Chemical characterization of paper surfaces by ESCA and TOF-SIMS

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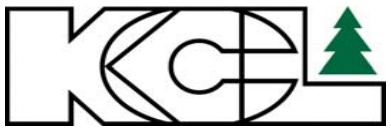
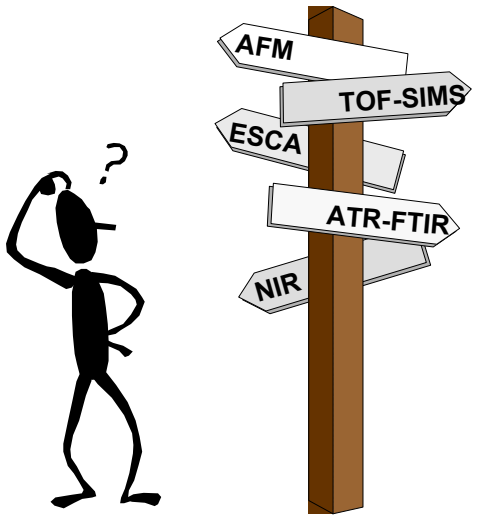


How to see surface molecules?

- **Isolation of surface material followed by analysis**
  - **mechanical peeling**
  - **enzymatic peeling**

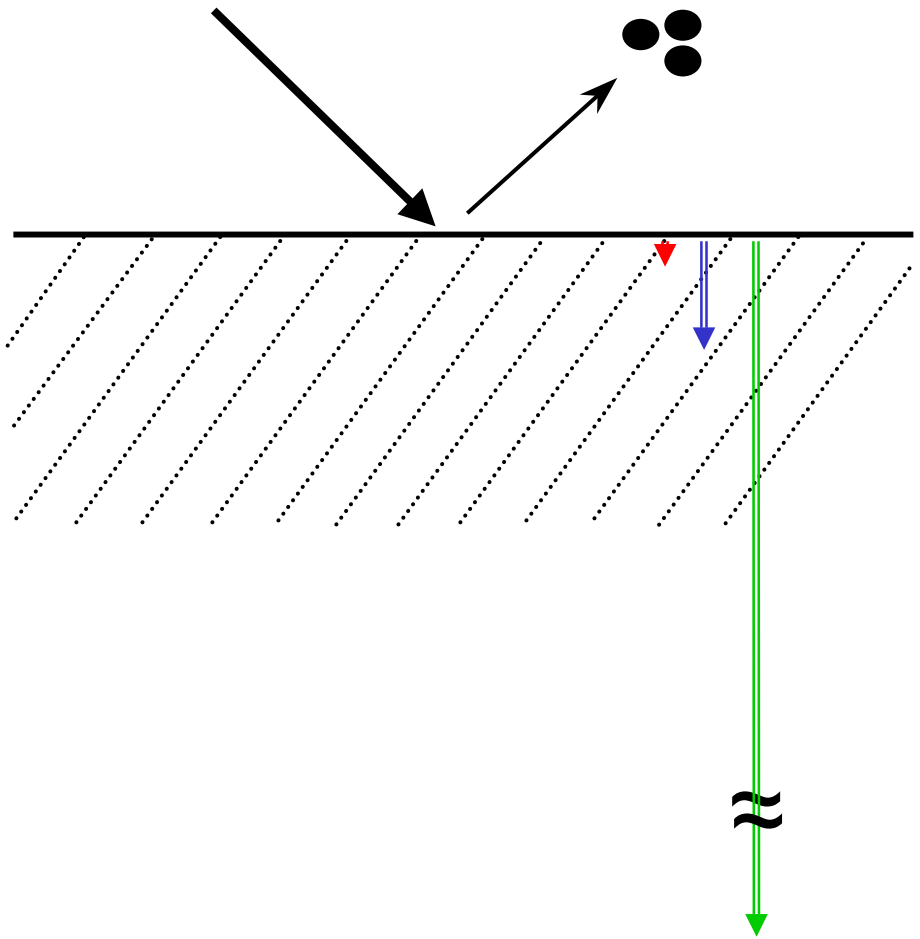


- **Direct analysis of surfaces**

Instrumentation for surface analysis

- ESCA (electron spectroscopy for chemical analysis, also called XPS)
- TOF-SIMS (time-of-flight secondary ion mass spectrometry)
- SEM (ESEM, FE-SEM)
- AFM
- FTIR, NIR

Surface analysis depth



TOF-SIMS (~1 nm)

