



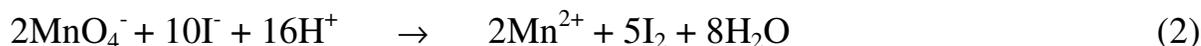
Kappa Number Determination

Introduction:

Kappa number is used to determine the amount of lignin in a sample of pulp. Lignin is one of three polymers in wood and the one that has to be removed in the chemical pulping process to liberate the fibers that are used in cellulosic products, such as paper and cardboard. The extent to which lignin is removed is important for the control of this process.¹

This method for the determination of Kappa number was developed through cooperation with PAPRICAN. PAPRICAN developed equations, calculations and methods which were then developed to work with our hardware and software. Kappa number is the amount of 0.02M potassium permanganate (KMnO₄) consumed by 1 g of pulp. This value is then corrected to 50% KMnO₄ consumption. The pulp samples are analyzed at various points in the paper making process. Different Kappa numbers are expected at different points in the process, dependant on the amount of lignin that has been removed from the sample during the pulping process. As lignin is removed from the sample, the Kappa number is reduced. Low Kappa numbers require less KMnO₄ for sample analysis, and the pulp is a lighter colour. The percentage of lignin in a pulp sample is calculated by multiplying the Kappa number of the pulp by 0.13².

The first reaction that takes place during the determination of Kappa number occurs between the lignin, the permanganate, and the acid. The lignin is oxidized and solubilised by permanganate in the presence of the acid (1) and the excess permanganate is used in the second reaction. The second reaction occurs when the potassium iodide is added. The iodide reacts with the excess permanganate to produce iodine (2). The third reaction occurs when the iodine reacts with thiosulphate to produce iodide and sulphate anions (3).³



This document shows the determination of the Kappa number by micro-Kappa method. This method uses 1/6 of the chemicals and sample volume versus the normal kappa method.² Micro-Kappa analysis is a simple, reliable, and precise method for the determination of Kappa number. The Man-Tech system uses a water bath to control the temperature of the samples during the titration to allow for more accurate Kappa number determination. The system has 16 locations that are available for samples and blanks. Automated chemical addition, wait time, end point determination, and calculation ensures reproducible results. Automation reduces variation in results due to human error and limits the volume of reagents required. All information from each titration is stored, allowing easy access to data from previous titrations. Custom reporting is easily set up and data can be exported for further analysis. Please contact your local Man-Tech sales representative to find out how this method can work for you.

Conforms To: Modified PAPTAC Standard Testing Methods Standard G.18
Kappa number with better repeatability and at a lower cost. *90th Annual meeting, PAPTAC.*
Montreal, Canada, Preprint Book C, p.111-115, 2004
TAPPI T236 om-99

Sample: Pulp/paper samples

Concentration Range: Suggested range: Kappa number 1-80
Range shown here: Kappa number 1-72

Apparatus:

1. 2 x Burivar - 1/2 Burette Module (PC-1104-00)
2. 2 x Titra-Rinse reagent addition pump (PC-1000-400)
3. Titra-Rinse slow speed reagent addition pump (PC-1000-408)
4. Interface (PC-1000-102/4)
5. Standard beaker autosampler with water bath (PCM-3000-223)
6. Redox electrode (PCE-80-OR1002)
7. Electrode cable (PCE-86-EX1001)
8. Waring commercial blender (PC-1000-803)
9. Waring blender vessel (PC-1000-804)
10. Tall-form 300mL beakers (PC-1000-357)
11. Shimadzu AUY120 analytical balance 0.0001g (SZ-321-62900-67)

Reagents:

1. Distilled water
2. Potassium permanganate (KMnO₄) 0.1 N
3. Sulfuric acid (H₂SO₄) 4 N
4. Potassium iodide (KI) 1 N
5. Sodium thiosulphate (Na₂S₂O₃) 0.1 N

Procedure:

All Samples:

1. All samples are weighed.
2. Pulp samples are dried at 104°C for at least 4 hours and allowed to cool in a desiccator for a minimum of 20 minutes before use (See Hints/Suggestions #9).
3. The amount of pulp required is calculated (see calculations section) and an appropriate sample size is accurately weighed.
4. The weighed pulp sample is placed in the Waring blender with 66.7 mL of deionized water.
5. 66.7 mL of deionized water is measured and placed aside for later use.
6. The lid of the blender is closed and the sample is blended for 5 sec on low speed and then immediately blended at high speed for 10 sec.
7. The mixture is quickly poured into a 300mL beaker.
8. Half of the deionized water set aside is poured into the blender. The lid is closed and the container is shaken to dislodge any pulp caught inside.
9. Water and sample are quickly poured into the beaker containing the sample.

