Surface chemistry and charge of cellulosic fibres

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Scots Pine (Pinus silvestris)

A renewable, biodegradable, environmentally benign material
Structure of the stem

Pith— the central part of the wood, that is formed during its first year of growth.

Xylem – the part between the pith and the cambium.

Cambium – a thin layer of cells, where cell division takes place.

Phloem (bast) - layer between cambium and bark.

Section of two years old tree
Wood cell (fibre) wall structure

middle lamella (filling the space between cell walls)
Softwood cells

Pine fibres (*Pinus sylvestris*). Pits in the walls of the tracheids can be clearly seen (T) and (CF). [KCL, 2002]
Wood fibre structure

Background

Microfibrillated cellulose can be obtained by disintegration of wood pulp in mills (not a very easy procedure). In the process, fibers are opened into their substructural fibrils and microfibrils. The resulting material is greatly expanded in surface area and highly crystalline. Large aspect ratios and hydrophillic surface of the microfibrils promote gel-like properties.
The chemical composition of wood

<table>
<thead>
<tr>
<th></th>
<th>Spruce</th>
<th>Pine</th>
<th>Birch</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extractives</td>
<td>2</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td>Lignin</td>
<td>27</td>
<td>27</td>
<td>20</td>
</tr>
<tr>
<td>Hemicelluloses</td>
<td>30</td>
<td>30</td>
<td>37</td>
</tr>
<tr>
<td>Cellulose</td>
<td>41</td>
<td>39</td>
<td>40</td>
</tr>
</tbody>
</table>
Wood extractives

- Several thousand low-molecular compounds soluble either in neutral organic solvents or water
- Terpenes, fatty acid esters, fatty acids, sterols and alkanes
- Many different functions in wood:
  - Fats, energy reserves of the tree
  - Rosin acids, terpenes, sterols, protect the tree from biological attack
  - Many other compounds with different functions
- 3-8 % by weight of wood, depending on species
Summary: Importance of fibre surface chemistry

• Porosity and flexibility of cell wall: bonding, beating, penetration

  - The lignin (and hemicellulose) is dissolved in the cook
    ➔ a porous structure is created and the importance of direct bonds between
    the microfibrils increases

  - Drying: new (irreversible) bonds are formed between the microfibrils
    ➔ stiffer structure ("hornification")

  - Swelling: Osmotic forces due to charges and hydration

  - Penetration: Consumption of additives (retention polymers etc.),
    absorption of water and other solvents

• Intrinsic bond strength: Bonding in paper, fibre interactions with pigments,
  printing inks, dyes and surrounding matrix in composites

  - Chemical composition of outer surface
  - Binding between S1 and S2 layers
  - Degree of coverage by hydrophobic material
  - Chemical groups in surface
Surface analysis of fibres

- Structure and crystallinity
  - Confocal microscopy (CSLM)
  - Electron Microscopy (TEM, SEM, ESEM)
  - X-ray diffraction
  - NMR (solid state)
  - Atomic Force Microscopy (scanning/AFM)
  - Porosimetry

- Chemistry
  - FTIR, NIR and Raman-spectroscopy (analysis depth > 0.5 nm)
  - Titrations and adsorption (ionizable groups in bulk and surface)
  - Secondary Ion Mass Spectroscopy (SIMS) (analysis depth < nm)
  - X-ray Photoelectron Spectroscopy/ Electron Spectroscopy for Chemical Analysis (XPS/ESCA) (analysis depth 0.5 - 2 nm)

- Surface energy
  - Adsorption (from gas or solution)
  - Contact angles (fibres and sheets)
  - Surface force measurements (model surfaces/surface force apparatus, and AFM)
Why is the charge important?

