LARISSE APARECIDA RIBAS BATALHA

ESTUDO COMPARATIVO DE PRODUÇÃO DE POLPA SOLÚVEL A PARTIR DE BAMBU E EUCALIPTO

Dissertação apresentada à Universidade Federal de Viçosa, como parte das exigências do Programa de Pós-Graduação em Agroquímica, para obtenção do título de *Magister Scientiae.*

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APROVADA: 26 de julho de 2011.

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RESUMO

BATALHA, Larisse Aparecida Ribas, M.Sc., Universidade Federal de Viçosa, julho de 2011. **Estudo comparativo de produção de polpa solúvel a partir de bambu e eucalipto.** Orientador: Jorge Luiz Colodette. Coorientadores: Luiz Claúdio de Almeida Barbosa e Célia Regina Alvares Maltha.

O aumento do consumo de papel tem causado escassez dos recursos florestais. Isso aliado com questões ambientais tem levado a pesquisa de matérias-primas alternativas para indústria de celulose e papel. Dentre as espécies estudadas, tem-se considerado o bambu como a matéria-prima mais promissora, especialmente em virtude da sua abundância, de seu crescimento rápido e da sua composição química adequada, que se assemelha à da madeira. Por outro lado, os altos custos do linter de algodão e da madeira aliado as restrições ambientais causaram aumento significativo no custo da produção de polpa solúvel a partir destas matérias-primas. Portanto, é necessário avaliar novas fontes de fibra para a fabricação desse tipo de polpa. Neste contexto, o bambu aparece como uma fonte alternativa para indústrias de celulose e papel. Portanto, esse trabalho avaliou cavacos comerciais de bambu como matéria-prima para produção de polpa solúvel. A pré-hidrólise foi usada como tratamento inicial do bambu para produção de polpa de dissolução. Foram realizadas cinco tratamentos com pH inicial igual a 1,5; 2,0; 2,5 e 6,9 em cavacos normais e outro em pH inicial igual a 2,5 em cavacos previamente tratados (70 ºC, 60 min e pH=2,5) para remocão de cálcio A temperatura e relação licor/madeira usadas foram as mesmas para as cinco pré-hidrólises. Os cavacos de bambu pré-hidrolisados na condição selecionada (auto-hidrólise) passaram por uma etapa de polpação NaOH/AQ e a polpa obtida foi branqueada utilizando a sequência: O-CCE-D-(EP)-D-P. A sigla CCE designa uma etapa de extração caústica a frio. Foi possível produzir polpa solúvel de boa qualidade a partir dos cavacos de bambu, comparativa àquela produzida a partir de cavacos de eucalipto, mesmo considerando-se que a química dos cavacos de bambu não era inteiramente favorável (22,4% de lignina; 19,5% de xilana; 49,3% de celulose; 16,8% de extrativos totais e 1,5% de cinzas). A polpa produzida apresentou alvura de 92,4% e teores de α-celulose, de xilanas, de extrativos e de cinzas de 94,9%, 5,1%, 0,041% e 0,13%, respectivamente. A polpa solúvel com estas características é adequada para a fabricação de viscose com vistas à produção de fios de raiona e outros derivados de menor exigência quanto ao teor de alfa-celulose.

ABSTRACT

BATALHA, Larisse Aparecida Ribas, M.Sc., Federal University of Viçosa, july of 2011. **Comparative study of production of soluble pulp from bamboo and eucalyptus**. Advisor: Jorge Luiz Colodette. Co-advisor: Luiz Claúdio de Almeida Barbosa and Célia Regina Alvares Maltha.

The increase of paper consumption has caused scarcity of forest resources. This coupled with environmental issues have led to research alternative raw materials for pulp and paper industry. Among the species studied, we have considered the bamboo as the most promising raw material, especially because of its abundance, its fast growth and of its adequate chemical composition that is similar to wood. On the other hand, the high cost of cotton linter and wood combined with environmental constraints caused a significant increase in the cost of pulp production from these soluble materials. Therefore, it is necessary to evaluate new sources of fiber for making this. In this context, bamboo appears as an alternative source for pulp and paper. Therefore, this work evaluated commercial bamboo chips as raw material for dissolving pulp production. The pre-hydrolysis was used as the first treatment of bamboo materials for the production of soluble pulp. It was carried out five treatments with initials pH equal to 1.5; 2.0; 2.5 and 6.9 (in H_2O without acidification- auto-hydrolysis); and other pre-hydrolysis in initial pH equal to 2.5 with a pretreatment in bath under the following conditions: 70 ºC and 60 min, pH= 2.5. The temperature and liquor/wood ratio were the same for five pre-hydrolysis. The prehydrolised bamboo chips at chosen condition (auto-hydrolysis: AH) went through a stage of NaOH/AQ pulping and the pulp obtained was bleached by sequence: O-CCE-D-(EP)-D-P. The CCE designates a cold caustic extraction stage. It was possible to produce good quality soluble pulp from the bamboo chips, comparative to that produced from eucalyptus chips, even considering that the chemistry of bamboo chips was not entirely favorable (22.4% lignin, 19.5% xylan, 49.3% cellulose, 16.8% of total extractives and 1.5% ash). The produced pulp showed the brightness of 92.4% and contents of α-cellulose, xylans, extractives and ashes of 94.9%, 5.1%, 0,041% and 0.13%, respectively. The soluble pulp with these characteristics is suitable for the fabrication of viscose aiming to the production of rayon wires and other derivatives of lower requirement on the content of alpha-cellulose.

1. INTRODUCTION

Dissolving pulps require high degree of purity. They are used for production of cellulose derivatives such as cellulose acetate, cellulose nitrate, viscose, rayon, methyl cellulose, carboxymethylcellulose among others. The overall fiber line yield for dissolving pulp production rarely exceeds 30–35% and compared to regular paper pulp their production costs are quite high. These pulps contain a high alpha-cellulose content (95–98%) and relatively low hemicelluloses (1–10%) and lignin (<0.05%) contents (Christov et al. 1998).

Dissolving pulps are produced from cotton linters (soda pulping) and from wood *via* the pre-hydrolysis Kraft and acid sulfite pulping processes (Barba et al. 2002). Wood pulps, especially those derived from the sulfite process, require a subsequent hemicellulose removal step; this is usually done through the so-called cold caustic extraction (CCE), which is performed during the bleaching operation. The current high costs of wood and cotton linters combined with environmental constraints against standard bleaching (chlorine and hypochlorite) have caused a significant increase in the cost of dissolving pulp derived from these raw materials. Therefore, it is appropriate to evaluate new sources of fiber for the manufacture of dissolving pulp.

In this context, bamboo appears as an alternative source for pulp and paper industries, particularly in the tropical areas of the world. Bamboo is the vernacular or common term for members of a particular taxonomic group of large woody grasses (subfamily Bambusoideae, family Andropogoneae=Poaceae). Bamboos encompass 1250 species within 75 genera, most of which are relatively fast-growing, attaining stand maturity within five years, but flowering infrequently (Scurlock et al. 2000). As an industrial raw material, bamboo has been used to produce both cellulosic fibers for paper and starch granules for saccharification and production or ethanol. Other potential applications include bamboo shoots for food and culms for production of charcoal (Beraldo and Azzini 2004). In general, the alpha-cellulose content in bamboo is 40-50%, which is comparable with the reported alpha-cellulose contents of softwoods (40-52%) and hardwoods (38-56%) (Dence 1992). Undoubtedly, bamboo is a potential alternative source of raw material for dissolving pulp production.

The auto-hydrolysis step has been commercially applied in the so-called pre-hydrolysis kraft pulping process, which produces dissolving pulp as a product (Liu et al. 2010). The introduction of auto-hydrolysis prior to any alkaline pulping process helps to produce pulp with a satisfactorily high content of alpha-cellulose and with low hemicellulose content, resulting from the destruction or degradation of hemicelluloses (Behin and Zeyghami 2009).

Recent literature (Liu et al. 2010) showed that the hemicelluloses may be extracted from the auto-hydrolysis liquor through its acidification and subsequent addition of ethanol, enabling the use of hemicellulose for the production of several value-added products such as biofuels, chemicals and materials. The black liquor derived from the pre-hydrolysis kraft process, which typically contains 30–34% of lignin is usually burnt to provide energy for mill operations, and to recover the cooking chemicals (Wallberg et al. 2005). A fraction of this black liquor can potentially be isolated and used as the starting material for a series of useful products, such as vanillin, phenols, benzene, dispersant, emulsifying and chelant agents, antioxidants, pesticides, fertilizers, vegetal charcoal, polymers, adhesives, concrete additives, component for resins, among others (Gargulak and Lebo 2000, Mussato et al. 2007).

In the biorefinery concept, the three main biopolymers, i.e., cellulose, hemicelluloses, and lignin, which are the dominant chemical constituents in lignocellulosic raw materials, are to be converted to the building blocks for biofuels, biochemicals and biomaterials (Saeed et al. 2010). In this context, recovery of hemicelluloses and lignin for using in these nobler purposes in dissolving pulp production is in line with the concept of biorefinery.

This study aimed at evaluating the feasibility of using bamboo to produce dissolving pulp with a vision of utilizing left over streams for manufacturing value added products. The results are compared with traditional eucalypt dissolving pulp production by the pre-hydrolysis Kraft process.

2. MATERIAL AND METHODS

2.1 Raw Material Preparation and Physical-Chemical Analyses

Depithed bamboo chips were provided by a paper pulp manufacturer located in the Brazilian Northeast. The eucalyptus chips were provided by a kraft pulp company located in the Brazilian Center East. The furnish of eucalyptus chips was comprised of 12, 9, 7 and 5 year old trees in the following proportion 8:47:28:17 w/w%. Both the bamboo and the eucalyptus chips were transported to UFV Pulp and Paper Laboratory, classified according to SCAN CN 40:94 standard procedures, dried to about 15% moisture and stored for further use. A fraction of the wood and bamboo chips were converted into sawdust, classified according to TAPPI T257-cm85 standard procedure, dried to 10% moisture and stored in glass jars. Bamboo and eucalyptus basic densities were measured on the chips whereas chemical analyses were done on the sawdust. Basic density, total extractives, ash, acid insoluble lignin, acid soluble lignin, lignin H:S:G ratio, and carbohydrates composition were measured according to TAPPI T258 om-94, TAPPI T264 cm-97, TAPPI T211 om-93, Gomide and Demuner (1986), Goldshmidt (1971), Lin and Dence (1992) modified, and Wallis *et al.* (1996), respectively. Total uronic acids, and acetyl groups were measured according to Scott (1979) and Solar et al (1987). The silica content of bamboo was measured according to TAPPI T245 cm-98 and the content of calcium, iron, manganese and magnesium of bamboo were determined by atomic absorption spectroscopy, according to the SCAN CM 38:96 procedures.

2.2 Pre-hydrolysis

The pre-hydrolysis stages for bamboo and eucalyptus were carried out in 7 liter M/K digester equipped with a heat exchanger, circulating pump and computer-controlled time and temperature, under the following conditions: 250 g chips, 4L/1kg liquid/fiber ratio, 170 °C maximum temperature, 90 min to maximum temperature, 15 min at maximum temperature, and initials pH equal to 1.5; 2.0; 2.5 and 6.9. One additional pre-hydrolysis treatment was done at initial pH of 2.5 on bamboo chips that were previously treated for calcium removal under the following conditions: 70 ºC, 60 min and pH= 2.5. For eucalyptus wood the pre-hydrolysis was carried out only at the initial pH of 6.9. In those cases where initial pH values were lower than 6.9, sulfuric acid was used to adjust the reaction pH. Bamboo and eucalypt chips obtained in pre-hydrolysis were characterized for their contents of carbohydrates, lignin, extractives, minerals, uronic acids, acetyl and uronic acid groups using the procedures previously described for the raw materials.

2.3 Cooking

After the pre-hydrolysis stage was completed, the digester was cooled to about 80 ºC and the residual liquor was drained and collected to determine its pH and the alkali requirement for raising the pH to 11. After removal of the residual liquor from the pre-hydrolyzed chips, the cooking liquor was added. The volume of pre-hydrolysis liquor retained by the chips was determined gravimetrically on the basis of the original feedstock dry weight; this determination was necessary to calculate the volume of cooking liquor to be injected into the system. The bamboo soda/AQ (sodium hydroxide/anthraquinone) cooking was performed under the following conditions: 30% active alkali (AA) on dry wood weight, 4L/1kg liquor/bamboo ratio, 162 ºC maximum temperature, 60 min to temperature, 45 min at temperature and 0.10% anthraquinone on dry wood weight. The eucalypt kraft (sodium hydroxide/sodium sulfide) cooking was performed under the following conditions: 17.4% active alkali, 35% sulfidity, 170 ^{o}C maximum temperature**,** 90 minutes to temperature and 90 min at temperature. After cooking completion, the spent liquor was drained and the cooked chips were thoroughly washed with tap water, the fiber separation was done in a 25 liter “hydrapulper”, and the pulp was screened using a laboratory 0.2 mm plate screener. Brown pulp obtained was characterized for their kappa number, viscosity and brightness, according to TAPPI T236 cm-85, T230 om-99 and T 525 om-92, respectively.

2.4 Bleaching

The bamboo AH-NaOH/AQ and the eucalypt AH-kraft pulps were bleached to full brightness with the O-CCE-D-(EP)-D-P and O/O-D-(EP)-D-D sequences, respectively, where: O=single-stage oxygen delignification, O/O= double-stage oxygen delignification without inter-stage washing, CCE=cold caustic extraction, D= chlorine dioxide bleaching, (EP)=oxidative extraction reinforced with hydrogen peroxide, P= hydrogen peroxide bleaching. Table 1 shows the conditions used for each bleaching stage.

The bleached pulps were characterized for their content of carbohydrates by high performance liquid chromatography (HPLC), according to the procedure described by Wallis *et al.* (1996). Pulp kappa number, viscosity, brightness, α-cellulose, ashes, and dichloromethane extractable contents were measured according to the Tappi procedures previously described. The content of metals of bamboo was determined by atomic absorption spectroscopy, according to the SCAN CM 38:96 procedures. The auto-hydrolysis, cooking and bleaching yields were measured gravimetrically.

Table 1. General bleaching conditions

Conditions	Bamboo Pulp						Eucalypt Pulp				
	O	CCE	D	(EP)	D	P	O/O	D	(EP)	D	D
Consistency (%)	10	12	12	12	12	12	10	10	10	10	10
Temperature, °C	105	40	60	80	80	80	95/100	55	90	75	75
Time, min	70	30	40	90	120	120	10/50	40	60	120	120
Pressure, kPa	600	-	-	-	-	-	500/350	-	-	-	-
O_2, kg/t	20	-	-	-	-	-	18/0	-	-	-	-
ClO_2 as Cl_2, kg/t	-	-	10	-	30	-	-	15.7	-	11	1.0
NaOH, kg/t	20	80	-	10	5.0	7.0	20/0	-	12.0	-	-
H_2SO_4, kg/t	-	-	10	-	-	-	-	5.0	-	-	0.5
$MgSO_4$, kg/t	1.5	-	-	1.5	-	-	1.5/0	-	1.5	-	-
H_2O_2, kg/t	-	-	-	3.0	-	3.0	-	-	3.0	-	-
Final pH	11.2	13.5	2.8	10.8	4.3	10.3	11.7	2.4	11.2	4.4	4.7

3. RESULTS AND DISCUSSION

3.1 Characterization of Raw Materials

The bamboo basic density was 553 kg/m^3 higher than that of the eucalypt wood (516 kg/m^3) evaluated. A high density is always favorable in pulp production because it increases pulp mill throughput, but may penalize pulping yield due to poor white liquor penetration when conditions are not properly optimized; the auto-hydrolysis treatment performed before cooking helps white liquor penetration significantly during the pulping operation. Therefore, the high density of the bamboo chips does not pose a significant problem for dissolving pulp production.

The chemical characteristics of bamboo and eucalyptus chips are presented in Table 2, where it is seen that bamboo glucans content (49.3%) is higher than that of eucalypt (47.9%). The bamboo xylan content (19.5%) was also higher than that of eucalypt (11.2%), and was compensated by its lower lignin content (22.4%); typically, lignin and xylan compensate each other in the chemical composition of biomass secondary wall, with the glucan content varying only slightly among different raw materials. The high glucan and xylan contents of bamboo turn this raw material interesting for production of dissolving pulp associated with subsequent use of the extracted xylan and xylan derivatives for biorefinery purposes. These can be recovered through collection and processing of the auto-hydrolysis liquor, after separation of the small fraction of lignin (Liu et al. 2010; Danielsson 2007). Bamboo showed very high extractive (16.2%) and mineral (1.5%) contents in relation to the eucalypt (4.1% extractives and 0.3% minerals). A large fraction of the extractives comes from starch but bamboo also presented high content of silica and calcium, 5500 ppm and 1821 ppm, respectively. The iron, magnesium and manganese contents were 299.4 ppm, 364.4 ppm, 9.6 ppm, respectively (Appendix 1). The high extractive and mineral contents is quite challengeable for dissolving pulp production. Besides causing a variety of operational problems (scaling, corrosion, pitch deposition, chemical degradation during bleaching, recovery boiler plugging, etc), minerals and extractives may cause severe difficulties during utilization of the dissolving pulp for production of cellulose derivatives, if not properly removed during the process.

Table 2. Quantitative chemical composition of *Bamboo and Eucalypt*, expressed in weight basis percentage of extractive free* dry raw materials.

Results	Glucan (%)	Xylan (%)	Galactan (%)	Arabinan (%)	Mannan (%)	Acetyl (%)	Uronic Acid (%)	Total Extractives** (%)	Ash** (%)	Total Lignin (%)
Bamboo	49.3	19.5	0.6	0.8	0.3	3.0	0.9	16.2	1. 5	22.4
Eucalypt	47.9	11.2	0.9	0.1	0.9	2.0	5.9	4.1	0.3	26.6

***** TAPPI T264 cm-97; **on total wood.

3.2 Pre-hydrolysis of Bamboo Chips

Biomass pre-hydrolysis aimed at removing some of its components is usually carried out at elevated temperature (150–180 ºC) with water or dilute (sulfuric acid or aqueous sulfur dioxide) for reaction times of up to about 2 h depending on the temperature (Behin and Zeyghami 2009). The pre-hydrolysis in water is, generally, referred as auto-hydrolysis and in mineral acid as acidhydrolysis. During the pre-hydrolysis in water acetyl groups are cleaved from the β-(1–4)-linked xylan backbone and the acetic acid released acts as a catalyst for the hydrolysis of glycosidic bonds. The resulting pH in the prehydrolyzate ranges between 3 and 4. The addition of a mineral acid catalyst will, of course, greatly increase the rate of solubilization of the xylan (Sixta 2006).

To determine the optimum pre-hydrolysis conditions for maximum removal of the xylans of bamboo, various pre-hydrolysis in different initial pH values were carried out. Some results obtained in the pre-hydrolysis are shown in Table 3.

Table 3. Bamboo chips pre-hydrolysis results

	Initial pH	Final pH	Hydrolysate solids (%)	Yield (%)
Pre-hydrolysis	1.5	2.0	7.4	67.7
	2.0	3.7	5.6	73.0
	2.5	4.3	4.4	81.5
	6.9	4.4	4.0	95.1

It was realized that the yield losses with decreasing pre-hydrolysis pH were reflected in increased hydrolysate solids content. Also, it was noticed that even for initial pH values lower than 2.5, it was found that final pH values were higher than the initial ones. The treatment at initial pH of 6.9 ended at pH 4.4. This drop in pH was anticipated since acetic acid is produced in the course of the pre-hydrolysis. In fact this pH value was expected to drop much more to a range of 3.0 as is usual for hardwood chips. Considering that the bamboo chips studied contained more acetyl groups than wood, a pH much lower than 4.4 should have occurred.

The large amount of Ca present in the bamboo (1821 ppm) may explain this less than ideal pH drop in the case of the pre-hydrolysis at initial pH 6.9, through formation of calcium hydroxide in reaction with water. Being a weak acid, the acetic would have no effect on reducing the pH of the treatments that started at pH 1.5, 2.0 and 2.5.

However the pH increase in these cases is difficult to explain. In order to determine the effect of calcium on the pH drop and, consequently, on the pre-hydrolysis efficiency, an attempt was made to remove calcium from the bamboo before the pre-hydrolysis treatment. The chips were treated with acid at mild conditions (70 ºC, 60 min and pH= 2.5). These chips depleted of calcium were prehydrolyzed at pH 2.5 under the same conditions used for the pre-hydrolysis of the original chips. With the calcium depleted chips the final pH was 3.8. This value is 0.5 units lower than the pre-hydrolysis in initial pH of 2.5 without pretreatment (pH 4.3), indicating that calcium does affect the drop of pH across the pre-hydrolysis and, consequently, the efficiency of the process. Metal analysis showed that the calcium content decreased 38.9% in the pretreatment plus pre-hydrolysis while the pre-hydrolysis alone reduced calcium content by only 24.6%. Consequently, the removal of acetyl groups, xylans, extractives, minerals and uronic acids during the pre-hydrolysis was more significant for the chips that were pretreated for calcium removal (Table 4). The lignin content increased (24.0%) and the yield (78%) decreased because of the more efficient xylan removal, which affected the mass balance.

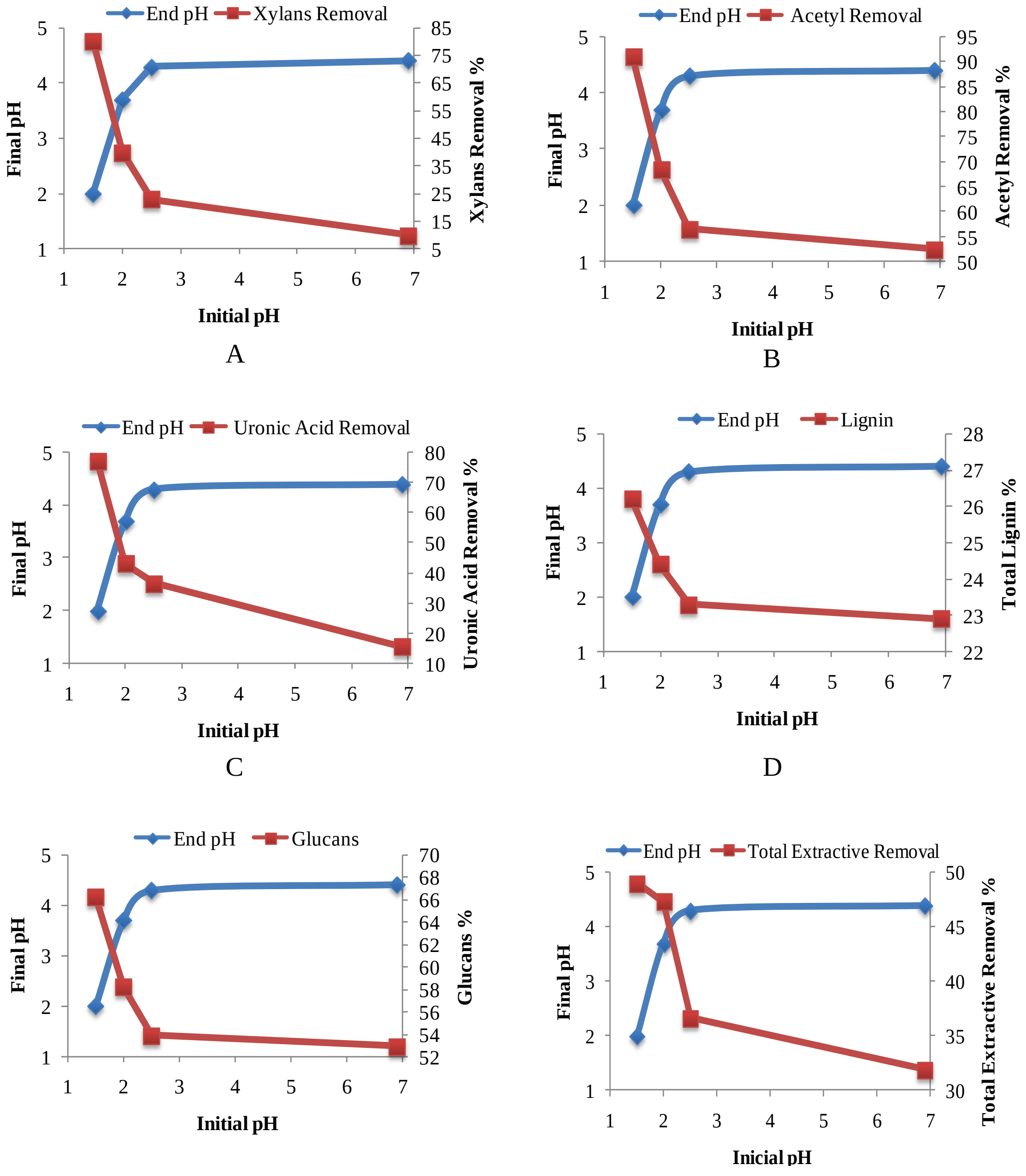
Table 4. Pre-hydrolysis at initial pH of 2.5 on regular Bamboo chips and chips pretreated for calcium removal.

