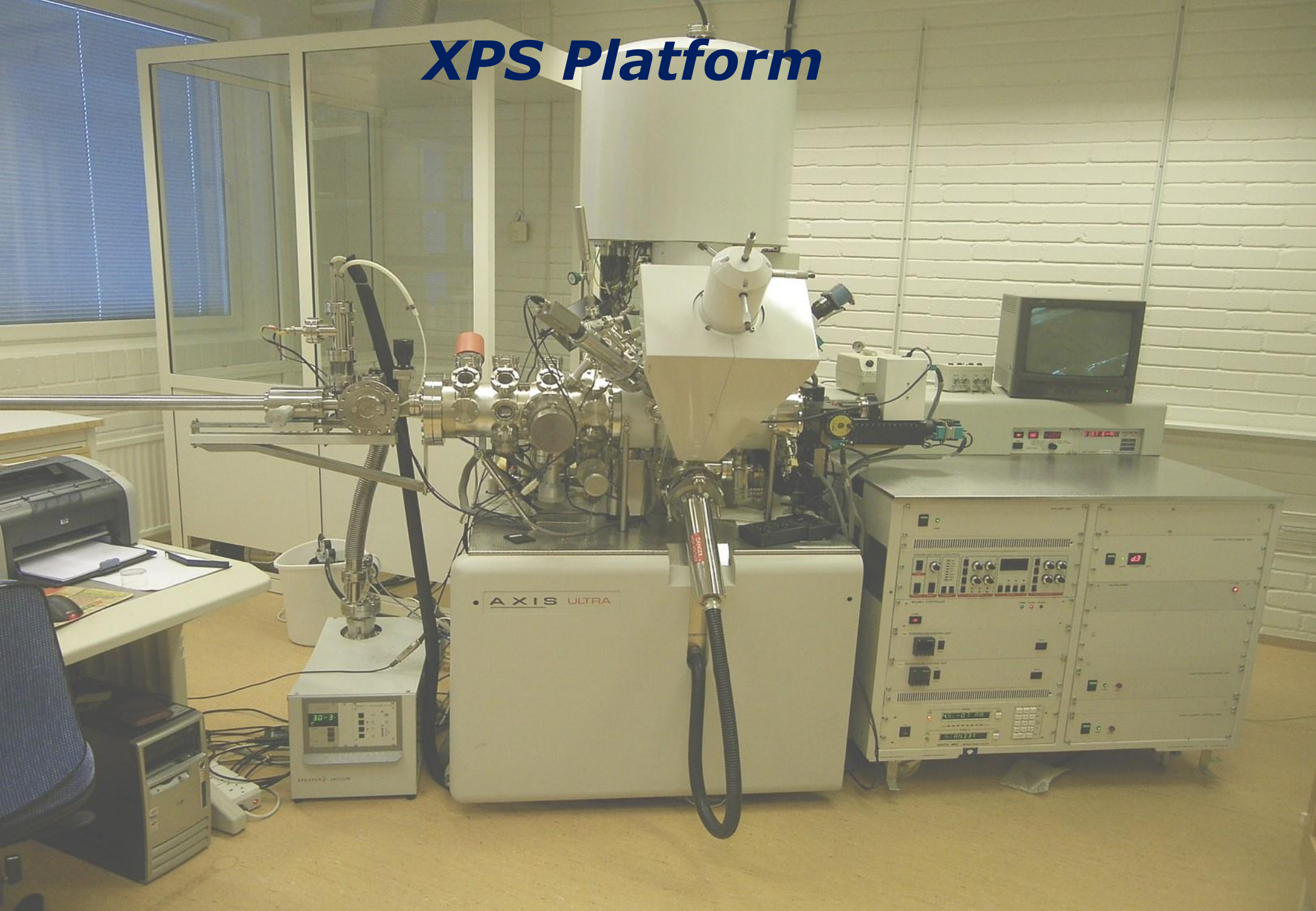
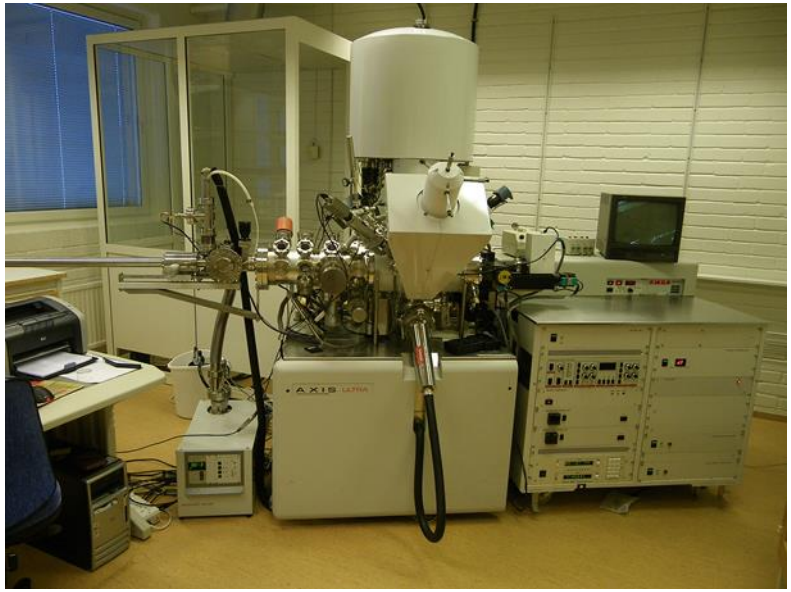
XPS Platform



PAST/History



Axis Ultra DLD electron spectrometer (Kratos Analytical Ltd, UK) installed Autumn 1999
Upgrades: 2005 and 2009
Covered by Bronze Service Contract - renewed yearly

21 years of operation:
3 books chapters
>140 peer-reviewed papers
>45 PhD thesis

X-ray Photoelectron Spectroscopy - XPS

- XPS/ESCA – X-Ray Photoelectron Spectroscopy/ Electron Spectroscopy for Chemical Analysis:

  X-Ray photons of precisely defined energy ($h\nu$) bombard the surface, electrons are emitted from the orbitals of the component atoms, electron kinetic energies (KE) are measured, their electron binding energies (BE) can be determined enabling the component atoms to be determined.

