Surface Chemistry of Papers
Surface chemical composition obtained by various spectroscopic techniques

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Paper Surfaces - Characterisation and Properties
FPIRC course September 15-18, 2014
Surface Analysis of paper and other materials

Examples:

- Mineral powder + fatty acid
  FT-IR: identify surface functional groups

- Pigment coated paper
  FT-IR, Raman, XPS, ToF-SIMS, AFM:
  latex distribution on surface, surface amount latex and pigments, etc.

- Polymer / plastic
  Confocal Raman, XPS:
  identification, fingerprinting

- PET
  XPS: identify surface functional groups

- Wood pulp fibres / Paper
  XPS / ESCA image of single fibre,
  surface coverage of lignin

- Water-borne coatings
  XPS / ESCA image + small spot:
  distribution of surfactants in latex films

- Sized paper
  XPS, ToF-SIMS:
  surface amount of sizing agent

- Barrier dispersion coated board
  XPS, SEM-EDX: composition in pinholes

Ref: Marie Ernstsson, SP
# Toolbox for Advanced Surface Analyses

## Surface sensitivity:

<table>
<thead>
<tr>
<th>Method</th>
<th>Sensitivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>XPS / ESCA</td>
<td>2-10 nm</td>
</tr>
<tr>
<td>X-ray Photoelectron Spectroscopy / Electron Spectroscopy for Chemical Analysis</td>
<td></td>
</tr>
<tr>
<td>ToF-SIMS</td>
<td>1-2 nm</td>
</tr>
<tr>
<td>Time-of-Flight Secondary Ion Mass Spectroscopy</td>
<td></td>
</tr>
<tr>
<td>FT-IR</td>
<td>0.5-5 ( \mu )m (ATR)</td>
</tr>
<tr>
<td>Fourier Transform Infrared Spectroscopy</td>
<td></td>
</tr>
<tr>
<td>Raman Spectroscopy</td>
<td>0.5 ( \mu )m</td>
</tr>
<tr>
<td>Confocal Raman – <em>depth sectioning with vertical resolution about</em> 0.5 ( \mu )m</td>
<td></td>
</tr>
<tr>
<td>ESEM - EDX</td>
<td>0.5-5 ( \mu )m</td>
</tr>
<tr>
<td>Environmental Scanning Electron Microscopy</td>
<td></td>
</tr>
<tr>
<td>Energy Dispersive X-ray detector</td>
<td></td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
</tr>
</tbody>
</table>

*For more details see Toolbox for Surface Analysis*

Ref: Marie Ernstsson, SP
Surface Analysis: Combine Methods

Some examples:

- Enrichment in surfaces: XPS (nm) + ESEM - EDX (µm)
- Detailed chemical info, e.g. functional groups: XPS (nm) + ToF-SIMS (nm), FT-IR (µm - nm), Confocal Raman Spectroscopy (µm)
- Structures, Topography: AFM, (E)SEM, Profilometry

Ref: Marie Ernåstsson, SP
Combination of surface analysis techniques

Micro scale:
Surface characterization of fibres, fines and vessel elements.

Surface chemistry and structure
large or small areas – fibres, fines & vessel elements

**(E)SEM:**
Surface structure.

**XPS:**
Chemical composition at top surface (nm) - over large areas or small area analysis.

Ref: Marie Ernstsson, SP
Surface sensitive technique(s) - some criteria for selection:

- **Surface sensitivity** – information from nanometer or micrometer level?
- **Chemical information** – elemental, functional groups, etc., what is required?
- **Quantification** – quantification in atomic %, semi quantitative or qualitative?
- **Lateral resolution in images / maps** – detection of small features, spots?
- **Topographical / Surface structure/ Other information** required?

Ref: M. Ernstsson and T. Wärnheim

“Surface Analytical Techniques Applied to Cleaning Processes”
in Handbook for Cleaning/Decontamination of Surfaces
## Toolbox for Advanced Surface Analyses

Comparison of some techniques that provide elemental and chemical information

Ref: M. Ernstsson and T. Wärnheim
“Surface Analytical Techniques Applied to Cleaning Processes”
in Handbook for Cleaning/Decontamination of Surfaces

