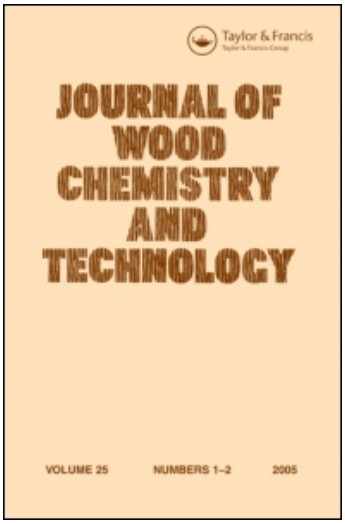


Journal of Wood Chemistry and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

Estimation of Phenolic Hydroxyl Groups in Wood by a Periodate Oxidation Method

Yuan-Zong Lai[a]; Xiao-Ping Guo[a]; Wei Situ[a]
[a] State University of New York College of Environmental Science and Forestry Empire State Paper Research Institute, Syracuse, New York

To cite this Article Lai, Yuan-Zong , Guo, Xiao-Ping and Situ, Wei(1990) 'Estimation of Phenolic Hydroxyl Groups in Wood by a Periodate Oxidation Method', Journal of Wood Chemistry and Technology, 10: 3, 365 — 377
To link to this Article: DOI: 10.1080/02773819008050245
URL: http://dx.doi.org/10.1080/02773819008050245

JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY, 10(3), 365-377 (1990)

ESTIMATION OF PHENOLIC HYDROXYL GROUPS IN WOOD BY A PERIODATE OXIDATION METHOD

Yuan-Zong Lai, Xiao-Ping Guo, and Wei Situ
State University of New York
College of Environmental Science and Forestry
Empire State Paper Research Institute
Syracuse, New York 13210

ABSTRACT

Oxidation of woodmeals with an excess of aqueous sodium periodate solution at 4°C released an amount of methanol approximately equivalent to the phenolic hydroxyl content of the lignin as determined by the aminolysis method. The periodate and aminolysis methods gave very comparable data for Norway spruce and aspen woodmeal samples.

INTRODUCTION

The phenolic hydroxyl group is one of the most important functionalities affecting the physical and chemical properties of lignin polymers.[1] It plays a prominent role in commercial pulping and bleaching processes by virtue of its ability to promote the base-catalyzed cleavage of interunit ether linkages, and the oxidative degradation of lignin.[2,3] The chemical reactivity of lignin in various modification processes is also profoundly influenced by its phenolic hydroxyl content (e.g., in the reaction with formaldehyde in the production of lignin adhesives).[4] On the other hand, the phenolic hydroxyl group reportedly contributed to the poor brightness stability of lignin-containing pulps which seriously limits their more widespread utilization.[5,6] Quantitative measurement of phenolic hydroxyl

groups thus provides pertinent information relating to the structure and reactivity of lignin as well as to the mechanism and extent of lignin degradation.

Survey of Analytical Approaches

Both physical and chemical methods, or a combination of both, have been used to estimate the phenolic hydroxyl content of lignin.[1,7] Physical methods include potentiometric and conductometric titration,[8,9] ionization UV spectroscopy,[10,11] and NMR spectroscopy.[12-14] A pyrolytic gas chromotographic technique based on the difference in yield of phenol and guaiacol resulting from the thermal degradation of lignin before and after methylation has also been used to estimate the phenolic hydroxyl content of softwood lignin.[15]

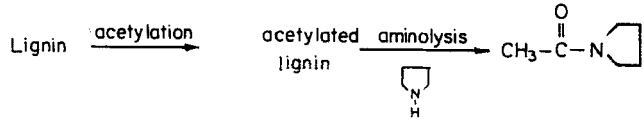
Chemical methods for the determination of phenolic hydroxyl groups include determination of the increase in methoxyl content resulting from diazomethane methylation,[16] of the phenolic acetyl group after acetylation,[17,18] and of low molecular weight compounds derived from the degradation of phenolic structures by procedures such as permanganate and hydrogen peroxide,[19,20] periodate,[21,22] or thioacidolysis.[23] The phenolic acetyl group of acetylated lignin may be determined by an NMR spectroscopic technique[17,24] or by a selective deacetylation in pyrrolidene (aminolysis).[18]

Of the various methods outlined above, the most widely used are those based on UV, periodate oxidation, and aminolysis. The UV method, based on the difference in absorption at 300 nm of phenolic units in neutral and in alkaline solutions, is very suitable for soluble lignin preparations[10,11] and has also been applied to the *in situ* measurement of the phenolic hydroxyl

content of lignin in wood[25] and in pulps.[26] But, it is not absolute in the sense that the measurement must be calibrated by using appropriate lignin model compounds or a lignin of known phenolic hydroxyl content. The principle of the two direct chemical methods, periodate oxidation and aminolysis, for determination of the phenolic hydroxyl content of lignin or lignin-containing materials is outlined below.

