

Spectroscopic Analysis of Fraké Treated with Periodic Acid.

I. Electron Spectroscopy for Chemical Analysis (ESCA)

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SYNOPSIS

Fraké, a tropical wood species from Cameroon, was reacted with 1% periodic acid solution at room temperature for 24 h. Untreated and treated woods were analyzed by ESCA. As expected, O_{1s} and C_{2s} were the predominant species in the spectra. While the O_{1s} peak is featureless, the C_{1s} peak can be decomposed into several components. These contributions were calculated, and it was observed that untreated and treated woods exhibit carbon atoms in classes C₁ (carbon atoms bonded by a C—C or a C—H bond), C₂ (carbon atoms bonded by a C—O bond), and C₃ (carbon atoms bonded by a C=O or by a O—C—O bond). Class C₄, which refers to carbon atoms bonded by O—C=O bonds, is completely absent. The periodic acid treatment produces a reduction in C₁, an increase in C₂, with C₃ remaining relatively small. Accordingly, the expected oxidation of hydroxyl groups to carbonyl groups is not observed. It can be postulated that wood-periodic acid intermediates, which are believed to be cyclic periodic esters, do not decompose to form carbonyl groups but rather remain as stable complexes. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Wood exhibits poor resistance to environmental degradation and needs to be protected in many service conditions. For that purpose, several formulations have been tested in terms of efficiency against natural organisms. Among those formulations, waterborne inorganic salts, organic solvent-type preservatives, and/or organic substances have been widely used.

To impart resistance and durability to treated woods, two prerequisites have to be met: penetration of the preservative into the wood, and permanence of its action against aging factors. The latter condition is rarely achieved, especially in tropical areas, because many of the waterborne preservatives leach out when wood is exposed to rain or wet soil or because the organic preservatives are lost by evaporation.

In this respect, the development of new wood preservatives, especially suited for tropical areas, must tend to improve their penetration into wood and their permanence. One such preservative is periodic acid, or its sodium salt, which is water soluble and reported to form addition compounds with polyalcohols.^{1,2} More recently, it has been shown that wood reacted with periodic acid or sodium periodate is resistant to attack by brown- and white-rot fungi and subterranean termites, and that after reaction, the chemicals are leach resistant.³ In view of the potential benefits that periodic acid and its salts can bring as wood preservatives, a fundamental understanding of the wood-periodic acid reactions is necessary.

In the current study, electron spectroscopy for chemical analysis (ESCA), also referred to as X-ray photoelectron spectroscopy (XPS), a nondestructive solid-state spectroscopic technique that has already been employed in the analysis of surfaces of synthetic polymers,⁴⁻⁶ natural and textile fibers,⁷⁻¹² and in the characterization of wood reactions,^{13,14} was used to investigate the nature of wood-periodic acid intermediates *in situ* and in an attempt to elu-

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cidate the nature of chemical reactions occurring between periodic acid and the constituents of wood. This article, the first of a series, presents results from ESCA analysis of untreated and treated woods.

EXPERIMENTAL

Sample Preparation

Fraké (*Terminalia superba*), a tropical species from Cameroon, was used in this study. Wood blocks of approximately $30 \times 30 \times 20$ mm were immersed in 1% periodic acid solution at room temperature and placed in a vacuum chamber. An initial pressure of about 10 mmHg was developed over the solution and maintained for 2 h. Air was then allowed into the chamber and the treating solution was forced to fill the pores previously occupied by air. This treatment was repeated until the blocks settled to the bottom, which means that they are saturated by the solution. In all cases, the soaking time was 24 h. After soaking, the blocks were conditioned at 27°C and 50% relative humidity for 15 days.

Specimen surfaces for ESCA were prepared by cutting a clean, smooth transverse surface from treated and untreated blocks using a sliding microtome. Cutting was performed such that all material for analysis originated from the core rather than the surface of the original sample. It was not possible to separate the specimens into earlywood and latewood portions, since tropical wood species usually display a diffuse porous structure, without regular annual growth rings.

Sample Analysis

ESCA analysis was performed using an ESCALAB II spectrometer fitted on a microlab system from Vacuum Generators and equipped with a nonmonochromatized dual Mg-Al anode X-rays source. Kinetic energy measurements were made using a hemispherical electrostatic analyzer ($r = 150$ mm) and a detector pass energy of 20 eV. Thin microtomed samples having a thickness of 500 μm or less were mounted onto an indium disk and introduced into the working chamber maintained at a pressure range of 10^{-8} – 10^{-6} torr.

