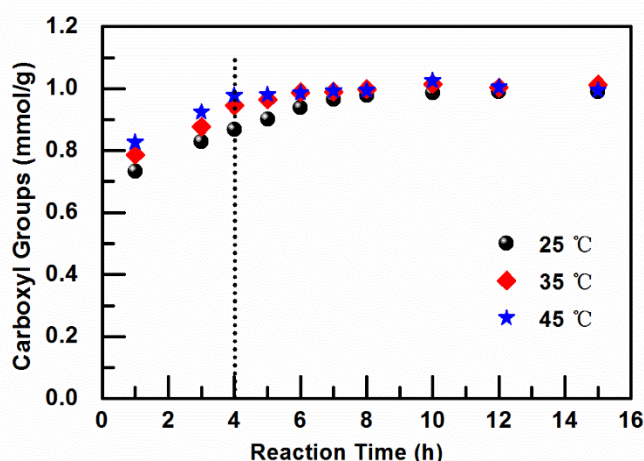


Fig. 4. Effects of reaction temperature and reaction time on the quantification of the carboxyl content in pulp

Method Evaluation

The repeatability testing of this method was investigated. The results showed that the repeatability was very good and the relative standard deviations (RSD) were within 1.50% (Table 1), in which the random errors were associated with uncertainties in both the sampling and UV measurement.

Table 1. Repeatability Testing

Samples	Carboxyl Groups (mmol/g)
1	0.991
2	0.985
3	0.994
4	1.018
5	0.979
Average	0.993
RSD (%)	1.50

The comparison of the results between UV spectrophotometry and conductimetric titration (Katz *et al.* 1984) are shown in Table 2. In brief, the pretreatment of pulp in conductimetric titration was the same within the UV spectrophotometry. An amount of 0.3 g OD pulp was dispersed in 50 mL of 0.1 mol/L NaCl and pH adjusted to 2.5 with 0.1 mol/L HCl, then the sample was titrated against 0.1mol/L NaOH in 0.1 mL increments. The carboxyl groups were calculated with equivalent point in titration curves and all results were the averages of three measurements which differed by less than 5%. The results showed that the relative deviation of this method was less than

4% and the UV spectrophotometry as conductimetric titration was acceptable for sample analysis. Thus, it is credible for UV spectrophotometry to determine the content of carboxyl groups in pulp.

Table 2. Comparison of the UV Spectrophotometry and Conductimetric Titration

Samples	UV Spectrophotometry (mmol/g)	Conductimetric Titration (mmol/g)	Relative Deviation (%)
1	0.387	0.385	0.517
2	0.716	0.703	1.816
3	0.838	0.858	-2.387
4	0.870	0.904	-3.908
5	1.042	1.003	3.743
6	1.193	1.206	-1.090

CONCLUSIONS

1. This study reports a new method to quantify the amount of carboxyl groups in pulp. The content of carboxyl groups was calculated with the exchanged capacity of copper ions.
2. The optimum conditions of quantification of the carboxyl groups were 4 h at 45 °C. The RSD of this method was only 1.50% and the maximum relative error was less than 4%.
3. This study contributed to accurate determination of carboxyl groups and the pulp that will be employed with the identified quantities of carboxyl groups. In comparison with traditional methods, it has good repeatability, high accuracy, and conventional operation for the quantification of carboxyl groups by UV spectrophotometry.

ACKNOWLEDGMENTS

The authors acknowledge the National Key R&D Program of China (2017YFB0308003), the Science and Technology Planning Project of Guangdong Province (2015A020215007, 2016A020221010), the Natural Science Foundation of China (No. 31670586), the Fundamental Research Funds for the Central Universities (2017ZD091), and the State Key Laboratory of Pulp and Paper Engineering Program (2016C05) for sponsoring this research.