Wood and fibres:
- Ion exchange capacities of fibres
- Modification of fibers by adsorption or chemical reactions
- Swelling of fibres with water
- Bonding between fibre surfaces

Papermaking:
- Beating
- Consumption of chemicals in the wet end of the paper machine
- Washing of pulp
Example 3: Effect of counter-ion on swelling and tensile strength of paper

Wood and pulp fibres carry a negative charge

- Carboxylic acids, \( \text{COOH} \rightarrow \text{COO}^- + \text{H}^+ \)
  - \( pK \approx 3 - 3.5 \) (uronic acids, cellulose, hemicelluloses)
  - \( pK \approx 4 - 5 \) (aliphatic acids, extractives, \( pK_1 \) for diacids)
- Functional groups in lignin: muconic acid \( pK_2 \), phenolic, alcoholic, etc.
  - \( pK \approx 6 - 10 \)
- Sulphonic acids, \( \text{SO}_3\text{H} \rightarrow \text{SO}_3^- + \text{H}^+ \)
  - \( pK \approx 2 \)
Effect of bleaching sequence on fibre charge

Determination of total charge

- Potentiometric titration
- Conductometric titration
- Complexation with dye and other small molecules
Determination of surface and total charge

- Polyelectrolyte adsorption
- Zeta potential
Choice of method

• Total charge:
  - Any of the direct titration methods can be used (only determination of equivalence point is required)
  - Conductometric titration is rapid and precise but cannot resolve a mixture of weak acids well
  - Adsorption methods: accessibility becomes important (for both polyelectrolytes and dyes

• Detailed determination of dissociation constants:
  - Potentiometric titration

• Distribution of charge (outer surface/pores):
  - Polyelectrolyte adsorption or adsorption of smaller molecules

• Zeta potential:
  - Gives indication of effective outer surface charge; interpretation may be difficult due to fibre swelling and complex structure of fibre surface
Pore size distribution in bleached softwood fibres, Inverse Size Exclusion Chromatography Chromatography

Probe molecules: series of pullulans (polysaccharide)

- Method probes very small pores
- Pore size distribution is shifted upwards by oxygen delignification after cook

J. Berthold, Thesis, STFI
Conductometric titration

- Total concentration can be calculated from $V_{eq}$.
- Rapid and simple measurement, applicable to low concentrations of weak acid. Method is extensively used for cellulose fibres.
- Sharp break points are obtained only if some background electrolyte is added so that electrostatic effects are screened.
- But break points become much less distinct at high electrolyte concentrations.

Contributions of different ions to conductance when a weak acid (HB) is titrated with a strong base (MB)
In a potentiometric titration of an acid, the potential $E$ of an electrochemical cell is measured. pH is calculated from

$$E = E^\circ + RT \ln 10 pH + E_j$$

The equivalence point is taken as the steepest point of a curve showing pH vs. added $[\text{OH}^-]$, or preferably determined by linearisation, i.e.:

$$\{\text{H}^+\} = 10^{\left(\frac{E^\circ - E_j}{RT}\right)} = \text{const.} \cdot 10^{\left(E - E_j\right)}$$

is plotted against added $[\text{OH}^-]$ (Gran diagram)


$E^\circ$ = standard potential
$E_j$ = diffusion potential
$\{\text{H}^+\}$ = hydrogen ion activity
Potentiometric titration of different pulps

$\text{pH}$

![Graph showing pH against added NaOH] / µmol]

→ actual location of equivalence point may be difficult to determine from slope when fibres (or polyelectrolytes) are titrated

Analysis of potentiometric titration

- Fitting of Z-function: determine experimentally the function
  \[ Z_{\text{exp}} = \frac{C_H - [H]}{C_B} \]
  - \( Z_{\text{exp}} \) = mean degree of dissociation of all acids
  - \( C_H \) = total concentration of hydrogen ions (free and in acids)
  - \( C_B \) = total concentration of acids
  - \( C_B \) and \( C_H \) can be determined with high precision from equivalence point of titration (Gran diagram)
  - \([H] = 10^{pH}\)
  - \([H]\), and hence \(Z_{\text{exp}}\), can be determined with high precision at each point of titration

