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Rapid and Direct Pulp Kappa Number Determination Using Spectrophotometry

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Rapid and Direct Pulp Kappa Number Determination Using Spectrophotometry

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ABSTRACT

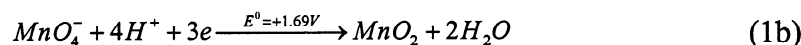
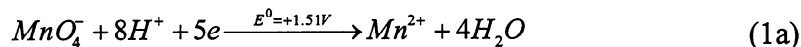
A spectrophotometric method has been developed for rapid pulp kappa number measurements under strongly acidic reaction conditions. Pulp kappa number is derived from the ratio of the absorption spectral intensities at a specific wavelength measured at the beginning and end of the reaction of the pulp with permanganate. Therefore, no calibration is necessary. Strong acidification is used to prevent MnO₂ precipitation and interference with the permanganate absorption spectrum. A method is proposed to determine the end of the pulp oxidation reactions with permanganate using the reaction kinetics and rate derived from the time-dependent spectrophotometric measurements of the reacting solution. It was found that the pulp oxidation was completed in less than 3 minutes. The measured kappa numbers of three pulp samples of two wood species, with and without bleaching, agreed well with those obtained by the current TAPPI standard method using thiosulfate titration. The present method is simple, rapid, and accurate.

Key Words: Kappa number; pulp; spectrophotometry; UV/Vis absorption;
lignin oxidation; permanganate.

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BACKGROUND

The kappa number of pulp is one of the important parameters in pulp manufacturing because it relates to the bleachability, or degree of delignification, of the pulp. The kappa number is defined as the volume of 0.02 mole/L (0.1 normality) potassium permanganate solution consumed by one gram of moisture-free pulp in an acidic medium through the following reactions, depending on the acidity of the medium:



The current, commonly used method for kappa number measurements, such as TAPPI Test Method T236 cm-85 [1], was first proposed in 1934 by Wiles [2] and later developed in the 1950's based on research by Watson [3], Valeur and Tornngren [4], and Tasman and Berzins [5]. The method calculates the volume of 0.02 mole/L (0.1 N) potassium permanganate consumed by one gram of moisture-free pulp by the difference between the initial and the final excess volumes of potassium permanganate after a 10-minute reaction at 25°C under weakly acidic conditions. The final excess volume of potassium permanganate after the 10-minute oxidation reaction is determined by titrimetry using a standard thiosulfate solution after adding an excess of potassium iodide to the slurry to react with the excess permanganate to form iodine.

The key assumptions of this method are: (1) the permanganate consumed was mainly due to reaction with lignin, and the rapid oxidation was completed in 10 minutes; (2) the effects of reaction temperature, time, and the variation in excess permanganate volume are not significant and can be corrected by a non-constant correction factor as tabulated in the TAPPI method [1]; and (3) the thiosulphate titration method is accurate. The disadvantages of this method are: (1) thiosulfate titration of iodine is tedious because a blank experiment (without pulp, and using exactly the same procedures) is needed to reduce the experimental error in the titration due to the high volatility of iodine; (2) the thiosulfate titration requires that the reaction be kept under weakly acidic conditions, which causes large variations in kappa measurements as reported by Valeur and Tornngren [4]; (3) the 10-minute oxidation

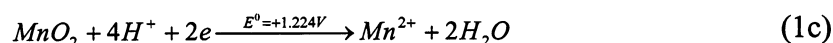
reaction time is arbitrary and can cause errors in determining kappa numbers for various pulps, because permanganate can be both oxidized and decomposed by other organic materials in pulp as explained by Tasman and Berzins [5]; the actual oxidation time is much shorter than 10 minutes, as found by Li and Gellerstedt [6] and in the present study; (4) the method requires that the volume of consumed permanganate after the 10-minute reaction should be around 50% of the initial volume to obtain good measurements; this is impossible because the final excess permanganate volume can only be known after the kappa number has been determined; (5) the non-constant correction factor is purely empirical, derived through experimental calibration, and can cause errors; and (6) compounds other than lignin in a pulp, such as a significant amount of hexenuronic acid in bleached pulps, can be oxidized by permanganate in the first 10-minute reaction. As a result, the existing kappa test methods have many shortcomings and the kappa number itself is not scientifically well defined; however, the kappa number of a pulp obtained by these methods has significant practical importance. A commercially available instrument, based on these methods, has been developed (KAPPAMAT, Kebo Lab, Sweden).