REFERENCES CITED

- Barbosa, L. C. A., Maltha, C. R. A., Demuner, A. J., Cazal, C. M., Reis, E. L., and Colodette, J. L. (2013). "A rapid method for quantification of carboxyl groups in cellulose pulp," *BioResources* 8(1), 1043-1054. DOI: 10.15376/biores.8.1.1043-1054
- Bhardwaj, N. K., Duong, T. D., and Nguyen, K. L. (2004). "Pulp charge determination by different methods: Effect of beating/refining," *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 236(1-3), 39-44. DOI: 10.1016/j.colsurfa.2004.01.024
- Chai, X. S., Hou, Q. X., and Zhu, J. Y. (2003). "Carboxyl groups in wood fibers. 2. The fate of carboxyl groups during alkaline delignification and its application for fiber yield prediction in alkaline pulping," *Industrial & Engineering Chemistry Research* 42(22), 5445-5449. DOI: 10.1021/ie0209733
- Chai, X. S., Zhang, D., Hou, Q., and Yoon, S. H. (2007). "Spectrophotometric determination of reducing aldehyde groups in bleached chemical pulps," *Journal of Industrial and Engineering Chemistry* 13(4), 597-601.
- Chen, Y., Wan, J., Dong, X., and Ma, Y. (2013). "Fiber properties of eucalyptus kraft pulp with different carboxyl group contents," *Cellulose* 20(6), 2839-2846. DOI: 10.1007/s10570-013-0055-8
- Fras, L., Stana-Kleinschek, K., Ribitsch, V., Sfiligoj-Smole, M., and Kreze, T. (2004). "Quantitative determination of carboxyl groups in cellulose polymers utilizing their ion exchange capacity and using a complexometric titration," *Materials Research Innovations* 8(3), 145-146. DOI: 10.1080/14328917.2004.11784850
- Haslam, E. (1980). "Recent developments in methods for the esterification and protection of the carboxyl group," *Tetrahedron* 36(17), 2409-2433. DOI: 10.1016/0040-4020(80)80219-5
- Hiller, L. A., and Pacsu, E. (1946). "Cellulose studies: VI. Determination of carboxyl groups in cellulosic materials," *Textile Research Journal* 16(8), 390-393. DOI: 10.1177/004051754601600805
- Hirosawa, S., Minato, K., and Nakatsubo, F. (2001). "Influence of carboxyl group on the acid hydrolysis of cellulose," *Journal of Wood Science* 47(2), 141-144. DOI: 10.1007/BF00780563
- Katz, S., Beatson, R. P., and Scallan, A. M. (1984). "The determination of strong and weak acidic groups in sulfite pulps," *Svensk Papperstidning* 87(6), 48-53.
- Kitaoka, T., Isogai, A., and Onabe, F. (1999). "Chemical modification of pulp fibers by TEMPO-mediated oxidation," *Nordic Pulp & Paper Research Journal* 14(4), 279-284.
- Lachenal, D., Perrin, J., Pouyet, F., and Chirat, C. (2014). "Formation of carbonyl and carboxyl groups on cellulosic pulps: Effect on alkali resistance," *BioResources* 9(4), 7299-7310. DOI: 10.15376/biores.9.4.7299-7310
- Scott, R. W. (1979). "Colorimetric determination of hexuronic acids in plant materials," *Analytical Chemistry* 51(7), 936-941. DOI: 10.1021/ac50043a036
- Snow, N. H., and Slack, G. C. (2002). "Head-space analysis in modern gas chromatography," *TrAC Trends in Analytical Chemistry* 21(9-10), 608-617. DOI: 10.1016/S0165-9936(02)00802-6

Zhu, J. Y., and Chai, X. S. (2005). "Some recent developments in headspace gas chromatography," *Current Analytical Chemistry* 1(1), 79-83. DOI: 10.2174/1573411052948488

Article submitted: November 23, 2017; Peer review completed: February 2, 2018;
Revised version received: February 12, 2018; Accepted: February 16, 2018; Published:
February 21, 2018.
DOI: 10.15376/biores.13.2.2670-2677