Aalto University

CHEM-E5140
Materials Characterization Laboratory

XPS Lecture

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Course content

Material Characterization techniques

Laboratory practice

What can I analyse?

Analysis of data

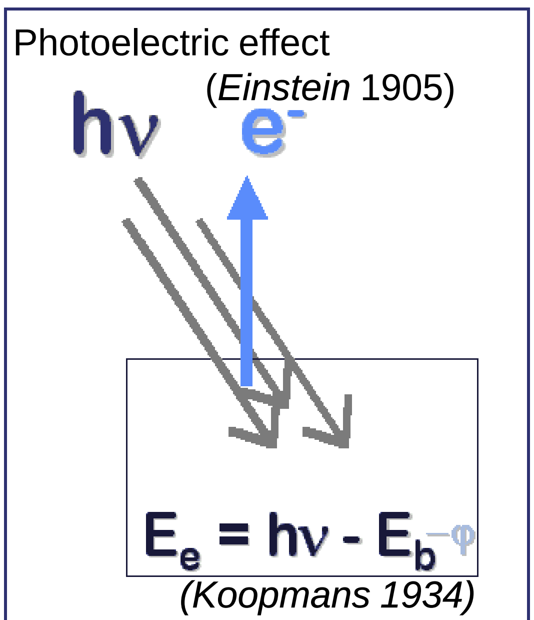
How to get the information needed?

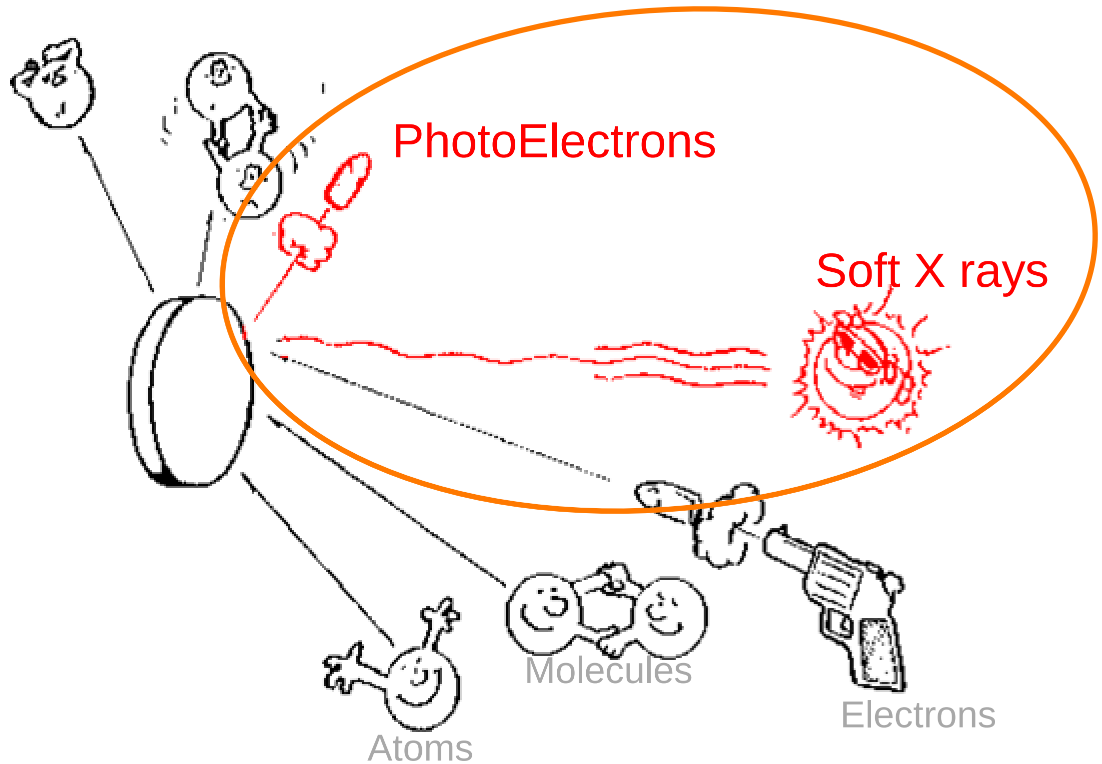
XPS

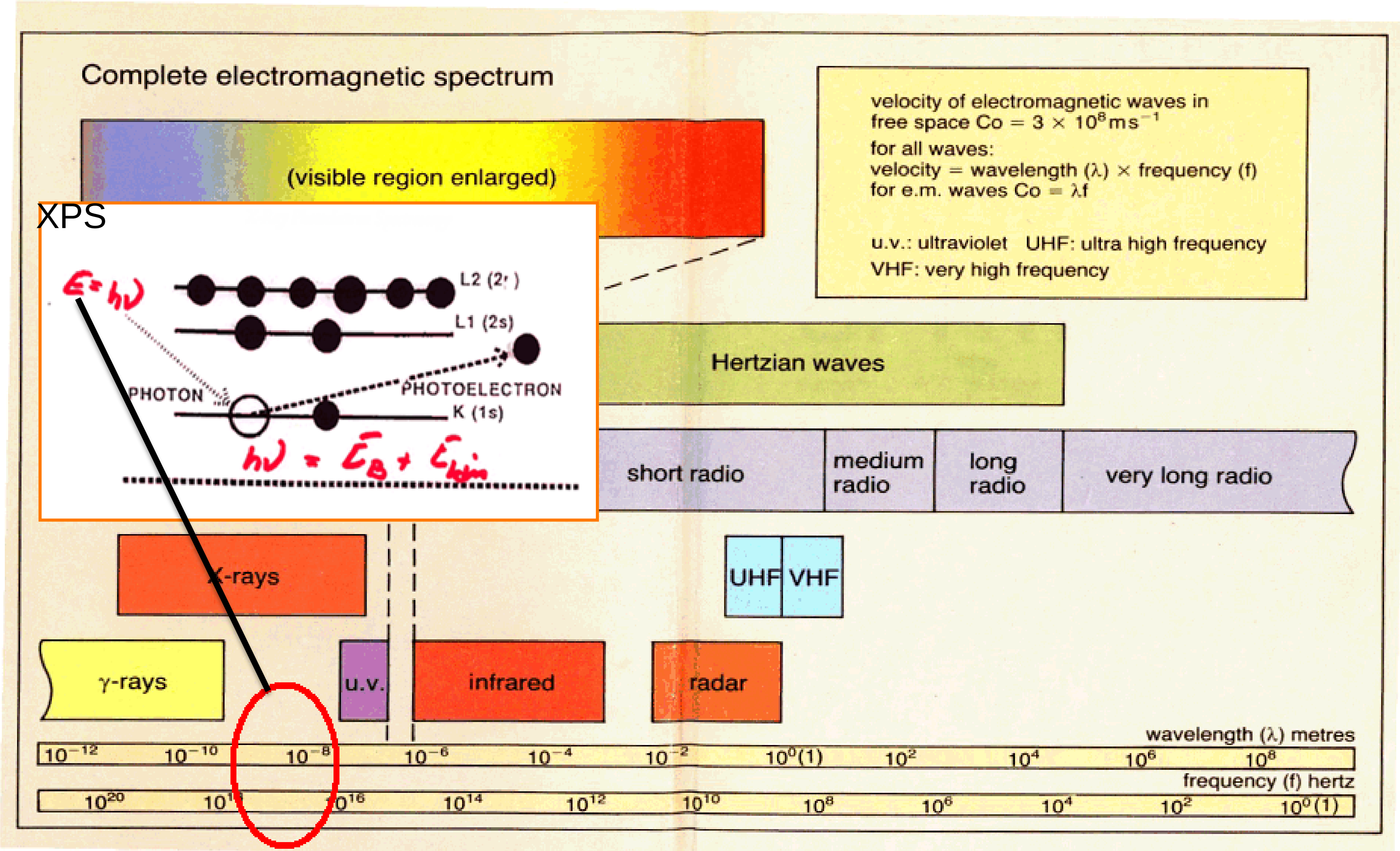
Material Characterization
techniques

XPS (X-ray Photoelectron Spectroscopy) … or

ESCA (Electron Spectroscopy for Chemical Analysis)







* In photoelectric effect, X-ray waves 1...100 nm ≅ 10..1500 eV, which matches binding energy of core orbitals.