Spectroscopic methods can provide direct and instantaneous measurement of chemical concentrations in reactions. Spectroscopic methods using UV and FTIR absorption to determine pulp kappa number have been reported [7, 8]. In these methods, the linear relationship between the lignin content of the pulp and the light absorption was used to determine pulp kappa number. Unfortunately, the permanganate consumption by different types of lignin is different. Therefore, calibration is required for a specific pulp sample using the traditional method of kappa number determination [1].

By the time the present study was completed, Li and Gellerstedt [6] had reported the results of a study on the kinetics and mechanism of pulp-permanganate reaction under conditions suggested in standard kappa testing methods. They directly measured the permanganate concentration in lignin-permanganate reaction solutions using UV/Vis spectrophotometry. According to Li and Gellerstedt [6] and Stewart [9], both reactions (1a) and (1b) can take place under conditions suggested in common kappa number test methods, such as TAPPI Test Method - T236 cm-85 [1] and SCAN-C1 Test Method [10], where the dominant reaction is an overall conversion of permanganate to MnO_2 according to reaction

(1b). Because the number of electrons required for these two reactions to take place is different (as shown in reactions (1a) and (1b)), and because the amount of permanganate consumed in the reactions varies with the initial amount of permanganate available in the pulp slurry, Li and Gellerstedt [6] concluded that the use of iodometric titration and the definition of a 30-70% permanganate consumption range prescribed in the commonly used kappa number test methods leads to erroneous results. Furthermore, they found the precipitated MnO_2 strongly interfered with the measured absorption spectrum of the reaction solution, and caused significant measurement difficulties in determining the excess permanganate in the final reaction solution. Nevertheless, they concluded that direct spectrophotometry can be used to calculate the kappa number of pulp samples.

We would like to point out that the conclusion drawn by Li and Gellerstedt [6], i.e., “iodometric titration and the definition of a 30-70% permanganate consumption range used in the commonly used kappa number testing methods is erroneous,” is not correct. The precipitated MnO_2 formed in reaction (1b) under the conditions used in these kappa number test methods is converted to Mn^{2+} with the addition of potassium iodide (KI) according to the following reaction,



which requires 2 electrons. The total number of electrons required for reactions (1b) and (1c) is 5, equal to that required for reaction (1a). Whether the pioneers who developed the current kappa test methods thought of this or not, these kappa number test methods, such as [1, 10], are valid. However, it is not possible to use spectrophotometry to determine pulp kappa number under the reaction conditions (weak acidification) used in these methods, as in the work by Li and Gellerstedt [6]. The amount of precipitated MnO_2 in the pulp-permanganate reaction solutions cannot be determined, and the errors caused by spectral interference from the precipitated MnO_2 cannot be ignored or eliminated.

In this study, we developed a spectrophotometric method for the rapid determination of pulp kappa number through direct measurement of the permanganate concentration in pulp-permanganate reaction solutions. Unlike the study by Li and Gellerstedt [6] that used weak acidification as in standard kappa testing methods [1, 10], we proposed the use of strong acidification to prevent the precipitation of MnO_2 . As a result, spectral interference

from the precipitated MnO_2 was eliminated and reaction (1a) then becomes the dominant oxidation reaction. Furthermore, we accurately determined a representative pulp oxidation reaction time and the final excess permanganate in the reaction solution from the measured permanganate absorption spectral intensities. We then directly determined pulp kappa numbers of several pulp samples using the permanganate absorption data without calibration and corrections. Because of strong acidification, we were able to eliminate the effect of the amount of excess permanganate or the mass of the pulp sample on the measured kappa number. The focus of the present research was to develop a method that can obtain kappa numbers consistent with existing methods because of the practical importance of the kappa number. Therefore, this study did not address the effect of oxidation reactions of compounds other than lignin, such as hexenuronic acid, on measured kappa number.

THEORY AND METHODOLOGY

Mathematically the pulp kappa number is defined as

$$K = p / w \quad (2)$$

where K is kappa number, p is the amount of 0.02 mole/L (0.1 N) permanganate solution actually consumed by the test sample in mL, and w is the mass of the moisture-free pulp sample in grams.