Aminolysis Method

The aminolysis method is based on the finding that the rate of deacetylation of aromatic acetates in pyrrolidene under mild conditions is considerably higher than that of aliphatic acetates.[18] Thus, the phenolic acetyl group of acetylated lignin can be selectively determined in pyrrolidene by a rapid formation of 1-acetylpyrrolidene [Eq. 1]. The method has been applied satisfactorily to acetylated lignin model compounds,[27] to milled wood lignin,[18] to kraft lignins,[18] to wood,[28] and to straw lignins.[29]



[1]

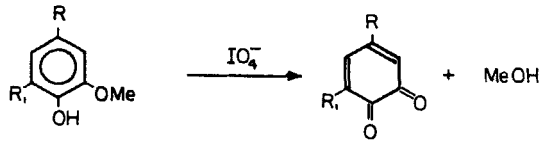
As discussed by Gellerstedt and Lindfors,[28] the accuracy of this method is critically dependent upon both a quantitative acetylation of phenolic hydroxyl groups and a selective deacetylation of the resulting phenolic acetyl groups. Although these requirements may not represent a serious concern in the analysis of soluble or reagent-accessible lignin preparations, they could present a problem in the case of lignocellulosic materials.

In addition, the reducing end groups of carbohydrates behave like phenolic hydroxyl groups in the aminolysis process. Thus, a

quantitative reduction of wood or pulp samples by borohydride prior to acetylation is essential.

Periodate Oxidation Method

The periodate oxidation method, developed originally by Adler et al.,[22] was based on the oxidation of simple phenolic quaiacyl compounds[21] with aqueous sodium periodate solution to ortho-quinone structures [Eq. 2]. In the process nearly one mole of methanol per mole of phenolic hydroxyl group is released [Eq. 2].



[2]

Where R = lignin side chain

R_1 = H, OCH_3 or lignin unit

A similar finding was later obtained for phenolic syringyl-type model compounds.[30] Since no methanol is formed when the oxidation is performed on etherified guaiacyl compounds, e.g., veratrole, measurement of the methanol formed in the oxidation thus is approximately equivalent to the amount of adjacent phenolic hydroxyl groups. However, the periodate method is based on methanol formation alone and cannot be applied to methoxyl-free phenolic units such as catechol-type structures or p-hydroxyphenyl units which are present in a large quantity in non-wood lignins.[1,31] The periodate method has been applied extensively to isolated lignins from softwoods,[1,22,25,26,32] and also has been shown to be suitable for hardwood lignins,[30] but it has not been extended to wood samples.

The objective of this study was to evaluate the extent to which the periodate oxidation method can be used to estimate the phenolic hydroxyl content of wood lignin *in situ*. Specifically, a comparison between the periodate oxidation and aminolysis methods for measurement of the phenolic hydroxyl groups of Norway spruce and aspen woodmeals is discussed.

EXPERIMENTAL

General

Samples of extractive-free woodmeals (40-60 mesh) were prepared by extraction with acetone overnight and then air dried. The species studied were Norway spruce (*Picea abies*), and aspen (*Populus tremuloides*). The borohydride reduction was conducted by treating woodmeals with an excess of $NaBH_4$ at ambient temperatures overnight, and the reduced samples were obtained by the usual procedure.

Lignin contents (Klason plus acid-soluble lignin) were determined by Tappi Standard Methods. A Varian 3700 gas chromatograph, equipped with flame ionization detectors and an electronic integrator for measuring peak areas, was used for analysis of reaction products.

