A Simple and Practical Pulp Kappa Test Method
for Process Control in Pulp Production

X.S. Chai, Q. Luo, and J.Y. Zhu

July 2000

Submitted to
Process Control and Quality
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A Simple and Practical Pulp Kappa Test Method for Process Control in Pulp Production

X.S. Chai, Q. Luo*, and J.Y. Zhu§
Institute of Paper Science and Technology
500 10th Street, N.W., Atlanta, GA 30318
(404) 894-5310, (404) 894-5752 (FAX), Junyong.Zhu@ipst.edu

ABSTRACT

Through permanganate measurements, this study demonstrates a simple, rapid, practical, and direct spectrophotometric pulp kappa test method through one calibration with a standard pulp sample of known kappa number. Two permanganate absorption measurements were made in both the testing and standard pulp-permanganate reacting solutions for kappa calculation, one at the beginning of the reaction and the other at about 2-3 minutes into the reaction. The measured kappa numbers of 13 blended hardwood pulps and another 45 pulps from laboratory pulping of 10 hardwood and softwood species in a kappa number range of 10-70 are reported. The results showed excellent agreement with those obtained by the standard TAPPI kappa method. The effect of pulp-permanganate reaction temperature on measured kappa number using the present method is also presented. The method has the potential for on-line kappa monitoring in pulp production.

Key Words: Kappa number; pulp; spectrophotometry; permanganate; lignin; hexenuronic acids; spectrochemical analysis; measuring instruments.

* Permanent address: State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou, China.
§ Author to whom correspondence should be addressed.

This paper has been accepted for Publication by Process Control and Quality
INTRODUCTION

Kappa number determination is a common practice performed numerous times daily in pulp mills and laboratories in the pulp and paper community. The kappa number is defined as the volume of 0.02 mole/L potassium permanganate solution consumed by 1 g of moisture-free pulp in an acidic medium. It is a measure of the reactivity of, or the chemical consumption in bleaching operations by, the total residue lignin in the pulp. First proposed in 1934 by Wiles [1], the most widely used methods for kappa-number measurements, TAPPI Test Method T236 cm-85 [2] or the SCAN-C1:77 [3] used by the Scandinavian countries, were later developed in the 1950's based on research by Watson [4], Valeur and Torngren [5], and Tasman and Berzins [6]. The method calculates the volume of 0.02 mole/L potassium permanganate consumed by 1 g of moisture-free pulp by the difference between the initial and the final excess volumes of potassium permanganate after a 10-min reaction at 25°C under weakly acidic conditions. The final excess volume of potassium permanganate after the 10-min 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 titration-based kappa test methods suffer from the random errors of human testers. Furthermore, process control is not possible using the offline titration method in pulping and bleaching operations in pulp mills. Alternative methods using spectroscopic technique, such as UV and FTIR have been developed for rapid prediction of pulp kappa number [7, 8]. However, these methods are based on indirect measurements, measuring the lignin content in pulps, not the kappa number itself. Because kappa number is not only
related to the lignin content in a pulp but also to lignin reactivity, which varies from pulp to pulp due to the variations of the lignin structure [9], a calibration procedure using the traditional titration-based methods must be carried out for each pulp of different wood species to determine the kappa number if methods based on lignin-content are used. Moreover, recent studies [9-11] have shown that the hexenuronic acid groups (IIexA) in pulps significantly contribute to the kappa number, especially for unbleached hardwood pulps that have a relatively high HexA content. Therefore, the validity of the principle of the lignin-based kappa test method through calibration is questionable.