In a permanganate-pulp reaction experiment, the initial volume of 0.02 mole/L permanganate added is a mL, and the amount of pulp used is w grams. At the end of the oxidation reaction, the excess volume of 0.02 mole/L permanganate is b mL. Therefore, the consumed volume, p , of 0.02 mole/L permanganate can be written as

$$p = a - b = a \left(1 - \frac{b}{a} \right) \quad (3)$$

The concentration of permanganate in the reaction solution at the beginning and the end of the oxidation can be written as

$$C_0 = \frac{0.1 \cdot a}{V_T} \quad (4)$$

and

$$C_e = \frac{0.1 \cdot b}{V_T} \quad (5),$$

respectively, where V_T is the total volume of the reaction solution, which includes the addition of sulfuric acid.

According to Beer's Law, the absorption is proportional to the concentration of the test sample; thus, we can have

$$A_0 = \varepsilon \cdot l \cdot C_0 \quad (6)$$

and

$$A_e = \varepsilon \cdot l \cdot C_e \quad (7),$$

respectively. Where A_0 and A_e are the permanganate absorbances (or spectral intensity) in the solution at the beginning and end of the oxidation reaction, ε and l are the molar absorptivity of the solution and the optical path-length of the cell, respectively.

From Eqns. (4) to (7),

$$\frac{b}{a} = \frac{A_e}{A_0} \quad (8)$$

Substituting Eqn. (8) into (3), the volume of permanganate consumed can be written as

$$p = a \cdot \left(1 - \frac{A_e}{A_0} \right) \quad (9)$$

We can determine the kappa number using the following expression:

$$K = \frac{a}{w} \left(1 - \frac{A_e}{A_0} \right) \quad (10)$$

Eqn. (10) indicates that kappa number can be calculated from the ratio of the permanganate absorption spectral intensities at a given wavelength at the beginning and end of the permanganate-pulp reaction and that absolute absorption measurements are not required. Therefore, quantitative calibration is not necessary, and the measurements will be much more reliable, accurate, and simplified than the existing quantitative titration method.

EXPERIMENTAL

Apparatus

All experiments were conducted using a flow loop. The flow loop consists of a peristaltic pump (RP-1, Rainin), tubing and connectors, a 25-mL beaker, a homemade net filter (200 mesh) to separate the fibers from the reaction solution, and a UV/Vis optical flow cell. Figure 1 shows a schematic diagram of the experimental setup. The permanganate-pulp reaction was carried out in the beaker. The reaction solution containing permanganate and sulfuric acid was recirculated by a peristaltic pump with a flow rate of 2 mL/min and flowed through the UV/Vis optical flow cell with a 1-mm optical path length. The pulp fibers were separated from the circulating solution by the stainless steel net filter to permit spectrophotometric measurements. All absorption measurements were continuously performed over the whole UV/Vis range by a spectrophotometer (UV-8453, Hewlett-Packard) equipped with an HP ChemStation for real-time data collection and analysis. The reaction solution was well mixed by magnetic stirring during the experiment.

Chemicals and Reagents

Standardized 0.02 ± 0.0001 mole/L (0.1 ± 0.0005 N) potassium permanganate solution was used to react with pulp samples under acidic conditions by adding standard sulfuric acid of concentration 2.0 mole/L.

Measurement Procedures

Distilled water was used as a blank solution for UV/Vis measurements. Pipettes of 5 mL (± 0.01 mL) of potassium permanganate solution and 20 mL of standard sulfuric acid solution were placed in a 25-mL beaker under strong magnetic stirring to make the 1.6 mole/L concentrated solution of sulfuric acid. The solution was circulated through the optical flow cell by the peristaltic pump. The required amount of moisture-free pulp (from 0.05 to 0.15 gram) was accurately weighed out and added to the beaker after the spectrophotometer had started to record real-time data. The time-dependent absorption spectra of the filtered solution were recorded by the ChemStation for 5 minutes with a time interval of 1 second.

RESULTS AND DISCUSSIONS

Time-Dependent Absorption Spectra of the Reaction Solution

The real-time absorption spectra collected during pulp oxidation by the permanganate solution allow us to obtain time-dependent concentrations of the chemicals under reaction. Figure 2 shows typical UV/Vis absorption spectra of a reaction solution after separation of pulp fibers using the net filter. Each spectrum is a superposition of absorption by various chemicals in the reaction solution. Because lignin and other organic molecules produced in the reaction do not absorb in the region of interest, the spectral intensity at 546 nm is due purely to the absorption of potassium permanganate. It is important to point out that the typical relative standard deviation of spectrophotometric measurements is only about 0.1%, which gives a negligible relative error in the ratio of the absorption spectral intensities in Eqn. (10) of 0.1%.

