

# Analysis of paper materials using modern FIB-SEM electron microscope

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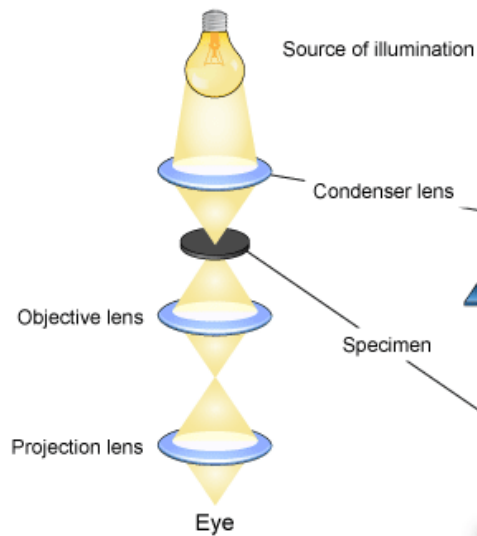
*<sup>2</sup>Pulp and paper institute, Bogišičeva 8, Ljubljana, Slovenia*



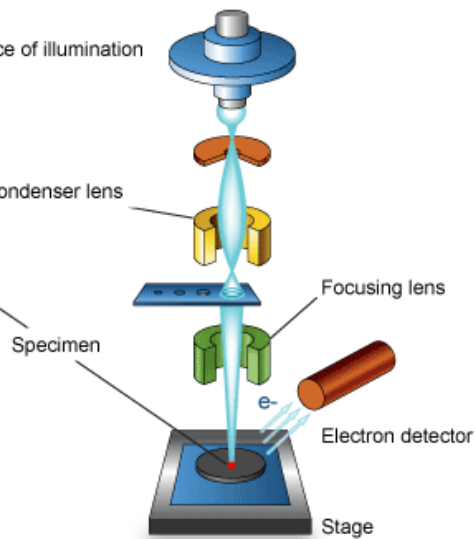
# Scanning Electron Microscopy as a tool for material analysis



## Optical microscope



## Scanning electron microscope



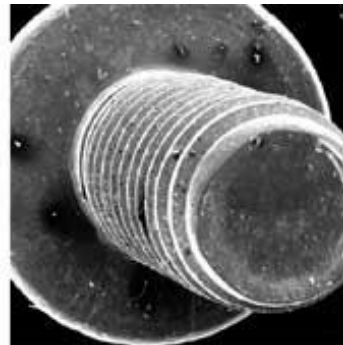
## The main advantages of SEM microscope

- High resolution (below 1 nm)
- High magnifications
- Large depth of field
- Analytical imaging
- Chemical analysis (EDXS)
- Crystallography analysis (EBSD)
- Several other upgradable extensions...

Image source: <http://www.ammrf.org.au/myscope/sem/background/>



plane image



depth image !

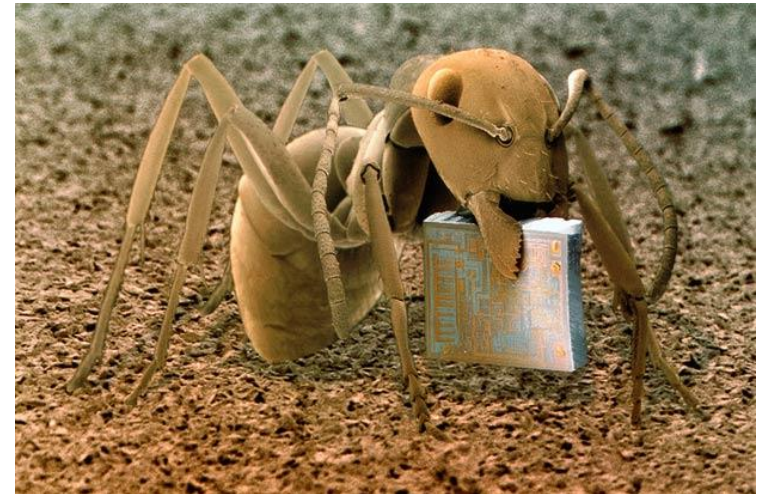
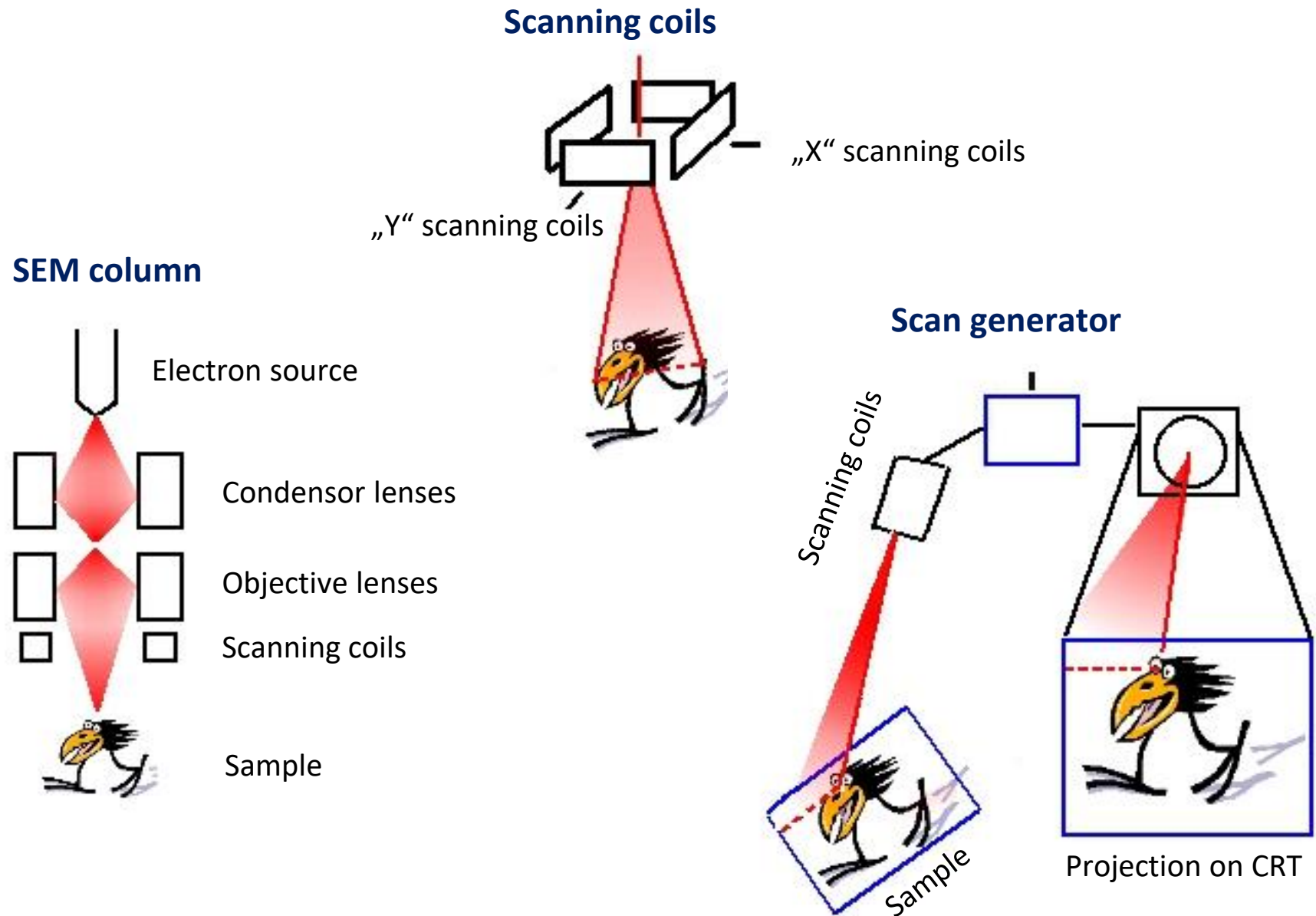
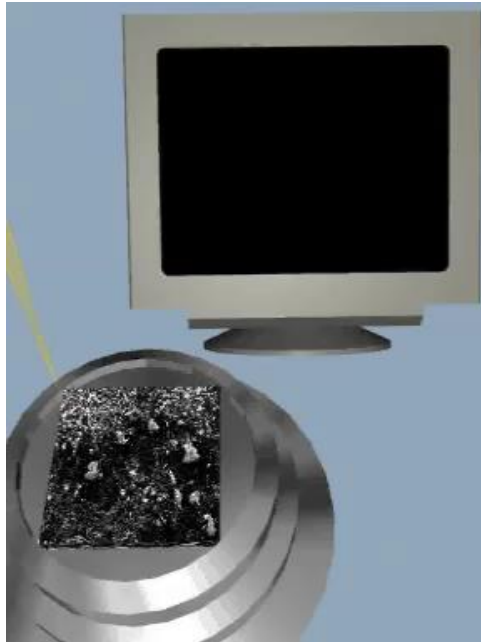


Image source: <http://www.telegraph.co.uk/>

# Scanning Electron Microscope – basic concept of operation



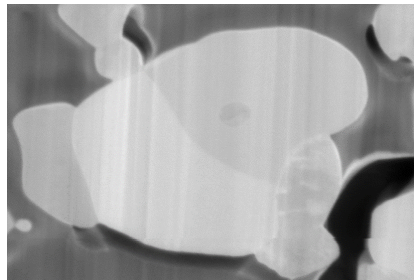
# Scanning Electron Microscope – basic concept of operation



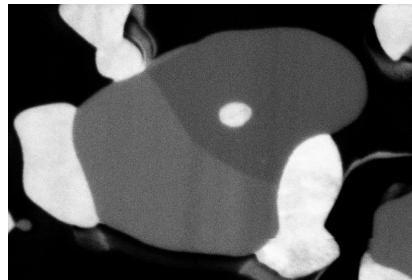
Area Scanned On Sample



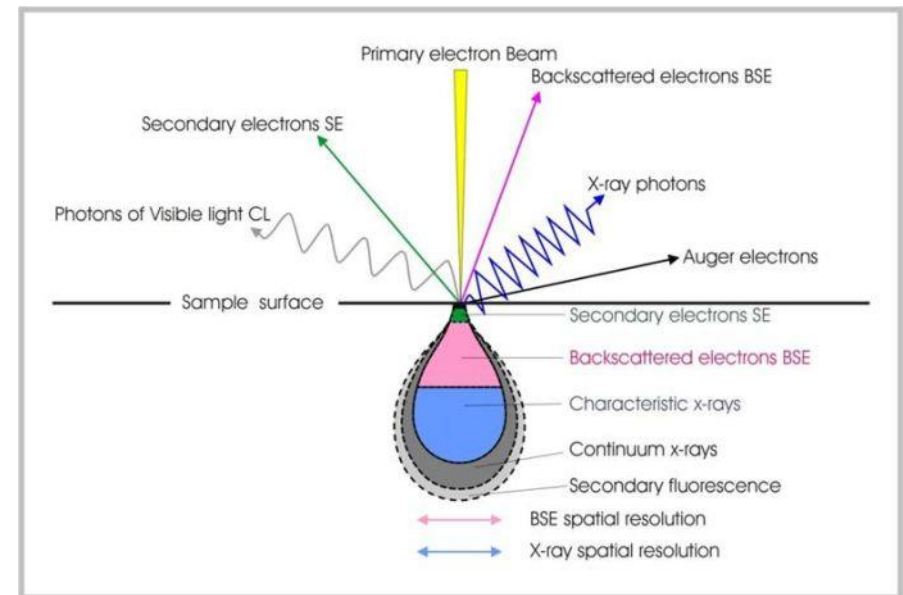
Image on CRT



SE image



BSE image





# Conventional SEM vs. modern high resolution SEM

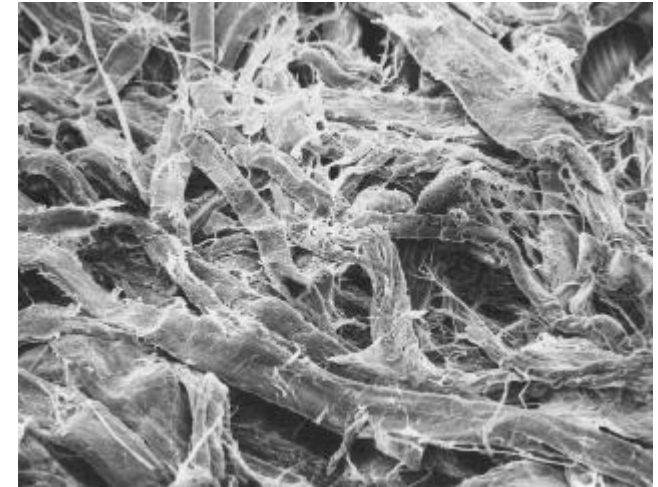


Conventional SEM



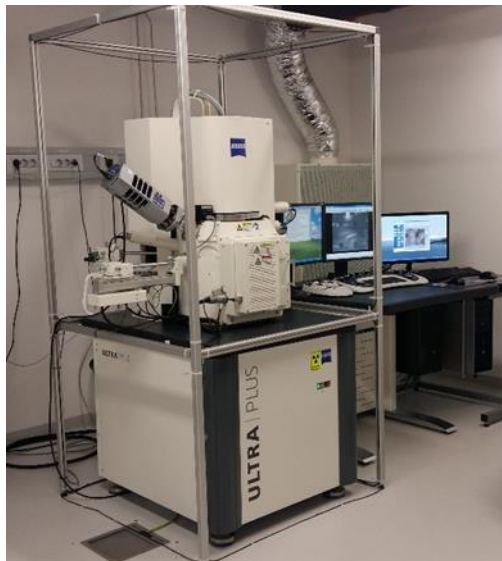
JEOL T300

Conductive layer  
is mandatory



high kV (gold coated sample)

