

Rapid Determination of Total Sulfur Content in Green Liquors by Turbidimetric Method

Renwei Xing,^{a,*} Zhiyong Yang,^a Yan Zhou,^a and Songlin Wang^b

A turbidimetric method for the determination of total sulfur content in green liquors was developed. The proposed method involves the quantitative conversion of reduced sulfur with hydrogen peroxide to form sulfate at room temperature for 2 min. After barium chloride is added, sulfate instantly reacts with barium chloride to form precipitated barium sulfate that is measured with a UV-Vis spectrophotometer. The interference from carbonate can be eliminated by adding hydrochloric acid. Proper analytical conditions were determined as follows: detection wavelength of 420 nm, the stabilizer of polyvinyl alcohol (PVA), and an analysis time of 10 min. The results showed that the method has an excellent measurement precision (RSD < 1.30%) and accuracy (recovery = 100.1 ± 1.7%) for the quantification of total sulfur content in green liquors. The present method is simple, rapid, and accurate, and can be used for the efficient determination of total sulfur in green liquors.

Keywords: Green liquor; Total sulfur; Reduction rate; Turbidimetry

Contact information: a: Shandong Peninsula Engineering Research Center of Comprehensive Brine Utilization, Weifang University of Science and Technology, Shouguang 262700, China; b: College of Chemical Engineering, Qingdao University of Science and Technology, Qingdao 266042, China;

* Corresponding author: 15964324097@163.com

INTRODUCTION

Sulfate pulping is the most commonly used chemical pulping method in the world, which not only has the advantages of high yield and good strength of pulp (Lachenal 2016), but also allows for efficient alkali recovery technology of the digestion liquid (black liquor). Kraft chemicals and heat energy can be recovered by burning thick black liquor (Gullichsen and Paulapuro 2000). During black liquor combustion, sodium sulfate is reduced to sodium sulfide, and its molten substance dissolves in water to become green liquor (Grace *et al.* 1989). The ratio of sodium sulfide content to total sulfur content in green liquor is called reduction efficiency, which represents the recovery rate of sodium sulfide in black liquor combustion (Biermann 1996; Silva *et al.* 2008; Josef 2016). Reduction efficiency can be used to regulate the combustion process of the boiler (*i.e.*, combustion temperature, air supply, and mirabilite dosage). The following formula is commonly used to calculate the reduction efficiency of green liquor in the factory (Biermann 1996).

$$\text{Reduction efficiency (\%)} = \frac{\text{Na}_2\text{S}}{\text{Na}_2\text{S} + \text{Na}_2\text{SO}_4} * 100 \quad (1)$$

The total content of sulfur-containing substances in the green liquor is represented by the sum of sodium sulfide and sodium sulfate (both measured as sodium oxide). Excluding sodium sulfide and sodium sulfate, other sulfur-containing substances including sodium sulfite and sodium thiosulfate also exist in green liquor (Kesler 1957; Kesler and

Reinke 1957; Grace *et al.* 1989; Jin *et al.* 2010). Therefore, the correct reduction efficiency should be calculated according to the following formula (TAPPI T1203 os-61 1961; Grace 1992).

$$\text{Reduction efficiency (\%)} = \text{Na}_2\text{S} / (\text{Na}_2\text{S} + \text{Na}_2\text{SO}_4 + \text{other sulfides}) * 100 \quad (2)$$

Other sulfur-containing compounds in green liquor are usually ignored in the current calculation methods adopted by factories. The reduction efficiency calculated by Eq. 1 is greater than the actual value. The content of sodium sulfide in green liquor can be easily determined by titration (MacDonald 1969), while sodium sulfate is usually measured by gravimetric method (TAPPI T 624 os-68, 1968). The gravimetric method always requires precipitation, aging, filtration, and high-temperature burning, which makes the operation tedious, time-consuming, and easy to bring large measurement errors.