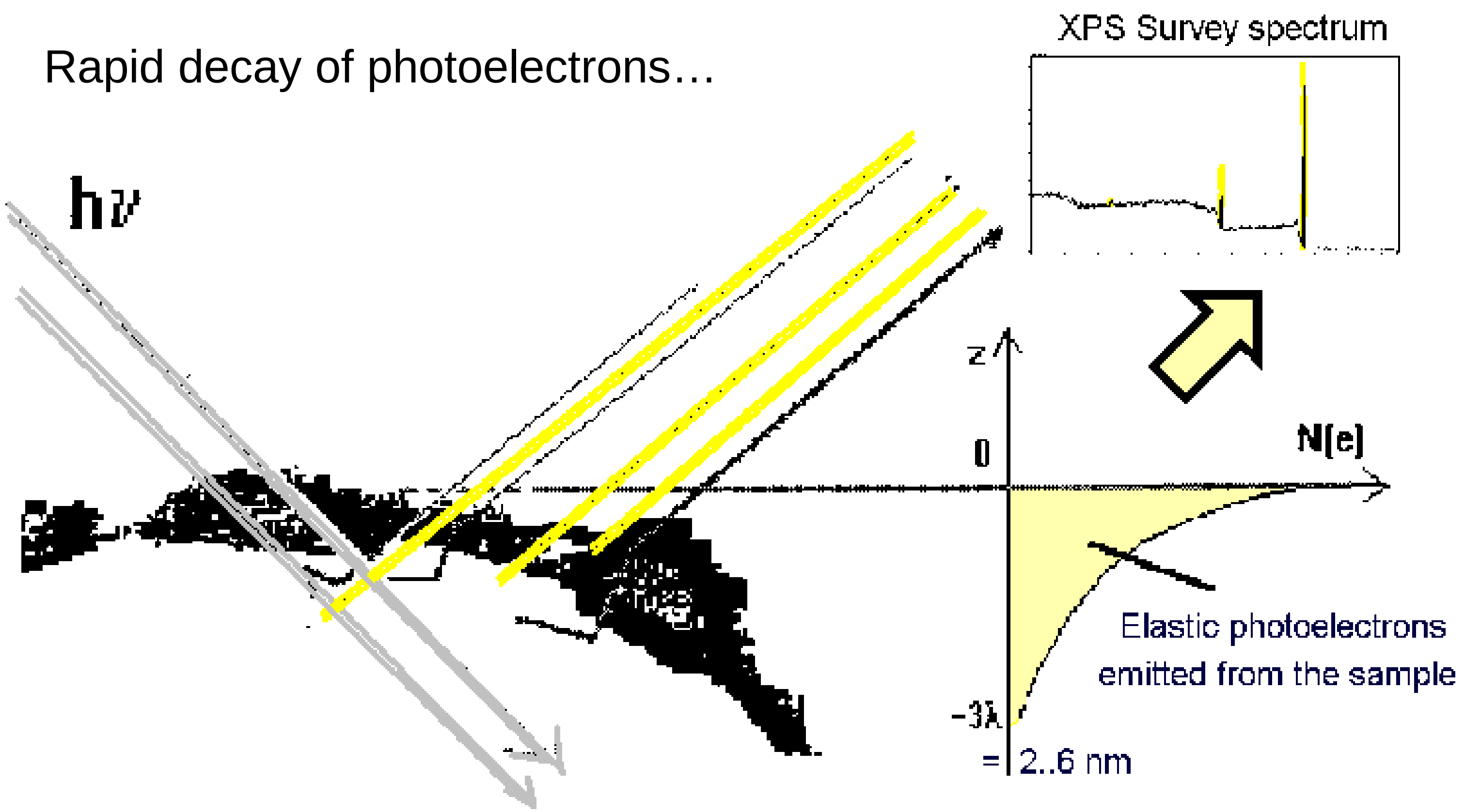
Cambridge illustrated thesaurus of physics, by Teresa Ricards, Cabridge Univ. Press 1984

XPS

How to obtain the information needed?

XPS is a surface technique

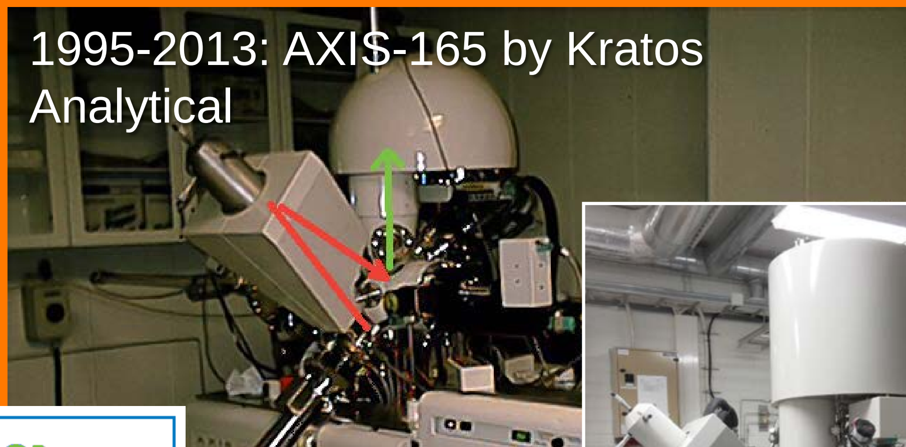
Rapid decay of photoelectrons…

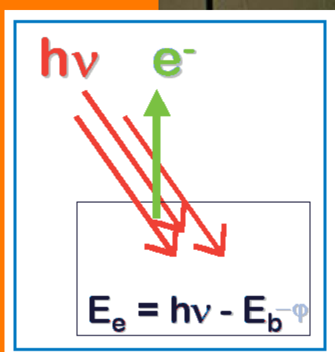


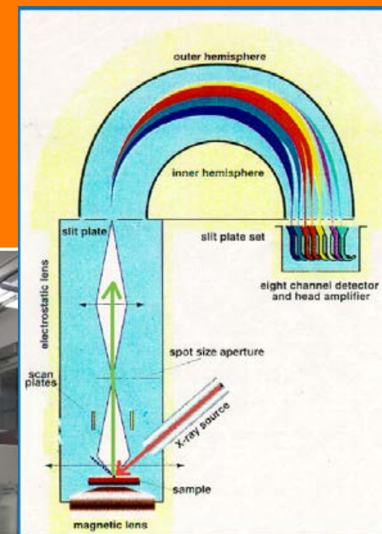
… makes the method very surface sensitive

… **but electron flux is so soft, that it is stopped effectively even in air.**
→ Kaj Siegbahn and <u>advances in Ultra High Vacuum tehcnology</u> (UHV) turned X-ray photoelectric effect into a surface analysis tool in 1960's, 50y after Einstein.

Aalto PUU: XPS tailored for soft materials







Note: All XPS experiments are done in Ultra High Vacuum!

XPS

What can I analyse?

XPS (ESCA) in applied surface analysis as a state-of-art technique, also for soft materials

Quantification of elements at the surface of materials

+ Analysis depth **less than 10 nm**

+ **Detection of all elements** but hydrogen

+ Chemical identification

+ Surface distributions in the first 10 nm (such as film vs islands?)

+ Allows insulating, conducting or heterogeneous samples, including **composites** and **organic,** even **biological** specimens

+ Easy sample preparation

+ Non-destructive (no particles, only very soft X-rays)

XPS in Aalto1995 - 2019
The database with more than 10,000 samples analysed in tailored, *in-situ* referenced experiments

AXIS 165 / AXIS Ultra^{DLD} at Aalto Chemical Technology 1995-2019

Cellulosic materials (ca 50 % of samples):

- Pulps surface analysis & process evaluations
- Paper coatings, contamination, fundamentals
- Model surfaces mono/multicomponent films formation and reaction dynamics
- Nanofibrillated cellulose nanofibrils, whiskers & bacterial cellulose, fundamentals & applications
- Wood hydrothermal modification, adhesion
- Derivatisations TEMPO, click, CMC, silylation …
- Functional surfaces biointerfaces, biological surfaces, biomimetic materials
- Composites cellulose and derivatives, polymers, clay, lignin, chitosan, graphene, CNTs
- Textiles flax, cotton, MMC, synthetic fibres
- Carburised celluloses e.g. in catalysis

Materials other than celluloses (50 % samples):

- Ultra-thin inorganic and organic films ALD deposited, spincoated, LB films, CVD, plasma, graphenes, CNTs, DLCs
- Surface analysis of metals, alloys, oxides, composites, polymers, powders, fibres, deposits
- Contamination analyses in e.g. semiconductor devices, quality control

Are there limitations? Yes.

- XPS is only for outmost surfaces (0 .. 20 nanometers)

  - It will NOT tell you average sample composition

  - Surface contamination is a **big** issue

  - Samples must tolerate Ultra High Vacuum (10^{-9} Torr)

- Samples

  - Almost any solid sample can be analysed, if it tolerates ultra high vacuum. Even insulating powders and fibers are ok

- Sample preparation: As little as possible. **Why?**

  - Samples are secured on the holder with springs or with vacuum compatible tape and then evacuated.

XPS

Analysis of the data

XPS analysis

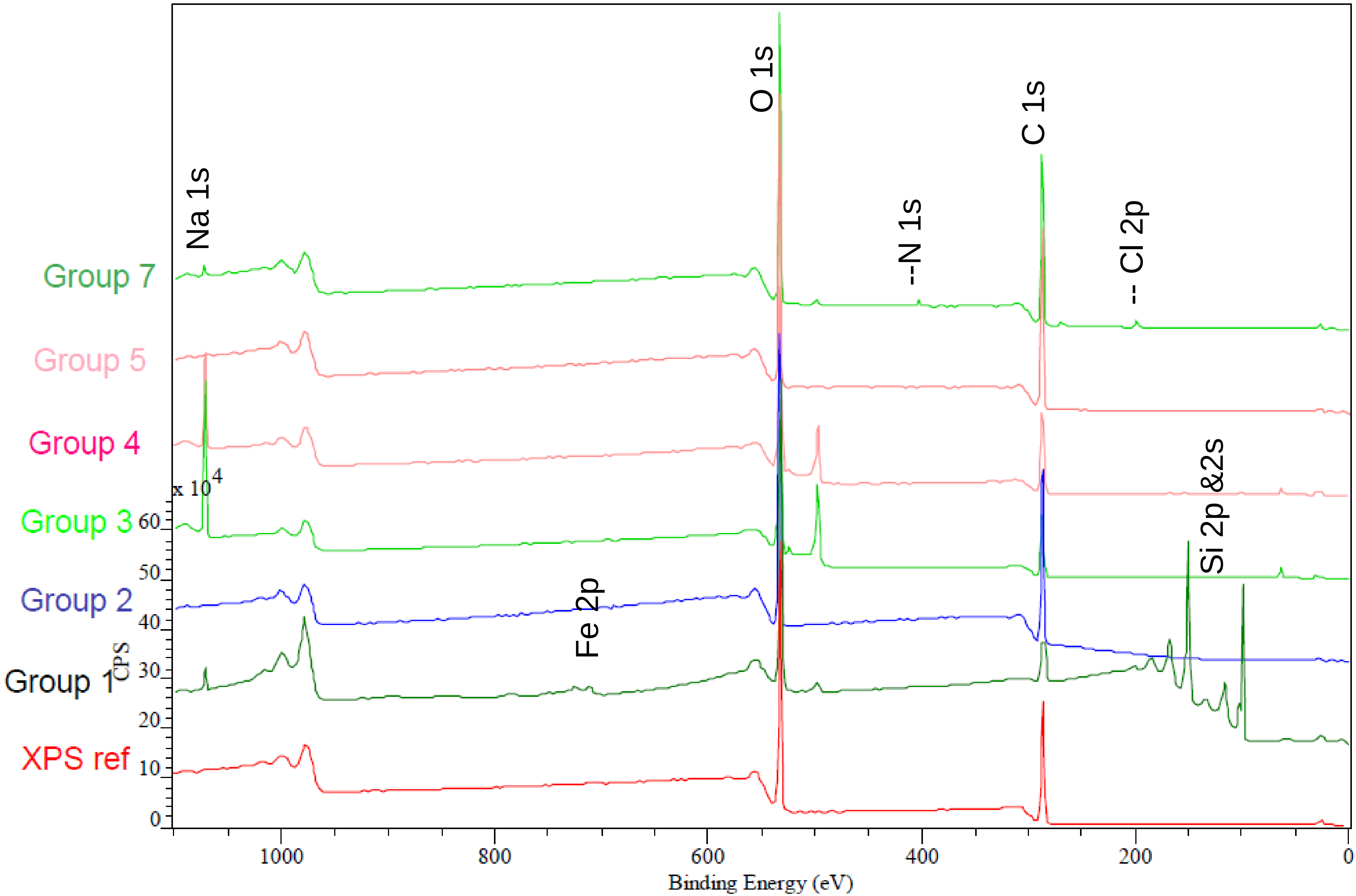
1. Elemental ID / quantification
wide scans (XPS sees all but hydrogen)

