

## A RAPID METHOD FOR DETERMINATION OF SILICON CONTENT IN BLACK LIQUOR BY UV SPECTROSCOPY

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This paper describes the development of a simple UV spectroscopic method for determination of silicon content in black liquor. The method is based on the fact that Si (IV) can react with ammonium molybdate to form Si-Mo heterophony acid in an acidic condition (pH=4). The absorption peak of  $\alpha$ -Si-Mo heterophony acid is 340 nm. To avoid the compensation of the instrument, 360 nm is used for spectroscopic quantification. A certain time (20 min) for the reaction is necessary. Moreover, it was discovered that 480 nm could be used to develop a dual-wavelength method to account for the spectral interference from dissolved lignin in black liquor. This method is simple, rapid, sensitive, accurate, and has the potential for on-line applications.

*Keywords:* *sa-Si-Mo heterophony acid; UV spectroscopy; Black liquor; Silicon content; Double wavelength*

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### INTRODUCTION

In a kraft pulping process, raw materials such as wood and non-wood are cooked in a digester that contains sodium hydroxide and sodium sulfide (Whitty et al. 2008). Lignin becomes dissolved into the pulping liquor during the cooking and cellulose fibers are liberated from each other as a result. The pulping liquor after separation is called black liquor (Preet et al. 2007). It is a highly viscous liquid containing sodium hydroxide and sodium sulfate combined with the non-cellulosic constituents of the raw material (Jarvinen et al. 2003; Ghatak et al. 2008), and also biomass wastes as by-products of chemical pulping. This mixture is concentrated by evaporation and then burned in recovery boilers to recover energy and chemicals (Sricharoenchaikul et al. 2003; Wallberg et al. 2003). The black liquor needs to be concentrated from 15% to about 70-75% of solids to become an adequate fuel. This recovery process is simple and very successful in wood pulping; however, when the process is considered for non-wood materials, such as wheat and rice straws, bagasse, or bamboo, the process is difficult (Jarvinen et al. 2003). The main problem is the high silicon content in non-wood material, which can cause deposits, lowers the coefficients of heat transfer, and causes pipeline blocking. Research on silicon reduction is under way, and promising approaches include a carbon dioxide and lime method (He 2008). Therefore, a rapid way to monitor silicon content in black liquor is needed.

At present, a gravimetric method is being used as the standard test in industrial practice for the determination of silicon in black liquor; however, there are several drawbacks when such a method is used. Firstly, the black liquor requires filtration and calcination (Paya et al. 2001), and the oven dry residual is considered as silicon content. Unfortunately, foreign ions are also calculated as silicon content. Secondly, the method involves no comparison with a standard to calibrate the preparation; therefore, the error cannot be evaluated. Thirdly, the gravimetric method is complex and time-consuming, a combination that can easily lead to errors. Therefore, a simple method is in urgent needed for silicon content determination. Recently, a  $\beta$ -Si-Mo heterophony acid method was developed to determine silicon content in black liquor (Tong Guolin et al. 2006). However, the stability of the complex is relatively low.

In this work, we have developed an  $\alpha$ -Si-Mo heterophony acid method for the determination of silicon content in black liquor. The major spectral interference from the dissolved lignin in the black liquor can be minimized through a dual-wavelength measurement technique. The present method is simple, rapid, accurate, and has the potential for on-line process monitoring.

## EXPERIMENTAL

### Chemicals

All chemicals used in the experiments were from commercial sources.  $1.000\text{g L}^{-1}$  Si (IV) solution prepared with 1.0119g of  $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$  in 100mL distill water, was used as the standard for calibration.  $\text{CH}_3\text{COOH-CH}_3\text{COONa}$  buffer solution (pH=4.0), 10% (w/v) molybdate was prepared by dissolving 0.1g of  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  in 100 mL of distill water.  $1.4\text{mol L}^{-1}$   $\text{CH}_3\text{COONa}$  solution was prepared by dissolving 47.6g of  $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$  in 250 mL distill water. 25%  $\text{H}_2\text{SO}_4$  (v/v) was prepared by diluting 25 mL sulfuric acid (98% v/v) into 100 mL of distill water.

