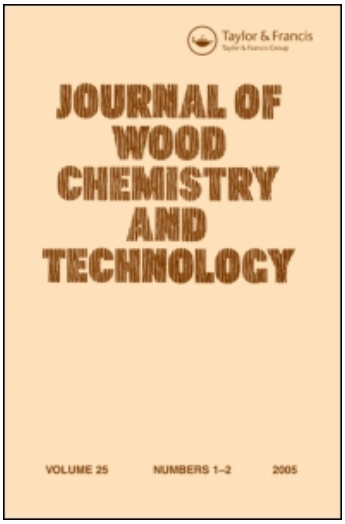

Journal of Wood Chemistry and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

The Study of Carbon-chlorine Bonds in Bleached Pulp with X-ray Photoelectron Spectroscopy

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To cite this Article Reeve, Douglas W. and Tan, Zheng(1998) 'The Study of Carbon-chlorine Bonds in Bleached Pulp with X-ray Photoelectron Spectroscopy', Journal of Wood Chemistry and Technology, 18: 4, 417 — 426
To link to this Article: DOI: 10.1080/02773819809349589
URL: http://dx.doi.org/10.1080/02773819809349589

JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY, 18(4), 417-426 (1998)

The Study of Carbon-chlorine Bonds in Bleached Pulp with X-ray Photoelectron Spectroscopy

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ABSTRACT

The bonding state of chlorine in chlorinated cellulosic materials and in chlorine-bleached pulp has been studied with X-ray photoelectron spectroscopy (XPS). Direct evidence of organically-bound chlorine is shown by high resolution Cl(2p) spectra.

INTRODUCTION

Organochlorine has been found in various cellulosic and carbohydrate materials which have been subjected to kraft pulping conditions and chlorine bleaching leading to the conclusion that chlorinated organic matter is formed from carbohydrate during kraft pulp bleaching.[1] The carbohydrate-originated organochlorine accounted for a significant part of the inextractable organochlorine in fully-bleached chemical pulp (50 to 200 ppm Cl), which had been previously ascribed entirely to a lignin origin.

The exact reaction mechanism of the formation of carbohydrate-originated organochlorine is not yet understood. Since hardly any organochlorine is produced from the chlorination of unmodified simple sugars, it has been proposed[1] that the major source of this organochlorine comes from chlorination of the unsaturated carbon-carbon bonds generated from carbohydrate during pulping. In the current work, the chemical structure of the carbohydrate and the bonding state of the organochlorine has been studied with X-ray photoelectron spectroscopy (XPS).

XPS, also referred to as electron spectroscopy for chemical analysis (ESCA), is a non-destructive surface analytical technique. It employs a characteristic X-ray source (Al Kα or Mg Kα) to excite photoelectrons from core levels of the specimen atom. The photoelectrons which escape from the specimen surface are analyzed by an energy analyzer. The difference between the X-ray source irradiation energy and the kinetic energies of the photoelectrons is a measure of the binding energies of the core level electrons within the specimen atom. The binding energies are characteristic of specific elements and therefore can be used for elemental identification.

XPS is also unique in providing information on the oxidation state or chemical bonding state of elements. This is based on the fact that the binding energies may be shifted by the charge distribution caused by various types of chemical bonding. For wood pulp fibres, there are mainly three types of carbon atoms in the C(1s) spectra: C-H or C-C carbon, C-O carbon and C=O (or O-C-O) carbon. The exact binding energies of C(1s) and O(1s) peaks for wood pulp fibres or bleached pulp and paper have been well documented in the literature and have been summarized by Hua *et al.*[2] The O(1s) peak of cellulose has a binding energy very close to 533.0 eV. The C(1s) peak for C-H (or C-C) carbon, which is located at 285.0 eV, is mainly from lignin. The C-O carbon is mostly from cellulose, with some contribution from lignin. The C(1s) peak of C-O carbon in cellulose has a maximum very close to 287 eV. The C=O or O-C-O C(1s) carbon, which lies between 288 eV and 290 eV, can be from either cellulose or lignin.