Knowing what acids (\(HA_j\)) are present and their dissociation constants \(K_j\), \(Z\) can be calculated theoretically from (Sillén L., Ingri, N.i et al, KTH, Stockholm 1960's)

\[ Z_{\text{theor}} = \frac{\sum_j [HA_j]}{C_B} = \frac{\sum_j [H][A_{j}^{-}]K_j}{C_B} \]

Curve-fitting by assuming the types of acids and using the \(K_j\) as adjustable parameters
Titration of unbleached kraft pulp

→ In unbleached fibres there are two types of acids:
  • uronic acids
  • carboxylic group very probably bound to lignin

The apparent dissociation constant

- The charge of the fibres increases as their degree of dissociation increases. As a result, the electrostatic attraction between hydrogen ions and the fibres increases.

- The acids apparently become weaker as the degree of dissociation increases. "Constant capacitance" model: The apparent dissociation constant is given by

\[ K_j' = K_j \cdot e^{\frac{zF\phi}{RT}} \]

\( \phi = \) surface potential of fibres, treated as additional adjustable parameter
\( z = \) valency of ion (+1 for hydrogen ion)

- Final equation for \( Z_{\text{theor}} \):

\[ Z_{\text{theor}} = \frac{\sum [H][A_j]K_j e^{\frac{zF\phi}{RT}}}{C_B} \]

- More advanced models (full electrical double layer models) sometimes used
Titration of unbleached kraft pulp (pine)

- Coulometric titration of unbleached kraft pulp (kappa = 19, alkali = 26 %).
- Points: experimental data.
- Dashed curve: Theoretical for a surface containing two acidic groups.
- Solid curve: no correction for electrostatic interactions
**Polyelectrolyte adsorption**

A highly charged polyelectrolyte adsorbs on the surface

The excess of polymer in solution after adsorption is titrated with an oppositely charged polymer

Assumptions:
- The adsorbed charge reacts stoichiometrically with the surface charge
- The oppositely charged polymer reacts stoichiometrically with the excess

Note: The accessibility of the surface charge depends on the molecular weight of the adsorbing polymer
Detection of end point

1) Reaction with dye indicator after complete reaction with polymer

\[ A + C \xrightarrow{k_1} AC \]
\[ A + I \xrightarrow{k_2} AI \]

A = Anionic polymer
C = Cationic polymer
I = Indicator

Requirement: \( k_1 \gg k_2 \)

This is the case for PE with high \( M_w \)

2) Detection of charge (electrophoretic mobility) of complex

- assumed to be 0 when polymer charges are equivalent

- requires strong interaction between polymers (low ionic strength, high charge of at least one polymer)
Standard chemicals used for colloid titrations

Titration of fibres

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Structure</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>KPVS</td>
<td><img src="image" alt="Structure" /></td>
<td>For titration</td>
</tr>
<tr>
<td>PDADMAC</td>
<td><img src="image" alt="Structure" /></td>
<td>Adsorbs, high $M_w$</td>
</tr>
<tr>
<td>Polybrene</td>
<td><img src="image" alt="Structure" /></td>
<td>Adsorbs, low $M_w$</td>
</tr>
<tr>
<td>OTB</td>
<td><img src="image" alt="Structure" /></td>
<td>Dye</td>
</tr>
</tbody>
</table>
Principle of pulp charge determination with colloid titration

Excess adsorption of cationic charge

Extrapolation to zero polyelectrolyte conc. ensures stoichiometry

Adsorption of cationic polymers with different molecular weight on unbleached kraft pulp

Accessibility of charge can be monitored by polyelectrolyte adsorption

Note: adsorption of high molecular weight polymer may change slowly with time (slow diffusion into fibres)

Binding of metal ions to fibres

Metal ion binding is a very important property of wood and cellulose fibres

- Heavy metal ions catalyse decomposition of peroxide used for bleaching
- Binding of calcium and other divalent ions very important when calcium carbonate or sulphate are used as fillers in paper
- Sorption of multivalent ions has strong effect on uptake of other chemicals
- Swelling of fibre and wood with water
- Multivalent aluminum ions are used as flocculants and in sizing
- Multivalent ions affect formation of harmful deposits
- Adsorption of toxic metal ions must be avoided
Models of ion binding

Good models of metal ion uptake by fibres (and wood) from aqueous solution are required.