### Apparatus

A UV-Vis spectrophotometer (HACH, made in USA) equipped with a 1 cm path length flow cell and a pH meter of PHS-3C made in Shanghai (China) were used for the experiments.

### Procedures

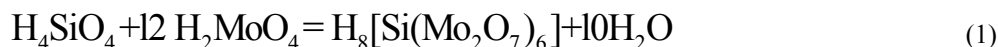
Calibration was conducted by preparing a set of standard solutions, i.e., by adding a certain volume of Si (IV) ( $1.000\text{g L}^{-1}$ ) into 100 mL of solution with 1 mL  $\text{H}_2\text{SO}_4$ , 5 mL  $\text{CH}_3\text{COONa}$  solution, 25mL buffer solution, and 10mL molybdate solution. The absorption spectrum for each solution was measured. Distilled water was used for all of the experiments. The agent without Si (IV) was used as the blank in the UV measurements.

## RESULTS AND DISCUSSION

### Spectral Characteristics of $\alpha$ -Si-Mo Heterophony Acid

#### *Principle and pH value effect*

Using presently available methods, the determination of silicon content in black liquor is difficult and time-consuming. Therefore, we developed a new method to determine the silicon content, using the principle that Si (IV) and ammonium molybdate can form Si-Mo heterophonic acid in an acidic condition. The relevant equation for formation of Si-Mo heterophonic acid is as follows:



The  $\alpha$ -Si-Mo heterophony acid is the main product when the solution pH value is greater than 2; however, the conversion from  $\beta$ -Si-Mo to  $\alpha$ -Si-Mo heterophony acid is not completed. It has been reported that with the presence of acetic acid (Wang et al. 2006), the conversion is favored by controlling the solution pH value between 3.6 and 4.4. The stable  $\alpha$ -Si-Mo heterophony acid can be formed faster when  $\text{CH}_3\text{COOH}-\text{CH}_3\text{COONa}$  is employed as a buffer. Hence, the solution pH value was maintained at 4 in this study.

#### *Spectral characteristics*

The complex of  $\alpha$ -Si-Mo heterophony acid has a yellow color and absorbs in the UV range with a maximum absorption at 340nm (as shown in Fig. 1). Therefore, silicon content can be determined by UV spectrophotometry based on its reaction with molybdate. Considering that the wavelength 340nm has error caused by instrumental limitations, which may lead to poor stability, a wavelength of 360nm was selected as the detection wavelength.

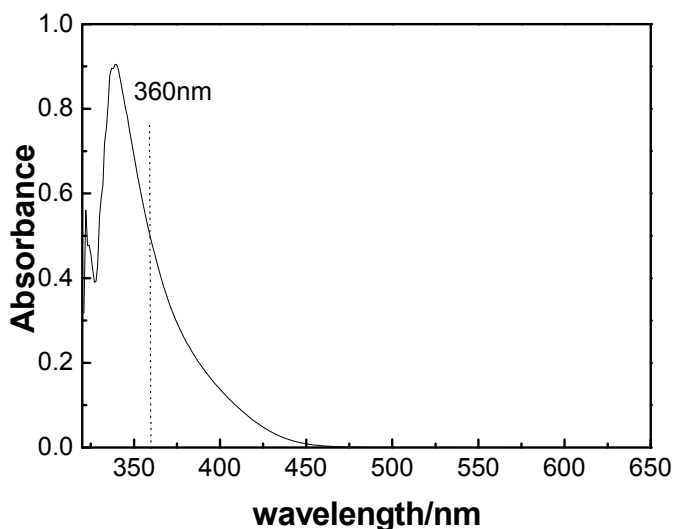


Fig. 1. Absorption spectrum of  $\alpha$ -Si-Mo heterophony acid

### Time for the reaction

As shown in Fig. 2, a certain time was needed to form  $\alpha$ -Si-Mo heterophony acid under the condition of pH=4 by using  $\text{CH}_3\text{COOH}-\text{CH}_3\text{COONa}$  as buffer. The absorbance at 360nm increased with time at first, and then the absorbance remained constant for times greater than 15 min. Hence, reaction time is another important factor affecting the measurement. For this reason, twenty minutes was selected for subsequent measurements.

