

A Rapid Method for Quantification of Carboxyl Groups in Cellulose Pulp

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Carbonyl and carboxyl groups are important components of bleached cellulosic pulp due to their significant effect on the mechanisms that cause paper aging. Pulp yellowing and the decrease in cellulose molecular weight during aging are usually linked to these two functional groups. Carbonyl groups initiate oxidative processes, but their effects are largely increased when carboxyl groups are also present in the pulp. This work presents an automated potentiometric method for quantitative determination of carboxyl groups in bleached kraft pulp. The results obtained were compared with those obtained by the TAPPI (T 237 om-93) standard method using the same samples. A good correlation ($r = 0.9956$) was observed between the methods, where the automated potentiometric titration method is most attractive due to its simplicity of execution and a shorter time required for the analysis. This method can be easily applied to quality control of a large number of samples in an industrial environment.

Keywords: Bleached kraft pulp; Eucalypt; Carboxyl groups; Potentiometric titration

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INTRODUCTION

Market demand for bleached pulps of high brightness has stimulated research into determination of the factors affecting pulp brightness stability, a parameter of great importance in the evaluation of pulp quality (Weir and Miller 2000). The papermaking process includes a series of chemical interactions that play an important role in consolidation and performance of the final product. The quality of such products can also be influenced by the composition of the lipophilic wood extractives (Silvério *et al.* 2007, 2008) and the appearance of impurity specks originated from various sources in the plant (Silvério *et al.* 2009).

Pulp brightness reversion (yellowing) is a consequence of the formation of chromophore groups and is directly related to the content of hexenuronic acids (Vuorinen *et al.* 1999; Sevastyanova *et al.* 2006a, 2006b; Eiras *et al.* 2008; Maltha *et al.* 2011) and carbonyl and carboxylic groups (Rapson and Hakin 1957; Sjostrom and Eriksson 1968; Buschle-Diller and Zeroniam 1993; Chirat and Lachenal 1994; Eldin and Fahmy 1994; Kolar *et al.* 1998; Tran 2002; Potthast *et al.* 2007). The presence of carbonyl groups in pulp potentiates the effect of hexenuronic acids in brightness reversion (Chirat and Lachenal 1994). In some cases, a positive correlation has been observed between the permanganate number, an indirect measure of pulp oxidizable materials, and the brightness reversion (Colodette *et al.* 2004).

Identification and quantification of pulp chromophores is very difficult by conventional analytical procedures due to their low concentration (scale of $\mu\text{mol g}^{-1}$) and also because they are connected within the pulp matrix (Jaaskelainen *et al.* 2009). Although many chromophores can be evaluated by spectroscopic methods (Loureiro *et al.* 2010), chemical methods can also be applied for quantitative analysis of carbonyl and carboxyl groups by titration or derivatization. In the latter procedure, the chromophore groups are converted into chemical structures that can be monitored by traditional spectroscopic techniques (Rohrling *et al.* 2002).

The main reactions that act on the cellulose fiber are responsible for altering its structure are photodegradation, acid hydrolysis, oxidation, and biodegradation (Vicini *et al.* 2004). However, the impact of chemical changes occurring on cellulose must be considered with respect to pulp brightness stability. Carbohydrates are quite vulnerable to attack by various oxidizing agents (Dence and Reeve 1996). The principal reactions of cellulose with ozone involve oxidation of the reducing end groups to carboxyl groups and oxidation of hydroxyl groups to carbonyl groups (aldehyde and ketone) (Lemeune *et al.* 2004; Silva *et al.* 1996). Oxidation with sodium periodate (NaIO_4) is highly specific and leads to selective cleavage of the bond between hydroxyl groups present in C_2 and C_3 carbons of the glycoside ring, as well as the formation of two aldehyde groups (Varma and Kulkarni 2002; Vicini *et al.* 2004; Princi *et al.* 2006). However, oxidation with NaIO_4 followed by oxidation with sodium chlorite (NaClO_2) introduces carboxyl groups mainly in positions 2 and 3 (Fig. 1) of the glycoside ring (Fras *et al.* 2005).