<table>
<thead>
<tr>
<th>Parameter</th>
<th>XPS/ESCA</th>
<th>ToF-SIMS</th>
<th>Raman</th>
<th>FT-IR - ATR*</th>
<th>EDX (from SEM or ESEM analysis)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Analysis depth</td>
<td>2-10 nm (static SIMS)</td>
<td>1-2 nm</td>
<td>0.5 µm</td>
<td>0.5-5 µm</td>
<td>0.5-5 µm</td>
</tr>
<tr>
<td>Chemical information</td>
<td>Elemental, functional groups, oxidation state</td>
<td>Elemental, molecular, functional groups, isotopical</td>
<td>Molecular, functional groups, crystallinity</td>
<td>Molecular, functional groups</td>
<td>Elemental</td>
</tr>
<tr>
<td>Quantification</td>
<td>Good</td>
<td>Semi</td>
<td>Semi</td>
<td>Semi</td>
<td>Semi</td>
</tr>
<tr>
<td>Detection limit</td>
<td>0.1 atomic %</td>
<td>ppm-ppb</td>
<td>1 %</td>
<td>1 %</td>
<td>0.1-0.5 wt %</td>
</tr>
<tr>
<td>Lateral resolution (in imaging/mapping)</td>
<td>&lt; 3 µm</td>
<td>0.2 µm</td>
<td>0.3 µm</td>
<td>1-2 µm</td>
<td>0.5 µm</td>
</tr>
<tr>
<td>Pressure</td>
<td>UHV*</td>
<td>UHV*</td>
<td>atm</td>
<td>atm</td>
<td>atm** (ESEM) HV (SEM)</td>
</tr>
<tr>
<td>Incident radiation</td>
<td>X-rays</td>
<td>Ions</td>
<td>Photons</td>
<td>Photons</td>
<td>Electrons</td>
</tr>
<tr>
<td>Analysed emission</td>
<td>Electrons</td>
<td>Ions</td>
<td>Photons</td>
<td>Photons</td>
<td>X-rays</td>
</tr>
</tbody>
</table>

*ATR = attenuated total reflection; IRAS = infrared reflection-absorption spectroscopy; UHV = ultrahigh vacuum
** Atmospheric pressure with respect to water vapour

**Confocal Raman** – depth sectioning with vertical resolution about 0.5 µm
**AFM** – topography, viscoelastic properties, force mapping (adhesion, stiffness, etc.)
**Infrared and Raman spectroscopy**

Both methods give molecular vibration information

**IR:**
- Light absorption
- IR molecular vibrations due to photon absorption are detected
- Polar molecules: e.g. C=O, C-O, N-H

**Raman:**
- Laser light scattering
- Photons frequency shifts due to scattering are detected, with the shifts corresponding to different molecular vibration
- Non-polar molecules: e.g. C-C, S-S

*Raman is not sensitive to water*

Ref: Marie Ernstsson, SP
FT-IR:

1. Transmission
2. ATR
3. RAS

Ref: Marie Ernstsson, SP
Trans FT-IR:
magnesium hydroxide + dodecanoic acid

Wavenumbers (cm$^{-1}$)

COO$^-$ Mg$^{++}$

- COOH

C-H

2931.6
2967.3
2860.3
1712.4
1577.0
1477.1

Ref: Marie Ernstsson, SP
FT-IR: Attenuated Total Reflectance (ATR) to increase surface sensitivity

Sampling depth: depends on crystal material: µm range
diamond, ZnSe, Ge

Ref: Marie Ernštsson, SP
Pigment coated paper and board

Why coating?
to improve optical and printing properties

Components in pigment coating colour:

- Mineral pigments
  - clay
  - calcium carbonate
- Binder
  - SB-latex
  - acrylate latex
- Dispersing agents, thickener, etc.

Ref: Marie Ernstsson, SP
FT-IR: Attenuated Total Reflectance (ATR) - to increase surface sensitivity

Sampling depth: μm range
crystal material: diamond, ZnSe > Ge

FT-IR spectra of coating components

Important with good contact between sample and crystal

Ref: Halttunen et al. at HUT, Tappi Coating Conference (2001)
FT-IR mapping: Scanning the surface with a diamond ATR crystal to determine surface latex content of different pigment coatings

Coating colour: calcium carbonate 100 ppw
SB-latex 12 or 15 ppw
CMC 1 ppw

Ref: Halttunen et al., proceedings Tappi Coating Conference (2001)
Confocal Raman Microscopy

Two pigment coated papers

Top map:
paper showing normal process behaviour

Lower map:
paper showing problem during production

Both pigment coating were expected to have the same composition.

In the lower paper sample two more components were detected, TiO2 and another, which explained the process problems.