Pre-hydrolysis	Yield (%)	Xylan Removal (%)	Acetyl Removal (%)	Uronic Acid Removal (%)	Total Extractives Removal (%)	Ash Removal (%)	Total Lignin (%)	Ca Removal (%)
Chips Pretreated for Ca Removal	78.0	31.2	61.0	39.4	40.8	70.4	24.0	38.9
Regular Chips	81.5	22.7	56.5	36.6	36.6	65.3	23.3	24.6

Figure 1A shows that decreasing initial pH favored xylan removal. The pre-hydrolysis in initial and final pH equal to 1.5 and 2.0, respectively, achieved the higher removal with almost 80%, decreasing from its original 19.5% to 5.8%. While the other pre-hydrolysis increased final pH around 1 point, that one increased 0.5 (Table 3), this is because the pre-hydrolysis in initial pH of 1.5 achieved 91% for acetyl group removal which by formation of acetic acid in middle it prevented a bigger increasing of final pH, decreasing from its original 3.0% to 0.4%.

Figures 1B shows that acetyl groups removal increases with decreasing initial pH. It is worth noting that increasing initial pH over 2.5 had on a slight impact on end pH and acetyl group and xylan removal (Figs 1A and 1B). Uronic acid removal was rather significant up to the initial pH of 2.5, and continued up to the initial pH of 6.9 (Fig. 1C). A 75% uronic acid removal was achieved at the 1.5 initial pH. The removal of uronic acid groups is important for dissolving pulps because they may cause pulp brightness instability after being converted into hexenuronic acids during Kraft pulping (Sixta 2006).

Figure 1D shows the effect of pre-hydrolysis initial pH on bamboo total lignin content. The original material contained 22.4% total lignin and its content increased with decreasing pre-hydrolysis initial pH up to 2.5. The increase in lignin content is explained by the decrease in xylan content, which affected the total mass balance and the relative lignin content. Obviously, there is no absolute increase in the bamboo original lignin content.



A B C D E F

Figure 1. Effect of pre-hydrolysis pH on xylan removal (A), acetyl groups removal (B), uronic acids removal (C), total lignin (D), glucans (E) and total extractive removal (F) from bamboo chips.

The Figure 1E shows the effect of pre-hydrolysis initial pH of bamboo glucans content. The original bamboo contained 49.3% glucans, and its content increased with decreasing pre-hydrolysis pH from 2.5 to 1.5. The glucans increase occurs as a consequence of xylan, mineral, uronic acid, and acetyl group removal, which in turn negatively affected the process yield. The lowest pre-hydrolysis yield (67.7%) occurred at initial pH of 1.5.

The pre-hydrolysis initial pH also affected extractives removal (Figure 1F). The extractives removed during the pre-hydrolysis consist, mainly, of substances soluble in hot water. These included tannins, gums, sugars, pigments, and starches (Liu 2004). In some bamboo species the starch content may reach 10%. Since starches are hydrolyzed in acid medium, it is believed that the increasing in extractive removal with decreasing initial pH is due mainly to starch removal. The extractive removal during pre-hydrolysis is desirable to minimize active alkali demand during the subsequent kraft pulping and improving white liquor impregnation. The highest extractive removal was 49% (from 16.2 to 12.2%).

The presence of certain inorganic compounds such as silicates, Ca salts, and catalytically active transition metal ions (Fe, Mn, Co, etc.) clearly impairs the filterability and spinnability of a cellulose spinning dope (e.g., viscose or lyocell type of fibers). Moreover, pulp contamination with inorganic compounds leads to a gradual clogging of the spinnerets, and this alters the uniformity of the fiber titer (Sixta 2006 b). So, mineral removal before pulping and bleaching processes is very important for dissolving pulp production processes.

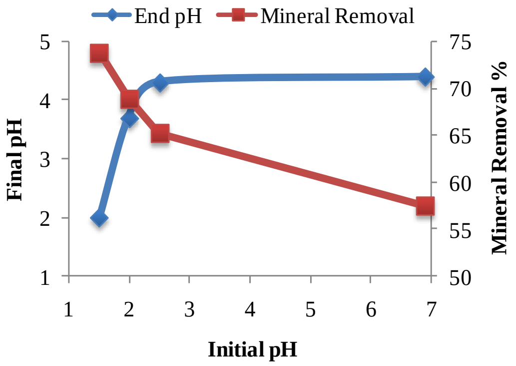
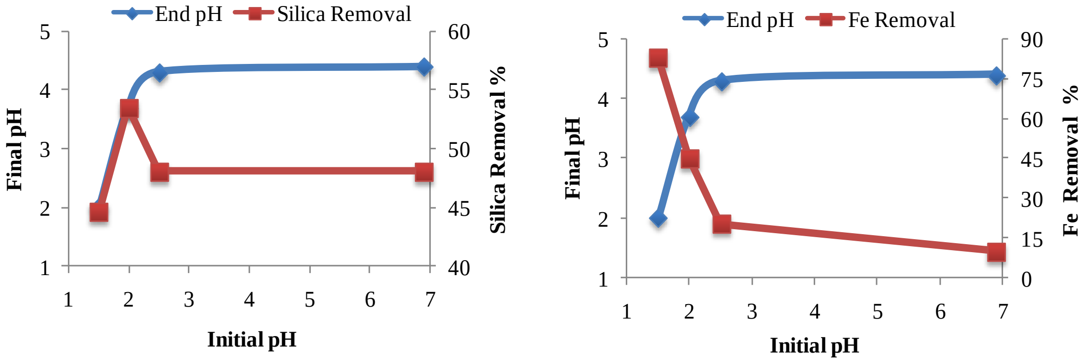


Figure 2. Effect of pre-hydrolysis pH on mineral removal from bamboo chips.

The bamboo mineral removal in the pre-hydrolysis increased with decreasing initial pH (Figure 2). A 73.8% removal (from 1.5 to 0.58%) was achieved at the initial pH of 1.5. This result was expected since minerals solubility increases with decreasing reaction pH; the only exception being for silica and silicates, which are more soluble under alkaline reaction conditions. Minerals may deposits in the digester during the pulping process, decreased pulp brightness stability and viscosity, chemicals decomposition, corrosion and scaling during bleaching. The minerals originate mainly from a variety of salts deposited in the fiber cell wall and lumen. Typical deposits are various metal salts, such as carbonates, silicates, oxalates, and phosphates (Sjöstrom 1993). The mineral content of bamboo is made up of inorganic minerals, primarily silica, calcium, and potassium. Manganese and magnesium are two other common minerals (Liu 2004). The metal cations are linked to the carboxyl groups of the wood components. As the pre-hydrolysis pH is lowered, most of these groups become protonated, which leads to the release of metal ions (Lindgren et al. 2002). Another factor that contributes to the removal of minerals at acid pH is metal salts dissolution.

Silica content in bamboo is higher in the epidermis, with very little in the nodes and absent in the internodes (Liu 2004). Figure 3A shows no relationship between pH of pre-hydrolysis and silica removal. When the operation of chipping bamboo is performed, crystals of silica are released from the cell wall, forming a dust. This represents part of the silica losses observed in most pre-hydrolysis treatments. During the washing of the chips resulting from of pre-hydrolysis, part of the silica may be leached with water, reducing the silica content, regardless of initial pH.

Transition metals may decompose hydrogen peroxide into water and oxygen due to their ability to change the oxidation state. The most reactive metals in the bleaching process are iron, manganese and copper (Devenyns et al. 1995). The relationship between iron removal and pre-hydrolysis initial pH is shown in Figure 3B. Iron removal increases with decreasing initial pH, reaching a maximum of 82.8% removal (from 299.4% to 76.0%) at the pH of 1.5. The pre-hydrolysis at initial pH of 6.9 removed only about 10% of the iron. The low iron removal at the higher pH range is explained by the strong bonds of this metal to wood components as reported by other authors (Colodette and Dence 1989). Thus, a strong acid medium is required to break the complexation and warrants sufficient iron removal.



A B

Figure 3. Effect of pre-hydrolysis pH on silica (A) and iron (B) removal from bamboo chips.

Calcium causes incrustation in various sectors of pulp and paper mill. Magnesium can also cause incrustation, but its presence in bleaching with oxygen and hydrogen peroxide is positive since it minimizes the degradation of carbohydrates. It is believed that the Mg precipitates with hydroxides, which absorbs other metal ions or form a complex with them, turning them unavailable to catalyze the decomposition of peroxide (Moreira 2006).

The highest removal of magnesium was also at the initial pH of 1.5, with 90.5% (Figure 4A). Magnesium minimizes the degradation of carbohydrates during pulp bleaching, but its removal is desirable to improve the dissolving pulp quality. The removal of manganese was around 87% at an initial pH of 1.5 and decreased with increasing pre-hydrolysis pH (Fig. 4B). Manganese has a negative effect on bleaching since it catalyzes the decomposition of oxygen-based reagents. The calcium removal was significant in the pre-hydrolysis at the initial pH 1.5, with almost 70% of removal (Figure 4C). High calcium concentrations favor scaling and corrosion during pulping and bleaching operations, in addition to their negative effect on dissolving pulp derivatives filterability and spinnability and loss of resistance of the wire.

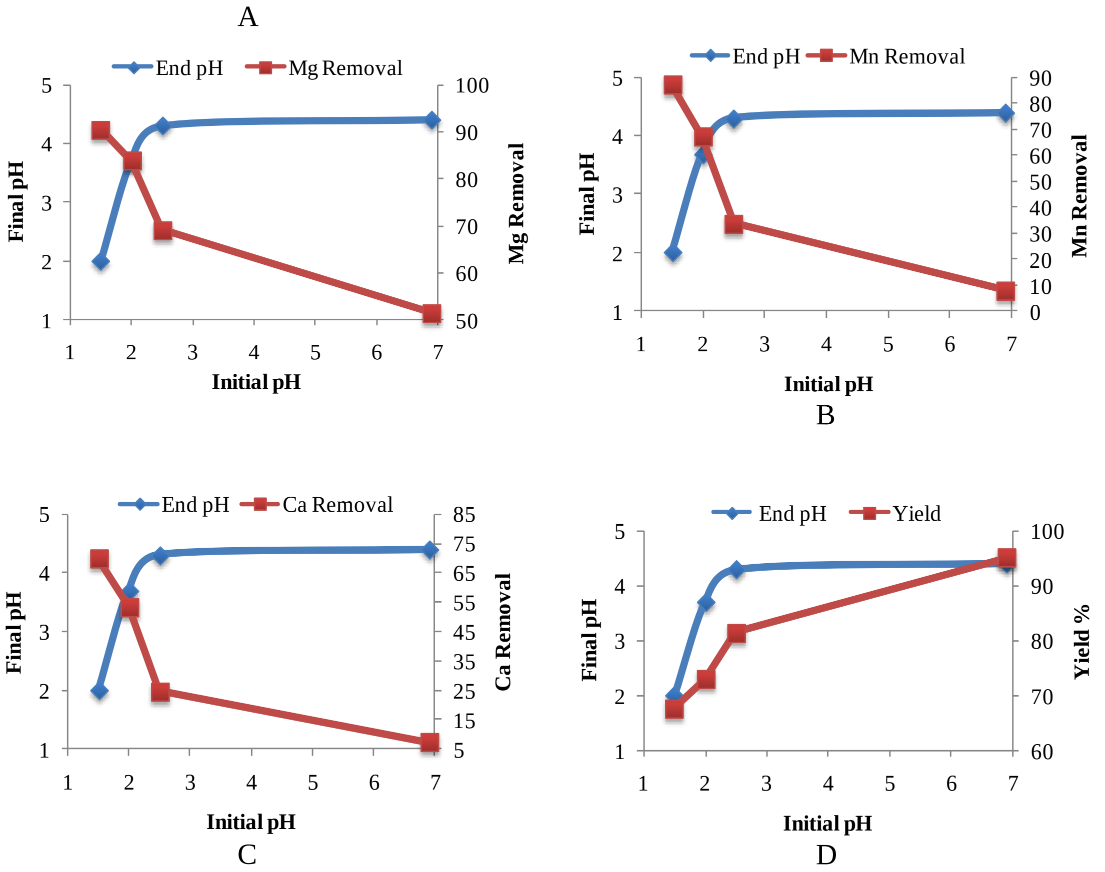


Figure 4. Effect of pre-hydrolysis initial pH on magnesium removal (A), manganese removal (B), calcium removal (C), and yield (D) from bamboo chips.

The Figure 4D represents yield loss with decreasing pre-hydrolysis pH. The overall fiber line yield for dissolving pulp production rarely exceeds 30–35% (Christov et al. 1998). Therefore, the yield of pre-hydrolysis should be used as the main factor to determine which treatment is chosen. The most efficient treatment for the removal of xylan and metals was the pre-hydrolysis at the initial pH of 1.5, but at this pH yield was only about 68%. On the other hand, the pre-hydrolysis at pH 6.9, in fact an auto-hydrolysis, showed the lowest removal of the bamboo components and, consequently, the highest yield. In addition, this treatment resulted in low environmental impact and lignin re-polymerization was largely avoided due to absence of mineral acids in the reaction system (no acid addition), which makes it an attractive for dissolving pulp producers. Thus, this work proceeded with the auto-hydrolysis treatment at an initial pH of 6.9 in order to produce dissolving pulp from bamboo.

3.3 Bamboo *versus* Eucalyptus Chip Auto-hydrolysis

The auto-hydrolysis (AH) treatment resulted in significant xylan removal for both bamboo and eucalypt, with the process being more effective for the latter. The bamboo xylan content decreased by 9.9%, from its original 19.5% in the wood to 18.5% in the AH chips taking into account the 5% yield loss, whereas the eucalypt xylan decreased by 29.4%, from 11.2% in the wood to 8.9% in the AH chips, taking into account the 11.1% yield loss (Table 5). The auto-hydrolysis of bamboo was less effective to remove xylans than the eucalypt one even though the bamboo acetyl group content was higher than that of eucalypt. This fact may be explained by bamboo high extractives and mineral contents (particularly starch and calcium), which prevented the natural pH drop of the reaction system, which is typical of auto-hydrolysis reactions; the end pH reached 4.4 only while the expected would have been 2.5-3.0. On the other hand the significant amount of starch existing in the bamboo chips may have hindered chip impregnation in the auto-hydrolysis. Another explanation is the more condensed nature of the bamboo lignin which may have impaired the xylan release since xylan is linked to lignin. The bamboo and eucalypt lignin H:S:G ratio were 1:2:2.1 and 0.1:2:1, respectively. The AH treatment increased bamboo and eucalypt lignin content from their original 22.4 and 26.6% to 23.2 and 27.6% in the hydrolyzed chips, respectively. This increase in explained by the partial removal of xylans which altered the relative mass balance in both feedstocks. It was obtained a total lignin removal of 1.5% and 7.8% for bamboo and eucalypt, respectively.

Table 5. *Bamboo* and *Eucalypt* chip auto-hydrolysis (AH) results.

AH Results	Yield (%)	Xylans (%)	Xylans Removal (%)	Lignin (%)	Spent liquor pH	Total Lignin Removal (%)
Bamboo	95.1	18.5	9.9	23.2	4.4	1.5
Eucalypt	88.9	8.9	29.4	27.6	2.8	7.8

3.4 Pulping Results

In order to cook the auto-hydrolyzed bamboo and eucalypt chips to kappa number 11.2 and 17.4, respectively, alkali charges of 30% and 17.4% as NaOH were required (Table 6). Pulp viscosity was quite satisfactory for both bamboo and eucalypt, with a higher value for the wood, reflecting its lower active alkali requirement.

Table 6. Kraft pulping results for auto-hydrolyzed *Bamboo* and *Eucalypt* chips (from Table 2)

Cooking Results	AA (%) NaOH	Kappa No.	Pulping Yield (%)	AH + Pulping Yield (%)	Pulp Viscosity (mPa.s)	Xylans (%)	BLS (%)
Bamboo	30	11.2	43.4	41.2	46.8	8.4	16.5
Eucalypt	17.4	17.4	44.6	40.5	61.1	3.3	15.3

The cooking screened yields were determined on the basis of the auto-hydrolyzed wood chip weight and they were 43.4% and 44.6% for bamboo and wood, respectively. Hence, the xylan removal from raw material by AH significantly decreased subsequent kraft pulping yield. For bamboo, screened yields of 45-46% have reported for the same kappa number range used in this work (Vu et al., 2004 and Guo et al., 2010). For the eucalypt Santiago and Neto (2007) found a screened yield of 56.0% for target kappa number in this study. The overall yield, including auto-hydrolysis (AH) plus pulping were 41.2% and 40.5% for bamboo and eucalypt, respectively. The low stability of the carbohydrates remaining in the raw materials after the AH treatment towards kraft cooking may be explained by two factors: (1) the xylans remaining in the auto-hydrolyzed chips are very sensitive to kraft cooking conditions because they are severely degraded, possessing very low molecular weight and high concentration of reducing end groups and thus very sensitive to alkali; (2) the cellulose chains become more susceptible to kraft cooking because the xylan layer existing over the cellulose fibrils is partially removed exposing the cellulose to alkali attack with consequent decrease in MW and increased polydispersity (Colodette et al. 2011). The xylan retained in the pulps derived from bamboo and eucalypt were 8.4% and 3.3%, respectively, after the pulping operation.

The eucalypt pulp containing only 3.3% xylan can be used for dissolving pulp applications grades after bleaching. However, the bamboo pulp containing 8.4 % xylans finds little application in the dissolving pulp industry due to its high xylan content, in spite of the harsh pulping conditions used. For this pulp a subsequent xylan removal step is required during the bleaching operation.

3.5 Oxygen Delignification and Bleaching

The oxygen delignification efficiencies of pulps derived from auto-hydrolyzed bamboo and eucalypt chips were 66.1% and 66.7%, respectively. The oxygen delignification efficiency is calculated on the basis of kappa number before and after the oxygen stage. The viscosity drop was higher for the bamboo pulp and resulted in lower oxygen stage selectivity for this pulp. The brightness out for the bamboo was comparable to eucalypt. In general, the performance of the oxygen delignification was quite high for both pulps if compared, for example, with conventional kraft pulps derived from wood. The Table 7 shows the results obtained for oxygen delignification.

The oxygen delignified pulps derived from bamboo and eucalypt AH chips were further bleached to ≥92% ISO brightness with the CCE-D-(EP)-D-P and D-(EP)-D-D sequences, respectively (Table 8). A fixed kappa factor was applied in the first chlorine dioxide stage and variable chlorine dioxide doses were applied in the second D-stage. The total chlorine dioxide dose required to produce full brightness was calculated by the sum of the ClO_2 applied in the D_0 Stage (kappa factor) plus the optimum ClO_2 dose obtained in the D_1 stage, which produced the target brightness. More detailed information about the operating conditions used in each bleaching stage is given in Table 1 and in the footnotes of Table 8. The brightness obtained for the bamboo (92.4%) was similar to that of acetate grade wood pulp (92.7%) reported in literature (He et al. 2008).The total active chlorine demand was higher for the bamboo pulp (52.5 kg/odt pulp) in relation to that for the eucalypt one (34 kg/odt pulp).

Table 7. Oxygen delignification performance for pulps derived from *Bamboo* and *Eucalypt* auto-hydrolyzed (AH) chips

Oxygen Delignification Results	Kappa drop (%)	Viscosity drop (%)	Brightness out (% ISO)	Selectivity*
Bamboo	66.1	62.2	47.2	1.1
Eucalypt	66.7	50.2	47.1	1.3

*Selectivity=kappa drop (%)/viscosity drop (%)

Note that the bamboo pulp had a kappa number of 3.8 after oxygen delignification while that of the eucalypt had a kappa of 5.8. Hence, the higher active chlorine demand of the bamboo pulp in relation to the eucalypt one can only be explained assuming that bamboo lignin is more condensed, particularly that fraction coming from *p*-hydroxyphenyl type lignin, which was significant in this bamboo sample (H:S:G = 1:2:2.1). The yield loss across bleaching was higher for the bamboo pulp. The bamboo pulp also presented lower brightness stability and viscosity than the eucalypt one. The low viscosity (6.2 mPa.s) of the bleached bamboo pulp somewhat limits its applications for certain dissolving grades applications such as acetate and nitrate; but it could be useful for production of viscose rayon and CMC derivatives. According to Henriksson et al. (2005) and Kvarnlöf et al. (2006) during the viscose process it is necessary to decrease pulp viscosity to values in the range of 200–300 dm^3/kg or 3.5–4.5 mPa.s via a pre-aging stage, since a high viscosity affects the cellulose process ability. Considering that the largest viscosity loss of the bamboo pulp occurred in the oxygen delignification stage, the use of magnesium in such stage could mitigate the problem to some extent. The eucalypt pulp viscosity (16.3 mPa.s) is quite acceptable for most dissolving pulp applications.

The CCE stage was included in the bleaching of bamboo pulp in order to meet the low hemicelluloses and extractives requirements of such pulps. The efficiency of conversion of cellulose into specific derivatives is dependent upon hemicelluloses content of the dissolving pulp (Christov et al. 1998). Hemicelluloses are undesirable impurities in dissolving pulps, affecting the cellulose processability, e.g. the filterability and the xanthanation in the viscose process, and properties of the cellulose- end products such as the viscose strength (Christov and Prior 1993). In this study, a bamboo bleached pulp containing 5.1% xylan was achieved (Table 8), a value which is acceptable for many dissolving pulp applications (Christov et al. 1998).

The mineral content of the bleached bamboo pulp were within acceptable levels. For example, Barba et al. (2002) showed that carboxymethylcellulose (CMC) can be produced from non-wood dissolving pulps an ash content about six times greater than the one found for the bamboo pulp of this work. A detailed study (Table 9) of the bamboo ash showed that it is mainly comprised of calcium, iron, manganese, copper and silica. The α-cellulose content (94.9%) is in agreement with the values (>90%)

reported in the literature for viscose grade pulps (Christov et al. 1998; Behin and Zeyghami 2009) and 90-99% (Ibarra et al. 2010).

The dichloromethane (DCM) extractive content of bamboo pulp obtained was 0.041% (Table 9). Recent literature (He et al. 2008) found that DCM extractive content for acetate and viscose grade bamboo pulp were 0.08% and 0.22%, respectively. This shows that the proposed cooking e bleaching method, including a CCE stage, was effective in achieving suitable pulp extractive levels for dissolving applications.