Modern HR-SEM

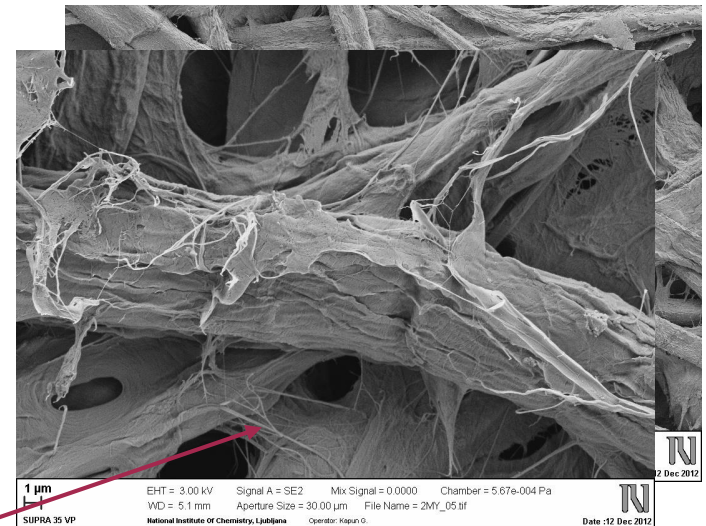


Zeiss Ultra+

Conductive layer  
not necessary

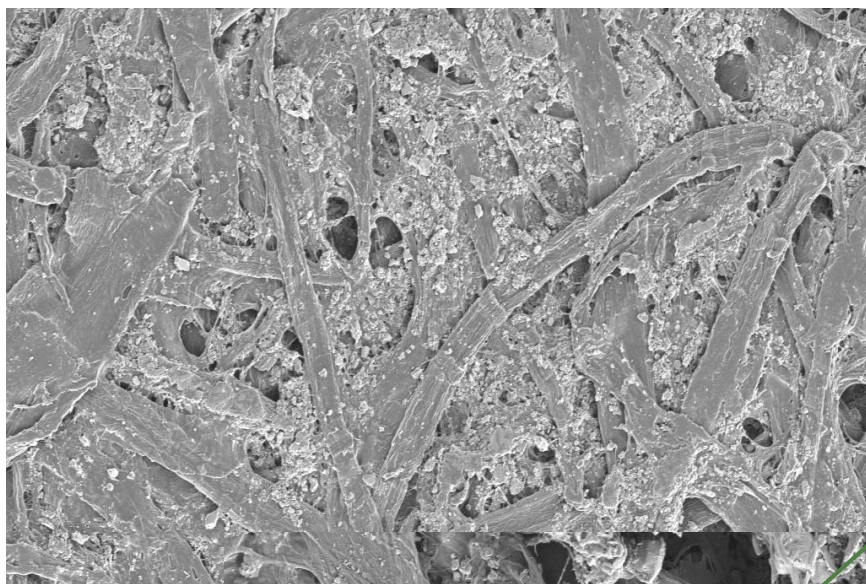


True surface information,  
revealing detailed structures!



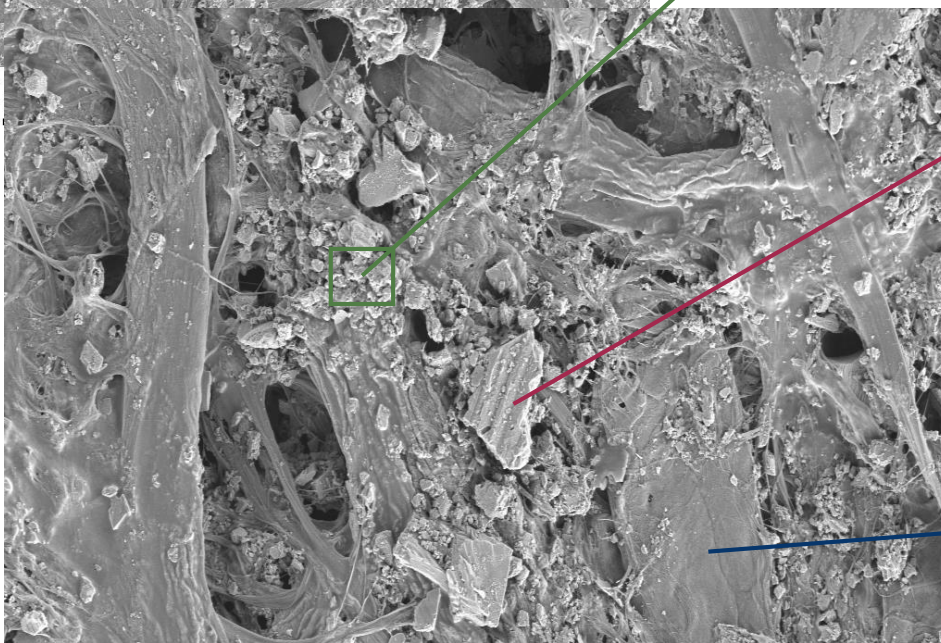
low kV (uncoated sample!)

# HR-SEM: surface analysis of commercial paper material



10  $\mu\text{m}$   
Zeiss, Ultra Plus

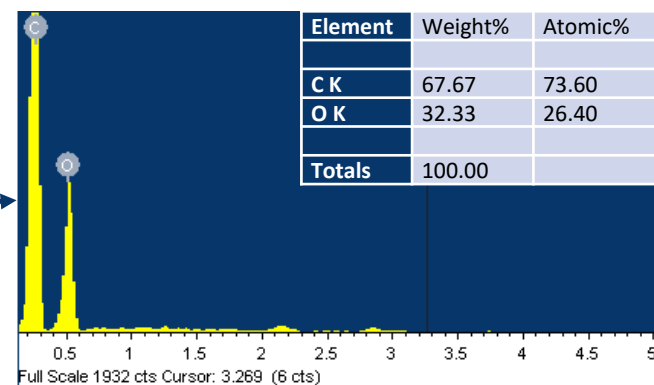
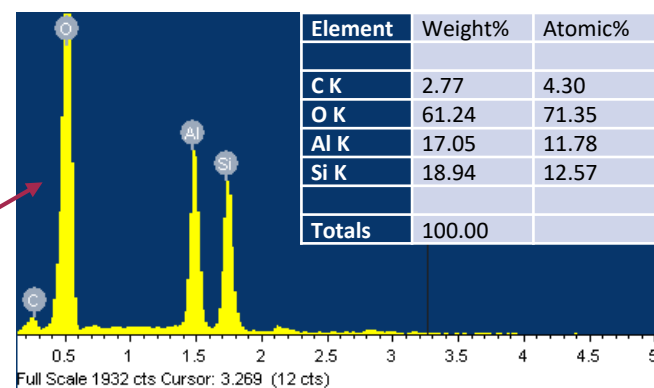
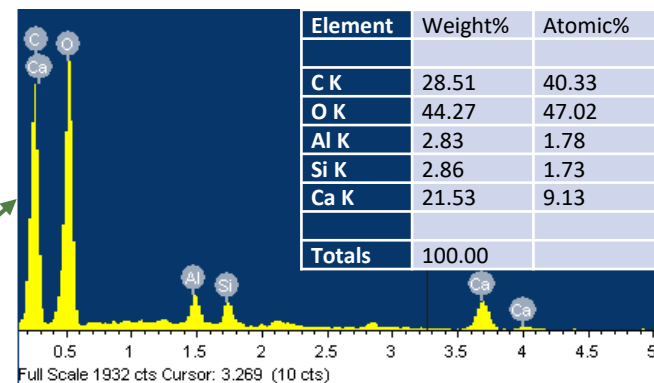
EHT =  
WD =  
National



10  $\mu\text{m}$   
Zeiss, Ultra Plus

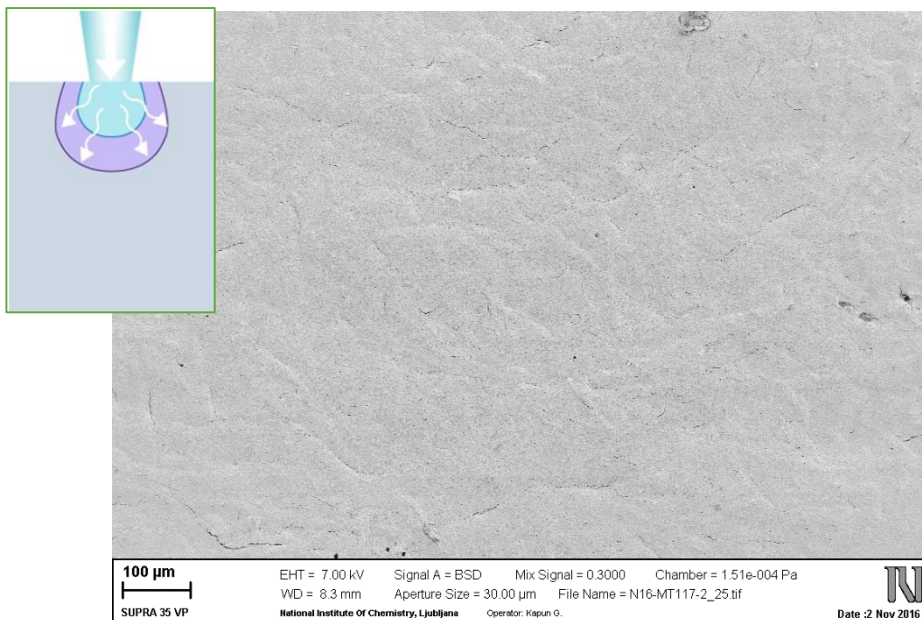
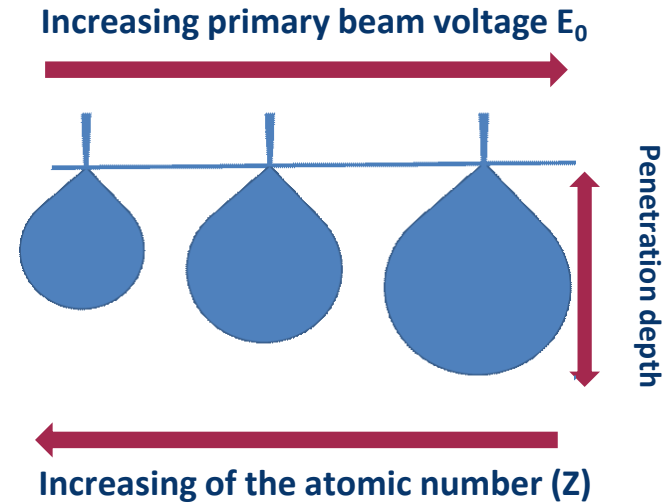
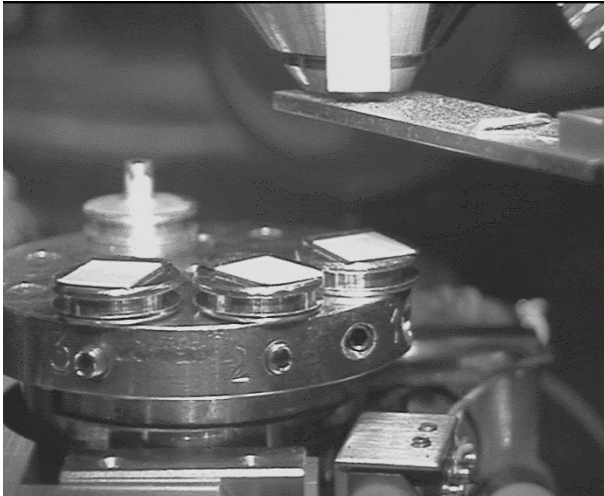
EHT = 3.00 kV Signal A = SE2 Mix Signal = 0.0000 ESB Grid = 859 V  
WD = 5.0 mm Aperture Size = 30.00  $\mu\text{m}$  File Name =  
National Institute of Chemistry, Ljubljana Operator: Kapun G.

