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Pulps — Determination of Kappa number

Pâtes — Détermination de l'indice Kappa

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT) see the following URL: Foreword - Supplementary information

The committee responsible for this document is ISO/TC 6, *Paper, board and pulps*.

This third edition cancels and replaces the second edition (ISO 302:2004), which has been technically revised.

Pulps — Determination of Kappa number

1   Scope

This International Standard specifies a method for the determination of the Kappa number of pulp. The Kappa number is an indication of the lignin content or bleachability of pulp.

This International Standard is applicable to all kinds of chemical pulps and semi-chemical pulps within the Kappa number range 1 to 100. For pulps with a Kappa number exceeding 100, use the chlorine-consumption procedure (ISO 3260) to describe the degree of delignification.

To achieve the greatest precision and accuracy, the sample size has to be adjusted so that the consumption of permanganate falls between 20 % and 60 % of the amount added.

NOTE   There is no general and unambiguous relationship between the Kappa number and the lignin content of pulp. The relationship varies according to the wood species and delignification procedure. All compounds oxidized by $KMnO_4$, not only lignin, will increase the consumption of $KMnO_4$, and thereby increase the Kappa number.[8] If the Kappa number is to be used to derive an index of pulp lignin content, specific relationships will have to be developed for each pulp type.

2   Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 638, *Paper, board and pulps — Determination of dry matter content — Oven-drying method*

ISO 7213, *Pulps — Sampling for testing*

3   Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1
oxidation capacity
relative amount of potassium permanganate reduced (expressed as MnO_2) of the total oxidation capacity

3.2
total oxidation capacity
oxidation capacity (permanganate consumption) when all permanganate is reduced into Mn^{2+}

3.3
Kappa number of pulp
number of millilitres of 0,02 mol/l potassium permanganate solution consumed under the specified conditions by one gram of pulp (calculated on an oven-dry basis)

Note 1 to entry: The results are corrected to a value corresponding to that obtained when 50 % of the total oxidation capacity of the permanganate is consumed in the test at a temperature of 25 °C.

4   Principle

Disintegrated pulp is allowed to react with a specified amount of potassium permanganate solution for a given time. The amount of pulp is chosen so that about 50 % of the total oxidation capacity of the permanganate is left unconsumed at the end of the reaction time.

The main reactions are as follows:

Residual lignin + other oxidizable compounds + MnO_4^- + $4H^+$ → oxidized lignin + other oxidized compounds + excess MnO_4^- + MnO_2 + $2H_2O$

$2MnO_4^-$ + $10I^-$ + $16H^+$ → $2Mn^{2+}$ + $5I_2$ + $8H_2O$

MnO_2 + $4H^+$ + $2I^-$ → Mn^{2+} + $2H_2O$ + I_2

$2S_2O_3^{2-}$ + I_2 → $S_4O_6^{2-}$ + $2I^-$

NOTE   By theoretical calculation and experimental observation, a consumption of 60 % (mass/mass) is actually the end point of the consumption for the permanganate ions, at which point the ions have been reduced to MnO_2. Further oxidation, performed by means of MnO_2 should be considered as "out of range". By adding potassium iodide solution, the reaction is terminated and the free iodine is titrated with sodium thiosulfate solution. The value so obtained is corrected to 50 % consumption of the total oxidation capacity of permanganate.

5   Reagents and materials

Use only chemicals of recognized analytical grade and only distilled water or water of equivalent purity.

5.1   Sulfuric acid, $c(H_2SO_4)$ = 2,0 mol/l.

Add with caution 112 ml of sulfuric acid, H_2SO_4, of density 1,84 g/ml to about 600 ml of water. Allow to cool and dilute to 1 litre with water.

5.2   Potassium iodide, $c(KI)$ = 1 mol/l.

Dissolve 166 g of potassium iodide, KI, in a 1 000 ml volumetric flask and fill up to the mark with water.

5.3   Potassium permanganate, $c(KMnO_4)$ = (0,020 ± 0,001) mol/l.

Dissolve 3,161 g of potassium permanganate, $KMnO_4$, in a 1 000 ml volumetric flask and fill up to the mark with water.

NOTE   Fresh solution is stable for at least 6 months if stored in a dark bottle.