4. CONCLUSIONS

The chip auto-hydrolysis process applied to dissolving pulp production improves the xylan removal but decreases pulp yield. The AH-NaOH/AQ pulping process and the O-CCE-D-(EP)-D-P bleaching sequence proved suitable for production of dissolving pulp from bamboo and resulted in bleached pulp of 94.9% α-cellulose, 92.4% brightness, 6.2 mPa.s viscosity, 5.1% xylans, 0.04% DCM extractives and 0.13% ash, which are acceptable specifications for many dissolving grade pups. The low viscosity limits the applications of the bamboo pulp for certain dissolving grades applications such as acetate and nitrate; but it is useful for production of viscose rayon and CMC derivatives. When compared to eucalypt dissolving pulp, the bamboo pulp is of slightly lower quality and its production is more costly. The use of a mineral acid in the auto-hydrolysis, converting it into an acid pre-hydrolysis is effective for bamboo xylan removal but result in very low fiber line yield.

Table 8. Bleaching and pulp quality results for *Bamboo* and *Eucalypt* dissolving pulps.

Conditions	Bamboo Pulp						Eucalypt Pulp				
	O	CCE	D_0	(EP)	D_1	P	O/O	D	(EP)	D_1	D_2
Reagent Consumed, %	-	-	98.4	100	99.3	100	-	100	100	100	100
Kappa Number	3.8	3.5	-	-	-	-	5.8	-	1.2	-	-
Brightness, % ISO	47.2	45.4	71.7	81.1	91.5	92.4	50.5	74.7	84.9	91.3	92.0
Brightness Reversion, % ISO	-	-	-	-	-	2.4	-	-	-	-	1.5
Viscosity, mPa.s	17.7	23.3	-	6.9	6.8	6.2	30.4	-	20.5	19.4	16.3
Yield, %	-	-	-	-		92.7	-	-	-	-	95.6
Xylans, %	-	-	-	-	-	5.1	-	-	-	-	-
Alpha-Cellulose	-	-	-	-	-	94.9	-	-	-	-	-
Ash, %	-	-	-	-	-	0.13	-	-	-	-	-
Ca, ppm	-	-	-	-	-	277	-	-	-	-	-
Fe, ppm	-	-	-	-	-	25.5	-	-	-	-	-
Mn, ppm	-	-	-	-	-	1.7	-	-	-	-	-
Si, ppm	-	-	-	-	-	24	-	-	-	-	-
Dichloromethane Extractable, %	-	-	-	-	-	0.041	-	-	-	-	-
[1]Total Active Chlorine, kg/bdt	52.5						34				
[2]Yield loss, %	7.3						4.3				

*__Bamboo: D_0-stage__:12% consistency, 60°C, 40 min, Kappa Factor 0.20, 2.8 end pH and 10 kg/bdt; **D_1-stage**:12% consistency, 80°C, 120 min, 4.5 end pH and 10, 15, 20 and 30 ClO_2; **Eucalypt: D_1-stage**:10% consistency, 75°C, 120 min, Kappa Factor 0.27, 4.5 end pH; **D_2-stage**:10% consistency, 75°C, 120 min, 4.5 end pH and 1, 2, 4 and 6 kg/bdt ClO_2.

[1] Total active chlorine (kg/bdt) = ClO_2(kg/bdt)*2.63 + H_2O_2(kg/bdt)*2.09;

[2] Includes yield loss across oxygen delignification stage

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Appendix 1

Table 1. Chemical Analysis for Pre-hydrolysis bamboo

Sample	**Glucans (%)**	**Xylans (%)**	**Galactans (%)**	**Mannans (%)**	**Arabinans (%)**	**Soluble Lig. (%)**	**Insoluble Lig. (%)**	**Total Lignin (%)**	**Uronic acid (%)**	**Acetyl (%)**	**Total Extractive (%)**	**Ash (%)**
Bambu original	49.2	19.7	0.6	0.2	0.7	0.8	21.5	22.3	0.9	3.0	16.2	1.5
	49.3	19.2	0.6	0.3	0.8	0.8	21.6	22.4	0.9	2.9	16.2	1.5
Average	49.3	19.5	0.6	0.3	0.8	0.8	21.6	22.4	0.9	3.0	16.2	1.5
Initial pH 6.9	53.2	18.6	0.4		0.6	0.8	22.3	23.1	0.7	1.5	11.4	0.69
	52.6	18.3	0.4		0.7	0.7	22.0	22.7	0.8	1.5	11.8	0.65
Average	52.9	18.5	0.4	ND	0.7	0.8	22.2	22.9	0.8	1.5	11.6	0.67
Initial pH 2.5 with pretreatment	56.3	17.3				0.5	23.7	24.2	0.7	1.5	12.5	0.58
	55.2	17.0				0.5	23.2	23.8	0.6	1.5	12.1	0.56
Average	55.8	17.2	ND	ND	ND	0.5	23.5	24.0	0.7	1.5	12.3	0.57
Initial pH 2.5	54.4	18.5				0.5	23.1	23.6	0.7	1.6	12.9	0.63
	53.4	18.4				0.5	22.5	23.0	0.7	1.6	12.3	0.64
Average	53.9	18.5	ND	ND	ND	0.5	22.8	23.3	0.7	1.6	12.6	0.64
Initial pH 2	58.6	16.3				0.3	24,0	24.3	0.7	1.3	11.4	0.64
	57.8	15.8				0.3	24.1	24.4	0.6	1.3	12.0	0.64
Average	58.2	16.1	ND	ND	ND	0.3	24.1	24.4	0.7	1.3	11.7	0.64
Inital pH 1.5	68.1	5.9				0.3	25.9	26.2	0.3	0.4	12.0	0.56
	64.2	5.7				0.3	26.3	26.6	0.3	0.4	12.4	0.59
Average	66.2	5.8	ND	ND	ND	0.3	26.1	26.4	0.3	0.4	12.2	0.58

Table 2. Chemical Analysis for Pre-hydrolysis bamboo

Sample	Fe (ppm)	Mg (ppm)	Ca (ppm)	Mn (ppm)	Si (ppm)
Bambu original	301.2	398.0	1823.2	9.6	6000
	297.5	330.7	1818.8	9.6	5000
Average	299.4	364.4	1821.0	9.6	5500
Initial pH 6.9	290.0	190.4	1782.2	8.9	3000
	276.8	181.1	1764.6	9.6	3000
Average	283.4	185.7	1773.4	9.3	3000
Initial pH 2.5 with pretreatment	281.0	94.9	1438.6	5.8	3000
	271.6	88.4	1415.6	5.8	3000
Average	276.3	91.7	1427.1	5.8	3000
Initial pH 2.5	288.8	136.3	1658.3	7.8	4000
	296.7	140.0	1709.5	7.7	3000
Average	292.8	138.2	1683.9	7.8	3500
Initial pH 2	222.9	81.7	1117.1	4.3	4000
	227.0	79.9	1204.6	4.2	3000
Average	224.9	80.8	1160.8	4.3	3500
Inital pH 1.5	79.4	50.8	822.0	1.8	4000
	72.6	51.9	795.3	1.7	5000
Average	76.0	51.4	808.6	1.8	4500

Table 3. Pre-hydrolysis

Sample	Hydrolysate solids (%)	Final pH	Yield (%)
Initial pH 6.9	4.0	4.4	95.1
Initial pH 2.5 with pretreatment	5.0	3.8	78.0
Initial pH=2.5	4.4	4.3	81.5
Initial pH=2.0	5.6	3.7	73.0
Initial pH=1.5	7.4	2.0	67.7

Table 4. Pulping

Sample	Active Alkali, %	Kappa	Pulping Yield, %			PHK+ Pulping Yield, %	Viscosity, mPa.s	Xylans, %
			Screened	Rejects	Total			
Eucalypt	17.4	17.6	45.1	0,1	45.2	40.2		---
	17.4	18.2	45.2	0.2	45.4	40.4		---
	17.4	18.0	44.7	0.1	44.8	39.8		---
	17.4	16.0	45.0	0.0	45.0	40.0		---
	17.4	16.7	44.3	0.1	44.4	39.5		---
	17.4	16.2	44.7	0.1	44.8	39.8		---
	17.4	17.7	44.3	0.1	44.4	39.5		---
	17.4	17.7	44.3	0.1	44.4	39.5		---
	17.4	17.7	43.9	0.1	44.0	39.1		3.4
	17.4	17.7	43.9	0.1	44.0	39.1		3.2
	17.4	17.4	44.5	0.1	45.6	40.5	61.1	3.3
Bamboo	30.0	9.7	42.6	0.0	42.6	40.0		---
	30.0	12.5	44.3	0.0	44.3	42.2		---
	30.0	12.2	43.5	0.0	43.5	41.4		---
	30.0	11.0	44.0	0.0	44.0	41.9		---
	30.0	11.4	43.7	0.0	43.7	41.6		---
	30.0	11.2	43.0	0.0	43.0	40.7	46.9	8.23
	30.0	9.2	42.8	0.0	42.8	40.3	46.5	8.54
	30.0	11.2	43.4	0.0	43.4	41.2	46.8	8.38

Table 5. Bleaching- Eucalypt

Conditions and Results		Bleaching Stage						
	O/O	**D**	**EP**	**D_1**	**D_2**	**D_2**	**D_2**	**D_2**
Consistency, %	10	10	10	10	10	10	10	10
Temperature, ^{o}C	(95+100)	55	90	75	75	75	75	75
Time, min	(10+50)	40	(15+45)	120	120	120	120	120
Kappa factor	-	0.27	-	-	-	-	-	-
ClO_2 as Cl_2, kg/t	-	15.66	-	11	1	2	4	6
H_2O_2, kg/t	-	-	3	-	-	-	-	-
NaOH, kg/t	(20+0)	-	12.0	-	-	-	-	0.3
$MgSO_4$, kg/t	(1.5+0)	-	1.5	-	-	-	-	-
H_2SO_4, kg/t	-	5	-	-	0.5	0.3	-	-
O_2, kg/t	(18+0)	-	-	-	-	-	-	-
Pressure, kPa	500	-	-	-	-	-	-	-
Final pH	11.7	2.4	11.2	4.4	4.7	4.6	4.6	4.5
Reagent Consumed, %	-	100.0	100.0	100	100	100.0	100.0	100.0
Kappa number	5.8	-	1.2	-	-	-	-	-
Bleaching Yield, %	98.1				97.5			
Brightness, % ISO	47.1	70.4	83.0	91.8	92.0	92.2	92.5	92.9
Reversion, % ISO	-	-	-	-	1.5	1.7	1.6	1.6
Viscosity, mPa.s	30.4	-	20.4	19.4	16.3	-	-	-

Table 6. Bleaching- Bamboo

Conditions and Results	Bleaching Stage											
	O	CCE	D	(EP)	D	D	D	D	P	P	P	P
Consistency, %	10	12	12	12	12	12	12	12	12	12	12	12
Temperature, ^oC	105	40	60	80	80	80	80	80	80	80	80	80
Time, min	70	30	40	90	120	120	120	120	120	120	120	120
Kappa factor	-	-	-	-	-	-	-	-	-	-	-	-
ClO_2 as Cl_2, kg/t	-	-	10	-	10	15	20	30	-	-	-	-
H_2O_2, kg/t	-	-	-	3	-	-	-	-	3	3	3	3
NaOH, kg/t	20	80	-	10	-	1	2	5	7	7	7	7
$MgSO_4$, kg/t	1.5	-	-	1,5	-	-	-	-	-	-	-	-
H_2SO_4, kg/t	-	-	10	-	-	-	-	-	-	-	-	-
O_2, kg/t	20	-	-	-	-	-	-	-	-	-	-	-
Presssure, kPa	600	-	-	-	-	-	-	-	-	-	-	-
Reagent Consumed, %	-	-	98.4	100	100	99.3	99.2	99.3	100	100	100	100
pH Final	11.2	13.5	2.8	10.8	3.9	4.2	3.9	4.3	10	10.2	9.9	10.3
Kappa Number	3.8	3.5	-	-	-	-	-	-	-	-	-	-
Bleaching Yield, %	-	-	-	-	-	-	-	92.7	-	-	-	
Brightness, % ISO	47.2	45.4	71.7	81.1	89.9	90.6	91	91.5	90.5	91	91.7	92.4
Reversion, % ISO	-	-	-	-	-	-	-	-	2.5	2.3	2.2	2.4
Viscosity, mPa.s	17.7	23.3	-	6.9	-	-	-	6.8	-	-	-	6.2
Yield, %	-	-	-	-	-	-	-	92.7	-	-	-	
Xylans, %	-	-	-	-	-	-	-	-	-	-	-	5.1

Appendix 2

T 211 om-93

TENTATIVE STANDARD – 1933
OFFICIAL STANDARD – 1934
OFFICIAL TEST METHOD – 1980
REVISED – 1985
REVISED – 1993

Ash in wood, pulp, paper and paperboard: combustion at 525°C

1. Scope

This method for determination of ash can be applied to all types and grades of wood pulp paper, and paper products. For the determination of ash by combustion at 900°C, see TAPPI T 413 "Ash in Wood, Pulp, Paper and Paperboard: Combustion at 900°C."

2. Summary

A test specimen is ignited in a muffle furnace at 525°C. A separate test specimen is analyzed for the percentage moisture. The resulting weight of ash and moisture level in the sample are used to calculate the percentage ash present at 525°C on a moisture-free sample basis.

3. Significance

3.1 The ash content of the sample may consist of: (1) various residues from chemicals used in its manufacture, (2) metallic matter from piping and machinery, (3) mineral matter in the pulp from which the paper was made, and (4) filling, coating, pigmenting and/or other added materials. The amount and composition of the ash is a function of the presence or absence of any of these materials or others singly or in combination. No specific *qualitative* meaning is attached to the term "ash" as used in this test method. Where a further qualitative examination of the ash is desired, this method may be used in combination with TAPPI T 421 "Qualitative (Including Optical Microscopic) Analysis of Mineral Filler and Mineral Coating of Paper," and major components of the ash identified.

3.2 The combustion of cellulose to form volatile combustion products occurs at about 300°C. For papers or pulp containing no added fillers or coatings, ignition at **either** 525°C or 900°C will yield essentially identical results of a few tenths percent ash or less. Examples of such papers include "ashless" filter papers manufactured for chemical analysis, or dissolving grade pulps.

3.3 For samples containing fillers, coatings or pigments *which undergo negligible change in weight upon ignition of either 525°C or 900°C*, such as the oxides of silicon or titanium, and where other fillers, coatings or pigments are known to be absent, ignition at either temperature may be taken as a semi-quantitative measure of the percentage of such material present in the sample.

3.4 In most cases, the ash content of paper and paperboard will contain inorganic residues from the pulp, inorganic residues from paper making chemicals, and loading or filling materials deliberately added. In such cases, the significance of the ash level determined will vary depending upon which ashing temperature is used and the identity of the materials added.

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3.5 For papers containing only cellulose and calcium carbonate, ignition at 525°C will remove cellulose, and moisture, but will leave as ash the calcium carbonate essentially intact. Ignition at 900°C will convert the calcium carbonate to calcium oxide. In such cases, these methods may be used in conjunction to provide a good estimate of added calcium carbonate levels.

3.6 For papers containing cellulose and clays or materials of indefinite composition and/or variable thermal decomposition, significance of ash level may require significant confirmation regarding the materials added, qualitative analysis of the ash as described in T 421, or both, and even then care in determining data significance will be required.

3.7 The user of this test method must confirm that 525°C is the correct ashing method to use and the significance of results based on an understanding of the composition of the sample ash and the information desired. This method may be used in conjunction with TAPPI T 413 "Ash in Wood, Pulp, Paper and Paperboard: Combustion at 900°C" for a more comprehensive understanding of the non-cellulosic materials present in the sample.

4. Definitions

4.1 *Ash,* the material remaining, calculated on the basis of the dry weight of the original sample, after the sample is ignited at a specified temperature.

4.1.1 *Ash at 525°C,* the ash content of the sample when the ignition temperature is 525°C.

5. Apparatus[1]

5.1 *Crucibles*, platinum, porcelain or silica, 50 to 100 mL, with covers.

5.2 *Electric muffle furnace*, suitable for maintaining a temperature of 525 ± 25°C.

6. Sampling

6.1 Obtain a sample of wood in accordance with TAPPI T 257 "Sampling and Preparing Wood for Analysis" and TAPPI T 264 "Preparation of Wood for Chemical Analysis" or a sample of pulp in accordance with TAPPI T 210 "Weighing, Sampling, and Testing Pulp for Moisture." Do not take cut edges or other parts of pulp where mineral contamination may have occurred.

6.2 Obtain a sample of paper or paperboard in accordance with TAPPI T 400 "Sampling and Accepting a Single Lot of Paper, Paperboard, Containerboard, or Related Product."

7. Test Specimens

7.1 Condition the sample in the atmosphere near the balance to the moisture equilibrium.

7.2 The test specimen shall consist of small pieces of the sample so selected as to be representative. The specimen weight shall be at least 1 g moisture-free and may be increased to sufficient size to yield an ash weight of not less than 10 mg and preferably over 20 mg.

7.3 Prepare sufficient test specimens so that the Procedure, Section 9.1 may be performed at least twice for each test unit.

7.4 The test specimen shall be weighed on an analytical balance to the nearest 0.1 mg.

8. Determination of Moisture

8.1 At the same time as the test specimen is being weighted (Section 7) weighing the sample for determination of moisture content shall be accomplished in accordance with T 264 "Preparation of Mechanical Pulps for Testing" (wood), T 210 (pulp) or T 550 "Determination of Equilibrium Moisture in Paper and Paperboard for Chemical Analysis" (paper and paperboard).

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[1] Names of suppliers of testing equipment and materials for this method may be found on the Test Equipment Suppliers list in the bound set of TAPPI Test Methods, or may be available from the TAPPI Technical Services Department.

9. Procedure

9.1 *Moisture determination*. Continue and complete moisture determination as described in the relevant procedure (see 8.1).

9.2 *Ash determination*

9.2.1 Carefully clean the empty crucible and ignite in a muffle furnace at 525 ± 25°C for 30-60 minutes. After ignition, cool slightly and then place in a desiccator, containing indicating-grade anhydrous alumina. When cooled to room temperature, weigh the ignited crucible on the analytical balance to the nearest 0.1 mg.

9.2.2 Transfer the test specimen to the crucible—and, with the lid ajar, gently carbonize the specimen in the crucible on the hearth of the furnace or directly over a low flame of a bunsen burner. Alternately, place the crucible, with lid removed, in a furnace at about 100°C. Raise the temperature to 525°C slowly so that the sample becomes carbonized without flaming. Sample must be charred, not burned so that the temperature of the sample does not exceed 525°C. If the crucible is too small to hold the entire specimen, gently char the portion added and add more as the sample chars, but in either case protect the contents of the crucible with a lid or cover so that a portion of the ash will not be blown from the crucible and/or the sample will not burn. When the residue has ceased to char, place the crucible with specimen into the furnace at 525 ± 25°C and remove the lid after the crucible seems to have reached the temperature of the furnace.

9.2.3 When the specimen is completely combusted as indicated by the absence of black particles, remove the crucible from the furnace, replace the cover, and allow to cool somewhat; then place in a desiccator containing indicating grade anhydrous alumina and cool to room temperature. Weigh the crucible with ash to the nearest 0.1 mg. Repeat the ignition and weighing until the weight of the ash is constant to ± 0.2 mg.

10. Calculation

Calculate the ash content as follows:

$$\text{Ash, \%} = \frac{A \times 100}{B}$$

where

A = weight of ash, g

B = weight of test specimen, g moisture-free

11. Report

Report the ash content in the sample as an average of two determinations to the nearest 0.01% when the ash content is below 10%, or to the nearest 0.1% if the ash content is 10% and higher.

12. Precision

12.1 Repeatability, as defined in TAPPI T 1206 "Precision Statement for Test Methods"

	Repeatability, absolute (as percentage of ash content)	*Repeatability, relative (as of ash content, %)*
Wood	0.03	6.6
Pulp	0.04	5.0

The data are derived by testing 60 wood and 50 pulp samples in one laboratory by several operators. The range of ash content in wood was from 0.16% to 0.84%, and in pulp from 0.24% to 1.60%. The actual temperature used for precision testing was 525°C. An experiment on two pulp and two wood samples at 525°C showed similar precision.

12.2 Reproducibility and comparability: not known

12.3 Precision for paper and paperboard are being determined.

T 230 om-99

SUGGESTED METHOD – 1946
OFFICIAL STANDARD – 1976
OFFICIAL TEST METHOD – 1982
REVISED – 1989
REVISED – 1994
REVISED – 1999

CAUTION:
This method may require the use, disposal, or both, of chemicals which may present serious health hazards to humans. Procedures for the handling of such substances are set forth on Material Safety Data Sheets which must be developed by all manufacturers and importers of potentially hazardous chemicals and maintained by all distributors of potentially hazardous chemicals. Prior to the use of this test method, the user should determine whether any of the chemicals to be used or disposed of are potentially hazardous and, if so, must follow strictly the procedures specified by both the manufacturer, as well as local, state, and federal authorities for safe use and disposal of these chemicals.

Viscosity of pulp (capillary viscometer method)

1. Scope

This method describes a procedure for determining the viscosity of 0.5% cellulose solutions, using 0.5*M* cupriethylenediamine as a solvent and a capillary viscometer. Measurements may be made on bleached cotton and wood pulps. Conventional kraft pulps with up to 4% lignin, as defined by TAPPI T 222 "Acid-Insoluble Lignin in Wood and Pulp" can also be analyzed. The applicability of this procedure to extended delignification pulps has not been determined.

2. Summary

2.1 This procedure describes the techniques for dissolving the pulp and measuring of the viscosity of the pulp solution. The procedure gives two alternative techniques for dissolving the pulp sample. This first technique involves mechanical shaking of the sample-solvent mixture in a closed bottle containing glass beads. The second technique involves stirring the sample and solvent in an open tube with a copper rod. A survey of users and an interlaboratory test program indicated an equal preference for the two techniques.

2.2 The second technique, which involves stirring the sample and solvent in an open tube, has the potential for oxidation of the cupriethylenediamine solution. If this occurs the method will give erroneous results. Caution should be taken to minimize the potential oxidation by continuous flooding of the open end of the dissolving tube.

3. Significance

3.1 The solution viscosity of a pulp gives an indication of the average degree of polymerization of the cellulose. Such a test therefore gives a relative indication of the degradation (decrease in cellulose molecular weight) resulting from the pulping and/or bleaching process.

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3.2 Caution should be exercised in drawing conclusions about pulp strength properties strictly from viscosity results unless previous investigation has identified the relationship.

4. Apparatus

4.1 *General.*

4.1.1 *Cylinder of nitrogen gas,* purity 99.998%, fitted with a pressure reducing valve to give 14 to 21 kPa (2 to 3 psi) pressure.

4.1.2 *Constant temperature bath*, capable of being maintained at 25.0 ± 0.1°C and equipped with clamps to support the viscometers in the thermostating fluid.

4.1.3 *Viscometer,* capillary type, size chosen according to expected viscosity range in compliance with the following characteristics for oil calibrations:

Size number	*Viscosity range, mPa•s (cP)*
50	0.8–3.2
100	3–11
150	7–27
200	19–76
300	48–190

In order to avoid correction for the kinetic energy effect, choose a viscometer with an efflux time of over 100 s, but less than 800 s. Viscometer calibration is given in Appendix A.

4.1.4 *Stopwatch or electric timer,* readable to 0.1 s.

4.1.5 *Buret,* 25 mL, automatic gravity fill, all openings sealed to air; for solvent.

4.1.6 *Buret or pipet,* 25 mL; for water.

4.1.7 *Büchner funnels,* for forming slush pulps into pads.

4.1.8 *Glass filter,* coarse, small diameter; and vacuum flask.

4.2 *Bottle technique.*

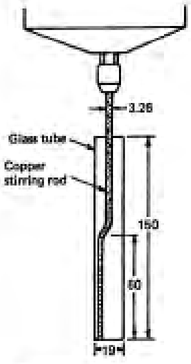
4.2.1 *Dissolving bottles,* 118-mL (4-oz) flat medicine bottles with plastic screw cap and polyethylene liner or rubber septa caps.