10. Steps 9 and 10 are repeated with the remaining deionized water.
11. One beaker with 200 mL of deionized water is placed in the second rinse station.
12. Two beakers with 133 mL each of deionized water are placed into the first and second sample positions to be run as blanks.

For samples with Kappa number less than 8:

1. The tips, electrode and stir rod (probe assembly) are placed in the flowing rinse.
2. The stirrer is turned on at 60 % speed.
3. The probe assembly is rinsed with deionized water in the flowing rinse station.
4. The probe assembly is moved to the stationary rinse station and rinsed, stirring at **30%** speed.
5. The probe assembly is moved to the sample and stirred at **20%**.
6. The burettes are filled with the appropriate solutions (potassium permanganate and sodium thiosulphate).
7. 16.666 mL of sulfuric acid solution is added to the sample, and the stir rate is increased to **80%**.
8. 16.666 mL of potassium permanganate solution is injected into the sample, and the reaction is allowed to sit for a total of 10 minutes including preparation time.
9. 3.333 mL of potassium iodide solution is added to the sample.
10. The mixture is titrated with sodium thiosulphate to the end point.
11. The analysis results are calculated and reported.

For samples with Kappa number between 8 and 20:

1. The tips, electrode and stir rod (probe assembly) are placed in the flowing rinse.
2. The stirrer is turned on at 60 % speed.
3. The probe assembly is rinsed with deionized water in the flowing rinse station.
4. The probe assembly is moved to the stationary rinse station and rinsed, stirring at **40%** speed.
5. The probe assembly is moved to the sample and stirred at **20%**.
6. The burettes are filled with the appropriate solutions (potassium permanganate and sodium thiosulphate).
7. 16.666 mL of sulfuric acid solution is added to the sample, and the stir rate is increased to **50%**.
8. 16.666 mL of potassium permanganate solution is injected into the sample, and the reaction is allowed to sit for a total of 10 minutes including preparation time.
9. 3.333 mL of potassium iodide solution is added to the sample.
10. The mixture is titrated with sodium thiosulphate to the end point.
11. The analysis results are calculated and reported.

For samples with Kappa number greater than 20:

1. The tips, electrode and stir rod (probe assembly) are placed in the flowing rinse.
2. The stirrer is turned on at 60 % speed.
3. The probe assembly is rinsed with deionized water in the flowing rinse station.
4. The probe assembly is moved to the stationary rinse station and rinsed, stirring at **30%** speed.
5. The probe assembly is moved to the sample and stirred at **20%**.
6. The burettes are filled with the appropriate solutions (potassium permanganate and sodium thiosulphate).
7. 16.666 mL of sulfuric acid solution is added to the sample, and the stir rate is increased to **50%**.
8. 16.666 mL of potassium permanganate solution is injected into the sample, and the reaction is allowed to sit for a total of 10 minutes including preparation time.
9. 3.333 mL of potassium iodide solution is added to the sample.
10. The mixture is titrated with sodium thiosulphate to the end point.
11. The analysis results are calculated and reported.

