Kappa number of pulp

1. Introduction

Kappa number is a key test method for determining the level of lignin remaining in a sample of finished or in-process pulp. It is thus a measure of the completeness of the pulping process for many kinds of chemical and semi-chemical pulps, both bleached and semi-bleached. Kappa number is based upon the reaction of a strong oxidizing chemical, potassium permanganate, with lignin as well as small levels of certain other organic impurities remaining in the pulp at various stages of its processing. Kappa number gives the maker of the pulp, as well as the papermaking user of the pulp, valuable information about the properties of the pulp as well as the paper made from it, particularly with regard to the level of residual lignin present.

2. Scope

2.1 This kappa number standard applies to many kinds of chemical, semi-chemical, unbleached and semi-bleached pulps within the kappa number range 1 to 100. Above a kappa number of 100, precision of the test may decrease, and the relationship between kappa number and lignin content may decrease, depending mainly upon the wood species from which the pulp is made. There is no general and unambiguous relationship between the kappa number and the content of lignin of other organic impurities in a particular pulp. The relationship varies according to the wood species and the pulping and delignification procedures used during the pulping process for a specific pulp. Kappa number is essentially a straight line relationship with both klasen lignin and chlorine number for pulps below 70% total pulp yields. The percentage of klasen lignin in a pulp sample whose kappa number is determined by the procedure in this standard test method may be approximated using the following equation

\[
\text{Lignin level (%) } = \text{Kappa number} \times 0.13
\]

If the kappa number is to be used to determine a precise numerical value regarding the amount of lignin present in a specific pulp of interest, a more precise relationship can be established by testing the specific pulp of interest.

2.2 As written, this standard is intended for use in the laboratory testing of pulps. It is recognized, however, that kappa number is widely used as an in-process test in the pulp and paper mill, in some cases with modifications.
Section 16 of this standard includes informative information regarding the unintended or unexpected impact that certain deviations from the standard can have on data accuracy, precision, or both.

2.3 Likewise, this standard does describe the use of automated instruments for measuring kappa number. The user of such equipment shall verify the applicability of such equipment for any intended use, and do such testing as may be required to determine the agreement of results from any automated testing equipment used with results obtained using the procedure in this test method.

3. Applicable documents

TAPPI T 550 “Determination of equilibrium moisture in pulp, paper and paperboard for chemical analysis”
TAPPI T 610 “Preparation of indicators and standard solutions”
ISO 302 “Pulps – Determination of kappa number:”
PAPTAC Standard G.18 “Kappa number of Pulp”
SCAN-C 1.00 “Kappa number” (withdrawn 2007)

4. Summary of the kappa number procedure

4.1 A sample of air-dried pulp of known weight is disintegrated in a known volume of distilled water, and the lignin and minor levels of other non-cellulose impurities in the sample are chemically oxidized in acidic solution by reaction with a known amount of potassium permanganate (KMnO₄) in a reaction vessel under atmospheric pressure for 10 minutes at 25°C Celsius. A separate test specimen will be used for moisture correction determination in order to calculate the equivalent oven-dry specimen weight. See section 16.7 regarding wet processed pulp samples.

4.2 After the 10-minute reaction period, a known amount of potassium iodide solution containing iodide in excess of the expected amount of permanganate remaining unreacted is added to the reaction vessel. The potassium iodide reacts instantaneously with all the remaining unreacted potassium permanganate, stopping or “quenching” any further oxidation of any remaining lignin and other oxidizable organic compounds that were present in the sample. An amount of iodine chemically equivalent to the amount of residual permanganate which remained in the reaction vessel at the time of the iodide addition is formed.

4.3 The resulting iodine formed is titrated with a standardized solution of sodium thiosulfate. From the amount of thiosulfate consumed, the amount of unreacted at the moment the oxidation reaction with the sample was quenched by the iodide addition can be calculated. From that information, the amount of permanganate that reacted with the original sample in the ten-minute reaction time is determined and the kappa number calculated.