4.2.2 *Glass beads,* approximately 6 mm diameter.

4.2.3 *Mechanical shaker,* such as Burrell wrist action shaker.

4.3 *Copper stirring rod technique.*

4.3.1 *Dissolving tube,* round flat-bottom glass tube, 19 mm (3/4 in.) inside diameter and 150 mm (6 in.) high (see Fig. 1), such as A.O.C.S. color comparison tubes, Kimbel #45290, or equivalent.



(Dimensions in mm)

Fig. 1. Dissolving tube.

4.3.2 *Copper stirring rod,* made from 3.2-mm (1/8-in.) diameter electrolytic copper rod (No. 8 B&S gauge) and shaped as shown in Fig. 1.

4.3.3 *Stirring motor,* capable of operation at 400 ± 25 rpm.

5. Reagents

5.1 *Standard viscosity oil*[1], Table 1 lists the viscosity standards available.

5.2 *Cupriethylenediamine solution,* 1.0 ± 0.02*M* in cupric ion and 2.0*M* in ethylenediamine. This solution can be purchased commercially[1] or prepared according to the procedure given in Appendix B. Cupriethylenediamine solutions must be stored under nitrogen at all times. *The concentrations of cupric ion and ethylenediamine should be checked as prescribed in Appendix B no less frequently than monthly.*

5.3 *Acetone*, reagent grade, if used for viscometer cleaning.

Table 1. Standard viscosity oils.

Viscosity standard	*Approximate viscosity, mPa•s (cP) at 25°C**
S3	4.0
S6	8.9
S20	34
S60	120

*Refer to specifications in ASTM D-446.

6. Safety

Sulfuric acid cleaning solution is a strong acid. Cupriethylenediamine solution is a strong caustic. Both require care in handling. Avoid contact of the solution with skin, eyes, and clothing or breathing its vapor.

7. Sampling and test specimen

Obtain a 5–7-g sample of the pulp and reduce to the air-dried state as follows. Form slush pulp specimens into thin sheets on a Büchner funnel or sheet mold and air dry. Slurry hard, dry specimens of pulp in water by shaking or by mixing in a blender and make into thin sheets. Tear apart the air-dry sheets by hand into small pieces. Thick pulp sheets could also be shredded by means of a clean, coarse file. Do not cut or use a mechanical shredder because the viscosity is likely to be lowered as the result of this process of disintegration. Where possible, the sample used for the actual viscosity measurement should be air-dried and never dried above 60°C.

8. Procedure

8.1 Allow the sample to attain moisture equilibrium in a constant temperature-humidity atmosphere according to TAPPI T 402 "Standard Conditioning and Testing Atmospheres for Paper, Board, Pulp Handsheets, and Related Products." Determine the moisture content of duplicate 2-g portions of the sample according to TAPPI T 550 "Determination of Equilibrium Moisture in Pulp, Paper, and Paperboard for Chemical Analysis." Use the average moisture content to calculate the specimen weight of conditioned pulp that must be weighed to give an amount of the sample that is equivalent to 0.1250 or 0.2500 ± 0.0005 g of oven-dry pulp depending on the dissolving technique to be used. *Duplicate specimens must be prepared.*

8.2 *Closed bottle procedure.*

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[1] Names of suppliers of testing equipment and materials for this method may be found on the Test Equipment Suppliers list in the bound set of TAPPI Test Methods, or may be available from the TAPPI Technical Operations Department.

8.2.1 Weigh into a dissolving bottle containing approximately eight 6-mm glass beads and an amount of air-dry pulp equivalent to 0.2500 g of moisture-free pulp. Add from a buret or pipet exactly 25.00 mL of distilled water, then cap the bottle and shake to disperse in the water. Allow the bottle to stand for about 2 min.

8.2.2 Add exactly 25.00 mL of the cupriethylenediamine solution. Purge with nitrogen for 1 min. Cap the bottle and shake until the fiber is completely dissolved. Usually, a period of 15 min is sufficient.

NOTE 1: Some difficult-to-dissolve pulps require preliminary shaker dispersion with only water or longer shaking time. It has been the experience of some workers that up to 90 min is required. The solution remaining after the viscometer has been filled can be filtered through a glass filter to verify that the pulp has been completely dissolved. The presence of gelatinous residue on the filter indicates that a repeat analysis employing more vigorous dissolving conditions is needed. A third technique for handling difficult-to-disperse pulps is to add 1/5 the prescribed amount of cupriethylenediamine, agitate until the pulp appears well dispersed, then complete the addition of the cupriethylenediamine.

NOTE 2: The sample preparation procedures give a final solution concentration of 0.5% pulp in 0.5*M* cupriethylenediamine.

8.2.3 At the end of the shaking time, place the solution bottle on its side for 2 min to allow the solution to degas.

8.3 *Copper rod stirring technique.*

8.3.1 Weigh into a dissolving tube an amount of air-dry pulp equivalent to 0.1250 g of moisture-free pulp. Add from a buret or pipet exactly 12.50 mL of distilled water and stir gently with the motor-driven copper rod for about 30 s. (See Note 1 for additional information).

8.3.2 After purging the dissolving tube with nitrogen for 1 min, add exactly 12.50 mL of the cupriethylenediamine solution, and stir the mixture for 15 min with the stirrer rotating at approximately 400 rpm. To prevent chances of oxidation the open end of the tube should be continuously flooded with nitrogen.

8.4 *Viscosity measurement.*

8.4.1 Fill the viscometer by immersing its small-diameter leg into the solution and drawing the liquid into the instrument by applying suction to the other end. Draw the liquid level to the second etch mark. Remove the tube from the solution, wipe the outside clean and return the instrument to a position within 1° of the vertical. Place the viscometer in the constant temperature bath at 25.0 ± 0.1°C and allow at least 5 min for the vessel to reach the temperature.

NOTE 3: The initial temperature of the solution will affect the time needed for the solution to reach the equilibrium temperature in the bath. Use a kinematic thermometer to verify that the time is adequate for the solution to reach the equilibrium temperature.

8.4.2 Draw the solution up into the measuring leg of the viscometer with a suction bulb, then allow the solution to drain down to wet the inner surfaces of the viscometer. Determine the efflux time by drawing the liquid above the upper mark and measuring the time required for the meniscus to pass between the two marks. Repeat the measurement of efflux time; the results should check within ± 2.0%. Poor repeatability can result from incomplete dissolution of the pulp, inadequate temperature control, a dirty viscometer, or impurities in the nitrogen gas.

NOTE 4: The viscometer size is selected to give efflux times of over 100 s, but less than 800 s. In practice, efflux times greater than 350 s should be avoided as reproducible results will be difficult to obtain. To adjust the efflux time, change the size of the viscometer accordingly.

8.5 *Viscometer cleaning.* Drain the CED solution from the viscometer immediately after the viscosity determination is complete. Rinse the tube well with water to remove all traces of the CED solution. Clean each tube with a sulfuric acid based cleaning solution designed for use with laboratory glassware. Soak especially dirty tubes for 24 hours or more to remove all traces of contaminants. Drain all cleaning solution from the tube and rinse well with deionized or distilled water. Viscometer tubes may be dried in two ways, by using a forced air oven or by rinsing with acetone with air drying. With either drying method, traces of moisture or condensation should not be visible in tube after drying.

8.5.1 To dry a viscometer in a forced air oven, place the viscometer in an oven set at 105 ± 2°C. Allow the viscometer tube(s) to remain in the air oven just until all traces of moisture are removed.

8.5.2 To dry a viscometer with acetone, rinse the tube well with reagent grade acetone, drain, and allow the tube to air dry.

NOTE 5: CED solution is highly alkaline and will etch the interior of the viscometer tubes over a period of time. This will change the calibration constant. For this reason, do not allow the CED solution to remain in the tube after the viscosity determination is complete. Drain all CED solution from the tube and rinse it with water to remove all traces of CED solution immediately after the determination is complete.

9. Calculation

Calculate the viscosity, *V*, of the pulp solution from the formula:

$$V = Ctd$$

where

V = viscosity of cupriethylenediamine solution at 25.0°C, mPa•s (cP)
C = viscometer constant found by calibration
t = average efflux time, s
d = density of the pulp solution, g/cm^3 (= 1.052)

10. Report

Report the average result of two determinations in mPa•s to three significant figures, and identify it as the cupriethylenediamine (CED) viscosity of the 0.5% pulp solution by the capillary viscometer method.

11. Precision

11.1 The values of repeatability and reproducibility provided below have been calculated for test results, each of which is an average of two test determinations. The values are based on data obtained in an interlaboratory test program with 18 participants using six materials. Table 2 gives a statistical summary of the data. The footnote to Table 2 lists a description of the materials tested.

Table 2. Statistical summary of data.

Statistical parameter	Sample*					
	A	*B*	*C*	*D*	*E*	*F*
Grand mean, mPa•s	6.04	11.18	43.2	15.8	19.6	22.6
Repeatability, mPa•s	0.109	0.327	2.63	0.60	0.95	1.02
Repeatability, %	1.8	2.9	6.1	3.8	4.8	4.5
Reproducibility, mPa•s	0.58	1.38	11.0	3.19	3.65	6.15
Reproducibility, %	9.6	12.3	25.4	20.1	18.6	27.2

*A = sulfite - cellophane grade; B = prehydrolyzed kraft; C = cotton linters; D = kraft bleached pine; E = kraft semi-bleached pine; F = sulfite paper grade.

11.2 Repeatability (within a laboratory) = 4.0%. The range of average repeatability for all materials in the study was between 1.8 to 6.1% (0.109 to 2.63 mPa•s) with the % repeatability increasing as the grand mean increases.

11.3 Reproducibility (between laboratories) = 19%. The range of average reproducibility for all materials in the study was between 9.6 to 27.2% (0.58 to 11.0 mPa•s).

11.4 The repeatibility and reproducibility are in accordance with the definitions of these terms in TAPPI T 1206 "Precision Statement for Test Methods."

12. Keywords

Pulp, Viscosity, Capillarity, Cuene, Cellulose

13. Additional information

13.1 Effective date of issue: September 2, 1999.

13.2 The 1999 revision includes a change in the requirements for check results for the viscosity measurement. Section 8.4.2 was changed from a "check within ± 0.25" to "a check within ± 2.0%." This change permits the use of this method on extended lignification pulps which have a wider range of times. The results with other chemical pulps is not significantly affected.

13.3 The falling ball viscometer method, as described in Useful Method 247 "Falling Ball Measurement of Cupriethylenediamine Disperse Viscosity of Pulp," may be applied as a control procedure. This is a less reliable procedure. Four laboratories used the falling ball viscometer method in the interlaboratory program and the results showed a repeatability of 10% and a reproducibility of 38%.

13.4 Related methods: CPPA G.24, "Cupriethylenediamine Viscosity of Pulp," Canadian Pulp & Paper Association, Montreal, Canada; SCAN-C 15-16, "Viscosity of Cellulose in Cupriethylenediamine Solution (CED)," Scandinavian Pulp, Paper and Board Testing Committee, Stockholm, Sweden; ISO Standard 5351/1; ASTM D 446-93, "Standard Specifications and Operating Instructions for Glass Capillary Kinematic Viscometer."

13.5 The 1966 edition of this method included provisions for delignifying unbleached pulps as a means to extend the scope of the method. Chlorite delignification does attack cellulose and when used in conjunction with this procedure may result in lower viscosity measurements. If delignification is used, the results should be considered only as approximations. It has been noted that pulps above 35 to 40 kappa number should be delignified with a mild treatment of sodium chlorite or chlorine dioxide to obtain meaningful results. A mild treatment will minimize cellulose degradation.

13.6 It has been observed that oxygen pulping and oxygen or ozone bleaching of pulps produces viscosity/strength relationships different from traditionally bleached sulfite and kraft pulps.

13.7 Methods for make-up of the required reagents have been simplified in this revision.

Reference

1. Sihtola, H., Kyrklund, B., Laamanen, L., Palenius, I., "Comparison and Conversion of Viscosity and DP-Values Determined By Different Methods," *Paperi ja Puu* **45**:225 (1963).

Appendix A
Calibration of viscometers

A.1 The calibration constant, *C*, for each viscometer is determined by the use of standard viscosity oils of known viscosity and density at 25.0 ± 0.1°C. Depending on the viscometer size, the appropriate oil is selected from Table 1.

A.2 Fill the viscometer by immersing its small diameter leg into the oil and drawing the liquid into the instrument by applying suction to the other end. Draw the liquid level to the second etch mark. Remove the tube from the solution, wipe the outside clean and return the instrument to a vertical position within 1° of vertical. Place the viscometer in the constant temperature bath at 25.0 ± 0.1°C and allow at least 5 min for the vessel to reach the temperature.

NOTE 6: The initial temperature of the solution will affect the time needed for the solution to reach the equilibrium temperature in the bath. Use a kinematic thermometer to verify that the time is adequate for the solution to reach the equilibrium temperature.

A.3 Draw the solution up into the measuring leg of the viscometer with a suction bulb, then allow the oil to drain back into the reservoir to wet the inner surface of the measuring vessel. Determine the efflux time by drawing the liquid above the upper mark and measuring the time required for the meniscus to pass between the reference lines. Make duplicate measurements; these should check within ± 0.2 s. Failure to obtain the required repeatability is indicative of a dirty viscometer or inadequate temperature control.

A.4 The viscometer constant, *C*, is calculated from the formula:

$$C = V/td$$

where

V = viscosity of standard oil, mPa•s
d = density of standard oil, g/cm^3 at 25°C
t = efflux time, s

Appendix B
Preparation of 1*M* cupriethylenediamine

B.1 *Preparation of* $Cu(OH)_2$.

B.1.1 Dissolve 250 g of reagent grade copper sulfate ($CuSO_4 \cdot 5H_2O$) in approximately 2000 mL of hot distilled water. Heat to boiling and add reagent grade NH_4OH slowly with vigorous agitation until the solution is faintly alkaline to pH (about 115 mL of NH_4OH are required). Let the precipitate settle, and wash by decantation with 1000-mL portions of distilled water, four times with hot water and twice with cold. Then add sufficient cold water to make the volume of the slurry 1500 mL; cool below 20°C (preferably below 10°C), and add slowly 850 mL of cold 20% NaOH solution with vigorous stirring. Wash the precipitated $Cu(OH)_2$ with distilled water by decantation until the washings are colorless to phenolphthalein indicator and give no precipitation of sulfate upon addition of $BaCl_2$ solution.

B.1.2 Cupric hydroxide purchased from chemical reagent suppliers may be used provided it is free from ammonia, chlorides, sulfates, and nitrates, and retains its blue-green color when heated 1 h at 100°C. In this case, 97.5 ± 0.5 g of cupric hydroxide shall be used beginning at step B.2.1. Cupric hydroxide of good quality has a blue-green color. If the sample is not pure, and particularly if it contains ammonia, it will gradually decompose and turn brown due to formation of the oxide. Such a discolored product is not satisfactory for the preparation of the reagent. If the hydroxide contains chlorides, sulfates, or nitrates, the determination of ethylenediamine will give too low results.

B.2 *Preparation of cupriethylenediamine (CED) solution.*

B.2.1 Transfer the washed $Cu(OH)_2$ slurries, using sufficient water to make a total volume of 500 mL, to a 1000-mL reagent bottle (see Fig. 2). The bottle is equipped with a rubber stopper carrying two glass tubes, one of which (A) is straight and extends to within approximately 50 mm of the bottom of the bottle, and the other having two side tubes (B and C) at right angles and extending just through the rubber stopper. One of the side tubes (B or C) is connected to a suction source and the other to the nitrogen supply.

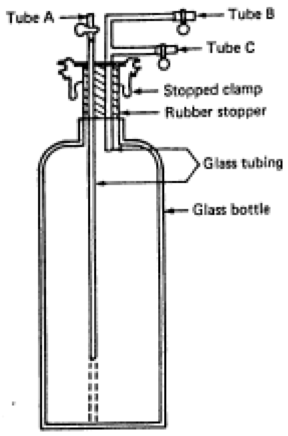

Fig. 2. Solution or stock bottle $Cu(En)_2$, viscosity solvent.

B.2.2 Clamp down the rubber stopper, exhaust the air with a laboratory water aspirator and refill the bottle with nitrogen at 14 kPa (2 psi) pressure three separate times. The rubber tubes and pinch clamps attached to the glass tubes of the solution bottle, as shown in Fig. 2, are used for this purpose. Draw a partial vacuum on the bottle and add 160 mL of 70% ethylenediamine, taking care that no air enters the bottle. This is accomplished by inserting a funnel in the rubber tube attached to the longer glass tube of the solution bottle and opening the pinch clamp just enough to allow the ethylenediamine to be drawn into the bottle. Since considerable heat is evolved at this point, it is desirable to keep cold water running over the bottle during the initial phase of the reaction. After the addition of the ethylenediamine, the gas over the liquid should be alternately evacuated and flushed three times with nitrogen at 14 kPa (2 psi) pressure.

B.2.3 Shake the contents of the bottle several times during the course of an hour, and then let stand 12 to 16 h. A clear supernatant liquor will usually be obtained, but if desired, the solution may be filtered through a fritted-glass Büchner funnel, using suction, and again stored under nitrogen.

B.3 *Standardization of $Cu(En)_2$ solution.*

NOTE 7: Visual observation during standardization of cupriethylenediamine (for cupric ion).

1. Perform the proper dilutions with the CED solution. Prepare and standardize 0.1*N* thiosulfate solution.
2. Pipet 25 mL of the diluted CED into a 250-mL Erlenmeyer flask. Add 3 grams KI and swirl to dissolve. Add 50 mL 4*N* sulfuric acid. The solution immediately takes on a dark brown color that quickly changes to a dark greenish-brown color. The color is the result of a precipitate formed in the reaction.
3. To perform the titration, it is necessary to constantly stir the mixture. This is achieved with best results via a magnetic stirrer.
4. The green color remains for about 70-75% of the titration. For example, if an end point of 25.0 mL is expected, the green color should remain until about 17-19 mL of the titrant is consumed. At this point, the mixture takes on a very creamy coffee color, and the effect of adding more of the titrant is like adding more cream to the coffee.
5. After addition of about 3-4 more mL, a mauve color will appear with each drop and quickly fade. The mixture remains a very light creamy color. At this point, the starch should be added. If the starch is not added, the mixture will become completely mauve, and it is extremely difficult to see the end point.
6. Addition of the starch results in a creamy purple color. The purple color should fade with the addition of more titrant. Only about 0.3-0.5 mL of titrant should be needed after the addition of the starch. This should be the point right before the end point.
7. Add 10 mL of 20% ammonium thiocyanate. The mixture becomes purple again. The titration should be carried out until the mixture fades to a mauve color and finally becomes white at the end point. However, the end point may appear as a salmon pink color with the white color of the precipitate developing only upon standing for a few minutes.

B.3.1 *Cupric ion concentration (Y).*

B.3.1.1 Pipet out a 25 mL sample of CED from a jar in the cold room and dilute to 250 mL in a volumetric flask. (Note: Save sample for Step B.3.2.)

B.3.1.2 Pipet out a 25 mL aliquot to a 250 mL flask.

B.3.1.3 Add 3 grams of KI (30 mL of 10% KI solution).

B.3.1.4 Add 50 mL of 4*N* H_2SO_4 to acidify.

B.3.1.5 Titrate with 0.1*N* thiosulfate near to the starch end point (add starch indicator at a proper time).

B.3.1.6 Just before the starch end point, add 10 mL of 20% ammonium thiocyanate solution to intensify the end point. (Note: 20% solution preparation: Dissolve 10 g of thiocyanate crystal to 50 mL of distilled H_2O.)

B.3.1.7 Continue to titrate to the starch end point.

B.3.1.8 Calculate cupric ion concentration (*Y*): $Y = 0.04$ (mL of 0.1*N* thiosulfate in mL consumed).

B.3.2 *Ethylenediamine concentration (X).*

B.3.2.1 Pipet out 25 mL of CED solution prepared in Step A.1 above to a 250 mL beaker.

B.3.2.2 Add 75 mL of distilled water.

B.3.2.3 Titrate to pH 3.0 using a pH meter with standard 1.0*N* H_2SO_4 while stirring.

B.3.2.4 Calculate ethylenediamine concentration (*X*): $X = 0.2$ (volume of 1*N* H_2SO_4 in mL consumed) *Y* (from B.3.1.8).

B.3.3 *Ratio ethylenediamine/cupric ion.*

Calculate the ethylenediamine and the cupric ion concentration and their ratio as follows:

$$X = [N_1a - 2N_2b]/[(2 \cdot V_1 \cdot V_3)/V_2]$$
$$Y = [N_2b]/[(V_1 \cdot V_3)/V_2]$$
$$R = X/Y$$

where

a = volume of sulfuric acid solution consumed, mL
b = volume of sodium thiosulfate solution consumed, mL
V_1 = volume of sample solution used for initial dilution, mL
V_2 = volume of sample dilution, mL
V_3 = volume of diluted solution used for titration, mL
N_1 = normality of sulfuric acid solution
N_2 = normality of sodium thiosulfate solution
X = mole ethylenediamine per 1000 mL of solution
Y = mole cupric ion per 1000 mL of solution
R = ratio ethylenediamine/cupric ion

B.3.4 *Dilution.* The ratio R must be 2.00 ± 0.04 and the cupric ion concentration $1.00 \pm 0.02M$. If the ratio exceeds 2.00:1, add fresh $Cu(OH)_2$ and repeat the agitation and standardization of the solution as given above. If the ratio falls below 1.92:1, start with fresh $Cu(OH)_2$ and increase the volume of ethylenediamine accordingly.

B.3.5 The solution should be stable for several months if stored under nitrogen. There is usually evidence of a small deposit of cuprous oxide after the solutions have been stored for varying periods of time. Usually this has a negligible influence on the copper and the solutions need not be discarded if the copper analysis checks within the required limits.

Your comments and suggestions on this procedure are earnestly requested and should be sent to the TAPPI Technical Operations Manager. ■

T 236 om-99

TENTATIVE STANDARD - 1960
OFFICIAL STANDARD - 1976
CLASSICAL METHOD - 1985
CORRECTION - 1993
OFFICIAL METHOD -1999

Kappa number of pulp

1. Scope and significance

This method applies to the determination of the relative hardness, bleachability, or degree of delignification of pulp. It may be used for all types and grades of chemical and semichemical, unbleached and semibleached pulps obtained in yields under 60%. This method may also be used for pulps obtained in yields up to 70%, provided the pulp has been well screened. See also Additional Information 10.5.

2. Definition

The *kappa number* is the volume (in milliliters) of 0.1*N* potassium permanganate solution consumed by one gram of moisture-free pulp under the conditions specified in this method. The results are corrected to 50% consumption of the permanganate added.

3. Apparatus

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

3.2 *Disintegration apparatus*, of 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.

3.3 *Constant temperature bath*, capable of maintaining a constant temperature of 25.0 " 0.2°C in the reaction vessel.

3.4 *Reaction beaker*, 2000-mL, glass or porcelain.

3.5 *Pipets*, two 100-mL automatic pipets are especially convenient when a large number of determinations are to be made.

3.6 *Buret*, 50-mL, graduated to 0.1 mL. A 52-mL buret will be found more convenient for titrating the reaction mixture in the blank test.

3.7 *Other apparatus*: a Büchner funnel and filter flask to dewater three to four grams of pulp; stopwatch or clock; 1000-mL and a 25- or 50-mL graduated cylinder; 250-mL beaker.

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4. Reagents

4.1 *Potassium permanganate solution*, standardized 0.1000 " 0.0005*N* $KMnO_4$.

4.2 *Sodium thiosulfate solution*, approximately 0.2*N* $Na_2S_2O_3$. Normality known with an accuracy of " 0.0005*N*.