When comparing Eqs. 1 and 2, the difference between the calculated and actual values of reduction efficiency is evident when other sulfur-containing compound content is high in green liquid. Thus, it cannot well guide sulfide transformation process conditions in the process of black liquor combustion. The transformation results in the decrease of effective sulfide component and the increase of non-process components in the process of white liquid recycling, which adversely affects normal pulp production. Therefore, a method based on the rapid and accurate determination of the total sulfur content to obtain the correct reduction efficiency is of great significance for boiler combustion during alkali recovery.

A simple turbidimetric method was developed for rapid determination of total sulfur in green liquor. The main goals were to explore the proper reaction conditions (*i.e.*, the dosage of hydrogen peroxide and reaction time) on the completion of reduced sulfur conversion and the analytical conditions. The precision and accuracy of the total sulfur quantification by the proposed method were evaluated.

EXPERIMENTAL

Chemicals and Materials

Green liquor was obtained from Chenming Paper Co. Ltd., China. Sodium sulfate, polyvinyl alcohol (PVOH), glycerol, ethanol, sodium thiosulfate solution, hydrogen peroxide, hydrochloric acid, and barium chloride were purchased from the Guangzhou Chemical Reagent Factory (Guangzhou, China). Deionized water was used for all of the experiments.

Method

Sample turbidity measurement

Five mL of 10% (w/v) barium chloride solution and 100 μL of 0.1 mol/L sodium sulfate standard solution were transferred to a set of 25 mL of volume bottle, after 5 min, 5 mL of water, 0.1% (w/v) PVA solution, ethanol and glycerin-ethanol with a volume ratio of 1:1 was added in the mixture, respectively. It took some time before the resulting cloudy was moved to a quartz vial and measured the absorbance was measured at 420 nm *via* a UV-visible spectrophotometer to determine the turbidity due to the presence of barium sulfate particles.

Drafting of standard sodium sulfate curve

Two point five mL of 10% (w/v) barium chloride solution was added to a set of 25 mL of volume bottle containing different amounts (0 to 80 μ L) of 0.1 mol/L sodium sulfate standard solution. After 5 min, 2.5 mL of 0.1% (w/v) PVOH solution was added to the mixture. Ten minutes later, the resulting solution was transferred to the quartz cuvette and 0.1% (w/v) PVOH solution was used as a blank sample. The absorbance of the turbidity of barium sulfate at 420 nm was measured in a UV-visible spectrophotometer. A linear standard curve was obtained between the absorbance value of turbidity solution of barium sulfate and the content of sulfate.

Reducible sulfide sample preparation and measurement

Fifty μ L of the 0.1 mol/L sodium thiosulfate solution was added to a set of 25 mL of volume bottle containing different amounts of 30% hydrogen dioxide. After a period of time, the sulfate content in the resulting solution was measured by ICP-OES, to calculate the percent conversion of reducible sulfide.

Green liquor sample preparation and measurement

Five mL of the green liquor and 25 mL of 30% hydrogen peroxide were added in a 100 mL beaker, and the mixed liquor was boiled for 10 min. Half a mL of the mixture solution was transferred to headspace vial containing 1 mL of 6 mol/L hydrochloric acid. After 5 min, 50 μ L of the resulting solution was added to another headspace vial containing 2.5 mL of 10% barium chloride and 2.5 mL of 0.1% (w/v) PVA solution. After 10 min, the resulting cloudy mixture was moved to a quartz or fused quartz glass, and the absorbance at 420 nm was measured in a UV-visible spectrophotometer to determine the turbidity barium sulfate.

Total Sulfur Content Calculation

The absorption value at 420 nm determined was substituted into the standard curve to calculate the total sulfur content in the solution.

RESULTS AND DISCUSSION

Effects of Reaction Conditions on Sulfate Conversion

The present method is based on measuring the sulfate that is generated by reaction between reducible sulfur compounds mainly including sodium sulfide, sodium sulfite, and sodium thiosulfate with hydrogen peroxide in the green liquor (SCAN-N 2:88 1988). The effects of the reaction conditions, such as the reaction time and dosage of hydrogen peroxide on the completion of the conversion, should be investigated. As sodium thiosulfate is the more difficult to be oxidized by hydrogen peroxide to sulfate ions compared with sodium sulfide, and only in acid conditions, it could be oxidized to sulfate. Sodium thiosulfate was selected for this work as the typical model of reducible sulfide to explore the reaction conditions on sulfate conversion.