We developed a simple and rapid spectrophotometric kappa test method through direct permanganate measurements [12]. In this novel method, the 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, it is a direct kappa method but without titrametric calibration. The method not only eliminates the titration procedures and therefore the random errors caused by human operations, but also reduces the reaction time through an increased acidity of the reaction medium. Because it is rapid, direct, and more accurate, it is superior to all the available methods. In this study, we present a one-point calibration method to simplify our direct spectrophotometric kappa test method called the Chai-Zhu kappa test method. Results from a wide range of kappa numbers of various wood species are presented using the simplified method. The effect of reaction temperature is also examined. The objective of the present study is to demonstrate the capabilities of the basic principles of the Chai-Zhu kappa test method [12] and the viability and simplicity of the present one-point calibration method for practical process control in pulp mills.
THE ONE-POINT CALIBRATION METHOD

The following equation was obtained in the original derivation of the Chai-Zhu method [12]:

\[ K = \frac{a}{w} \left( 1 - \frac{A^e}{A^0} \right) \quad \text{or} \quad K = \frac{a}{w} \left( \frac{A^0 - A^e}{A^0} \right) \]  \hspace{1cm} (1)

where \( K \) is the kappa number of a pulp sample, \( a \) is the volume of the 0.02 mol/l permanganate solution used in the kappa experiment, \( w \) is the mass in grams of the moisture-free pulp sample used, \( A^0 \) and \( A^e \) are the spectral intensities (at a given wavelength, e.g., 546 nm) of the permanganate blank solution (before pulp is being added, or time \( t=0 \)) and the pulp-permanganate reacting solution at the end of the oxidation reaction, or time \( t' \), respectively.

From Eqn. (1), we have,

\[ \frac{K}{(A^0 - A^e)/w} = \frac{a}{A^0} = \text{constant} \] \hspace{1cm} (2)

For given \( n \) different pulps to be tested for kappa, as long as we use the same reaction medium and same volume of the reaction solution, we have the following equation:

\[ \frac{K_1}{(A^0 - A^e)/w_1} = \frac{K_2}{(A^0 - A^e)/w_2} = \ldots = \frac{K_i}{(A^0 - A^e)/w_i} = \ldots = \frac{K_n}{(A^0 - A^e)/w_n} \] \hspace{1cm} (3)

For a two-sample (sample \( i \) and \( j \)) experiment, Eqn (3) can be simplified as

\[ K_i = K_1 \cdot \frac{w_j}{w_i} \cdot \frac{(A^0 - A^e)}{(A^0 - A^e)} \] \hspace{1cm} (4)
Normalize the time-dependent absorption spectral intensities, \( A_t^e \) and \( A_i^e \), using the following normalization parameter, \( y \), as used in the Chai-Zhu method [12],

\[
y = \frac{A - A^E}{A^0 - A^E}
\]  

(5)

where \( A \) is spectral intensity a variable reaction time \( t \), \( A^E \) is the absorption spectral intensity at a given reaction time \( t^E \) (usually \( t^E > t \) to obtain a positive \( y \)). Then, Eqn (4) can be expressed as

\[
K_i = K_1 \cdot \frac{w_i \cdot [(A^0 - A_i^E)(1 - y_i^e)]}{w_i \cdot [(A^0 - A_i^E)(1 - y_i^e)]}
\]

(6)

If \( y_i^e = y_i^e \), Eqn. (6) becomes

\[
K_i = K_1 \cdot \frac{w_i}{w_i} \cdot \frac{(A^0 - A_i^E)}{(A^0 - A_i^E)}
\]

(7)

From a purely mathematical point of view, Eqn. (7) and Eqn. (4) are exactly the same. However, Eqn. (7) has significant practical importance. It indicates that the kappa number of pulp sample \( i \), \( K_i \), can be measured without the knowledge of the end point of the oxidation reaction, \( t^E \), for the determinations of \( A_t^e \) and \( A_i^e \) from the absorption data as demonstrated in the Chai-Zhu method [12]. The kappa number of pulp sample \( i \), \( K_i \), can be determined using any spectral intensities \( A_t^e \) and \( A_i^e \) on the kinetic curves corresponding to pulp samples \( I \) and \( i \), respectively, at time \( t^E \) given that \( y_i^e \approx y_i^e \), or \( (1 - y_i^e)/(1 - y_i^e) \approx 1 \). Therefore, Eqn. (7) does not require time-resolved absorption measurements for the determination of the end of the pulp oxidation reaction, \( t^E \), that are required when using the
Chai-Zhu method [12] Eqn. (1) or Eqn. (4). Eqn. (7) is called the one-point calibration kappa method or the simplified Chai-Zhu method.

