Estimating the concentration of phenolic hydroxyl groups in wood pulps

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ABSTRACT *The aminolysis method reliably measures the concentration of phenolic hydroxyl groups in lignins. However, the method is tedious and time-consuming. The periodate oxidation method is much simpler and provides comparable results for pulps with low concentrations of methoxyl-free phenolic structures. This report shows that both methods provide similar results for softwood kraft pulps with lignin contents in the range 1.5–5.5% as well as for unbleached and peroxide-bleached hardwood and softwood thermomechanical and chemithermomechanical pulps.*

KEYWORDS
Chemical analysis
Chemithermomechanical pulping
Lignins
Methoxyl groups
Phenolic groups
Phenylpropane units
Test methods
Thermomechanical pulping

The phenolic hydroxyl (PhOH) group is one of the most important functional groups affecting the physical and chemical properties of lignin polymers (*1*). These units contribute to the kraft, soda, and sulfite pulping reactions by converting to quinone methides, which are the key intermediates in alkaline pulping (*2, 3*). The delignification or prebleaching of kraft pulps is accelerated by phenolic hydroxyl groups (*4–6*). Conversely, it has been shown that alkylation of these groups significantly retards both the rate and extent of delignification with chlorine dioxide, oxygen, and hydrogen peroxide (*7, 8*). With mechanical pulps, phenolic units consume oxidant during H_2O_2 bleaching and contribute significantly to the poor brightness stability of lignin-rich pulps (*9*).

Lai *et al.* (*10*) surveyed the literature and concluded that the two methods best suited for *in situ* determination of the concentration of phenolic hydroxyl groups are those involving aminolysis (*11, 12*) and periodate oxidation (*13, 14*). They also showed that the two methods gave comparable results for both spruce and aspen wood meal (*10*).

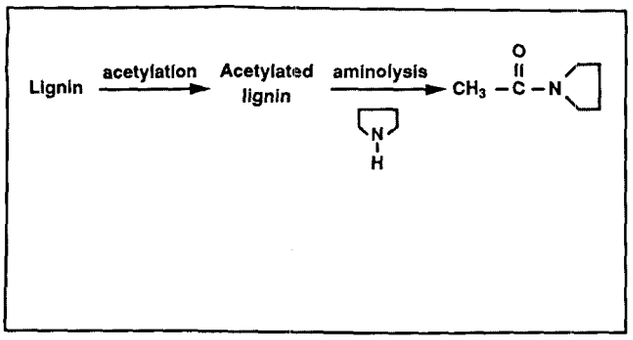
The aminolysis method is based on the finding that the rate of deacetylation of aromatic acetates by pyrrolidine under mild conditions is considerably higher than that of aliphatic acetates (*11*). Thus, the phenolic acetyl group of acetylated lignin can be selectively and rapidly deacetylated by pyrrolidine to 1-acetylpyrrolidine via the reaction depicted in **Fig. 1**. The method has been applied satisfactorily to acetylated lignin model compounds (*15*), to milled wood lignin and kraft lignins (*11*), to wood and kraft pulps (*12*), to high-yield sulfite pulps (*16*), and to straw lignins (*17*).

The advantages of the aminolysis method are its applicability to a wide range of lignins and its proven success during *in situ* determinations. However, the procedure is extremely time-consuming and tedious.

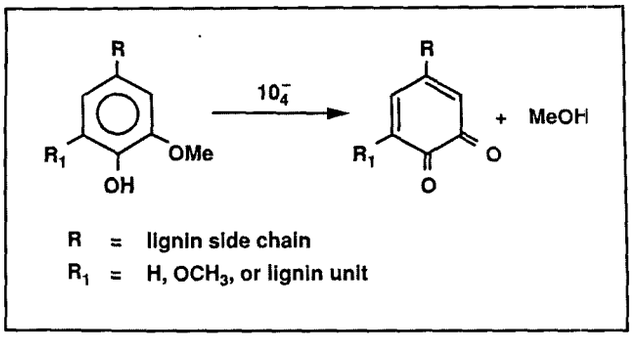
The periodate oxidation method, developed originally by Adler *et al.* (*14*), is based on the oxidation of simple phenolic guaiacyl compounds (*13*) with aqueous sodium periodate solution to *o*-quinone structures, as seen in **Fig. 2**. In the process, nearly one mole of methanol per mole of phenolic hydroxyl group is released.