5.4   Sodium thiosulfate, $c(Na_2S_2O_3)$ = (0,200 0 ± 0,000 5) mol/l.

Dissolve 49,65 g of sodium thiosulfate, $Na_2S_2O_3 \cdot 5H_2O$, in a 1 000 ml volumetric flask and fill up to the mark with water.

5.5   Starch indicator, 2 g/l solution.

NOTE   Commercially available standard solutions may be used.

6   Apparatus and equipment

Ordinary laboratory equipment and the following.

6.1   Agitator, of the propeller type, made of glass or other noncorrosive material (a plastic- or glass-covered magnetic stirrer may be used instead).

6.2   Wet-disintegration apparatus or **blender**, high-speed mixer, capable of disintegrating the pulp completely with minimum damage to the fibres.

6.3   Water bath, capable of maintaining a temperature of (25,0 ± 0,2) °C in the reaction vessel (see 8.3 regarding temperature correction).

6.4   Timing device, capable of measuring 10 min to the nearest 1 s.

NOTE   Automatic Kappa number analysers can be used if they follow this International Standard and give the same results.

7   Sampling and preparation of sample

7.1   Sampling

If the test is being made to evaluate a pulp lot, the sample shall be selected in accordance with ISO 7213. If the test is made on another type of sample, report the source of the sample and if possible the sampling procedure used.

Make sure that the test portions taken are representative of the pulp.

As the presence of small amounts of spent cooking liquor affects the Kappa number, ensure that the sample is well washed.

7.2   Sample preparation

Prepare the test material according to one of the following procedures.

7.2.1   Air-dry pulp. Tear or cut the pulp into small pieces.

7.2.2   Screened slush pulp. Dewater the pulp sample by filtering on a Büchner funnel or by centrifuging, avoiding any loss of fibres or fines. Air-dry the pulp sample, or dry it at a temperature not exceeding 105 °C, and tear it into small pieces.

7.2.3   Unscreened pulp. If the sample is taken from unscreened pulp, which is normally screened before bleaching or other processing, remove the shives and knots from the sample by screening. Choose a procedure that gives results similar to those obtained by industrial screening. State the method of screening in the test report. Continue the sample preparation as described in 7.2.2.

NOTE   If the pulp sample contains a considerable amount of shives, the screening procedure may give rise to incorrect results. A more reliable value may be obtained by defibrating the pulp sample before the determination. State the method of defibration in the test report.

8   Procedure

8.1   General

This International Standard includes two different procedures. One is used in the Kappa number range 5 to 100 and the other in the Kappa number range 1 to 5.

The main difference between the procedures is the added amounts of pulp and of $KMnO_4$, and the calculation. Due to stirring problems when determining Kappa numbers below 5, decrease the amounts of pulp and permanganate.

Use 8.2 and 8.3 in both procedures. The separate procedures are described in 8.3.2 and 8.3.3.

Run the determination in duplicate.

NOTE   Experimental work in Nordic countries has shown that the Kappa number determination according to the procedure for Kappa number 5 to 100 gives results equivalent to those obtained by the procedure for Kappa number 1 to 5, within the Kappa number range from 4 to 6.

8.2 Blank

Carry out a blank determination using exactly the procedure described in 8.3, but without the pulp. Read off the volume, V_1, to the nearest 0,1 ml, of the sodium thiosulfate (5.4) consumed at the inflection point. The consumption of sodium thiosulfate solution may vary by at most ± 1 % from its theoretical value (25,0 ml).

Divide the blank value of the Kappa number determination in the range 5 to 100 by two, for use in the Kappa number determination in the 1 to 5 range.

8.3 Determination

8.3.1 General

Condition the test specimens for at least 20 min, or until constant weight has been reached, in an atmosphere near the balance prior to weighing the samples for determination of Kappa number and dry matter content.

Weigh, to the nearest 0,001 g, the amount of pulp which will consume approximately 50 % of the potassium permanganate (5.3). Examples of suitable amounts of pulps are given in Table 1 and Table 2. Ensure that the consumption of permanganate is between 20 % and 60 % (mass/mass) of the amount added (see Reference [11]).

At the same time, weigh a separate test specimen for determination of the dry matter content in accordance with ISO 638, or any other method for determination of the dry matter content giving a similar result.