4.4 The size of the pulp sample used for the test is chosen such that about 50% of the total oxidation capacity of the amount of added permanganate, as measured by the procedures in 4.2 and 4.3, is consumed by reaction with lignin and other impurities in the sample by the end of the 10-minute reaction time. If the amount of permanganate consumed is greater than or less than specified limits, the sample size shall be adjusted and the test shall be repeated to assure accuracy of the results.

5. Significance

The level of lignin and other impurities in pulp is very important in pulp production, as it is directly related to the amount and type of bleaching chemical required to produce a finished pulp of specified end use properties, particularly pulp brightness. Kappa number may be used as a specification for pulp used in various end use paper products such as bag papers, printing and writing papers and others.

6. Definition

Kappa number: the volume (in milliliters) of 0.1N potassium permanganate solution consumed by the equivalent of one gram of oven dried pulp under the conditions specified in this method. The results are corrected to the grams of sample which would react with 50% of the potassium permanganate added. Kappa number is expressed as a unitless number.
7. Interferences

The test procedure is based upon oxidation of lignin by permanganate and reduction of excess permanganate by thiosulfate, hence any chemically oxidizable or reducible contaminant not typical of the pulp itself may cause errors in the measured result. In general, such interferences come from samples which contain residues of pulping and bleaching operations that have not been properly or completely washed prior to sampling or sample preparation. This is rarely a problem in the case of air-dried sheet pulps, but should be considered when slush pulps or any in-process pulp samples are being tested.

8. Apparatus

8.1 Agitator, propeller type, made of glass or other noncorrosive material (a plastic or glass-covered magnetic stirrer may be used instead).
8.2 Disintegration apparatus, wet, high-speed type, which disintegrates the pulp completely with a minimum of damage to the fibers. Avoid disintegrators that may contaminate the sample with grease.
8.3 Water bath or constant temperature bath, capable of maintaining a constant temperature of 25.0 ± 0.2°C in the reaction vessel. It is convenient if the bath is of sufficient size to hold not only the reaction vessel but also the sulfuric acid and potassium permanganate solutions (9.1, 9.4).
8.4 Beaker 2000-mL.
8.5 Pipets, two 100-mL automatic pipets are especially convenient when a large number of determinations are to be made.
8.6 Buret, 50-mL, graduated to 0.1 mL. A 50-mL buret will be found more convenient for titration of the reaction mixture in the blank test.
8.7 Analytical balance, accurate to ± 0.0002 g.
8.8 Büchner funnel and filter flask to dewater three to four grams of pulp.
8.9 Filter paper, coarse pore size, 150-mm diameter.
8.10 Stopwatch, accurate to the nearest second.
8.11 Graduated cylinders, 1000, 25 and 50 mL.
8.12 Beaker, 250 mL.

9. Reagents

9.1 Potassium permanganate solution, analytical reagent grade, standardized with a normality of 0.1000 ± 0.0005N KMnO₄. Normality shall be as stated, that is, between 0.0995N and 0.1005N. Care shall be taken in the preparation and standardization of the potassium permanganate solution. In cases where the potassium permanganate solution is used infrequently (less than twice per week) or where the amount prepared lasts for more than a week, standardized of the solution shall be checked weekly and a new batch of the standard solution prepared when the normality deviates from the limits stated above. Refer to TAPPI T 610 “Preparation of indicators and standard solutions.” The “aging” of potassium permanganate solution is a recognized problem which must be guarded against if precision and accuracy of test results are to be achieved.
9.2 Sodium thiosulfate solution, 0.2000 ± 0.0005N Na₂S₂O₃.
9.3 Potassium iodide solution, 1.0N KI.
9.4 Sulfuric acid, 4.0N H₂SO₄.
9.5 Starch indicator solution, 0.2%.
9.6 Water, distilled.

10. Sampling

10.1 If the test is being made to evaluate a pulp lot, the sample shall be selected in accordance with TAPPI T 400 “Sampling and accepting a single lot of paper, paperboard, containerboard, or related product.”
10.2 If the test is made on another type of sample, report the source of the sample and the sampling plan or procedure used. Make sure the test portions taken are representative of the pulp.
10.3 When testing in-process samples, it is important to remember that the presence of small amounts of spent cooking liquor may cause errors in the measured kappa number. Ensure that any sample which may be contaminated with
process liquids or other sources of oxidizable or reducible material not typical of the pulp are free of such materials. When necessary, this can be completed by washing the pulp with distilled water prior to sample preparation, and then treating as in 11.2.