Energy conservation law:

$$h\nu = BE + KE + \varphi$$

$$BE = h\nu - KE - \varphi$$

X-ray Photoelectron Spectroscopy - XPS

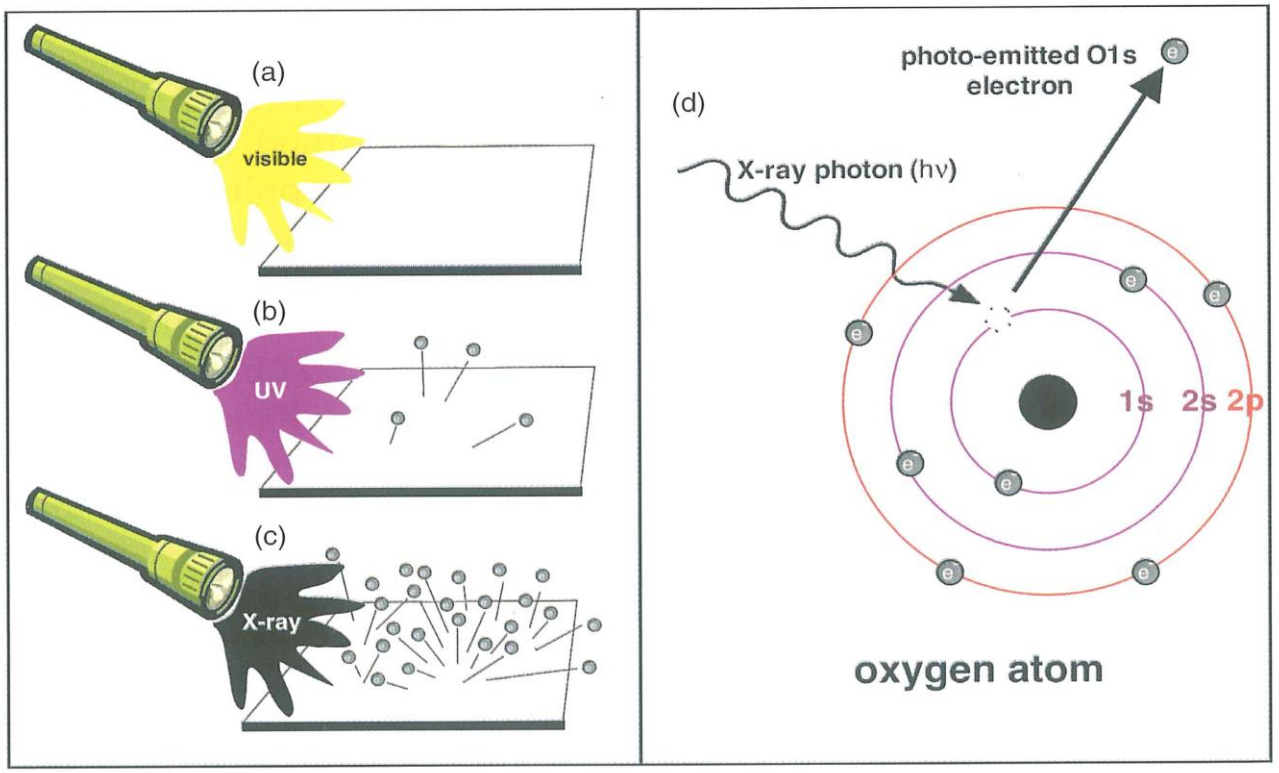
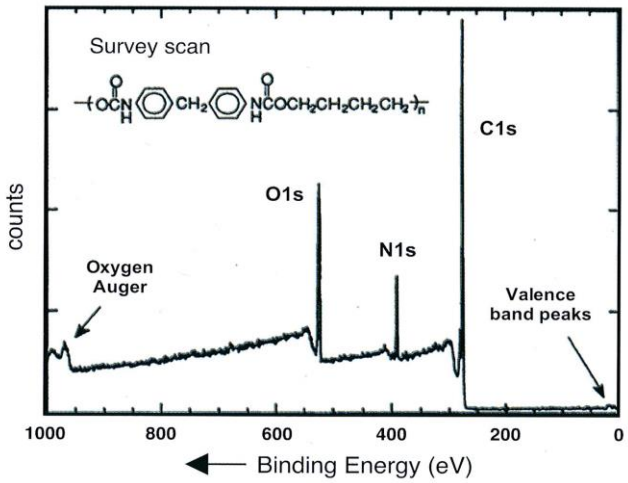


Figure 3.1 (a–c) A surface irradiated by a photon source of sufficiently high energy will emit electrons. If the light source is in the X-ray energy range, this is the ESCA experiment. (d) The X-ray photon transfers its energy to a core-level electron imparting enough energy for the electron to leave the atom

X-ray Photoelectron Spectroscopy - XPS



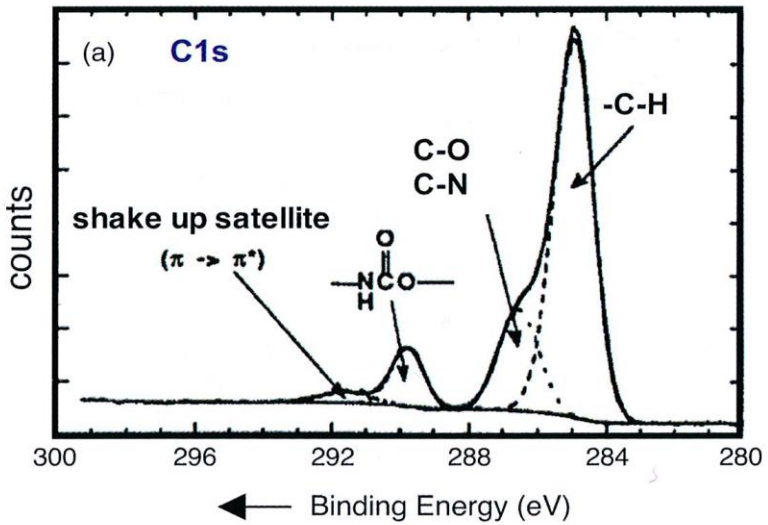
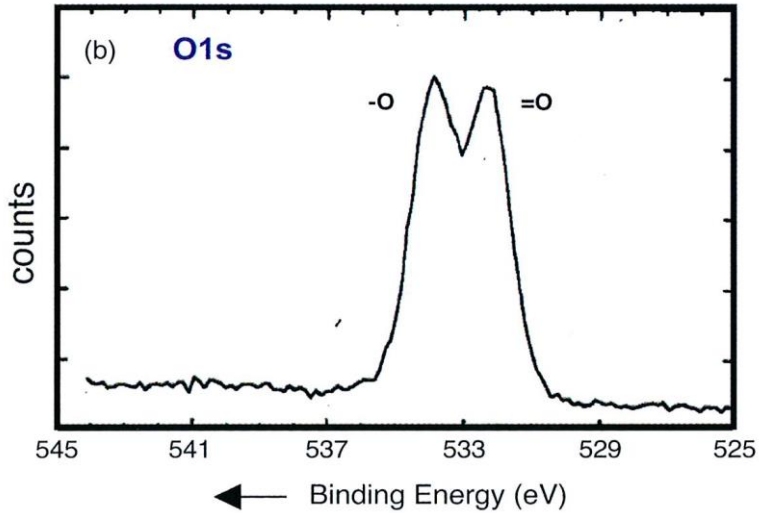
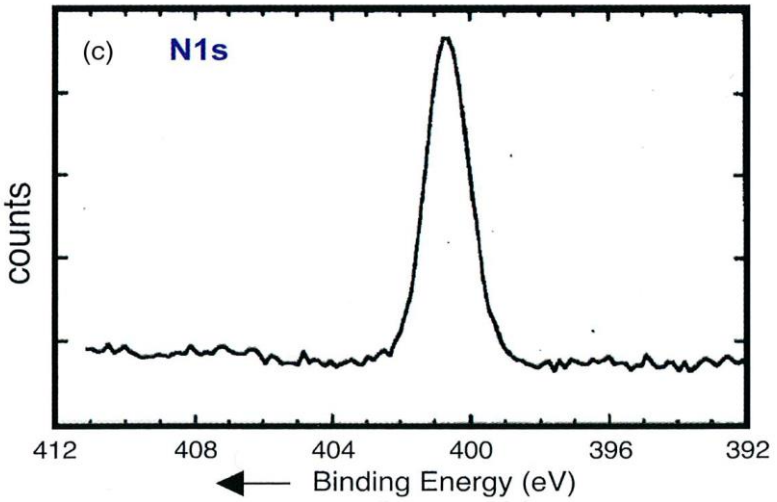