Determination of the End of the Oxidation Reactions and Pulp Kappa Number

One problem associated with the existing method [1] for kappa number determination is that the pulp oxidation reaction time is arbitrarily taken as 10 minutes, irrespective of the reaction conditions, such as acidity, the species, the amount of pulp, and the excess volume of permanganate used in the reaction. With the time-dependent concentrations of the reaction chemicals determined from spectrophotometric measurements, we should be able to accurately determine an effective end point of any given pulp oxidation reaction with permanganate. According to Beer's Law, or Eqns. (6) and (7), the permanganate concentration in the reaction solution is linearly proportional to the absorption spectral intensity A ; therefore, we call the plot of time-dependent spectral intensity A a kinetic curve. We can describe the permanganate reaction kinetics using the time-dependent permanganate absorption at 546 nm. We found that all the kinetic curves from reactions with different amounts of pulp and pulp species fall on a single curve after proper normalization as shown in Fig. 3, indicating that the normalized reaction rate (or permanganate consumption per gram of pulp) does not change with the absolute amount of excess permanganate or pulp and the pulp species used. From Fig. 3, we then can calculate the time derivative of the normalized permanganate absorption or concentration, or the reaction rate. Figure 4 plots the normalized reaction rates that are averaged over the 7

experiments shown in Fig. 3. According to Tasman and Berzins [5], there are generally two main (groups of) reactions occurring simultaneously in a pulp-permanganate solution, i.e., rapid oxidation of lignin (recent studies [6, 11] indicate that other compounds, such as hexenuronic acid, can also be oxidized) by permanganate and slow decomposition of permanganate by other organic materials. Our data shown in Fig. 3 validate this assumption. The activation energies of these two groups of reactions are different. Lignin and hexenuronic acid can be easily oxidized by permanganate; the decomposition reactions between permanganate and some other organic materials will dominate only after the oxidation reactions are over. We can therefore fit the normalized kinetic data to a two-rate model. We found that the following equation fits the data in Fig. 3 very well,

$$y = 1.0 - m[1 - \exp(-Et)] - Bt, \quad (11)$$

where $m = 0.615$, $E = 0.029$, $B = 0.0015$, y is the non-dimensional permanganate absorption at 546 nm, and t is the reaction time in seconds. In this two-rate model, we used an exponential function to represent permanganate consumption by the group of rapid oxidation reactions of lignin, hexenuronic acid, etc., early in the reaction, and a linear decay function for the slow decomposition by other organic materials. Eqn. (11) clearly indicates that the exponential decay function is important only during an initial short time period, while the linear decay function will dominate later in the reaction at a longer value of t . The time derivative of Eqn. (11) is then used to obtain the fitted normalized reaction rate equation as follows:

$$\frac{dy}{dt} = -m \cdot E \exp(-Et) - B \quad (12)$$

The purpose of the above analysis is to determine an effective reaction time t_e when oxidation reactions (lignin oxidation in particular) end, so that the permanganate absorption A_e at time t_e can be determined from Fig. 3 and used to calculate the sample pulp kappa number by Eqn. (10). If the reaction energies of the two permanganate reactions differ significantly, a clear break point in the curves of the permanganate consumption and of the reaction rate can be seen. Unfortunately, this is not the case in this reaction system, as shown in Figs. 3 and 4 where the solid lines are Eqns. (11) and (12), respectively. Because

of the asymptotic nature of the oxidation reaction rate curve, we define the end point of the oxidation reactions as the point at which the rapid oxidation reaction rate (the exponential decay function part of Eqn. (12)) is reduced to only $q\%$ of its maximum rate (at $t = 0$), or $m \cdot E = 0.0178$, according to Eqn. (12)). Mathematically, we can define t_e as

$$\left. \frac{dy}{dt} \right|_{t=t_e} = -m \cdot E \frac{q}{100} - B = [-m \cdot E \exp(-Et_e)] - B \quad (13)$$

By solving Eqn. (13) for t_e , we have

$$t_e = -\frac{\ln(q/100)}{E} = -\frac{\ln(q/100)}{0.029} \quad (14)$$

In this study we arbitrarily take $q = 1$ as a good approximation from an engineering point of view. For a given temperature of 25°C and strong acidification, as used in this study, the oxidation reaction end point t_e is a constant and is equal to 159 seconds for all experiments conducted with different amounts of pulp, pulp species, and final excess permanganate volume. This time of 159 s (or 2.65 minutes) is only about one quarter of the 10 minutes required in the current TAPPI test method [1]. It is also much shorter than the 5 minutes suggested by the recent modified method [12] proposed by the Canadian Pulp and Paper Association.