2. Chemical info / quantification
HighRes data (especially C 1s)

3. Depth distributions info
Surface modelling via Tougaard

XPS, elemental identification:

Case, student demo data, spring 2015: Celluloses and cellulose derivatives



XPS, elemental quantification

Instrument & element

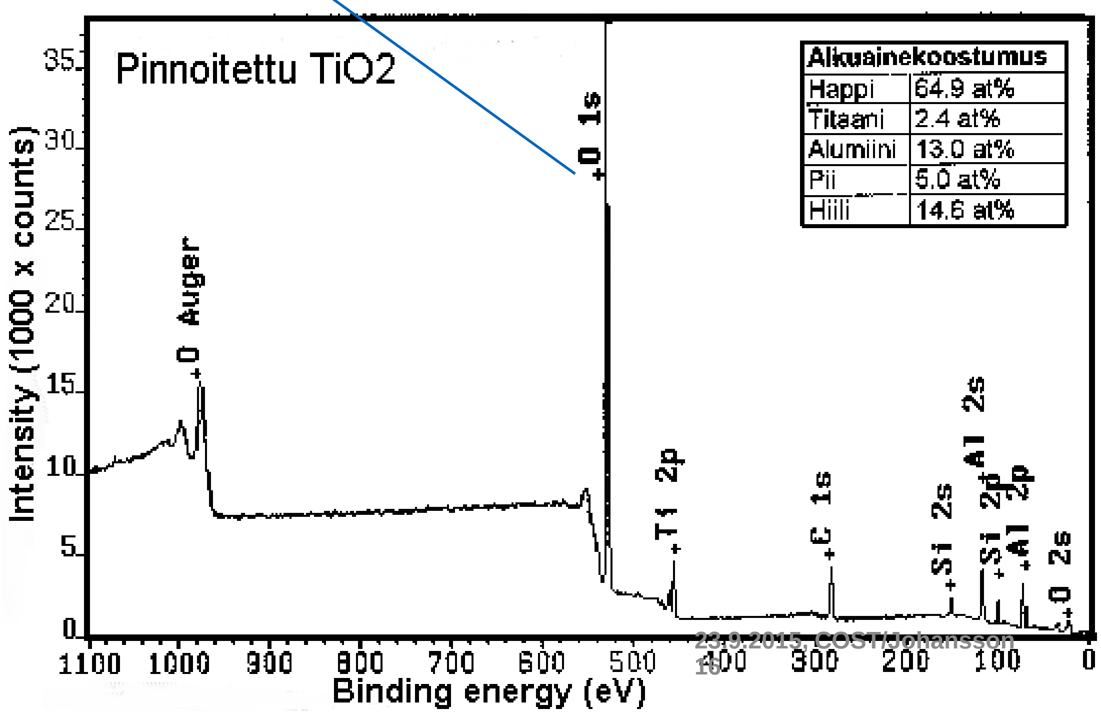
Distribution in sample

O 1s peak:

$$I_A^{nl}(E) = K\sigma_A^{nl}\, L_A \int_x n_A(x)\, e^{\frac{-x}{\lambda_M(E)\cos\theta}}\, dx$$

$= S_A X_A$ (for <u>homogeneous</u> samples)

$$x_a = \frac{I_a/S_A}{\Sigma I_i/S_i}\cdot 100\%$$



Alkuainekoostumus	
Happi	64.9 at%
Titaani	2.4 at%
Alumiini	13.0 at%
Pii	5.0 at%
Hiili	14.6 at%

Note: **In this formula the chosen intensities are summed to 100%, is typically used in XPS quantification.**
However it is correct only for homogeneous samples

1. Elemental ID / quantification
wide scans (XPS sees all but hydrogen)

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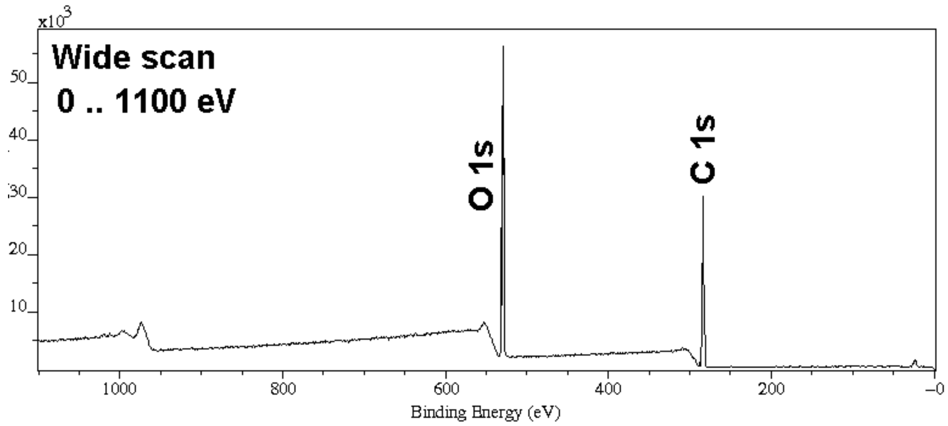
Carbon C 1s and the *cellulose signature*



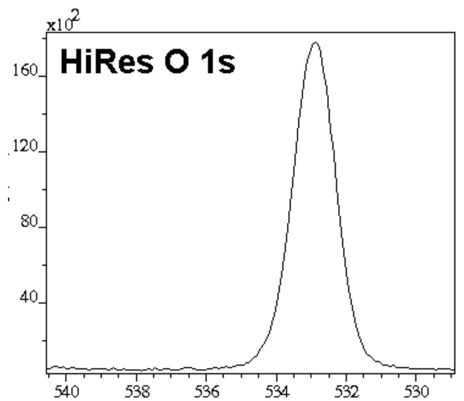
Cellulose molecule:

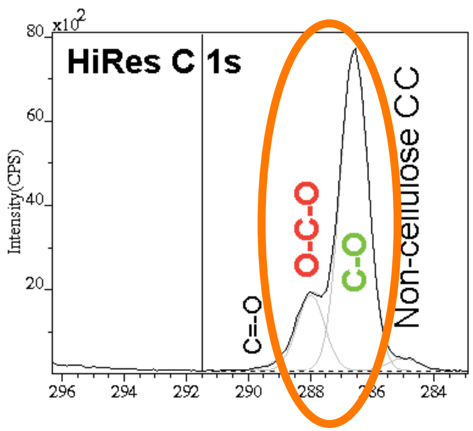
5 oxygen atoms

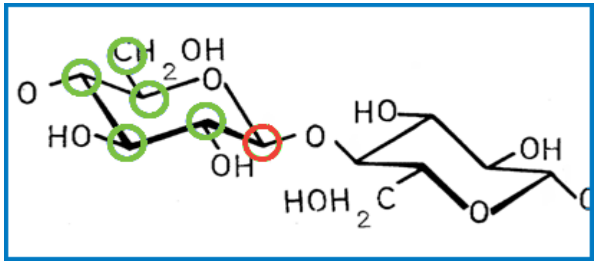
5 carbon atoms with one bond to oxygen neighbor

1 carbon atom with two bonds to oxygen neighbors

10 hydrogens (not seen XPS)







18

L.-S. Johansson: Monitoring fibre surfaces with XPS in papermaking processes. Microchimica Acta 138, pp 217-223 (2002)

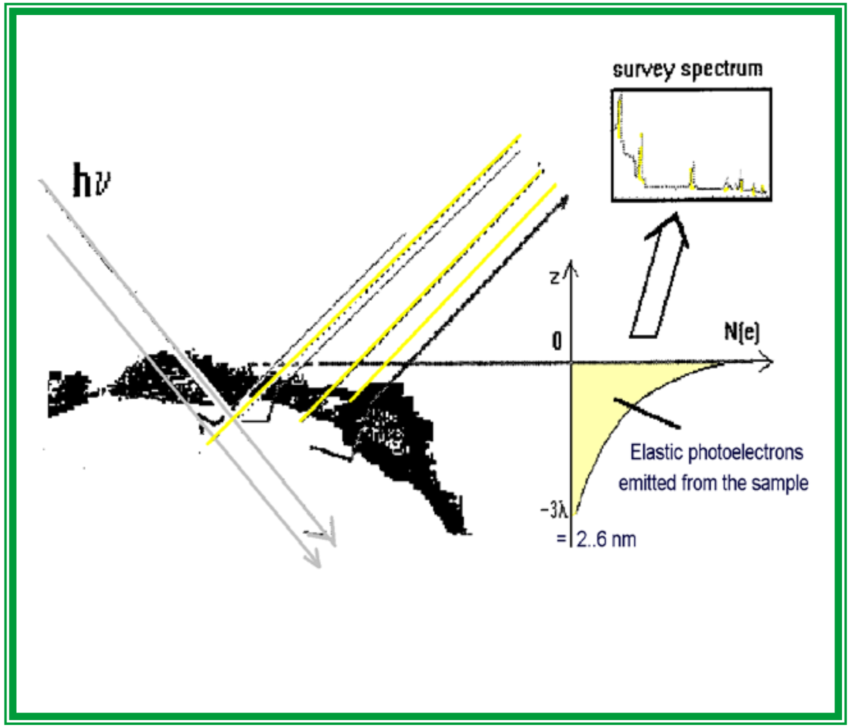
1. Elemental ID / quantification
wide scans (XPS sees all but hydrogen)