Figure 3.10 The ESCA survey scan of a hard-segment polyurethane





X-ray Photoelectron Spectroscopy - XPS

Analytical performance:

- Depth of analysis: metals - 5 – 25 Å, oxides – 30 – 60 Å, organic materials – 100 Å

- Analysis area from 0.3 x 0.7 mm^2 up to 15 micron in diameter

- Sensitivity - 0.1 monolayer

-Practically non-destructive

-Depth profiling up to 1 micron

-UHV technique (better than 10^{-8} Torr)!

XPS Platform

The platform provides surface analysis by X-ray Photoelectron Spectroscopy (XPS or ESCA) technique.

Equipment

AXIS Ultra DLD is an electron spectrometer manufactured by Kratos Analytical, Ltd. (UK). The instrument was installed at the Department of Chemistry in 1999 and upgraded twice.

Service

In the outermost 10 nm of a surface (10 atomic layers), XPS provides:

- Identification of all elements (except H and He) present in concentrations >0.1 atomic %
- Semi quantitative determination of the elemental surface composition
- Information about the molecular environment (oxidation state, bonding atoms, etc.)
- Non-destructive elemental depth profile 10 nm into the sample and surface heterogeneity assessment
- Lateral variations in surface chemical composition (XPS imaging with spatial resolution of 5 microns)
- Studies on wet/hydrated (frozen) samples

Our unique field of scientific research is an investigation of fast-frozen samples including mineral-aqueous solution interfaces (Electrical Double Layer), interfaces of biomaterials with biologically relevant media, and surface of viable microorganisms (top of the cell wall).

Present

We are first XPS facility in the world and the only in Sweden which has developed special fast-freezing protocol and provides unique cryogenic measurements of fast-frozen wet samples (Cryo-XPS):

- mineral suspensions (Biogeochemistry, Dentistry, Linnaeus University)
- bacterial cultures (Biogeochemistry, microbiology)
- algae (Biochemistry)
- lake sediments (Biogeochemistry, EMG)
- frozen environmental soil samples (Biogeochemistry, SLU, Uppsala University, Linnaeus University)

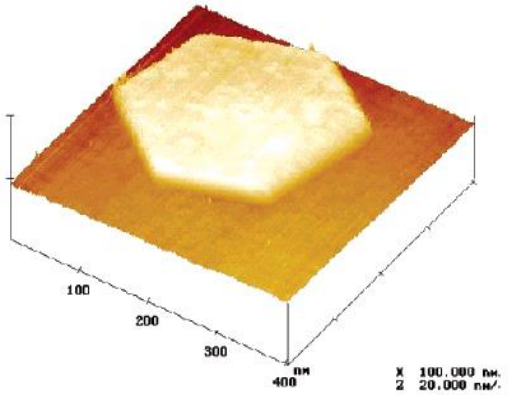
XPS applications – Fast-Freesing Technique

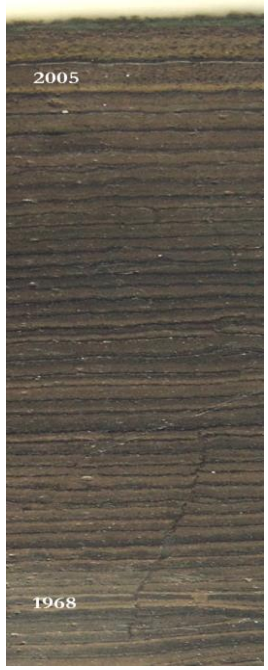
Wet samples: Suspensions, Sediments, Soils, microorganisms, etc.

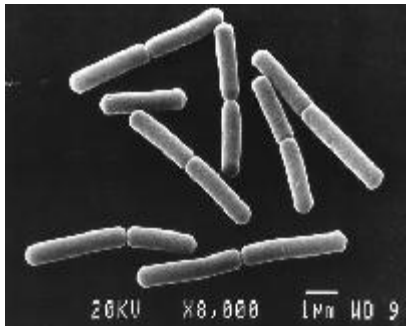
Solid-Aqueous Solution Interface: Composition and Structure

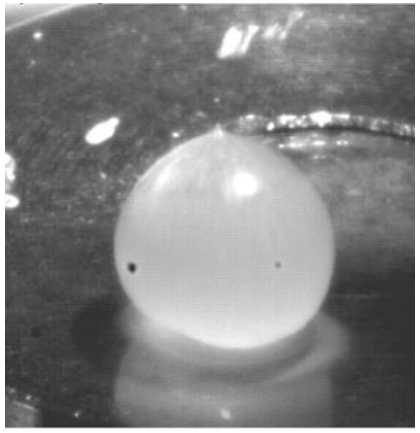
Electrical Double Layer: Composition, Structure, Potentials, Protonation constants, etc.