Effects of Reaction Time

Figure 1 shows the time-dependent sulfate formation from the sodium thiosulfate conversion reaction with hydrogen peroxide. The percent conversion gradually increased to achieve equilibrium with increasing reaction time.

It was observed that a minimum of 2 min was required for complete conversion of reducible sulfide to sulfate. Therefore, a time of 5 min was used in subsequent experiments.

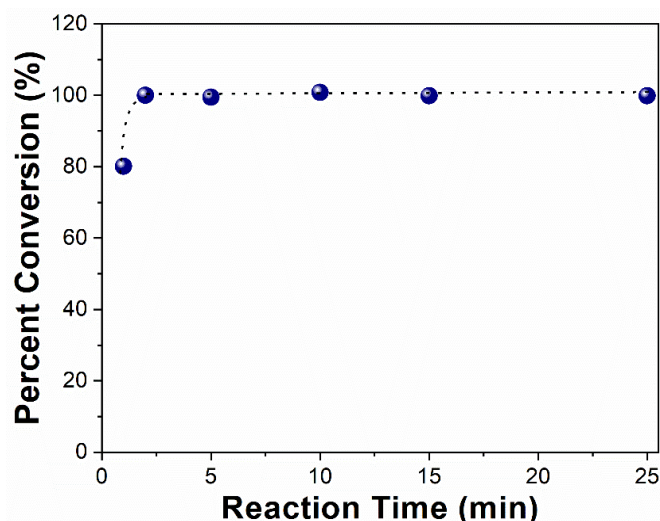


Fig. 1. The relationship between reaction time and reduced sulfur conversion (with a H_2O_2 dosage of 5 mL)

Effects of H_2O_2 Dosage

For a complete conversion of sodium thiosulfate to sulfate, an excess amount of hydrogen peroxide is necessary. As shown in Fig. 2, a percent conversion equilibrium was obtained by adding 0.5 mL of hydrogen peroxide for the sample at the given conditions. Therefore, more than 0.5 mL hydrogen peroxide was used in the following experiments.

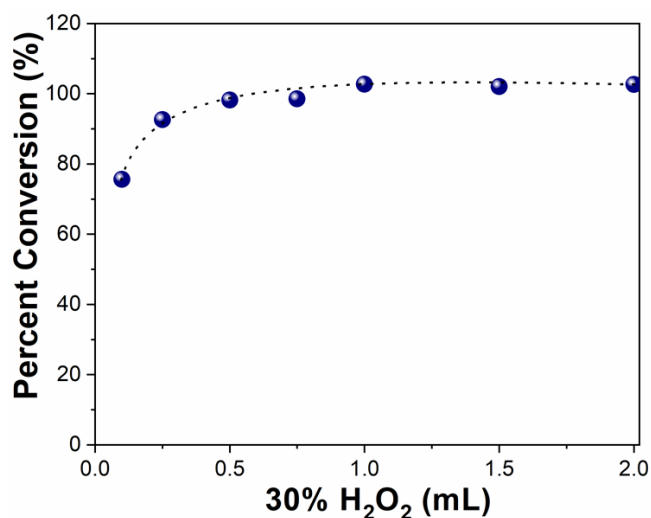


Fig. 2. The relationship between H_2O_2 usage and reduced sulfur conversion (with a reaction time of 15 min)

Sample Turbidity Selection

Due to the small particles and high surface energy of barium sulfate precipitation, it is easy to accumulate and sink in water. Therefore, a stabilizer should be added to form a stable dispersion system. An appropriate stabilizer controls the size of barium sulfate grain, prevents precipitation, and makes it disperse evenly in the system for a long time (Grace *et al.* 1989). Figure 3 shows the stabilizing effect of polyvinyl alcohol (PVOH), ethanol, and gelatin on barium sulfate particles. Clearly, PVOH had the best stabilizing effect on barium sulfate precipitation and was selected as the stabilizer in the following studies.