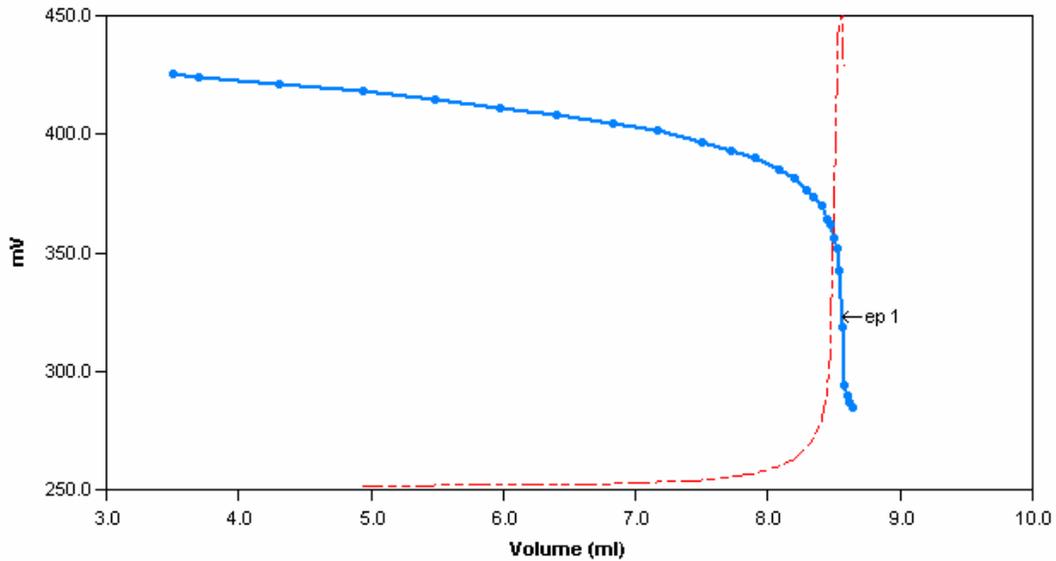


Figure 1: Sample Titration Curve for a sample with a Kappa Number of 7.1

Calculations:

Kappa Number:

Amount of pulp required per sample for Kappa number determination:

8.333/estimated Kappa = mass of dry pulp to be weighed

$$K = \frac{\left[16.666 - \left(\frac{VE1 * 16.666}{BLANK} \right) \right] * \left[10^{\left(0.00093 \left(6 * \left(16.666 - \left(\frac{VE1 * 16.666}{BLANK} \right) \right) - 50 \right) \right) \right]}{SWGHT}$$

K = Kappa Number

VE1 = total volume of sodium thiosulphate titrant added at the endpoint (mL)

BLANK = volume of sodium thiosulphate titrant added to the blank at the endpoint (mL)

SWGHT = weight of pulp in the sample (g)

Quality Control

Replicates were run for samples with Kappa values of 3.1, 7.7, 12.7, 16.2, 27.5, 33.8 and 40, as well as common paper products such as printer paper, binder dividers, manila envelopes, file folders and cardboard boxes. Statistical data is displayed below.

Kappa Number 3.1:

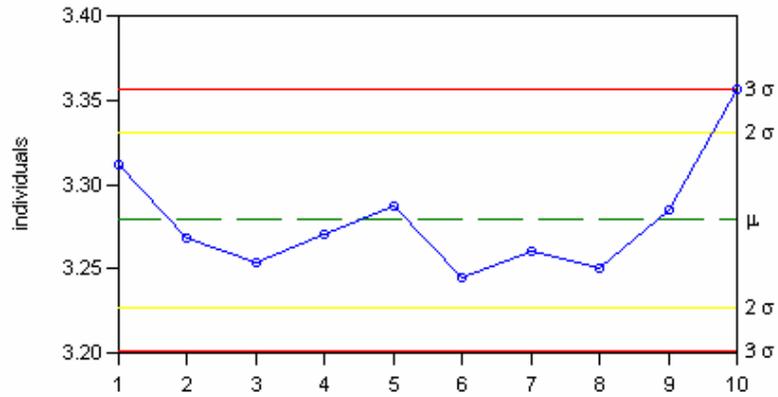


Figure 2: Control Limits plot for a sample with a Kappa Number of 3.1

Control Limits – Individuals

$\mu = 3.279$
 $\sigma = 0.026$
 CV= 0.793 %

95% Confidence Limits

$\mu - 2\sigma = 3.227$
 $\mu + 2\sigma = 3.331$

99.7% Confidence Limits

$\mu - 3\sigma = 3.201$
 $\mu + 3\sigma = 3.357$

Kappa Number 7.7:

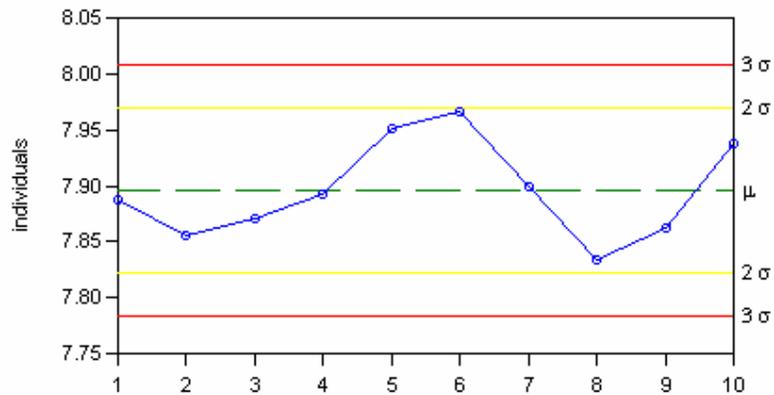


Figure 3: Control Limits plot for a sample with a Kappa Number of 7.7

Control Limits – Individuals

$\mu = 7.896$
 $\sigma = 0.037$
 CV= 0.469 %

95% Confidence Limits

$\mu - 2\sigma = 7.821$
 $\mu + 2\sigma = 7.970$

99.7% Confidence Limits

$\mu - 3\sigma = 7.784$
 $\mu + 3\sigma = 8.007$

Kappa Number 12.7:

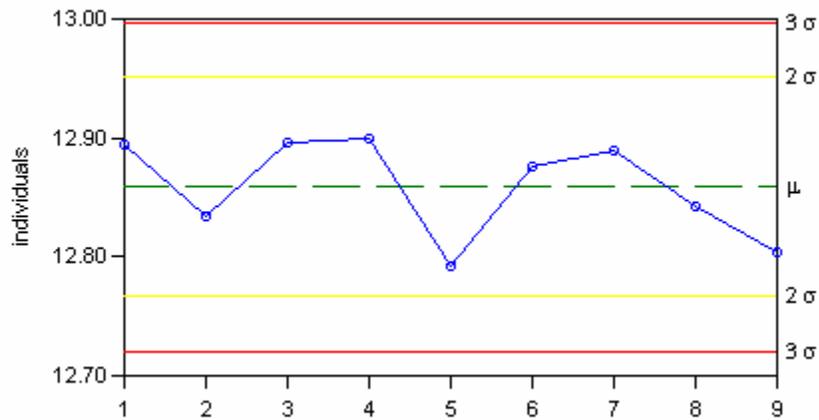


Figure 4: Control Limits plot for a sample with a Kappa Number of 12.7

Control Limits – Individuals

$\mu = 12.859$
 $\sigma = 0.046$
 CV = 0.358 %

95% Confidence Limits

$\mu - 2\sigma = 12.767$
 $\mu + 2\sigma = 12.951$

99.7% Confidence Limits

$\mu - 3\sigma = 12.721$
 $\mu + 3\sigma = 12.997$

Kappa Number 16.2:

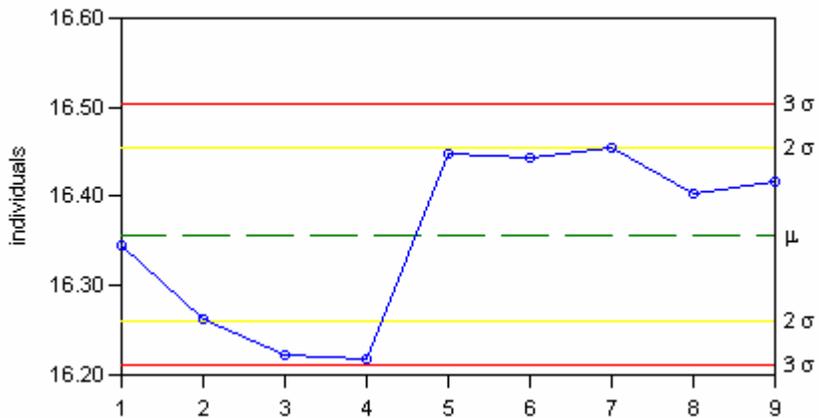


Figure 5: Control Limits plot for a sample with a Kappa Number of 16.2

Control Limits – Individuals

$\mu = 16.357$
 $\sigma = 0.049$
 CV = 0.299 %

95% Confidence Limits

$\mu - 2\sigma = 16.260$
 $\mu + 2\sigma = 16.455$

99.7% Confidence Limits

$\mu - 3\sigma = 16.211$
 $\mu + 3\sigma = 16.504$

Kappa Number 27.5:

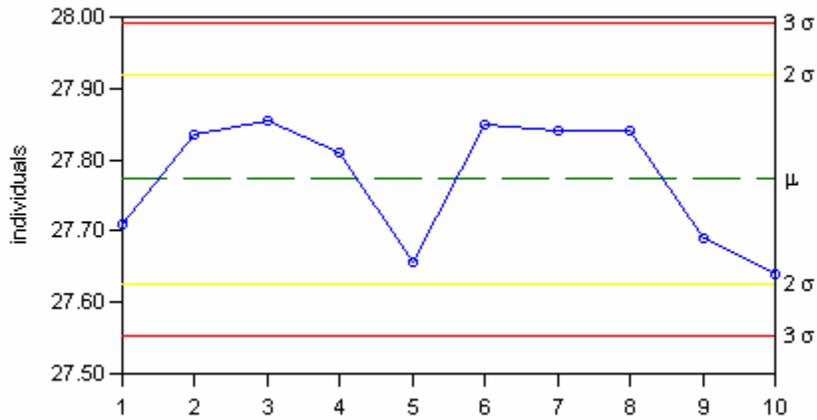


Figure 6: Control Limits plot for a sample with a Kappa Number of 27.5

Control Limits – Individuals

$\mu = 27.773$
 $\sigma = 0.073$
 CV = 0.263 %

95% Confidence Limits

$\mu - 2\sigma = 27.626$
 $\mu + 2\sigma = 27.919$

99.7% Confidence Limits

$\mu - 3\sigma = 27.553$
 $\mu + 3\sigma = 27.992$

Kappa Number 33.8*:

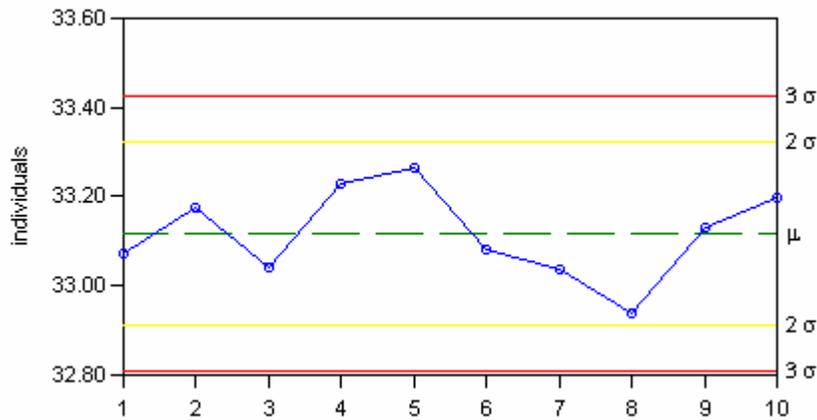


Figure 7: Control Limits plot for a sample with a Kappa Number of 33.8

Control Limits – Individuals

$\mu = 33.117$
 $\sigma = 0.103$
 CV = 0.311 %

95% Confidence Limits

$\mu - 2\sigma = 32.911$
 $\mu + 2\sigma = 33.323$

99.7% Confidence Limits

$\mu - 3\sigma = 32.808$
 $\mu + 3\sigma = 33.426$

*This sample was aged, potentially causing slightly low values.

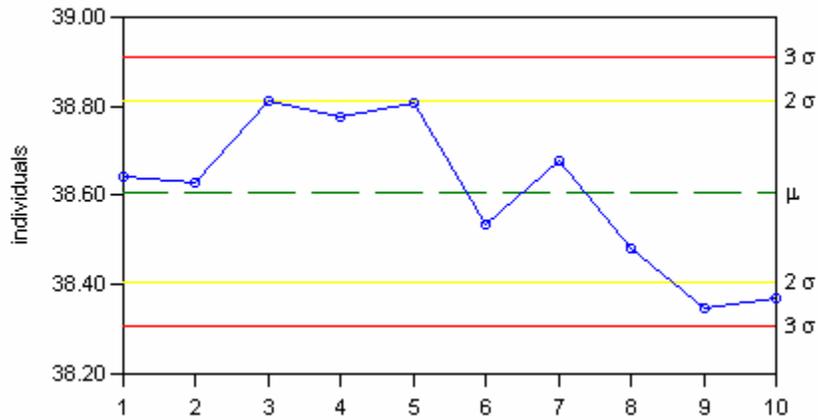


Figure 8: Control Limits plot for a sample with a Kappa Number of 40

Control Limits – Individuals

$\mu = 38.608$
 $\sigma = 0.101$
 CV = 0.262 %

95% Confidence Limits

$\mu - 2\sigma = 38.406$
 $\mu + 2\sigma = 38.810$

99.7% Confidence Limits

$\mu - 3\sigma = 38.305$
 $\mu + 3\sigma = 38.911$

*This sample was aged, potentially causing slightly low values.