For chlorine atoms, it has been shown that the Cl(2p) spectra can be used to differentiate between organically bound chlorine and inorganic chloride. Normally, the Cl ($2p_{3/2}$) peak from organochlorine is slightly above 200 eV while the Cl ($2p_{3/2}$) from inorganic chloride is below 200 eV,[3,4,5] usually between 198 eV to 199 eV. The Cl ($2p_{1/2}$) peak is also present and is also useful in distinguishing organically bound chlorine from inorganic chloride.

EXPERIMENTAL

Five samples were used for XPS analysis: 1) chlorinated, kraft-cooked glucose precipitate, 6510 ppm Cl; 2) chlorinated, severely cooked cotton fibres, 710 ppm Cl; 3) chlorinated, severely cooked micro crystalline cellulose precipitate, 510 ppm Cl; 4) α-cellulose from chlorine-bleached wood pulp, 200 ppm Cl; and 5) chlorinated and extracted softwood kraft pulp, 2410 ppm Cl. Preparations of the first four samples have been described in detail in reference 1. The fifth sample, a CE-bleached pulp, was made under normal bleaching conditions in this laboratory. Each sample was spread onto copper tape and mounted on the XPS sample holder.

XPS analysis was carried out on a Leybold MAX 200 XPS system. The spectra were obtained using a Mg Kα X-ray source operating under 12 or 15 kV, at 15-25 mA current. The XPS spectrometer had been calibrated to the Ag ($3d_{5/2}$) and Cu ($2p_{3/2}$) peaks at 368.3 eV and 932.7 eV respectively.[3] The binding energy scale was then adjusted against the C(1s) peak at 285.0 eV. This procedure, using the same instrument, has been used for the examination of chlorhexidine.[3] In the absence of 285.0 eV peak, the scale was adjusted against the O(1s) peak of cellulose at 533.0 eV. In this case, the C(1s) peak at 287 eV was also cross-checked for confirmation.

RESULTS AND DISCUSSION

Figure 1 is an XPS survey spectrum of the chlorinated, kraft-cooked glucose precipitate. The C(1s) peak is higher than the O(1s) peak and the chlorine peak in

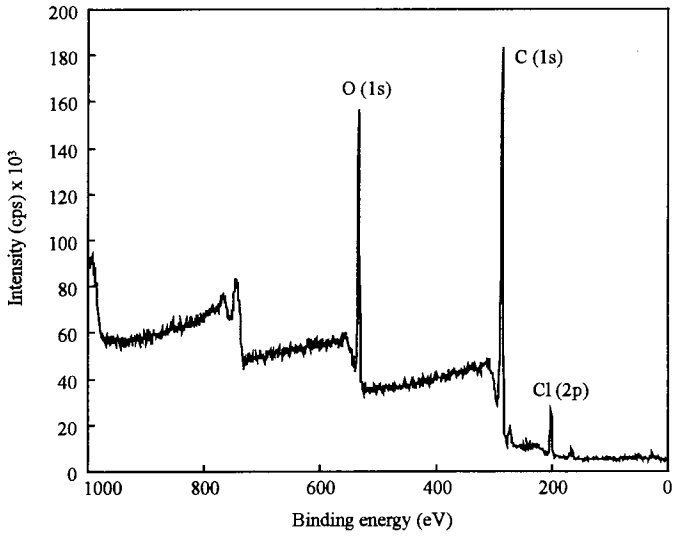

FIGURE 1. XPS survey of chlorinated, cooked glucose precipitate.

Figure 1 is relatively high. A high resolution spectrum of the C(1s) peak shows predominantly C-H (or C-C) carbons, which are produced during cooking. The high resolution Cl(2p) spectrum in Figure 2 is deconvoluted into $Cl(2p_{1/2})$ and $Cl(2p_{3/2})$ peaks by a curve fit routine provided by the XPS instrument. The $Cl(2p_{3/2})$ peak is located above 200 eV, indicating that the chlorine atoms are covalently bound.