Solutions: Liquid-gas interface composition, etc.



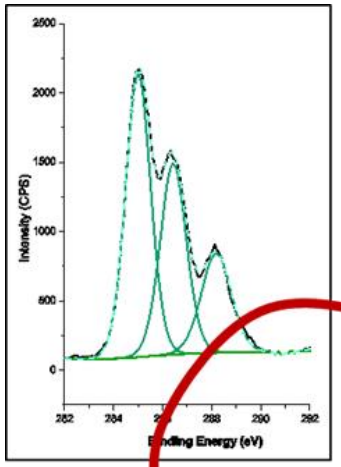


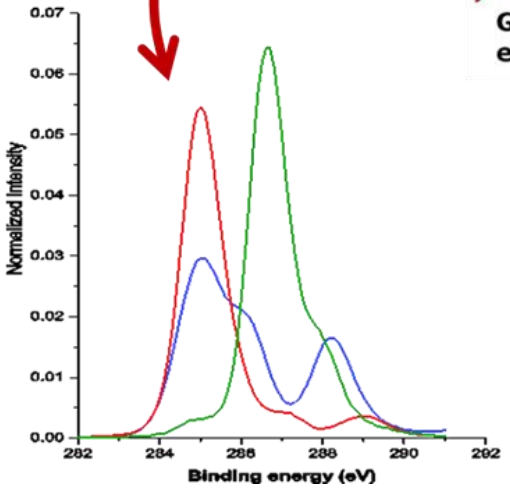


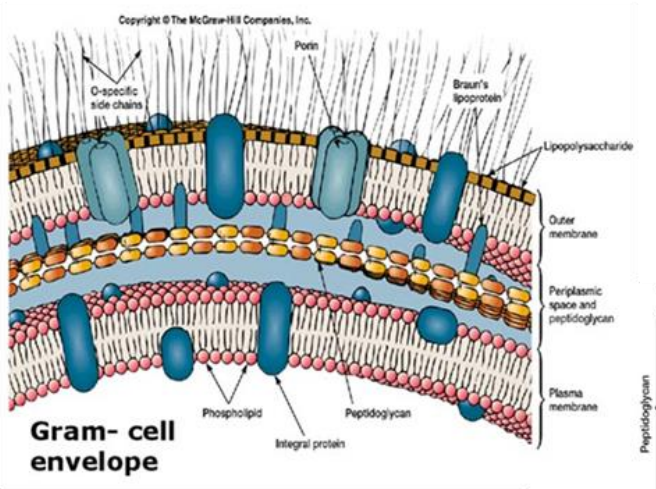


XPS applications – Biology

Living Cells: Cell wall composition, surface charge, acid-base properties, metabolic activity, etc.



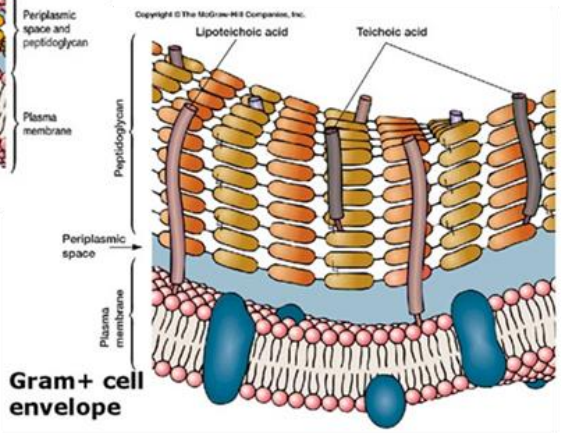




Gram- cell envelope

Lipid,
Peptide,
Polysaccharide

Lipoteichoic acid,
Lipid,
Peptidoglycan,
protein,
Teichoic acid,
Polysaccharide



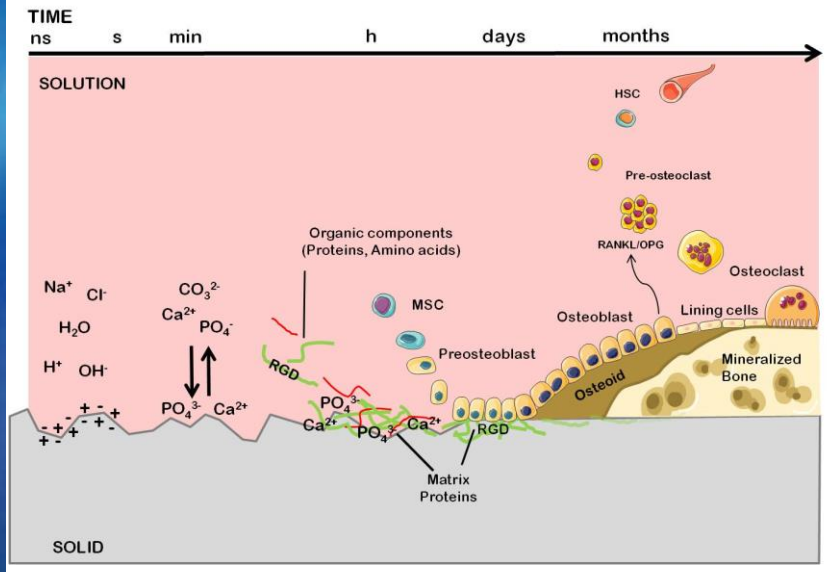
Gram+ cell envelope

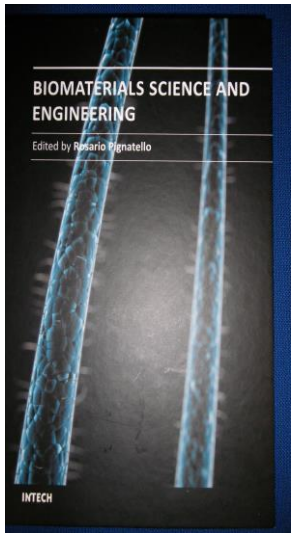
Contact: Madeleine Ramstedt

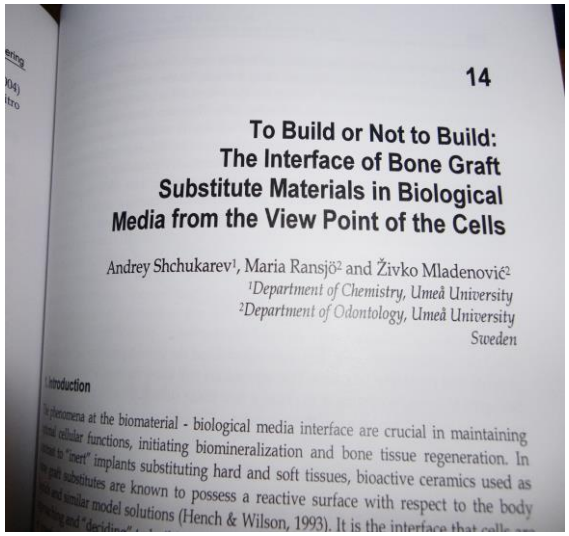
XPS Applications - Biomaterials

Real Biomaterials in Cell Culture medium:

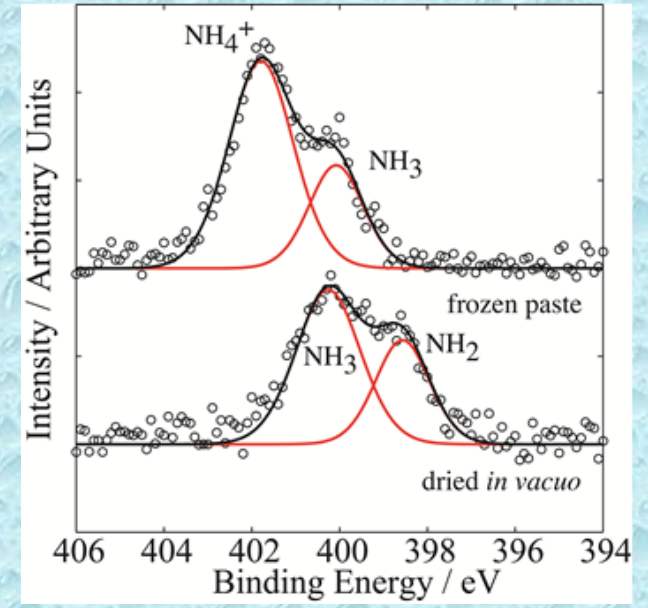
Interface composition, biomaterial particles surface charge, amino acids and protein adsorption, time dependent protein orientation, etc.



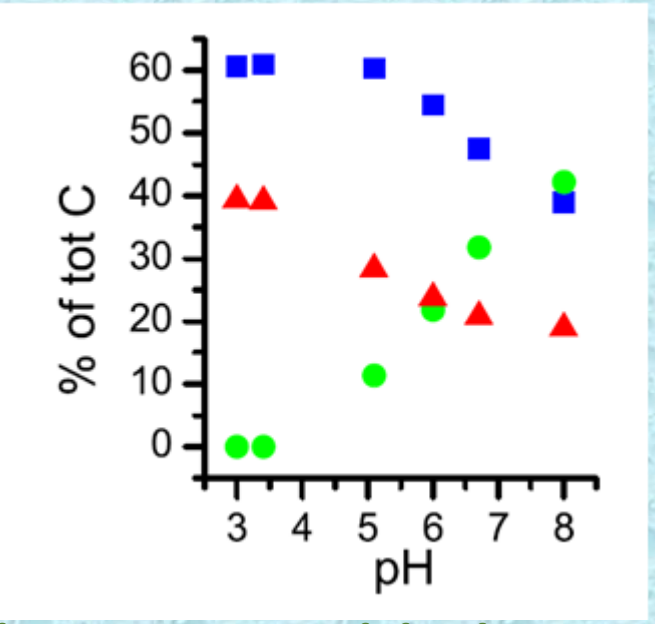




XPS Platform



N 1s spectra of hematite treated in 50 mM NH_4Cl at pH 6.2. The top spectrum originate from frozen paste and the bottom spectrum represents the same paste after sublimation of water inside the spectrometer



Surface composition of fast-frozen *Bacillus subtilis* bacteria in saline (0.1 M NaCl) as a function of pH: ■ - peptide, ▲- sugar, ● - lipid

A. Shchukarev, M. Ramstedt. **Cryo-XPS: probing intact interfaces in nature and life**. *Surface and Interface Analysis*, **2017**, *49, 349-356*. DOI: 10.1002/sia.6025

Cryo-XPS analyses give clues to understand flocculation affinity of microalgae

Andrey Shchukarev, Zivan Gojkovic, Christiane Funk and Madeleine Ramstedt

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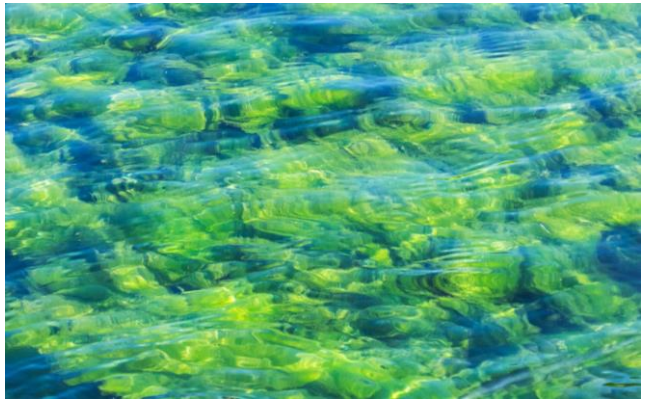
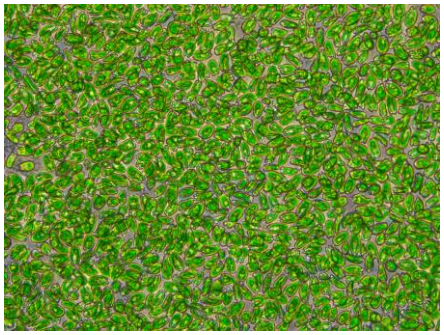
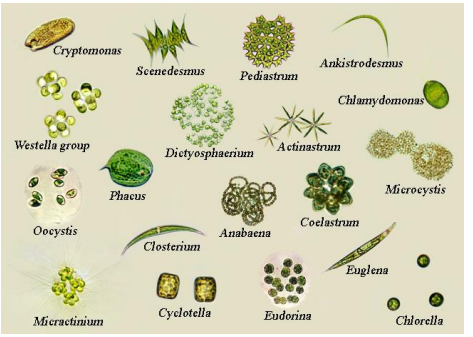
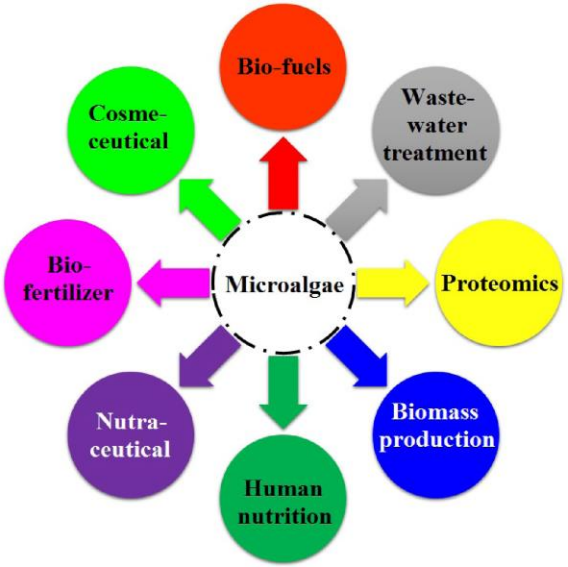
MICROALGAE









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HARVESTING OF MICROALGAE

Centrifugation consumes a lot of energy (about 69% of 1 kg dry algae biomass energetic value).