NI  
Date :11 Dec 2015

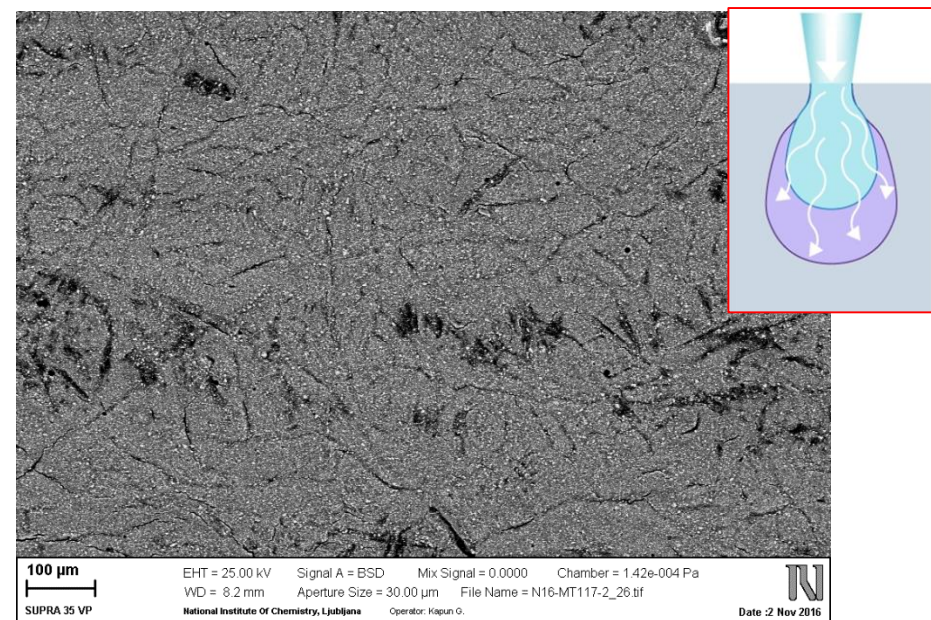




# SEM-BSD: coating homogeneity on the paper surface



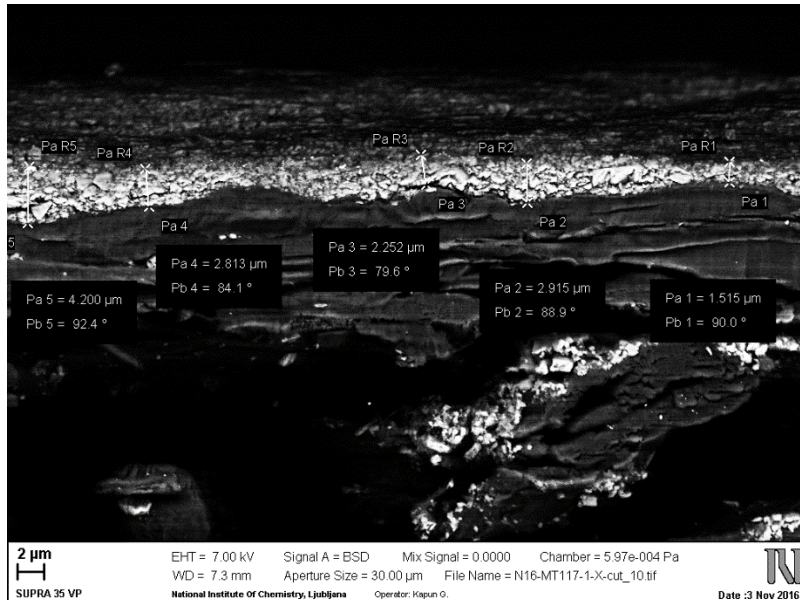
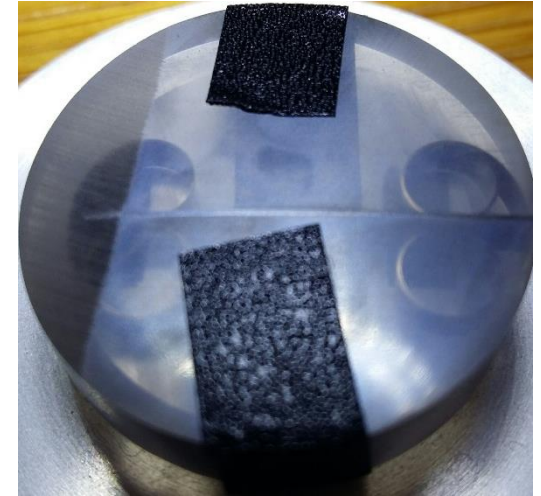
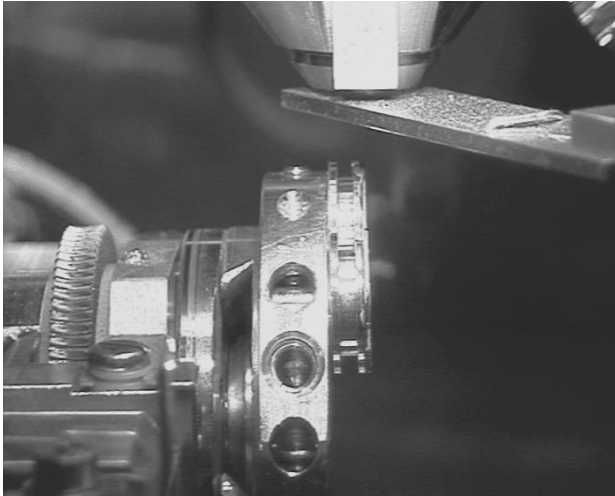
Surface of commercially coated paper: **BSD @7kV**



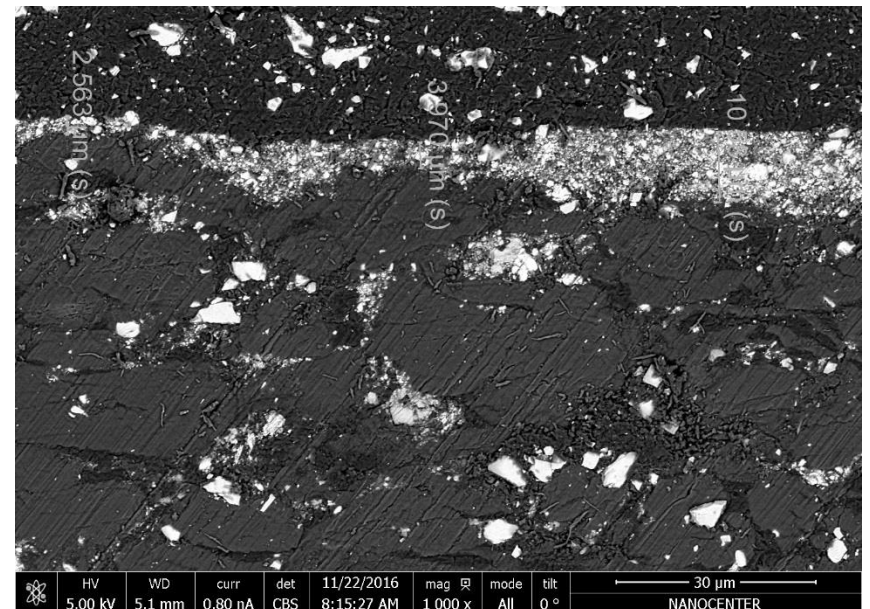
Surface of commercially coated paper: **BSD @25kV**



# HR-SEM: conventionally cross-section analysis of paper material



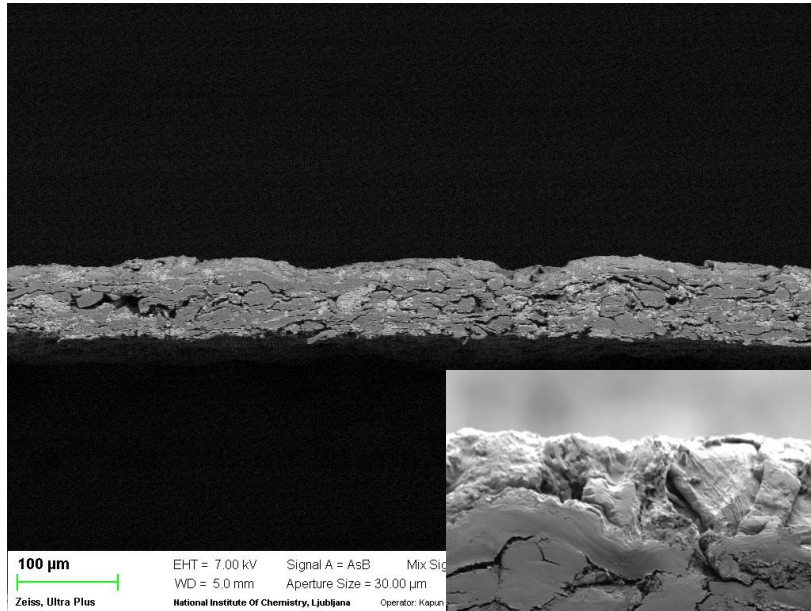
Mechanically prepared cross-section: **BSD @7kV**