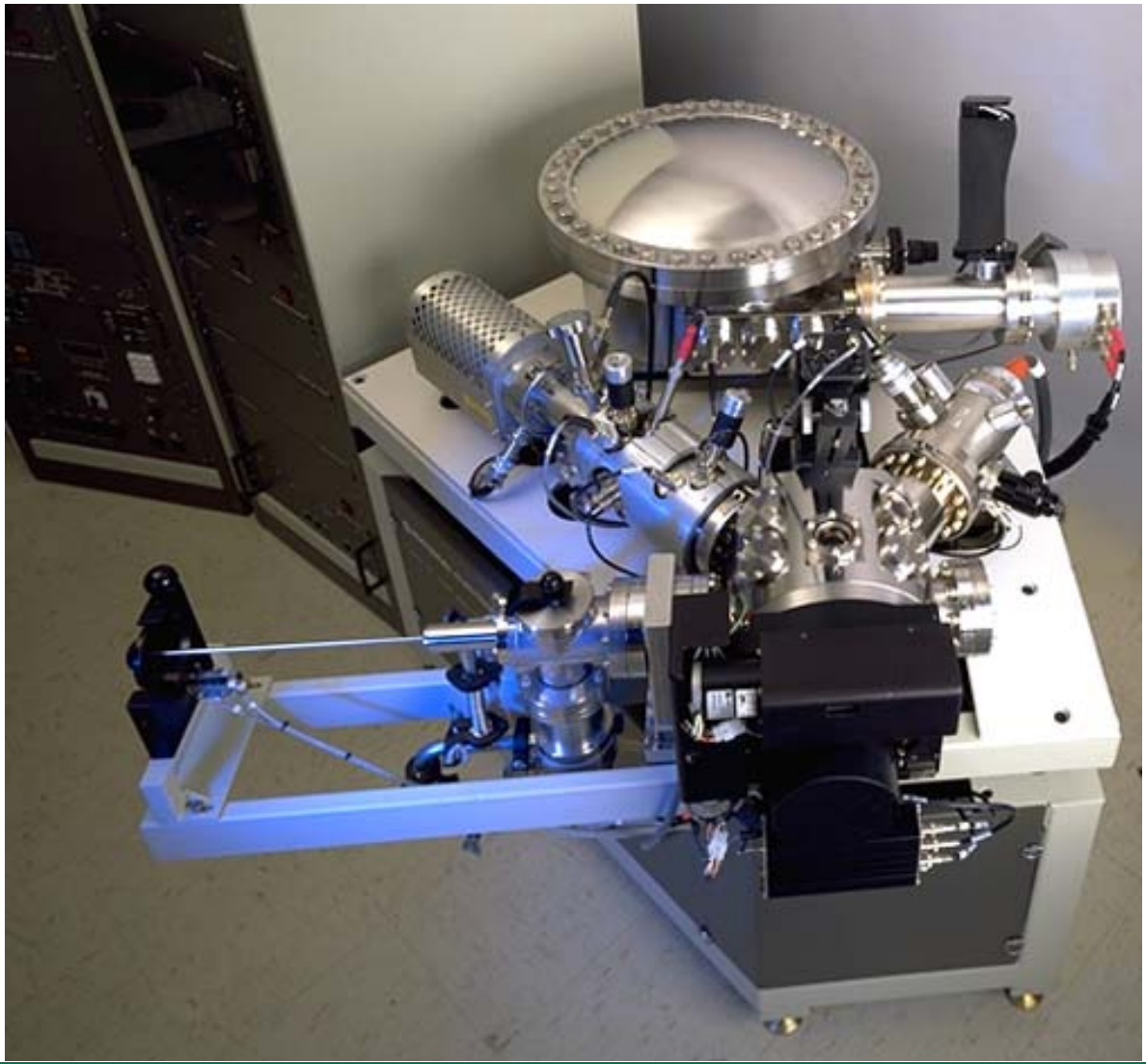
ESCA (~10 nm)

IR (~1000 nm)

SEM (~1000 nm)

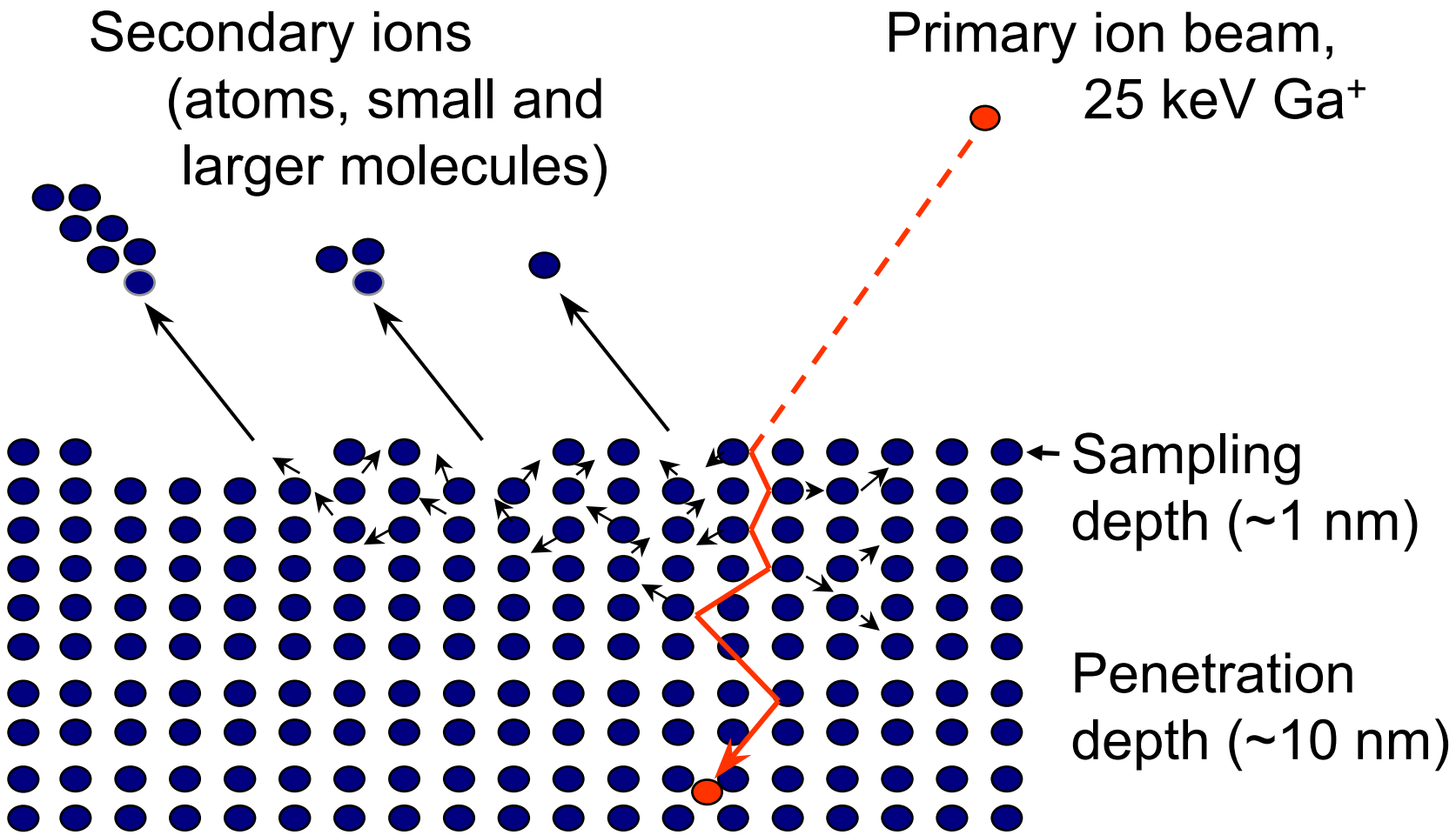
TOF-SIMS

(time-of-flight secondary ion mass spectrometer)