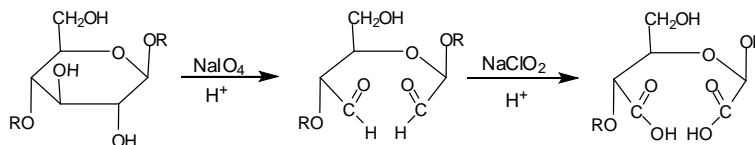


Fig. 1. Oxidation reactions of cellulose with NaIO_4 and NaClO_2

Hydroxyl groups in the cellulose structure make the molecule very reactive with respect to the numerous chemical reactions occurring during pulping and bleaching, resulting in the formation of carbonyl and carboxyl groups (Rohrling *et al.* 2002; Vicini *et al.* 2004). The presence of oxidized groups in cellulose is not desirable, since several parameters for evaluating the quality of the pulp and other cellulosic materials, especially strength properties (Rohrling *et al.* 2002), are affected by its occurrence. It is also considered that these groups are those most responsible for induction of brightness reversion in bleached pulp (Weir and Miller 2000; Potthast *et al.* 2003).

Although the loss of pulp brightness stability is related to the presence of carboxyl and carbonyl groups, it is known that ion exchange capacity of cellulose is mainly determined by the content of carboxylic groups in the pulp (Fras *et al.* 2004). These anionic groups play an important role in the production of paper because they are considered sites of cationic retention additives, used to improve retention on the paper machine (Chen *et al.* 2004). Therefore, it is important to know the content of carboxyl groups in order to understand the conditions of its formation, as well as for evaluating the advantages and disadvantages of maintaining such groups in the pulp and paper.

Among the various laboratory methods developed for determining the content of carboxylic groups in cellulose pulp, the most commonly used are the potentiometric (Fras *et al.* 2005) and conductometric titrations (Buchert *et al.* 2001; Fras *et al.* 2005) and the

methylene blue method (Davidson 1948a; Fardim and Holmbom 2003). Imprecision of the results may occur in the case of the methylene blue method (interaction of the dye with OH groups present in the pulp) and conductometric titration (difficulty in determining the equivalence point for weak acids at low concentration).

The determination of the carboxylic acid content in industrial pulps is of great practical importance. The most currently used method for this analysis is the procedure described by TAPPI standard protocol T237 om-93. Although this procedure has been largely employed, it is based on an indirect titration and involves a lengthy sequence of steps, which allows for the analysis of three samples a day for those skilled in the art. Also, the visualization of the titration end-point is subjective and can lead to poor reproducibility. Considering our experience in developing an automated potentiometric system for the analysis of very weak humic acids in soil (Reis *et al.* 2010), we envisaged that such system could be successfully adapted for the quick analysis of carboxylic groups in pulp.

In this paper we present a methodology for quantitative determination of carboxyl groups in kraft pulps obtained from the Brazilian industry using a fully automated system. The results obtained by the potentiometric titration method were compared with those obtained by the TAPPI method, recognized by the Technical Association of Pulp and Paper Industry and widely used in the pulp and paper industry.

MATERIAL AND METHODS

Sample Preparation

Samples of kraft pulps bleached by different bleaching sequences (Samples 1-7) were obtained from the Brazilian industry. In the case of samples 8 to 12, more extensive oxidation conditions were used to obtain pulp with unusually high content of carboxyl groups. All these samples were submitted initially to an O/OA/D(PO) DP bleaching sequence. For samples 8, 9, and 10 a subsequent treatment with ozone was carried out. Sample 11 was treated with NaIO₄. This oxidizing reagent is known to cleave diol groups into aldehydes. Sample 12 was also treated with NaIO₄ followed by a further oxidation of the aldehyde groups into COOH by reaction with NaClO₂ (Table 1).