For the chlorinated, severely cooked cotton fibres, the XPS survey spectrum is shown in Figure 3. The chlorine Cl(2p) peak is small, but can be clearly identified. The intensity of C(1s) peak is lower than that of the O(1s) peak. The high resolution C(1s) spectrum shows predominantly cellulose features, with the highest peak centered at 287 eV. However, there is a slight shoulder at 285 eV which suggests that a small amount of C-H and C-C carbons (most likely unsaturated carbon-carbon bonds) are produced during severe kraft cooking of the cotton fibres. The deconvoluted high resolution Cl(2p) spectrum in Figure 4 shows predominantly organically bound

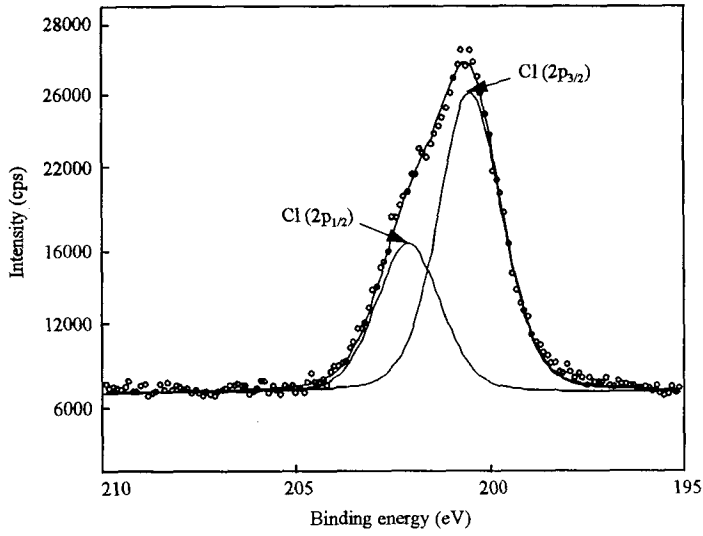

FIGURE 2. Cl(2P) spectrum of chlorinated, cooked glucose precipitate.

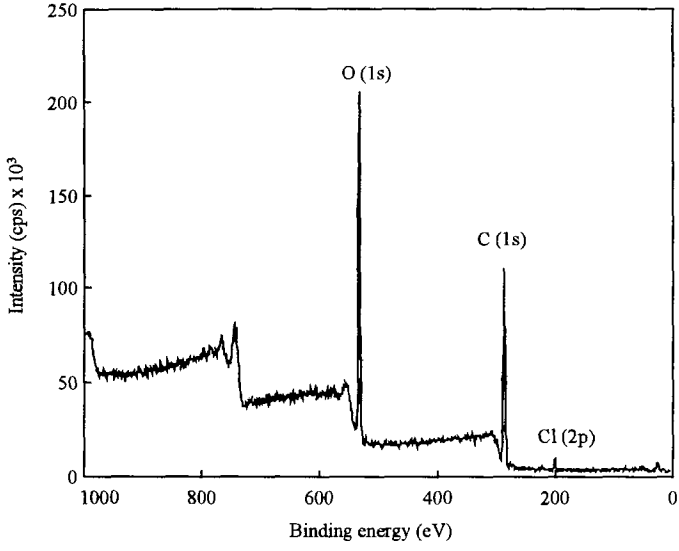

FIGURE 3. XPS survey spectrum of chlorinated, severely cooked cotton.

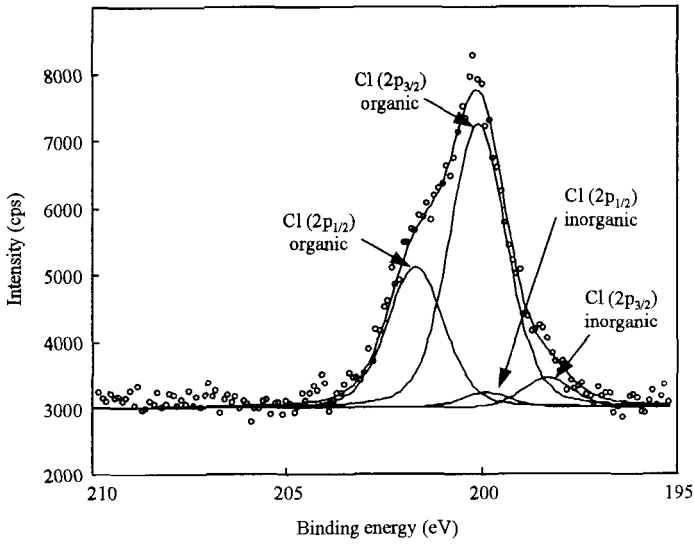

FIGURE 4. Cl(2P) spectum of chlorinated, severely cooked cotton.

chlorine; the Cl($2p_{3/2}$) peak is above 200 eV. Small amounts of inorganic chloride are also shown; Cl($2p_{3/2}$) at 198-99 eV.