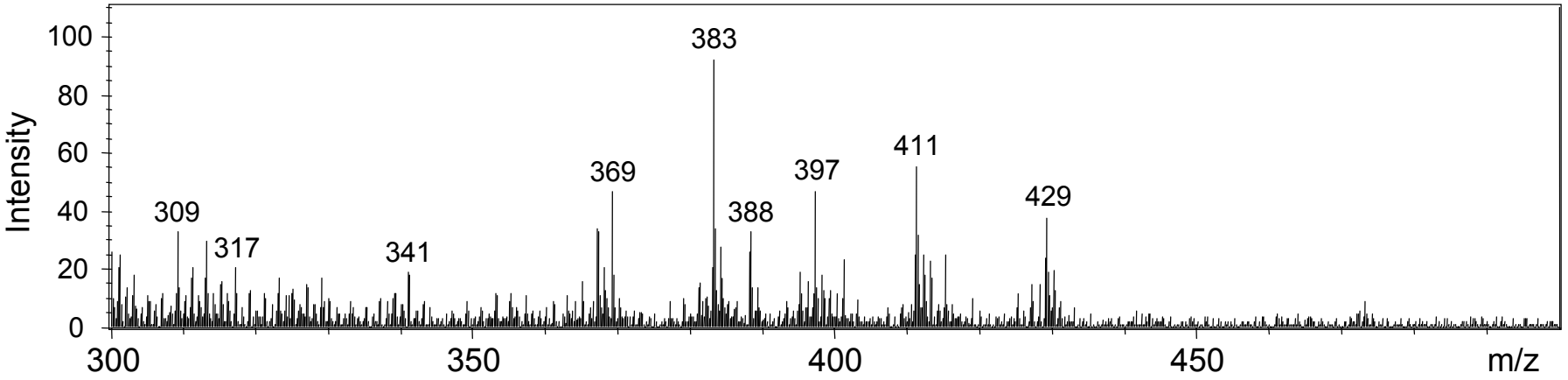


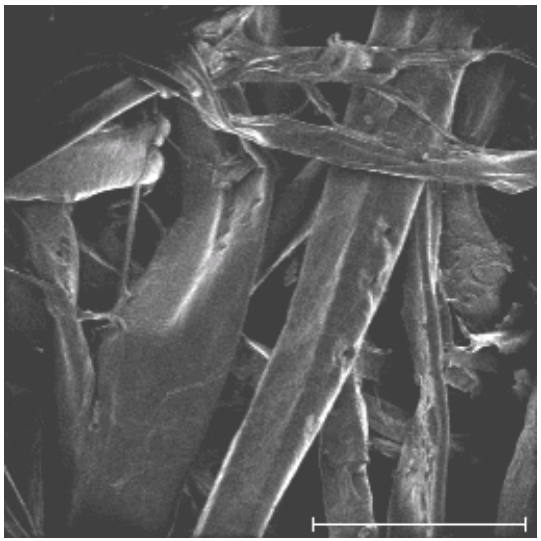
PHI TRIFT II
TOF-SIMS

Principle of secondary ion formation



TOF-SIMS gives…

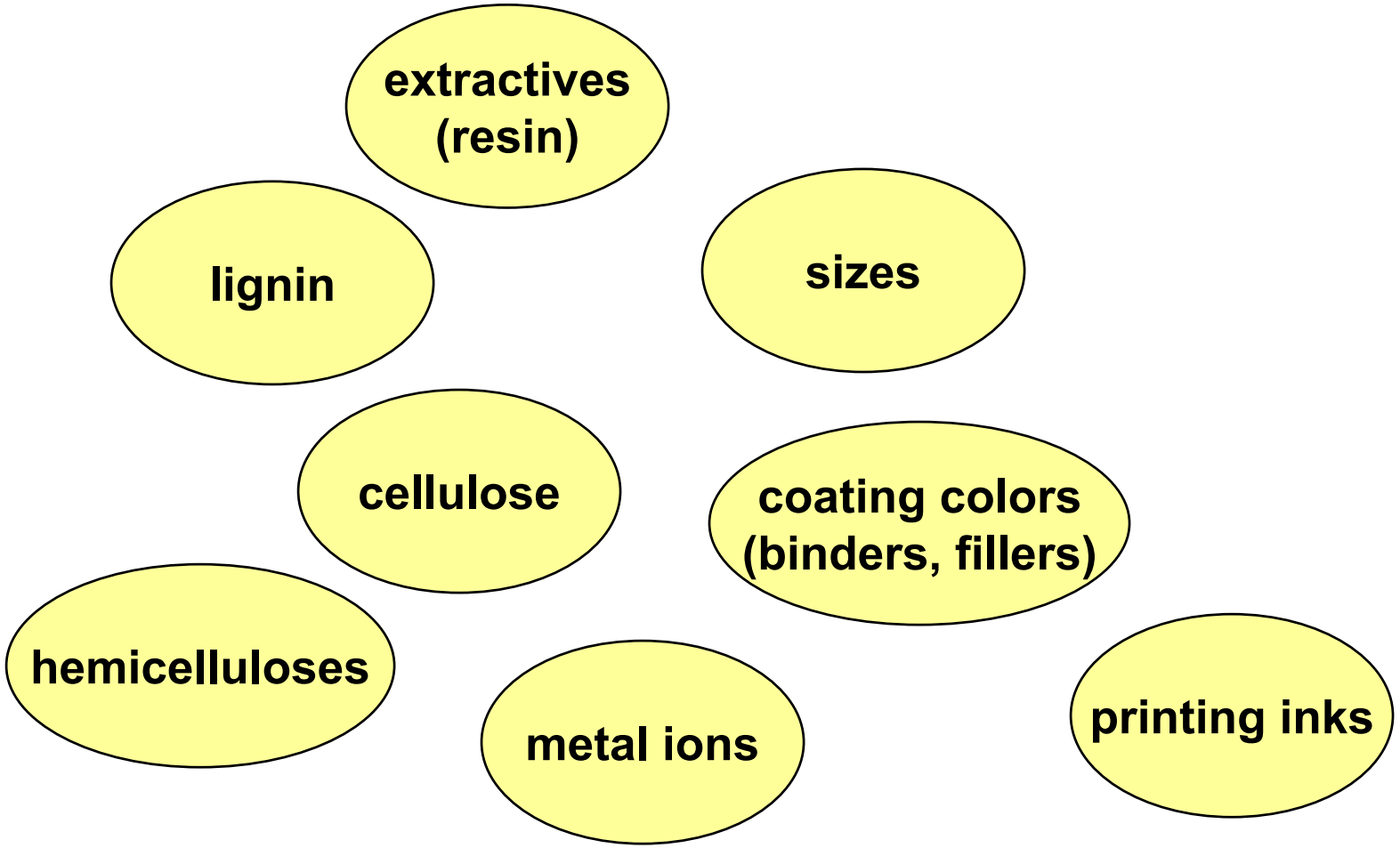