Data Treatment

When a sample is irradiated by X-rays that collide with the inner shell electrons of the atoms at the

surface of a solid sample, the kinetic energy E_k of the photoelectrons ejected is expressed as

$$E_k = E_x - (E_b + E_c + \phi) \quad (1)$$

where E_x is the energy of the incident photon (1353.6 eV for the Mg_k anode source and 1486 eV for the Al_k anode source), E_b is the binding energy of the electron on its original level, ϕ is the work function of the spectrometer, and E_c is the energy lost in counteracting the potential associated with the steady charging of the surface. Uncorrected binding energies are expressed by $E_b + E_c$ and are obtained from Eq. (1). During measurement, E_c can be minimized by using a floodgun¹³ or by wrapping the sample in an aluminum foil.⁷ The use of a known reference is necessary to obtain an absolute value of the binding energy. Following the suggestion of Doris and Gray, the O_{1s} peak of cellulose⁷ can be set at 533.2 eV, and this is equivalent to a value of 285.0 eV for the binding energy of the C_{1s} component of the C_{1s} peak. The chemical shifts ΔE_b of the C_{1s} peak components were evaluated relative to this value.

The ratio of two elements present in the surface region can be estimated from the ratio of their ESCA peak intensities:

$$\frac{\text{O}}{\text{C}} = \frac{\sigma_c D_c \lambda_c I_{\text{O}_{1s}}}{\sigma_0 D_0 \lambda_0 I_{\text{C}_{1s}}} \quad (2)$$

where σ is the cross section of the photoelectrons generation, λ the mean-free path of the photoelectrons, D the spectrometer transmissions, and I the integrated peak intensity. Using the cross sections reported by Scofield,¹⁵ the O/C ratio can simply be written as:

$$\frac{\text{O}}{\text{C}} = \frac{1}{2.85} \times \frac{I_{\text{O}_{1s}}}{I_{\text{C}_{1s}}} \quad (3)$$

The peak synthesis was performed using a product of Gaussian and Lorentian functions¹⁶ at a Gaussian-Lorentian ratio of 60%.

RESULTS AND DISCUSSION

Measurements

Figures 1(A) and (B) show ESCA spectra of electron intensity as a function of binding energy for untreated and treated Fraké samples, respectively. As expected for woody materials, O_{1s} and C_{1s} are the

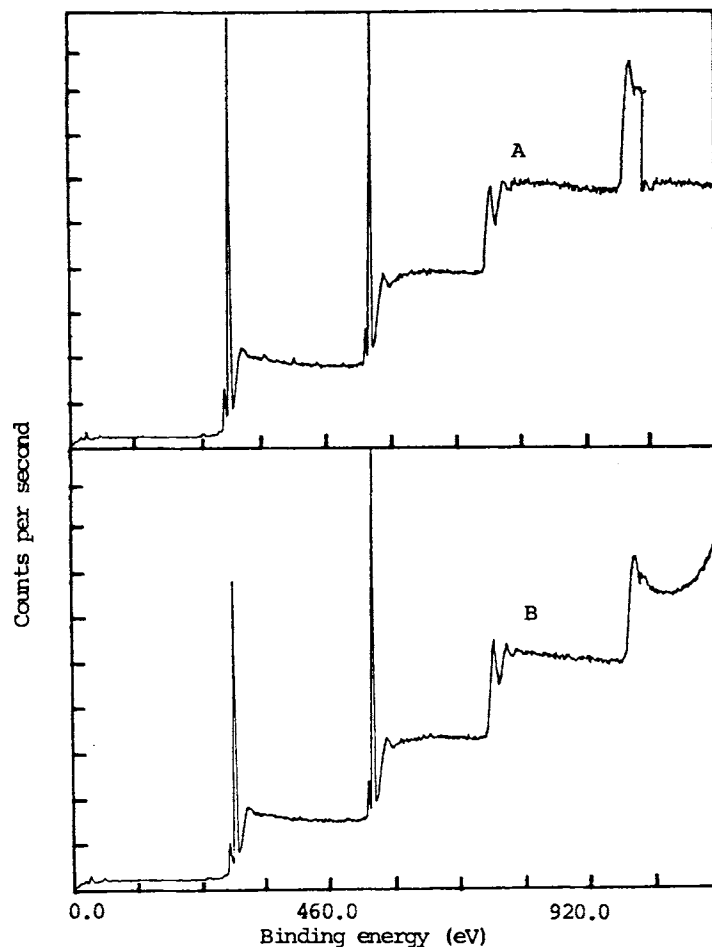


Figure 1 Survey of ESCA spectra for (A) untreated and (B) treated Fraké samples.