Colour code:
SB-latex, CaCO3, TiO2, Stearate

Scale bar: 8 µm
Raman spectroscopy of Uncoated Copy paper
Distribution of starch – pigment - cellulose

yz-scan
xy-scan through the middle of the yz-scan

raw data

Starch
Cellulose
CaCO_3

evaluated

Parameters:
laser: 785 nm, 0.07 s/spectrum,
range:15x100 or 100x100 µm,
2 pixel/µm (40000 spectra)

Ref: Birgit Brandner, SP
Confocal Raman Microscopy

Depth profile
three-layer polymer film

Chemical image
Paper coating surface

PET
Glue
PP

CaCO₃  SB-latex

SP Technical Research Institute of Sweden
Chemical composition of surface layers

**XPS**
X-ray Photoelectron Spectroscopy

**ESCA**
Electron Spectroscopy for Chemical Analysis

X-ray  
\[ e^- \text{ out} \]

2-10 nm

Ref: Marie Ernstsson, SP
Irradiating a sample with a well defined x-ray energy results in emitted photoelectrons.

By analysing the kinetic energy of these photoelectrons, their binding energy can be calculated, thus giving their origin in relation to the element and the electron shell.

\[ h\nu = E_k + E_b + \phi \]

- \( h\nu \) = photon energy
- \( E_k \) = kinetic energy of photoelectron
- \( E_b \) = binding energy
- \( \phi \) = spectrometer work function

Ref: Marie Ernstsson, SP
Surface analysis with XPS / ESCA

• chemical composition of surface layers: 2-10 nm

• easy to quantify

• identification of all elements (except H and He) present at concentrations > 0.1 atom%

• information of chemical bonding, oxidation state, etc. from chemical shifts

• depth profiling - e.g. thickness of surface layers

• chemical distribution across surfaces:
  – imaging: < 3 µm lateral resolution
  – small spot spectroscopy (15, 27, 55, 110 µm selected area)

Ref: Marie Ernstsson, SP
XPS - Wide and Detail Spectra for Element Identification and Quantification

Example:
Pigment-coated paper - surface composition in atomic %:

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>45.7</td>
</tr>
<tr>
<td>O</td>
<td>38.8</td>
</tr>
<tr>
<td>Ca</td>
<td>2.1</td>
</tr>
<tr>
<td>Si</td>
<td>7.1</td>
</tr>
<tr>
<td>Al</td>
<td>6.3</td>
</tr>
</tbody>
</table>

Ref: Marie Ernstsson, SP
XPS - quantification

\[ 100\% = \frac{A_{O\ 1s}}{S_{O\ 1s}} + \frac{A_{C\ 1s}}{S_{C\ 1s}} + \ldots \]

\[ 100\% = \text{atom}\% \ O\ 1s + \text{atom}\% \ C\ 1s + \ldots \]

\[ \textbf{S} = \text{sensitivity factor} \]

value depends on:
- instrument  
  eg: x-ray flux, area analysed
- element (material)  
  eg: \( \lambda \) (inelastic mean free path)

relative values - often on a scale with \( S_{F\ 1s} = 1.00 \)

Ref: Marie Ernstsson, SP
**XPS: Water-borne Coatings - Distribution of Surfactants in Latex Films**

**XPS image and 27µm small spot analysis** of latex film cross-section (microtomed) - acrylate latex with anionic surfactant (S)

Latex film thickness about 300 µm

Enrichment of anionic surfactant at the air interface easy to detect by XPS small spot spectroscopy

<table>
<thead>
<tr>
<th>27 µm selected area – position number:</th>
<th>Relative surface composition (atomic %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>4</td>
<td>88.2</td>
</tr>
<tr>
<td>3</td>
<td>83.1</td>
</tr>
<tr>
<td>2</td>
<td>80.8</td>
</tr>
<tr>
<td>1</td>
<td>80.7</td>
</tr>
</tbody>
</table>

Ref: Marie Erntsson and Anders Larsson, SP
XPS- High resolution spectroscopy and Valence band data for "fingerprinting"

Valence band spectra for fingerprinting of organic components which are hard to separate using normal XPS spectra, e.g. certain polymers, latex systems, etc.

Relevant to projects where polymers, coatings, biomaterials, etc. are used.

Different valence spectra – even if similar surface chemical composition:
- PE, PP and PS
- also other polymeric samples, e.g. PET and PMMA

Ref: Marie Ernstsson, SP
**XPS** - High-resolution spectra for Functional Group Identification and Quantification

**Example: PET** poly(ethylene terephthalate)

Surface composition in atomic % from high-resolution carbon spectrum

- C-C, C=C, C-H 60 % of C$_{\text{tot}}$
- C-O, C-O-C 20 % of C$_{\text{tot}}$
- O-C=O 20 % of C$_{\text{tot}}$

High resolution carbon spectra – useful for materials such as paper, coatings, polymers, etc.