4.3 *Potassium iodide solution*, 1.0*N* KI.

4.4 *Sulfuric acid*, 4.0*N* H_2SO_4.

4.5 Starch indicator solution, 0.2%.

5. Preparation of sample

5.1 *Air-dried pulp sheets*. Tear small pieces from the sample sheets to weigh a total of three to four grams.

5.2 *Screened slush sheets*. Mix and make three to four grams (dry weight) into a pad by filtering on a Büchner funnel; avoid any loss of fibers. Air-dry the pad and tear it into small pieces.

5.3 *Unscreened pulps*. 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 5.2.

6. Procedure

6.1 Prior to weighing the test samples, condition them for at least 20 min in the atmosphere near the balance.

6.2 Weigh out to the nearest 0.001 g that amount of pulp specimen which will consume approximately 50% of the potassium permanganate solution. The permanganate consumption must be between 30 and 70%. At the same time weigh out a second specimen and determine its moisture content in accordance with TAPPI T 550 "Determination of equilibrium moisture in pulp, paper and paperboard for chemical analysis."

6.3 Disintegrate the test specimen 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.

6.4 Transfer the disintegrated test specimen to a 2000-mL reaction beaker and rinse out the apparatus with enough distilled water to bring the total volume to 795 mL. The distilled water should be at least 25.0 " 0.2°C.

6.5 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 10.1).

6.6 Pipet 100.0 " 0.1 mL of potassium permanganate solution and 100 mL of the sulfuric acid solution into a 250-mL beaker. Bring this mixture to 25°C quickly and add it immediately 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.

6.7 At the end of exactly 10.0 min, stop the reaction by adding 20 mL of the potassium iodide solution from a graduated cylinder.

6.8 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 (see 10.3).

6.9 Carry out a blank determination using exactly the same method as above but omitting the pulp (see 10.3)

7. Calculations

7.1 Calculate kappa number as follows:

$$K = \frac{p \text{ x } f}{w}$$

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 1)
w = weight of moisture-free pulp in the specimen, g
p = amount of 0.1N 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

7.2 Factors in Table 1 are based on the equation: $\log K = \log p/w + 0.00093\,(p-50)$.

Table 1. Factors f to correct for different percentages of permanganate used

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

8. Report

8.1 Report the kappa number as follows:
8.1.1 Under 100, to the nearest 0.1.
8.1.2 Over 100, to the nearest whole number.

9. Precision

9.1 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.

Kappa Measurements

Material	Grand Mean	Repeatability r		Reproducibility R		Labs Included
Pulp A	5.76	0.30	5.2%	1.20	20.8%	5
Pulp B	12.33	0.27	2.2%	0.28	2.3%	5
Pulp C	24.48	0.55	2.2%	1.23	5.0%	5
Pulp D	44.52	3.01	6.8%	11.67	26.2%	6
Pulp E	115.45	8.37	7.3%	15.07	13.0%	5

9.2 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.

10. Additional information

10.1 Effective date of issue: October 19, 1999.

10.2 This revision differs from the 1960 edition as follows: (a) a precision statement has been added; (b) the use of smaller quantities of specimen and reagents has been eliminated; and (c) the conversion table from 40 mL kappa numbers (T 214) to kappa numbers has been deleted.

10.3 Iodine volatization has been found to be an important variable in the kappa number determination. The timing between the reaction and subsequent titration completion should be as short as possible. Blank determinations should duplicate the testing of the specimen as nearly as possible (omitting the pulp, of course).

10.4 *Correction for reaction temperature.* When a constant temperature bath is not available, determine the temperature after the reaction has been taking place for 5 min and assume this to be the average reaction temperature throughout the test. If this temperature is not higher than 30°C nor lower than 20°C, correct the kappa number as follows:

$$K = \frac{pf}{w}\ [1 + 0.013\ (25 - t)]$$

where t = actual reaction temperature in degrees Celsius. If temperature is outside this range, redo the determination maintaining temperature in proper range.

10.5 *Relationship with lignin.* The kappa number gives essentially a straight line relationship with both klason lignin and chlorine number for pulps below 70% total pulp yields (*1*). The percentage of klason lignin approximately equals *K* H 0.13.

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

10.7 Related methods: Australian Standard AS 1301. P 201m , "Kappa Number of Pulp," Technical Association of the Australian and New Zealand Pulp and Paper Industry, Parkville, Australia; CPPA G.18, "Kappa Number of Pulp," Canadian Pulp and Paper Association, Montreal, Canada; ISO R 302, "Determination of the Kappa Number of Pulp (Degree of Delignification)," International Organization for Standardization, Geneva, Switzerland; SCAN C1, "Kappa Number of Pulp" (essentially identical), Scandinavian Pulp, Paper and Board Testing Committee, Stockholm, Sweden, ISO Standard ISO 302.

10.8 This method, formerly T 236 os-76, has been 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. This method was upgraded to an Official Method in 1999.

11. Keywords

Pulp, Lignin, Kappa number

Literature cited

1. Tasman, J. E., and Berzins, V., "The Permanganate Consumption of Pulp Materials," *Tappi* **40** (9): 691 (1957); *Pulp Paper Mag. Canada* **58**(10): 145 (1957).

Your comments and suggestions on this procedure are earnestly requested and should be sent to the TAPPI Technical Operations Manager.

T 245 cm-98

SUGGESTED METHOD – 1970
OFFICIAL STANDARD – 1977
OFFICIAL TEST METHOD – 1983
REVISED – 1988
REVISED – 1994
CLASSICAL METHOD – 1998

Silicates and silica in pulp (wet ash method)

1. Scope and summary

1.1 This method describes a procedure for determining the silicates and silica content of pulp.

1.2 The pulp is wet-ashed using nitric and sulfuric acids. The insoluble residue is filtered, washed, ignited, and weighed as silicon dioxide.

1.3 For a faster but less accurate procedure for measuring all acid insoluble material see TAPPI T 244 "Acid-Insoluble Ash in Pulp."

1.4 The ashing temperature used in this method has been changed from 575°C (T 245 om-88) to 525°C. This is consistent with recent changes in TAPPI T 211 "Ash in Wood and Pulp," and is also consistent with current ASTM and ISO ash methods. The purpose behind this is to prevent the degradation of calcium carbonate that can occur at the higher temperature. Please note that the precision statement contained in section 10 was developed using an ashing step at 575°C, and has not been repeated at the lower ashing method of 525°C.

2. Significance

Silica or silicates are normally present in pulp in very small quantities. If excessive amounts are present and carried into the finished paper of some "fine" or specialty grades, they may cause undesirable abrasion of metal repeatedly applied to the paper, such as punches, dies, knives, or type.

3. Apparatus

3.1 *Kjeldahl flask*, 500 mL.
3.2 *Heating mantle*, sized to accommodate a 500-mL flask and with a variable heat controller.
3.3 *Platinum dish*, 50 mL.
3.4 *Muffle furnace*, maintained at 525 ± 25° C.

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3.5 *Filter paper*, ash-free, double acid-washed, extremely close in texture, of a type recommended for use with the finest precipitates, for example, Whatman No. 42 or Munktell No. 00.

3.6 *Other apparatus*, graduated cylinders, 10-, 25-, and 100-mL.

4. Reagents

4.1 *Nitric acid*, concentrated HNO_3.

NOTE 1: Fuming HNO_3 has been used in the related method for paper; however, concentrated HNO_3 is suggested as a substitute because of the even more hazardous nature of the fuming acid.

4.2 *Sulfuric acid*, concentrated H_2SO_4.

5. Sample

5.1 Select a sample of pulp representative of the shipment or batch to be tested and tear it into pieces.

5.2 If the moisture content is not known, determine the moisture content of another sample in accordance with TAPPI T 210 "Sampling and Testing Wood Pulp Shipments for Moisture." Use percent moisture to determine the oven dry weight of the sample, expressed in grams.

6. Test specimen

The size of the specimen, approximately 25 g, depends on its silica content and should be adjusted so that the weight of the silica will be at least 0.01 g. Weigh duplicate specimens to the nearest 0.01g.

7. Procedure

CAUTION: 1) Because of the corrosive fumes, carry out the digestion in a well-ventilated hood.
2) Because of the danger of adding water to concentrated acid, perform steps 7.2 and 7.3 while wearing chemical goggles, face shield, long heavy rubber gloves, and use a splash shield in front of the flask.

7.1 Place the weighed specimen in a clean 500-mL Kjeldahl flask. Add 100 mL of concentrated HNO_3, warm until the pulp becomes a thin paste, then boil gently until a low-viscosity solution results. Evaporate the solution to a volume of 40-50 mL, cool, and add 20 mL of concentrated H_2SO_4.

7.2 Heat until white fumes of SO_3 are evolved. Clarify the solution by adding, with extreme caution and without cooling the flask, small volumes (10-20 mL) of concentrated HNO_3, allowing the acid to run slowly down the inside wall of the flask. Reheat the flask after each addition until white SO_3 fumes are again evolved. Repeat this operation as often as necessary to produce a clear, straw-colored solution, which does not darken on further heating. Complete the wet oxidation by heating until SO_3 fumes reappear. This will remove the last traces of HNO_3 from the solution.

7.3 Cool the solution to room temperature and carefully dilute to approximately 250 mL with distilled water using a squirt bottle for the distilled water. Boil gently for a few minutes. Filter through the recommended filter paper, being careful to quantitatively transfer the solids. Wash the residue with a few small portions of boiling distilled water (normal use calls for 100-125 mL total).

NOTE 1: If trace metals (Cu, Fe, Mn, or Ca) are to be determined in the same pulp specimen, collect the filtrate in a volumetric flask for further treatment.

7.4 Place the filter paper containing the residue in a platinum dish, previously ignited to a constant weight (to the nearest 0.1 mg). Heat the dish very carefully until the water has evaporated and then ignite the paper and residue in the muffle furnace at 525 ± 25° C until free from black carbon particles. Allow the dish to cool in a desiccator and reweigh it.

8. Calculation

Calculate the silica content as:

$X = 1000\ a/m$

where

X = silicates and silica in parts per million (mg/kg) as SiO_2.
a = weight of insoluble residue, mg.
m = weight of the oven-dry pulp, g.

9. Report

Report the average result for the silicates and silica in pulp in ppm of SiO_2, to the nearest 10 ppm (mg/kg).

10. Precision

NOTE 2: This precision statement was generated using the higher ashing temperature of 575°C and has not been redone at the current ashing temperature of 525°C.

10.1 Repeatability (within a laboratory) = 20 ppm.

10.1.1 The repeatability value is based on an intralaboratory study conducted in accordance with TAPPI T 1200 "Interlaboratory Evaluation of Test Methods Used with Paper and Board Products," using pulp samples containing these levels of silica (ppm): 10, 100, 200, 300, etc., up to 2000.

10.2 Reproducibility (between laboratories) = not known; in accordance with the definitions of these terms in TAPPI T 1206 "Precision Statement for Test Methods."

11. Keywords

Silica, Silicates, Pulp, Impurities, Wet ash method

12. Additional information

12.1 Effective date of issue: February 26, 1998.

12.2 This method has been revised to include an ashing step at 525°C. Please see Scope and Precision statements that discuss this change.

12.3 For pulp samples containing minute amounts of silica (less than 10 ppm), ASTM Standard Method D 2438 "Silica in Cellulose" should be used.

12.4 Related methods: SCAN-C9 (Silicates and Silica in Pulp); ANSI P3.17; ASTM D 2438.

12.5 This method was reclassified as a Classical method in 1998.

Your comments and suggestions on this procedure are earnestly requested and should be sent to the TAPPI Technical Operations Manager. •

T 257 cm-85

TENTATIVE STANDARD – 1942
OFFICIAL STANDARD – 1945
REVISED – 1974
REVISED – 1976
CLASSICAL METHOD – 1985

Sampling and preparing wood for analysis

1. Scope and summary

1.1 This method is applicable to the sampling of wood for all chemical tests.

1.2 The procedures given describe the sampling of wood in all forms, i.e., logs, chips, or sawdust.

1.3 Two sampling plans are described: A probability sampling plan which provides test units from which some property of the wood may be determined within known and controlled limits at a minimum total cost; an economic or engineered sampling plan which minimizes errors due to variations in the raw material or the quality of the lot.

2. Significance

2.1 The physical procedures for obtaining the sample vary because of differences in form and in the condition of the wood (in bulk, in piles on the ground or in bins, in transit, in flumes, on conveyor belts, or separated into sublots in trucks, railroad cars, or containers). The various sampling devices used also affect the sampling procedure. The governing principle for obtaining an economical sampling is the use of a random selection procedure for the shipment or lot as a whole or for obtaining subsamples proportionally for subdivisions of the lot.

2.2 A probability sampling plan generally requires an estimate of the standard deviation of the lot, determination of the maximum allowable difference between the estimate of the average quality and the actual value, and selection of a probability factor to give a selected level of confidence to the decision regarding the lot.

2.3 In many commercial situations, there are significant economic consequences depending on the quality of the lot; for example, proper payment may depend upon the precise determination of some property; or in subsequent use of the wood, the acceptability of the final product may be sensitive to variation in the raw material. If the economic penalties of a wrong decision regarding the lot are considered to be significantly large, care should be exercised in selection of the sample according to a probability-based sampling plan. In some circumstances, however, where the economic differences are of minor consequence, and thus the penalty for making an erroneous decision is small, by mutual agreement an empirical or engineered sampling plan may be adopted.

3. Definitions

3.1 The term *random* carries the statistical implication of planned equality in the probability of selecting appropriate samples, not haphazard or subjective selections.

3.2 An *engineered sampling plan* is one using procedures based on a study of the physical aspects of obtaining samples in an unbiased manner and on experimentation to determine how to exercise maximum control over errors in sampling.

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3.3 A *probability sampling plan* is one giving procedures for use of the theory of probability to combine a suitable method of selecting the sample with an appropriate method for summarizing the test results so that inferences may be drawn and risks calculated.

3.4 A *homogeneous lot* is one in which all the items are from the same statistical population or from populations with the same mean, standard deviation, and skewness.

4. Apparatus

4.1 *Saw*, power driven, for cutting disks from logs.

NOTE 1: The use of an electric handsaw or band saw is quite appropriate for cutting discs from small diameter logs, i.e., less than 150 to 200 mm. Diameters greater than 200 mm, however, dictate the use of an electric or gas-powered chain saw. These saws are now frequently equipped with an automatic chain lubrication system which must be cleaned up with a suitable solvent before use. The chain should be resharpened frequently during use to minimize heating.

4. 2 *Screen,* 40 mesh (0.40 mm), for sifting finer material.

NOTE 2: A power-driven screen is preferable.

4.3 *Mill*, hand-driven or Wiley type (see 5.4.1)
4.4 Mason jar, for keeping sample air-tight.
4 5 *Shovel or scoop*, for use in taking samples of chips.

5. Procedures

5.1 *Engineered sampling plan*

5.1.1 Divide the lot into at least two subdivisions (on a rational basis considering its form and condition) and take at least two subsamples from each subdivision.

5.1.2 For logs, a practical way to attain randomness is to subdivide the shipment into approximately equal quantities by carloads, truckloads, or cords, identify each subdivision by number, and select the subdivisions to be included in the sample by the use of a random number table. From each equal subdivision so selected an equal number of logs are to be taken at random during unloading or stacking. The number of logs comprising the complete sample should be sufficient to produce at least twice the amount of sawdust or raspings required for the moisture content test and the chemical analyses desired. The amount of material obtained by sampling should be reduced to the amount necessary for analysis by quartering (see TAPPI T 605 "Reducing a Gross Sample of Granular or Aggregate Material to Testing Size").

5.1.3 Subsamples of chips may be taken using a shovel or scoop after identifying subdivisions of the lot in the same way as for logs.

5.1.4 An engineered sampling plan requires accepting broad assumptions regarding the relative unimportance of, or the lack of, differences in variation between and within subdivisions of the lot. It avoids questions regarding the limits of uncertainty in the decision made based on the sample, and it provides no real control over that uncertainty. It does not ensure a least-cost balance of sampling against the risk of economic loss due to a bad determination.

5.2 *Probability sampling plan*

5.2.1 If the lot can be assumed to be homogeneous and a prior estimate of the standard deviation of the lot (derived from subsampling) is available, the number of subsamples (n) may be calculated by

$$n = \left[\frac{t\sigma'}{E} \right]^2 \qquad (1)$$

where

σ = the prior estimate of the standard deviation of the lot.
E = the maximum allowable difference between the estimate to be made from the sample and the actual value
t = a probability factor to give a selected level of confidence that the difference is greater than E

See any standard statistical text for values of *t*. The value for *t* should be based on the number of degrees of freedom used to calculate the standard deviation. If the standard deviation is based on calculations made on previous samplings of similar materials and the number of degrees of freedom is unknown, it is suggested that a value of 2.0 be used for 95% probability.

5.2.2 *Example:* Assume that repeated sampling in the past had resulted in a standard deviation of 0.187 in measurements of the property of interest. The number of subsamples required to assure with 95% confidence that the average quality of a shipment lies within limits of ± 0.15 of the mean of the determinations is, from Eq. 1,

$$n = \left[\frac{2.00 \times 0.187}{0.15} \right] = 6.25 \text{ or } 7 \text{ subsamples}$$

5.2.3 Within the physical limitations of handling equipment, the subsamples may be selected with the entire lot considered as a whole. An alternative practical way is to make a random selection of subdivisions and, from them, a random selection of subsamples, using always a random number table.

5.2.4 In a lot assumed to be homogeneous, the balance between number of subdivisions to be sampled and the equal number of subsamples from each may be adjusted to the relative ease, or cost, of selecting the subdivision and of selection of the subsamples therefrom. It is essential, however, that selections made at each stage be random.

5.2.5 If it is known that the lot is not homogeneous, it should be subdivided into rational subdivisions such as opposite quarters of a pile, carloads, or cords. The number of subdivisions to be selected for the sample and the equal number of subsamples to be selected from each may be determined according to the following formulas:

Number of subsamples (*k*) per subdivision:

$$k = \frac{\sigma_w}{\sigma_b} \left[\frac{c_1}{c_2} \right]^{1/2} \qquad (2)$$

Number of subdivisions (*n*) in sample:

$$n = \frac{N(\sigma_w + k\sigma_b^2)}{Nk(E/t)^2 + k\sigma_b^2} \qquad (3)$$

where:

σ_w^2 = variance between subsamples averaged over all subdivision units
σ_b^2 = variance between subdivisions
c_1 = cost of identifying and preparing a subdivision
c2 = cost of taking a subsample
N = number of subdivisions in lot
E = allowable uncertainty in the sample result
T = probability factor

5.2.6 The total cost of the sample can be represented by

$$c = nc_1 + nkc_2$$

Accordingly, sampling schedules can be set up for any set of conditions for which variances and costs can be determined, to make possible the selection of samples with predetermined precision at minimum cost.

5.2.7 If the standard deviation of a lot is not known, or if the variances between and within subdivisions have not been determined previously, sampling experiments must be performed to provide data for use in subsequent calculations of sample size.

5.3 *Preparation of laboratory sample.* Obtain a composite sample of wood from the selected logs by either of the following procedures:

5.3.1 Use a power-driven, sharp saw having a guide to permit cuts being made across the end of each log just the width of the saw teeth, and fitted with a clean box or other device for collecting all the sawdust without contaminating the sample. With the guide removed from the saw, cut about one-third of the length off one or both ends of each sample log across a portion free from knots or decayed wood.

NOTE 3: If the shipment is to be analyzed for its quantity of decay, for example by TAPPI T 265 "Natural Dirt in Wood Chips," take special care in selecting the sample logs. Take double the number specified above and take cuts across five cross sections of each log at intervals of one-sixth of its length.

Remove any bark from the sawed ends of the logs. Replace the guide. Completely clean the box or collecting device. Take one or more cuts across each of the sawed ends of all the logs and collect all the sawdust.

5.3.2 Using the power-driven saw, cut a sample disk 6.4 to 25 mm (1/4 to 1 in.) thick from each log. Take the disk from a point not nearer the end than one-third the total length of the log. If only a single log is provided for analysis, cut three such disks from the log. Take one from approximately the center of the log and the other two about 152 mm (6 in.) from the ends. Cut all the disks into two semicircles or into four sectors by two cuts at an angle depending upon the amount of sample required. Include opposite equal sectors in the final sample. Separate and discard all bark and knots, decayed portions, compression wood and other abnormalties. From each semicircle reduce equal sectors situated opposite in the log to sawdust by means of the specially equipped power-driven saw described above. Use the portion to be discarded for feeding the selected sector to the saw. Alternatively use a hand rasp to produce a satifactorily divided sample from the sectors. In this case, take care to keep the teeth of the rasp clean and not to heat the wood unduly by vigorous rasping. In each case reduce a complete sector to sawdust or raspings to ensure maintaining unchanged the correct proportions of sapwood and heartwood.

5.4 *Grinding and screening*

5.4.1 If moist, let the composite sample air-dry thoroughly. Separate the finer material by sifting on a 40-mesh (0.40-mm) screen. Grind the coarser material in a mill of the Wiley type or in a hand-driven grinding mill. In any case, however, avoid using a mill which heats the material appreciably during grinding or which produces many fines.

NOTE 4: The use of a laboratory refiner equipped with a "pyramid" plate is a convenient means of reducing chip samples to a suitable size for Wiley milling.

NOTE 5: The Wiley-type mill is not satisfactory for all "green"' hardwoods and it is sometimes necessary to use a hammer-type mill or to prepare shavings of the wood using a rotary-knife cutter. Green hardwood can become contaminated if the mill is mild steel *(1)*, and stainless steel construction is recommended for such wood.

5.4.2 Preferably use a power-driven screen because the fine material may then be more effectively separated. Again separate the finer material by sifting. Discard the portion which does not pass through the screen. Do not regrind any material. Continue grinding and sifting until sufficient material has been prepared or until all the available material has been ground.

5.4.3 Place the entire sample so prepared in an airtight container, e.g., a Mason jar, from which portions may be withdrawn for analysis as desired. It is good practice to expose the prepared sample to average atmospheric conditions (see TAPPI T 402 "Standard Conditioning and Testing Atmospheres for Paper, Board, Pulp Handsheets, and Related Products") for a period before closure. This is in order to minimize changes in the moisture content of the material during subsequent handling and weighing operations.

6. Additional information

6.1 Effective date of issue: January 2, 1985.

6.2 The particle size to which wood should be reduced for the purpose of certain analyses has been the subject of differences of opinion and complete agreement with respect to the most suitable size has not yet been reached.

6.3 Moisture content. If the percentage moisture-free wood in the sample is required, proceed according to TAPPI T 264 "Preparation of Wood for Chemical Analysis."

6.4 This revision differs from the previous version in that regrinding coarse material is not recommended. Regrinding can significantly alter the chemical composition of the wood material. This method was first issued as a tentative standard in 1942; an official standard in 1945; was corrected in 1959 and revised in 1974.

6.5 This method had been placed in the Classical Method category due to lack of timely review. In 1995-96, the Test Methods Subcommittee of the Quality and Standards Management Committee required all committees to review such methods and either confirm as Classical or revise as Official or Provisional. The responsible committee for this method confirmed that this version is properly classified as a Classical Method, in accordance with the current test method regulations.

Literature cited

1. Stewart, C. M., *et al.*, "The Selection and Preparation of a Reproducible Wood Sample for Chemical Studies," *Australian Pulp and Paper Ind., Tech. Assoc. Proc.* **5**:267, 312 (1951); also abridged as "Species Sampling on a Reproducible Basis," *Tappi* **35** (4): 129 (1952).