11. Preparation of sample

11.1 Air-dried pulp sheets. Tear small pieces from the sample sheets to obtain a total weight of sample given in Table 1 for the expected kappa number.

11.2 Screened slush sheets. Be sure sample is free of any remaining process liquid. Mix and filter using a Büchner funnel avoiding any loss of fibers. Air-dry the pad and tear it into small pieces.

11.3 Unscreened pulps. Be sure sample is free of any remaining process liquid. If the pulp sample is taken from unscreened pulp which is normally screened before bleaching and other processing, then remove the shives and knots from the sample by screening. State method of screening along with the test results and choose the method which would give results similar to those obtained by the industrial screening of the pulp. Proceed as in 11.2.

12. Procedure

12.1 Prior to weighing the air-dried test samples, condition for at least 20 min in the immediate vicinity and atmosphere of the balance (8.7).

12.2 Weigh a separate test specimen for moisture determination using TAPPI T 550 “Determination of equilibrium moisture in pulp, paper, and paperboard for chemical analysis.”

12.3 Adjust the temperature of the potassium permanganate solution, the distilled water and the sulfuric acid solution to a temperature of 25.0 ± 0.2°C.

12.4 Weigh out to the nearest 0.001 g that amount of pulp specimen which will consume approximately 50% of the potassium permanganate solution. Generally, a sample of 1.0 g will be suitable. A requirement of the procedure is that the permanganate consumption, as measured by back titration with thiosulfate at the end of the required 10-minute reaction time, shall be between 30% and 70% of the volume originally added. See 13.2.

12.4.1 Table 1, from SCAN-C 1.00 (withdrawn 2000), gives guidance regarding the weight of oven-dried sample typically required for performing the kappa number test on pulps of various kappa number. Similar suggested test specimen amounts are found in ISO 302. The values in the table may be used as a guide for the sample weight to be taken in 12.3, depending upon the expected kappa number. The final decision on test specimen weight, however, must be made upon experimental data. If the calculated value of \((b - a)\) (Table 2) is outside the range 30 – 70, repeat the determination on a larger or smaller test specimen.

12.4.2 For measuring kappa number below 5, increasingly larger amounts of sample must be used. Care must be taken to adjust the stirring for the thicker pulp suspensions such that it is adequate to adequately mix the added permanganate solution with the pulp suspension during the ten minute reaction period, however stirring shall not be such that air is drawn into the solution being stirred. While the kappa number procedure in this standard may be used for measuring kappa numbers above 100, for some wood pulps precision, accuracy, or both, of the method may be decreased. (1)

12.5 Disintegrate the first test specimen from 12.4 in 500 mL or less of distilled water until free of fiber clots and undispersed fiber bundles. Avoid methods of disintegration which involve extensive cutting of the fibers. The disintegration shall be sufficient to produce pulp fibers that are evenly dispersed during the reaction with the permanganate solution. For lower levels of fibers, the magnetic stirring bar (8.1) may be adequate. For higher levels of fiber, the propeller type stirrer may be required. In each case, stirring shall be done in a manner that does not draw air into the mixture of pulp and potassium permanganate (12.4.2). Adequate fiber disintegration and mixing with the permanganate during the test are required for good reproducibility of data.

12.6 Transfer the disintegrated test specimen to a 2000-mL reaction vessel and rinse out the apparatus with enough distilled water to bring the total volume to 795 mL.

12.7 Place the beaker in a constant temperature bath adjusted so that the reaction temperature stays at 25.0 ± 0.2°C during the entire reaction. Continuously stir the suspension so as to produce a vortex about 25 mm deep but not fast enough to introduce air into the mixture (see 12.4.2).
Table 1. Suitable amounts of oven-dry pulp in the kappa number range 5 to 100