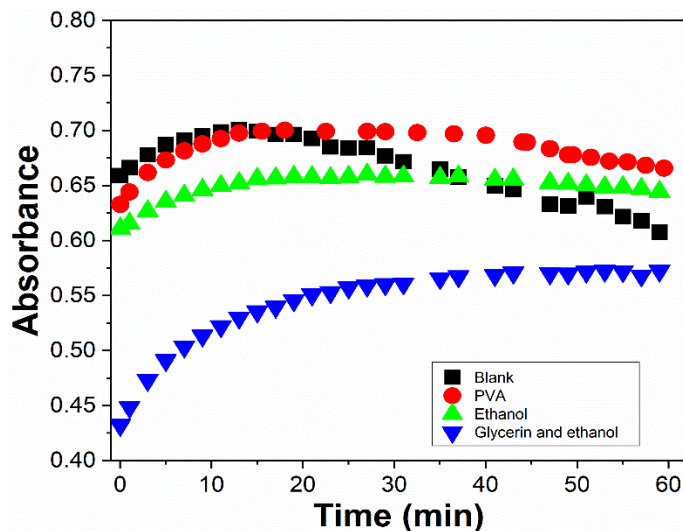


Fig. 3. Effects of different stabilizers on BaSO₄ particles

Measurement Wavelength

Because the intensity of scattered light (I) of the dispersion system is inversely proportional to wavelength to the four power (λ^4), and the PVOH dispersion system of barium sulfate is a colorless suspension, a short wavelength with low absorption interference and good linear relation should be selected as the measurement wavelength (Wiethoff *et al.* 2001). Considering the sensitivity of the determination, and the interference of coexisting ions in the visible region and reagent in the ultraviolet region, respectively, 420 nm was assigned as the measurement wavelength of the PVOH dispersion system of barium sulfate (Iwasaki *et al.* 1957; Kolmert *et al.* 2000).

Measurement Time

The formation time has great influence on the result of turbidimetric method. Because 0.1% (w/v) PVOH was found to have a better stabilizing effect than the other stabilizers (Fig. 3), it was further used to investigate the relationship between turbid formation time and the absorbance value of barium sulfate. As shown in Fig. 4, the absorbance value of turbidity solution increased with the extension of time, and reached a stable value after 10 min. Therefore, a time of 10 min was selected as the formation time of turbidity.

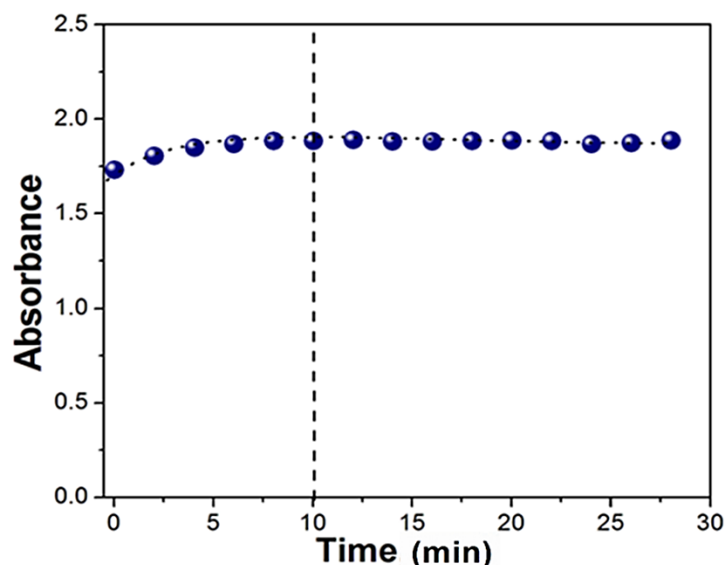


Fig. 4. Effects of turbidity time on the absorbance value of barium sulfate turbid solution (with a 0.1% (w/v) PVA dispersion system)

Method Precision and Validation

Sample preparation and spectroscopic determination were carried out under certain experimental conditions. The measurement reproducibility of the present method was investigated by the quintuplicate determination of absorbance of barium sulfate turbidity in a green liquor sample. The relative standard deviation was less than 1.3%.