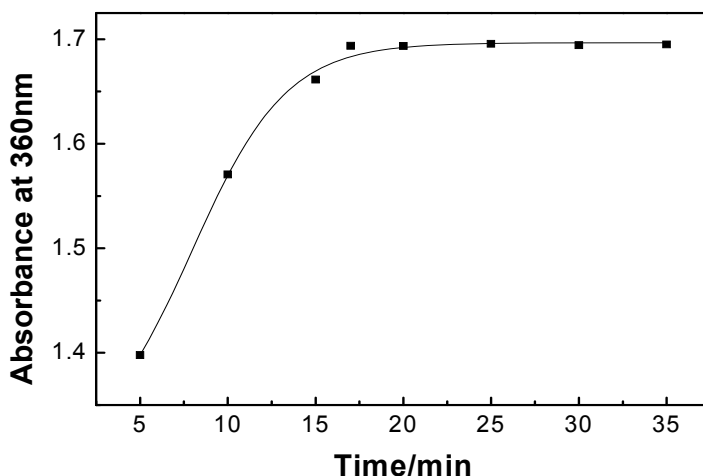


Fig. 2. Absorbance versus time at 360nm

### Determination of $\alpha$ -Si-Mo Heterophony Acid

For cases where spectral interference from other species at 360 nm is insignificant, a simple calibration procedure was developed for silicon content determination in acid solutions, which was based on the measurement of the absorbance of  $\alpha$ -Si-Mo heterophony acid in the solution. Figure 3 shows a response plot of UV absorbance at 360 nm vs. silicon content introduced.

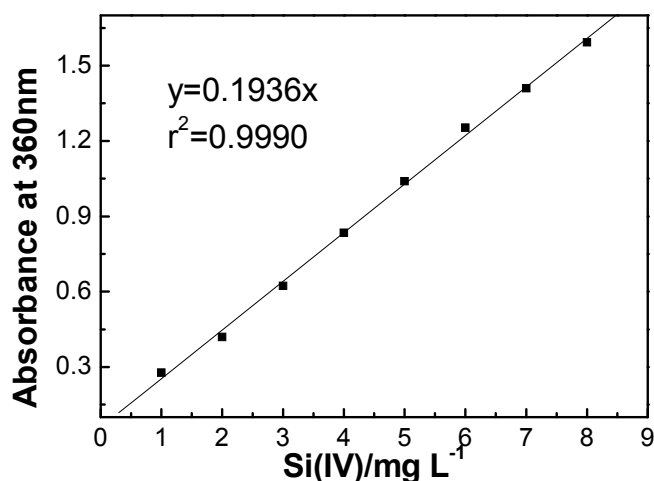


Fig. 3. An absorbance response plot for Si(IV) determination

Based on Beer's law, the concentration of silicon in the sample can be calculated according to the following equation,

$$A_{360} = k_1 C_{Si} \quad (2)$$

where  $A_{360}$  is the absorbance at 360nm,  $C_{Si}$  is the silicon content of dilute test sample, and the factor  $k_1$  is 0.194, as determined from Fig. 3.

Silicon content of dilute test sample can be obtained as follows,

$$C_{Si} = \frac{C V_{\text{sample}}}{V_{\text{sample}} + V_{\text{solution}}} \quad (3)$$

where  $C$  is the concentration of silicon content (in  $\text{mg L}^{-1}$ ) in black liquor,  $V_{\text{sample}}$  is the black liquor volume (mL) added to the dilute test sample, and  $V_{\text{solution}}$  is the dilute test sample volume (mL).

Hence, from Eqs. (1) and (2), the silicon content in black liquor can be derived as follows:

$$C = k_2 A_{360} \frac{V_{\text{solution}} + V_{\text{sample}}}{V_{\text{sample}}} (\text{mgL}^{-1}) \quad (4)$$

where the factor  $k_2$  is 5.15, calculated from Eq. (1).