Table 1. Bleaching Sequences and Subsequent Oxidative Treatments of Pulps

Samples	Bleaching sequence	Oxidative Treatments
1	CCE-D(EPO) DD	-
2	O/OA/D(PO) DP	-
3	OD(EPO)DP	-
4	OD _{HT} (PO)D	-
5	OD _{HT} (PO)D	-
6	OA/Z/EDP	-
7	OD _{HT} (EP)D(PO)	-
8	O/OA/D(PO) DP	O ₃ , 0.5%
9	O/OA/D(PO) DP	O ₃ , 2.5%
10	O/OA/D(PO) DP	O ₃ , 5.0%
11	O/OA/D(PO) DP	NaIO ₄
12	O/OA/D(PO) DP	NaIO ₄ /NaClO ₂

CCE (cold alkaline extraction), D (oxidation with chlorine dioxide), EPO (oxidative extraction with oxygen and peroxide), O (oxygenation), A (hot acid hydrolysis), (PO) (pressurized peroxidation with oxygen), P (peroxidation), D_{HT} (oxidation with chlorine dioxide at high temperature), Z (ozonolysis), E (alkaline extraction), (EP) (oxidative extraction with hydrogen peroxide).

Oxidation of the Cellulose Pulps

The oxidation procedures were conducted using sample 2, oven dry (o.d.) pulp. Oxidation with ozone (3 x 250 g o.d.) was performed in the reactor/mixer Mark V (Quantum Technologies) coupled to an ozone compressor (Ozone Cart). The resulting oxidized pulps (samples 8, 9, and 10) were washed with distilled water (9 m³/ton of pulp), and the excess water was removed by centrifugation.

To obtain sample 11, 1.5 L of a 0.01 mol L⁻¹ NaIO₄ solution was added to sample 2 (2 x 15 g o.d.). The mixture was maintained under magnetic stirring at 20 °C for 12 h in the dark, then filtered and washed with distilled water until reaching a pH of approximately 7.

Sample 12 was prepared by adding 1.5 L of a NaClO₂ 0.2 mol L⁻¹ solution to 15 g o.d. of sample 11. The mixture was maintained under magnetic stirring at 20 °C for 48 h in the dark, then filtered and washed with distilled water until reaching a pH of approximately 7.

Pulp Analysis

Determination of carboxyl groups in the pulps was performed according to the procedure described in the TAPPI standards (T 237 om-93) and by direct potentiometric titration (Fras *et al.* 2005). The hexenuronic acids content was determined according to the procedure described in the literature (Tenkanen *et al.* 1999).

The equipment for potentiometric titration included the potentiometer ORION, Model 901, equipped with combined electrodes of glass and the reference electrode of Ag/AgCl was used. A peristaltic pump was used to propel the titrant solution and flow was controlled using Teflon® solenoid valves (Fig. 2). The program manager, in Visual Basic, permits real-time visualization of the potentiometric data and the titration curve, as well as recovery of data stored for posterior comparisons. This equipment has been successfully used for potentiometric titration of carboxyl groups in humic acids (Reis *et al.* 2010).

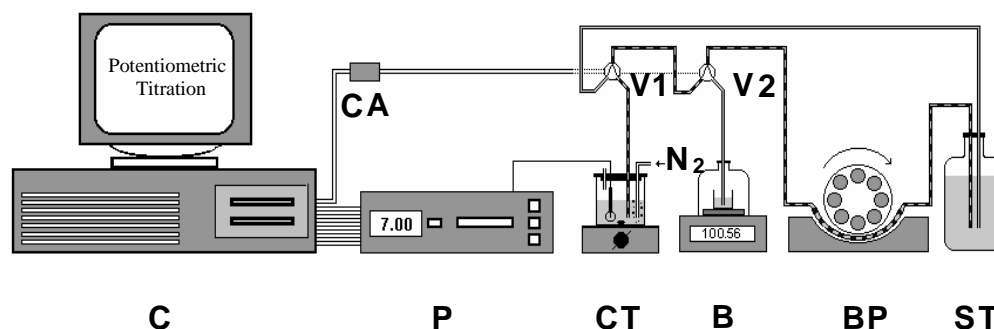


Fig. 2. Schematic representation of the potentiometric titration apparatus: C (PC-486 microcomputer), P (potentiometer), CT (titration cell), B (semi-analytical balance), PB (peristaltic pump), ST (titrant solution), CA (auxiliary circuit for the control valves), V1 and V2 (Teflon solenoid valves).