The high resolution Cl(2p) peak for the chlorinated severely cooked microcrystalline cellulose precipitate is shown in Figure 5. The deconvoluted peak shows characteristics clearly due to organochlorine as the Cl($2p_{3/2}$) peak is above 200 eV.

The α-cellulose from wood pulp, when thoroughly washed, had a chlorine content of 200 ppm Cl. In the present experiment, it was intentionally soaked in the spent chlorine bleaching liquor containing chloride ion and was only briefly rinsed. The chlorine signal in the XPS survey spectrum was very weak. But at high resolution (Figure 6), organochlorine (Cl $2p_{3/2}$ at 200 eV and Cl $2p_{½}$ at 202 eV) and inorganic chlorine (Cl $2p_{3/2}$ at 198 eV) can be clearly distinguished.

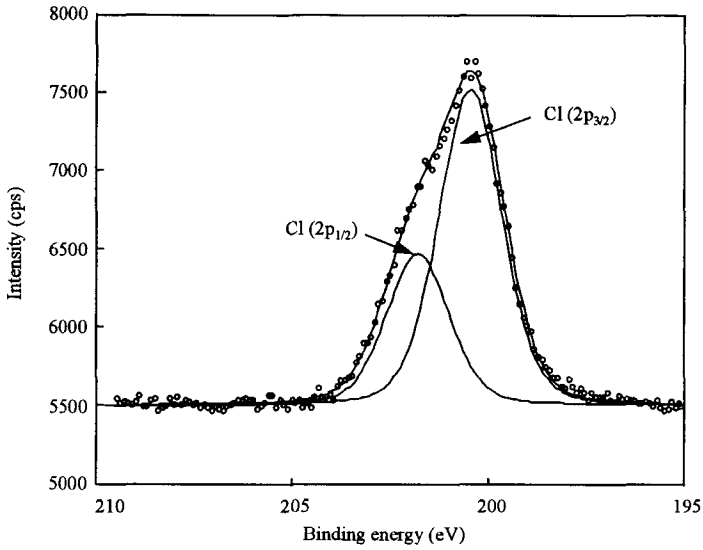

FIGURE 5. Cl(2P) spectrum of chlorinated, severely cooked, microcrystalline cellulose precipitate.

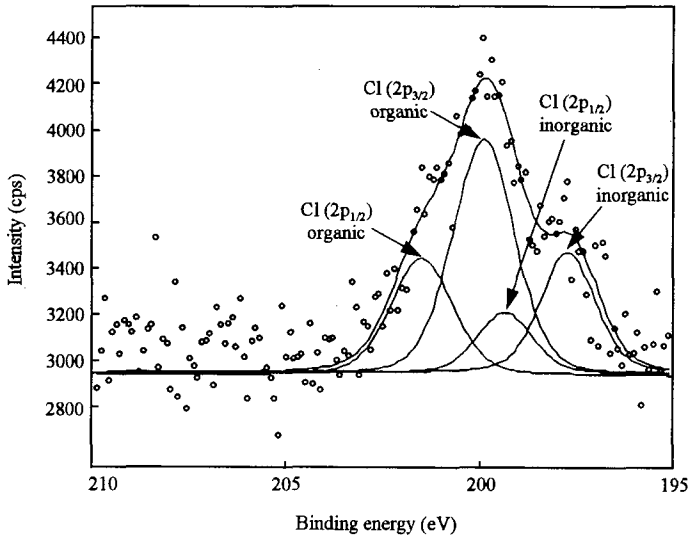

FIGURE 6. Cl(2P) spectrum of chlorinated α-cellulose from wood pulp.