## Spectral Interferences and Determination

### *Spectral interferences*

It is well known that dissolved lignin in black liquor has a strong spectral absorption covering the whole UV range. Therefore, it will interfere in the determination of silicon content by UV spectrophotometry. Although most dissolved lignin in the black liquor can be precipitated in an acidic medium and removed by centrifugal separation, such a procedure is insufficient to eliminate its spectral interference in silicon content determination.

As shown in Fig. 4, we can see that acid-soluble lignin has significant absorbance within the range 340 to 600 nm. It will interfere with the determination of silicon content at 360nm. Fortunately, the  $\alpha$ -Si-Mo heterophony acid has no absorbance above 450nm; the absorbance in that range is contributed only by soluble lignin. As reported by Chai et al. (2004), the ratio of lignin absorption at two wavelengths of 350nm and 297nm was found to be a constant of 0.331. Based on this conclusion, the ratio of the lignin absorbance at 360 nm and 480 nm in the lignin concentration range tested was carried out, and the results revealed that the  $A_{360}/A_{480}$  is also a constant. Therefore, the spectral contribution from lignin at 360nm can be accounted by using the lignin contribution at 480nm.

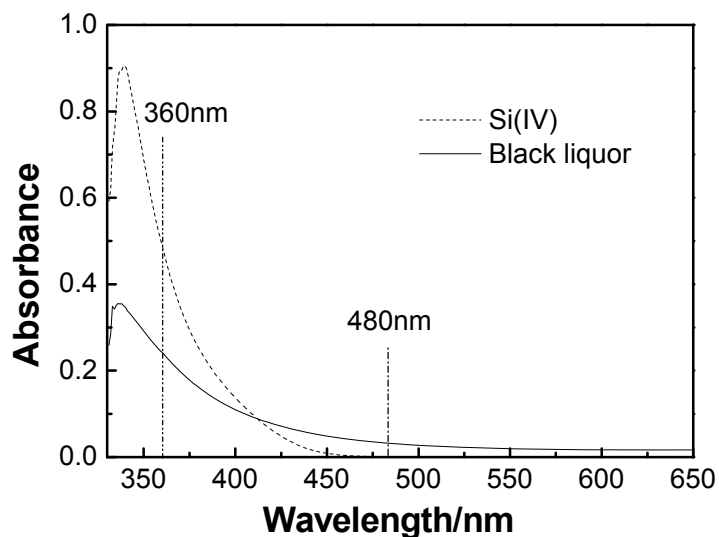


Fig. 4. Spectra of the acidic soluble lignin

#### *Spectral interference determination*

Different raw materials were prepared to determine the interference, including eucalyptus, mixed poplar, bagasse, and wheat straw. The acid-soluble lignins of the four materials spectral absorbance are shown in Fig. 5.

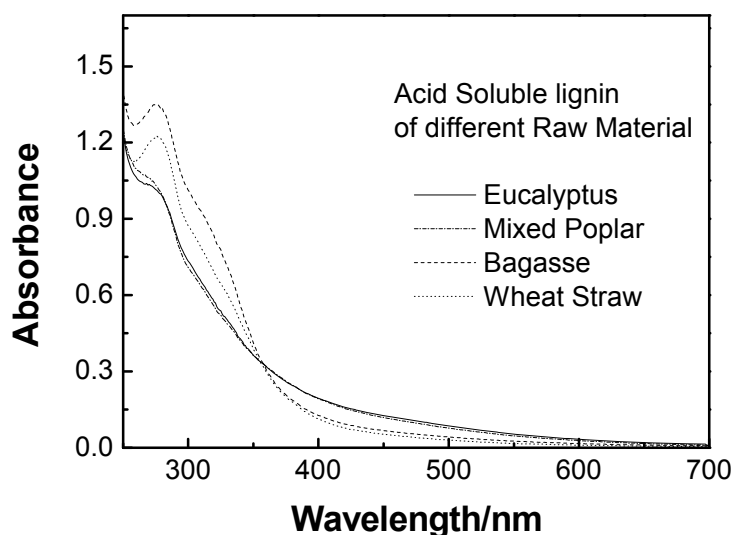


Fig. 5. Spectra of the acidic soluble lignin from different raw material

As shown in Fig. 5, the spectra of acid-soluble lignin from wood and non-wood material were obviously different. However, the spectra were similar when raw material was from the same category. Based on Fig. 5, we can calculate the absorbance ratio ( $k_3$ ) of acidic soluble lignin at 360nm and 480nm, i.e.:

$$k_3 = \frac{A_{\text{lignin}}^{360}}{A_{\text{lignin}}^{480}} \quad (5)$$

where  $A_{\text{lignin}}^{360}$  and  $A_{\text{lignin}}^{480}$  are the acidic soluble lignin absorbances at 360nm and 480nm, respectively.

Therefore, the interference of acidic soluble lignin at 360nm can be determined by the absorbance at 480nm.

### A Dual-Wavelength Method

By deducting the interference from acidic soluble lignin at 360nm, silicon content can be calculated as follows:

$$A_{360} - A_{\text{lignin}}^{360} = k_1 C_{\text{Si}} \quad (6)$$

Therefore, from Eqs. (4), (5), and (7), an equation to calculate silicon content in black liquor can be derived as follows:

$$C = k_2 (A_{360} - k_3 A_{480}) \frac{V_{\text{solution}} + V_{\text{sample}}}{V_{\text{sample}}} \text{ (mgL}^{-1}\text{)} \quad (7)$$

### The Coefficient Determination ( $k_3$ ) of Acid-Soluble Lignin

Based on Fig. 5, the  $k_3$  value of the four materials was calculated and the results are listed in Table 1. From Table 1 it can be shown that wood (i.e., eucalyptus and mixed poplar) had the similar  $k_3$  values, which were quite different from those of the non-wood materials. The silicon content can be determined from Eq. (6).

**Table 1.**  $k_3$  Value of the Four Raw Materials

	Wood		Non-wood	
	Eucalyptus	Mixed Poplar	Wheat Straw	Bagasse
$K_3 = A_{360}/A_{480}$	3.08	3.43	7.8	6

### Precision and Validation

The repeatability tests for the new method were conducted using black liquor from bagasse pulping. The pulping conditions were as follows: maximum temperature 175°C, solid liquor ratio 1:20, 10% NaOH, and cooking time 120min. According to the experimental procedure and the spectral test described above, the silicon content in black liquor was calculated by Eq. (7). Based on triplicate measurements, the relative standard deviation (RSD) was less 5.00%.

We also used Chinese standard method (CSM) (Shi et al. 2003) for the determination of silica content in black liquor of bagasse, wheat straw, and rice straw. The results from this determination were compared with those provided by UV method.

**Table 2.** Silicon Content Obtained by CSM Method and UV Method

Sample number	CSM Measured (g L <sup>-1</sup> )	UV Measured (g L <sup>-1</sup> )	Error (%)
Bagasse	0.96	0.91	4.17
Wheat straw	1.43	1.36	4.90
Rice straw	3.25	3.14	3.38

$$\text{Error(\%)} = \frac{(\text{CSM Measured} - \text{UV Measured})}{\text{CSM Measured}} \times 100\%$$

As shown in Table 2, good agreement was obtained between the results derived using the Chinese standard method and the UV method.

**Table 3.** Recovery Test of the Method

	Sample number	Added (mg*L <sup>-1</sup> )	Measured (mg L <sup>-1</sup> )	Recovery (%)
Bagasse	1	0.5	0.492	98.4
	2	1.0	1.04	104
	3	1.5	1.61	107
	4	2.0	2.06	103
	5	2.5	2.52	101

The method was validated by adding a volume series of Si (IV) into bagasse black liquor. According to the experimental procedure and spectral test, the silicon content was calculated from Eq. (6). The results are listed in Table 3.

As shown in Table 3, the recovery was between 98% and 106%. Therefore, the present method has been validated. It can be used for silicon content determination in black liquor and has the potential for on-line applications.

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