Three main approaches:
- Modelling based on separate binding constants of each metal ion to each type of ionic group in fibre.
- Donnan equilibrium (non-specific sorption due to osmotic effects).
- Combination of both (most useful).
Fibre ion binding and swelling: Donnan equilibrium

(Neale, 1929, Scallan et. al. 1979, 1996)

Assumptions:

• All ions except those specifically bound to fibre surface groups are freely mobile between the solution in the fibres (f) and the external phase (e)

• Ion distribution is determined by mass equilibrium and electroneutrality conditions

• The fibres contain a number of fibre-bound acid groups $HA_i$

$$HA_i \rightarrow H^+ + A_i^-$$

• Both the fibre phase and the external phase are electrostatically neutral

• Ions are point charges, characterised only by their valency $z$

Because fibre-bond ions cannot move into bulk phase, concentrations of mobile ions in bulk and in the fibre solution are not equal (but chemical potentials are)
Distribution of ions

- For any freely mobile ion $X^z$ the distribution between the external and fibre phases is given by
  \[ [X]_f = \lambda^z [X]_e \]
  \( \lambda \) = distribution coefficient, valid for all freely mobile ions

- The dissociation constants of the acid groups in the fibre are given by
  \[ K_i = \frac{[H^+]_f[A^-]_f}{[HA_i]_f} = \frac{\lambda \cdot [H^+]_e[A^-]_f}{[HA_i]_f} = \lambda K'_i \]

- \( \lambda \) depends on the degree of dissociation of the fibres, i.e. the concentration of fibre-bound ionic groups.
- Hence the apparent dissociation constant \( K' \), which is calculated from measurements of the external pH, depends on the degree of dissociation.
- pH in the fibres $<$ pH in the bulk!!
- This dependence is analogous to the dependence on surface potential assumed in the constant capacitance model used to interprete potentiometric titrations.
Sorption of ions to hardwood kraft fibres

Unbleached kraft pulp containing 2860 ppm Na\(^+\), 680\(^+\) ppm K\(^+\), 165 ppm Mg\(^{++}\), 1100 ppm Ca\(^{++}\), 1 ppm Mn\(^{++}\)

Only parameter needed to describe distribution is \(\lambda\)
- All three ions distribute in the same way → no specific binding
- Added sodium ions decreases divalent ion concentration in fibres
- Dissociation of uronic acids and acid groups in lignin clearly distinguishable

Prediction of pH from Donnan model

Experimental and calculated external pH in metal ion sorption studies, Dissociation constants determined by potentiometric titration
Concentration of Ca\(^{++}\) in bulk solution (AAS)

\[ [\text{Ca}^{++}]_{\text{tot}} = 86 \text{ mmol/l}, \text{two acid groups in fibres, } pK_{a1} = 3.6, pK_{a2} = 7.4, \text{total charge of fibres } 157 \text{ mmol/kg (125 mmol/kg} + 32 \text{ mmol/kg)} \]

- Donnan model is a simple and accurate mode that is able to predict metal ion sorption into fibres.
- Solution equilibria (complexation) can be taken into account by standard methods of calculating complex equilibria.
- Multivalent ions may bind specifically; then dissociation constants must be known
Conclusions

- Fibre charge is an essential property of fibres

- A full determination of fibre charge properties requires
  - Detailed analysis by potentiometric titration
  - Determination of charge distribution on fibres by polyelectrolyte adsorption
  - Verification by chemical analysis

- Equilibrium distribution of ions in fibre suspension can be successfully modelled using the Donnan approach

- However, kinetics (not discussed here) can be of importance in practice
Important:

- Charge models should always be verified by independent determinations of chemical composition!
Spectroscopies of organic surfaces: limiting factors