Analysis of polished paper cross-section: **BSD @5kV**



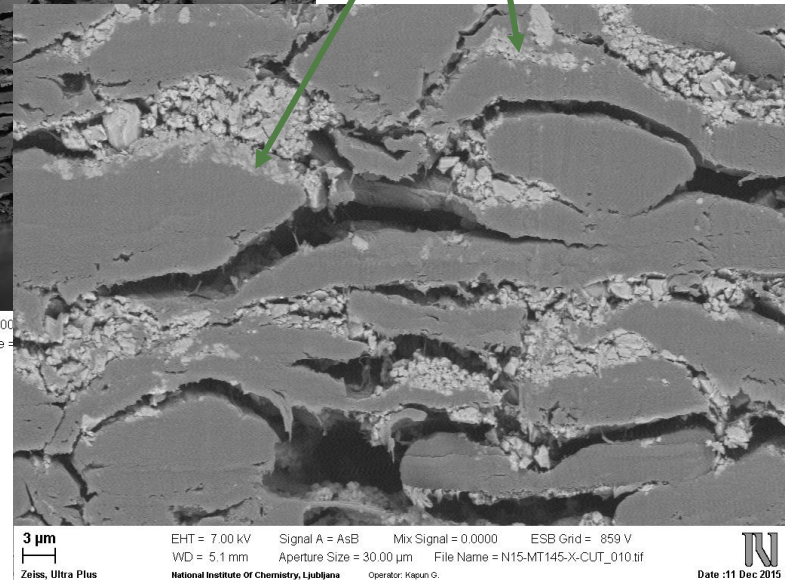
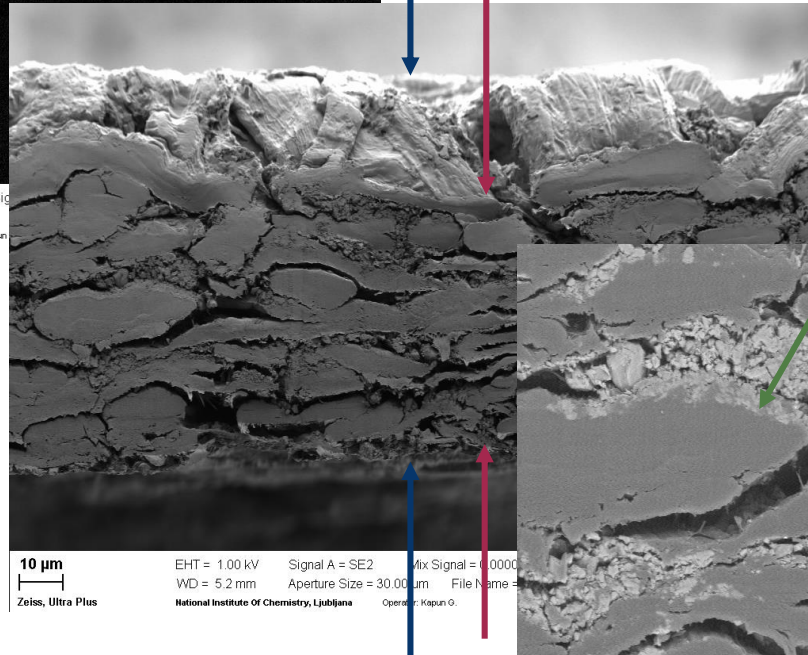
# HR-SEM: conventionally cross-section analysis of paper material



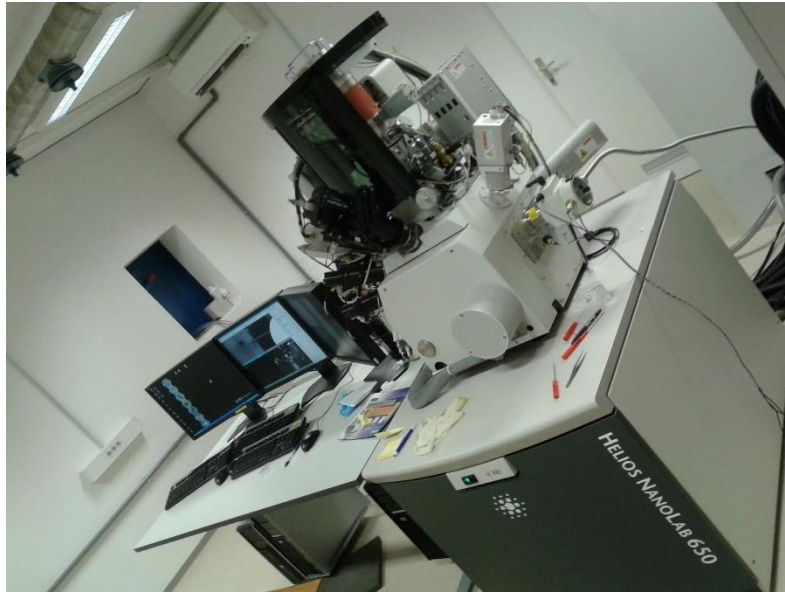
Real thickness

Mechanical deformation!

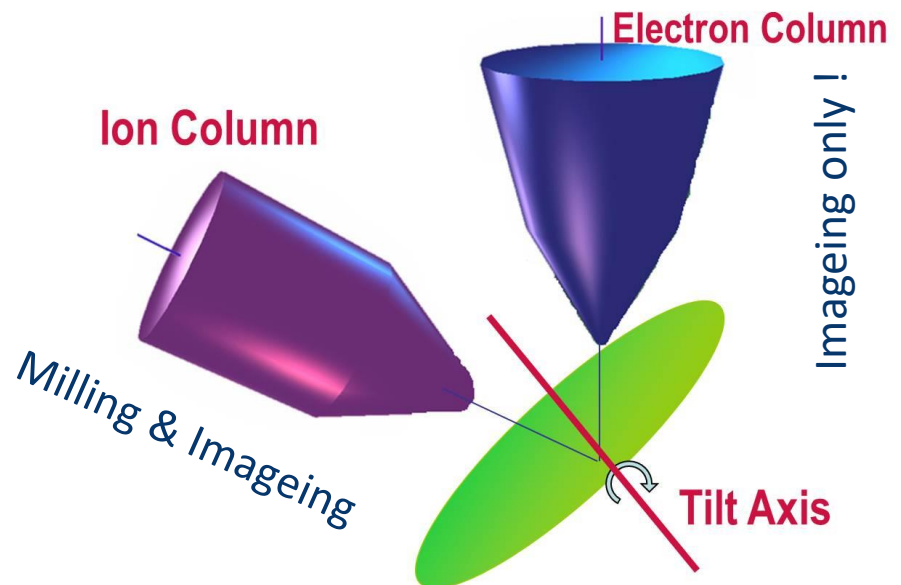
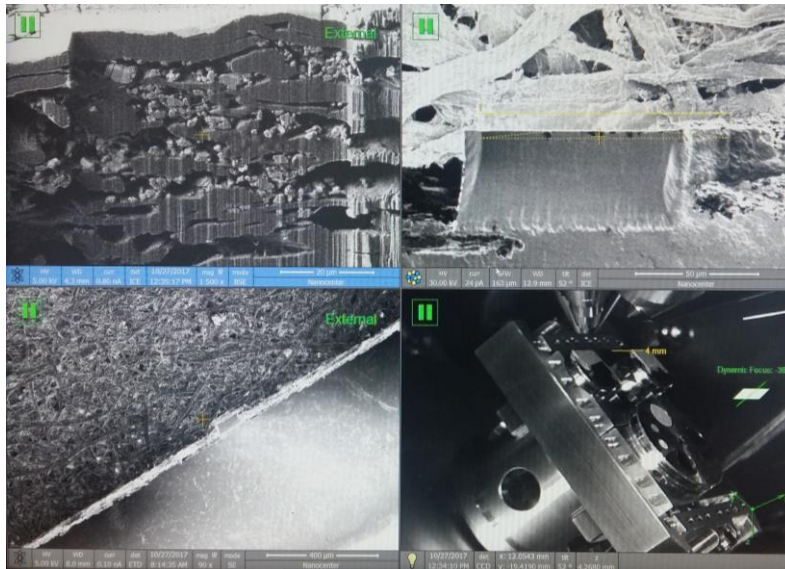
Displacement of harder material across soft matter during preparation of mechanical cross-section



# Focused Ion Beam – Scanning Electron Microscope (FIB-SEM)

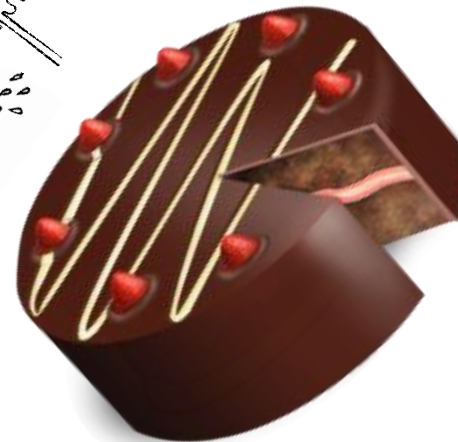
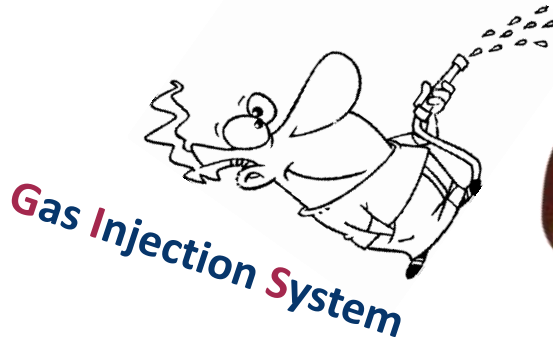
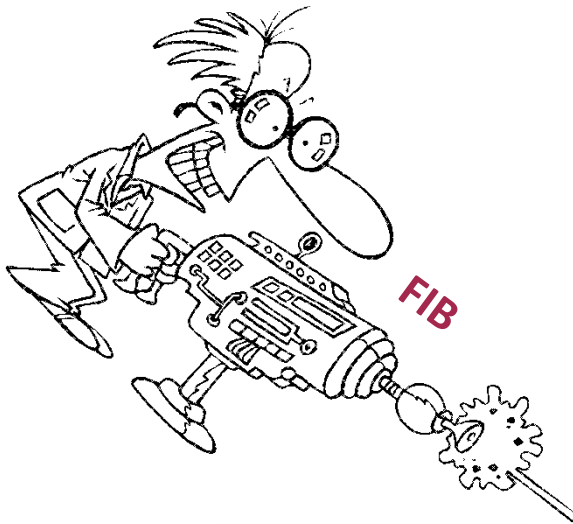
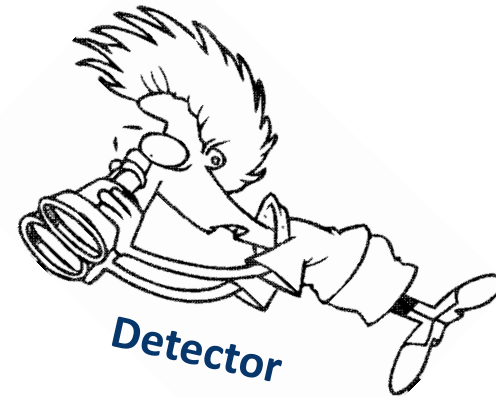
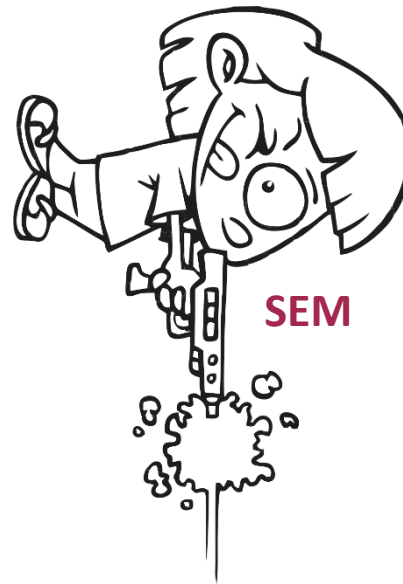
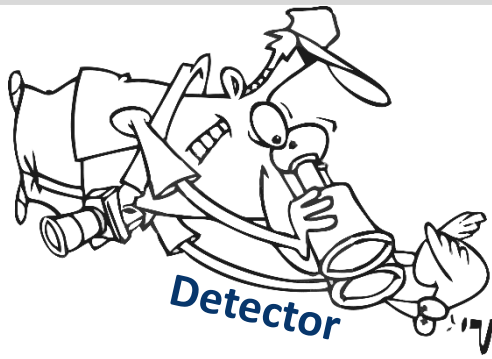


- FIB-SEM dual beam system incorporates:  
electron column → **focused electron source**  
+  
ion column → **focused ion source**
- Instrument is used for nano-patterning, TEM sample preparation, 3D tomography and deposition of thin conductive or dielectric films via ion-beam induced deposition.