Total ion image

Extractives

What can we see?

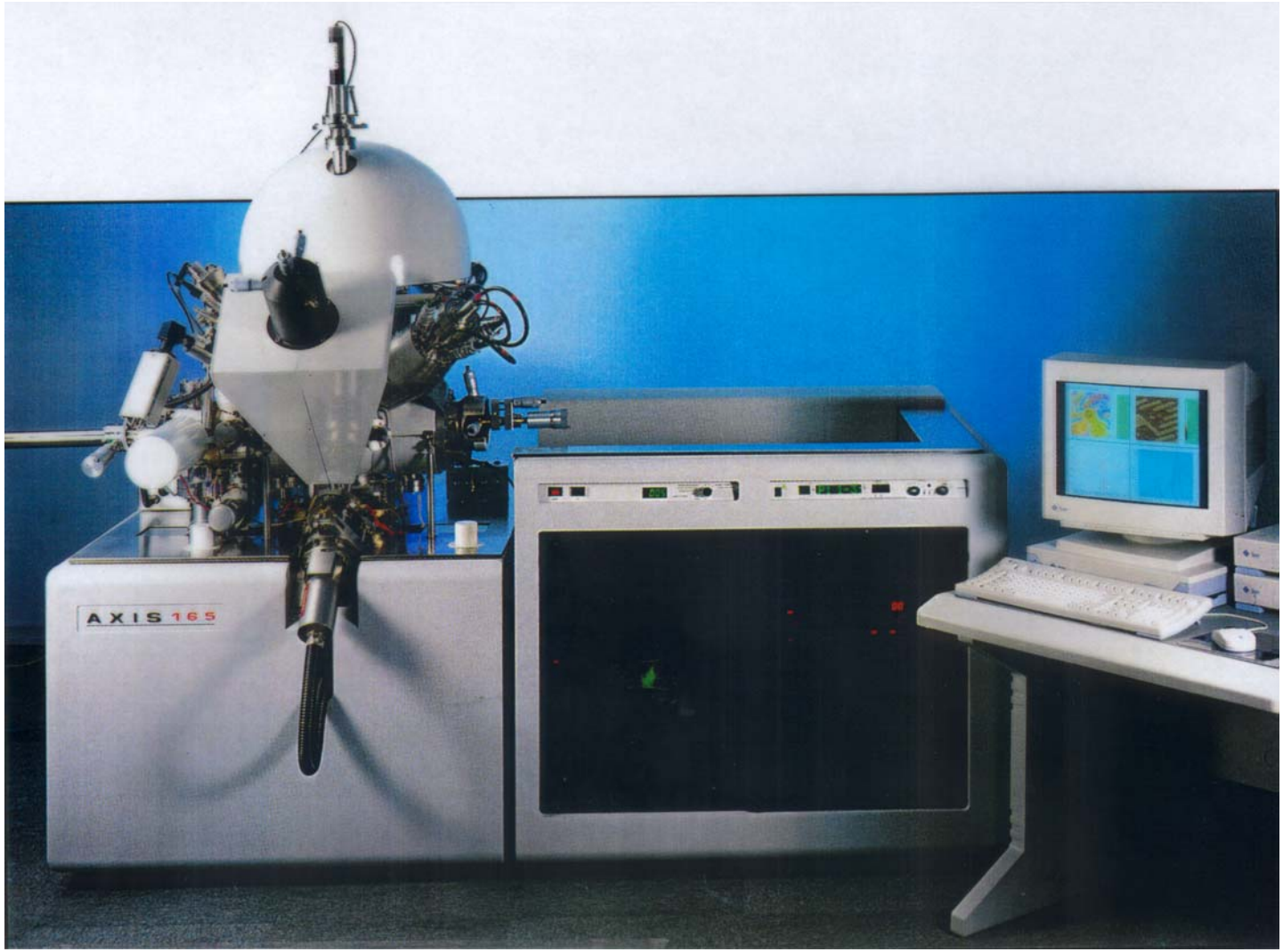


TOF-SIMS

+ can analyze complex mixtures
+ identification of several molecules simultaneously
+ elemental and molecular imaging