To perform the analysis, 0.5 g o.d. of each pulp sample were used and placed in a flask containing 60 mL of a 0.1 mol L⁻¹ HCl solution. The mixture was maintained under magnetic agitation until complete dispersion and then left still at room temperature for 2 h. After filtration, the sample was washed with deionized water saturated with CO₂ until

observing that a 10 to 20 mL aliquot of the filtrate, containing 2 drops of methyl red indicator solution under boiling, did not consume more than 1 or 2 drops of the 0.01 mol L⁻¹ NaOH solution for persistence of its yellow color. The sample was then transferred to a 100 mL cuvette, where 50 mL of 0.5 mol L⁻¹ solution of NaCl for controlling the ionic strength was added. This mixture was maintained under magnetic stirring until complete dispersion. After bubbling nitrogen (N₂) in the mixture, titration was performed in triplicate using a 0.02 mol L⁻¹ NaOH standardized solution in 0.5 mol L⁻¹ solution of NaCl. The criterion of stability for recording the pH after addition of NaOH aliquots was drift of less than 0.002 pH unit/10 seconds.

During potentiometric titration, the amount of titrant volume added and pH of the solution were recorded after each addition. The titrant solution was slowly added (0.1 mL per addition), permitting that the titration curves were plotted with 51 points. Exceptions occurred in the case of pulps 1 and 12, where 31 and 151 points were necessary, respectively. The content of carboxyl groups was determined according to the following expression,

$$C_0 = \left(\frac{N * V * 100}{M} \right) \quad (1)$$

where C_0 is the content of carboxyl groups (meq/100 g), N is the titrant concentration, V is the volume (mL) at the equivalence point, and M is the oven-dried pulp mass (g).

Analyses for determining the concentration of hexenuronic (Vuorinen *et al.* 1996) and uronic acids (Scott 1979) in the bleached and oxidized pulps were performed according to methods adapted from procedures described in the literature.

RESULTS AND DISCUSSION

The system used for the potentiometric analysis was set up as described in Experimental, and all data collection and analysis were performed by a Visual Basic program developed in house.

Considering the low quantities of COOH groups present in the pulps, some preliminary experiments were performed in order to establish the concentration of NaOH solution for the titration, the amount of sample and the volume of NaCl aqueous solution used to suspend the pulp.

A direct titration of 0.5 g o.d. of pulp containing all carboxylic groups protonated suspended in 50 mL of 0.5 mol L⁻¹ aqueous solution of NaCl and titrated with a 0.02 mol L⁻¹ NaOH standardized solution was found suitable. The preparation of the sample for the titration requires approximately 2.5 h. On the other hand, the TAPPI protocol involves 2 filtrations and takes approximately 10 to 12 h to analyze 2 to 3 samples, depending upon the analyst skills. In order to evaluate the adequacy of the proposed procedure for pulps with different content of COOH groups, samples treated under different bleaching sequences and conditions were used. Samples with higher content of COOH groups were obtained by direct oxidation of bleached pulp with ozone and NaIO₄/NaClO₂ as described in the experimental.

The automated potentiometric titration was performed with around 51 points per curve for most of the samples. For sample 12 with a very high COOH content up to 151 points were taken.

In the potentiometric titrations performed with the bleached and oxidized pulps, the end point was determined automatically from an inflection point of the titration curves. This procedure reduces the errors associated with the visual observation of the equivalent point using an indicator as in the TAPPI method. As an example, Figs. 3 and 4 show respectively, the potentiometric titration curve and curves of the first (dpH/dV vs. V_{mean}) and the second ($\text{d}^2\text{pH/dV}^2$ vs. V) derivatives, as well as the equivalence volume calculated from the second derivative of sample 2. The maximum position of the first derivative curve corresponds to the inflection point of the original titration curve (Lindberg and Kowalski 1988). The end point can also be found from the second derivative. The potentiometric titration curve and curves of the first (dpH/dV vs. V_{NaOH}) and second ($\text{d}^2\text{pH/dV}^2$ vs. V) derivatives from all samples showed similar behavior to that of sample 2.