To demonstrate the effect of the above-proposed method of determining the oxidation reaction end point, t_e , on measured kappa number, we calculated the kappa numbers of three different pulp samples from the measured spectral intensity data using different q or oxidation reaction end point, t_e . We found that the relative differences in measured kappa numbers of these three pulp samples (based on $q = 1$) were less than 10% when varied from 0.32 to 3.3 (more than an order of magnitude variation), corresponding to an effective oxidation reaction end point, t_e , of 198 to 118 seconds (about 70% variation) as shown in Fig. 5. This calculation demonstrates the accuracy, versatility, and validity of the proposed method to determine the end of the oxidation reactions for kappa number calculations using the present spectrophotometric method.

Comparison of the Present Method with the Traditional Titration Method

Although the existing kappa measurement method based on titration [1] has many problems, and the measurement results for the same pulp sample are a strong function of the operator, the existing method has been widely accepted by the pulp and paper industry as well as by academic researchers throughout the world. From a practical point of view, the pulp and paper industry will benefit from any new kappa determination method that can give results consistent with the existing method. To demonstrate the agreement of kappa measurements using the proposed spectrophotometric method with the existing method, we measured three pulp samples derived from two wood species (pine and birch), with and without bleaching, with significant variation in kappa numbers (from 4 to 26). We found that the measured kappa numbers of these three samples agreed with those obtained using the traditional TAPPI Test Method - T236 cm-85. The maximum relative difference in kappa numbers between the two methods was less than 5% at low kappa numbers as shown in Table I.

Effect of Pulp Sample Size on Measured Kappa Number

One of the problems of the existing kappa number measurement method [1] is that the measured kappa number for a given pulp varies with the amount of pulp sample or the excess volume of permanganate solution used. However, with strong acidification, this effect on kappa number is diminished, as shown by Valeur and Tornngren [4]. The mechanism of the effect of acidification on measured kappa number has not been understood and is not the subject of the present study. We eliminated the variation in measured kappa number by using strong acidification (the initial sulfuric acid concentration in the reaction solution was 1.6 moles/L), and the effective pulp oxidation reaction end point was determined using the method described above. We used birch pulp of sample size from 50 mg to 150 mg to test the effect on the measured kappa number of the amount of pulp sample or the excess permanganate used. We found that the measured kappa number of the pulp sample using the present method and apparatus based on Eqn. (1) does not change with the amount of pulp sample used. The results are listed in Table II. The mean kappa number was 25.8 with a relative standard deviation of only 2.3%. Compared with the measured kappa number of 25.4 using the traditional method [1], the difference is only 1.6%. We also

found that the measured volume of permanganate consumed is linearly proportional to the amount of pulp sample used in the experiments because the same pulp sample was used. Furthermore, we were able to reduce the oxidation reaction end point to only 2.65 minutes.

CONCLUSIONS

Absorption spectrophotometry has been used to analyze the permanganate concentration in pulp-permanganate reaction solutions. By using strong acidification, the precipitation of MnO_2 was prevented and the reaction was forced to follow reaction (1a); as a result, spectral interference from precipitated MnO_2 was eliminated. We found that the normalized time-dependent permanganate absorption spectral intensity (or kinetic curve) in the reaction solution is not dependent on either the pulp species or the sample size. We also found that an empirical two-rate model (an exponential and a linear decay function) fits the normalized kinetic data very well. The pulp kappa number was derived from the ratio of permanganate absorption spectral intensities at a specific wavelength measured at the beginning and the end of the pulp oxidation reactions. Therefore, it was possible to determine the pulp kappa number from spectral analysis without calibration. Unlike the traditional titration kappa number measurement method in which the pulp oxidation time is arbitrarily taken as 10 minutes, a method was developed to determine the end of the pulp oxidation reaction using reaction kinetics and the two-rate model derived from the spectral measurements. We found that an oxidation reaction duration of less than 3 minutes is sufficient to obtain reliable kappa number measurements. The method also eliminates the effect of pulp sample size or final excess volume of permanganate on the measured kappa number. Using the present spectrophotometric method, the measured kappa numbers of three pulp samples from two wood species with and without bleaching agreed well with those obtained by the current TAPPI test method using thiosulfate titration. The present method is simple, rapid, versatile, and accurate.