Periodate Oxidation

The procedure used was a slight modification of the method developed by Adler *et al.*[22] and that employed by Gierer *et al.*[32] In general, a sample of woodmeal (~ 400 mg) in a 20-mL glass centrifuge tube with a Teflon screw cap was treated with sodium periodate (800 mg), dissolved in 6 mL of distilled water, and with 1 mL of distilled water containing 3 mg of acetonitrile as an internal standard. Both solutions were cooled to 4°C prior to addition to the sample. The sealed 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. Methanol and the internal standard (acetonitrile) were determined with a 1.8 m x 0.32 cm stainless steel column packed with Tenax GC. The Tenax column (obtained from Alltech Associates, Inc., Deerfield, IL.) was operated at 80°C with an injection port temperature of 150°C and a detector temperature of 250°C. A nitrogen flow of 30 mL min^{-1} was maintained.

The mixture was homogenized and centrifuged to obtain a clear solution prior to sampling and was homogenized again after sampling.

The methanol formation generally levels off after two days' reaction as indicated in Figure 1B for Norway spruce woodmeals. The phenolic hydroxyl content of lignin is calculated from the maximum amount of methanol formed.

Calculations of the phenolic hydroxyl content as percent phenylpropane (C_9) unit were based on that the average weight of a C_9 unit is 184 and 206 for Norway spruce and aspen MWL, respectively.[33]

Aminolysis Procedures

The aminolysis procedures used for the determination of phenolic hydroxyl group of wood was essentially that of Gellerstedt and Lindfors[28] and included a borohydride reduction step prior to acetylation.

During the aminolysis step, an acetylated wood sample (- 400 mg) in a centrifuge tube was treated with 3 mL of dioxane and 1 mL of dioxane containing 5 mg of an internal standard (1-

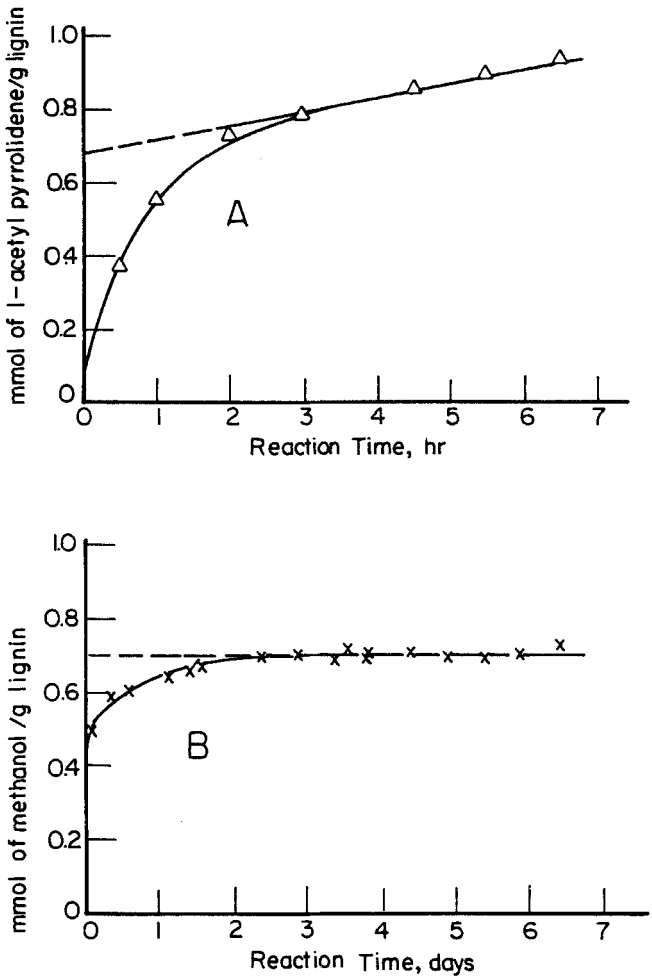


FIGURE 1. Rate of formation of 1-acetylpyrrolidene on (A) aminolysis of acetylated woodmeal and of methanol on (B) periodate oxidation of woodmeal from Norway spruce.

methylnaphthalene). The mixture was homogenized in an ultrasonic bath for 10 minutes and then treated with 1 mL of a 1:1 (v/v) dioxane-pyrrolidene solution. With the cap firmly tightened on the reaction tube, the mixture was again homogenized by vigorous shaking and then allowed to stand with stirring.