Flocculation is the most economically effective pre-concentration step

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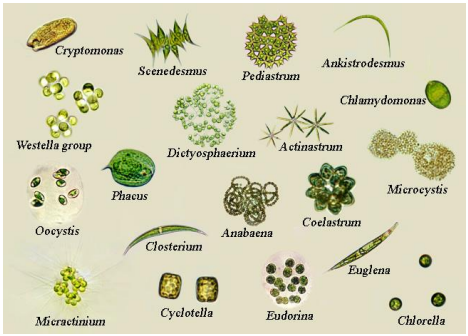
MICROALGAE UNDER STUDY

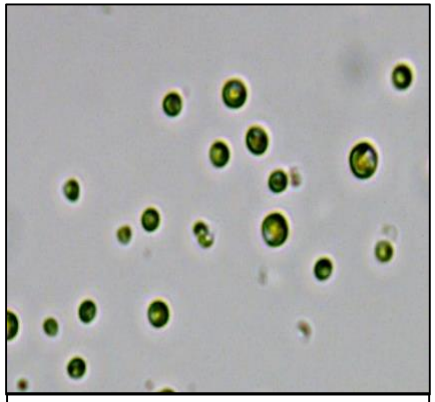


Two locally isolated Nordic microalgae plus *S. obliquus* RISE (UTEX 417)

$d_{13\text{-}1}$ = 3.8 µm

$d_{3\text{-}4}$ = 8.2 µm

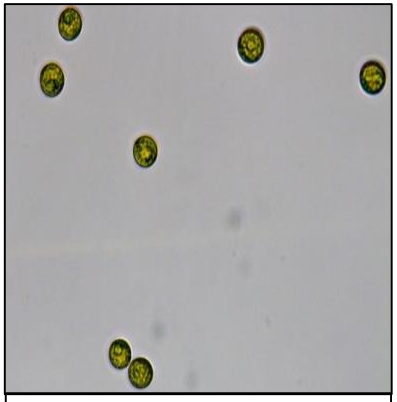
d_{RISE} = 8.0 µm



Chlorella vulgaris

13-1

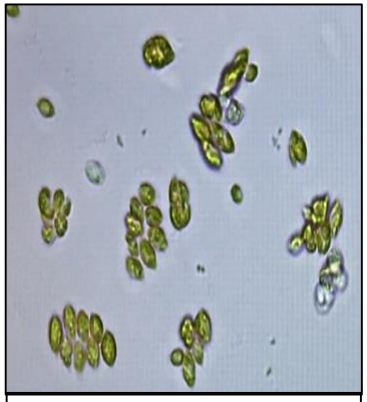
Non-flocculating



Coelastrella sp.

3-4

Auto-flocculating



Scenedesmus obliquus

RISE

Mildly auto-flocculating

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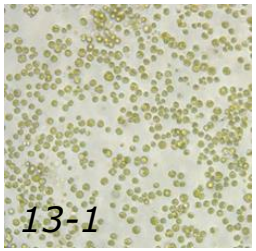
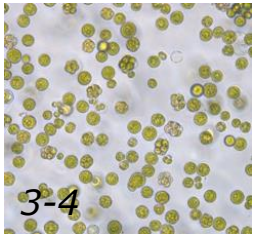
FLOCCULATION AFFINITY



Non-flocculating



Auto-flocculating

Mildly auto-flocculating

Same ζ–potential
Similar cell size

WHY flocculation behavior is different?

Surface properties/composition???

Surface analysis by cryogenic XPS with fast-frozen samples!

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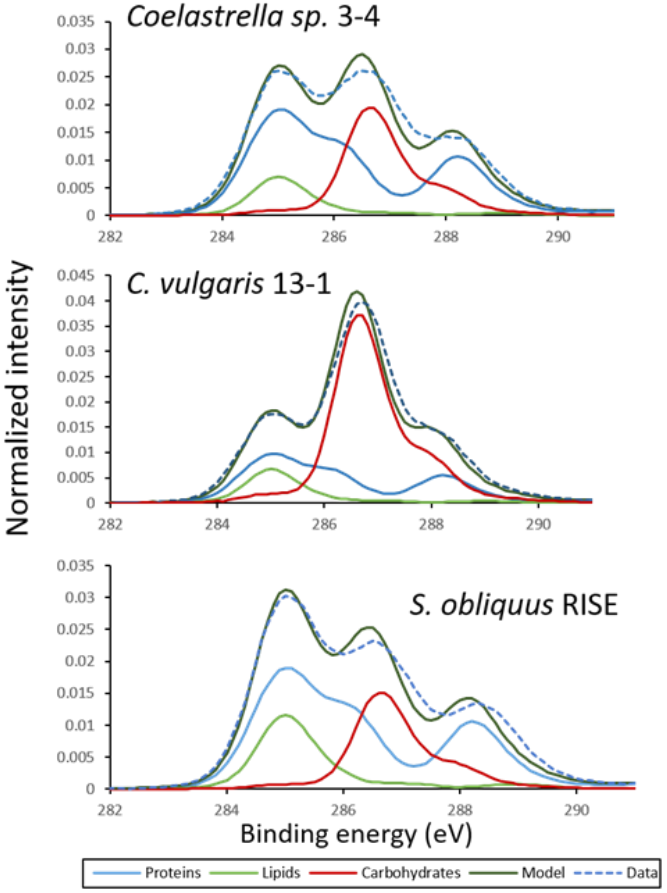
Microalgae cell wall - Biochemical analysis with C 1s spectra



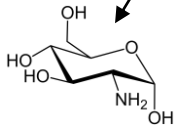
Surface of the auto-flocculating *Coelastrella sp.* 3-4 is significantly enriched in proteins (hydrophobic!)