2. Chemical info / quantification
HighRes data (especially C 1s)

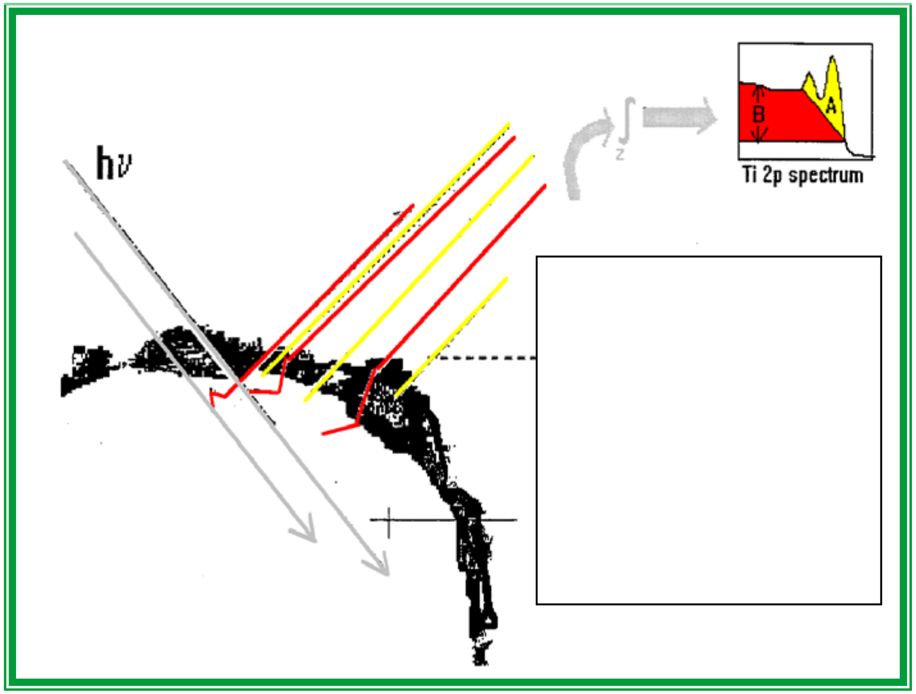
3. Depth distributions info
Surface modelling via Tougaard
Note: sputtering damages organics!

Depth distributions & modelling with Tougåård

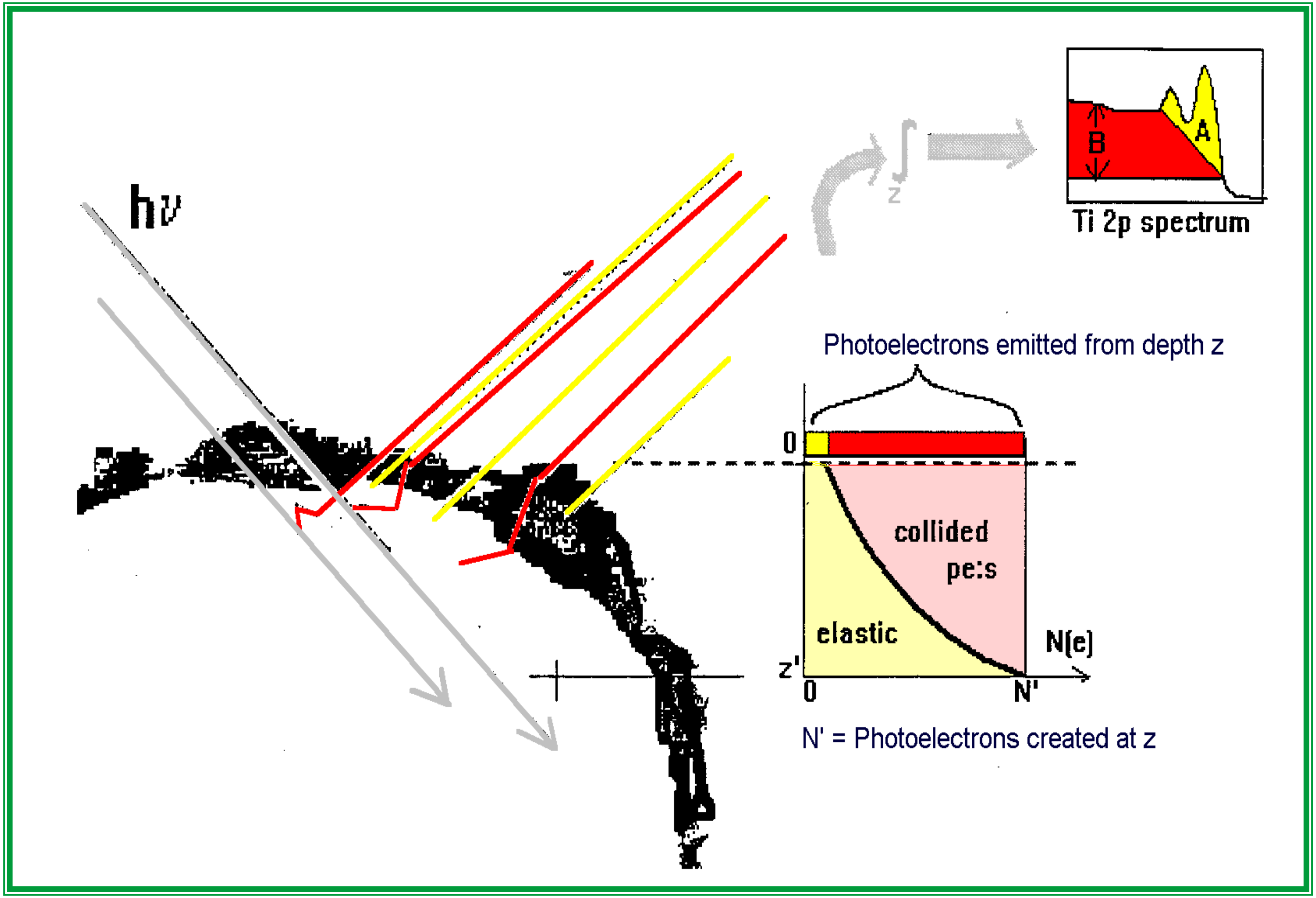
Conventional XPS core lines



Peaks & collided electrons (Tougaard)



L.-S. Johansson: Analyzing coated powders with XPS Surf.Int.Anal. 17 (1991).


hν
Ti 2p spectrum
B
A
z
Photoelectrons emitted from depth z
0
collided
pe:s
elastic
N(e)
z'
0
N'
N' = Photoelectrons created at z

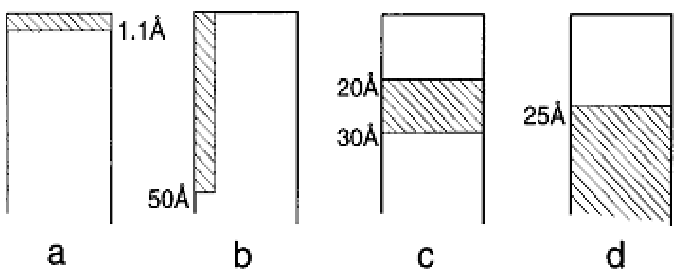
Background size & shape in evaluation

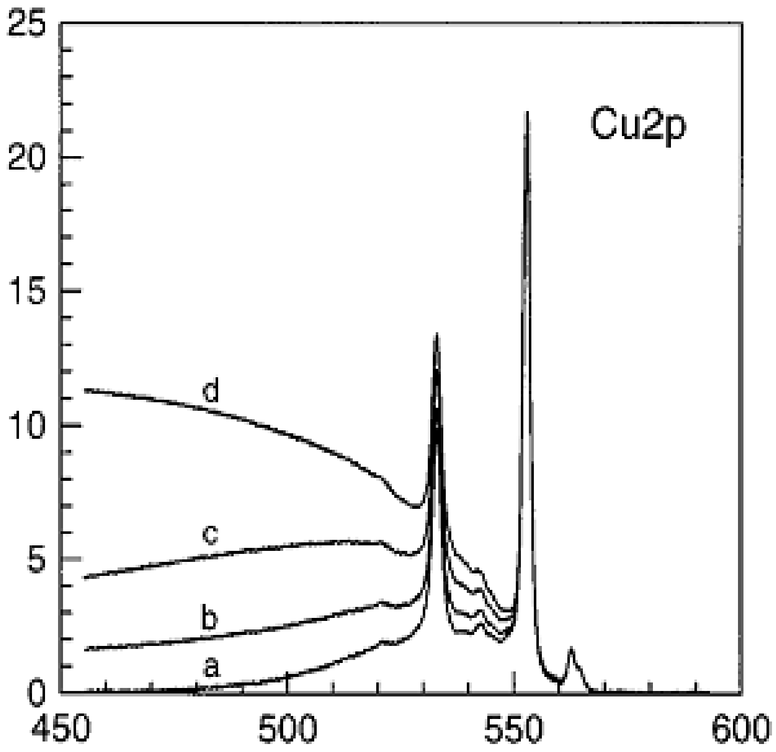
From spectral features to modelling: Theory

S. Tougaard:

Simulated & experimental spectra of Copper in/on Gold

Four surface distributions of Cu:





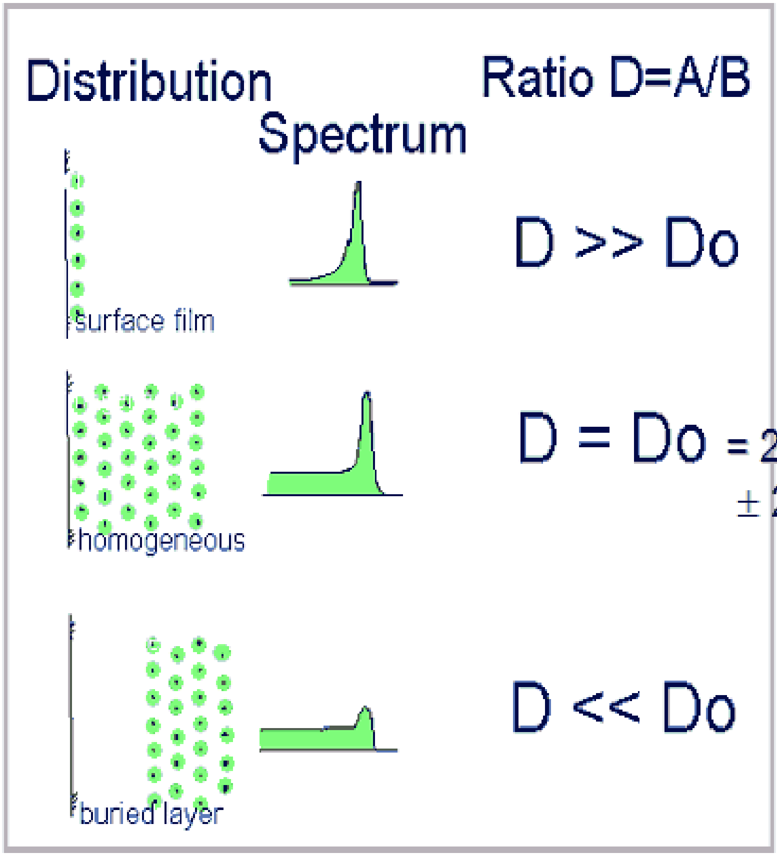
Peak intensity + background shape

→ Cu content and distribution determined without pre-information

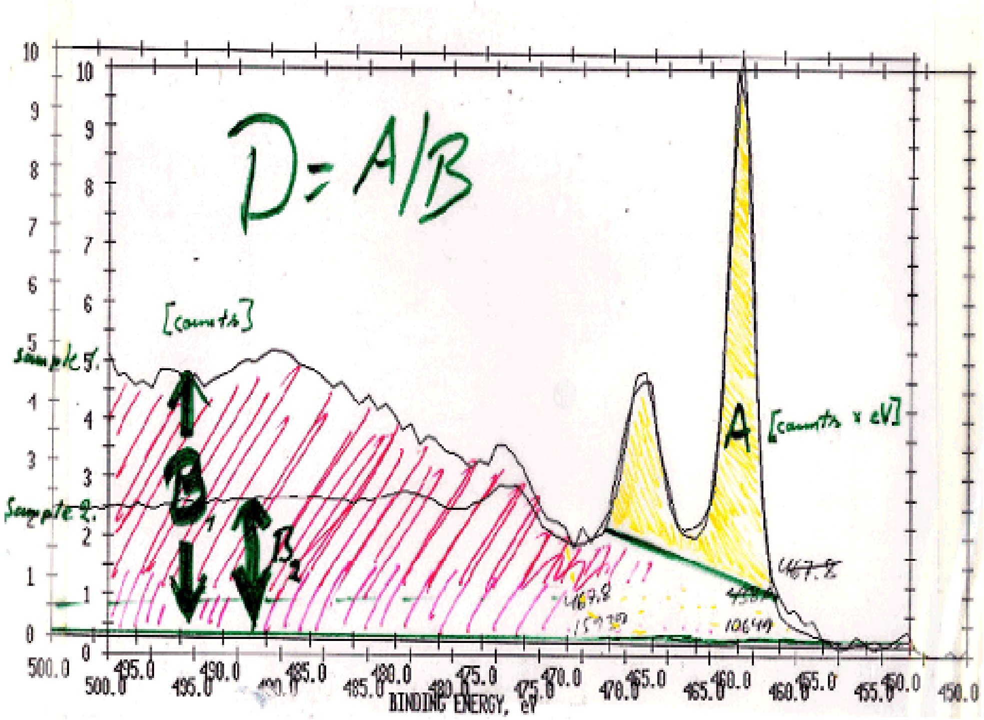
S. Tougaard: Surf.Int.Anal 26, 249-269 (1998)

Background size & shape in evaluation

From spectral features to <u>modelling</u>: practice1



Peak-to-background ratio D:
is very similar for most solid matrices.
It depends mainly on the surface distribution.