- charging of electrically isolating surfaces
- decomposition (thermal or caused by radiation)
- evaporation of volatile components (in methods requiring high vacuum)
## Surface spectroscopies, organic surfaces

<table>
<thead>
<tr>
<th></th>
<th>Emission or scattering</th>
<th>Transmission</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Electrons Radiation Ions</td>
<td>Electrons Radiation</td>
<td></td>
</tr>
<tr>
<td>Electrons</td>
<td>SEM, ESEM</td>
<td>TEM EDX</td>
<td></td>
</tr>
<tr>
<td>Radiation</td>
<td>XPS(ESCA) AES</td>
<td>FTIR FT-Raman Raman</td>
<td>FTIR NIR</td>
</tr>
<tr>
<td>Ions</td>
<td></td>
<td>SIMS</td>
<td></td>
</tr>
</tbody>
</table>

SEM = Scanning Electron Microscopy  
TEM = Transmission Electron Microscopy  
EDX = Energy Dispersive X-ray Analysis  
ESCA (XPS) = Electron Spectroscopy for Chemical Analysis (X-ray Photoelectron Spectroscopy)  
AES = Auger electron spectroscopy  
FTIR = Fourier Transform Infrared Spectroscopy  
FT-Raman = Fourier Transform Raman Spectroscopy  
Raman = Raman spectroscopy (dispersive)  
NIR = Near infrared spectroscopy  
SIMS = Secondary Ion Mass Spectroscopy
X-ray Photoelectron Spectroscopy, XPS

The electrons adsorb energy $E_s$ from the X-rays so that they are emitted from the atom.

The spectrometer measures their kinetic energy $E_{kin}$.

The difference gives the binding energy $E_b$

$$E_b = E_s - E_{kin}$$
Electrostatic attraction between the nucleus and an electron:

\[ E_b = \mu - \frac{Z e_0^2}{r} \]

- \( r \) = distance between electron and nucleus
- \( e \) = charge of proton
- \( Z \) = number of protons in nucleus (atomic number)

Because the binding energy is proportional to the atomic number, any element bound in the surface (except hydrogen) can be identified and quantified.
XPS of solid surfaces

The X-rays penetrate deeply into the surface, but the escape depth of the electrons is very small

\[ \delta = 1 - 7 \text{ nm} \]

(95% of the electrons come from a depth that is < 3\( \delta \))

→ Only the outermost molecular layers of the surface are analysed

For very smooth surfaces, depth profiles can be determined by analysis of intensity dependence on emission angle
Wide scan XPS spectrum of cellulose surface

Unbleached pine kraft pulp

Note: Auger electrons have a low kinetic energy and therefore are interpreted by XPS software as having a high binding energy. They are useful for confirmation of elementary analysis.
Chemical analysis: chemical bonds

- The electron density around the atom is important.
- The higher the ionisation of the atom, or the more electronegative its neighbors, the higher is the binding energy of the core electrons.
- It becomes possible to identify the types of bond in which the atom participates.
- E.g., based on the detailed carbon spectrum, the total amount of carbon in a fibre surface and the relative amounts of lignin, polysaccharides, extractives and different metal ions in the surface can be identified.
High resolution C1s spectrum of unbleached pine kraft pulp
## Chemical shifts in the XPS spectrum

<table>
<thead>
<tr>
<th>Atom/electron</th>
<th>Chemical bond</th>
<th>Binding energy</th>
<th>Chemical shift$^{1)}$</th>
<th>eV</th>
<th>eV</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>C 1s</strong></td>
<td>Only to carbon or hydrogen</td>
<td>285.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>One bond to oxygen</td>
<td></td>
<td>1.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Two bonds to oxygen</td>
<td></td>
<td>3.0</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>(O-C-O, C=O)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Carboxyl group</td>
<td></td>
<td>4.0-5-0</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>-COOH</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CO$_3^{2-}$ (carbonate)</td>
<td></td>
<td>5</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>“Shake-up” (aromatic carbon)</td>
<td></td>
<td>$\approx$ 7</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>S 2p$_{1/2}$</strong></td>
<td>R-SO$_3$H</td>
<td>169</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>R-SO$_2$-R</td>
<td></td>
<td>-2.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>O 1s</strong></td>
<td>Different bonds</td>
<td>533</td>
<td></td>
<td></td>
<td>±2</td>
</tr>
<tr>
<td><strong>N 1s</strong></td>
<td>-N(CH$_3$)$_2$, -NH$_2$, -C≡N</td>
<td>399-401</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>-NH$_3^+$, -N(CH$<em>3$)$</em>+^+$</td>
<td></td>
<td>1.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>-NO$_2$</td>
<td></td>
<td>7</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The amount of different carbons in wood components