Prior to the work of Lai *et al.* (*10*), the periodate method had been applied extensively to isolated lignins from softwoods (*1, 14, 18–20*) and to hardwood lignins (*21*), but it had not been applied to wood or pulps. The main advantage of the periodate method is its simplicity. However, since the periodate method is based on

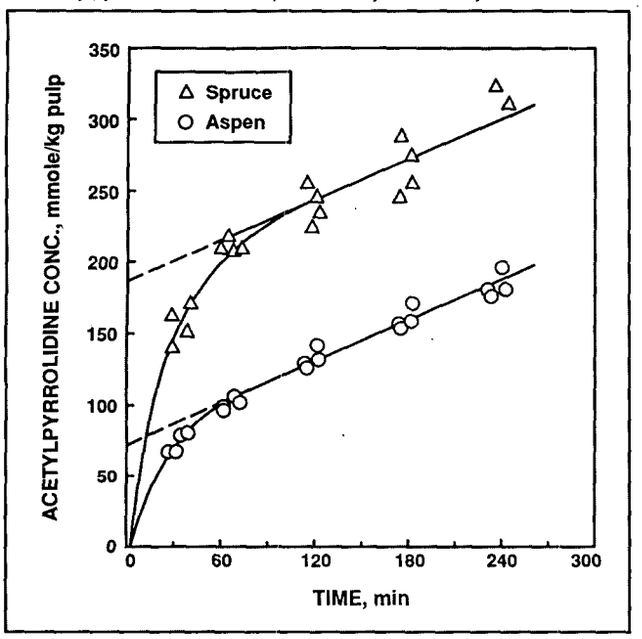
1. Chemical reaction—aminolysis method. Phenolic acetyl group of acetylated lignin is deacetylated by pyrrolidine to 1-acetylpyrrolidine.



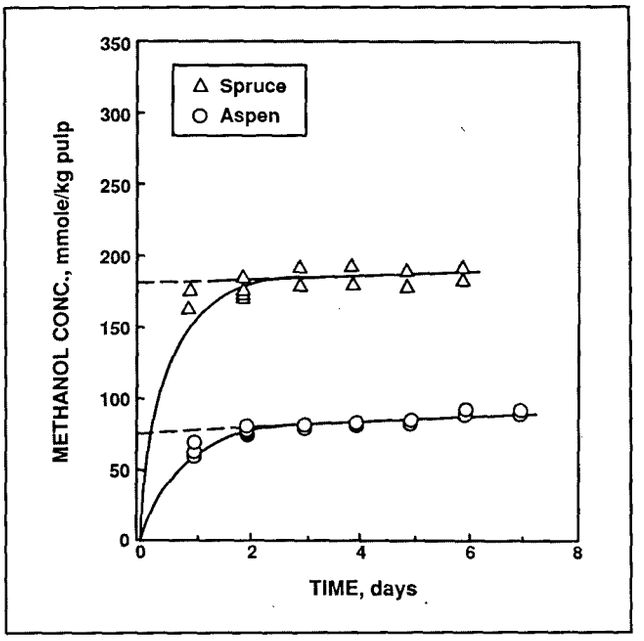
2. Chemical reaction—periodate oxidation method. Aqueous sodium periodate solution oxidizes simple phenolic guaiacyl compounds to o-quinone structures and methanol.



3. Acetylpyrrolidine formed upon aminolysis of acetylated TMP



4. Methanol formed upon periodate oxidation of TMP



methanol formation alone, it cannot be applied to methoxyl-free phenolic units such as catechol-type structures or to *p*-hydroxyphenyl units, which are abundant in nonwood lignins (*1*, *22*).

The objective of this study was to extend the comparison between the aminolysis and periodate oxidation methods to several relevant pulp types including bleached and unbleached softwood and hardwood thermomechanical pulp (TMP) and chemithermomechanical (CTMP) pulp and to softwood kraft pulps with lignin contents in the range of 1.5–5.5%.