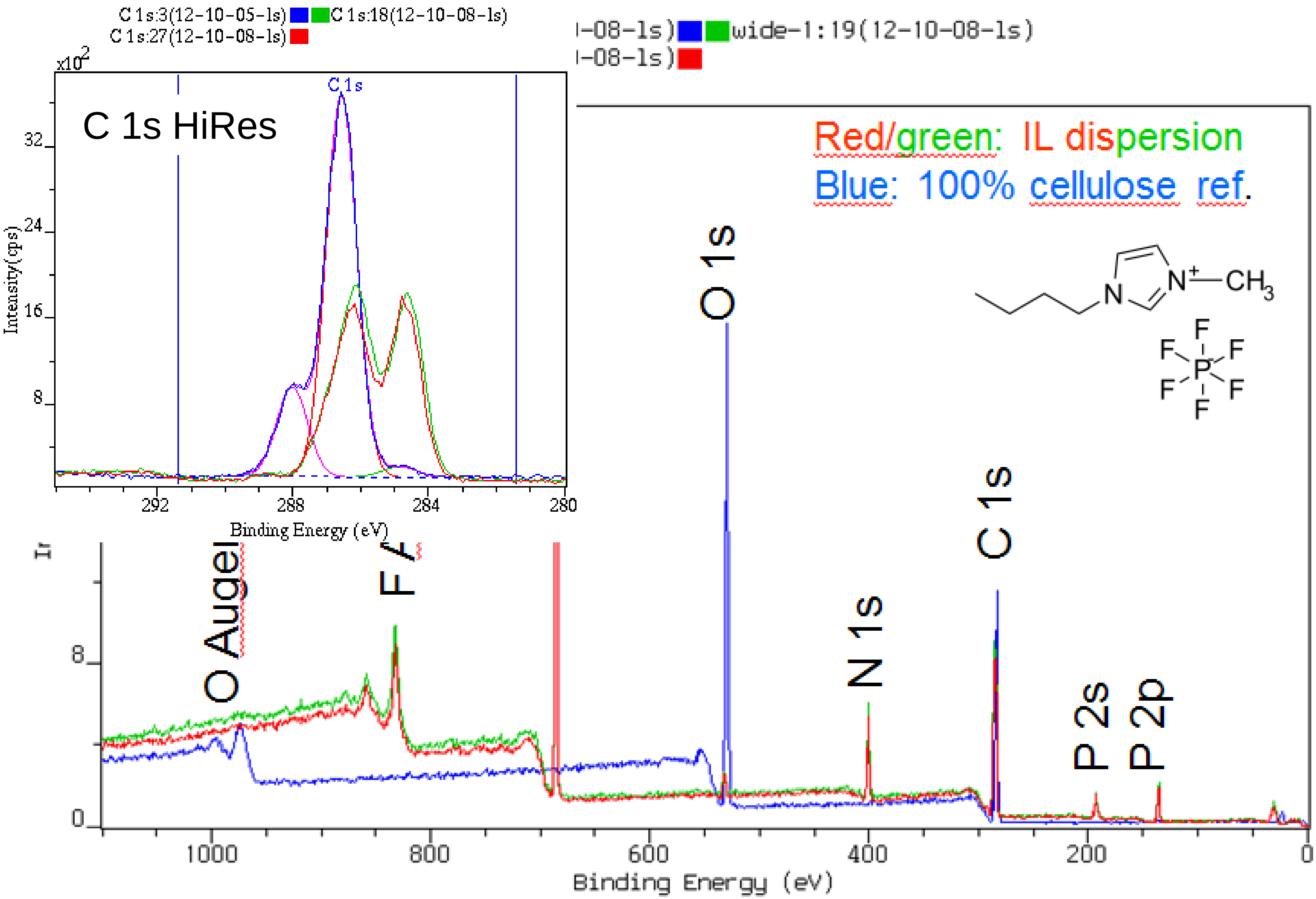


S. Tougaard, H.S. Hansen: Surf.Int.Anal 14, 730 (1989)

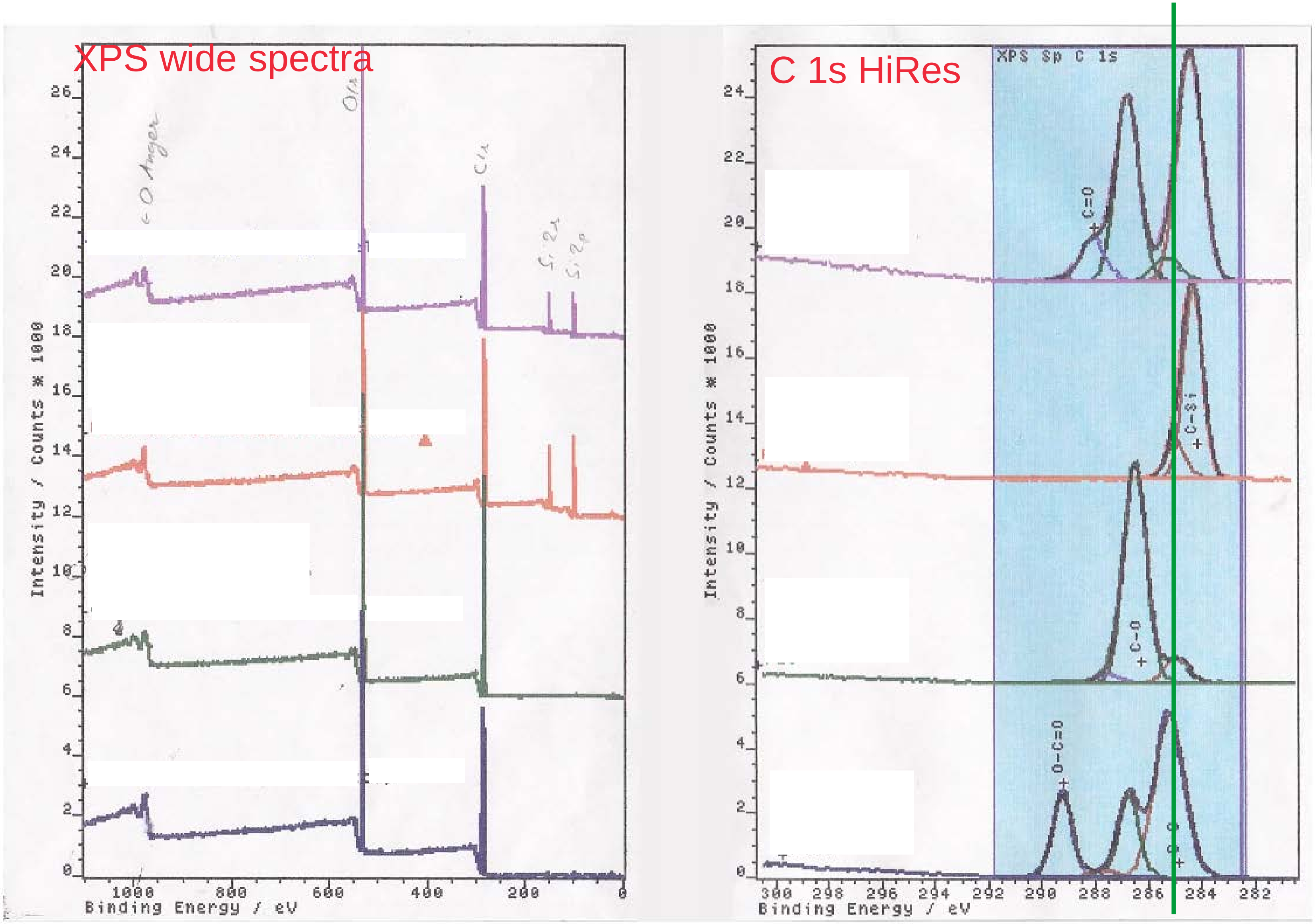
XPS

Example/Case study

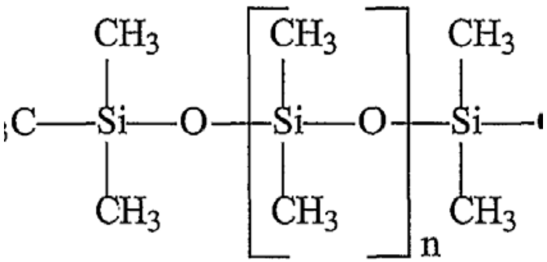
Case 1. Is cellulose seen in PMIM-PF_6 dispersion ?

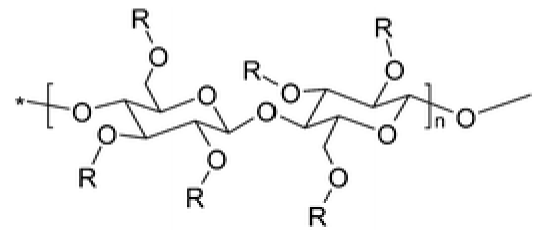


Case 2: Identification of polymers



Polydimethylsiloxane (PDMS)



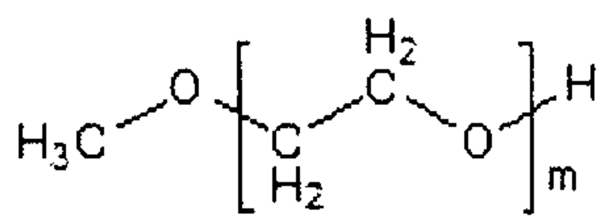


Cellulose R=H

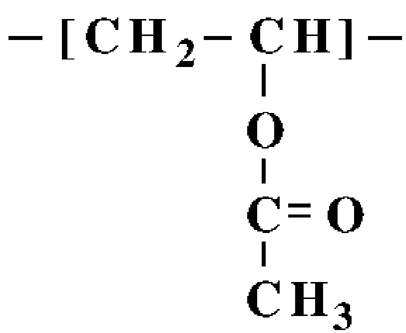
Trimethylsilyl cellulose R=Si(CH_3)$_3$

Cellulose triacetate R=$COCH_3$

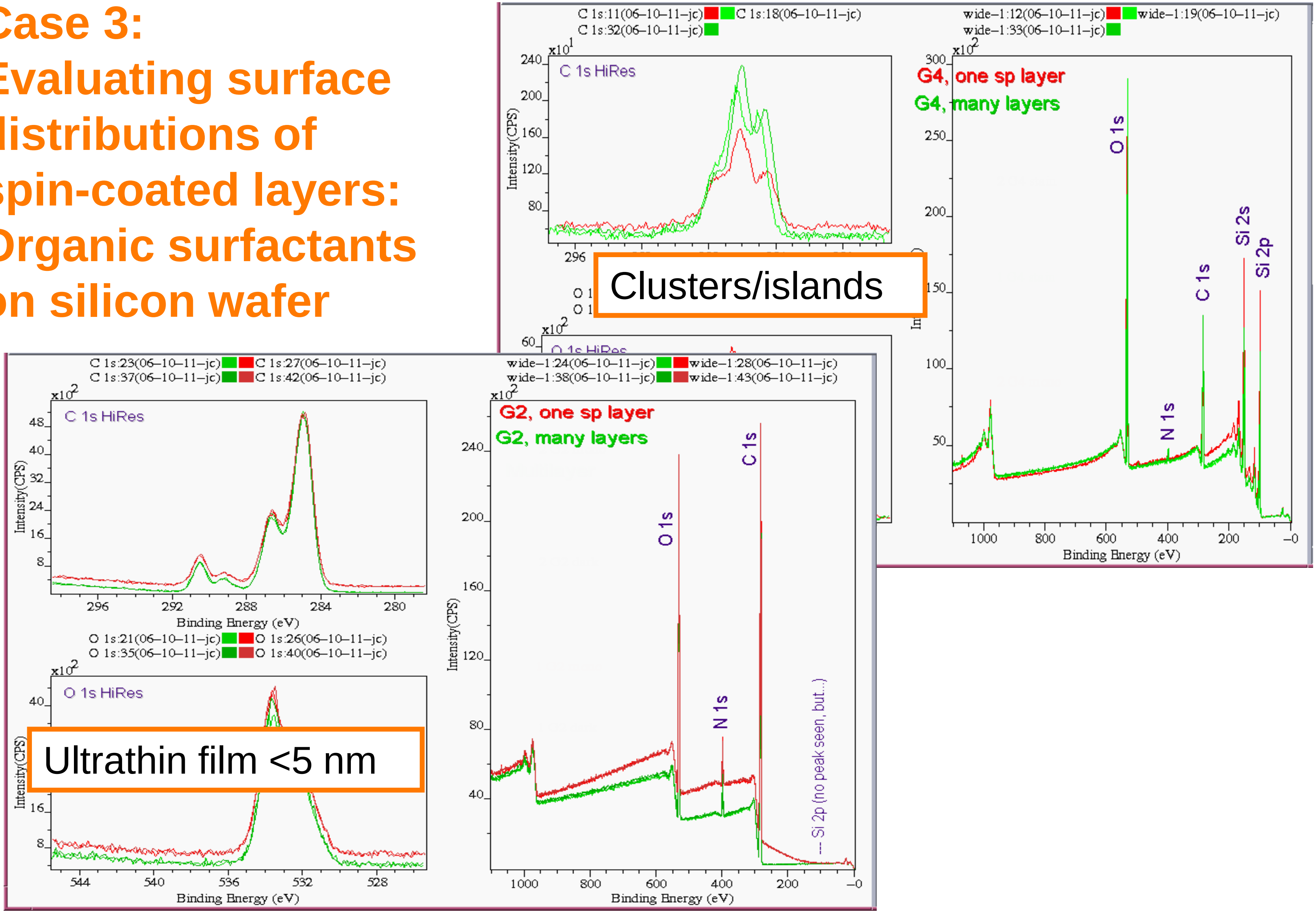
Polyethyleneglycol (PEG)



Polyvinyl acetate (PVAc)