Your comments and suggestions on this procedure are earnestly requested and should be sent to the TAPPI Technical Divisions Administrator. ■

T 258 om-94
TENTATIVE STANDARD – 1947
OFFICIAL STANDARD – 1953
REVISED – 1976
OFFICIAL TEST METHOD – 1985
REVISED – 1989
REVISED – 1994

CAUTION:
This method may require the use, disposal, or both, of chemicals which may present serious health hazards to humans. Procedures for the handling of such substances are set forth on Material Safety Data Sheets which must be developed by all manufacturers and importers of potentially hazardous chemicals and maintained by all distributors of potentially hazardous chemicals. Prior to the use of this test method, the user should determine whether any of the chemicals to be used or disposed of are potentially hazardous and, if so, must follow strictly the procedures specified by both the manufacturer, as well as local, state, and federal authorities for safe use and disposal of these chemicals.

Basic density and moisture content of pulpwood

1. Scope and summary

1.1 This method describes the measurement of the basic density (bone-dry weight per unit of maximum volume) of pulpwood in the form of chips or disks from the cross section of logs. The method also gives procedures for determining the moisture content of wood in either form.

1.2 For moisture content of wood in the form of sawdust see TAPPI T 264 "Preparation of Wood for Chemical Analysis (Including Procedures for Removal of Extractives and Determination of Moisture Content)."

1.3 Moisture content is determined by the difference in weight as received and after drying at 105 ± 3°C.

1.4 Volume is determined by the amount of water displaced by the test specimen of wood.

1.5 Because wood swells or shrinks, respectively, with absorption or loss of water, it is necessary to express the density at a specified moisture content and corresponding volume. The usual conditions are the minimum (oven-dry or moisture-free) weight and the maximum (green) or the minimum (oven-dry or moisture-free) volume. For most purposes, the maximum volume basis is sufficient. In the present method the specimen is considered to have swollen to its maximum volume when its moisture content exceeds the "fiber-saturation point," which lies between 18 and 26% by weight (wet basis) for most species. Procedures for obtaining the volume, both green and oven-dry, are described in this method.

NOTE 1: Many wood technologists consider the density of wood is best expressed only on the basis of oven-dry weight and maximum volume, because at moisture contents above the fiber-saturation point the maximum volume is essentially constant.

2. Significance

Pulpwood, as logs or chips, is often purchased on a volume basis. It is also normally charged to the digester by volume. The moisture content and density of the wood are significant values for comparative pulpwood costs, for inventory control, and for proper processing such as digester load and alkali charge.

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3. Definitions

3.1 *Density* is the ratio of the mass of a quantity of a substance to its volume and is expressed in terms of weight per unit volume.

3.2 The density of the wood portion of pulpwood and chips may be expressed as:

3.2.1 *As-received density*, obtained by dividing the as-received weight by the as-received volume.

3.2.2 *Green density*, obtained by dividing the green (maximum swollen) weight by the green (maximum swollen) volume.

3.2.3 *Basic density*, obtained by dividing the oven-dry weight by the green (maximum swollen) volume.

3.2.4 *Oven-dry density*, obtained by dividing the oven-dry weight by the oven-dry volume.

3.2.5 *Bulk density*, obtained by dividing the weight (at specified conditions) of the specimen (chips) by the bulk volume at the conditions indicated. It can be expressed in the same terms as basic density (see TAPPI UM 23 "Bulk Density of Wood Chips").

NOTE 2: At initial moisture contents above the fiber saturation concentration (18-26% moisture), as-received and green densities will be identical.

TEST PROCEDURES FOR DISKS

4. Apparatus

4.1 *Balance*, capacity 1 kg, sensitivity 0.1 g.

4.2 *Balance*, minimum capacity 500 g, sensitivity 0.05 g. This balance has a weighted hook substituting for the left balance pan and hanger, and so mounted on a support that the hook will be suspended above an open 114-L (30-gal) container (see Fig. 1). Electronic balances such as Ohaus GT series, or equivalent, equipped with a hanger to permit below-the-balance weighting are also suitable when mounted in an appropriate manner above the 114-L container. The weighted hook should be exactly the weight of the pan and hanger which has been replaced or sufficiently close to the same weight so that it can be counterbalanced by the adjusting screws.

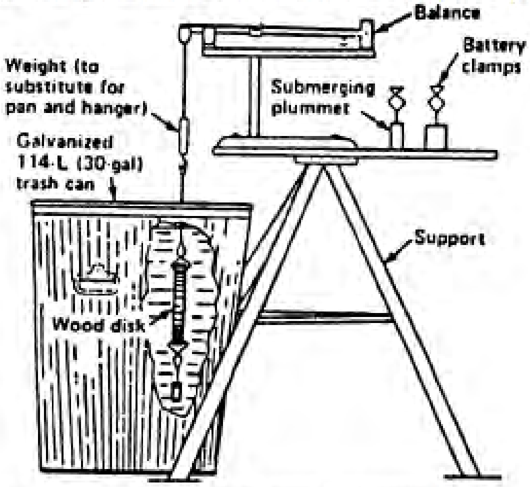

Fig. 1. Apparatus for suspended submergence method for volume determination of disks.

4.3 *Container*, for holding water for submerging disks. A 114-L (30-gal) galvanized or plastic trash container is satisfactory for the purpose.

4.4 *Holding clamp*. This clamp, such as a 200-A battery clamp, should be attached to a fine wire or thread, which, in turn, is attached to an eye for hanging the clamp from the weighted hook on the balance. The wire or thread must be long enough that the clamp and the eye to which the wire is attached are completely submerged in the water held in the container.

4.5 *Submerging plummets* (3 or 4), in the range of 50 to 500 g (as for example 50, 100, 200 and 500 g). Each of these plummets must be attached to a clamp (200-A battery clamps are suitable).

4.6 *Drying oven*, forced air, constant temperature 105 ± 3°C, with drying rack of wire, so constructed that the disks can be placed on edge in the oven, and several thus held without touching one another.

4.7 *Saw*, circular or chain.

5. Materials

Paraffin wax, commercial grade.

6. Sampling

Select a number of sample logs according to TAPPI T 257 "Sampling and Preparing Wood for Analysis."

7. Test specimens

7.1 From each sample log, with a sharp saw, cut a specimen disk of solid wood 20-25 mm (3/4-1 in.) thick from an undamaged, sound, and knot-free section. Preferably cut the disks from the center or at least 300 mm (at least 12 in.) from the end of each log so as to avoid end checks. Quickly remove any bark, adhering splinters, and sawdust from each disk. Reduce the size of any disks too large for the available vessel for obtaining the submerged weight by cutting a wedge or half disk section and mark the pieces for identification.

NOTE 3: The volume of the specimen required is the outside boundary, exclusive of surface depressions; therefore, cleanly cut the disks.

7.2 Place the specimen disks in a covered container as soon as cut to prevent loss of moisture.

8. Procedures

8.1 *Moisture content.*

8.1.1 Determine the moisture content from the as-received weight and the oven-dry (or moisture-free) weight. If the moisture content alone is desired, it is necessary only to determine the as-received weight as described in Section 8.1.2 and then immediately proceed to the measurement of oven-dry weight in Section 8.2.4.

8.1.2 *As-received weight of disks.* Brush off sawdust and dirt from surfaces of disk and weigh disk promptly. If the disk is too large in diameter to be weighed readily, cut it into pie-shaped segments, weigh each segment and total the weights of the segments. Record as-received weight of disk in grams.

8.2 *Basic density.*

8.2.1 *Soaking.* Unless the wood is green, submerge the disk in water at 23 ± 2°C for a minimum of 1 h.

NOTE 4: The purpose of soaking the wood is two-fold: first, to ensure that the specimen is swelled to its green volume, with its internal cavities filled, and second, to eliminate an error resulting from the wood absorbing water while being weighed to obtain its volume. If the moisture content is above the fiber-saturation point, a 1-h soaking period is usually sufficient to accomplish both these conditions; otherwise the soaking should be prolonged until 1 h after checks, if any, are closed.

8.2.2 *Green weight.* Drain the free water from the soaked disks by patting them lightly with a cloth or piece of blotting paper and allowing them to stand 5 min prior to weighing. Brush off sawdust and dirt from surfaces of disk and weigh each disk promptly. If a disk is too large in diameter to be weighed readily, cut it into pie-shaped segments, weigh each segment and total the weights of the segments. Record green (water-soaked) weight of disk in grams. While draining, do not expose the disks to a draft, fan, or direct heat. Return to the soaking vessel those disks whose surfaces show signs of drying out before the weighings can be completed.

8.2.3 *Green volume.* As shown in Fig. 1, set the scales on the left end of a table so constructed that specimens can be suspended in place of the left-hand pan. Place a vessel of sufficient size containing water at room temperature below the scales directly under the left side of the balance. Hang on the left-hand arm a stirrup and chain or other convenient device with large battery clamp attached. Counterbalance the stirrup, clamps and plummet, immersed in water, and record this tare weight.

8.2.3.1 Suspend the disk edgewise (vertically) by clipping it to the large battery clamp attached to a light chain or cord which is hung from the left-hand pan of the scales. Clip the large battery clamp, to which is fastened the weight or plummet, to the lower edge of the disk. Carefully lower disk and plummet into the water so as not to entrap air.

Adjust and clamp the disk so that it is completely immersed and not touching the sides of the vessel. Balance the scale by adding weight to the right-hand pan. The green volume in mL of the disk is equal to the weight of the water displaced by the disk. The weight of the volume of water equivalent to the volume of the disk is the green weight plus the tare weight of apparatus and plummet immersed in water minus the weight of the system obtained here. If density of disk is less than 1.0 (and most are) the weight of the system will be less than the tare weight.

NOTE 5: Raise and lower the disk in the water several times to dislodge any adhering air bubbles before attaching it to the balance. Neither the disk nor the submerging plummet must be allowed to touch the walls or bottom of the vessel during the weighing.

NOTE 6: Another technique for determining green volume is described by Heinrichs and Lussen (1).

8.2.4 *Oven dry (or moisture-free) weight.* Dry disk in an oven at 105 ± 3°C to constant weight. Record that weight as the oven-dry (or moisture-free) weight in grams.

8.2.5 *Oven-dry (or moisture-free) volume.* Dip the dried disk (still warm or even reheated) in hot paraffin, remove it at once and allow it to drain thoroughly. When the paraffin has solidified, conduct the volume determination by the steps outlined in Section 8.2.3 using the weight of the paraffined disk in air for the weight in the computation of volume. Compute the volume in mL as directed in Section 8.2.3 and record it.

NOTE 7: As skill with the basic procedure is developed, the final weighing can be completed in 15 s or less. The expansion of the disk in this length of time is negligible and the paraffin dip can be eliminated. Use oven-dry weight obtained in 8.2.4 for computation.

TEST PROCEDURES FOR CHIPS

9. Apparatus

9.1 *Those items listed in Section 4* (4.1, 4.6) and:

9.2 *Pycnometer*, a can of 1 L (1 qt) or slightly smaller capacity, with a tight lid, with a screen near its top and an opening in its lid (see Fig. 2). Ordinary glass pycnometers are unavailable in the size required for this determination. However, some scientific supply houses list a pycnometer top for determining specific gravity of sand and gravel. Such a top fits a quart screw cap jar, and this combination when equipped with a suitable screen as shown would be satisfactory. Polyethylene containers are also quite acceptable. A commercially available cocktail shaker can easily be adapted for this use by inserting the screen, drilling the hole and fixing the outlet tube as shown.

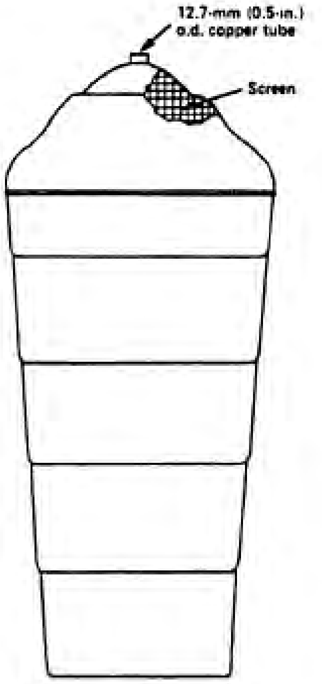

Fig. 2. Apparatus for pycnometer method for volume determination of chips.

9.3 *Screen*, 6-7 mm openings (3 mesh), 450-600 mm square or diameter.
9.4 *Screen shaker*.
9.5 *Mixer*, twin-cone or twin-shell.

10. Reagents

10.1 *Shellac solution*, commercial shellac (containing 0.6 g of ordinary orange shellac per mL of denaturated alcohol) diluted with an equal volume of alcohol (i.e., 1.1-kg cut).
10.2 *Kerosene*, commercial grade.

NOTE 8: These chemicals are flammable and appropriate cautions should be taken by the user of this method.

11. Sampling and test specimens

11.1 From 300 to 350 g (0.60 to 0.75 lb) of chips are required for a determination. Run duplicate determinations. Select the chips to be as representative as possible of the lot being tested. If the chips have been previously screened to the desired size, step 11.3 can be eliminated.

11.2 Store the chips in reasonably air-tight containers until ready for further preparation. Cans such as 114-L (30-gal) trash receptacles (if provided with close fitting lids) are satisfactory for the purpose. Specimens which are to be used within two or three hours can be stored safely in these cans without additional covering. Place those to be stored a longer time into moisture-proof bags and securely tie them before placing in the storage cans. Brush sawdust and dirt from the surfaces before use.

NOTE 9: Procedures for the determination of wood properties should be carried out as rapidly after sampling as possible so as to avoid changes in these properties while the chip sample is in storage.

11.3 Before the determination of any of the several values herein described, chips, as sampled, should be screened to the desired size.

11.3.1 Screen the sample used for determinations through a three-mesh standard screen (9.3). Discard the dust which is passed by this screen. Use only the material retained on the screen.

11.3.2 Thoroughly mix the screened chips in a closed dry solids mixer such as a twin-shell mixer.

12. Test procedures

12.1 The computation of density requires figures to be developed describing the weight and volume of the same sample of wood chips. Also, on occasion, information relating to moisture content becomes important; therefore, methods are presented below for making these three measurements. If the moisture content alone is desired, it is necessary only to determine the as-received weight as described in Section 8.1.2 and then immediately to proceed to the measurement of oven-dry weight in Section 8.2.4. Because the values to be used for the various density computations must (unless moisture content is appropriately applied) relate to the same wood sample, it is recommended that the measurements on a specimen of chips be made in the following sequence:

As-received weight (12.2)
As-received volume (12.3)
Green (water-soaked) weight (12.4)
Green (water-soaked) volume (12.5)
Oven-dry weight (12.6)
Oven-dry volume (12.7)

NOTE 10: Make certain that chips are not lost during the conduct of the several steps.

12.2 *As-received weight.*

12.2.1 Weigh the empty pycnometer and record this tare weight.

12.2.2 Place chips in pycnometer and weigh. Subtract the tare weight of the pycnometer to determine the as-received weight in grams.

12.3 *As-received volume.*

12.3.1 After determining as-received weight, carefully fill the pycnometer with water to the extent that when the cover is replaced the water overflows through the top outlet hole. Shake the pycnometer to dislodge air bubbles. Add water to the outlet hole as necessary to restore the water level.

12.3.2 Weigh the pycnometer with chips and water.

12.3.3 Determine weight of pycnometer when filled with water without chips (water filled weight).

NOTE 11: Be sure pycnometer does not leak when lid is positioned and that lid is similarly positioned for above weighings.

12.3.4 Chip volume in mL is obtained by subtracting the unfilled or void volume (the weight of the pycnometer when filled with chips and water, minus the chip-filled weight) from the volume of the pycnometer (the water filled weight minus the tare weight).

12.4 *Green weight*. After soaking as in 8.2.1, sponge off surface water from chips with several thicknesses of paper towels. Place chips in pycnometer and weigh. Subtract the tare weight of the pycnometer to determine the green weight in grams.

12.5 *Green volume*. After determining green weight in grams, proceed as in 12.3 to determine green volume and green density in grams.

12.6 *Oven-dry weight*. Spread out the chips in a wire-mesh tray or basket in the oven. Dry the chips to constant weight in grams at 105 ± 3°C, which will require from 24 to 48 h.

12.7 *Oven dry volume*. Because of the proportionately high volume of paraffin coating on a quantity of chips as compared to that on an equal quantity of wood in the form of disks, as well as the difficulty of immersing paraffined chips in water without entrapping air, the determination of the volume of dried chips by the method used for disks is not recommended. The volume, however, can be obtained satisfactorily by coating the chips with shellac and immersing them in kerosene. Weigh the dried chips, and while still warm, place them in the wire basket, immerse them in the alcoholic solution of commercial shellac for a period of 3-5 min, then spread them out to air-dry. Obtain the weight of the shellac-coated chips in air before obtaining the weight suspended in kerosene. Make weighings with the shellac-coated chips as described in the basic procedure, except substitute kerosene for water in the submergence bath. Compute the volume in mL as directed in Section 12.3.4. Divide the volume as calculated by the density of the kerosene to obtain the oven-dry volume and record it.

NOTE 12: The density of the kerosene in g/mL must be known or must be determined by standard liquid density procedures.

13. Calculations

13.1 Let the following equal the quantities as indicated:

a = as-received weight of disks (from 8.1.2), g
b = oven-dry weight of disks (from 8.2.4), g
c = as-received weight of chips (from 12.2), g
d = oven-dry weight of chips (from 12.6), g
e = green volume (from 8.2.3), mL
f = oven-dry volume of disks (from 8.2.5), mL

13.2 Calculate the moisture content of the disks ("as-received basis") as follows:
Moisture, % = $[(a - b)/a] \times 100$

13.3 Calculate the moisture content of chips (as-received basis) as follows:
Moisture, % = $[(c - d)/c] \times 100$

13.4 Compute the basic density as determined by the various procedures described by the formulas given below. Calculate the density separately for each specimen of disks as follows:

13.4.1 Calculate the basic density, g/mL, as follows:
Basic density = b/e

13.4.2 If desired, calculate the bone-dry density, g/mL, as follows:
Bone-dry density = b/f

13.4.3 *Volume of the pycnometer* in mL is obtained by subtracting the tare weight (in grams) from the water-filled weight (in grams):
Pycnometer volume = water-filled weight - tare weight

13.4.4 *Weight of the chip* sample is obtained by subtracting the tare weight (in grams) from the chip-filled weight (in grams):
Weight of chip sample = chip-filled weight - tare weight

13.4.5 *Unfilled volume* or void volume is obtained by subtracting the chip-filled weight (in grams) from the weight of the pycnometer (in grams) when filled with chips and water:
Unfilled volume = chip and water-filled weight - chip-filled weight

13.4.6 *Chip volume*, as described in 12.3.4.

13.4.7 *Oven-dry weight*, as determined in 12.6.

13.4.8 *Green volume*, as determined in 12.5.

13.4.9 *Oven-dry volume*, as determined in 12.7, is the difference in weight between the pycnometer when filled with chips and kerosene and the weight when filled with shellacked chips which must be divided by the density (in g/mL) of the kerosene. This gives the volume (in mL) occupied by the liquid kerosene, and the difference between this figure and the total volume (13.4.3) gives the volume of the chips.
Bone-dry volume = pycnometer volume - (weight of kerosene/density of kerosene)

14. Report

14.1 *Moisture content.* For disks or chips, report the results on the "as received" basis to the nearest 0.1% moisture.

14.2 *Density.* For disks or chips, report the basic or oven-dry density in g/mL to three significant figures.

15. Precision

15.1 *Disks* (*2*, *3*, *4*). A series of 156 tests of green volume basic density in duplicate on disks was conducted by one laboratory for a repeatability of 6%.

15.2 *Chips (4)*. Within one laboratory, the density of 12 specimens of sweetgum chips measured an average of 0.460 g/mL with a repeatability of 0.00556 g/mL.

15.3 These values are in accordance with the definitions in TAPPI T 1206 "Precision Statement for Test Methods."

16. Additional information

16.1 Effective date of issue: May 17, 1994.
16.2 Related method: CPPA A.8.

References

1. Heinrichs, J. F., and Lassen, L. E., "Improved Technique for Determining the Volume of Irregularly Shaped Wood Blocks," *Forest Prod. J.* **20**(4): 24 (1970).
2. United States Department of Agriculture Forest Service Research Paper FPL, "Properties of Major Southern Pines," U.S. Department of Agriculture, Forest Products Laboratory, Madison, Wisconsin, 176 (1972).
3. Saucier, J. R., "Wood Specific Gravity of Eleven Species of Pine," *Forest Prod. J.* **22**(3): 32 (1972).
4. Eslyn, W. E., "Reliability of a Method for Measuring Specific Gravity to Determine Wood Losses in Outside Deep Storage," *Tappi* **54**(8): 1269 (1971).

Your comments and suggestions on this procedure are earnestly requested and should be sent to the TAPPI Technical Divisions Administrator. ■

T 264 cm-97

TENTATIVE STANDARD – 1942
OFFICIAL STANDARD – 1945
OFFICIAL TEST METHOD – 1982
REVISED – 1988
CLASSICAL METHOD – 1997
FORMERLY – T 12

CAUTION:
This method may require the use, disposal, or both, of chemicals which may present serious health hazards to humans. Procedures for the handling of such substances are set forth on Material Safety Data Sheets which must be developed by all manufacturers and importers of potentially hazardous chemicals and maintained by all distributors of potentially hazardous chemicals. Prior to the use of this test method, the user should determine whether any of the chemicals to be used or disposed of are potentially hazardous and, if so, must follow strictly the procedures specified by both the manufacturer, as well as local, state, and federal authorities for safe use and disposal of these chemicals.

Preparation of wood for chemical analysis

1. Scope

1.1 This method describes a procedure for further preparation of wood that has been sampled for analysis in accordance with TAPPI T 257 "Sampling and Preparing Wood for Analysis."

1.2 A method for determination of moisture content in wood is described.

1.3 Due to the highly hazardous nature of the solvents used in this procedure, the committee is working on a new procedure that will replace this method at a later date utilizing alternative solvents.

2. Summary

The neutral solvents, ethanol and benzene, are employed to remove materials which are not part of the wood substance or which may interfere with some analysis (see 11.2).

3. Significance

3.1 *Classification*

3.1.1 Wood for chemical analysis should be ground to a fine particle size to permit complete reaction of the wood with the reagents used in the analysis. T 257 specifies that the wood should be ground to pass a 0.4-mm (40-mesh) screen.

3.1.2 Chemical methods for analysis of wood typically call for utilization of the entire amount of material without further fractionation. The fine material might contain a disproportionate quantity of some wood constituents, and its removal could alter the chemical composition as analyzed.

3.1.3 In some chemical methods, the fine material interferes with the analysis. It clogs fine filters or passes through coarse filters, producing erroneous results. UM 249 "Holocellulose in Wood" requires comminuted wood samples to have fines removed by fractionation.

3.2 *Extraction*

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3.2.1 Wood extractives are materials soluble in neutral solvents and are not generally considered as part of the wood substance. These materials should be removed before any chemical analysis of wood substance, except where the extraction process and subsequent washing could interfere with certain chemical analysis.

3.2.2 Ethanol-benzene is used to extract waxes, fats, some resins, and possibly some portions of wood gums. Hot water is used to extract tannins, gums, sugars, starches, and coloring matter.

NOTE 1: Significant quantities of benzene and ethanol are absorbed by the treated material; these are difficult to remove.

4. Apparatus

4.1 *Extraction thimbles*, alundum or fritted glass, coarse porosity; or pre-extracted paper.

4.2 *Extraction apparatus*, with ground glass joints, consisting of:

4.2.1 *Extraction flask*, 250 mL.

4.2.2 *Soxhlet extraction tube*, inside diameter 30-40 mm, capacity to top of siphon about 100 mL.

4.2.3 *Graham or Allihn type condenser.*

4.3 *Glassware,* weighing bottle, glass, preferably "shallow" type or weighing dish, aluminum; filtering flask, 1000 mL; Büchner funnel.

4.4 *Heating device*, to contain hot water; or steambath or electric heating mantle.

4.5 Chemical fume hood, having a face velocity of at least 24.4 m/min (80 ft/min) or as required by local safety regulations.