<table>
<thead>
<tr>
<th>Kappa number</th>
<th>Amount of sample, g</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>10.0</td>
</tr>
<tr>
<td>6</td>
<td>8.3</td>
</tr>
<tr>
<td>8</td>
<td>6.3</td>
</tr>
<tr>
<td>10</td>
<td>5.0</td>
</tr>
<tr>
<td>15</td>
<td>3.3</td>
</tr>
<tr>
<td>20</td>
<td>2.5</td>
</tr>
<tr>
<td>25</td>
<td>2.0</td>
</tr>
<tr>
<td>30</td>
<td>1.7</td>
</tr>
<tr>
<td>35</td>
<td>1.4</td>
</tr>
<tr>
<td>40</td>
<td>1.3</td>
</tr>
<tr>
<td>45</td>
<td>1.1</td>
</tr>
<tr>
<td>50</td>
<td>1.0</td>
</tr>
<tr>
<td>55</td>
<td>0.9</td>
</tr>
<tr>
<td>60</td>
<td>0.8</td>
</tr>
<tr>
<td>70</td>
<td>0.7</td>
</tr>
<tr>
<td>80</td>
<td>0.6</td>
</tr>
<tr>
<td>90</td>
<td>0.6</td>
</tr>
<tr>
<td>100</td>
<td>0.5</td>
</tr>
</tbody>
</table>

12.7.1 This test as written is a standardized test written for laboratory testing of pulp. It is recognized that this test, with appropriate modifications, is widely used in process testing in pulp and paper mills throughout the pulp and paper production operation.

12.7.2 One such modification is to perform the test in certain locations in the pulp and paper producing location where a constant temperature bath having a temperature of 25 ± 0.2°C is not available or difficult to maintain. In such cases, determine the temperature of the material in the reaction vessel at the beginning and at the end of the 10-min reaction time, average the two values, and assume this to be the average reaction temperature throughout the test. Correct the kappa number using the average of the beginning and ending temperature, \( t \), as shown in 13.4. However, if either of the temperatures measured during the 10-min reaction period is below 20.0°C or above 30.0°C, the test must be repeated after obtaining a temperature bath or in some other way controlling the temperature within the required temperature range.

12.8 Pipet 100.0 ± 0.1 mL of potassium permanganate solution and 100 mL of sulfuric acid solution into a 250-mL beaker. Bring this mixture to 25°C quickly and immediately add to the disintegrated test specimen, simultaneously starting a stopwatch. Rinse out the beaker, using not more than 5 mL of distilled water, and add the washings to the reaction mixture. The total volume should be 1000 ± 5 mL.

12.9 At the end of exactly 10 min, stop the reaction by adding 20 mL of the potassium iodide solution from a graduated cylinder.

12.10 Immediately after mixing, but without filtering out the fibers, titrate the free iodine with the sodium thiosulfate solution, adding a few drops of the starch indicator toward the end of the reaction. Iodine volatization has been found to be an important variable and source of error (lack of precision) in the kappa number determination. The timing between the potassium iodide addition and subsequent titration completion should be as short as possible.

12.11 Carry out a blank determination using exactly the same method as above but omitting the pulp. Blank determinations should duplicate the testing of the specimen as nearly as possible, particularly with regard to timing.

13. Calculations

13.1 Calculate kappa number as follows:
\[ K = \frac{p \times f}{w} \]

and

\[ p = \frac{(b - a) N}{0.1} \]

where:

- \( K \) = kappa number
- \( f \) = factor for correction to a 50\% permanganate consumption, dependent on the value of \( p \) (see Table 2)
- \( w \) = weight of oven-dried pulp in the specimen as calculated from the air-dried specimen used (see Note 1), g
- \( p \) = amount of 0.1\( N \) permanganate actually consumed by the test specimen, mL
- \( b \) = amount of the thiosulfate consumed in the blank determination, mL
- \( a \) = amount of the thiosulfate consumed by the test specimen, mL
- \( N \) = normality of the thiosulfate

**NOTE 1:** \( W = \) Air-dried weight \( \times (100 - \% \text{ moisture}) \)/100, weight, g

13.2 Where \((b - a)\) is greater than 70 (test specimen weight is too large) or below 30 (test specimen too small), the test shall be repeated with a larger or smaller test specimen.