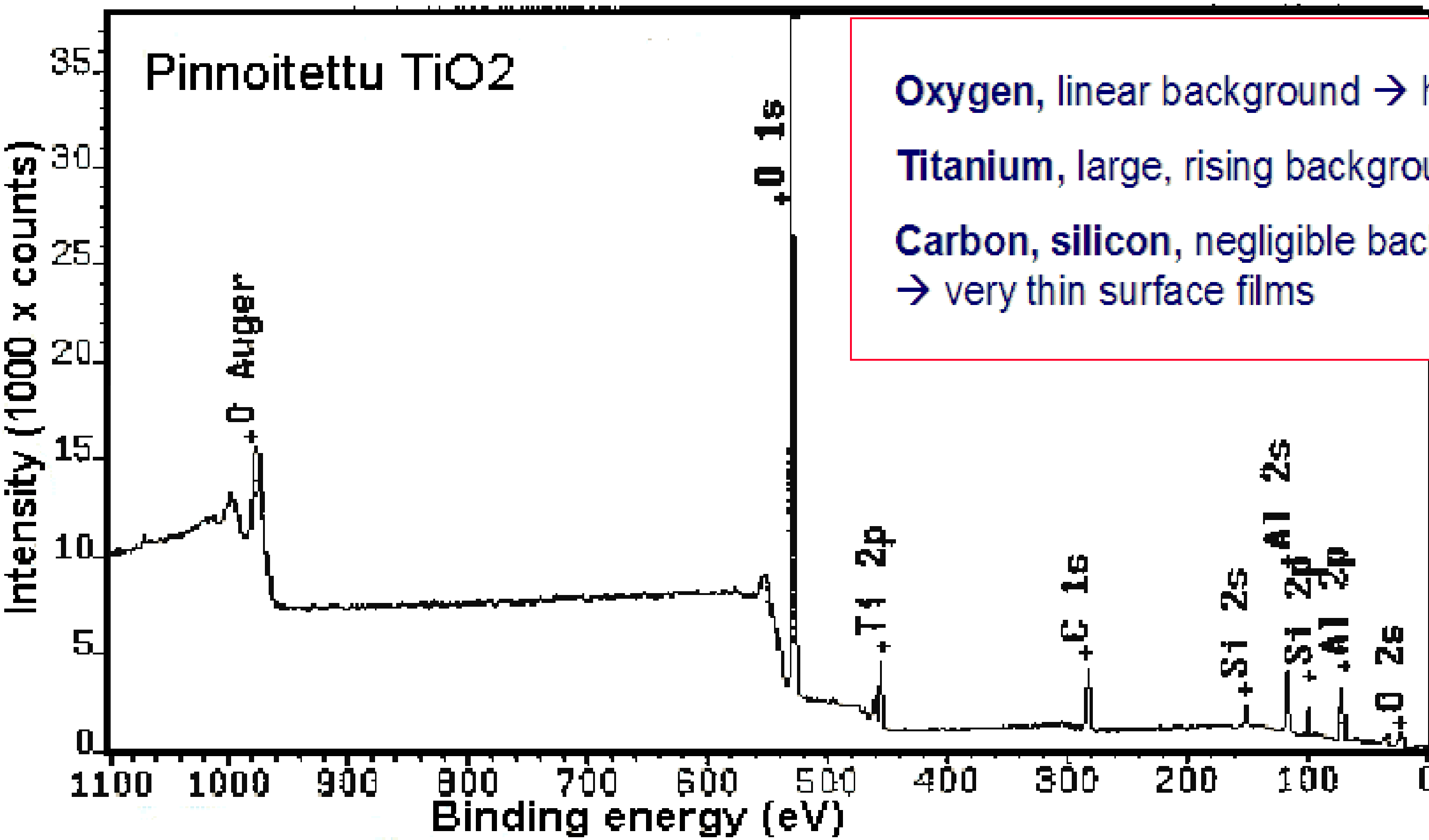


Case 3: Evaluating surface distributions of spin-coated layers: Organic surfactants on silicon wafer



Case 4: TiO_2 pigment powder

The XPS background evaluation on surface distributions:
homogeneous / buried / surface film – or none of the above?

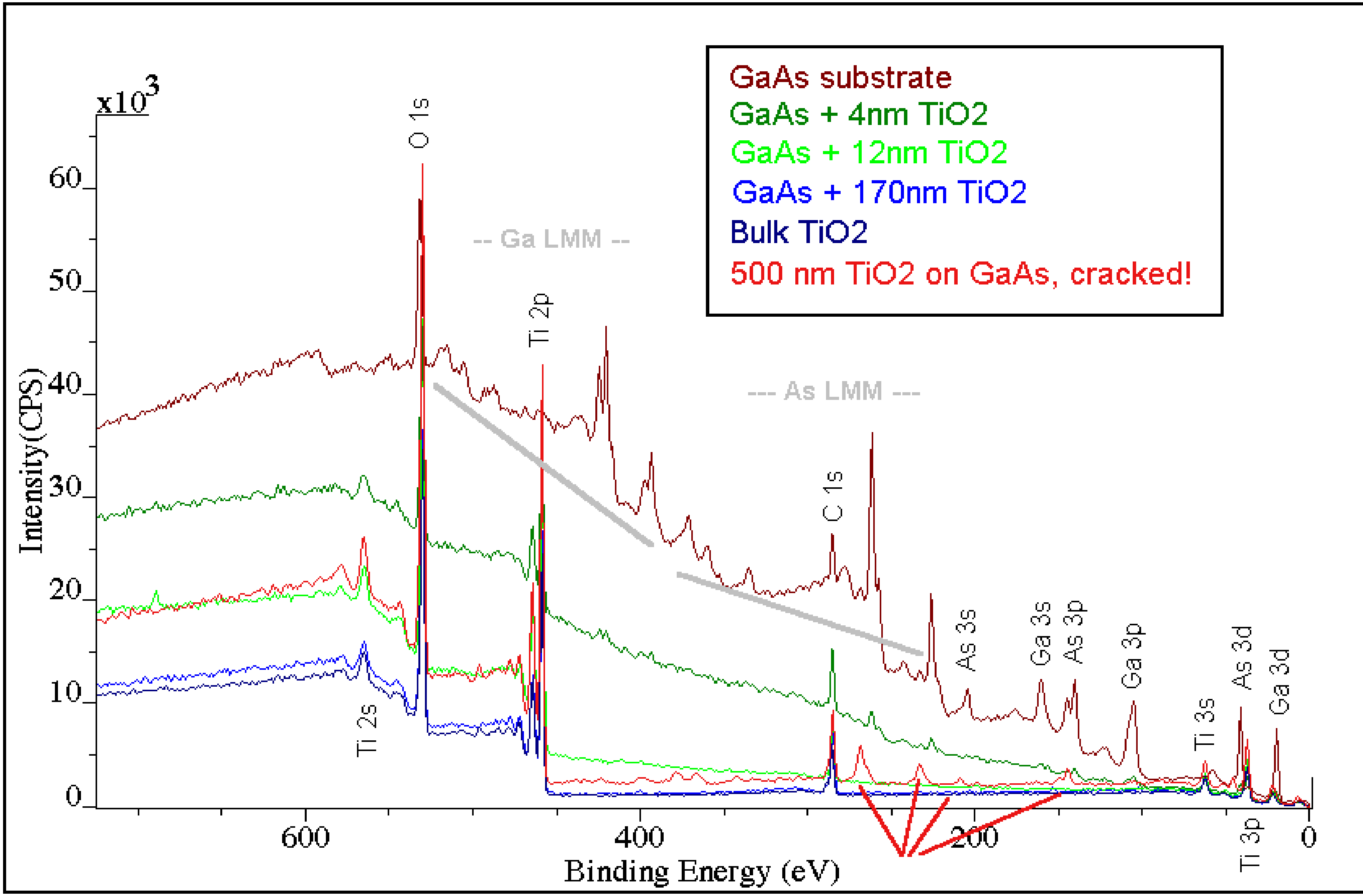


Oxygen, linear background → homogeneous

Titanium, large, rising background → covered

Carbon, silicon, negligible backgrounds
→ very thin surface films

Case 5: ALD thin film analysis



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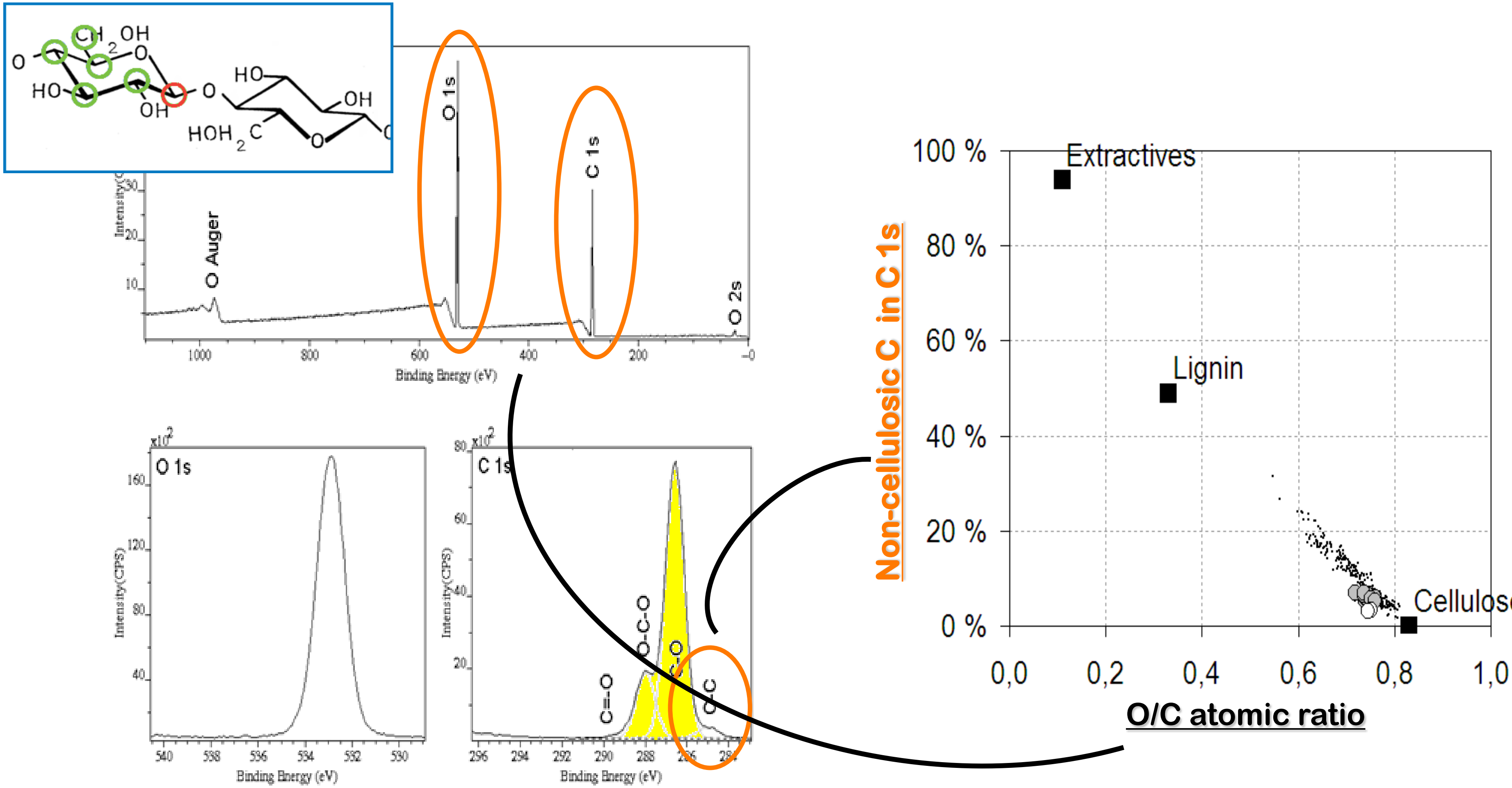
Case 6