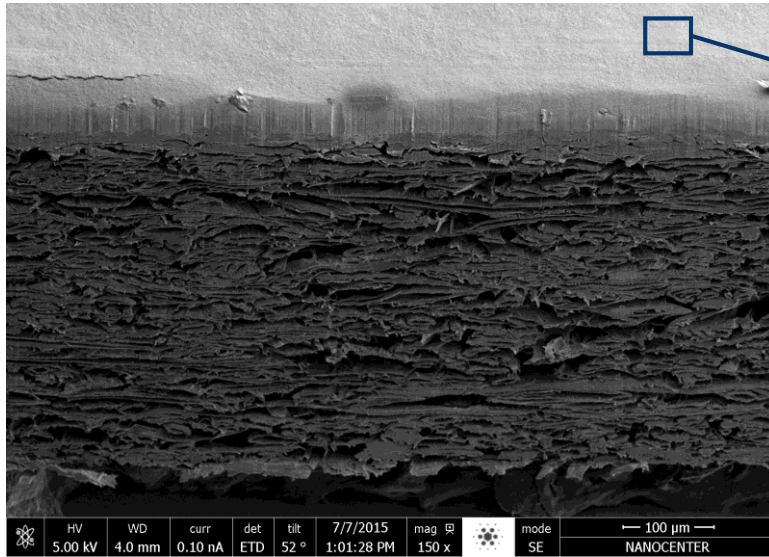




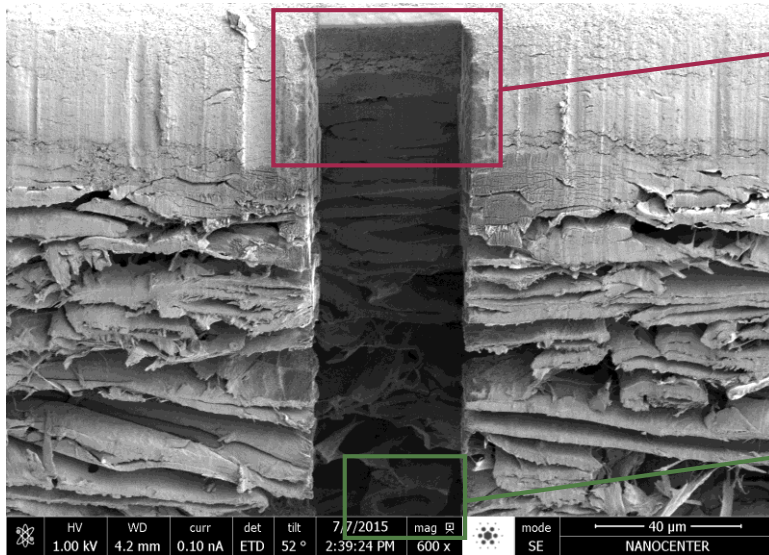
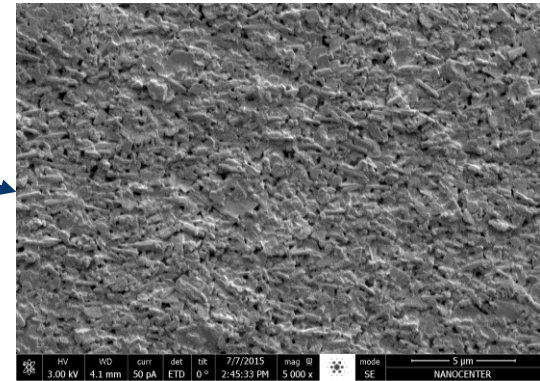
# FIB-SEM – basic concept of operation



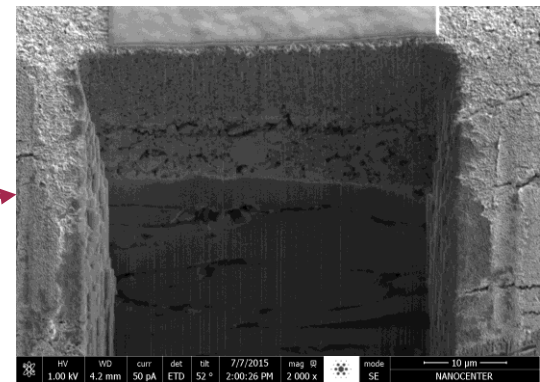
# FIB-SEM: ion polished cross-section of cardboard packaging



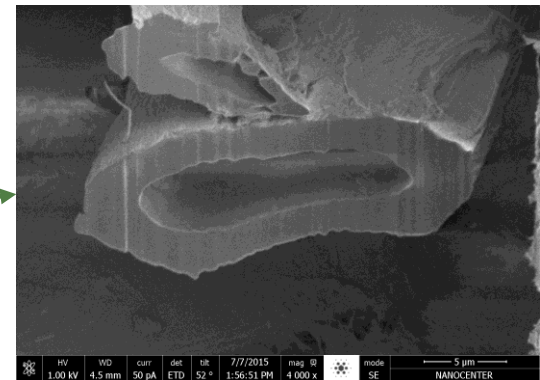
Surface



Coating-paper interface



paper fibre cross-section

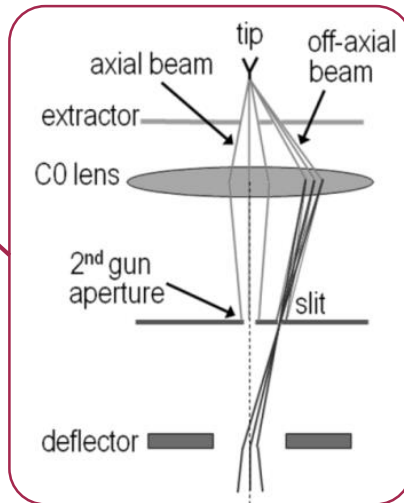
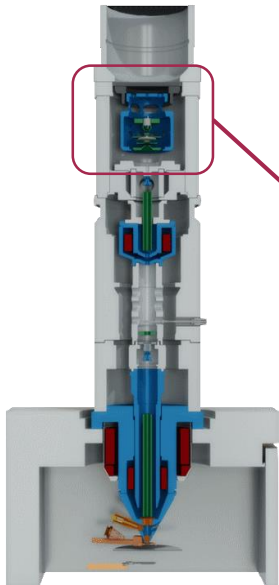
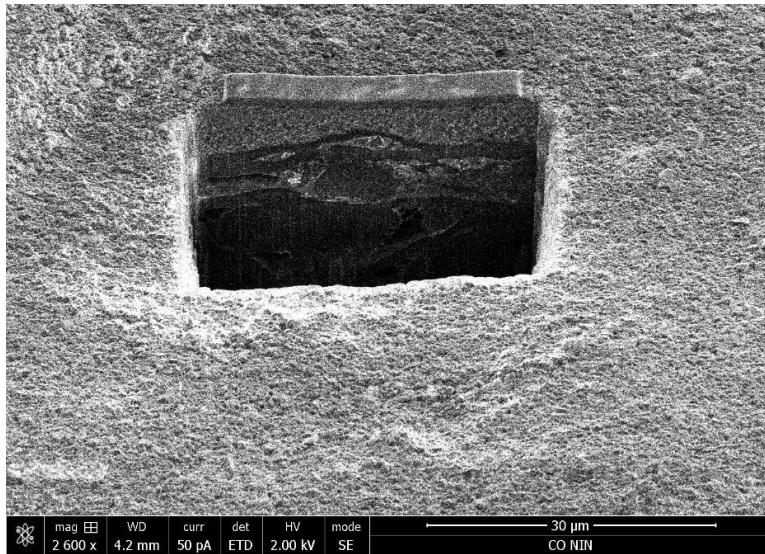




# FIB-SEM: paper material – very challenging for electron imaging



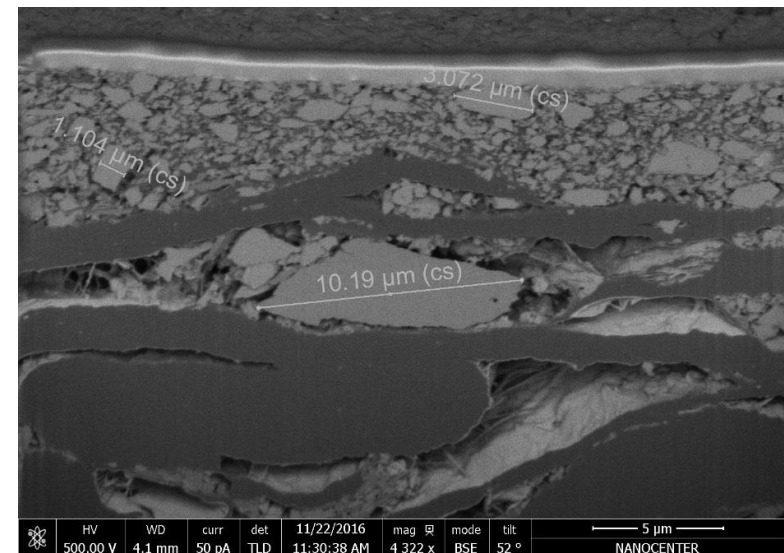
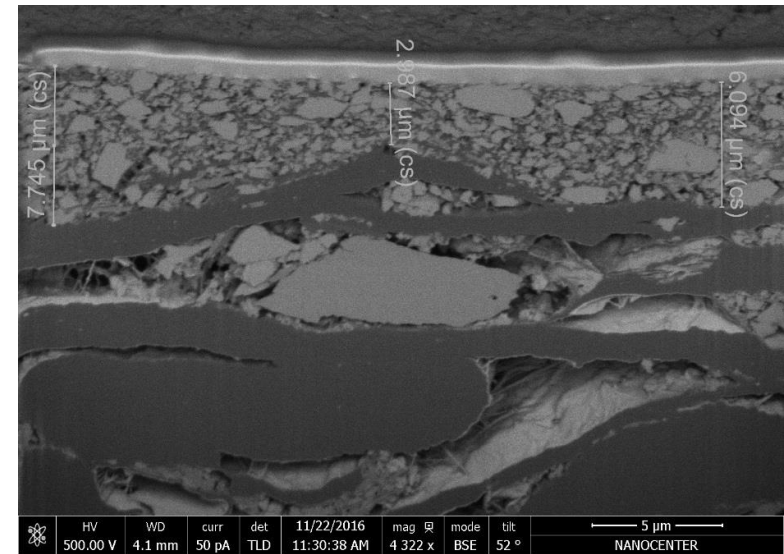
## Conventional low kV e-beam imaging

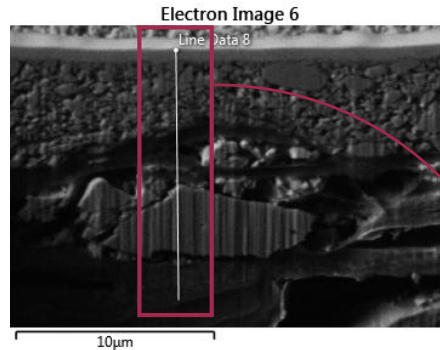


## monochromator

Analytical image with Z-contrast information!

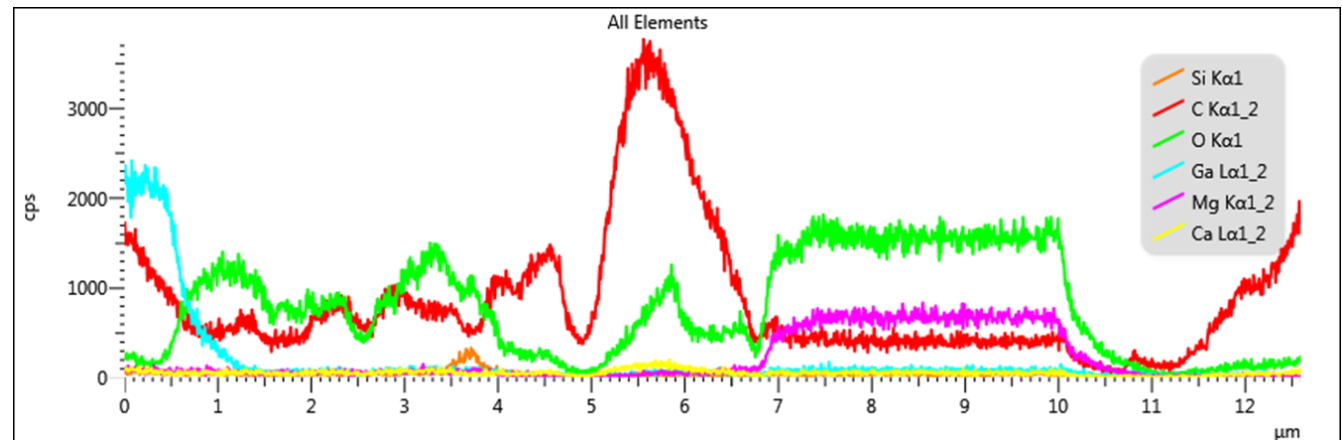
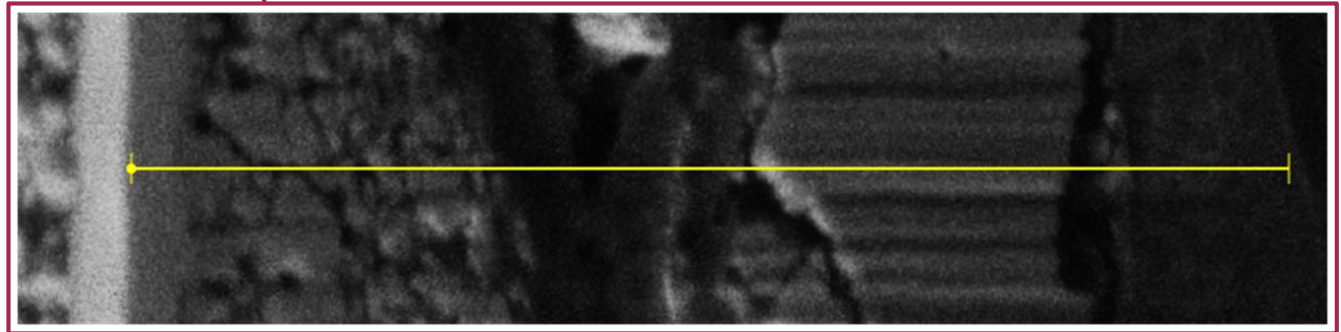
## Very low kV e-beam imaging + U-mode