13.2.1 Factors in Table 2 are based on the equation: \( \log K = \log p/w + 0.00093 (p-50) \).

**Table 2. Factors \( f \) to correct for different percentages of permanganate used**

<table>
<thead>
<tr>
<th>( p )</th>
<th>+</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>0.958</td>
<td>0.960</td>
<td>0.962</td>
<td>0.964</td>
<td>0.966</td>
<td>0.968</td>
<td>0.970</td>
<td>0.973</td>
<td>0.975</td>
<td>0.977</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>0.979</td>
<td>0.981</td>
<td>0.983</td>
<td>0.985</td>
<td>0.987</td>
<td>0.989</td>
<td>0.991</td>
<td>0.994</td>
<td>0.996</td>
<td>0.998</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>1.000</td>
<td>1.002</td>
<td>1.004</td>
<td>1.006</td>
<td>1.009</td>
<td>1.011</td>
<td>1.013</td>
<td>1.015</td>
<td>1.017</td>
<td>1.019</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>1.022</td>
<td>1.024</td>
<td>1.026</td>
<td>1.028</td>
<td>1.030</td>
<td>1.033</td>
<td>1.035</td>
<td>1.037</td>
<td>1.039</td>
<td>1.042</td>
<td></td>
</tr>
<tr>
<td>70</td>
<td>1.044</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

13.4 Where a temperature correction is required for reasons described in 12.7.2, use the following formula to make the correction:

\[ K = \frac{p \times f}{w \left[ 1 + 0.013 (25 - t) \right]} \]

where \( t \) = average reaction temperature in degrees Celsius. If either temperature from 12.7.2 is higher than 30.0°C, or lower than 20.0°C, the data shall not be used, and a repeat determination shall be made.

**14 Report**

14.1 Report the kappa number as follows:
14.1.1 Under 100, to the nearest 0.1.
14.1.2 Over 100, to the nearest whole number.
14.1.3 Report any deviations from the requirements of this standard, particularly with regard to temperature control of the reaction vessel during the test, and with regard to handling or treatment of any samples which were not air dried prior to testing.
15. Precision

15.1 The following estimates of repeatability and reproducibility are based on data from a limited interlaboratory trial involving 6 laboratories and five different pulps. The trial was conducted in November 1997 using the “cm-88” revision of this method. Testing is based on one determination per test result and three results per lab, per material.

<table>
<thead>
<tr>
<th>Material</th>
<th>Grand Mean</th>
<th>Repeatability r</th>
<th>Reproducibility R</th>
<th>Labs included</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pulp A</td>
<td>5.76</td>
<td>0.30</td>
<td>5.2%</td>
<td>5</td>
</tr>
<tr>
<td>Pulp B</td>
<td>12.33</td>
<td>0.27</td>
<td>2.2%</td>
<td>5</td>
</tr>
<tr>
<td>Pulp C</td>
<td>24.48</td>
<td>0.55</td>
<td>2.2%</td>
<td>5</td>
</tr>
<tr>
<td>Pulp D</td>
<td>44.52</td>
<td>3.01</td>
<td>6.8%</td>
<td>6</td>
</tr>
<tr>
<td>Pulp E</td>
<td>115.45</td>
<td>8.37</td>
<td>7.3%</td>
<td>5</td>
</tr>
</tbody>
</table>

15.2 Repeatability and reproducibility are estimates of the maximum difference (at 95%) which should be expected when comparing test results for materials similar to those described above under similar test conditions. These estimates may not be valid for different materials or testing conditions.

16. Additional information

16.1 Effective date of issue: November 5, 2013.

16.2 The 1960 edition made the following changes: (a) a precision statement was added; (b) the use of smaller quantities of specimen and reagents was eliminated; and (c) the conversion table from 40 mL kappa numbers (T 214) to kappa numbers was deleted.

16.3 The 1976 version of the method was reclassified as a Classical Method by the Test Methods Management Committee of the TAPPI Board of Directors. This reclassification was made necessary since the last revision was over five years ago and no revision or reaffirmation has been accomplished by the responsible committee. The method was upgraded to an Official Method in 1999.

16.4 This 2013 edition of the method has undergone extensive editorial revision in an effort to clarify the importance of controlling temperature and test specimen weights when the method is used for process samples. Table 1 reflects the use of 100 mL of KMnO₄ instead of the 50 mL used by ISO.