It should be pointed out that the one-point calibration method Eqn. (7) has significant advantages over any lignin-content-based spectrophotometric kappa methods [7, 8]. First of all, the lignin-content-based methods [7, 8] are indirect kappa methods and require calibrations for wood-species effects because the lignin reactivities differ for different woods. However, Eqn. (7) only needs to calibrate once using a standard pulp sample of known kappa number regardless of the wood species of the pulp to be tested because direct permanganate is measured. Secondly, the HexA groups, present especially in hardwood pulps, consume permanganate and bleaching chemicals, making calibration of lignin based kappa test methods problematic. Furthermore, the methods based on lignin content [7, 8] require absolute measurements of lignin absorption, which will always cause measurement errors in practice, while absolute measurements are not necessary in using Eqn. (7). Finally, Eqn. (7) also significantly reduces errors due to baseline shift in spectroscopic measurements by the subtracting terms in the equation. Therefore, Eqn. (7) provides much more accurate and reliable results than any spectrophotometric methods based on lignin content. If both the standard and unknown pulp samples are conditioned properly in a same room overnight, the difference of moisture content among these pulp samples may be neglected; therefore; moisture content may not need to be measured in using Eqn. (7).
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. 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 200-mesh 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, now Agilent Technologies) 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 mol/L potassium permanganate solution was used to react with pulp samples under acidic conditions by adding standard sulfuric acid of 2.0 mol/L concentration. The volume ratio of the permanganate solution to sulfuric acid is 1:4.

Measurement Procedures

The measurement procedure has been described in our previous study [12]. Distilled water was used as a blank solution for UV/VIS measurements. Pipettes of 5 mL (± 0.01mL)
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 g) 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 min with a time interval of 1 s.

RESULTS AND DISCUSSION

Operating Window of the One-Point Calibration Method

The major simplification of the present one-point calibration method (Eqn.(7)) is that it is not necessary to know the end point of the pulp oxidation reaction with permanganate for kappa number determination; therefore, the operating window of the present method is eliminated. To validate this experimentally, seven kinetic curves measured at 546 nm conducted in our previous study [12] were plotted in Figure 1. The first two kinetic curves were from an unbleached birch pulp of kappa number 14.9; the other five were from an unbleached southern pine pulp of kappa number 25.8. Different sample sizes were used in these seven experiments. We then normalized these seven kinetic curves according to eqn. (5) by using various intensities $A^E$ taken at different reaction times $t^E$. We found that all the kinetic curves fall into a single curve when $A^E$ is taken at reaction time greater than 50 s with only very small deviations. Therefore, $y^*_i = y^*_i$, which indicates that it will give approximately the same correct answer of the kappa number of the testing pulp sample $i$. 
from Eqn. (7), when $A_i^E$ and $A_i^*$, corresponding to pulp samples $I$ and $i$, respectively, are taken from any time greater than 50 s on the kinetic curves. In other words, the operating window of reaction time is a semi-open range of greater than 50 s. For clarity, only two normalized curves using $A_i^E(t^E = 159)$ and $A_i^E(t^E = 260)$ are shown in Fig. 2. The normalization results indicate that the reaction is kinetically controlled rather than mass transfer (diffusion) controlled. Any deviations in the normalized curves are due to (1) imperfect mixing of the pulp with the reaction solution in the experiments, (2) differences in pulp internal diffusion of the oxidant caused by the differences in the pulp physical structure, and (3) experimental errors.