<table>
<thead>
<tr>
<th>Substance</th>
<th>O/C</th>
<th>C₁</th>
<th>C₂</th>
<th>C₃</th>
<th>C₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose</td>
<td>0.83</td>
<td>-</td>
<td>83</td>
<td>17</td>
<td></td>
</tr>
<tr>
<td>Galactoglucomannan</td>
<td>0.82</td>
<td>3</td>
<td>79</td>
<td>16</td>
<td>3</td>
</tr>
<tr>
<td>Lignin</td>
<td>0.33</td>
<td>49</td>
<td>49</td>
<td>2</td>
<td>–</td>
</tr>
<tr>
<td>Linolic acid</td>
<td>0.11</td>
<td>94</td>
<td>-</td>
<td>-</td>
<td>6</td>
</tr>
<tr>
<td>Abietic acid</td>
<td>0.10</td>
<td>95</td>
<td>-</td>
<td></td>
<td>5</td>
</tr>
</tbody>
</table>
A model of extracted and unextracted wood pulp fibre surfaces
Surface coverage of lignin vs. total content of lignin in kraft pulps bleached by different sequences

O = oxygen
Z = ozone
P = hydrogen peroxide
D = chlorine dioxide
E = washing with alkali

Surface composition of mechanical pulp fines

“fines” = fine material formed during mechanical pulping

(J. Mosbye et al.(2003), Nordic Pulp Paper Res J)
SIMS,
Fast atom bombardment FAB,
Laser decomposition LD
SIMS
Secondary Ion Mass Spectroscopy

"Static" SIMS: As little damage to the surface as possible.
- Depth of analysis 0.3 - 1 nm
- Sweep: < 1 mm resolution
- Sensitivity: 10 - 100 times that of ESCA

"Dynamic" SIMS: Molecular layers are peeled off by the ion source

Mass spectrometry: principle the same as for standard mass spectrometry
Time-of-Flight SIMS, ToF-SIMs

Mass detection in SIMS

(a) Quadrupole detector, similar to the one used in standard mass spectrometers, useful for metal ions and low molecular weight fragments ($M_w < 6000$)

(b) Time-of-flight detector, based on kinetic energy of molecular fragments: if ions with different mass all have the same k.e. they will arrive at different times to the detector

$$E_{kin} = \frac{1}{2} mv^2$$
SIMS: The distribution of calcium and silicon in the surface of bleached groundwood finres

(Saastamoinen et al, Pap. Puu 1994)

Calcium

Silicon and calcium

Yellow: Calcium, Green: silicon; → calcium silicate used as additive in bleaching has adsorbed on fibres
Lignin coverage and structure on thermomechanical fibres and fines

**XPS**

Surface coverage, %

<table>
<thead>
<tr>
<th></th>
<th>extractives</th>
<th>lignin</th>
</tr>
</thead>
<tbody>
<tr>
<td>TMP orig</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TMP peeled</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TMPp</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TMPs</td>
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</tbody>
</table>

**ToF_SIMS**

127 = hexosaccharides
77/127 = aromatic units (lignin)
31/77 = methoxyl/aromatic (in lignin)
(137+51)/77 guaiacylic (in lignin)

The changes in surface chemistry resulting from different treatments can be followed in detail by combining XPS and SIMS

Kleen, Kangas et al, 1th ISWPC, Nice, 2001, 1