Results and discussion

Precision of the methods

Data obtained from the analysis of spruce (*Picea abies*) and aspen (*Populus tremuloides*) thermomechanical pulps by the aminolysis and periodate methods are plotted in **Figs. 3 and 4**, respectively (four samples per pulp). For the aminolysis method, the concentration of phenolic hydroxyl groups was determined from the curve of acetylpyrrolidine formation by extrapolating the linear region of the curve to zero time (*11*). For the periodate method, the concentration of phenolic hydroxyl groups was determined based on the maximum methanol formation (*10*). Linear regression was used to obtain intercepts.

Averages and standard deviations for spruce and aspen TMP are shown in **Table I**. It can be seen that the two methods gave comparable results for both spruce and aspen TMP. The value of 12 PhOH per 100 phenylpropane (C_9) units compares favorably with the value of 13 obtained for extractive-free spruce and pine woods (*10*, *12*). The value of 8 PhOH/100 C_9 for aspen also agrees well with the value of 10 obtained by Lai *et al.* (*10*). The lower concentration of phenolic hydroxyl groups in aspen as compared with spruce is consistent with the finding of Beatson *et al.* (*24*, *25*) that the concentration of phenolic hydroxyl groups in aspen lignin is approximately one-half that in spruce lignin.

The data for spruce in Fig. 3 consist of duplicate analyses of TMP made from two different logs and analyzed at different times. The low standard deviation indicates that the precision and reproducibility of the aminolysis

I. Precision of aminolysis and periodate oxidation methods for softwood and hardwood TMP

	Aminolysis		Periodate oxidation		
	PhOH, mmole/kg pulp	Std. dev. (PhOH), mmole/kg pulp	PhOH, mmole/kg pulp	Std. dev. (PhOH), mmole/kg pulp	PhOH per 100 C_9
Spruce	188	4.33	183	4.00	12[a]
Aspen	72	2.23	78	1.18	8[b]

[a]Lignin content of 28.6% and C_9 molecular weight of 183 (12)
[b]Lignin content of 21.1% and C_9 molecular weight of 220 (23)

II. Comparison of aminolysis and periodate oxidation methods for TMP

	Aminolysis	Periodate oxidation
	PhOH, mmole/kg pulp	PhOH, mmole/kg pulp
Unbleached spruce	188	183
Bleached spruce	164	168
Methylated spruce	12	8
Unbleached aspen	72	78
Bleached aspen	75	70
Unbleached *P. nigra*	...	97
Bleached *P. nigra*	97	92

method is excellent. However, the reproducibility and precision of this method are strongly dependent on an efficient reduction of the sample prior to acetylation.

The spruce TMPs were chelated and reduced with borohydride as suggested by Gellerstedt and Lindfors (*12*, *26*). The suggested reduction procedure calls for an initial 1-h sodium borohydride treatment. After this treatment, additional $NaBH_4$ is added to give a total charge equivalent to the weight of the wood meal or pulp. The sample is centrifuged for 2 h and then allowed to stand for two days with gentle magnetic stirring. This method was effective with the spruce TMPs, which contained low concentrations of transition metals after chelation (<1 ppm Mn, 2.5 ppm Cu, and 45 ppm Fe). However, when this reduction procedure was applied to the aspen TMP, phenolic hydroxyl concentrations in the range of 150–250 mmole/kg pulp were obtained for the bleached and unbleached samples. The apparent reason for the unreasonable results was incomplete reduction of the pulp. Based on gas evolution, which resulted in flotation of the wood particles, it was obvious that the rate of $NaBH_4$ decomposition was much higher for aspen than for spruce TMP.

Without stabilization by diethylenetriaminepentaacetic acid (DTPA) (*27*) or NaOH (*27*, *28*), $NaBH_4$ reacts and/or decomposes completely in the presence of some pulps in about 6 h at room temperature. Modified reduction procedures were conducted on four aspen samples, results for which are shown in Fig. 3. After the initial addition of 50 mg for 1 h, additional $NaBH_4$ (25% on pulp) was added in four increments at 12-h intervals. Two of the samples in Fig. 3 were reduced in a 1-g/L Na_5DTPA solution, while the other two were reduced in deionized water. The results for aspen shown in Fig. 3 and Table I confirm the excellent precision of the aminolysis method when the pulp meal is effectively reduced.