The results in Fig. 2 clearly indicate that the kinetic curves of the two birch pulp samples consistently deviate from the five pine-pulp samples in both of the normalization curves, which should not be a concern, because the requirement of the normalized kinetic curves falling to a single curve is more than sufficient (not necessary) for the one-point calibration method (Eqn. (7)) to be valid. The necessary condition for Eqn. (7) to be valid is $y_i^* = y_i^*$. When $t^E = 159$ seconds ($= t^E$, the end of the pulp oxidation reaction time determined in our previous study), $y_i^* = y_i^* = 0$, Eqn. (7) will be exactly the same as Eqns. (6) and (4). Therefore, Eqn. (7) must be valid. Let us examine the effect of $t^*$, an operating window parameter, on the measurement errors of the kappa numbers (relative to the Chai-Zhu method, or Eqn. (4)) of the birch and pine pulp samples from the absorption spectra shown in Fig. 1 in using the one-point calibration method (Eqn. (7)). It should be noticed from Eqn. (6) that the effect (or error) is really caused by the difference in the normalized spectral intensities $y_i^*$ and $y_i^*$. Here, $y_i^*$ is calculated using the unbleached
birch of 0.05 g spectrum and $y^f_1$ is calculated using the rest of the spectra. Recall, when $t^E = 159$, Eqn. (7) and Eqn. (4) are identical; therefore, the error is zero. The results clearly show that even when a birch sample is used for calibration, the relative measurement errors for the pine-pulp samples were less than 10% as long as the spectral intensity $A^E$ used for spectral normalization was taken at reaction time, $t^E$, greater than 50 s, in a semi-open operating window. For comparison purposes, Fig. 3 also plots the operating window of the same pine-pulp using the Chai-Zhu method [12], i.e., an operating window of 118-198 s if the same 10% error range is allowed. Figure 3 also indicates that the operating window of the birch pulp is much wider than that of the pine because the calibration sample is also a birch, which eliminates the difference in internal permanganate mass diffusion within the pulps.

**Comparisons with the Traditional Titration Method**

We measured the kappa numbers of 14 blended hardwood pulps using the present one-point calibration method and the standard TAPPI kappa test method [1]. The moisture contents of the 14 pulps were measured to determine kappa number. One of the pulp samples, with kappa number of 42.9 was used as the calibration pulp. In using Eqn. (7) to calculate the kappa numbers of the remaining 13 pulps, the 13 spectral intensities, $A^E$, are taken at reaction time, $t^E = 159$ s (= $t^f$ found in Chai-Zhu [12]) from the corresponding kinetic curves. Therefore, the results obtained from the one-point calibration method should be very close to those obtained using the original Chai-Zhu method [12]. The possible small deviations between the one-point calibration and the Chai-Zhu methods come from two factors: the kappa number of the calibration pulp sample and the deviation of true $t^f$ of the present experiments (was not determined) from 159 seconds (determined in previous study.
The comparisons demonstrate that the direct spectrophotometric kappa methods (including both the Chai-Zhu [12] and the one-point calibration methods) agree very well with the standard TAPPI kappa test method as shown in Fig. 4 over a wide kappa number range of 10–65.

To further demonstrate the validity of the true one-point calibration kappa test method, which eliminated the wood-species or lignin reactivity effect, we measured 45 pulp samples of 6 hardwoods and 4 softwoods obtained in our laboratory pulping experiments. The kappa numbers of these pulps were also measured in our previous pulping experiment [13] using the standard TAPPI kappa test method [1]. The moisture contents of the 45 pulps were measured in our previous study [13]; however, the results were not used in the determinations of the kappa numbers using the one-point calibration method in the present study. One of the 45 pulp samples, the aspen pulp with kappa number 26.8 was used as the calibration pulp. Figure 5 shows the comparisons of the kappa numbers of these 45 pulp samples obtained by the TAPPI method and the one-point calibration without moisture content measurements. Excellent agreements were obtained in a kappa number range of 10-70, indicating the validity of the present one-point calibration. An aspen pulp was used to calibrate all the other 44 pulps from 9 different wood species. Again, we did not determine the true \( t^c \) for these 45 pulp samples and the spectral intensities, \( A^E \), were taken at reaction time \( t^E = 159 \) seconds in this calculation.