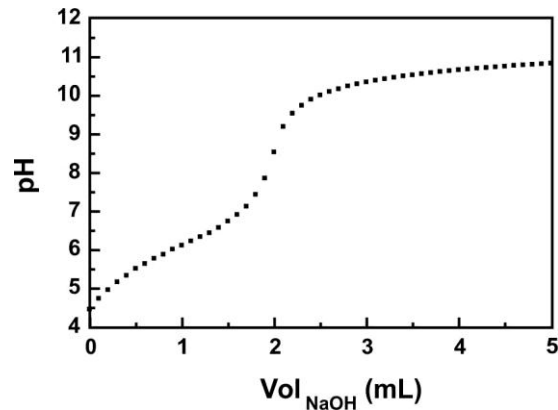


Fig. 3. Potentiometric titration curve of sample 2

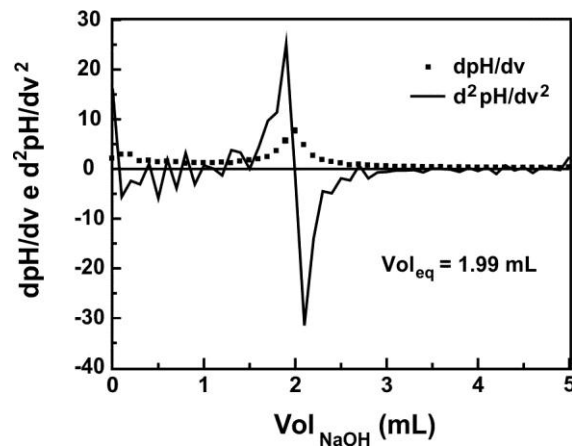


Fig. 4. Curves of the first (dpH/dV vs. V_{NaOH}) and second ($\text{d}^2\text{pH/dV}^2$ vs. V) derivatives of sample 2

A good correlation ($r = 0.9956$) was observed between the methods used for determining the content of carboxyl groups in cellulose pulp (Fig. 5). The content of carboxylic groups reported in the literature for bleached kraft pulp varies from 4.0 to 8.7 meq/100 g of pulp. In this work, an average value of 5.83 ± 0.80 meq/100 g pulp was encountered with the TAPPI method, and 6.57 ± 0.92 meq was observed for pulps 2 to 7 using the potentiometric titration method. A lower concentration of carboxyl groups was found in sample 1 (Fig. 6), because it is a dissolving pulp resulting from specific treatments (pre-hydrolysis kraft pulping and CCE-stage bleaching) aimed at maximum removal of hemicelluloses from the pulp. In this sample, the values of carboxylic groups were 1.37 meq/100 g of pulp (TAPPI method) and 1.29 meq/100 g of pulp (potentiometric titration). This observation suggests that most carboxyl groups present in the pulp were derived from hemicelluloses.

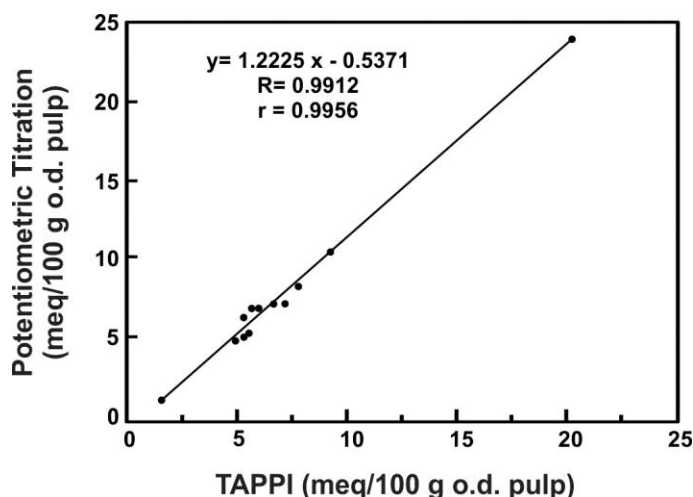


Fig. 5. Correlation of the results for determination of carboxyl groups (meq/100 g o.d. pulp) using the TAPPI method and direct potentiometric titration