predominant species and occur, respectively, at 533.2 and 285.1 eV. In case of periodic acid treatment, the presence of iodine at the wood surface is revealed by the peaks at 620.0 and 632.0 eV ascribed to I_{3d_5} and I_{3d_3} , respectively. Other species are present but only in very small concentration: This is the case of Ca_{2p} at 350.4 eV, Ca_{2s} at 437.9 eV, and N_{1s} at 402.4 eV.

The presence of nitrogen has to be noted since it has been previously reported that this species does not exhibit an ESCA peak even at contents of about 1.5% by weight in wood.¹³ Since the wood blocks did not exhibit signs of decay, fungi or endosymbiotic bacteria that may fix the nitrogen of the air could not have contributed to an enrichment in nitrogen compounds. The amino acids in wood are the most

Table I C_{1s} Peak Analysis of Untreated and Treated Fraké Samples

Sample	O/C	Fractional Area			Binding Energy Corrected (eV)			WHH (eV)			Chemical Shifts (eV)		
		C_1	C_2	C_3	C_1	C_2	C_3	C_1	C_2	C_3	C_1	C_2	C_3
Fraké untreated	0.27	0.66	0.30	0.04	285.1	286.9	288.5	1.9	2.0	2.2	0.1	1.9	3.5
Fraké treated	0.38	0.53	0.41	0.06	285.1	286.8	288.4	1.9	1.9	2.2	0.1	1.8	3.4
Maple wood ¹²	0.15	0.50	0.43	0.07	285.2	287.0	288.8	—	—	—	0.2	2.0	3.8
Whatman paper ⁶	0.80	0.06	0.83	0.11	285.3	286.9	288.6	2.2	1.8	1.7	0.3	1.9	3.2
CTMP pulp ⁸	0.46	0.41	0.52	0.07	285.1	286.8	288.3	1.9	1.9	2.1	0.1	1.8	3.8

probable source of this nitrogen as will be discussed in the following sections.

O/C Ratio

A determination the O/C ratio provides useful information on the surface composition of the samples. From the determination of peak areas and the calculation of the O/C peak area ratio [Eq. (3)], as shown in Table I, the untreated wood has a rather low O/C ratio of 0.27 as compared to 0.38 for the treated wood. A low O/C ratio suggests a surface rich in extractives and lignin materials that exhibit low O/C ratios. The observed increase of O/C values upon periodic acid treatment is a logical consequence of the increased accessibility of polysaccharides onto the wood. Partial elimination of extractives, which have low O/C ratios, may contribute to this effect.

Peak Assignments

In order to get more information, O_{1s} and C_{1s} peaks have been expanded and deconvoluted into their component peaks. The results are shown in Figures 2 and 3. The O_{1s} peak is symmetrical in all cases and is described as a single peak. The C_{1s} peak shows evidence of shoulders, indicating that it is made up of several components, which is justified since wood contains different constituents, polysaccharides, lignin and extractives, each of which has carbon atoms in different chemical environments.

On the basis of their chemical shifts, the carbon atoms in woody materials have already been classified into four categories as illustrated in Table II.⁷ The contribution of these different carbon atoms to the C_{1s} peak has been calculated and is reported in Table I. It is noted that chemical shifts, ΔE_b , binding energies, E_b , and width at half height (WHH) of