**Measurement Errors**

We calculated the measurement errors of kappa numbers, measured by the one-point calibration method, of the 13 pulp samples shown in Fig. 4 relative to the corresponding
kappa numbers measured by the TAPPI kappa test method. For each pulp sample, 10 spectral intensities, $A^E$, taken at different operating-window parameter (or reaction times), $t^E$, were used to calculate 10 kappa numbers corresponding to each $A^E$ using Eqn. (7) along with the corresponding errors relative to the TAPPI method. We then averaged the absolute values of the relative errors of the 13 pulp samples (with a kappa number range of 10-65) obtained using the same $A^E$ (or $t^E$). The effect of $t^E$ on the kappa-measurement error is shown in Fig. 6. Unlike the results presented in Fig. 3, the zero error is no longer observed at $t^E = 159$ s ($\equiv t^r$, the end of the oxidation reaction), because the error is relative to the kappa numbers determined by TAPPI method in Fig. 6. The errors are relative to the kappa numbers determined using spectral intensity, $A^E$, taken at $t^r = 159$ in Fig. 3. Furthermore, unlike the results presented in Fig. 3 where both positive and negative errors are presented, the absolute values of errors for the 13 pulp samples were used in averaging to obtain the final results shown in Fig. 6. Figure 6 clearly indicates that as long as the spectral intensities, $A^E$ used in Eqn. (7), are taken at reaction times greater than 120 s, the one-point calibration method produces relative errors less than 10% when averaged over the 13 pulps, though the wood species of the calibration pulp is different from the 13 testing pulps.

The Effect of Temperature on Kappa Measurements

In the standard TAPPI titration kappa test method, it is suggested that the reaction should be conducted at a temperature of 25°C because temperature can affect the reaction rate and therefore the measured kappa number. The following equation is provided to correct the effect of temperature on measured kappa number using the TAPPI kappa test method [1]:
where \( f \) is a temperature-correction factor and \( T \) is the temperature (°C) of the reaction solution. According to this equation, a maximum error of ±6.5% will occur in the TAPPI kappa test method if the reaction temperature varies between 20 and 30°C.

The temperature effect on measured kappa number using the direct spectrophotometric kappa methods, including both the Chai-Zhu [12] and the present one-point calibration methods, was investigated in this study using a southern pine pulp sample with a known kappa number of 36. Spectroscopic measurements of permanganate concentrations were conducted under 9 reaction temperatures from 20 to 34°C. The size of the pulp sample was 0.05g. The kappa numbers were calculated from the measured spectral intensities of the blank solution and that taken at reaction time of 159 s using Eqn. (7). The results indicate that the reaction temperature does not significantly affect the measured kappa number. A temperature-correction factor, \( f \), was determined from the measured kappa numbers at 9 different temperatures as shown in Fig. 7. A linear equation, similar to Eqn. (8), for correcting temperature effect was obtained,

\[
f_{\text{TAPPI}} = 1 + 0.013 \times (25 - T) \tag{8}
\]

\[
f_{\text{Eqn.(7)}} - 1 + 0.024 \times (25 - T) \tag{9}
\]

The slope of Eqn. (9) is greater than the slope of Eqn. (8) because the reaction rate in the present method is faster than that in the TAPPI method with strong acidification. In real on-line process control applications, the operating temperature may be higher than 34°C. This study demonstrates that the effect of temperature on the measured kappa number can be accounted for using a corrected factor.
CONCLUSIONS

A simple, direct, rapid, and practical spectrophotometric kappa test method using one standard pulp sample for one-point calibration has been developed based on the principles of the Chai-Zhu kappa test method [12]. In this one-point calibration kappa test method, the kappa number of a pulp sample is calculated using Eqn. (7) that requires only one absorption measurement of the blank (without pulp) permanganate reacting solution and one measurement of the pulp-suspended permanganate solution at any time in the later stage of the reaction. For the reaction conditions provided in this study, the second absorption measurement is suggested at about 2-3 minutes into the reaction. It has been verified that the operating window of the second absorption measurement is very wide and determination of the end point of the pulp oxidation reaction is not needed in using the one-point calibration method. Therefore, the technique is very suitable for process control in pulp productions.