Low kV EDXS line profile:

- Thickness of layers according to their elemental composition
- In particular case coating layer and filler material has different composition

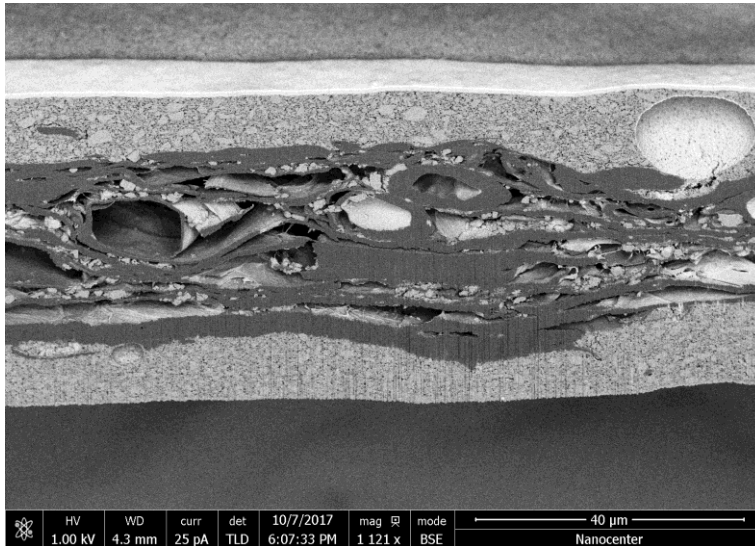
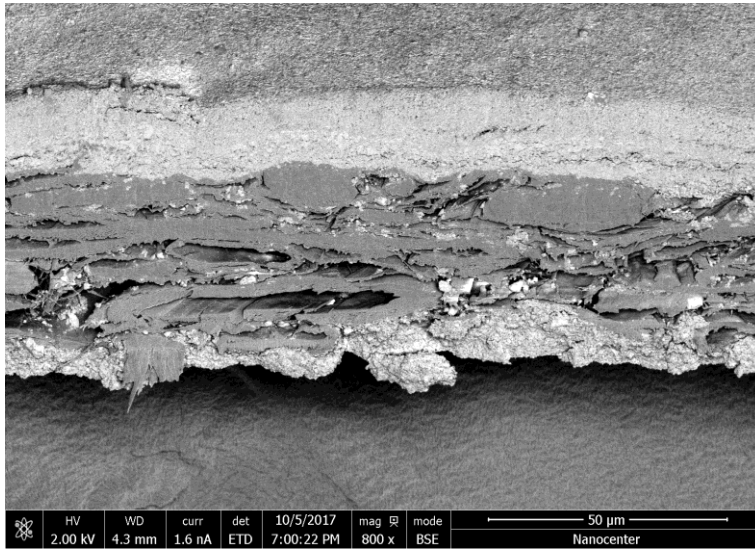




# FIB-SEM: paper material – very challenging for electron imaging

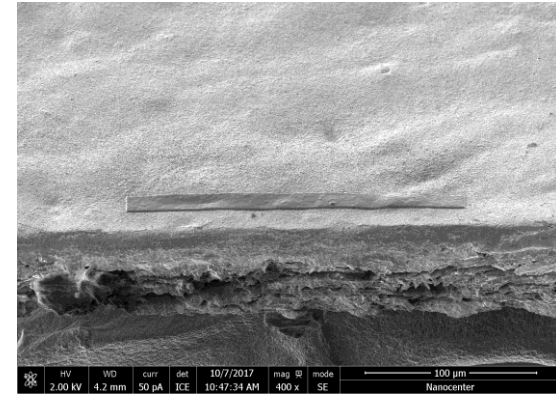


## Mechanical prepared cross-section

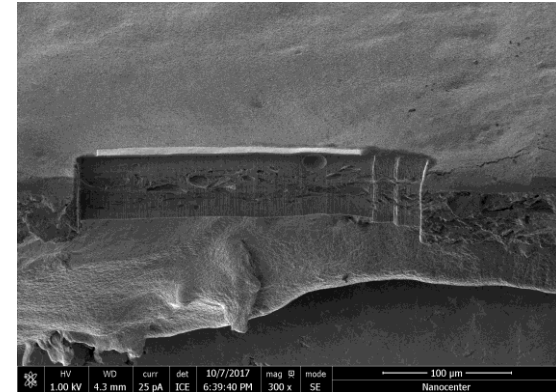


## FIB-SEM prepared cross-section

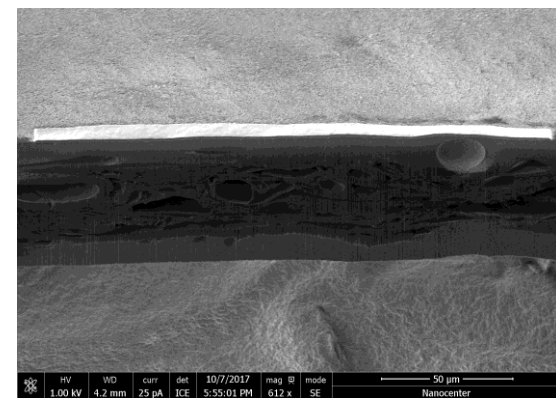
FIB-SEM cross-section preparation steps



„in situ“ Pt protection  
layer deposition



Rough cut using high  
current focused ions



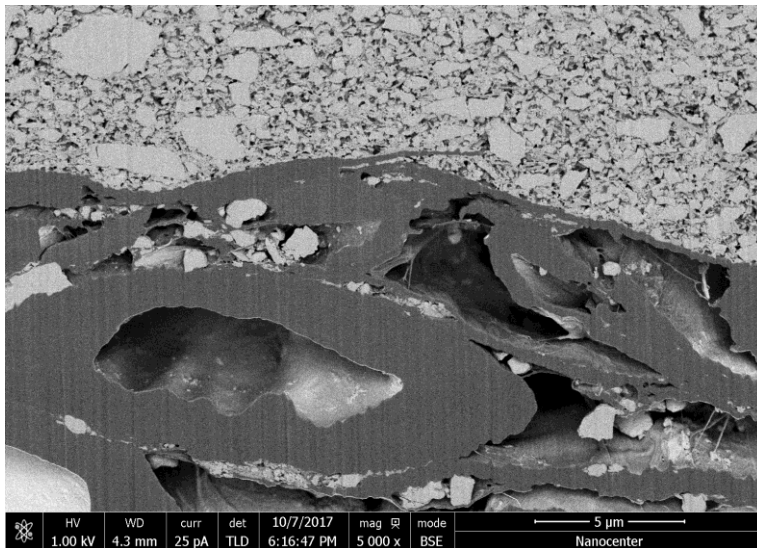
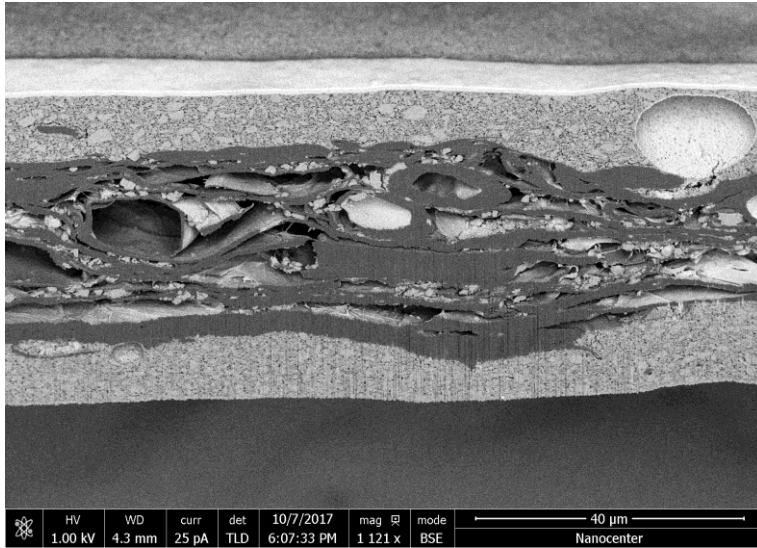
Polishing using low  
current focused ions



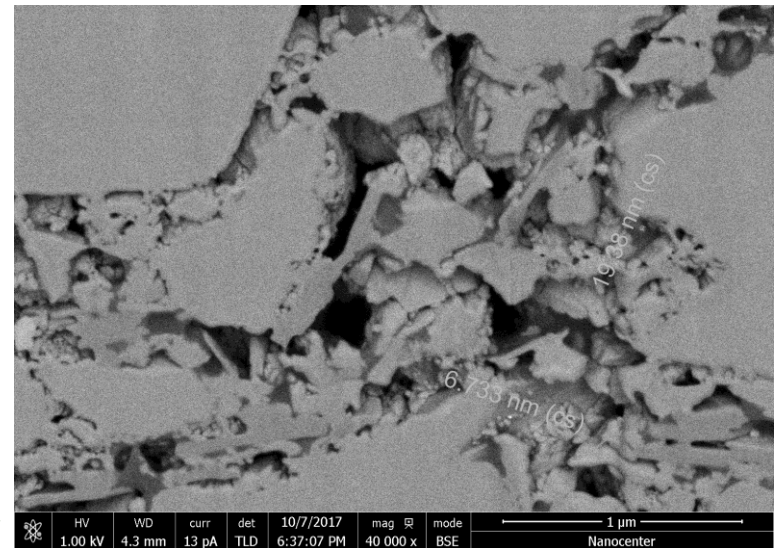
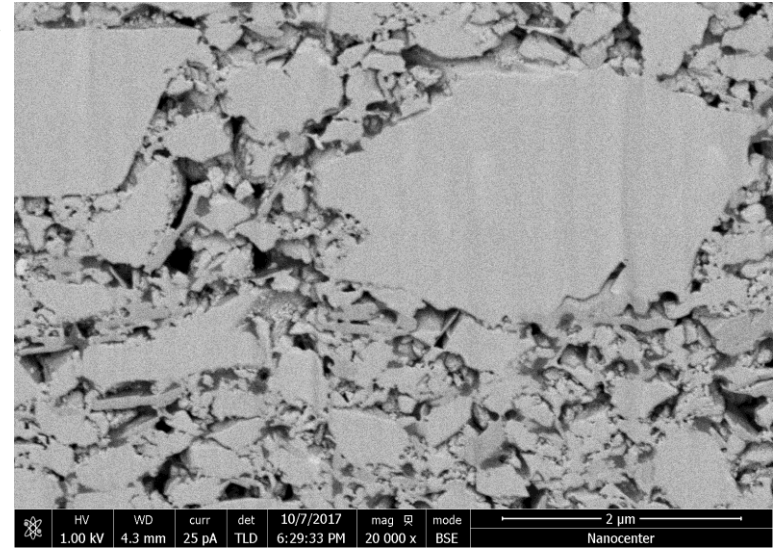
# FIB-SEM: paper material – very challenging for electron imaging