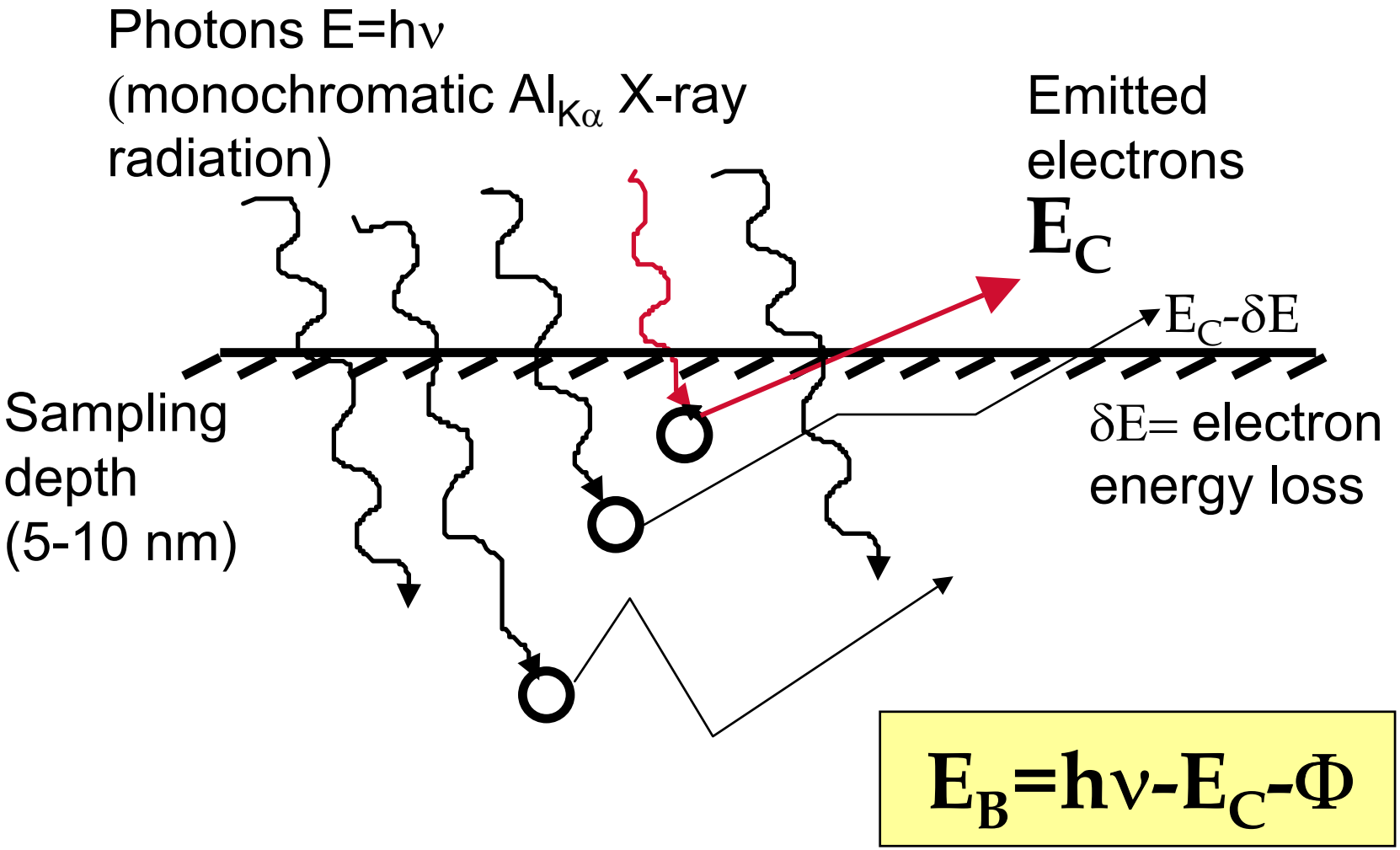
– identification demanding
– not quantitative
– sensitive to surface impurities
– not suitable for all organic compounds