The first sample was taken after approximately 30 minutes and subsequently, 5-6 samples were analyzed gas chromatographically at suitable intervals of about 30-60 minutes. The deacetylation products, 1-acetylpyrrolidene, and an internal standard (1-propionylpryrrolidene or 1-methylnaphthalene) were determined with a 1.83 m x 0.32 cm stainless steel column packed with 5% Carbowax 20 M on 80/100 mesh chromosorb G[5] which was obtained from 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^{-1}. The pyrrolidene amides (1-acetylpyrrolidene and 1-propionylpyrrolidene) were prepared from the appropriate acid chloride and pyrrolidene.[34]

The rate of 1-acetylpyrrolidene formation was followed as a function of time which may require a total of 6-7 h reaction period as illustrated in Figure 1A for Norway spruce woodmeals. The phenolic acetyl content (equivalent to the phenolic hydroxyl content) is calculated by extrapolating the linear region of the kinetic curve to zero time.

RESULTS AND DISCUSSION

Periodate Oxidation of Woodmeals

Figure 1B illustrates the formation of methanol from the oxidation of extractive-free Norway spruce woodmeals in aqueous periodate solution at 4°C. It is evident that the kinetic curve

of woodmeals, like that of lignin preparations,[22] displayed a two-stage process showing an initial fast phase followed by a slow one. A similar pattern was also obtained for aspen extractive-free woodmeals sample. The slow-phase reaction, which was generally complete after two days, accounted for about 20 and 30% of the overall methanol formation for Norway spruce and aspen, respectively.

As discussed by Adler *et al.*,[22] the causes of the slow-phase reaction may be partially attributed to the presence of free-phenolic units containing carbonyl groups. We have observed that borohydride-reduction of woodmeals prior to periodate treatments has practically no effect on the overall methanol formation. Interestingly, such a reduction significantly reduced the methanol formation (from 20 to 10%) for the slow-phase reaction of Norway spruce while having little influence in the case of aspen.

Under experimental conditions, the contribution of methanol from the degradation of carbohydrate components appears to be negligible, because periodate oxidation of acetylated woodmeals from Norway spruce or aspen gave virtually no detectable formation of methanol. The data also indicated that the mild periodate solution used did not cause any deacetylation of phenolic acetate groups.

Previous analysis of lignin samples by the periodate oxidation method was generally conducted in a homogeneous solution using 80% acetic acid.[22,25,26,32] Under these conditions, methanol was partly converted to methyl acetate thus giving rise to two gas chromatographic peaks corresponding to each of these two products. In addition, acetic acid passed through the Triton column slowly, exhibited marked tailing, and required proper conditioning of the column after each injection.[32]

In the current procedure, distilled water was used as the reaction medium thus obviating the problems associated with the presence of acetic acid. Results obtained with water and with 80% acetic acid were practically identical for phenolic model compounds.[21]

Comparison of Aminolysis and Periodate Methods

Table 1 summarizes the phenolic hydroxyl content of extractive-free Norway spruce and aspen woodmeal samples determined by the aminolysis and periodate methods. It is evident that both methods gave very comparable data. However, the periodate oxidation method yields consistently higher values (8 and 10% for Norway spruce and aspen woodmeals, respectively) for phenolic hydroxyl content than are obtained using the aminolysis procedure. The reasons for these variations are not clear. However, in a series of replicate determinations, the aminolysis method has a considerably higher standard deviation compared to the periodate method, which may be partly attributable to the large number of steps involved in the aminolysis analysis.

The aminolysis is a laborious procedure, e.g., for wood samples, a 6-7 h reaction period may be required for the aminolysis step alone. In addition, the process requires a thorough reduction of reducing end-groups of carbohydrates and a complete acetylation of phenolic hydroxyl groups.

On the other hand, the periodate oxidation method is a relatively simple process and is unaffected by the presence of carbohydrates. In contrast to aminolysis, construction of a kinetic curve is not necessary in the periodate oxidation procedure which requires only determination of the maximum amount of methanol formation for calculation of the phenolic hydroxyl

TABLE 1

A Comparison of the Aminolysis and Periodate Oxidation Methods for Determination* of the Phenolic Hydroxyl Content of Norway Spruce and Aspen Woodmeals

Species	Method	Phenolic hydroxyl content mmol/g lignin		Nos./100 C_9
		Avg.	Std. Dev.	Avg.
Spruce	Aminolysis	0.649	0.029	11.9
	Periodate Ox.	0.702	0.005	12.9
Aspen	Aminolysis	0.445	0.031	9.2
	Periodate Ox.	0.493	0.008	10.2

* The number of replication was 11 and 8 for Norway spruce and aspen, respectively.

content. Thus, for routine analysis, the periodate oxidation method may require only measurement of the amount of methanol liberated after 2 and 3 days' reaction for isolated lignin[22,25,26,32] and wood samples, respectively. Furthermore, this oxidation method has been applied satisfactorily to thermomechanical and chemithermomechanical pulp samples.