Ref: Marie Ernstsson, SP
Shake-up lines in XPS spectra

- from ions left in an excited state a few eV above the ground state (aromatic: \( \pi \) to \( \pi^* \))
- the \( E_k \) of the emitted electrons is reduced with the difference corresponding to the energy difference between ground and excited state

Shake-up peak detected at higher \( E_b \)

Shake-up lines can be useful in identifying the chemical state of an element

For PET: Shake up from aromatic ring

Ref: Marie Ernstsson, SP
Monochromatic x-ray source instead of traditional x-ray source

- Better energy resolution – high resolution spectra, such as the C 1s spectrum for PET

- Less damage to sensitive samples – such as pharmaceutical and food powders, polymers, papers, biomaterials, etc.

Ref: Marie Ernstsson, SP
Schematic diagram
XPS / ESCA spectrometer

XPS / ESCA – Surface chemical composition for the top 2-10 nm of surfaces

XPS at SP Chemistry, Materials and Surfaces

Ref: Marie Ernstsson, SP
XPS wide spectrum of Paper Pulp

Unbleached Kraft Pulp

Binding energy (eV)

Intensity

Intensity / Counts * 1000

11
10
9
8
7
6
5
4
3
2
1

1300 1200 1100 1000 900 800 700 600 500 400 300 200 100

Binding energy (eV)

C KLL  O KLL  C 1s  O 1s

Ref: Marie Ernstsson, SP
**XPS high-resolution carbon spectra for spruce kraft pulp fibres - before and after extraction**

- **C1**: C-C, C=C or C-H
  - Unoxidised carbon
- **C2**: C-O or C-O-C
  - C with one bond to O
- **C3**: C=O or O-C-O
  - C with two bonds to O
- **C4**: O-C=O or C(=O)OH
  - C with three bonds to O

*Ref: Marie Ernstsson, SP*
## XPS - Components in Wood Pulp Fibres

<table>
<thead>
<tr>
<th>Sample</th>
<th>Atomic ratio</th>
<th>C 1s = 100 %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O / C</td>
<td>C1</td>
</tr>
<tr>
<td><strong>Theoretical values:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cellulose</td>
<td>0.83</td>
<td>-</td>
</tr>
<tr>
<td>Lignin</td>
<td>0.33</td>
<td>49</td>
</tr>
<tr>
<td>Oleic acid</td>
<td>0.11</td>
<td>94</td>
</tr>
<tr>
<td><strong>Example of measured values:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Extracted Bleached Kraft pulp</td>
<td>0.81</td>
<td>5</td>
</tr>
</tbody>
</table>

Ref: Marie Ernstsson, SP
Model of wood pulp fibre surface:
- extracted
- unextracted

Assumption thickness of patches > depth of analysis (ca 10 nm)

Surface Coverage of Lignin from XPS data - for extracted samples:

\[
\phi_{\text{lignin}} = \frac{O/C_{\text{afterextraction}} - O/C_{\text{carbohydrates}}}{O/C_{\text{lignin}} - O/C_{\text{carbohydrates}}}
\]

\[
\phi_{\text{lignin}} = \frac{C_1_{\text{afterextraction}} - a}{49}
\]

\[
\phi_{\text{softwoodlignin}} = \frac{\text{atom\% Hg}}{5.48}
\]

Comparison of different XPS quantification methods for Fiber Surface Analysis

Co-operation between Chalmers, Eka Chemicals, Södra Cell and YKI

Softwood kraft pulp: unbleached, O₂-delignified, TCF bleached
Thermo mechanical pulp: unbleached, H₂O₂ bleached
Wheat straw: unbleached

Three XPS quantification methods were used and compared in order to quantify the surface coverage of lignin and extractable material on the different pulp fibers.

Also studied were for example the methods’ sensitivity to fiber preparation, i.e. drying technique (air-dried or freeze-dried).