The periodate oxidation method is characterized by a relatively high rate of methanol formation for the first two or three days, followed by a slower phase (following zero-order kinetics). The rate in the slower phase is extremely low (Fig. 4), and analysis after a three-day reaction period serves as a good estimate of total methanol formation.

The low standard deviations listed in Table I for the periodate oxidation method were typical for all the pulps and woods tested in our laboratory.

Results for TMP and CTMP

The results for softwood and hardwood TMP are shown in **Table II**. It can be seen that the two methods give comparable results for both unbleached and modified TMP over a wide range of concentrations.

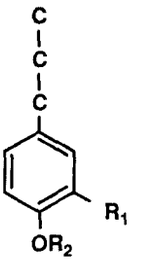
The comparison between methods was equally favorable for CTMP, as seen in **Table III**. The difference between the two methods was less than 10% for the three pulps tested. The higher concentration of phenolic hydroxyl groups in CTMP as compared with TMP is consistent with previous results (*16*, *29*). Also, when an extended reaction time is used in the neutral sulfite treatment, most of the phenylpropane units containing phenolic hydroxyl groups become sulfonated, resulting in approximately equal concentrations of phenolic hydroxyl and sulfonate groups (*16*, *29*).

Based on the concentration of sulfonate groups, maximum sulfonation was not achieved under our cooking conditions. Heitner and Hattula (*30*) sulfonated spruce chips with a 63-g/L solution of Na_2SO_3. All other conditions were similar to ours with the exception that they had a 30-min hot impregnation stage, giving their cooks a longer retention time. The sulfonate content obtained by them

III. Comparison of aminolysis and periodate oxidation methods for CTMP

	Aminolysis	Periodate oxidation	SO_3H groups,
	PhOH, mmole/kg pulp	PhOH, mmole/kg pulp	mmole/kg pulp
Unbleached spruce	250	240	188
Bleached spruce	250	232	...
Unbleached aspen	98	90	79

5. Methoxyl-free phenolic structures in kraft lignin



Structure 1: $R_1 = R_2 = H$

Structrure 2: $R_1 = OH$, $R_2 = H$

Structrure 3: $R_1 = OH$, $R_2 =$ lignin

was 227 mmole/kg (*30*). Beatson *et al.* (*24*) sulfonated aspen wood meal at 140°C and found the maximum sulfonate content in the pH range 7–10 to be approximately 100 mmole/kg. The concentrations of sulfonate groups obtained by these researchers are in the same range as the concentrations of phenolic hydroxyl groups obtained in our research.

Results for kraft pulps

The periodate oxidation method cannot be used to detect methoxyl-free phenolic structures. Chang *et al.* have analyzed milled wood lignin (*31*) and kraft residual lignin (*32*) from loblolly pine (*Pinus taeda*). Based on elemental and methoxyl analyses, the milled wood lignin contained ≅97 OCH_3/100 C_9 units, while the kraft residual lignin contained ≅91 OCH_3/100 C_9 units, confirming the expected higher concentration of methoxyl-free C_9 units in kraft residual lignin as compared with milled wood lignin.

The demethylation reaction (*33*) that occurs during kraft pulping produces methoxyl-free phenolic units, e.g., Structures 2 and 3 in **Fig. 5**. *p*-Hydroxyphenylpropane structures (Structure 1) are another source of methoxyl-free phenolic hydroxyls in kraft pulps. Of the three phenolic structures listed in Fig. 5, Structures 1 and 2 have been detected and quantified. Gellerstedt *et al.* (*6*) analyzed kraft residual lignin for various phenolic structures using permanganate oxidation followed by hydrogen peroxide oxidation. The procedure detected 1058 μmole of PhOH/g lignin or ≅20 PhOH/100 C_9 for kraft residual lignin. Structure 1 made up 2.6% of the phenolic units, while Structure 2 made up only 0.3% of the total. Therefore, nondetection of Structures 1 and 2 by periodate oxidation should not result in a major error. However, quantitative data for Structure 3 are not available.