16.5 The reaction of potassium permanganate with lignin as a means of determining pulping completeness and bleachability has a long history in the pulp and paper industry. Permanganate number and K number are names for tests for pulp similar to kappa number based on permanganate oxidation of pulp. TAPPI T 214 “Permanganate number of chemical and lightly lignified pulp” was formally introduced as a TAPPI test method in the 1930s. In 1957, Tasman and Berzins (1) proposed a procedure for the reaction of lignin in pulp with permanganate which they called kappa number. This test was relatively simple to perform, could be used for pulps varying over a wide range of lignin levels, and eliminated some of the difficulties encountered with the TAPPI T 214 test. The initial TAPPI version of Tasman’s and Berzins’ work, T 236, kappa number of pulp, was published in 1960. TAPPI T 214 was formally withdrawn by TAPPI in 1976, and reissued as TAPPI Useful Method 251 at that time. Kappa number tests based on the work of Tasman and Berzins are found in various collections of standardized pulp tests including ISO Standard Test Method 302 and PAPTAC Standard Method G.18, to name only two. Both the ISO 302 and PAPTAC G.18 kappa number tests differ from this TAPPI standard mainly in the units used to calculate reagent chemical concentrations. The ISO and PAPTAC methods express standard concentrations as moles of reagent chemical per liter, while this TAPPI standard uses equivalents of reagent chemical per liter. The calculations of the methods are adjusted for this difference such that the
reported kappa number of milliliters of standardized potassium permanganate solution per gram of oven dried pulp is numerically identical. Similar differences may exist among other published kappa number tests. Various versions of permanganate number and K number methods (essentially the same as kappa number) and test results are found in publication today. Careful review of published data is appropriate when test results based upon the oxidation of pulp with permanganate to determine lignin levels are reviewed, as various different tests give data which are similar, but differ on an absolute basis.

16.6 In certain reactions such as that of an inorganic acid and base (for example, sodium hydroxide with hydrochloric acid), the reaction takes place between ions, and it occurs essentially instantaneously. In the kappa number test, where one of the components of the reaction (such as lignin and other pulp organic impurities) is present as a suspended solid material, the key reaction in the test is between the permanganate ion in solution with lignin (or other) compounds present as insoluble organic compounds in the molecular state. In this case, the reaction takes place at a non-instantaneous rate which is dependent upon time, temperature, pressure, concentration of the reacting materials and in some cases additional variables. These variables are all controlled in the pulping process, and their control in the procedure in this TAPPI standard kappa number test is also very important if reliable results are to be achieved. These control limits are stated in the procedure in this standard test method, and shall be exactly followed.

16.7 Wet processed pulp samples. This test as written is a standardized test written for laboratory testing of pulp. It is recognized that this test, with appropriate modifications, is widely used in process testing in pulp and paper mills throughout the pulp and paper production operation. Such modification is to perform the test on test specimens of pulp that have not been air or oven dried. This modification will give satisfactory results as long as the approximate oven dried mass of the test specimen is known and the specimen weight adjusted accordingly. For example, if a suitable test specimen (Table 2) is two grams (estimated kappa number about 25) of oven dried pulp, and the test specimen is known to contain 50% water, a four-gram sample of the specific sample may be suitable for the test. The added water (two grams or approximately 2 mL) is insignificant with regard to the total volume of the reaction mixture (1000 mL; see 12.7) so no adjustment of the water level is required. It must be remembered, however, that if the process sample contains any chemicals, particularly process liquid chemicals (11.2-11.3), it shall be washed free of all such material before performing the test or significant errors can result.

16.8 Aging. Freshly made pulp has slightly higher permanganate consumption than pulp which has aged. The change is rather rapid immediately after the pulp is made but reaches a relatively stable stage after two or three days.


17. Keywords

Pulp, Lignin, Kappa number, Permanganate number

Literature cited


References

Watson, A.J., Stamp, C., “Influence of different operating procedures on the permanganate number determination.” APPITA, 11(1957):1, pp. 4-11

*Your comments and suggestions on this procedure are earnestly requested and should be sent to the TAPPI Standards Department.*