FIB-SEM prepared cross-section of double side coated commercial paper using focused ions and imaged with low energy pre-monochromated electron beam (UHR U-mode, 1kV@25pA – Z contrast)

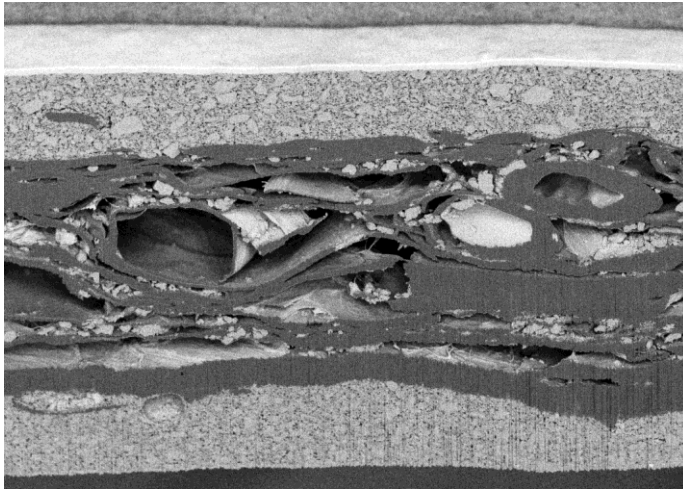


Cross-sectional images of coating acquired at UHR conditions

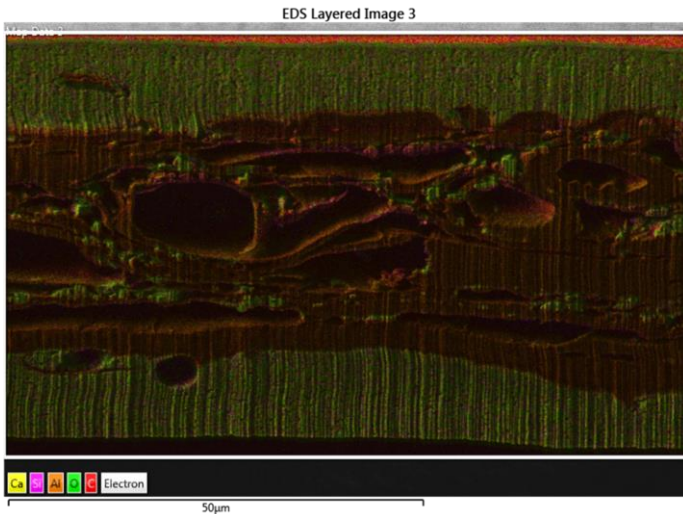




# FIB-SEM: paper material – very challenging for electron imaging



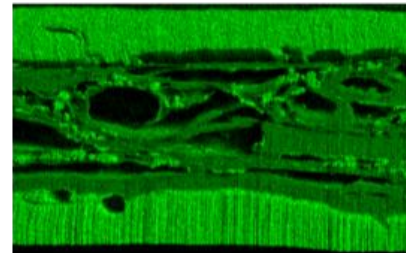
FIB-SEM prepared cross-section of double side coated commercial paper using focused ions and imaged with low energy pre-monochromated electron beam (UHR U-mode, 1kV@25pA, Z contrast)



Low kV EDXS TrueMap analysis

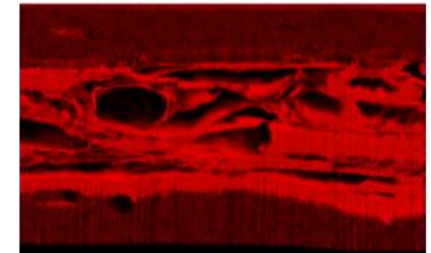


O K series



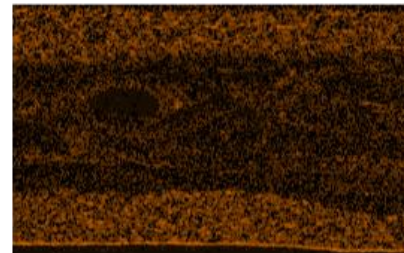
25µm

C K series



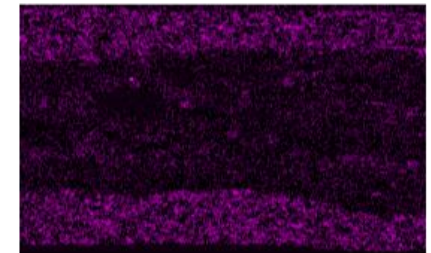
25µm

Al K series



25µm

Si K series



25µm

Expensive fillers



Side products as cost effective fillers



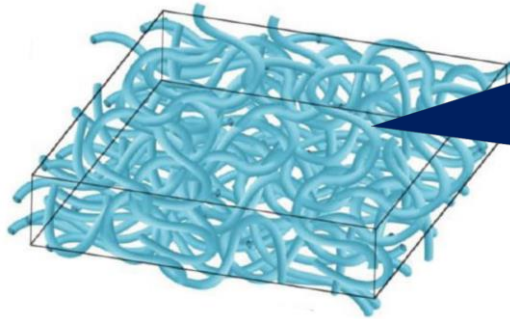
OR

**BUT !**

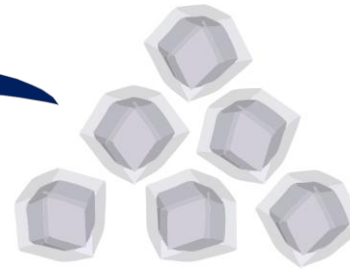
**CHALLENGE**

Cost effective  
Industrial process

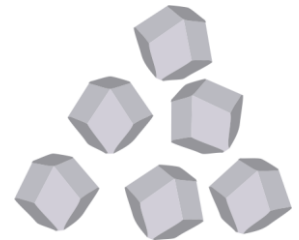
**SOLUTION**



Cellulose fibers



Coated  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$   
(stable)



Raw  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$   
(soluble)



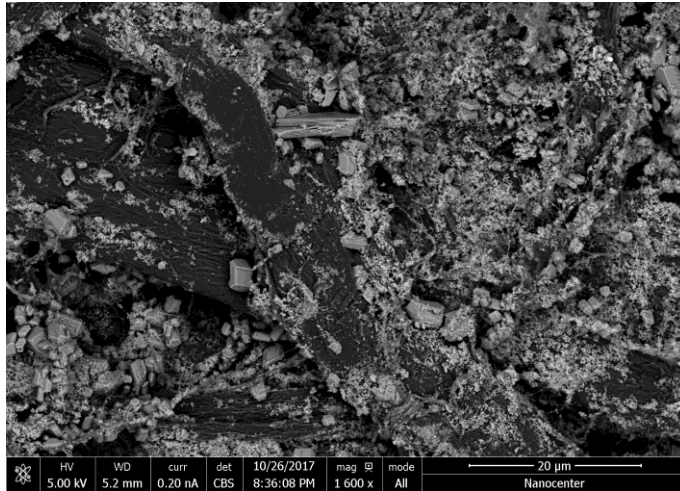
Research + Good analytical support!



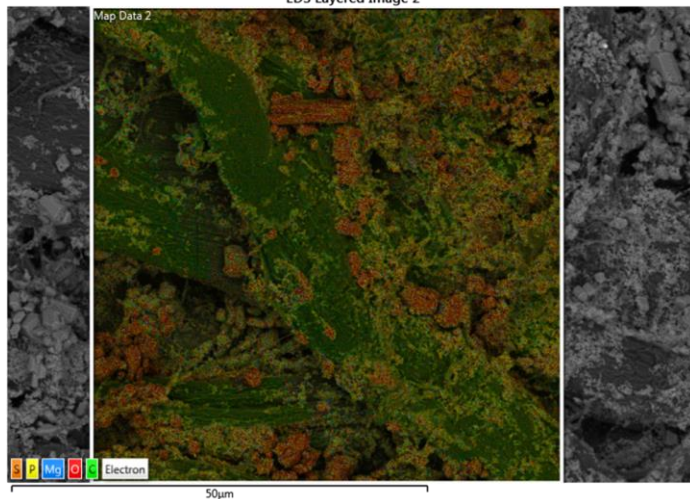
# „in situ“ coating of the filler particles formulated directly in paper mass



„in situ“ preparation of  $\text{Na}_2\text{HPO}_4$   
coating on  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  filler

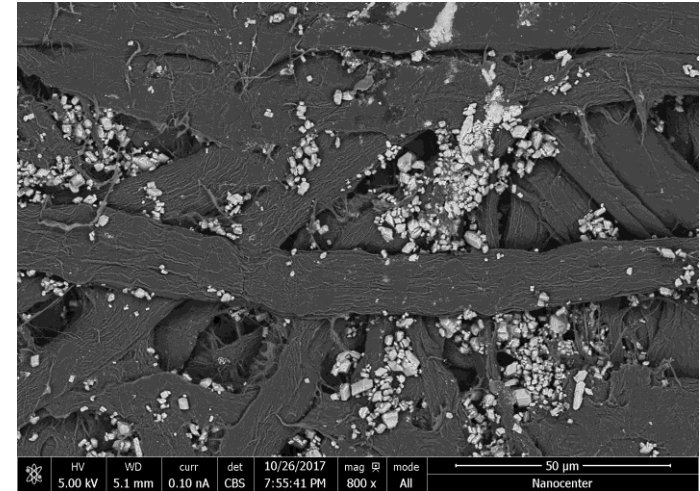


EDS Layered Image 2

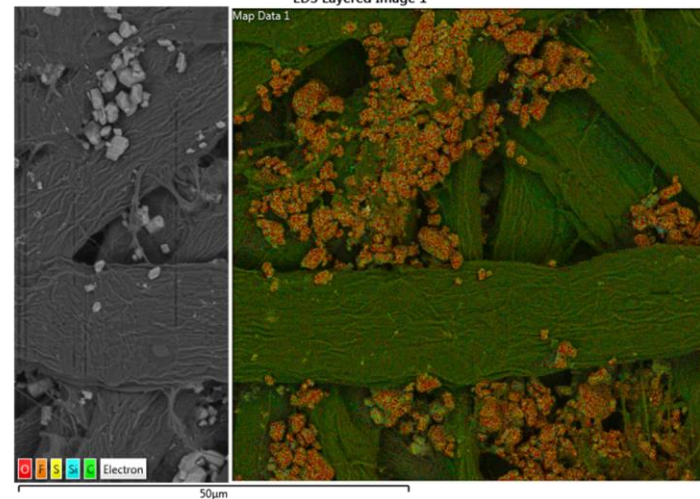


SEPARATED

„in situ“ preparation of  $\text{Na}_2\text{CO}_3$   
coating on  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  filler