Common Paper Products

Printer Paper:

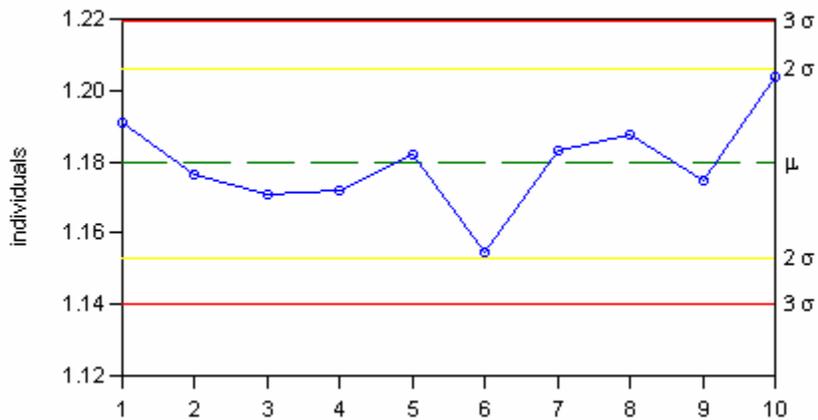


Figure 9: Control Limits plot for a Printer Paper Sample

Control Limits – Individuals

$\mu = 1.180$
 $\sigma = 0.013$
 CV = 1.102 %

95% Confidence Limits

$\mu - 2\sigma = 1.153$
 $\mu + 2\sigma = 1.206$

99.7% Confidence Limits

$\mu - 3\sigma = 1.140$
 $\mu + 3\sigma = 1.219$

Binder Divider:

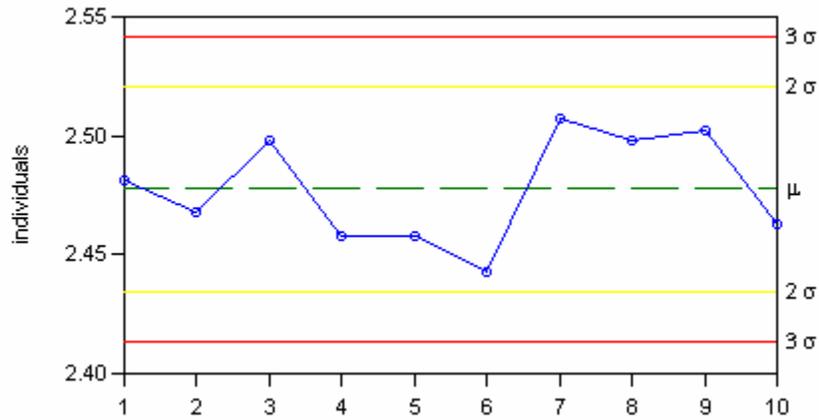


Figure 10: Control Limits plot for a Binder Divider Sample

Control Limits – Individuals

$\mu = 2.478$
 $\sigma = 0.021$
 CV = 0.847 %

95% Confidence Limits

$\mu - 2\sigma = 2.435$
 $\mu + 2\sigma = 2.520$

99.7% Confidence Limits

$\mu - 3\sigma = 2.413$
 $\mu + 3\sigma = 2.542$

Manila Envelope:

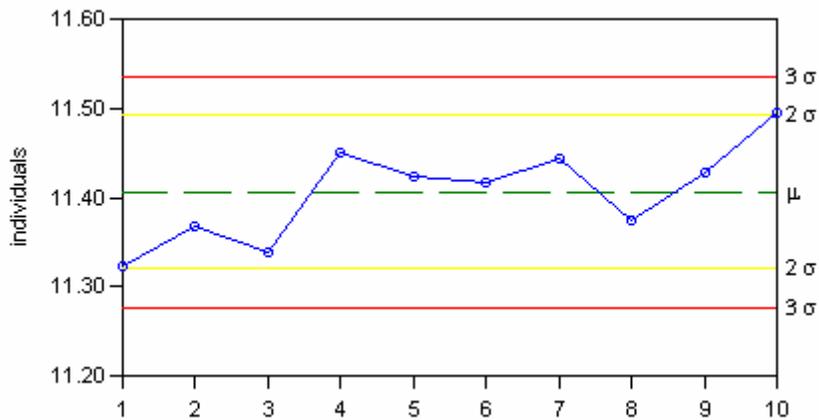


Figure 11: Control Limits plot for a Manila Envelope Sample

Control Limits – Individuals

$\mu = 11.406$
 $\sigma = 0.043$
 CV = 0.377 %

95% Confidence Limits

$\mu - 2\sigma = 11.320$
 $\mu + 2\sigma = 11.492$

99.7% Confidence Limits

$\mu - 3\sigma = 11.276$
 $\mu + 3\sigma = 11.535$

File Folder:

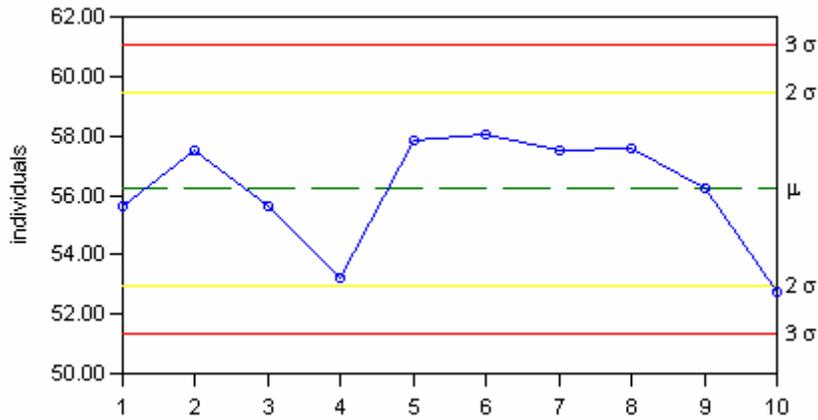


Figure 12: Control Limits plot for a File Folder Sample

Control Limits – Individuals

$\mu = 56.204$
 $\sigma = 1.620$
CV = 2.882 %

95% Confidence Limits

$\mu - 2\sigma = 52.963$
 $\mu + 2\sigma = 59.444$

99.7% Confidence Limits

$\mu - 3\sigma = 51.343$
 $\mu + 3\sigma = 61.065$

Cardboard Box:

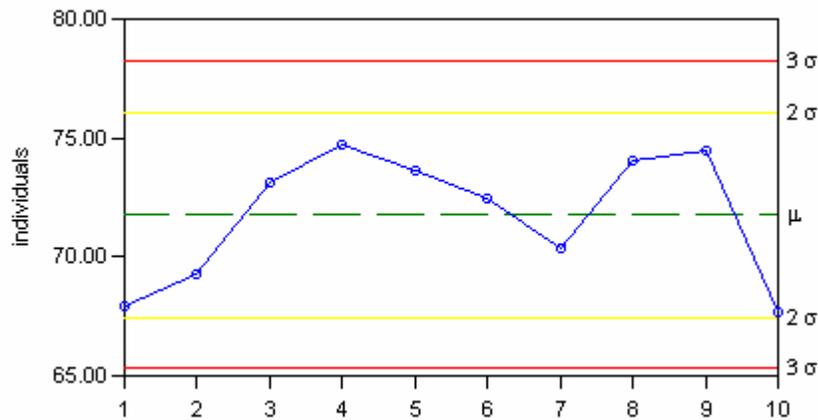


Figure 13: Control Limits plot for a Cardboard Box Sample

Control Limits – Individuals

$\mu = 71.765$
 $\sigma = 2.155$
CV = 3.003 %

95% Confidence Limits

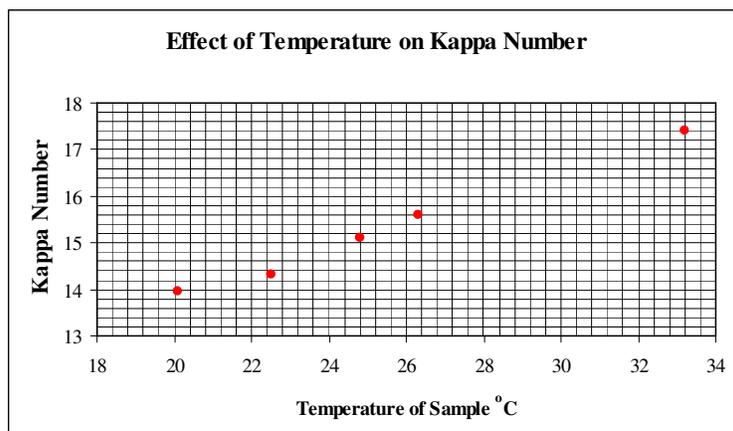
$\mu - 2\sigma = 67.454$
 $\mu + 2\sigma = 76.076$

99.7% Confidence Limits

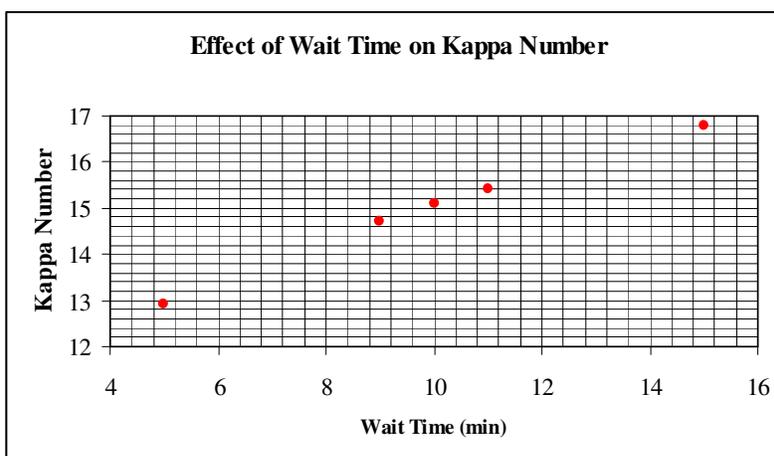
$\mu - 3\sigma = 65.299$
 $\mu + 3\sigma = 78.231$