Figure 5 showed that the plot of standard curve of barium sulfate. Using the standard curve, a standard calibration curve was obtained by,

$$A = -0.01062(\pm 0.00177) + 0.0128(\pm 0.0002) \times C \quad (3)$$

where A and C represent the absorbance value and the absolute amount of sulfate (mg/L), respectively.

A standard addition method was used to verify the accuracy of the present method. The total sulfur content of green liquor was 23.5 g/L, and Table 1 lists the addition amount of the sulfate and test value of sulfate calculated by Eq. 3 in green liquor, respectively. The recovery ranged from 98.8% to 101.7%, which is appropriate for the determination of total sulfur content in green liquor. Detection and quantification limits (LOD and LOQ) of this method is 4.55 mg/L and 13.78 mg/L, respectively.

Table 1. Method Validation

Sample No.	Amount of Sulfate (mg)		Recovery (%)
	Measured	Added	
1	0.95	0.96	99.1
2	1.90	1.92	98.8
3	2.90	2.88	100.9
4	3.81	3.84	99.2
5	4.88	4.80	101.7

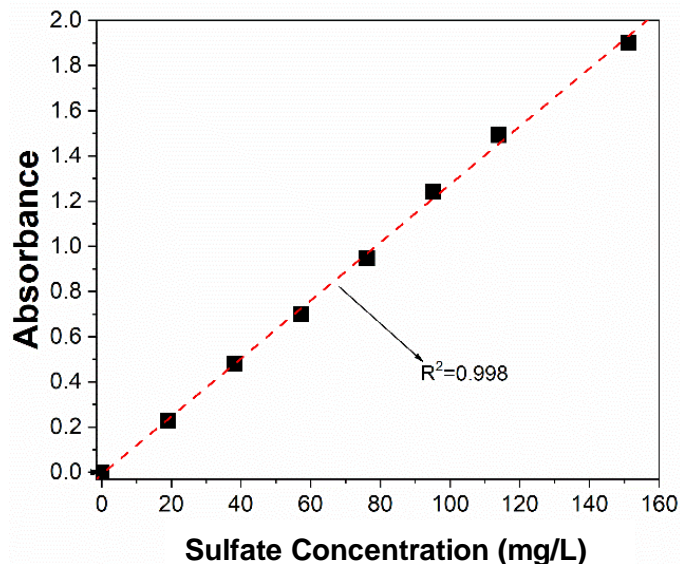


Fig. 5. The plot of the standard curve (b) of barium sulfate

Measurement Interferences

Because the present method is based on the detection of absorbance value for turbidity converted from sulfate with barium chloride, the presence of carbonate in the green liquor, which could react with barium chloride to form barium carbonate precipitation, is the major source of species interference. Hydrochloric acid was added to remove carbonate during the sample preparation.

CONCLUSIONS

1. This paper presents a spectrophotometry method for the determination of total sulfur in green liquor based on light scattering technique. In the experiment, hydrogen peroxide was used to convert S^{2-} , SO_3^{2-} and $S_2O_3^{2-}$ in green liquid into SO_4^{2-} , so that the result was better close to the real value.
2. The method is simple, reliable, rapid, accurate, and cheap. This can be used in industrial field.

ACKNOWLEDGMENTS

The authors acknowledge Doctoral Fund Project of Weifang University of Science and Technology (No. 2018KJBS02) for sponsoring this research.