Ref: A. Heijnesson Hultén, J. Basta, P. Larsson, M. Ernstrsson; Holzforschung 60, 14-19 (2006)
Surface coverage of Lignin (XPS) vs Total Lignin content

Softwood kraft pulp, TMP and wheat-straw fibers:

Surface coverage of lignin was calculated from XPS data using three different methods

Ref: A. Heijnesson Hultén, J. Basta, P. Larsson, M. Ernstsson; Holzforschung, 60, 14-19 (2006)
XPS - Chemical State Imaging of Single Fibres

Wood pulp fibres
Image:
- unbleached (left)
- bleached (right)

Carbon spectra:
- unbleached (green)
- bleached (red)

In XPS image:
- green: C-C, C=C, C-H
- red: C-O, C-O-C

XPS imaging: elemental or chemical states (different functional groups), also for small particles, patches, etc. on a surface
XPS - Depth profiling

Ar ion sputtering: steel surface

destructive depth profiles - several 100 nm into sample

Angle resolved XPS: Si oxide on Si

non-destructive depth profiles - 10 nm into sample

from depth profiling it is possible to get thickness of surface layers

Ref: Marie Erntsson, SP
XPS wide spectra of a Steel surface

before Ar ion sputtering

after 9 min sputtering

Ref: Marie Ernstsson, SP
Angle Resolved XPS – AR-XPS:
Enhanced surface sensitivity

Probability of Electron Emission as a function of Depth

X-ray photons
penetrates to µm depths

Photoelectrons
from outermost 2-10 nm

θ = electron take-off angle

1λ

3λ

**XPS - Exponential Decay of Electron signal as a function of Depth**

1\(\lambda\) = electron inelastic mean free path, escape depth
*depth from which 63% of total signal arises*

3\(\lambda\) = sampling depth, depth of analysis
*depth from which 95% of total signal arises*

The emission of photoelectrons from element in substrate \((I_s)\) or overlayer \((I_o)\) as a function of depth \((d)\) is predicted by:

\[
I_s = I_\infty \exp\left(-\frac{d}{\lambda \sin \theta}\right)
\]

\[
I_o = I_\infty \left[1 - \exp\left(-\frac{d}{\lambda \sin \theta}\right)\right]
\]

Ref: Marie Ernstsson, SP
IMFP – Inelastic Mean Free Path

The average distance (in nanometer) that an electron with a given energy travels between successive inelastic collisions.

Value of IMFP (=1λ) can be estimated from different equations - often with: \( \lambda \propto \frac{E_{\text{kin}}}{\text{density}} \)

Depth of analysis, sampling depth 3\( \lambda \) is:
- about 10 nm for polymers and paper
- lower for metal oxides and metals

Ref: Marie Ernestsson, SP
Angle Resolved XPS – AR-XPS:
thickness of a thin overlayer on a flat substrate

flat surface (e.g. mica, silicon wafer) is essential

\[ I_s = I_\infty \exp\left(-\frac{d}{\lambda \sin \theta}\right) \]

In \( I(\theta) \) for substrate element plotted against \( -1 / \sin \theta \)
slope of resulting line equals the reduced thickness \( \frac{d}{\lambda} \)

if know \( \lambda \): possible to estimate layer thickness \( d \)

Ref: Marie Ernstsson, SP
Surface chemical composition of Pilot Coated Paper - XPS

Same formulation of coating colour but different latex binders:

70 parts CaCO3
30 parts clay
17 parts latex \[\rightarrow\] bulk composition 15 wt%

+ polyvinylalcohol, hardener, optical whitening agent

Surface chemical composition (XPS) of pigment coated paper - 2 models:

- CaCO₃
- Latex
- Clay

Surface concentration (atomic %)

Take off angle, $\alpha$ [°]

- Ca
- Si
- C
Effect of Sampling Depth on the Surface Composition from XPS analysis of Pilot Coated Paper

Conclusion:
Model with no thin carbon overlayer can be used

Possible to estimate paper surface composition in terms of $\text{CaCO}_3$, clay and latex
**XPS: Paper Surface Composition**

Assume only pigments and latex in surface layer:

\[
100\% = \text{area}\% \text{ CaCO}_3 + \text{area}\% \text{ clay} + \text{area}\% \text{ latex}
\]

Area\% of CaCO\(_3\) = \(\frac{\text{Ca in paper (atom\%)} \times 100}{\text{Ca in CaCO}_3 (\text{atom\%})}\)

Area\% of clay = \(\frac{\text{Si + Al in paper (atom\%)} \times 100}{\text{Si + Al in clay (atom\%)}}\)

**XPS: Surface Chemical Composition for Pilot Coated Papers**

Latex:
- bulk 15 wt%
- surface 43-53 area%

Pigment coated paper and board

Why coating?
to improve optical and printing properties

Components in pigment coating colour:

- Mineral pigments
  - clay
  - calcium carbonate
- Binder
  - SB-latex
  - acrylate latex
- Dispersing agents, thickener, etc.