ACKNOWLEDGEMENT

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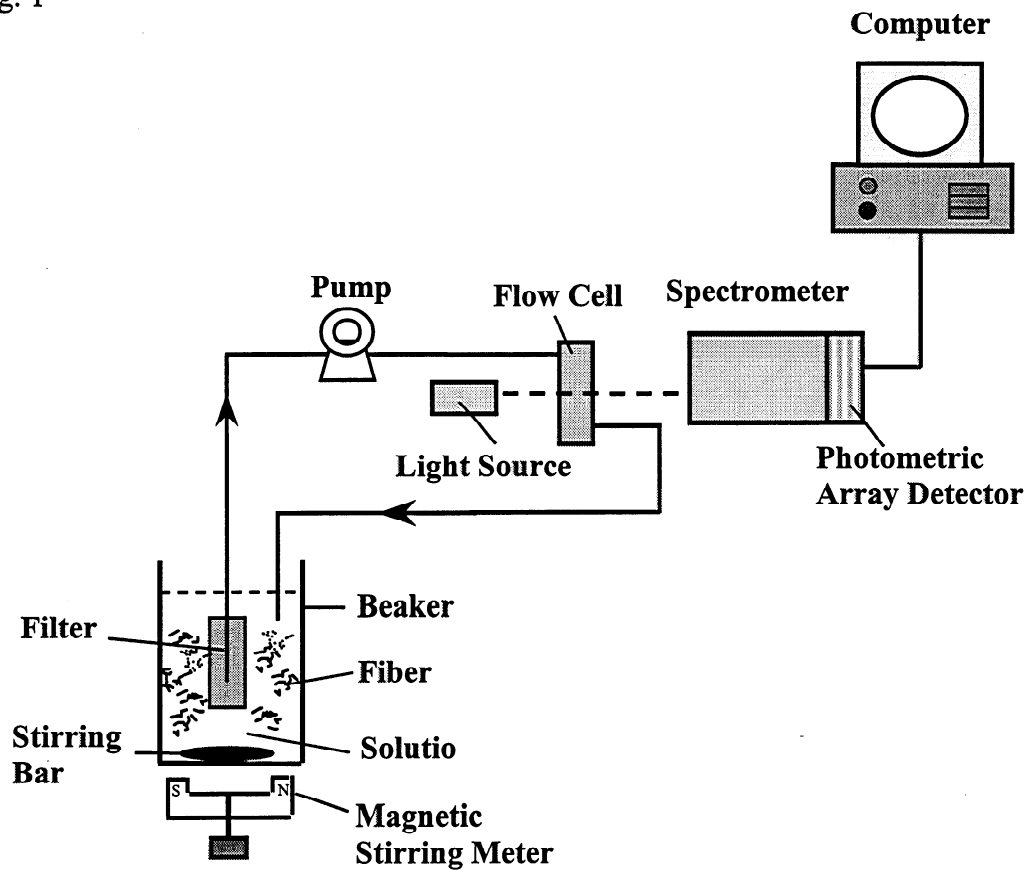