Kappa measurements of 45 pulp samples obtained from laboratory pulping of 10 different hardwood and softwood species and 13 blended hardwood pulps with a kappa number range of 10-70 demonstrate that the present one-point calibration method agrees with the standard TAPPI kappa test method very well. This study also demonstrates that the effect of permanganate reaction temperature on measured kappa number using the one-point calibration method is not significant and can be corrected using a correction factor similar to that used in the TAPPI method. A ragged and inexpensive on-line kappa sensor can be developed using the one-point calibration method presented.
ACKNOWLEDGEMENT

This work was supported by the U.S. Department of Energy through Grant No. DE-FC07-96ID13418.

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List of Figures

Fig. 1 Time-dependent permanganate absorption spectral intensities at 546 nm measured in seven pulp oxidation reactions with permanganate for pulp kappa number determination (reaction kinetic curves).
- △ Unbleached birch, 0.0500 g; ▽ Unbleached birch, 0.1540 g;
- ○ Unbleached pine, 0.0516 g; ◇ Unbleached pine, 0.0612 g;
- ▼ Unbleached pine, 0.0832 g; ▶ Unbleached pine, 0.1184 g;
- □ Unbleached pine, 0.1403 g.

Fig. 2 Normalized seven reaction kinetic curves shown in Fig. 1

Fig. 3 The effect of the operating window parameter (reaction time) of the one-point calibration method on the relative error in kappa measurements

Fig. 4 Comparisons of the kappa numbers of 13 blended hardwood pulps between the TAPPI and the one-point calibration kappa methods.

Fig. 5 Comparisons of the kappa numbers of 45 pulps from laboratory pulping of 10 hardwood and softwood species between the TAPPI and the one-point calibration kappa methods.

Fig. 6 The effect of the operating window parameter (reaction time) on the averaged relative deviations of the kappa numbers of the 13 pulps measured by the one-point calibration method presented in Fig. 4.

Fig. 7 The effect of temperature on the measured kappa number using the one-point calibration method.
Fig. 1

![Graph of Spectral Intensity at 546 nm vs Reaction Time (s).]  

Fig. 2

![Graph of Normalized Spectral Intensity vs Reaction Time (s).]  

**Curve I:** Normalized by $A(t=159 \text{ s})$

**Curve II:** Normalized by $A(t=260 \text{ s})$

- △ Unbleached birch, 0.0500 g
- ▽ Unbleached birch, 0.1540 g
- ○ Unbleached pine, 0.0516 g
- ◊ Unbleached pine, 0.0612 g
- □ Unbleached pine, 0.0832 g
- ▼ Unbleached pine, 0.1184 g
- □ Unbleached pine, 0.1403 g
Fig. 3

![Graph showing relative measurement error vs. operating window parameter, $t^E$, (s).](image)

Operating window: One-Point Calibration method

Birch .1540 g
A Pine .0516 g
Pine .0516 g
Pine .0620 g
Pine .0832 g
Pine .1184 g
Pine .1403 g

Fig. 4

![Graph showing Kappa vs. Kappa (TAPPI Method).](image)

Pulp: Blended hardwood pulps
Moisture content: measured
Fig. 5

![Graph showing the relationship between Kappa (One-Point Calibration Method) and Kappa (TAPPI Method). The graph is divided into hardwoods and softwoods. Hardwoods include Aspen, Basswood, Birch, Maple, Oak, and Sweetgum. Softwoods include Southern pine, Douglas-fir, White spruce, and Western hemlock.](image)

Fig. 6

![Graph showing the averaged relative deviation (%). The graph plots the operating window parameter, $t^E$, against the averaged relative deviation. The data points indicate a decreasing trend with increasing parameter values.](image)
Experimental Data, Present Method

- $f = 1 + 0.024(25 - T)$, Present Method
- $m_w - f = 1 + 0.013(25 - T)$, TAPPI Method

Fig. 7