Ref: Marie Ernstsson, SP
XPS high-resolution carbon spectra for spruce kraft pulp fibres - before and after extraction

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  - unoxidised carbon

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  - C with one bond to O

- **C3**: C=O or O-C-O
  - C with two bonds to O

- **C4**: O-C=O or C(=O)OH
  - C with three bonds to O

Ref: Marie Erntsson, SP
## XPS - Analysis of organic components

<table>
<thead>
<tr>
<th>Component</th>
<th>C1 [%]</th>
<th>C2 [%]</th>
<th>C3 [%]</th>
<th>C4 [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>styrene</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>butadiene</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>vinyl acetate</td>
<td>50</td>
<td>25</td>
<td>0</td>
<td>25</td>
</tr>
<tr>
<td>acrylic acid</td>
<td>66.7</td>
<td>0</td>
<td>0</td>
<td>33.3</td>
</tr>
<tr>
<td>carboxymethyl cellulose</td>
<td>0</td>
<td>75</td>
<td>12.5</td>
<td>12.5</td>
</tr>
<tr>
<td>polyvinyl alcohol</td>
<td>50</td>
<td>50</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>cellulose</td>
<td>0</td>
<td>83</td>
<td>17</td>
<td>0</td>
</tr>
</tbody>
</table>

Increase in organic carbon (latex) is observed with increasing GCC particle size.

**XPS- High resolution spectroscopy and Valence band data for “fingerprinting”**

Valence band spectra for *fingerprinting of organic* components which are hard to separate using normal XPS spectra, e.g. *certain polymers, latex systems*, etc.

Relevant to projects where polymers, coatings, biomaterials, etc. are used.

Different valence spectra – even if similar surface chemical composition:

- PE, PP and PS
- also other polymeric samples, e.g. PET and PMMA

---

**Ref:** Marie Ernstsson, SP
X-ray Photoelectron Spectroscopy / Electron Spectroscopy for Chemical Analysis

Surface chemical composition in atomic% at top nanometer level - outermost 2-10 nm of surfaces

Examples: Paper & Packaging Coatings Paint

Adhesion / Delamination problems Where is the locus of failure?

Adhesional or cohesive failure determined by XPS analysis of failure surfaces

Ref: Marie Ernstrsson, SP
AFM Force Mapping – XPS data
Pigment-coated paper - with kaolin clay pigment

<table>
<thead>
<tr>
<th>XPS data:</th>
<th>Surface Chemical composition in atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>O</td>
</tr>
<tr>
<td>44.1</td>
<td>39.9</td>
</tr>
</tbody>
</table>

AFM images 2 x 2 micrometer

Topography

Adhesion force

Ref: Marie Ernstrsson and Viveca Wallqvist, SP
More detailed chemical info of surface layers

ToF-SIMS

Time-of-Flight Secondary Ion Mass Spectrometry

ions in

ions out

1-2 nm

Ref: Marie Ernstsson, SP
ToF-SIMS principle

Primary ion

Secondary ions and neutrons

Upper most monolayer

Substrate
XPS / ESCA

- chemical composition of surface layers: 2-10 nm
- easy to quantify, composition expressed in atomic %
- identification and quantification of elements and different chemical states - functional groups, oxidation state - from chemical shifts
- chemical distribution across surfaces:
  - imaging: < 3 µm lateral resolution
  - small spot spectroscopy: 15, 27, 55, 110 µm selected area

ToF-SIMS

- chemical information of surface layers: 1-2 nm
- not straightforward to quantify
- detailed chemical information:
  - functional groups
  - molecular fragments (oligomers, monomers)
- chemical distribution across surfaces - imaging: 0.2 µm lateral resolution
ToF-SIMS positive mass spectra for Paper and Starch

Peak at 58 m/z from cationized end group of starch (C$_3$H$_8$N)

Cationic starch on paper surfaces detected by ToF-SIMS:
Often very low amounts of N in cationic starch - if below the noise level for XPS (0.1 atomic %) – then it may be possible to detect specific end groups by ToF-SIMS

Ref: Marie Ernstsson, SP
Surface analysis of natural fibres using ToF-SIMS, XPS / ESCA and AFM

Co-operation between Innventia, YKI and SP

Characterisation of wood fibre surfaces: chemical and morphological properties

Spruce kraft pulp fibres with high (85) and low (20) kappa number

XPS and ToF-SIMS:
Chemical composition of fibre surfaces + distribution of extractable materials (before + after extraction, different solvents)

Ref: S. Svanberg, M. Lindström, Innventia; M. Ernstsson R. Seppänen, YKI; J. Lausmaa, SP; Report
XPS carbon spectra for pulp fibres (kappa 20)