Fig. 2

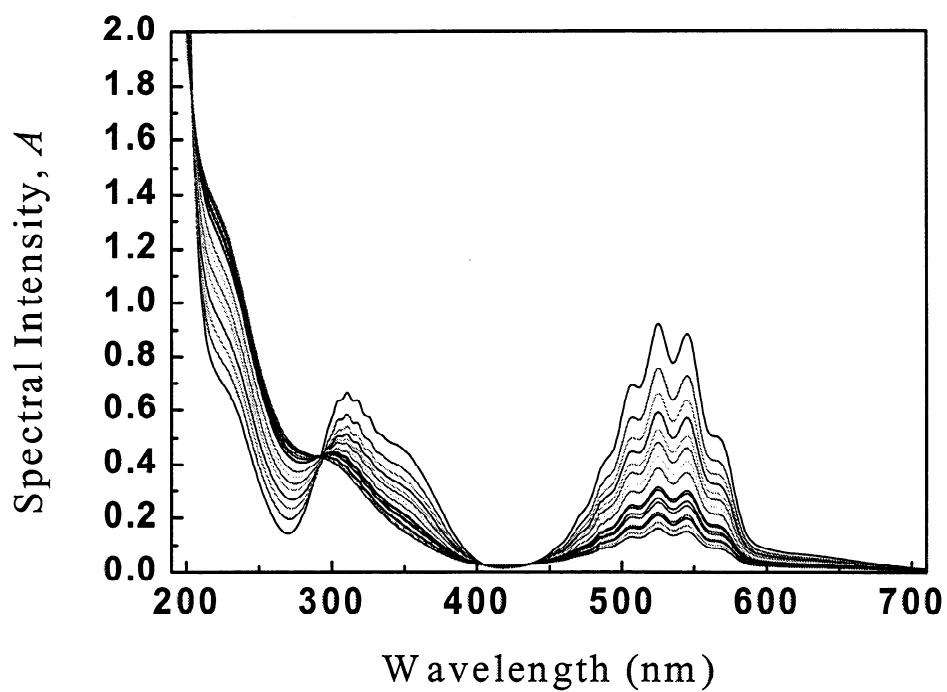


Fig. 3

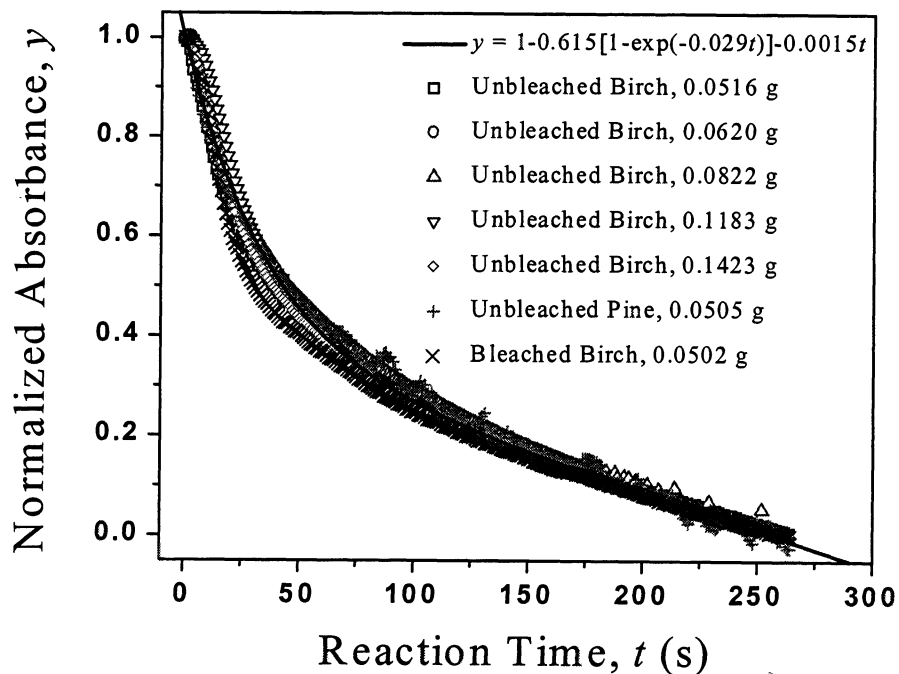


Fig. 4

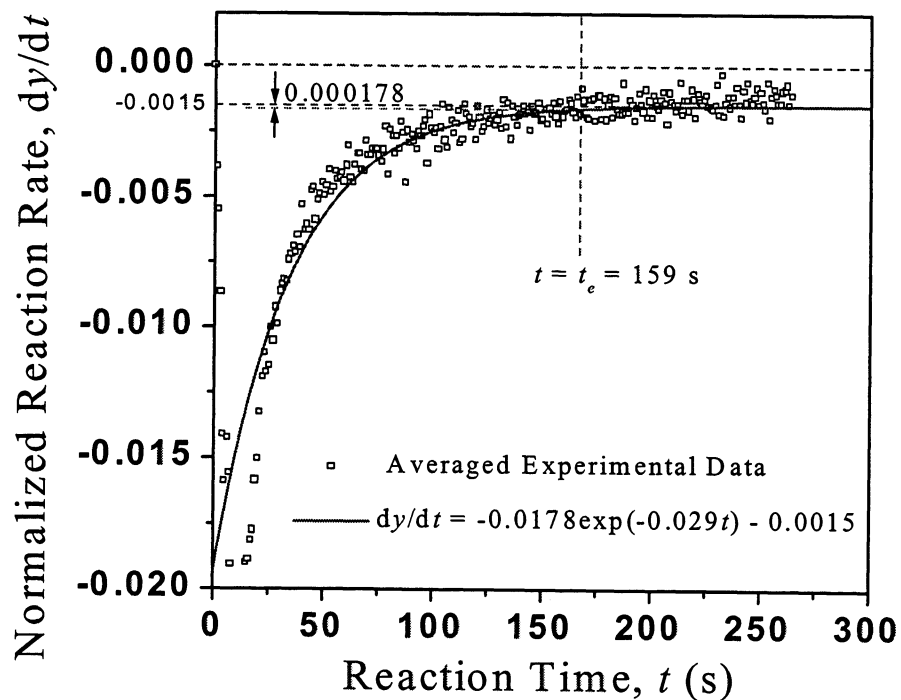


Fig. 5

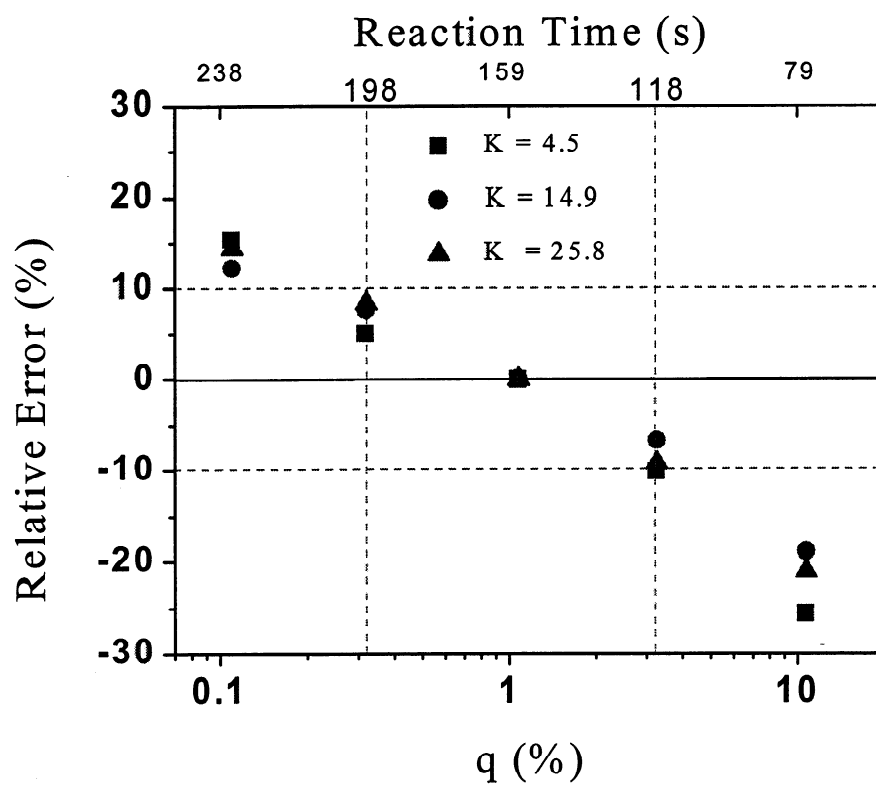


Table I. Comparison of measured kappa number with those obtained using the traditional TAPPI Test Method - T236 cm-85

No.	Pulp	Pulp Mass (g)	Measured Kappa Number		
			Present Method	Tappi Method [1]	Relative Difference (%)
1	birch, bleached	0.0501	4.5	4.3	4.5
2	pine, unbleached	0.0505	14.9	15.3	-2.6
3	birch, unbleached	0.0516	25.8	25.4	1.6

Table II. Measured kappa number using different amounts of pulp sample

No.	Pulp Mass (g)	A_0	A_e	KMnO ₄ Consumed (mL)	Measured Kappa No.
1	0.0516	0.922	0.682	1.302	25.2
2	0.0620	0.921	0.619	1.636	26.4
3	0.0832	0.922	0.519	2.217	26.3
4	0.1183	0.920	0.356	3.071	25.9
5	0.1403	0.919	0.272	3.515	25.1
Mean					25.8
RSD					2.3 %