ESCA



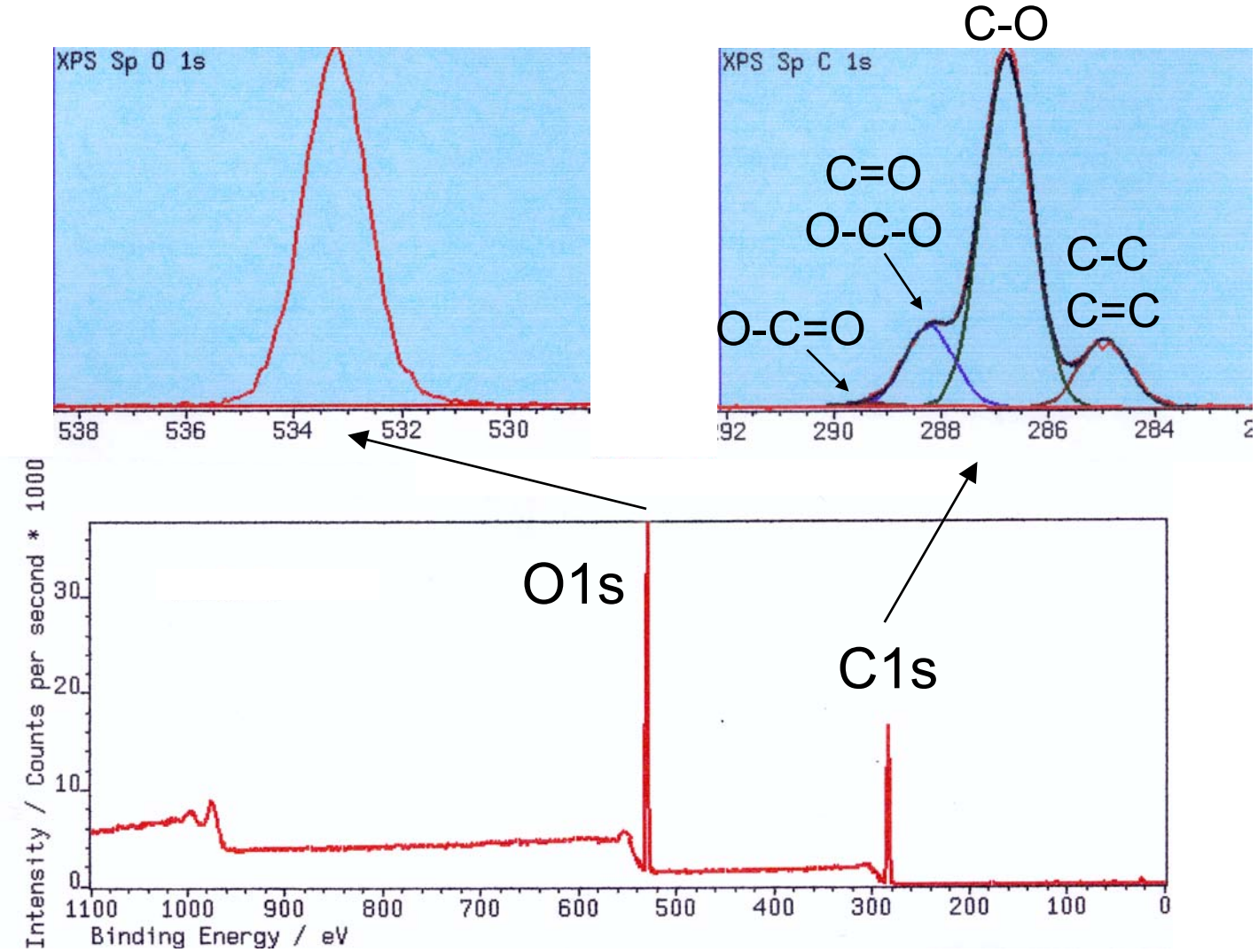
Kratos Analytical AXIS 165

Principle of ESCA



$$E_B = h\nu - E_C - \Phi$$

ESCA on pulp surface



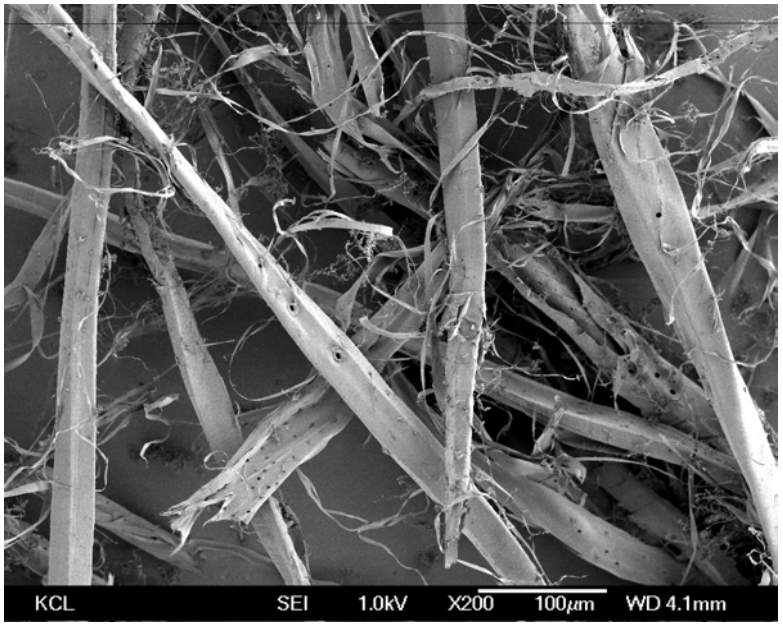
ESCA

+ quantitative (coverage by extractives, lignin and polysaccharides)

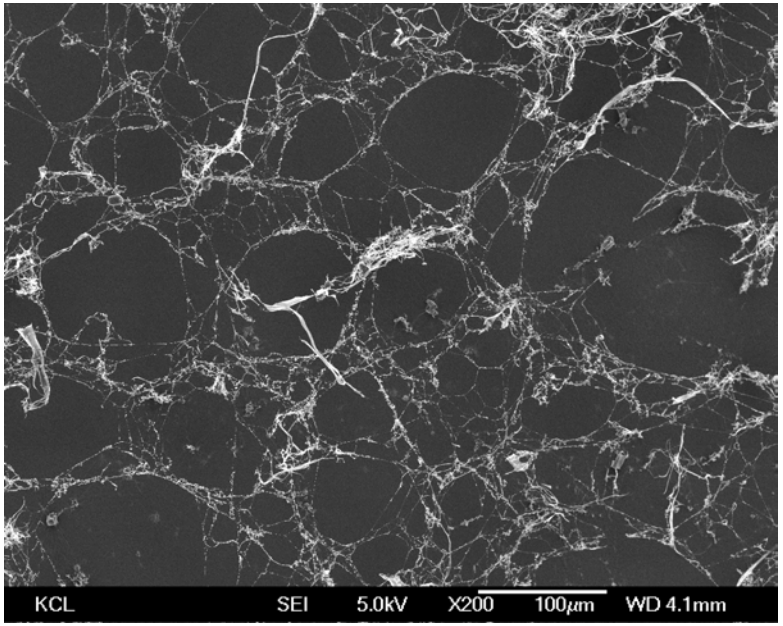
– reliability in determination of the coverage depends on:
  - ✓ all extractives are removed in extraction
  - ✓ no lignin is extracted
  - ✓ no lignin exposed under extractives
  - ✓ layers of lignin and extractives are thicker than the analysis depth