REFERENCES CITED

- Biermann, C. J. (1996). *Handbook of Pulping and Papermaking* (2nd Ed.), Academic Press, San Diego, CA, USA.
- Grace, T. M., Kocurek, M. J., and Malcolm, E. W. (1989). "Alkaline Pulping, Pulp, and Paper Manufacture 5(3), Joint Textbook Committee of the Paper Industry, Atlanta,

- GA, USA, pp. 17-18.
- Grace, T. M. (1992). *Chemical Recovery Process Chemistry, Chemical Recovery in the Alkaline Pulping Processes* (3rd Ed.), TAPPI Press, Atlanta, GA, USA.
- Gullichsen, J., and Paulapuro, H. (2000) *Papermaking Science and Technology, Book 6B: Chemical Pulping*, Fapet Oy Helsinki.
- Iwasaki, I., Utsumi, S., Hagino, K., Tarutani, T., and Ozawa, T. (1957). "Spectrophotometric method for the determination of small amounts of sulfate ions," *Bull. Chem. Soc. Jpn*, 30(8), 847-851. DOI:10.1246/bcsj.30.847
- Jin, Y., Jameel, H., Chang, H., and Phillips, R. (2010). "Green liquor pretreatment of mixed hardwood for ethanol production in a repurposed kraft pulp mill," *J. Wood Chem. Technol.* 30(1), 86-104. DOI: 10.1080/02773810903578360
- Josef, P. (2016). *Measurement of Reduction Efficiency in Green Liquor using a NIR Spectrometer*, University essay, Luleå University of Technology, Luleå, Sweden.
- Kesler, R. B. (1957). "Analysis of alkaline pulping liquors," *Tappi* 40(10), 802-809.
- Kesler, R. B., and Reinke, P. A. (1957). "Preparation and analysis of polysulfide cooking liquor," *Tappi* 46(5), 310.
- Kolmert, A., Wikstrom, P. and Hallberg, K.B. (2000). "A fast and simple turbidimetric method for the determination of sulfate in sulfate-reducing bacterial cultures," *J. Microbiol. Methods*, 40(3), 179-184. DOI: 10.1016/S0167-7012(00)00154-8
- Lachenal, D. (2016). "Kraft pulping," in: *Lignocellulosic Fibers and Wood Handbook: Renewable Materials for Today's Environment*, Scrivener Publishing LLC, Austin, TX, USA, pp. 207-223.
- MacDonald, R. G. (1969). *Pulp and Paper Manufacture, The Pulping of Wood* (2nd Ed.), McGraw-Hill, New York, NY.
- SCAN-N 2:88 (1988). "White and green liquor- total, active and effective alkali titration with indicators," Scandinavian Pulp, Paper, and Board Committee, Stockholm, Sweden.
- Silva, W. L., Ribeiro, J. C. T., Costa Jr, E. F.da., and Costa, A. O. S.da. (2008). "Reduction efficiency prediction of CENIBRA's recovery boiler by direct minimization of Gibbs free energy," *Brazilian Journal of Chemical Engineering* 25(3), 603-611. DOI: 10.1590/S0104-66322008000300017
- TAPPI T 624 os-68 (1968). "Analysis of soda and sulfate white and green liquors," TAPPI Press, Atlanta, GA.
- TAPPI T1203 os-61 (1961). "Active alkali charge, AA, defined as $m_{(\text{NaOH}+\text{Na}_2\text{S})}/m_{\text{woodo.d.}}$; Effective alkali charge, EA, defined as $m_{(\text{NaOH}+1/2\text{Na}_2\text{S})}/m_{\text{woodo.d.}}$ and sulphidity, S, defined as $m_{\text{Na}_2\text{S}}/m_{(\text{NaOH}+\text{Na}_2\text{S})}$," TAPPI Press, Atlanta, GA.
- Wiethoff, C. M., and Middaugh, C. R. (2001). "Light-scattering techniques for characterization of synthetic gene therapy vectors," *Methods Mol. Med.* 65, 349-376. DOI: 10.1385/1-59259-139-6:349

Article submitted: July 12, 2019; Peer review completed: October 10, 2019; Revised version received and accepted: December 4, 2019; Published: December 9, 2019.
DOI: 10.15376/biores.15.1.721-728