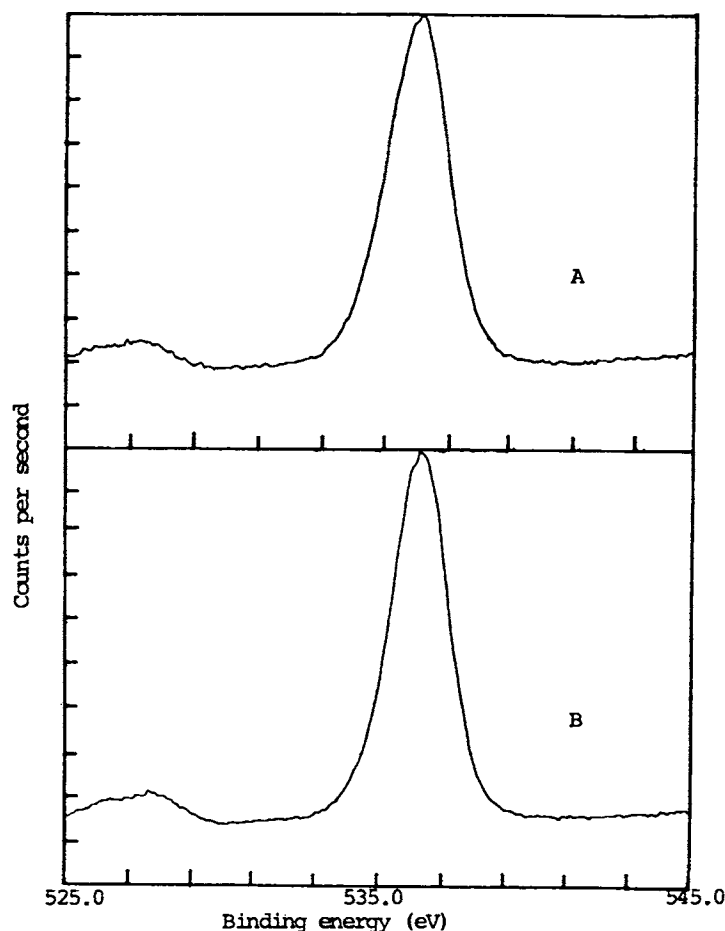


Figure 2 Expansion of O_{1s} peaks obtained from ESCA spectra of (A) untreated and (B) treated Fraké samples.

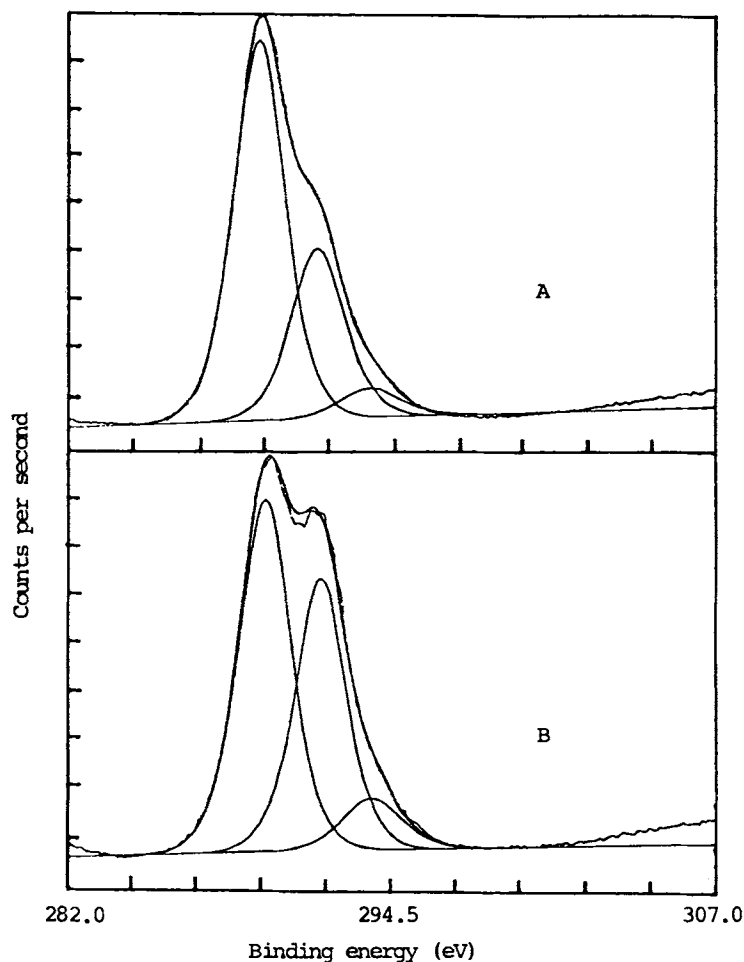


Figure 3 Expansion and deconvolution of C_{1s} peaks obtained from ESCA spectra of (A) untreated and (B) treated Fraké samples.