Monitoring paper-making process with XPS

Basics: two way analysis



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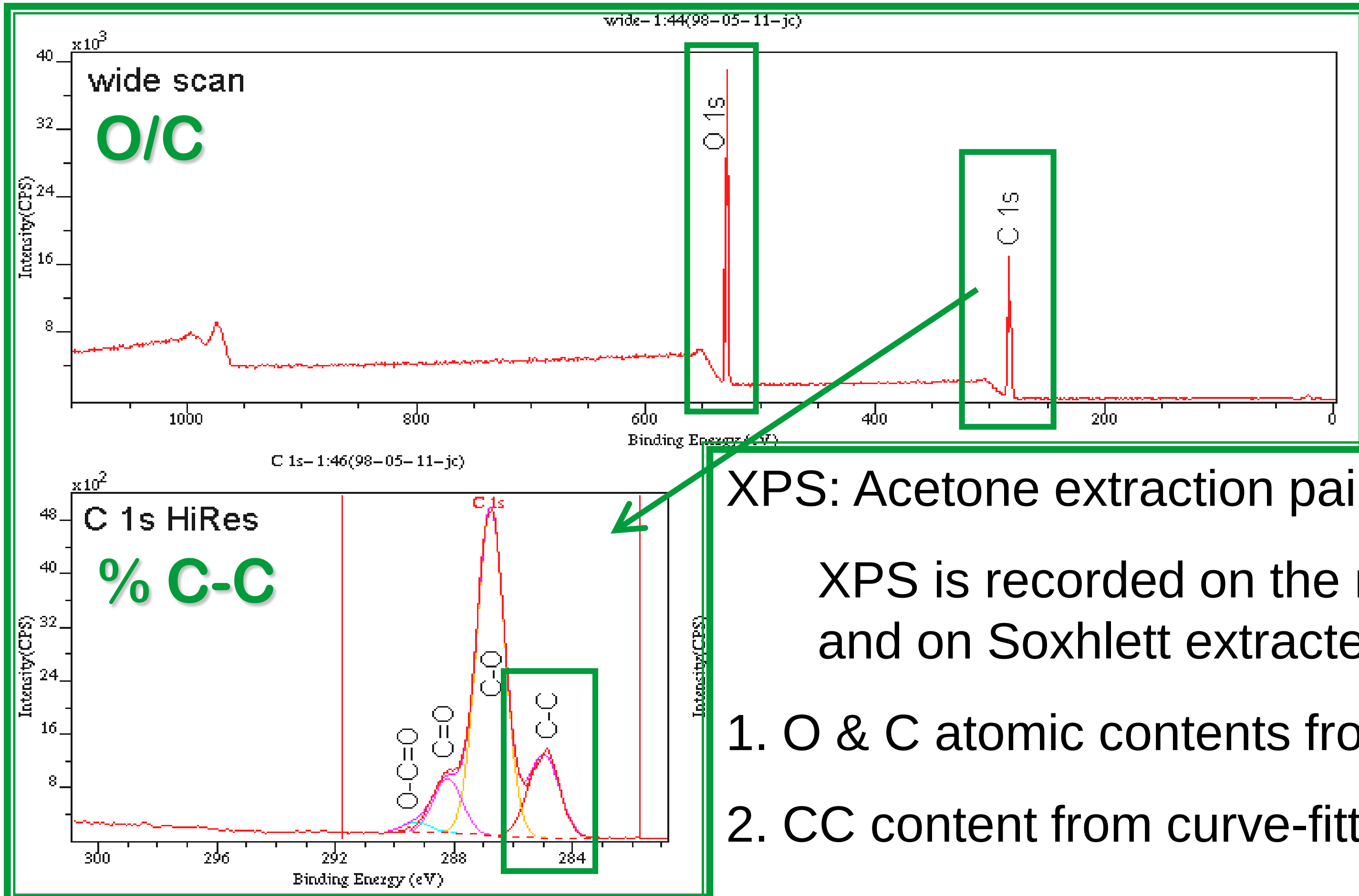
Johansson, Campbell, Koljonen, Stenius: Appl.Surf.Sci. 144-145, 92-95 (1999)
Johansson, Campbell: Surf.Int.Anal 36 1018-1022 (2004)
XPS Round Robin on cellulose: Surf.Sci. 584 (2005), Holzforschung (2006)

Surface lignins vs extractives



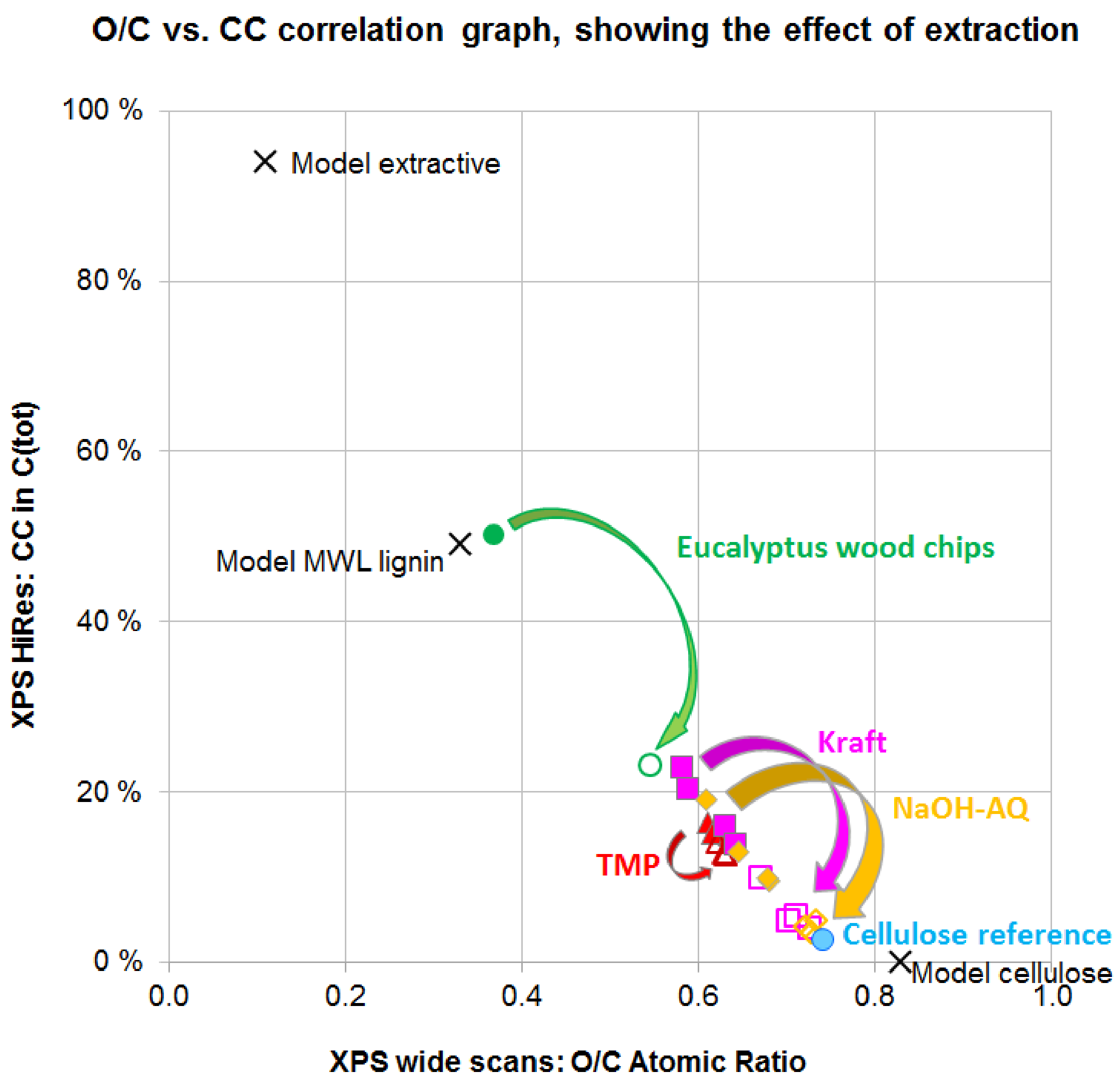
XPS: Acetone extraction pairs:

XPS is recorded on the non-extracted and on Soxhlett extracted sample

1. O & C atomic contents from wide scan
2. CC content from curve-fitted C 1s HiRes

→ data to correlation graph

Eucalypt, from wood to cellulose



X's:
Model compounds

Filled marks:
Non-extracted
(lignin and extractives)

Open marks:
Extracted
(only lignin)

M. Muguet et al, Holzforschung 2014; 68(3): 273–282

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XPS

Additional reading

Additional reading

Practical materials characterisation using complementary XPS, AES and Tof-SIMS

- http://www.spirit-ion.eu/tl_files/spirit_ion/files/Training%20course/Analysis%20V.pdf

  Erityisesti alustus sekä XPS ja Tof-SIMS -osuudet

  Lähde: Prof. John Watts, U of Surrey

More on UHV (Ultra High Vacuum), XPS and SIMS

- http://www.chem.qmul.ac.uk/surfaces/scc/

  Part 4. UHV & Effects of Gas Pressure
  Part 5. Surface Analytical Techniques, especially 5.1, 5.3 and 5.5
  Part 7. Surface Imaging & Depth Profiling

  (muutkin voi tietenkin lukea, mutta osa soveltuu paremmin kiinteän olomuodon fyysikoille eikä niinkään käytännön pintatekniikan soveltajille)

  Lähde: Dr. Roger M. Nix, Queen Mary U of London