Examples

TMP fibers and fiber surface material



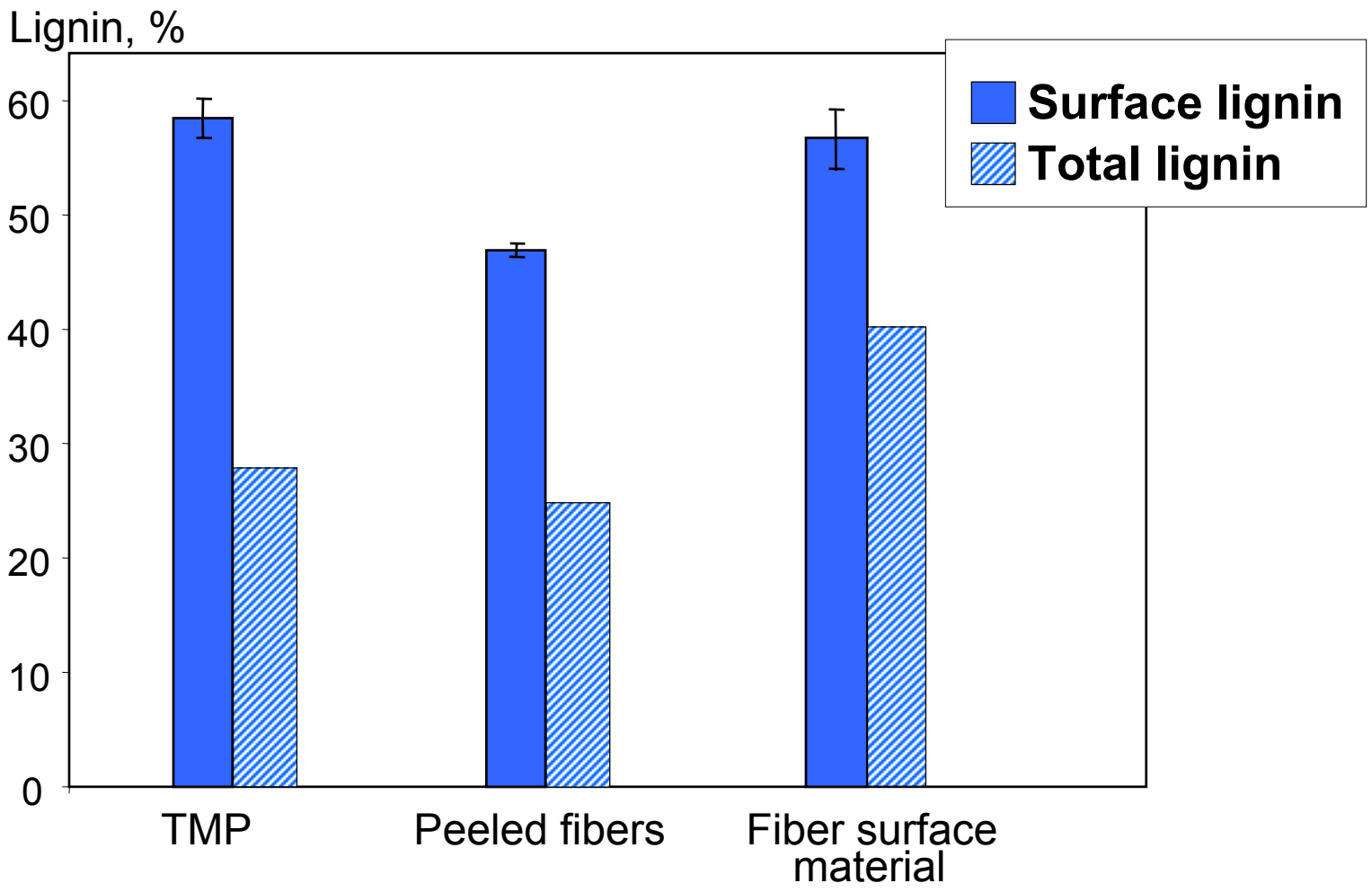
TMP fibers



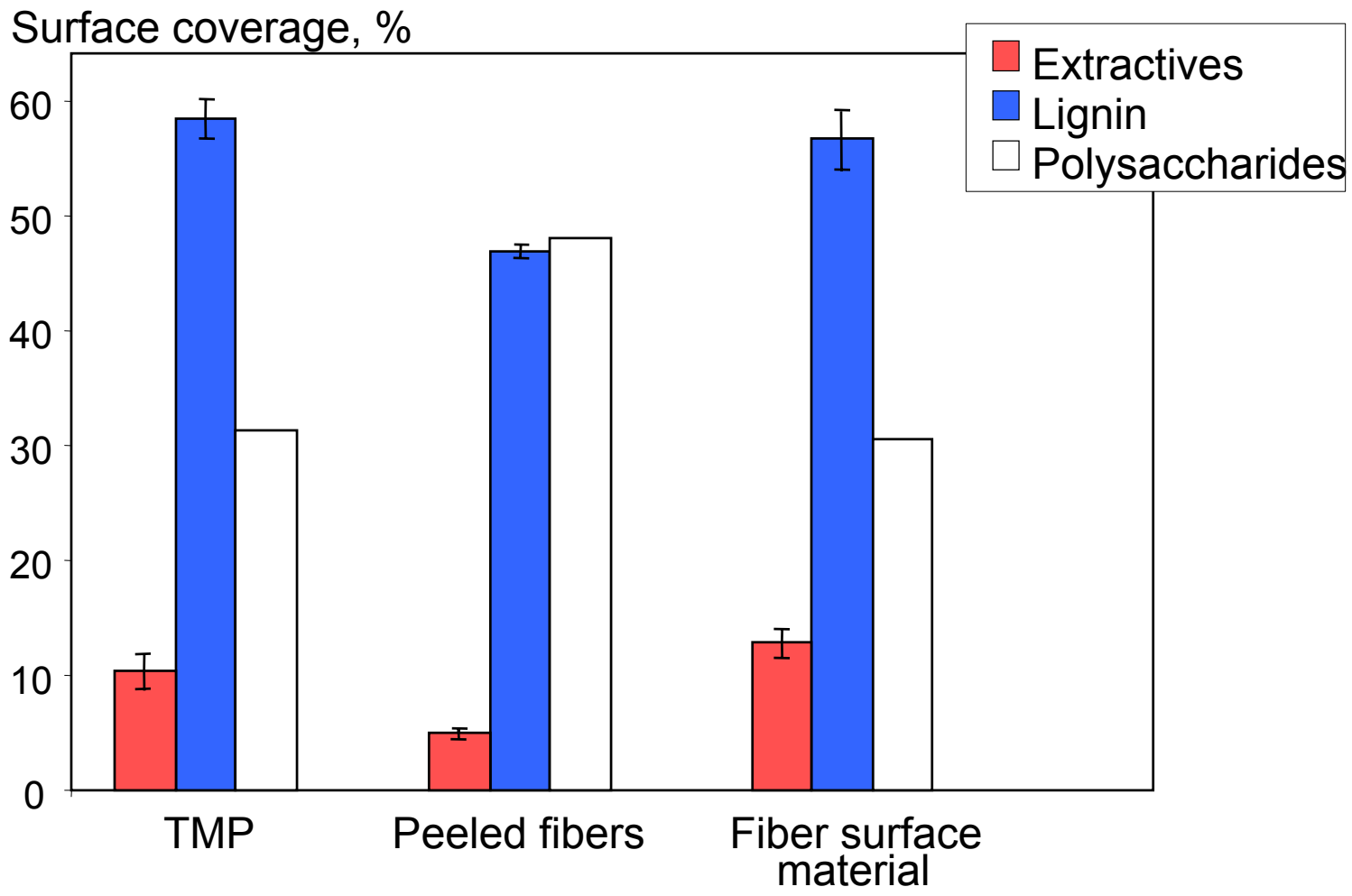