Unoxidised carbon (C-C, C=C) is reduced by extraction

From pyrolysis GC / MS: the acetone extracts contain fatty acids, fatty alcohols and sterols

Ref: S.Svanberg, M.Lindström, Innventia; M. Ernstsson R.Seppänen, YKI; J.Lausmaa, SP; Report
ToF-SIMS positive mass spectra for unextracted pulp fibres (kappa 20)

Identification of extractive components such as sterols at 383, 397, 411, 415, 429

Ref: S.Svanberg, M.Lindström, Innventia; M. Ernstsson R.Seppänen, YKI; J.Lausmaa, SP; Report
ToF-SIMS positive ion images for unextracted pulp fibres (kappa 20)

500 x 500 µm

The total ion image shows the fibre structure

Image at 397 amu shows an even distribution of sterols on the fibre surface

**XPS and ToF-SIMS:**
Clear differences before and after acetone extraction.
Sterols, distributed even over surface, identified before extraction.

Ref: S.Svanberg, M.Lindström, Innventia; M. Ernstsson R.Seppänen, YKI; J.Lausmaa, SP; Report
AFM height image of spruce kraft pulp fibres

Kappa number 85:
granular surface structure, bundles of microfibrils

Kappa number 20:
no granules, separate microfibrils

Ref: M. Ernstsson R. Seppänen, YKI; S. Svanberg, M. Lindström, STFI; J. Lausmaa, SP; Report
Why are paper and paper board hydrophobized (sized)?

To control wettability of paper and board by aqueous liquids

Wettability by paper and board affects, e.g. Inkjet printing

High liquid resistance is needed in Packaging materials

Sizing agent AKD - alkyl ketene dimer:

$$R-\text{CH}=\text{C-CH-R'}$$

$$\text{O-C=O}$$

R and R’: often C14-, C16- or/and C18-hydrocarbon chains
Hydrophobizing (sizing) of paper and board

**XPS analysis AKD or ASA sized papers**

C1: C-C, C-H or C=C unoxidised carbon - *sizing agents AKD or ASA*

C2: C-O or C-O-C carbon with one bond to oxygen

C3: C=O or O-C-O carbon with two bonds to oxygen

C4: O-C=O carbon with three bonds to oxygen
XPS analysis of AKD sized papers

Information of surface coverage

Good estimate of Surface coverage, area-%

C1 (sized)-C1 (unsized)

Added AKD, wt. -%

ToF-SIMS ion images for PCC-filled paper: Signals for unreacted AKD wax (533,5) and hydrolysed AKD (ketone form, 507,5)

XPS - stitched images and small spot analysis

Distribution of different chemical components across the surface
Paper & Packaging – Coatings – Pharmaceutical - etc.

Hydrophobic sizing agent (AKD) covers most of the paper
(middle - right) - clean paper towards left end.
XPS stitched image covers a total area of 8 x 0.8 mm.

C-C, C-H signal: high intensity = mainly AKD (hydrocarbon chains)

O 1s signal: high intensity = mainly filter paper

Right end of paper dipped in 1% AKD in heptane.
Wetting front at about 5.6 mm after a few sec.

10 stitched XPS images:
10 x 800 x 800 micrometer

Ref: Marie Ernstsson, SP
**XPS / ESCA**

- chemical composition of surface layers: 2-10 nm
- easy to quantify, composition expressed in atomic%
- identification and quantification of elements and different chemical states - functional groups, oxidation state - from chemical shifts
- chemical distribution across surfaces:
  - imaging: < 3 µm lateral resolution
  - small spot spectroscopy (15, 27, 55, 110 µm selected area)

**ESEM - EDX**

- elements detected from surface layers: 0.5-5 µm
- quantification: at best semi-quantitative evaluation
- only elemental information
- elemental distribution - imaging: 0.5-5 µm lateral resolution

*Point analysis: very useful for contaminant identification*

*Ref: M. Ernstsson, SP*
Barrier dispersion coated board

**Applications:** e.g. food packaging industry

Co-operation between Karlstad University (Caisa Andersson, Lars Järnström) and YKI (Marie Ernstsson)

**Barrier coating:**
clay filler + styrene/butyl acrylate latex (surfactants)

Barrier coating 5-6g/m²
Pigment coating, 14g/m²
CaCO₃ + SB latex
Top layer 54 g/m²
60% pine
40% birch
Middle layer ca 100 g/m²
50% CTMP
50% broke
Bottom layer 30g/m²
100% pine
Starch+CMC