CONCLUSIONS

Periodate oxidation of woodmeals released an amount of methanol approximately equivalent to the phenolic hydroxyl content of lignin as determined by the aminolysis method.

The periodate oxidation method, based on the maximum amount of methanol formed, has been shown to be a convenient procedure for estimating the average phenolic hydroxyl content of lignin in wood, including both softwood and hardwood.

ACKNOWLEDGMENTS

This work was supported by a grant from the Empire State Paper Research Associates (ESPRA).

REFERENCES

1. E. Adler, Wood Sci. Technol., 11, 169 (1977).
2. J. Gierer, Wood Sci. Technol., 19, 289 (1985).
3. J. Gierer, Wood Sci. Technol., 20, 1 (1986).
4. M. Olivares, J. A. Guzman, A. Natho, and A. Saavedra, Wood Sci. Technol., 22, 157 (1988).
5. U. Tschirner and C. W. Dence, Pap. Puu., 70, 338 (1988).
6. G. Gellerstedt and E.-L. Pettersson, Svensk Papperstidn., 77, 15 (1977).
7. B. L. Browning, in Methods of Wood Chemistry, Vol. II, p. 755-786, Interscience Publishers, 1967.
8. H. Pobiner, Anal. Chim. Acta., 155, 57 (1983).
9. Q. Pu and K. V. Sarkanen, J. Wood Chem. Technol., 9, 293 (1989).
10. G. Aulin-Erdtman, Svensk Papperstidn., 57, 745 (1954).
11. A. S. Wexler, Anal. Chem., 36, 213 (1964).
12. D. R. Robert and G. Brunow, Holzforschung, 38, 85 (1984).
13. G. J. Leary, J. A. Lloyd, and K. R. Morgan, Holzforschung, 42, 199 (1988).
14. J. A. Hemmingson and F. H. Dekker, J. Wood Chem. Technol., 7, 229 (1987).
15. P. Whiting and D. A. I. Goring, Pap. Puu., 64, 592 (1982).
16. A. Björkman and B. Person, Svensk Papperstidn., 60, 285 (1957).
17. B. Lenz, Tappi 51, 511 (1968).
18. P. Månsson, Holzforschung, 37, 143 (1983).
19. G. Gellerstedt and K. Gustafsson, J. Wood Chem. Technol., 7, 65 (1987).
20. G. Gellerstedt, K. Gustafsson, and R. A. Northey, Nordic Pulp Pap. Res. J., 3, 87 (1988).
21. E. Adler and S. Hernestam, Acta. Chem. Scand., 9, 319 (1955).

22. E. Adler, S. Hernestam, and I. Walldén, Svensk Papperstidn., 61, 641 (1958).

23. C. Lapierre, B. Monties, and C. Rolando, Holzforschung, 42, 409 (1988).

24. D. R. Robert, G. Gellerstedt, and M. Bardet, Nordic Pulp Pap. Res. J., 1, 18 (1986).

25. J.-M. Yang and D. A. I. Goring, Can. J. Chem., 58, 2411 (1980).

26. J.-M. Yang and D. A. I. Goring, Cellulose Chem. Technol., 15, 337 (1981).

27. P. Månsson, Tetrahedron Lett., 23, 1845 (1982).

28. G. Gellerstedt and E. Lindfors, Svensk Papperstidn., 87, R115 (1984).

29. X. Liu and Z. Li, Zhongguo Zaozhi 6, 34 (1987).

30. H.-M. Chang, E. B. Cowling, W. Brown, E. Adler, and G. Miksche, Holzforschung, 29, 153 (1975).

31. J. H. Feng and Z. H. Wang, In Proceedings of Fourth International Symposium on Wood and Pulping Chemistry, Vol. 1, 61 (1987).

32. J. Gierer, B. Lenz, I. Noren, and S. Soderberg, Tappi, 47, 233 (1964).

33. S. A. Rydholm, Pulping Processes, p. 186, Interscience, New York, 1965.

34. P. Månsson and L. Westfelt, J. Appl. Polym. Sci., 25, 1533 (1980).