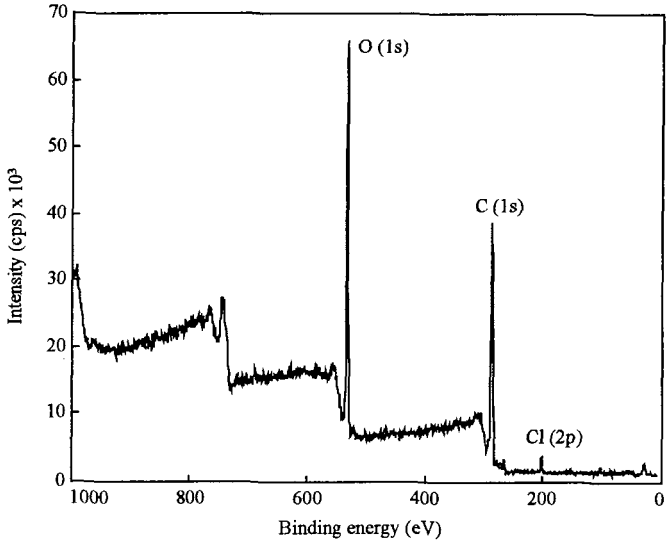

FIGURE 7. XPS survey spectrum of the CE-bleached kraft pulp.

The XPS spectrum of CE-bleached pulp was studied for comparison. Figure 7 is a survey spectrum of the CE-bleached pulp. The Cl(2p) peak is small but evident. The high resolution C(1s) spectrum with curve-fitting indicates three types of carbon: C-H (or C-C) carbon, C-O carbon and C=O (or O-C-O) carbon. The C-H (or C-C) carbon at 285.0 eV is mainly from lignin. The C-O carbon at 287 eV is mostly from cellulose, also with some contribution from lignin. Figure 8 is the high resolution Cl(2p) spectrum. $Cl(2p_{3/2})$ is located above 200 eV, which indicates organically bound chlorine. Most of this organochlorine (2410 ppm Cl) is expected to be bound to the lignin, since chlorolignin is known to be present in the CE-bleached pulp. The moderately strong intensity of C(1s) peak at 285 eV is most certainly the contribution of residual lignin.

XPS analysis was performed on fully bleached kraft pulp containing 200 ppm Cl inextractable by water or solvent. However, at high resolution the Cl (2p) peak was

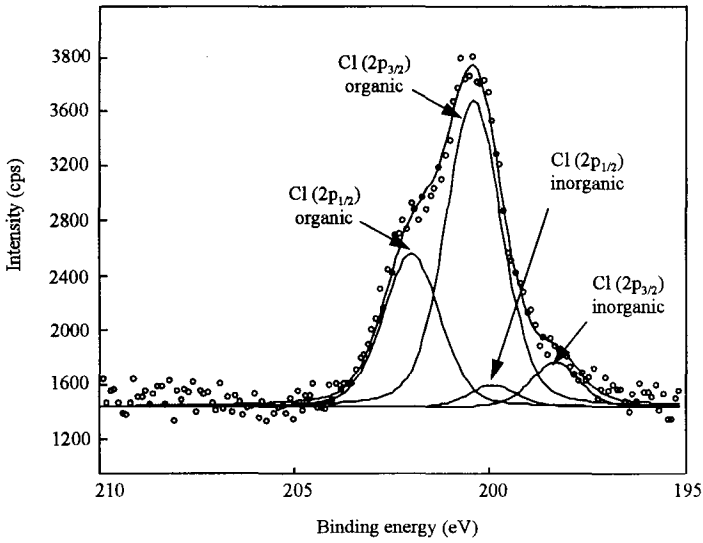

FIGURE 8. Cl(2p) spectrum of the CE-bleached kraft pulp.

not detectable. In this case, most of the organochlorine is probably located in the middle of the fibre wall[6] and therefore not detected.

SUMMARY

X-ray photoelectron spectroscopy (XPS) has provided unique information about the chemical bonding state of the carbohydrate-originated carbon-chlorine bonds in chlorinated carbohydrate materials and bleached pulp. First of all, it is shown directly that the "organochlorine" in chlorinated cellulosic material and CE-bleached pulp is covalently bound to carbon. Previously such "organochlorine" has been defined as the chlorine which is not removed by vigorous water washing. Secondly, high resolution C(1s) spectra verify the fact[1] that hydrocarbons (either olefinic or aromatic) should serve as reaction sites for chlorination, thus contributing to the carbohydrate-originating organochlorine.

ACKNOWLEDGMENTS

We thank Dr. R. N. S. Sodhi for XPS measurements and for valuable discussions. The authors are grateful to D. A. I. Goring for his valuable discussions and editorial comments.

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