Table 1 — Suitable amounts of oven-dry pulp in the Kappa number range 5 to 100

Kappa number	Amount of sample, g
5	4,5
6	4,0
8	3,0
10	2,5
15	1,5
20	1,2
25	1,0
30	0,9
35 to 45	0,6
50 to 55	0,5
60 to 70	0,4
80 to 90	0,3
100	0,25

Table 2 — Suitable amounts of oven-dry pulp in the Kappa number range 1 to 5

Kappa number	Amount of sample, g
1	5,5
2 to 3	4,0
4	3,0
5	2,5

In order to avoid stirring problems when the Kappa number is low (i.e. five in the Kappa number range 5 to 100, and 1 to 2 in the Kappa number range 1 to 5), the amount of sample must be smaller than the amount corresponding to approximately 50 % of the total oxidation capacity of permanganate. However, the amount of sample should still correspond to at least 20 % of the total oxidation capacity of permanganate.

Disintegrate the test specimen in 300 ml of distilled water until it is free from fibre clots and from large fibre bundles. Avoid methods of disintegration which involve extensive cutting of the fibres. Rinse the disintegrator with approximately 90 ml of distilled water. If a combined disintegration and reaction beaker is used, perform the disintegration in 390 ml of distilled water.

Place the beaker in a water bath (6.3) adjusted to maintain a reaction temperature of (25,0 ± 0,2) °C during the entire reaction.

NOTE   A constant temperature bath must be used in order to perform this test under standardized conditions. It is recognized, however, that a constant temperature bath may not be available, or a constant temperature may be difficult to maintain, as may be the case for process testing, or in certain locations of a pulp and paper mill. 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, as shown in 9.1 and 9.2. However, if either of the temperatures measured during the 10-min reaction period is below 20 °C or above 30 °C, the test must be repeated after obtaining a temperature bath or in some other way controlling the temperature within the required temperature range. If a temperature correction is used, it must be reported in Clause 10 (test report). The results must also be validated by comparison with those obtained under constant temperature and using the same type of sample, since there might be some variability in results if a temperature correction is used.

Adjust the agitator (6.1) to produce a vortex approximately 25 mm deep in the reaction mixture. It is very important that the stirring is adequate.

8.3.2   Kappa number range 5 to 100

Pipette (50 ± 0,1) ml of the potassium permanganate solution (5.3) and 50 ml of the sulfuric acid (5.1) into a beaker. Bring this mixture to 25 °C, quickly add the mixture to the disintegrated specimen and simultaneously start the timing device (6.4). Rinse the beaker with approximately 10 ml of distilled water, and add the washings to the reaction mixture. The total volume shall be 500 ml. At the end of 10,0 min ± 15 s, terminate the reaction by adding exactly 10 ml of the potassium iodide solution (5.2).

Immediately after mixing, but without filtering out the fibres, titrate the free iodine with the sodium thiosulfate solution (5.4). Add a few drops of the starch indicator solution (5.5) toward the end of the titration. Do not add the starch until the majority of the iodine is reduced by the thiosulfate, because the starch ties up the free iodine liberated from the potassium iodide. Read off the volume, V_2, to the nearest 0,1 ml of the sodium thiosulfate (5.4) consumed at the inflection point.

Iodine volatilization has been found to be an important variable in the determination of the Kappa number. The time between the addition of potassium iodide solution to terminate the reaction, and the completion of the subsequent titration, should be as short as possible, particularly when titrating the blank.

If the titration is performed in an automatic titrator using a platinum electrode, it is not necessary to add starch as an indicator.

8.3.3   Kappa number range 1 to 5

Pipette (25,0 ± 0,1) ml of the potassium permanganate solution (5.3) and 50 ml of the sulfuric acid (5.1) into a beaker. Bring the mixture to 25 °C, quickly add the mixture to the disintegrated specimen and simultaneously start the timing device (6.4). Rinse the beaker with approximately 35 ml of distilled water, and add the washings to the reaction mixture. The total volume shall be 500 ml. At the end of 10,0 min ± 15 s, terminate the reaction by adding exactly 10 ml of the potassium iodide solution (5.2).