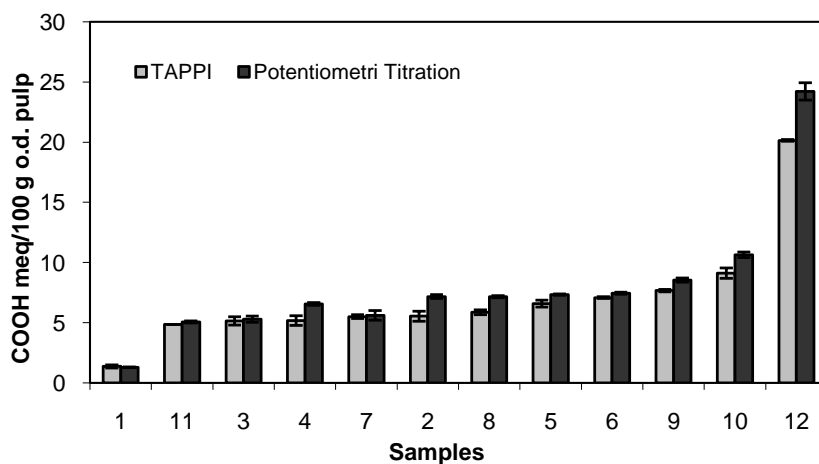


Fig. 6. Concentration of carboxyl groups (meq/100 g o.d. pulp) present in the bleached kraft pulps, utilizing the TAPPI method and direct potentiometric titration

Among the oxidized pulps (samples 8 to 12), the highest content of carboxyl groups was found in samples 9, 10, and 12 (Fig. 6), in accordance with the conditions employed for their oxidation. Similar results to those of sample 2 (non-oxidized pulp) were obtained in samples 8 and 11. In this case, it is observed that oxidation of the pulp with NaIO_4 (sample 11), as well as mild oxidation with 0.5% ozone (sample 8), did not significantly contribute to the formation of carboxylic groups. As expected, samples 9 and 10, obtained by oxidation with 2.5% and 5% ozone, respectively, and sample 12, resulting from oxidation with $\text{NaIO}_4/\text{NaClO}_2$, produced very high concentrations of carboxyl groups.

The results in general showed that potentiometric titration gave on average 22% greater values in relation to those obtained by the TAPPI method (Fig. 6). Although we have no clear explanation for such results, all the analyses were carried out with the same samples for both procedures. The first step for the sample preparation for both analyses involves stirring the pulp in HCl aqueous solution and filtration, followed by washing with water saturated with carbon dioxide. The solid washed pulp was then resuspended in water and submitted to a potentiometric titration in one case. For the TAPPI procedure, further resuspension of the pulp in an aqueous solution of $\text{NaCl}/\text{NaHCO}_3$, followed by filtration and titration of the excess of bicarbonate with a standardized solution of HCl, was carried out. As the difference in results between the two methods is systematic, one could in principle attribute such differences to the better capacity of the NaOH to swell the pulp fibers compared to the NaHCO_3 , resulting in a more efficient neutralization of the acid groups in the case of potentiometric method. As the quantities of COOH groups are very small, the visualization of the titration end point is relatively difficult and could also result in error for the TAPPI method. In a study comparing the amount of carboxylic groups measured by different methods, Fras *et al.* (2005) obtained systematic higher results for the potentiometric analysis compared to the conductometric one. The differences were attributed to the uncertainty in the evaluation of the equivalence points.

Considering the origin of carboxyl groups present in bleached cellulose fibers, they may originate from wood or be created during the cooking and bleaching processes (Ruusumo *et al.* 2008). 4-*O*-methyl- α -D-glucuronic acids are found in native wood linked to the xylan chain, and hexenuronic acids result from the partial conversion of 4-*O*-methyl- α -D-glucuronic acids during kraft pulping (Teleman *et al.* 1995; Buchert *et al.* 2001; Sjostrom 2006). The other carboxylic acids were derived from reducing end groups and hydroxyl groups that were oxidized during bleaching. Figure 7 shows the variation of hexenuronic, 4-*O*-methyl- α -D-glucuronic, and other carboxylic acid contents in function of bleaching and oxidation of cellulose pulp.