5. Reagents and materials

5.1 *Ethanol (ethyl alcohol)*, approximately 95% C_2H_5OH by volume, or denatured with 5% methanol or isopropanol, having a residue after evaporation not more than 0.001%.

5.2 *Benzene*, reagent grade or purified C_6H_6, having a residue after evaporation not more than 0.001%.

5.3 *Ethanol-benzene mixture*, mix together one volume of the ethanol and two volumes of the benzene.

6. Safety precautions

6.1 Avoid any contact of benzene with skin and inhalation of benzene vapor. Use plastic gloves and a respirator suitable for removal of benzene vapor. Carry out the procedure of extraction in a chemical fume hood with good ventilation.

6.2 Ethanol and benzene are flammable and constitute a fire and explosion hazard. Use water, steam, or oil baths or electric heating mantles. Avoid open flame in the vicinity of the extraction.

7. Sampling and test specimens

7.1 In accordance with T 257, obtain a composite sample of wood meal.

7.2 Take a specimen for extraction, sufficient for the chemical analyses to be performed including moisture determination.

8. Procedures

8.1 *Preparation of extractive-free wood*

8.1.1 Clean and dry the extraction flask. Place the material to be extracted in the extraction thimble and place the thimble in position in the Soxhlet apparatus. Place a small cone of fine mesh screen wire in the top of the thimble to prevent any loss of the specimen.

8.1.2 Extract with 200 mL of solvent for 6 to 8 h, keeping the liquid boiling briskly so that siphoning from the extractor is no less than four times per hour.

8.1.3 After extraction with ethanol-benzene, transfer the wood to a Büchner funnel, remove the excess solvent with suction, and wash the thimble and wood with ethanol to remove the benzene. Return the wood to the extraction thimble and extract with 95% ethanol for 4 h or longer if necessary, until the alcohol siphons over colorless.

8.1.4 Again transfer the sample to a Büchner funnel, remove the excess solvent with suction, and wash the thimble and wood sample with distilled water to remove the ethanol. Transfer the sample to a 1000-mL Erlenmeyer flask and add 500 mL of boiling distilled water. Heat the flask for 1 h in the hot water bath. Keep the water at boiling temperature and surround the flask in the bath with boiling water. After extraction, filter on a Büchner funnel and wash with 500 mL of boiling distilled water. Allow the wood to air-dry thoroughly.

8.1.5 Mix and store in an air tight container. Determine the moisture content in wood (8.2) and withdraw specimens for analysis as required.

8.2 *Moisture content*

8.2.1 Weigh a specimen from 8.1.5 of approximately 2 g to the nearest 0.001 g *(A)* in a tared weighing bottle. Dry for 2 h in an oven at 105 ± 3°C, cool in a desiccator, replace stopper, and open the stopper momentarily to equalize the air pressure and weigh. Return bottle to the oven for 1 h; repeat the cooling and weighing as above for successive hourly periods until constant weigh (*B*) is reached, that is, until successive weighings do not change by more than 0.002 g.

8.2.2 Calculate the percentage of moisture in wood to the nearest 0.1%:

$$\text{Moisture content, \%} = [(A-B)/A] \cdot 100$$

where A and B are the sample weights after subtracting the weight of the sample bottles.

9. Keywords

Sample preparation, Wood, Analysis, Chemical analysis, Moisture content, Ethanol, Benzene

10. Precision

10.1 Precision, in accordance with the definitions in TAPPI T 1206 "Precision Statement for Test Methods," is not applicable to the preparation of extractive-free wood.

10.2 Repeatability of moisture content by oven-drying was found in one laboratory to be 0.2% in terms of moisture content. Reproducibility and comparability = not known.

11. Additional Information

11.1 Effective date of issue: April 7, 1997.

11.2 A mixture of ethanol and toluene, $C_6H_5CH_3$, was found in some laboratories as removing the same materials from wood as ethanol-benzene. However, the boiling point of toluene is higher than that of benzene, and the mixture of ethanol-toluene does not boil and reflux at a constant temperature and rate.

11.3 Related methods: ASTM D1105 (ANS) "Preparation of Extractive-Free Wood;" CPPA G.31P, "Preparation of Wood for Chemical Analysis."

11.4 This method was reclassified as Classical by committee action in 1997.

Your comments and suggestions on this procedure are earnestly requested and should be sent to the TAPPI Technical Divisions Administrator. •

T 525 om-92

SUGGESTED METHOD – 1972
HISTORICAL METHOD – 1985
OFFICIAL TEST METHOD – 1986
REVISED – 1992

Diffuse brightness of pulp (*d*/0°)

1. Scope

1.1 This method is to be used to evaluate the diffuse blue reflectance factor (diffuse brightness) of pulp by measuring handsheets prepared according to TAPPI T 218 "Forming Handsheets for Reflectance Tests of Pulp." The measurement of handsheets is the most commonly accepted procedure for obtaining pulp brightness; however, machine-dried sheets can also be used.

NOTE 1: The brightness of a handsheet will usually be 0.5 to 1.0 unit higher than that of a machine-dried sheet made from the same pulp.

1.2 This method utilizes an integrating sphere to provide diffuse illumination and perpendicular (0°) observation geometry *(1)*. With this geometry, specimen surface structure and azimuthal orientation have negligible effect on brightness.

1.3 The instrument has a relatively large specimen aperture for the purpose of averaging small area variations in reflectance, making it possible to obtain a reliable average value with only a few individual measurements.

1.4 This method is not intended for use with colored materials.

1.5 Although this method does not specifically exclude naturally fluorescent pulps or the use of optical brighteners, paper manufacturers may wish to limit their pulp suppliers in their use of optical brighteners. Such additives may reduce the potential for paper manufacturers to control brightness by the use of additional optical brighteners.

2. Summary

Diffuse reflectance is measured at an effective wavelength of 457 nm by using a suitable filter set or an equivalent device for modifying the spectral response and an instrument having diffuse illumination and perpendicular observation geometry. The measurements are made in terms of absolute reflectance.

3. Significance

3.1 Blue-light reflectance measurements were originally designed to provide an indication of the amount of bleaching that has taken place in the manufacture of pulp. The higher the blue-light reflectance, generally the whiter the products will appear. The method provides a simple, single-number index useful for comparing similar white materials; however, colored materials are better identified by using a standardized three-dimensional color space [see TAPPI T 442 "Spectral Reflectance Factor, Transmittance, and Color of Paper and Pulp (Polychromatic Illumination)," T 524 "Color of White and Near-White Paper and Paperboard by *L, a, b* 45° 0° Colorimetry," and T 527 "Color of Paper and Paperboard in CIE *Y; x, y*, or *Y*, Dominant Wavelength and Excitation Purity"].

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TAPPI

3.2 Because the instrument geometry of this method is different from that of TAPPI T 452 "Brightness of Pulp, Paper and Paperboard (Directional Reflectance at 457 nm)," there is no simple relationship between the two brightness scales.

3.3 Specularly reflected light (gloss) is excluded from the measurement of diffuse brightness by the use of a gloss trap (specular reflectance absorber) as required in 5.1.1.3.

NOTE 2: Material containing fluorescent brightening agents will exhibit higher reflectance values to a degree which is dependent upon the ultraviolet (UV) content of the radiation incident on the specimen. Control of such UV content is essential to maintain continuity of measurement among optically brightened pulps.

NOTE 3: No known material is both perfectly reflecting and perfectly diffusing, but standards can be calibrated in terms of absolute reflectance (2). Standards with calibrations based on this reference can be obtained from ISO authorized laboratories[1].

4. Definitions

4.1 *Diffuse reflectance factor*, the ratio of the radiance of a specimen to that of a perfectly reflecting diffuser, each being irradiated hemispherically and viewed identically.

4.2 *Absolute brightness*, the diffuse reflectance factor for blue light in terms of a perfectly reflecting, perfectly diffusing specimen as determined on an instrument as described in section 5.

5. Apparatus

5.1 *Reflectometer*, an instrument designed for the measurement of diffuse reflectance which employs the following geometric, photometric, and spectral characteristics:

5.1.1 *Geometric characteristics*

5.1.1.1 Diffuse illumination of the specimen by means of an integrating sphere of 150 mm diameter. The sphere shall be equipped with screens to eliminate direct illumination of the specimen.

5.1.1.2 The sum total of the areas of the apertures in the sphere does not exceed 10% of the area of the sphere.

5.1.1.3 The receptor aperture is surrounded by a gloss trap (black circular area) of external diameter subtending a half-angle of 15.5 ± 0.5° at the center of the specimen aperture.

5.1.1.4 No light reflected from the rim of the specimen aperture shall reach the receptor.

5.1.1.5 The measured test area on the specimen is circular with a diameter 30 mm ± 1 mm.

5.1.1.6 The specimen aperture diameter shall not exceed 35 mm and the edge thickness shall not exceed 2 mm.

5.1.1.7 The specimen is viewed perpendicularly (0°). Only reflected rays within a solid cone, whose vertex is in the specimen aperture and of half-angle not greater than 4°, shall fall on the receptor.

5.1.1.8 Stray light from all sources shall not exceed 0.5%.

5.1.2 *Photometric characteristics.* The accuracy of the photometer, whether mechanical or electronic, is such that the departure from photometric linearity after calibration does not exceed 0.1% reflectance factor.

5.1.3 *Spectral characteristics.* The effective wavelength of the reflectometer, 457.0 nm ± 0.5 nm, is arrived at with a combination of lamps, integrating sphere, glass optics, filters or other spectrally selective device and photoelectric cells. The filters should be such that the relative spectral distribution function $F(\lambda)$ of the reflectometer is as indicated in Table 1: $F(\lambda)$ is the product of the following variables:

a) the relative spectral distribution of the radiant emittance of the integrating sphere,
b) the spectral transmittance of the glass optics,
c) the spectral transmittance of the filters or other spectrally selective device, and
d) the spectral response of the photoelectric cells, each being a function of the wavelength.

Table 1 The relative spectral distribution function F (λ) of a reflectometer equipment for measuring diffuse brightness of pulp.

Wave-length, nm	F(λ), arbitrary units	Wave-length, nm	F(λ), arbitrary units
380	0.0	450	82.5
390	0.0	460	100.0
400	1.0	470	88.7
410	6.7	480	53.1
420	18.2	490	20.3
430	34.5	500	5.6
440	57.6	510	0.3

5.2 The following ancillary items must be available:

5.2.1 *Instrument standards*, two or more opal glass or ceramic standards calibrated relative to a Level 2 (ISO) or Level 3 reference standard (see 7.3).

5.2.2 *Black cavity*, a black cylindrical cavity, with centering device, having a known reflectance of less than 0.5%.

5.2.3 *Lens tissue*, non-fluorescent, non-abrasive lens paper or tissue.

6. Reagents

Cleaning solution, distilled water and detergent free from fluorescing or abrasive ingredients.

7. Calibration and standardization

7.1 *ISO reference standard of level 1 (IR1)*, the perfect reflecting diffuser. Ideal spectrally uniform Lambertain diffuser with a reflectance equal to 100.0 at all wavelengths.

7.2 *ISO reference standard of level 2 (IR2)*, standard whose reflectance factor has been determined by a standardizing laboratory in relation to the IR1. These standards are used by authorized standardizing laboratories for the calibration of their reference instruments.

7.3 *ISO reference standard of level 3 (IR3)*, standard where the reflectance factor has been determined by an authorized standardizing laboratory in relation to any IR2. These standards are employed by instrument users for the calibration of their instruments.

7.4 *Instrument standards*, two opal glass or ceramic instrument standards are required. Wash standards with a solution of distilled water and detergent which is free from fluorescing or abrasive ingredients. Rub surface with a soft cloth or brush with synthetic fiber bristles. Rinse thoroughly with distilled water. Dry by blotting with filter paper. Place in a desiccator for additional drying until ready for use.

NOTE 4: An instrument standard in frequent use should be cleaned regularly, at least weekly, and it should be cleaned at any time that there is reason to suspect that the surface has become contaminated.

7.5 *Calibration of instrument standards*

7.5.1 Turn instrument on and allow it to come to operating equilibrium. Consult instruction manual for manufacturer's recommended warmup time and use of any lamp-house cooling technique that may be provided.

7.5.2 Clean two opal glass or ceramic instrument standards as described in 7.2.1, if they have not been cleaned recently.

7.5.3 Place the 457 nm filter set in position or select modified spectral equivalent.

7.5.4 Adjust instrument to read black cavity value with black cavity in specimen position.

7.5.5 Place the IR3 reference standard in the specimen position. Adjust the instrument to read the assigned value.

7.5.6 Place an opal glass or ceramic instrument standard in the specimen position and read the calibration value for this standard. Repeat the procedure to obtain the value for standard No. 2.

NOTE 5: The reflectance of opal-glass or ceramic standards is relatively stable; however, they must be calibrated at regular intervals on the specific instrument with which they will be used by making use of Level 3 reference standards and the procedures described in Section 7.

8. Use of instrument standards

Calibrate the instrument with standard No. 1 and then read standard No. 2. If the reading for standard No. 2 is not within 0.1% of its assigned value, clean it and reread. Use this reading as the new value for standard No. 2, and use this standard for the regular calibration of the instrument. Use standard No. 1 only to verify the calibration of standard No. 2.

NOTE 6: The relation between the calibrated values of the two instrument standards should remain constant. If a difference greater than 0.1% is observed, it is reasonable to assume that the calibration of standard No. 1 is more reliable because it has been used least. However, if the difference is greater than 0.2%, even after careful cleaning of both new standards, it would be advisable to procure a new Level 3 reference standard and to determine by this means whether the reflectance of one of the instrument standards has actually changed.

9. Test specimens

Prepare handsheets according to T 218. Remove the filter paper cover from the dried handsheets. Cut the handsheets into tabs large enough to cover the measurement aperture of the instrument. Use a pad of tabs of sufficient number that doubling it will not change the brightness reading. Six tabs may be sufficient.

10. Procedure

10.1 Place the 457 nm filter in position or select modified spectral equivalent and check black cavity reading (7.5.4). Place instrument standard No. 2 in position. Calibrate the instrument relative to this standard using the value obtained from the procedure described in Section 8.

NOTE 7: A single 150 mm diameter handsheet can be conveniently cut into six pre-shaped tabs using a paper cutter with a special template. The six tabs can be stored in the folded filter paper cover until ready to read the brightness.

10.2 Remove the top cover tab and place it on the bottom of the stack of tabs. Place the tabs, with the smooth side up, on a clean specimen holder.

10.3 Read the brightness of the first tab and record to the nearest 0.1%. Transfer the top tab to the bottom of the stack and make a brightness reading on the second tab. Repeat this procedure until five tabs have been read.

NOTE 8: Handle the specimens by the edges to avoid contamination. With many instruments, the brightness measurement must be made with reasonable speed because the reflectance may change as the moisture content of the surface of the specimen changes when heated by the instrument lamps. Color reversion also is possible with unstable material, so do not leave the stack of tabs against the specimen aperture while recording results.

NOTE 9: Since moisture content of the specimen has a slight effect on brightness, the best reproducibility is obtained by conditioning and making the tests in an atmosphere in accordance with TAPPI T 402 "Standard Conditioning and Testing Atmospheres for Paper, Board, Pulp Handsheets, and Related Products."

11. Report

11.1 Report a precise identification of the sample.
11.2 Reference TAPPI Official Method T 525.
11.3 Report the brightness of the sample as the average of five tab readings to the nearest 0.1%.
11.4 Indicate whether data were obtained from measurement of a machine sheet or handsheet.

12. Precision

12.1 Data on the precision of measurement have been obtained from the published reports of the TAPPI-NBS Collaborative Reference Program *(4)* in which approximately 15 laboratories participated in the measurement of papers. The brightness values ranged between 75 and 81. The within-laboratory repeatability and the among-laboratory reproducibility were computed from the averages of the reported standard deviations in accordance with TAPPI T 1206 "Precision Statement for Test Methods." It is assumed that the measurement precision for pulp would be comparable.

SCAN-CM 40:94

Revised 1994

SCANDINAVIAN PULP, PAPER AND BOARD
TESTING COMMITTEE

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Wood chips for pulp production

Size distribution

0 Introduction

This SCAN-test Standard replaces SCAN-CM 40:88, from which it differs in that way that mainly editorial changes have been made. In addition to that the Standard has been provided with precision data.

1 Scope

This Standard describes the apparatus and procedure for classification of wood chips, intended for the production of chemical and mechanical pulps. The Standard is applicable to the determination of the quality of wood chips with regard to chip sizes and fines content.

2 References

SCAN-CM 39	Wood chips for pulp production – Dry matter content
SCAN-CM 41	Wood chips for pulp production – Sampling

3 Definitions

For the purpose of this Standard, the following definitions apply:

3.1 *Size distribution* – The content of chips in different classes, grouped according to size and shape.

3.2 *Size classification* – A procedure for separating, by means of a series of screens, a sample of wood chips into fractions according to size or shape.

3.3 *Chip classifier* – Apparatus for chip size classification.

3.4 *Oversize chips* – Chips that do not pass the first screen of the classifier when chip size classification is performed as specified in this Standard.

3.5 *Overthick chips* – Chips that pass the first screen of the classifier, but are retained on the second screen, when chip size classifaction is performed as specified in this Standard.

3.6 *Accept chips* – Chips that pass the two top screens of the classifier, but are retained on the third screen, when chip size classification is carried out as specified in this Standard.

3.7 *Pin chips* – Chips that pass the three top screens of the classifier but are retained on the fourth screen when chip size classification is performed as specified in this Standard.

3.8 *Fines* – Particles that pass all four screens of the classifier when chip size classification is performed as specified in this Standard.

4 Principle

A test sample of chips is placed on the top screen of a stack of four screen trays. The screens have holes or slots of specified dimensions and the stack is kept in a reciprocating motion. After a specified time the screening is stopped and the five fractions obtained are weighed separately. The size of each fraction is its mass, expressed as a percentage of the total mass of all five fractions.

5 Apparatus

5.1 *Chip classifier,* having 4 screen trays and a fines tray, *Figure 1.*

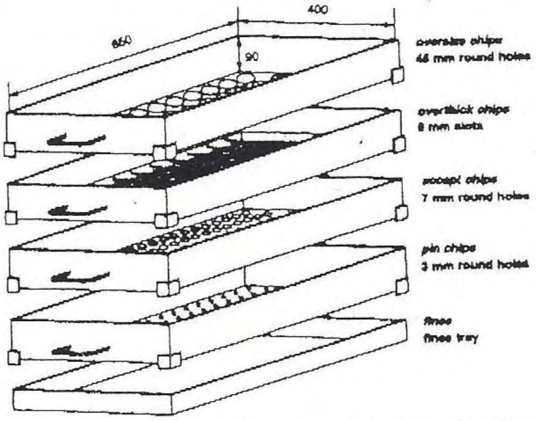

Figure 1. The four screens in the chip classifier (measures in millimetres).

The inside bottom of each screen tray is a screen 650 mm by 400 mm in size. The tray rims are 90 mm high. The fines tray has the same dimensions as the screen trays. The four trays can be mounted on top of the fines tray to form a stack.

> *Note 1* – In some classifiers the fines tray is larger than specified above and mounted in a fixed position under the shaking frame. Such a classifier is considered as complying with this Standard, provided that measures have been taken to avoid loss of sample by dusting and when emptying the tray before weighing the fines.

The four screens meet, in numerical order from the top, the following specifications (maximum and minimum values):

First screen, Figure 2: Made of aluminium or stainless steel, plane and having circular holes, (45,0 ± 0,1) mm in diameter. The holes are placed in a triangular pattern and the distance between the centres of adjacent holes is (60,0 ± 1,0) mm. All holes must be complete circles, parts of holes, i.e. at the edges of the screen, are not allowed.

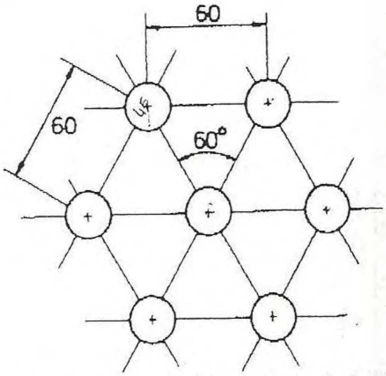

Figure 2. Arrangement of the holes in the hole screens. The distance 60 mm refers to the first screen.

Second screen, Figure 3: Parallel, cylindrical rods of stainless steel, 5 mm in diameter; the free distance between two adjacent rods does not exceed 8,3 mm or fall short of 7,7 mm in any place [(8,0 ± 0,3) mm]. The mean free distance between adjacent rods shall be (8,0 ± 0,1) mm. Each second rod is in a lower level than the others. The vertical distance, *w*, between the two sets of rods is 6,25 mm (centre to centre). The rods are parallel to the short side of the screen and may be supported by a vertical plate, parallel to the longer rims of the screen. This plate must not protrude more than 5 mm over the top rods. The maximum thickness of this plate is 4 mm.

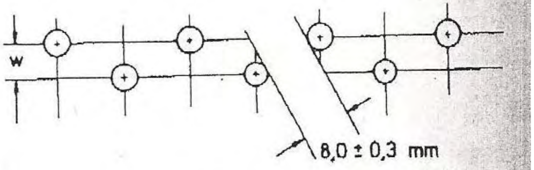

Figure 3. Arrangement of the rods in the second screen. w = 6,25 (measures in millimetres).

Third screen: Similar to the first screen, hole diameter (7,0 ± 0,1) mm, distance between the centres of adjacent holes (8,5 ± 0,3) mm.

Fourth screen: Similar to the first screen, hole diameter (3,0 ± 0,1) mm, distance between the centres of adjacent holes (8,0 ± 0,3) mm.

The other parts of the trays may be made of aluminium, stainless steel or other suitable material.

The stack, with the fines tray, can be firmly fastened on a shaking frame. The frame has a mechanism which gives it a reciprocating motion along a line, parallel to the longer side of the trays. The frame must be guided so that it cannot move in the direction parallel to the shorter side of the trays. The motion in the vertical direction must not exceed 5 mm.

The stroke (the movement in the direction parallel to the longer side of the trays) is 120 mm and the frequency is (160 ± 10) cycles per minute.

> *Note 2* – The dimensions of the screens should be checked regularly. Deposits of sticky material (resin etc.) shall be removed with the aid of a suitable solvent, such as acetone or alcohol.

5.2 *Balance,* accurate and readable to 0,1 g.

6 Sampling and preparation of sample

The sampling procedure is not covered by this Standard. A suitable sampling procedure is described in SCAN-CM 41.

The dry matter content of the sample should be within the range 40 to 70 %. If the sample is wet and has a dry matter content of less than 40 %, dry it to a dry matter content within that range in air of room temperature. The method for determination of dry matter content is described in SCAN-CM 39.

The test portion for each fractionation is 8 to 10 litres. If the sample has to be subdivided to obtain test portions of that size, take precautions to avoid any fractionation of the material. A suitable procedure for subdividing a sample is described in SCAN-CM 41.

7 Procedure

Arrange the trays in the order given in Section 5 to form a stack. Mount the stack on the shaking frame. Distribute the test portion, 8 to 10 litres of chips, on the top tray. Start the shaking mechanism and shake the stack for 10 min. Remove the five fractions obtained and weigh them immediately to the nearest 0,1 g.

> *Note* – No determination of the dry matter content is required, but it is essential for the accuracy of the result that the material does not gain or lose moisture after the fractionation. Therefore, weigh the fractions as quickly as possible on a balance placed near the chip classifier.

8 Calculation and report

Calculate the total mass of all five fractions and then the mass of each fraction as a percentage of the whole, with one decimal. Name the fractions in the trays as follows:

First tray:	oversize chips
Second tray:	overthick chips
Third tray:	accept chips
Fourth tray:	pin chips
Bottom tray:	fines

The test report shall include reference to this SCAN-test Standard and the following particulars:

(a) date and place of testing;
(b) identification mark of the sample tested and an indication as to whether or not sampling has taken place in accordance with SCAN-CM 41;
(c) the results;
(d) any departure from the standard procedure and any other circumstances that may have affected the test results.