Two kraft pulps were analyzed for phenolic hydroxyl concentrations. Kraft pulp I was made in our laboratory from loblolly pine, while kraft pulp II was a commercial pulp made from a furnish that was predominantly loblolly pine. The periodate and aminolysis methods gave similar results for both of the unbleached pulps, as seen in **Table IV**. This indicates that, in kraft residual lignin, the overall concentration of phenylpropane units containing phenolic hydroxyl groups and no methoxyl groups is low.

The laboratory pulp contained ≅31 PhOH/100 C_9 units, and the mill pulp contained ≅33 PhOH/100 C_9 units. These values fall in the range of 20–36 PhOH/100 C_9 units obtained for kraft residual lignin (*5, 6, 12, 26, 31*) and are close to the value of 36 PhOH/100 C_9 units obtained for the same wood species grown in the same region (*31*).

Table IV also shows that oxygen delignification to kappa no. 17.7 and 19.2 for kraft pulps I and II decreased the concentration of phenolic hydroxyl groups in the residual lignin, as observed previously (*5, 6*). However, the phenolic hydroxyls remaining in the pulp after this initial delignification were less reactive to oxygen, also as noted previously (*5, 6*). The kappa no. 19.2 for pulp II was obtained by reacting it with 2.5% NaOH and 0.5% $MgSO_4 \cdot 7H_2O$ for 1 h at 10% consistency, 90-psig O_2 pressure, 90°C. Despite the fact that the lignin in the O_2-bleached pulp still contained 23 PhOH/100 C_9 units, washing and a second oxygen treatment under similar conditions decreased the kappa number only 4.3 units to kappa no. 14.9. Phenolic biphenyl structures have been identified as units that are unreactive to oxygen (*5, 6*).

Summary

The aminolysis method is known to give reliable results for the concentration of phenolic hydroxyl groups in various lignins and lignin-containing materials. However, the procedure is extremely tedious and time-consuming. A much simpler method based on the oxidation of phenolic guaiacyl and syringyl units with sodium periodate to produce methanol has been found to give results comparable with those of aminolysis (±10%) for softwood and hardwood TMP, CTMP, and softwood kraft pulps. The periodate oxidation method cannot be used to detect methoxyl-free phenolic structures. It appears that the pulps studied for this

IV. Comparison of aminolysis and periodate oxidation methods for kraft pulps

	Kappa no.	Lignin content, %	Aminolysis PhOH, mmole/kg pulp	Periodate oxidation PhOH, mmole/kg pulp	PhOH per 100 C_9*
Kraft pulp I (lab)					
Unbleached	35.0	5.3	93	86	31
Oxygen delignified	17.7	2.8	34	33	22
OPO delignified	10.0	1.7	18	15	18
Kraft pulp II (mill)					
Unbleached	35.8	5.4	96	96	33
Oxygen delignified	19.2	3.1	34	42	23
OPO delignified	10.2	1.7	14	12	14

*C_9 molecular weight of 183 (*12*)

report contain insignificant amounts of free-phenolic units having no adjacent methoxyl group.

Experimental

Pulp samples

High-yield pulps. TMP was made by preheating wood chips for 3 min at 120°C prior to pressurized refining in a KRK refiner (Kumagai Riki Kogyo Co. Ltd., Tokyo). Atmospheric second-stage refining was conducted in the same refiner. All pulps were chelated with 0.4% Na_5DTPA in the presence of $NaHSO_3$ (4% SO_2) at 3% consistency and 90°C for 30 min prior to analysis and further modification.

CTMP was produced by reacting the chips with a 60-g/L solution of Na_2SO_3 in an M&K digester. A liquor-to-wood ratio of 6:1 was used. The liquor temperature was increased to 130°C in 30 min and maintained at that temperature for another 30 min. Refining and chelation were performed as described for TMP.

Peroxide bleaching. Hydrogen peroxide bleaching was conducted using 4% H_2O_2, 4% sodium silicate (41° Be), 3.0–4.5% NaOH, and 0.5% $MgSO_4 \cdot 7H_2O$ (o.d. pulp basis) for 4 h at 60°C and 15% consistency.