Immediately after mixing, but without filtering out the fibres, titrate the free iodine with the sodium thiosulfate solution (5.4). Add a few drops of the starch indicator solution (5.5) toward the end of the

titration. Do not add the starch until the majority of the iodine is reduced by the thiosulfate, because the starch ties up the free iodine liberated from the potassium iodide. Read off the volume, V_2, to the nearest 0,1 ml, of the sodium thiosulfate (5.4) consumed at the inflection point.

Iodine volatilization has been found to be an important variable in the determination of the Kappa number. The time between the addition of potassium iodide solution to terminate the reaction, and the completion of the subsequent titration, should be as short as possible, particularly when titrating the blank.

If the titration is performed in an automatic titrator using a platinum electrode, it is not necessary to add starch as an indicator.

8.4 Reference pulp

To be sure that the result is correct, it is recommended that a reference pulp with a known Kappa number in the same range as the sample be analysed. Keep the reference pulp sample in a dry, cool and dark place.

9 Calculations

9.1 Kappa number 5 to 100

The Kappa number X, expressed as a numerical value only, is given by the following formulae:

$$V_a = \frac{(V_1 - V_2)c}{0,1} \tag{1}$$

$$X_1 = \frac{V_a d}{m} \tag{2}$$

$$X_2 = \frac{V_a d}{m}\left[1 + 0,013(25 - t)\right] \tag{3}$$

where

X_1 is the Kappa number without a temperature correction;

X_2 is the Kappa number with a temperature correction;

V_a is the volume of the potassium permanganate solution (5.3) consumed in the determination, in millilitres;

V_1 is the volume of the sodium thiosulfate solution (5.4) consumed in the blank test, in millilitres;

V_2 is the volume of the sodium thiosulfate solution (5.4) consumed in the determination, in millilitres;

c is the concentration of the sodium thiosulfate solution (5.4), expressed in moles per litre;

0,1   is the numerical factor, which takes into account the molarity of potassium permanganate and the stoichiometry of the reaction during the titration ($f = 0,02 \times 5$);

d is the correction factor to 50 % (mass/mass) permanganate consumption; d is dependent on the value of V_a, (see Table 3);

m is the oven-dry mass of the test specimen, in grams;

t is the actual temperature of reaction, in degree Celsius.

Table 3 — Correction factor d, expressed as a function of V_a
(Kappa number 5 to 100)

V_a ml	d									
	0	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
10	0,938	0,942	0,946	0,950	0,954	0,958	0,962	0,966	0,970	0,975
20	0,979	0,983	0,987	0,991	0,996	1,000	1,004	1,009	1,013	1,017
30	1,022									

NOTE   The correction factor d is based on an experimental study which gave the following formula:

$$\log_{10} X = \log_{10} \frac{V_a}{m} + 0{,}000\,93\left(2V_a - 50\right)$$

9.2   Kappa number 1 to 5

The Kappa number X, expressed as a numerical value only, is given by the following formulae:

$$V_b = \frac{\left(\dfrac{V_1}{2} - V_2\right)c}{0{,}1} \tag{4}$$

$$X_1 = \frac{V_b d}{m} \tag{5}$$

$$X_2 = \frac{V_b d}{m}\left[1 + 0{,}013\left(25 - t\right)\right] \tag{6}$$

where

X_1 is the Kappa number without a temperature correction;

X_2 is the Kappa number with a temperature correction;

V_b is the volume of the potassium permanganate solution (5.3) consumed in the Kappa number determination range 1 to 5, in millilitres;

V_1 is the volume of the sodium thiosulfate solution (5.4) consumed in the blank test in the Kappa number determination range 5 to 100, in millilitres;

V_2 is the volume of the sodium thiosulfate solution (5.4) consumed in the Kappa number determination range 1 to 5, in millilitres;

c is the concentration of the sodium thiosulfate solution (5.4), expressed in moles per litre;

0,1   is the numerical factor, which takes into account the molarity of potassium permanganate and the stoichiometry of the reaction during the titration ($f = 0{,}02 \times 5$);

d is the correction factor to 50 % (mass/mass) permanganate consumption; d is dependent on the value of V_b, (see Table 4);

m is the oven-dry mass of the test specimen, in grams;

t is the actual temperature of reaction, in degrees Celsius.