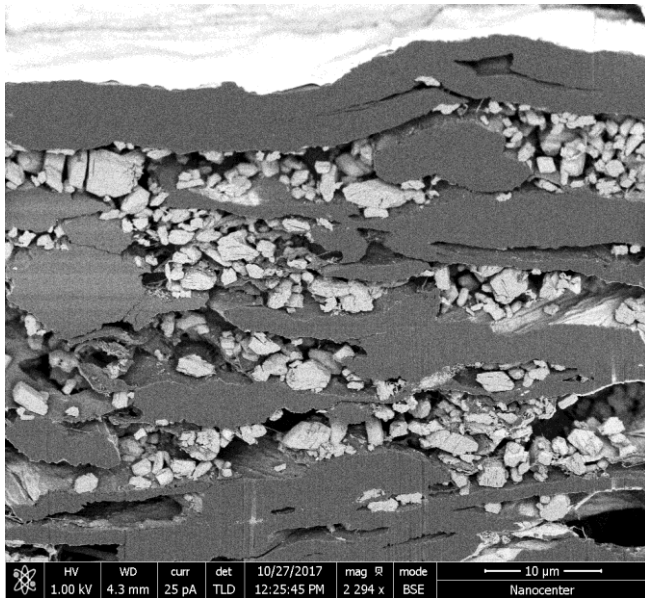


EDS Layered Image 1



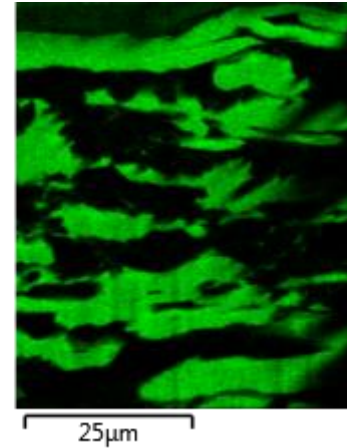
SUCCESSFUL COATING PROCEDURE

# FIB-SEM: cross-sectional analysis of paper with $\text{CaCO}_3$ coated filler

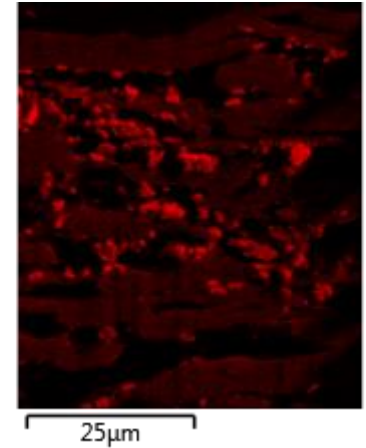


## Low kV EDXS TrueMap analysis

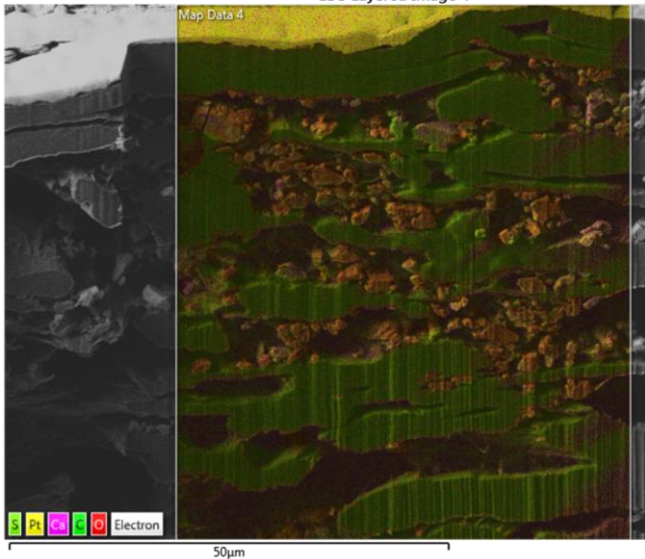
C K series



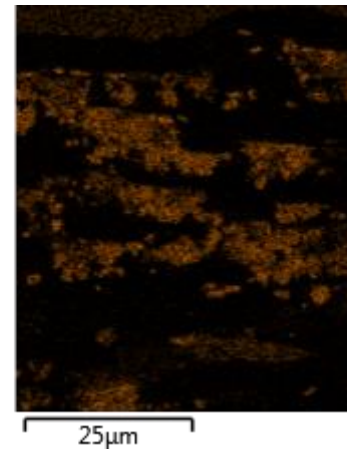
O K series



EDS Layered Image 4



S K series



Ca K series

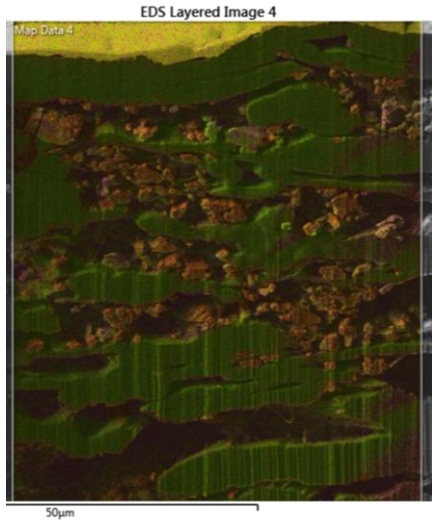




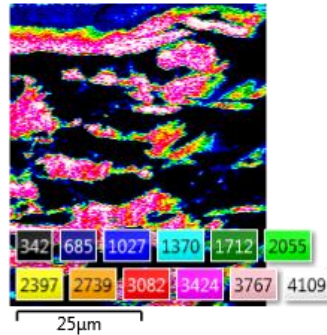
# FIB-SEM: cross-sectional analysis of paper with $\text{CaCO}_3$ coated filler



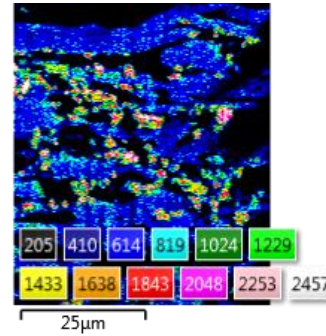
## Low kV EDXS spectrum imaging – quantitative results



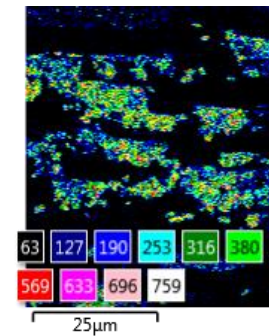
C K series



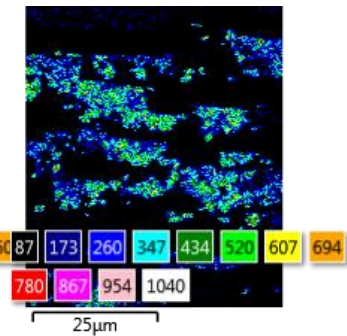
O K series



S K series

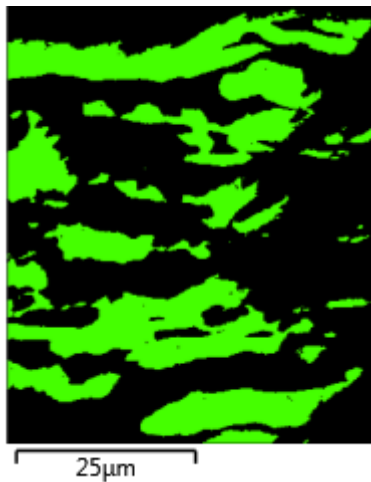


Ca K series



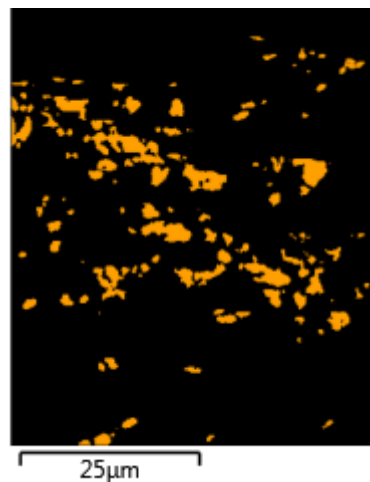
## Phase analysis of quantitative spectrum imaging data

Phase 1 CO



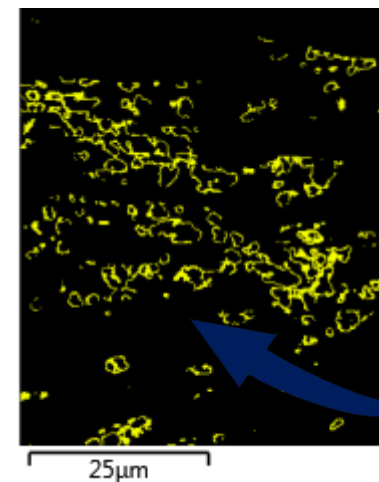
Celulose fibers

Phase 2 CaSO



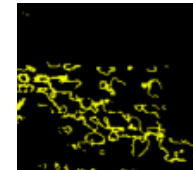
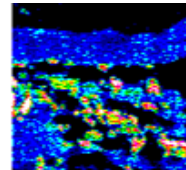
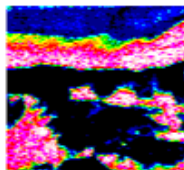
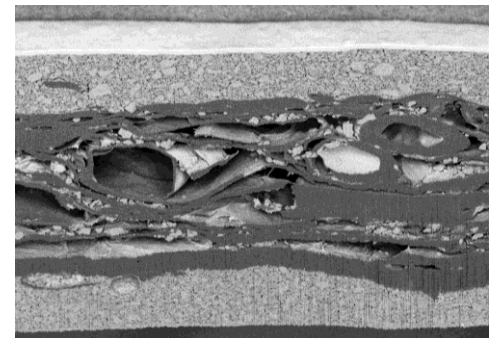
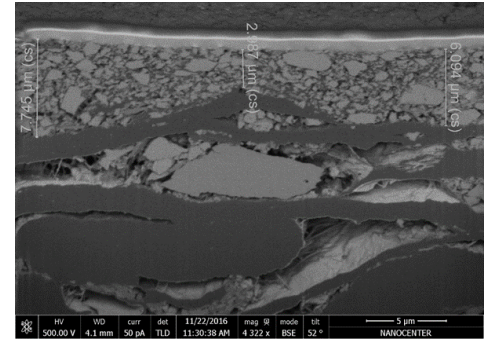
Calcium sulphate

Phase 3 CCaSO



Calcium carbonate  
coating on top of  
filler

- FIB-SEM can be used for producing clean cross-sections of various paper materials while preserving their original form,
- In addition to SEM microscope, FIB-SEM provides surface and cross-sectional material analysis at the same time,
- Use of Low kV e-beam energies enables true-surface imaging of all present morphological forms within the paper material,
- Introduction of monochromator enables use of very low kV e-beam energies which eliminates beam damage and charging effects. It further provides UHR analytical imaging (Z-contrast),
- Combination of FIB-SEM and EDXS techniques offers elemental analysis of surface and cross-section of various paper materials (quantitative identification and distribution of any component),
- Use of advanced EDXS techniques such as spectrum imaging in addition provides detailed quantitative analysis and/or phase analysis of any present component within paper material.





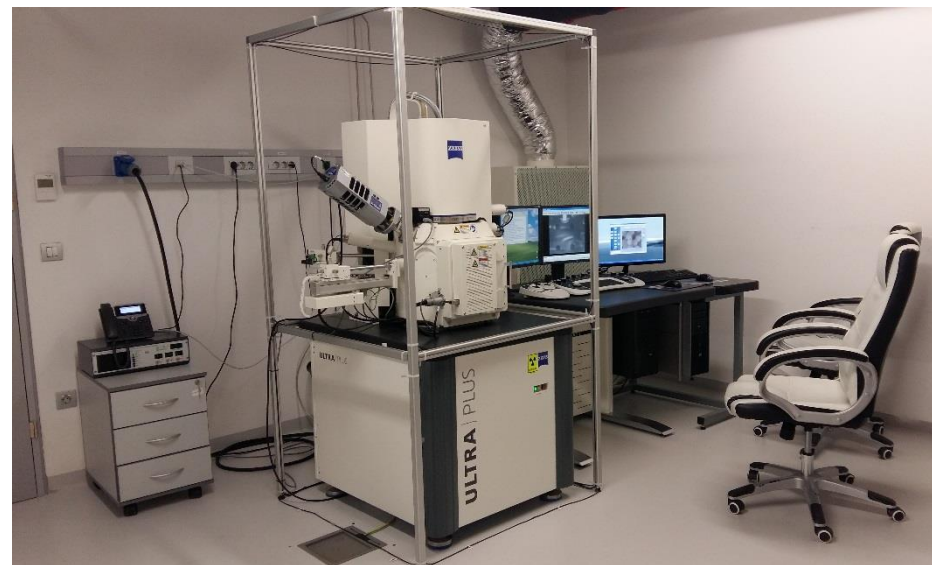
# High end HR-SEM's and FIB-SEM instruments available to NIC



## FE-SEM SUPRA 35 VP



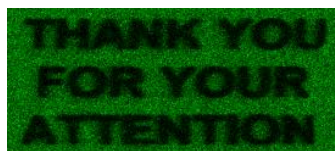
## FE-SEM Ultra+



10µm



10µm



10µm

## FIB Helios Nanolab 650i