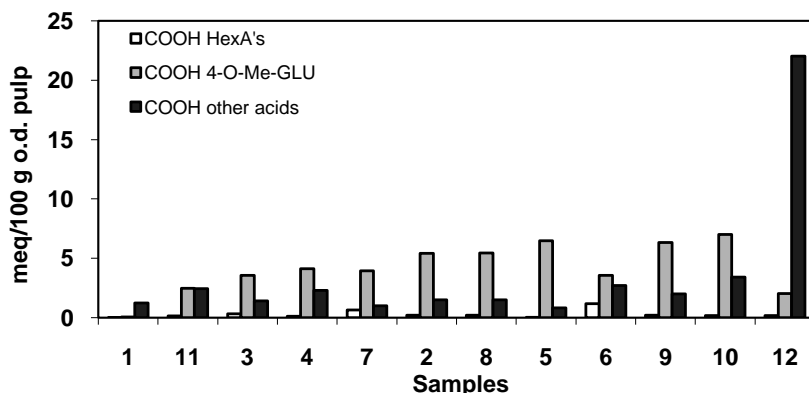


Fig. 7. Quantitative contribution of the various carboxyl groups (meq/100 g o.d. pulp) present in the bleached kraft pulps

In general, the content of carboxyl groups derived from hexenuronic acids represents a small fraction of the total content of carboxyl groups in bleached pulp. This observation is very relevant since the presence of hexenuronic acids in pulp favors the brightness reversion process (Sevastyanova 2006a,b).

The major contributor to the total content of carboxyl groups present in the pulp is the 4-*O*-methyl- α -D-glucuronic acids (Fig. 7), except in samples 1 and 12. In sample 1, which is the pulp with minimal hemicellulose content, practically all acid groups (95%) were derived from the other acids groups category. In sample 12 – pulp obtained from exhaustive oxidation with $\text{NaIO}_4/\text{NaClO}_2$ – the content of other acid groups reached 91%.

Considering oxidation with ozone, a small decrease in the content of hexenuronic acids was observed among samples 8, 9, and 10 in relation to sample 2. On the other hand, a small increase observed in the content of 4-*O*-methyl- α -D-glucuronic acids in these samples was proportional to the concentration of ozone used. The increases observed in the content of other carboxylic acids were 0.06%, 31.5%, and 127% for samples 8, 9, and 10, respectively. This result is consistent with the degree of oxidation of the pulp, as a function of the ozone concentration used for their acquisition.

The oxidative treatment with NaIO_4 caused a decrease of 31% and 55%, respectively, in the contents of hexenuronic and 4-*O*-methyl- α -D-glucuronic acids, compared to sample 2. Under conditions of exhaustive oxidation ($\text{NaIO}_4/\text{NaClO}_2$), a substantial increase was observed in the content of other carboxylic acids in sample 12, a result expected based on the reactions which occurred.

CONCLUSIONS

The presence of carboxyl groups in the pulp significantly contributes to induction of the brightness reversion and degradation of bleached pulp over time. In this work, carboxyl groups in commercial cellulose pulps and pulps submitted to different oxidative treatments were quantified by a fully automated potentiometric titration. The results obtained from this automated analysis were compared with results obtained for the same samples analyzed by the TAPPI procedure for determination of the carboxyl groups in cellulose. A good correlation between the methods was found ($R^2 = 0.9956$), but the

automated potentiometric titration provided a systematic higher content of COOH groups (22%), which was attributed to the more efficient neutralization of the acid groups provided by the potent fiber swelling NaOH solution used as the titrant. In general the automated potentiometric system requires less time for analyses and can be used for the study of samples with a large range of COOH group contents. The equipment can be easily assembled at low cost, and all the analysis and results are controlled by homemade software.

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