Methylation. Bleached or unbleached pulps were dispersed in water at 2.0% consistency. The slurry was vigorously stirred, and dimethyl sulfate was added at 0.5 mL/min from a Fisher model 395 dispenser. Using a Drummond microburette, 0.25 mL of 4N NaOH was added whenever the pH fell to approximately 9.5. The alkali addition increased the pH to approximately 10.5. A pH of 11.0 was not exceeded. The experiments were conducted at room temperature under a nitrogen atmosphere.

Kraft pulps. Pulp I was made from loblolly pine (*Pinus taeda*) with the following cooking conditions: active alkali, 18%; sulfidity, 30%; time to temperature (170°C) 90 min; time at temperature, 90 min; yield, 48%. Pulp II was a commercial pulp made from a furnish that was predominantly loblolly pine.

Oxygen delignification. Oxygen delignification was carried out in a Quantum Mark IV reactor at 10% consistency using 2.5% NaOH and 0.5% $MgSO_4 \cdot 7H_2O$ on pulp at 90°C and 90-psig O_2 pressure for 1 h.

Peroxide delignification. Peroxide delignification was carried out in a Quantum reactor or in plastic bags at 10% consistency with 0.2% Na_5DTPA, 250 ppm Na_2MoO_4, and 0.5% H_2O_2 on pulp at 85°C for 1 h.

Aminolysis

The aminolysis procedure was similar to that of Gellerstedt and Lindfors (*12*), with some minor but important modifications. After the initial 1-h treatment of the pulp with sodium borohydride (50 mg), instead of adding additional borohydride equivalent to the weight of the pulp meal and allowing it to react for 48 h as suggested previously (*12*), four additions—each of 25% $NaBH_4$ on pulp—were made. Each addition was followed by centrifugation and a retention time of approximately 12 h. Also, the reduction was carried out in a solution of Na_5DTPA (1 g/L) for improved stability of the borohydride (*27*). There were no changes in the acetylation and deacetylation procedures.

Periodate oxidation

The procedure (*10*) used was a slight modification of the method developed by Adler *et al.* (*14*) and that employed by Gierer *et al.* (*20*). In general, a sample (≅400 mg) of chelated pulp or pulp meal (40 mesh) in a 20-mL glass centrifuge tube was treated with sodium periodate (800 mg), dissolved in 6 mL of distilled water, to which 1 mL of distilled water containing 3 mg of acetonitrile was added as an internal standard. Both solutions were cooled to 4°C prior to addition to the sample. The suspension was homogenized and kept in the dark at 4°C in a refrigerator with occasional stirring.

The rate of methanol formation was followed gas chromatographically by periodically injecting a 1–2 μL aliquot of the reaction mixture. The mixture was homogenized and centrifuged to obtain a clear solution prior to sampling and was homogenized again after sampling.

Analytical methods

Sodium borohydride concentration was determined by potassium iodate oxidation (*28*). Lignin contents (Klason plus acid-soluble lignin) were determined using appropriate TAPPI test methods. Sulfonate groups were determined by the conductometric method of Katz *et al.* (*34*). A Varian 3700 gas chromatograph, equipped with a flame ionization detector and an electronic integrator for measuring peak areas, was used for analysis of the reaction products.

In periodate oxidation experiments, methanol and the internal standard (acetonitrile) were determined with a 1.8-m × 0.32-cm stainless steel column packed with Tenax GC. The Tenax

column (Alltech Associates, Inc., Deerfield, Ill.) was operated at 80°C with an injection-port temperature of 150°C and a detector temperature of 250°C. A nitrogen flow of 60 mL/min was maintained.

In aminolysis experiments, the deacetylation products, 1-acetylpyrrolidine, and an internal standard (1-propionylpryrrolidine or 1-methylnaphthalene) were determined with a 1.83-m × 0.32-cm stainless steel column packed with 5% Carbowax 20 M on 80/100-mesh Chromosorb G (*9*) (Supelco Chromatography Products, Bellefonte, Pa.). The column was heated isothermally at 180°C, with the injection port and detector temperatures set at 210°C and 250°C, respectively. The carrier gas, N_2, was delivered at a flow rate of 20 mL/min. The pyrrolidine amides (1-acetylpyrrolidine and 1-propionylpyrrolidine) were prepared from the appropriate acid chloride and pyrrolidine (*35*).□

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