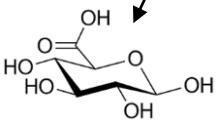
Surface of the non-flocculating *Chlorella vulgaris 13-1* cells are dominated by carbohydrates (hydrophilic!)

The reference strain, *Scenedesmus obliquus RISE*, shows similar content of proteins as the auto-flocculating, but has an increased amount of lipids (hydrophobic)

Flocculation affinity of mildly auto-flocculating reference strain seems to be regulated by protein orientation at the surface and/or biology of the cell – formation four-celled colonies

Deviation of resulting envelope from experimental spectrum (dashed line) is due to additional chemical compounds in the algae cell wall, e.g. glucosamine and glucuronic acid, which are not present in bacterial cell walls.





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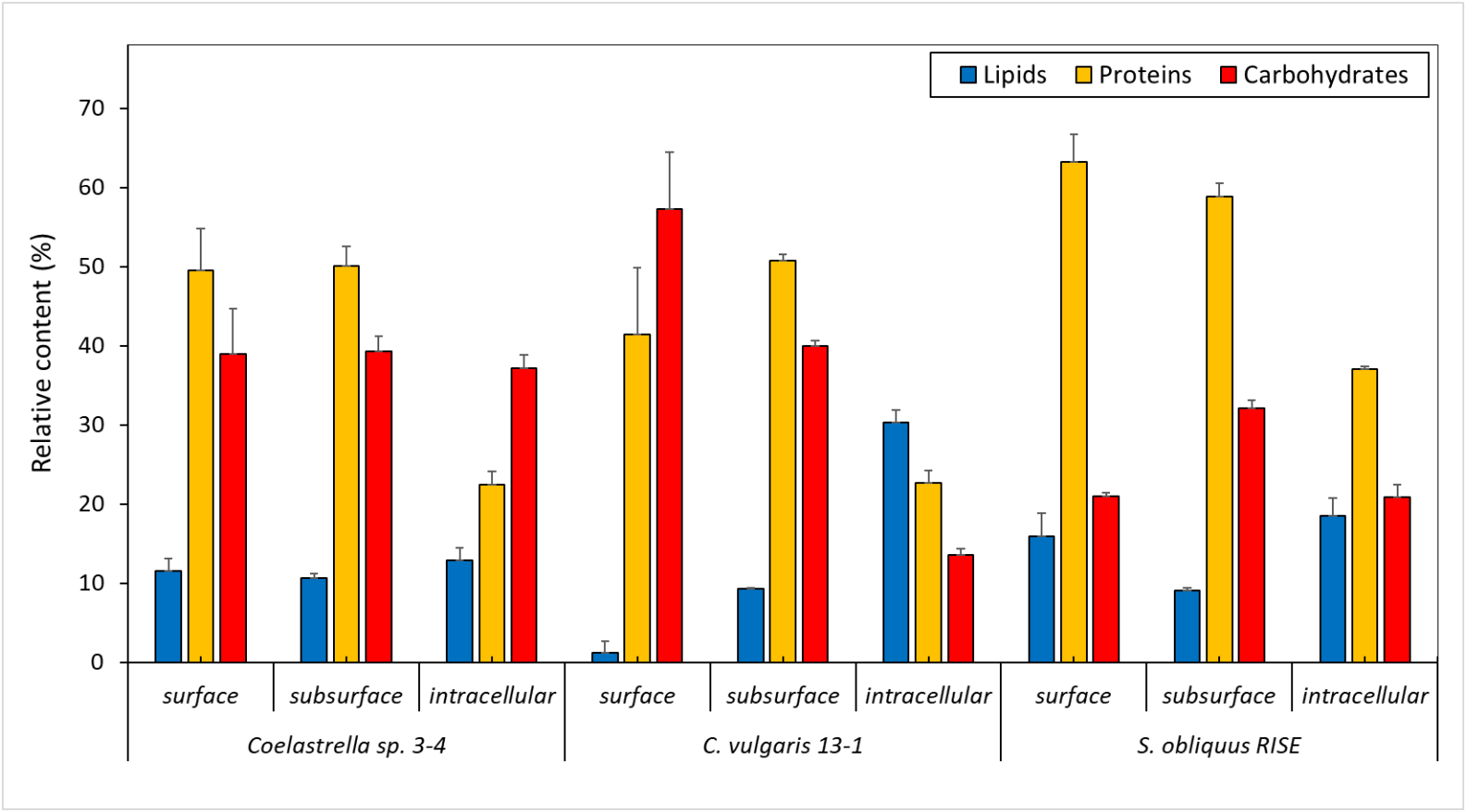
Microalgae – Surface, subsurface and bulk composition



Surface
Cryo-XPS

Subsurface
DR-FTIR

Bulk (intracellular)
Biochemical analysis

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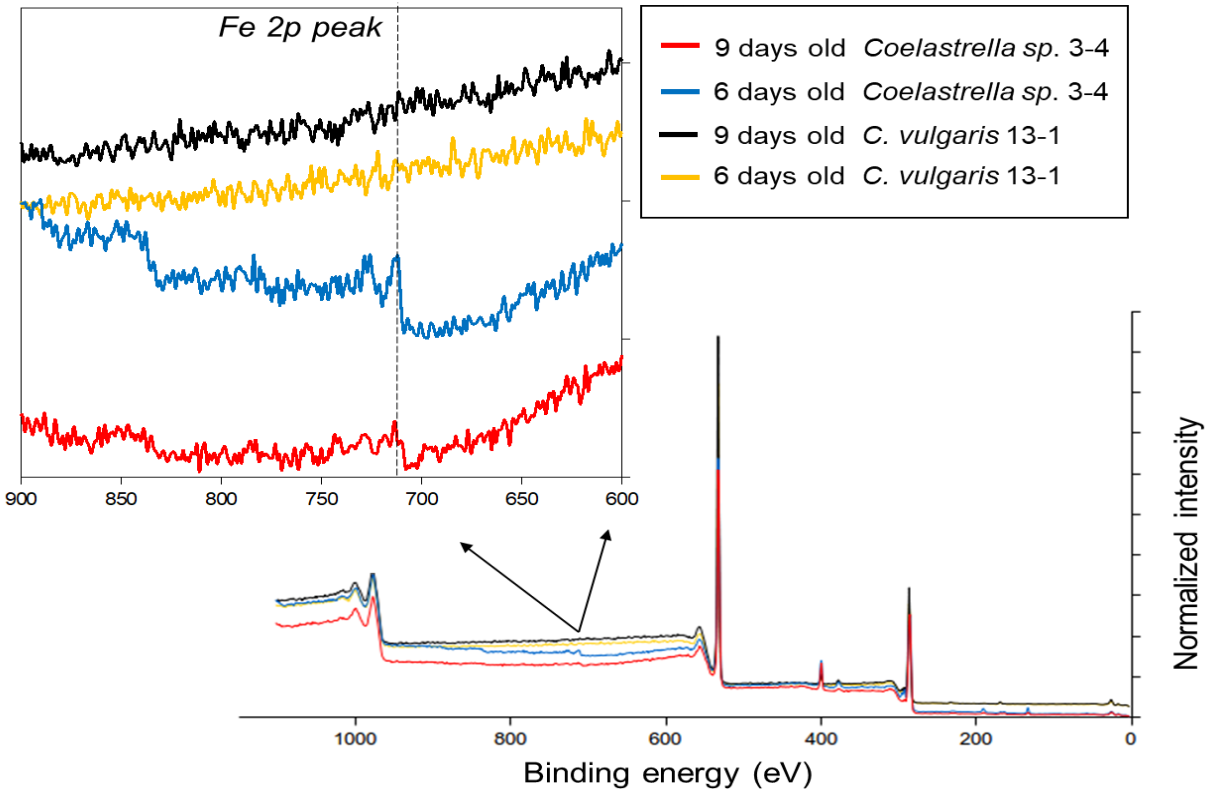
Microalgae cell wall development