## XPS - surface composition

<table>
<thead>
<tr>
<th>Sample</th>
<th>Atom%</th>
<th>C</th>
<th>O</th>
<th>Ca</th>
<th>Si</th>
<th>Al</th>
<th>S</th>
<th>Na</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barrier coating 1</td>
<td></td>
<td>80</td>
<td>18</td>
<td>0.2</td>
<td>0.4</td>
<td>0.2</td>
<td>0.8</td>
<td>0.4</td>
<td>0.6</td>
</tr>
<tr>
<td>Pigment coating</td>
<td></td>
<td>69</td>
<td>25</td>
<td>6</td>
<td></td>
<td></td>
<td></td>
<td>0.4</td>
<td>0.2</td>
</tr>
</tbody>
</table>

*Weak Ca signal in barrier coating 1 - from ???

ESEM - EDX: Barrier coating 1

pinhole: Ca detected

no Ca

Ca from CaCO₃ in the pigment coating layer

Surface sensitive technique(s) - some criteria for selection:

- **Surface sensitivity** – information from nanometer or micrometer level?

- **Chemical information** – elemental, functional groups, etc., what is required?

- **Quantification** – quantification in atomic %, semi quantitative or qualitative?

- **Lateral resolution in images / maps** – detection of small features, spots?

- **Topographical / Surface structure/ Other information** required?

Ref: M. Ernstsson and T. Wärnheim
“Surface Analytical Techniques Applied to Cleaning Processes”
in Handbook for Cleaning/Decontamination of Surfaces
## Toolbox for Advanced Surface Analyses
Comparison of some techniques that provide elemental and chemical information

<table>
<thead>
<tr>
<th>Parameter</th>
<th>XPS/ESCA</th>
<th>ToF-SIMS</th>
<th>Raman</th>
<th>FT-IR - ATR* (IRAS*)</th>
<th>EDX (from SEM or ESEM analysis)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Analysis depth</td>
<td>2-10 nm (static SIMS)</td>
<td>1-2 nm</td>
<td>0.5 µm</td>
<td>0.5-5 µm (IRAS: nm)</td>
<td>0.5-5 µm</td>
</tr>
<tr>
<td>Chemical information</td>
<td>Elemental, functional</td>
<td>Elemental, molecular</td>
<td>Molecular, functional</td>
<td>Elemental</td>
<td></td>
</tr>
<tr>
<td></td>
<td>groups, oxidation state</td>
<td>groups, functional</td>
<td>groups, crystallinity</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Quantification</td>
<td>Good</td>
<td>Semi</td>
<td>Semi</td>
<td>Semi</td>
<td></td>
</tr>
<tr>
<td>Detection limit</td>
<td>0.1 atomic %</td>
<td>ppm-ppb</td>
<td>1 %</td>
<td>1 %</td>
<td>0.1-0.5 wt %</td>
</tr>
<tr>
<td>Lateral resolution (in imaging/mapping)</td>
<td>&lt; 3 µm</td>
<td>0.2 µm</td>
<td>0.3 µm</td>
<td>1-2 µm</td>
<td>0.5 µm</td>
</tr>
<tr>
<td>Pressure</td>
<td>UHV*</td>
<td>atm</td>
<td>atm</td>
<td>atm** (ESEM)</td>
<td>HV (SEM)</td>
</tr>
<tr>
<td>Incident radiation</td>
<td>X-rays</td>
<td>Ions</td>
<td>Photons</td>
<td>Photons</td>
<td>Electrons</td>
</tr>
<tr>
<td>Analysed emission</td>
<td>Electrons</td>
<td>Ions</td>
<td>Photons</td>
<td>Photons</td>
<td>X-rays</td>
</tr>
</tbody>
</table>

*ATR = attenuated total reflection; IRAS = infrared reflection-absorption spectroscopy; UHV = ultrahigh vacuum
** Atmospheric pressure with respect to water vapour

### Confocal Raman
- depth sectioning with vertical resolution about 0.5 µm

### AFM
- topography, viscoelastic properties, force mapping (adhesion, stiffness, etc.)

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Ref: M. Ernstsson and T. Wärnheim
“Surface Analytical Techniques Applied to Cleaning Processes”
in Handbook for Cleaning/Decontamination of Surfaces
Surface Analysis: Combine Methods

Some examples:

Enrichment in surfaces
XPS (nm) + ESEM - EDX (µm)

Detailed chemical info
e.g. functional groups
XPS (nm) + ToF-SIMS (nm)
FT-IR (µm - nm)
Confocal Raman Spectroscopy (µm)

Structures, Topography
AFM, (E)SEM, Profilometry

Ref: Marie Ernstsson, SP