Hints/Suggestions:

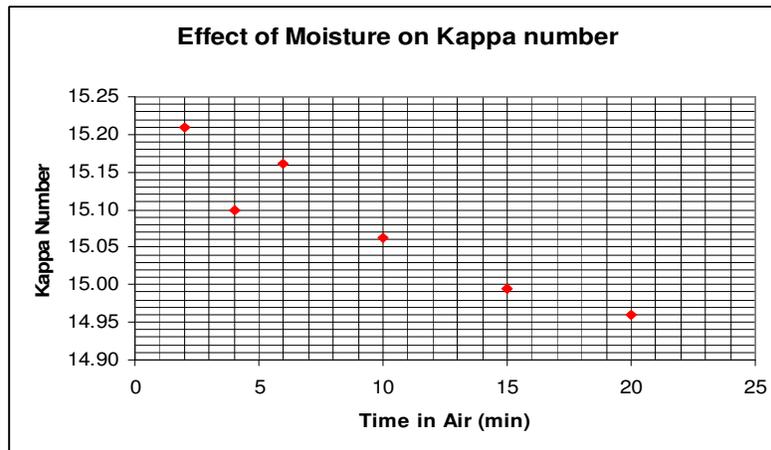
1. At the beginning of each day, purge the burets and pumps. Also, replace the stationary rinse and storage solutions before any samples are run. The redox electrode can be cleaned by emptying the fill solution with the supplied pipette, quickly rinsing it with deionized water, then refilling it with the 4 M KCl fill solution. All reagent bottles should be checked daily to ensure that they are full.
2. For better results, two blanks should be run at the beginning of each run. Based on our analysis, the first blank is usually different from all other blanks, mainly due to “warm up” of the system. Two blanks are run in succession and only the data from the second blank is used in the calculations.
3. When the system will not be used for a long period of time such as over a weekend, run air through the pumps to help ensure the longevity of your system.
4. Potassium permanganate and potassium iodide should be stored in amber bottles due to light degradation. Opaque tubing should also be used for the potassium iodide. Users may want to cover the bottles and the potassium permanganate buret for extra protection from the light.
5. The samples must be at 25°C for accurate results. Temperature and Kappa number are proportional as seen below.



6. The reaction time prior to KI addition must be kept at 10 minutes for standard results. Wait time and Kappa number values are proportional as seen below.



7. If samples are oven-dried and many samples are run together, all samples should be weighed at the same time to ensure that the weight is all from pulp and not from accumulated moisture in the air. If samples contain varying amounts of moisture, reported kappa numbers will be altered as seen below.



8. It is recommended that the tubing and the tip carrying the potassium permanganate are rinsed at least once each month to prevent them from becoming blocked. To do this, run deionized water through the tip and tubing and allow the water to drain. Reconnect the tubing and purge the buret twice with potassium permanganate before running samples.
9. The data compiled in this application note was determined by analyzing the Kappa of an oven dried sample. In a mill location (or any laboratory looking to follow Paprican prescribed methods for Kappa²), customers may choose to analyze air dried samples for Kappa. A correction can then be calculated to provide an oven dried weight and obtain better repeatability in a mill setting.
10. The various procedures for Kappa number analysis (steps 14-24 in the Procedure section), differ slightly based on stirring speeds designed to help ensure homogenous samples. All other procedural steps remain identical.

¹ <http://www.rfu.org/KraftPulp.htm>

² PAPTAC Standard Testing Methods. *Pulp & Paper Technical Association of Canada*. Montreal, Canada. Kappa Number of Pulp, pg 1-2.

³ Li and Gellerstedt, NPPRJ 13 (2), 147-152, 1998

⁴ Jiang, Zhi-Hua; Audet, Andre; van Lierop, Barbara; Berry, Richard; Menegotto, Robert. Kappa number with better repeatability and at a lower cost. *90th Annual meeting, PAPTAC*. Montreal, Canada, Preprint Book C, p.111-115, 2004