Fe origins from Fe-binding proteins within the cell, e.g. cytochrome complexes of the thylakoid membranes in the chloroplast

Cell wall of auto-flocculating *Coalestrella sp. 3-4 (*cell diameter - 8.2 µm) is thinner than for non-flocculating *C. vulgaris 13-1* (cell diameter -3.8 µm)

Mildly auto-flocullating *S. obliquus* RISE is similar to auto-flocculating *Coalestrella sp. 3-4*

Cell wall of *Coalestrella sp. 3-4* and *S. obliquus* RISE becomes thicker than 10 nm (XPS depth of analysis) during the cell development

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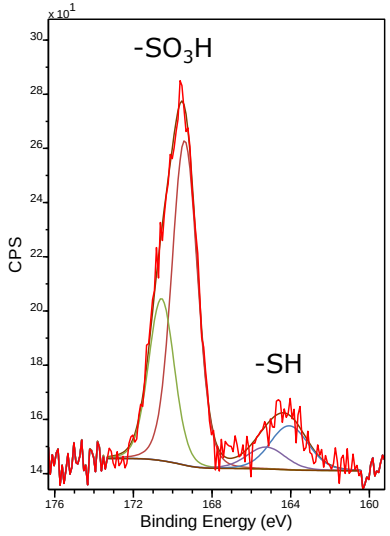
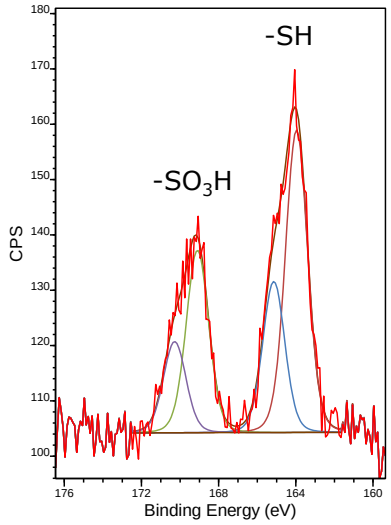
Clue to proteins identification – S 2p spectra



Chlorella vulgaris

13-1

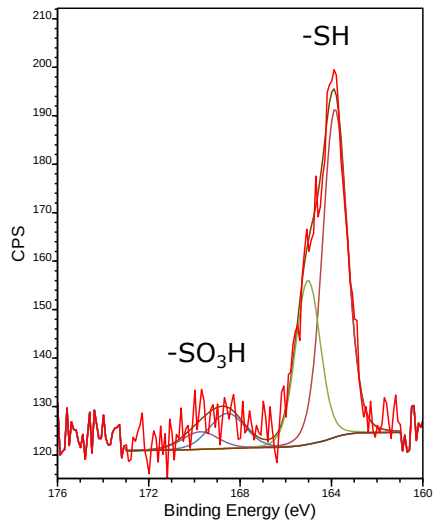
Non-flocculating



Coelastrella sp.

3-4

Auto-flocculating



Scenedesmus obliquus

RISE

Mildly auto-flocculating

One or two
S-containing proteins

Different protein orientation
at the surface?

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X-Ray Photoelectron Spectroscopy Platform

Collaboration:

Department of Chemistry:

Environmental Biogeochemistry – J.-F. Boily, K. Irgum, S. Jansson.
Technical Chemistry – J.-P. Mikkola.
Biological Chemistry – M. Ramstedt, C. Funk

Umeå University:

Department of Physics – T. Wågberg, A. Talyzin.
Department of Ecology and Environmental Science
Department of Medical Chemistry

Sweden:

Stockholm University, Uppsala University, LTU (Luleå), KTH (Stockholm), Mitt University (Sundsvall), RISE (Stockholm), FOI (Umeå), SLU (Umeå)

International:

The Hebrew University of Jerusalem, Weizman Institute of Science, Technical University of Košice, University of Barcelona, Copenhagen University, Aalto University, Helmholtz Zentrum Dresden-Rossendorf, University of Grenoble, Silicon Valley.

XPS Platform

Steering Committee:

Dr. A. Shchukarev, Dr. M. Ramstedt, Prof. J.-F. Boily, Prof. K. Irgum, Prof. L. Morozova-Roche

User fees 2020:

Instrument running cost – 750 kr/hour

Umeå University/SLU – 1650 kr/hour

External users – 1840 kr/hour

Industry – 3680 kr/hour

Finance 2020 (Jan – Oct):

Income (XPS analysis) – 700 000 sek, Support from the Department of Chemistry – 30% of salary (AS), KBC – 200 000 sek

XPS running cost – 254 914 sek (service contract, spares, consumables, etc.)

XPS Platform

Upcoming projects and future plans

Surface composition of viable viruses and fungi - already started

New XPS spectrometer with fast-freezing and LEIPS (Low Energy Inverse Photoemission) options.

Acquiring and training of new employee(s)

Thank you for your attention
and see your samples soon!

Contact information: Andrey Shchukarev
Chemistry Department, C6, room B6-35-07 (XPS lab) and B6-33-07 (office), tel. 090-786 5361.
E-mail: andrey.shchukarev@umu.se