the different carbon classes obtained in this work are in very good agreement with values reported for woody materials.^{7-9,13}

From Table I, it is observed that treated and untreated woods exhibit carbons in classes C_1 , C_2 , and C_3 , while class C_4 is completely absent. In untreated wood, 66% of the carbon bonds are C_1 carbon bonds. A similar pattern is exhibited by maple wood,¹³ that is, large contributions to C_1 and C_2 and a small frac-

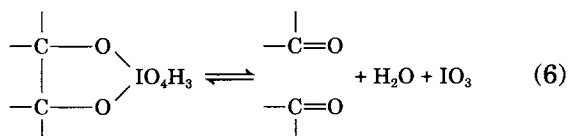
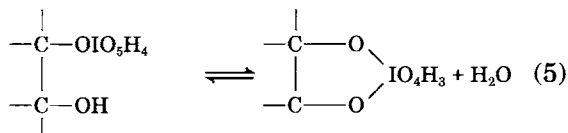
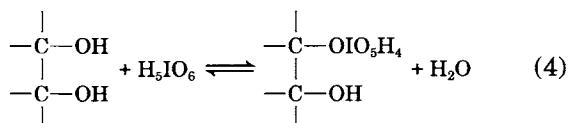
tion of C_3 . Oxidation of the wood with periodic acid significantly alters this distribution. It produces a reduction in C_1 , representing the group of carbon atoms not bonded to oxygen, and an increase in C_2 , with C_3 remaining relatively small but showing a slight increase from 4 to 6% upon treatment.

Known mechanisms of periodic oxidation should result in a large increase of C_3 and C_4 at the expense of C_2 atoms.^{1,17} Throughout this study, C_4 atoms were absent, while C_3 atom fractions remained relatively small and C_2 atoms increased with treatment. Accordingly, the expected oxidation of hydroxyl groups to carbonyl groups by periodic acid was not observed. However, periodic acid is known to be a selective reagent for diols, forming an intermediate that is believed to be a cyclic periodic ester, which is only possible if the hydroxyl groups are spatially adjacent.^{1,2} It is possible, therefore, that wood-periodic acid intermediates formed by the addition of periodic

Table II Classification of Carbon Atoms in Woody Materials⁷

Group	Symbol	Carbon Bonds Involved
I	C_1	C-C or C-H
II	C_2	C-O
III	C_3	C=O or O-C-O
IV	C_4	O-C=O

acid on vicinal diols do not decompose to form carbonyl groups but rather remain as stable complexes. For example, if periodic acid reacts with the hydroxyl groups of wood components such that an addition compound having C—O—I bonds is formed, as illustrated by Eqs. (4)–(6):



the C_{1s} peak should not be significantly affected because the carbon atom is still bonded to a simple nonketonic oxygen. But if a decrease in the carbon atomic fraction not bonded to oxygen C₁ implies a partial elimination of extractives, then the corresponding increase of the carbon atomic fraction bonded to oxygen, especially C₂, will be observed. This would explain why the action of periodic acid on wood did not result in an increase in C₃ atoms with a concomitant decrease in C₂ component. It would explain also why periodic acid is considered to be a preservative for woods because it blocks some of its hydroxyl functions and remains there covalently attached to the cellulose.

CONCLUSIONS

Periodic acid and its sodium salt have been reported to be potential preservatives for woods; but their association with wood constituents is not yet understood. This study was undertaken in an attempt to elucidate the nature of the chemical reactions occurring between periodic acid and the constituents of wood. ESCA data did not show evidence of the expected oxidation of hydroxyl groups. Throughout this study, C₄ atoms were absent, while C₃ atoms remained relatively small and C₂ atoms increased with treatment. It was then postulated that wood-periodic acid intermediates are formed by the addition of periodic acid on vicinal diols of wood constituents. These intermediates are believed to be

cyclic periodic esters that do not decompose to form carbonyl groups but rather remain as stable complexes. Other researchers^{2,3} using infrared (IR) spectroscopy arrived at the same results that the reaction of periodic acid with wood involves bond formation between wood constituents and periodic acid, and at low concentrations of the acid, there was no change in the IR spectrum in the carbonyl region.

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