9 Precision

Three laboratories tested the same four test samples from a chip pile. At each laboratory one of the samples were analysed ten times. The reproducibility, calculated as the coefficient of variation, is given in *Table 1.*

The repeatability, calculated as the coefficient of variation, is given in *Table 2.*

Table 1. The reproducibility, calculated as the coefficient of variation (between labs and between samples).

	Between labs (n = 3)	Between samples (n = 4)
Oversize chips	0,34	1,27
Overthick chips	0,05	0,16
Accept chips	0,03	0,07
Pin chips	0,18	0,12
Fines	0,24	0,26

SCAN-CM 38:96
SCAN-P 74:96
Revised 1996

SCANDINAVIAN PULP, PAPER AND BOARD
TESTING COMMITTEE

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Pulps, papers and boards

Calcium, magnesium, iron, manganese and copper content

Atomic absorption spectroscopy

0 Introduction

This SCAN-test Standard replaces SCAN-CM 38:87 which included only the determination of copper, iron and manganese in pulps and not in paper and board. In addition, SCAN-CM 38:87 only related to the acid-soluble part of the incineration residue. This revised Standard also refers to the acid-soluble part of the incineration residue, i.e. that part of the ignition residue obtained after incineration which is soluble in hydrochloric acid. In addition, an Annex describes the analysis of the insoluble part of the ignition residue.

1 Scope

This Standard describes the procedure for the determination of calcium, magnesium, iron, manganese and copper by atomic absorption spectroscopy. It is applicable to all types of pulp, paper and board.

> *Note 1* – The determination can also be made by plasma emission spectroscopy.

If the residue from the incineration is completely soluble in hydrochloric acid, the results are taken as the totalamount of the element in the sample. If, after treatment with acid, an insoluble residue remains, the total amount can be determined only by applying both the procedure described in the Standard and the procedure described in the Annex.

> *Note 2* – The reason for including in the standard the option of determining only the acid-soluble fraction of the elements in samples with an unsoluble ignition residue is that in a number of cases the acid-soluble fraction is more informative than the total content. Elements bound so firmly that they are not leachable in acid often have no relevance in the use of the material. For example, they are not likely to contaminate food in food-packaging, to enhance the formation of odorous compounds or to promote yellowing.

2 References

SCAN-C 3	Pulp – Dry matter content
SCAN-C 6	Ash in pulp
SCAN-P 4	Moisture in paper and paperboard

3 Definitions

For the purpose of this Standard, the following definitions applies:

3.1 *Acid-soluble element content* – The element content in the solution obtained after incinerating the sample at 575 °C and treating the residue with 6 mol/l hydrochloric acid as specified in this Standard.

3.2 *Total element content* – The sum of the acid-soluble element content and the acid-insoluble element content.

4 Principle

The sample is incinerated and charred at 575 °C. The charred residue is treated with 6 mol/l hydrochloric acid and the acid-soluble element content in the solution is determined by flame atomic absorption spectroscopy.

5 Reagents and chemicals

Use only chemicals of analytical grade.

5.0 *Water*, of high purity, deionized or distilled water.

5.1 *Hydrochloric acid*, $c(HCl)$ about 6 mol/l. Dilute 500 ml of hydrochloric acid (density 1,19 g/ml) in 500 ml of water (5.0).

5.2 *Reference solutions*. Reference solutions have a shelf-life of several months if stored in polyethylene bottles.

Commercially available reference solutions may be used.

5.2.1 *Calcium reference solution*, $c(Ca) = (1000 \pm 2)$ mg/l. In a 1000 ml volumetric flask, dissolve 2,497 g of dry $CaCO_3$ in 50 ml hydrochloric acid (5.1) and fill up to the mark with water (5.0).

5.2.2 *Magnesium reference solution*, $c(Mg) = (1000 \pm 2)$ mg/l. In a 1000 ml volumetric flask, dissolve 1,000 g of magnesium in 50 ml of hydrochloric acid (5.1) and fill up to the mark with water (5.0).

5.2.3 *Copper reference solution*, $c(Cu) = (1000 \pm 2)$ mg/l. Dissolve 1,000 g of electrolytically pure copper in a minimum volume of nitric acid (HNO_3, density 1,4 g/ml). Boil the solution to expel all nitrous gases and allow it to cool. Transfer the solution quantitatively to a 1000 ml volumetric flask and fill up to the mark with water (5.0).

5.2.4 *Iron reference solution*, $c(Fe) = (1000 \pm 2)$ mg/l. In a 1000 ml volumetric flask, dissolve 1,000 g of pure oxide-free iron wire in a minimum volume of hydrochloric acid (density 1,19 g/ml). Fill up to the mark with water (5.0).

5.2.5 *Manganese reference solution*, $c(Mn) = (1000 \pm 2)$ mg/l. In a 1000 ml volumetric flask, dissolve 2,748 g of manganese sulphate, $MnSO_4$, dried at 300 °C, in water (5.0). Add 5 ml of hydrochloric acid (5.1) and fill up to the mark with water (5.0).

5.3 *Cesium solution*, $c(Cs) = 50$ g/l. In a 1000 ml volumetric flask, dissolve 63,5 g of ultra-pure cesium chloride, CsCl, in water (5.0) and fill up to the mark with water.

> *Note 1* – This solution is used to suppress ionization of calcium and magnesium in the nitrous oxide/acetylene-flame.
>
> The solution is normally not required when the air/acetylene-flame is used.

5.4 *Lanthanum solution*, $c(La) = 50$ g/l. In a 1000 ml volumetric flask, dissolve with caution 59 g of lanthanum oxide, La_2O_3, in 250 ml of hydrochloric acid (density 1,19 g/ml) and fill up to the mark with water (5.0).

> *Note 2* – This solution is used to eliminate interference from phosphates when determining calcium or magnesium in an air/acetylene-flame.
>
> The solution is normally not required when the nitrous oxide/acetylene-flame is used.

6 Apparatus

6.1 *Ordinary laboratory equipment*. Laboratory vessels made of plastics are recommended as well as ash-free filter paper (particle retention 20 µm - 25 µm). Clean all equipment in 0,1 mol/l hydrochloric acid.

6.2 *Dishes* of platinum or quartz.

> *Note* – Wash the dishes thoroughly. Remove any spots in the platinum dishes by cleaning with fine sand. Boil the dish with hydrochloric acid (5.1) and avoid any possible contact with metals other than platinum. If necessary, clean platinum dishes by melting sodium carbonate in them.

6.3 *Atomic absorption spectrometer*, with a burner for air/acetylene and/or for nitrous oxide/acetylene and with hollow-cathode lamps for the elements to be determined (multi-element lamps may be used).

7 Incineration and dissolution of the residue

7.1 *Sample preparation.* The sampling procedure is not covered by this Standard. Make sure that the test pieces taken are representative of the sample received.

Carry out the determination at least in duplicate. Tear the air-dry sample into pieces of suitable size. Do not use cut edges, punched holes or other parts where metallic contamination may have occurred.

7.2 *Weighing.* Select the amount of sample with regard to the anticipated element content. Normally an amount of between 2 to 5 g is suitable but, if copper is to be determined in pulp, a larger amount of sample is recommended (10 g - 20 g) because the copper content of such samples is normally very low.

In a clean dish (6.2) with known weight, weigh the sample to the nearest 0,01 g. At the same time, weigh a separate test portion for the determination of dry matter content in accordance with SCAN-C 3 or SCAN-P 4, as relevant.

7.3 *Incineration.* Use a hot plate, a program-controlled oven or a low flame of a gas burner and char the sample until it is well carbonized. The temperature must not exceed 575 °C.

If the dish is too small to hold the entire sample, gentle burn it off in portions. Take care not to let any ash blow from the dish. Then place the dish in a furnace and incinerate at a temperature of (575 ± 25) °C for a period of 3 h, or longer if needed to burn away all the carbon.

> *Note 1* – In order to avoid flames, the dish can be covered by a lid. The lid must not be so tight that reducing conditions occur in the dish, in which case acid-insoluble compounds may be formed. Under reducing conditions, e.g. copper may be lost due to the formation of a platinum alloy.

Weigh the incineration residue (*a*). If the residue exceeds 0,5 g, after thoroughly mixing with a glass rod, take a fraction of the residue and weigh it (*b*).

7.4 *Blank.* Run a blank with the same chemicals as those added to the incineration residue but without any residue (see Clause 7.5).

7.5 *Dissolving the incineration residue in acid.* To avoid splattering, with caution moisten the residue (or the fraction of the residue) with water (5.0) and add 5 ml of hydrochloric acid (5.1) to the dish. Evaporate to dryness on a boiling water-bath or equivalent device. Repeat this procedure once.

> *Note 2* – For samples with a high carbonate content, more than 10 ml of acid (2 x 5 ml) may be required. In such a case, the blank should be run using the same amount of acid.

Add 2,5 ml of the acid (5.1) to the dry residue and heat the dish, if needed covered by a watch glass.

Use the filter (6.1) and filter the contents of the dish into a 25 ml volumetric flask. To ensure that the transfer is quantitative, add another portion of 2,5 ml of acid (5.1) to the dish and heat it again. Filter this last portion of acid to the main portion in the volumetric flask with the aid of some water (5.0).

Wash the insoluble residue with water (5.0) into the volumetric flask. Fill up to the mark and mix.

If the total content is to be determined, keep the filter with the insoluble residue for the analysis of the insoluble part of the residue, as described in the Annex. The insoluble residue should be treated in the same dish without intermediate cleaning. Further instructions are given in the Annex.

8 Determination

8.1 *Preparation of calibration solutions.* It is important that the acid concentration is the same in the calibration and in the sample solutions since the acid concentration influences the signal.

> *Note 1* – Usually it may be preferable to prepare multi-element calibration solutions. When required, add cesium or lanthanum solutions as specified in 8.2.

At least three calibration solutions and one zero solution should be used for the construction of the calibration graph. (The zero solution is similar to the calibration solutions, but contains no added elements. It should not be confused with the blank). An example of suitable calibration solutions is given in *Table 1*.

Table 1. Example of suitable calibration solutions. All concentrations are given in milligrams per litre.

	Zero	I	II	III
Ca	0	1,0	2,0	4,0
Mg	0	0,25	0,5	1,0
Cu	0	0,5	1,0	2,0
Fe	0	1,0	3,0	5,0
Mn	0	1,0	2,0	3,0

8.2 *Measurement.* Carry out the spectrometric measurements of the calibration solutions, of the sample solutions and of the blank solution. Operate the instrument as instructed by the manufacturer.

If any value obtained exceeds the range covered by the calibration solutions, the measurement must be repeated with a more dilute sample solution. Add acid (5.1), cesium (5.3) or lanthanum (5.4) as required.

> *Note 2* – Cesium (5.3) and lanthanum (5.4) solutions are not needed and shall therefore not be used in the determination of iron, copper and manganese. Cesium (5.3) and lanthanim (5.4) solutions shall only be used for the determination of calcium and magnesium.

If a nitrous oxide/acetylene-flame is used, add cesium solution (5.3) so that $c(\mathrm{Cs})$ in the solution used for measurement will be 1 g/l to prevent ionization. If an air/acetylene-flame is used, add lanthanum solution (5.4) so that $c(\mathrm{La})$ will be 5 g/l.

Most instruments have a system for automatic evaluation of results. If the instrument has no automatic evaluation of results, plot the absorbance, corrected for the blank, against the element content (in milligrams per litre).

9 Calculation

9.1 *Acid-soluble element content.* Calculate the acid-soluble element contents, X, from the expression:

$$X = \frac{c\,f\,V\,a}{m\,b} \qquad [1]$$

where

X is the element content, in milligrams per kilogram;
c is the concentration of the element in the sample solution, as obtained from the calibration plot corrected for the blank, in milligrams per litre;
f is the dilution factor (flask volume/aliquot);
V is the volume of the sample solution (standard 25 ml);
m is the amount of sample taken, oven dry basis, in grams;
a is the total weight of the residue, in grams;
b is the weight of the residue fraction taken, in grams.

Calculate the mean element content for each element, with two significant figures for values above 1 mg/kg and with one significant figure in the range 0,1 mg/kg to 1 mg/kg.

9.2 *Total element content.* To obtain the total amount of the element in the sample, add the amount of the element which is soluble in hydrochloric acid, X, determined as described in this Standard, to the result, Z, obtained by the melt procedure described in the Annex.

10 Report

The test report shall include reference to this SCAN-test Standard and the following particulars:

(a) date and place of testing;
(b) identification mark of the sample tested;
(c) the results, element by element, and a statement as to whether acid-soluble element content or total element content is reported;
(d) any departure from the standard procedure and any other circumstances that may have affected the test results.

11 Precision

The precision data given includes results for the determination of the acid soluble element content as well as results for the total element content. The precision of the results when measuring the total amount of the determinand is influenced by both the precision of the results for the acid-soluble part of the sample and the precision of the results for the melt-soluble part of the sample. The part of the elements which does not dissolve in acid sometimes remains in the melt-soluble part in such a way that the two parts compensate each other. In such situations, the deviation in the total amount of the determinand is often less than the deviations for the acid-soluble part and the melt-soluble part separately.

11.1 *Repeatability.* A sample of uncoated paperboard was analysed in one laboratory nine times. The following results, mean value and coefficient of variation (CV) were obtained:

Element	Acid-soluble element content	
	Mean, mg/kg	CV, %
Calcium	730	10
Magnesium	210	7
Iron	13	8
Manganese	33	2
Copper	0.5	24

11.2 *Reproducibility.* Four samples were analysed in eight laboratories. In the samples from bleached pulp and uncoated paperboard, 100 % of the total element content was found in the acid-soluble fraction. For the acid-insoluble residue, two different melt chemical mixtures were used (sodium carbonate-boric acid melt and sodium carbonate-potassium carbonate melt). The total element results presented here are based on the mean value for the two melt chemical procedures. The following results, mean value and coefficient of variation (CV), were obtained:

Results for the determination of calcium:

Sample type	Acid-soluble element content		Total element content	
	Mean, mg/kg	CV, %	Mean, mg/kg	CV, %
Bleached pulp	160	6	160	6
Coated paperboard	10 500	5	11 000	6
Uncoated paperboard	640	9	640	9
Copy paper	86 400	11	88 000	3

Results for the determination of magnesium:

Sample type	Acid-soluble element content		Total element content	
	Mean, mg/kg	CV, %	Mean, mg/kg	CV, %
Bleached pulp	16	11	16	11
Coated paperboard	58	15	67	4
Uncoated paperboard	190	9	190	9
Copy paper	1 600	16	2 100	5

Results for the determination of iron:

Sample type	Acid-soluble element content		Total element content	
	Mean, mg/kg	CV, %	Mean, mg/kg	CV, %
Bleached pulp	3,6	45*	3,6	45*
Coated paperboard	430	19	590	13
Uncoated paperboard	13	28*	13	28*
Copy paper	180	4	210	8

* The high CV-value for iron is due to an uneven distribution of the element in the sample.

Results for the determination of manganese:

Sample type	Acid-soluble element content		Total element content	
	Mean, mg/kg	CV, %	Mean, mg/kg	CV, %
Bleached pulp	0,2	19	0,2	19
Coated paperboard	7,4	18	8,1	14
Uncoated paperboard	32	10	32	10
Copy paper	19	15	21	16

Results for the determination of copper:

Sample type	Acid-soluble element content		Total element content	
	Mean, mg/kg	CV, %	Mean, mg/kg	CV, %
Bleached pulp	0,4	73*	0,4	73*
Coated paperboard	2,2	29*	3,4	31*
Uncoated paperboard	0,4	63*	0,4	63*
Copy paper	1,6	28*	2,8	37*

* The high CV-value for cupper is due to an element content close to the lower limit of detection and by an uneven distribution of the element in the sample.

Note – The limit of detection in the acid-insoluble procedure (using a melt mixture) is higher than in the acid-soluble procedure due to the fact that the sample solution is more dilute in relation to the amount of sample weighed. This must be taken into consideration when the accuracy of the procedure is estimated, especially for copper, which usually occurs at a concentration lower than that of the other elements. For example, a deviation in the sample solution of 0,02 mg/l corresponds to a deviation in the final result of 0,1 mg/kg for a 20 g sample and a deviation in the final result of 1 mg/kg for a 2 g sample.

Annex –
Content of elements in the insoluble ignition residue

A.1 Introduction

If an insoluble residue remains after the incineration residue has been dissolved in hydrochloric acid, the residue can be analysed using the procedure described in this Annex.

The procedure makes it possible to determine the total element content in pulps, papers and boards yielding a large incineration residue or an incineration residue which is difficult to dissolve.

A.2 Principle

The insoluble residue which remains after dissolution of the incineration residue in 6 mol/l hydrochloric acid is filtered, ignited together with the filter paper, and mixed with melt chemicals. The mixture is melted with the aid of a gas burner and then in an oven, and is then cooled and dissolved. After dissolution, the element content is determined by flame atomic absorption spectroscopy.

Two alternative melt mixtures are described;

A. Sodium carbonate - potassium carbonate melt;
B. Sodium carbonate - boric acid melt

Alternative A:
Sodium carbonate - potassium carbonate melt;

A.3 Reagents and chemicals

All reagents and chemicals used in Clause 5 in this Standard and the following *melt chemical mixture:*

A.3.1 *Sodium carbonate-potassium carbonate melt.* Mix sodium carbonate, Na_2CO_3, and potassium carbonate, K_2CO_3, in the required amounts in the proportions 106:138 (equimolar mixture). The mixture is commercially available.

A.4 Procedure

A.4.1 *Blank.* Run a blank with the same chemicals as those added to the sample but without any sample.

A.4.2 *Procedure for the insoluble residue.* Transfer the filter paper with the insoluble residue to a platinum dish (6.2) and dry it. Incinerate with a gas burner and ignite in a furnace at 575 °C. Let it cool in a desiccator. Add 2 g of the melt mixture (A.3.1). The amount of melt mixture must not be less than 10 times the weight of the ash.

> *Note 1* – If the amount of ash is too large, a weighed portion of it can be taken after thorough mixing with a glass rod. The proportion taken shall be considered when calculating the result.

Stir with a glass rod. Heat the mixture over a gas burner until it has melted. If a transparent melt is not obtained, place the dish in a furnace at 900 °C and keep it there for 15 minutes. Allow the dish to cool. Leach the melt with water by putting the dish including the melt in a 250 ml beaker with 50 ml - 100 ml water (5.0) and heating in a water bath. Sometimes a red-blue colour develops in the solution, caused by the formation of permanganate. The permanganate can be removed by reduction with ethanol. Add a few drops of ethanol until the colour disappears.

Filter the mixture, wash the dish and filter 3 to 5 times with 1 % sodium carbonate-potassium carbonate solution. This solution is used to reduce the solubility of carbonates in the precipitation on the filter. Do not use the filtrate.

Add 5 ml of hydrochloric acid (5.1) in the dish to dissolve the carbonates of the elements. Transfer the acid carefully to the filter and collect the filtrate in a 50 ml volumetric flask. Repeat the procedure once. Wash the filter with water acidified with hydrochloric acid. Fill up to the mark with water.

A.5 Measurement

A.5.1 *Preparation of calibration solutions.* When the above procedure is used, the sample solution does not contain any melt chemicals, since they have been removed by washing. Therefore use the calibration solutions described in Clause 8.1. The concentration of acid should be the same in the calibration and sample solution.

A.5.2 *Measurement.* Carry out the measurements as described in Clause 8.2, page 3.

If any value obtained exceeds the range covered by the calibration solutions, the measurements must be repeated with a more dilute sample solution.

Calculate the result as described in A.9.

Alternative B:
Sodium carbonate - boric acid melt

A.6 Reagents and chemicals

All reagents and chemicals used in Clause 5 in this Standard and the following *melt chemical mixture:*

A.6.1 *Sodium carbonate-boric acid melt.* Mix sodium carbonate, Na_2CO_3, and boric acid, H_3BO_3, in the required amounts in the weight proportions 3:1.

A.6.2 *Matrix solution.* Use the matrix solution for the preparation of calibration solutions and for dilution of the sample solutions. The matrix solution contains the same reagents, in the same concentrations as the sample solutions, when these are prepared as described in Clause 5.

A.6.2.1 *Sodium carbonate-boric acid melt.* Dissolve 5 g of boric acid, H_3BO_3, and 15 g of sodium carbonate, Na_2CO_3, in water in a 1000 ml volumetric flask. Add 100 ml of hydrochloric acid (5.1).

Add 20 ml of cesium solution (5.3) and 10 ml of lanthanum solution (5.4) and fill up to the mark with water (5.0).

A.7 Procedure

A.7.1 *Blank.* Run a blank with the same chemicals as those added to the sample but without any sample.

A.7.2 *Procedure for the insoluble residue.* Transfer the filter paper with the insoluble residue to a platinum dish (6.2) and dry it. Incinerate with a gas burner and ignite in a furnace at 575 °C. Let the dish and the residue cool in a desiccator. Add 2 g of the melt mixture (A.6.1). The amount of the melt mixture must not be less than 10 times the weight of the ash.

> *Note 1* – If the amount of ash is too large, a weighed portion of it can be taken after thorough mixing with a glass rod. The proportion taken shall be considered when calculating the result.

Stir with a glass rod. Heat the mixture over a gas burner until it has melted. If a transparent melt is not obtained, place the dish in a furnace at 900 °C and keep it there for 15 minutes. Allow the dish to cool. Dissolve the melt in water using a magnetic stirrer and transfer the solution to a 100 ml volumetric flask. If a larger melt than 2 g has been prepared, use a correspondingly larger volumetric flask in order to maintain the proportion between salts and water volume. Carefully add 10 ml of hydrochloric acid (5.1) to dissolve the carbonates. Add a part of the hydrochloric acid to the dish to dissolve remaining carbonates. Wash the dish carefully with hydrochloric acid. If the determination is to be carried out by the atomic absorption technique, add 2 ml of cesium solution (5.3) and 1 ml of lanthanum solution (5.4). If a larger melt has been prepared, add these reagents in a corresponding proportion. Fill up to the mark. Mix and let the solution stand until remaining solid material has settled. Use the transparent solution for the measurements.

> *Note 2* – If the sample contains a large amount of silicon, silicic acid may precipitate. The elements remain in solution under acid conditions, if the precipitation is not too extensive.

A.8 Measurement

A.8.1 *Preparation of calibration solutions.* Prepare the calibration solutions using the matrix solution described in A.6.2.1.

> *Note* – It is important that calibration and sample solutions are matrix matched to each other. It is usually practical to prepare multi-element standards. The matrix solution is used as zero-solution.

A.8.2 *Measurement.* Carry out the measurements as described in Clause 8.2, page 3.

If any value obtained exceeds the range covered by the calibration solutions, the measurements must be repeated with a more dilute sample solution. Use the matrix solution as zero-solution.

A.9 Calculation (alternatives A and B)

A.9.1 *Elements in the acid-insoluble residue.* Calculate the element content, Z, in the insoluble residue, from the expression:

$$Z = \frac{c\,f\,V\,a}{m\,b} \qquad [A1]$$

where

Z is the acid-insoluble element content in the original sample, in milligrams per kilogram;
c is the concentration of the element in the sample solution, as obtained from the calibration plot corrected for the blank solution, in milligrams per litre;
f is the dilution factor, if dilution is used;
V the volume of the sample solution (normally 100 ml);
m is the amount of original sample of pulp, paper or board taken (not residue), oven dry basis, in grams;
a is the total amount of the ash, in grams;
b is the weighed amount of the ash, in grams.

A.10 Report

Report the results according to instructions given in Clauses 9.2 and 10, page 4. The mean value of the acid-soluble part and the total amount of the element should be reported.