Table 4 — Correction factor d, expressed as a function of V_b (Kappa number 1 to 5)

V_b ml	d									
	0	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
0						1,022	1,026	1,030	1,035	1,039
10	1,044	1,048	1,053	1,057	1,062	1,066				

NOTE   The Kappa number can also be calculated using the following formula:

$$\log_{10} X = \log_{10} \frac{V_b}{m} + 0{,}000\,93 \times 2V_b$$

9.3   Expression of results

Report the Kappa number of the pulp as the mean of two determinations to the following precision:

Kappa number ≤ 50: to the nearest 0,1;

50 < Kappa number ≤ 100: to the nearest 0,5.

9.4   Example of calculation

Air-dry mass of the test specimen	1,100 g
Dry matter content of the sample	91,5 % (mass/mass)
Oven-dry mass of the test specimen	$\frac{91{,}5}{100} \times 1{,}100 \text{ g} = 1{,}006 \text{ g}$
Volume of the sodium thiosulfate solution (5.4) consumed in the blank test, V_1	25,2 ml
Volume of the sodium thiosulfate solution (5.4) consumed in the determination, V_2	9,5 ml
Concentration of the sodium thiosulfate solution (5.4), c	0,191 0 mol/l
Volume of the potassium permanganate solution (5.3) consumed in the test V_a	$\frac{(25{,}2 - 9{,}5) \times 0{,}191\,0}{0{,}1} = 30{,}0 \text{ ml}$
Correction factor, d	1,022
Kappa number, X_1	$\frac{30{,}0 \times 1{,}022}{1{,}006} = 30{,}5$

10 Test report

The test report shall give the following information:

a)   all information for complete identification of the sample;

b)   a reference to this International Standard, i.e. ISO 302;

c)   date and place of testing;

d)   the result, as specified in 9.3;

e)   whether or not an automatic device is used;

f)   the procedure (8.3.2 or 8.3.3) used;

g)   whether or not a temperature correction was used

h)   the mass of pulp tested;

i)   if the sample has been screened, the procedure used;

j)   if the sample has been disintegrated, the disintegration procedure;

k)   any unusual features observed during the work;

l)   any departure from this International Standard, or any other circumstances or influences regarded as optional, that could have affected the results.

Annex A
(informative)

Precision

A.1 General

The precision data are based on four pulp samples with different kappa numbers ranging from 4 to 40.

The calculations have been made according to ISO/TR 24498.

The repeatability and reproducibility limits reported are estimates of the maximum difference which should be expected in 19 of 20 instances, when comparing two test results for material similar to those described under similar test conditions. These estimates may not be valid for different materials or different test conditions.

Note Repeatability and reproducibility limits are calculated by multiplying the repeatability and reproducibility standard deviations by 2,77, where 2,77 = 1,96 $\sqrt{2}$.

A.2 Repeatability

Four pulp samples were analysed in two different laboratories with a manual device and in seven different laboratories with an automatic device. Each laboratory analysed the different pulp samples 10 times. The repeatability data are shown in Table A.1

Table A.1 — Repeatability for determination of Kappa number

Kappa number level	Manual device			
	Mean	Standard deviation S_r (%)	Coefficient of variation CoV_r (%)	Repeatability limit r (%)
4	4,0	0,038	0,95	0,10
10	10,4	0,088	0,85	0,24
16	16,3	0,18	1,1	0,50
40	41,7	0,25	0,60	0,69

Kappa number level	Automatic device				
	Mean	Grand mean[a]	Standard deviation S_r (%)	Coefficient of variation CoV_r (%)	Repeatability limit r (%)
4	4,3 to 4,5	4,4	0,026 to 0,14	0,6 to 3,1	0,072 to 0,39
10	10,2 to 10,7	10,4	0,062 to 0,16	0,6 to 1,5	0,17 to 0,44
16	16,1 to 16,7	16,4	0,082 to 0,28	0,5 to 1,7	0,23 to 0,78
40	42,3 to 42,8	42,6	0,17 to 0,51	0,4 to 1,2	0,47 to 1,41

[a] Since only the range of mean values was available for the laboratories using an automatic device, the grand mean, standard deviation and repeatability limit could not be calculated exactly, but were estimated based on the average value of the two extreme mean values. However, since the mean values cover a narrow range, any possible deviation from the true values are not considered to be significant.