Fiber surface material (fibrils)

Image area 590x440 μm^2

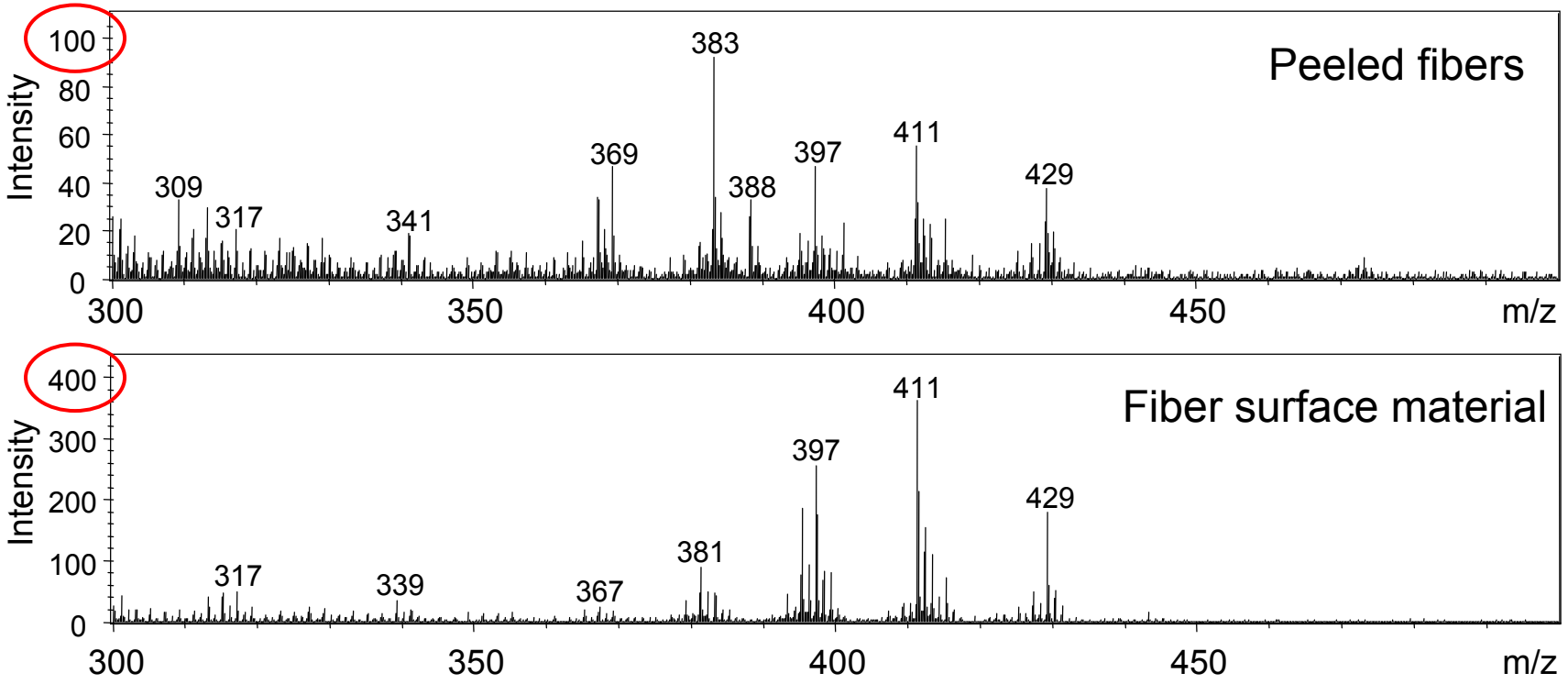
Surface lignin and total lignin



Surface chemical composition by ESCA

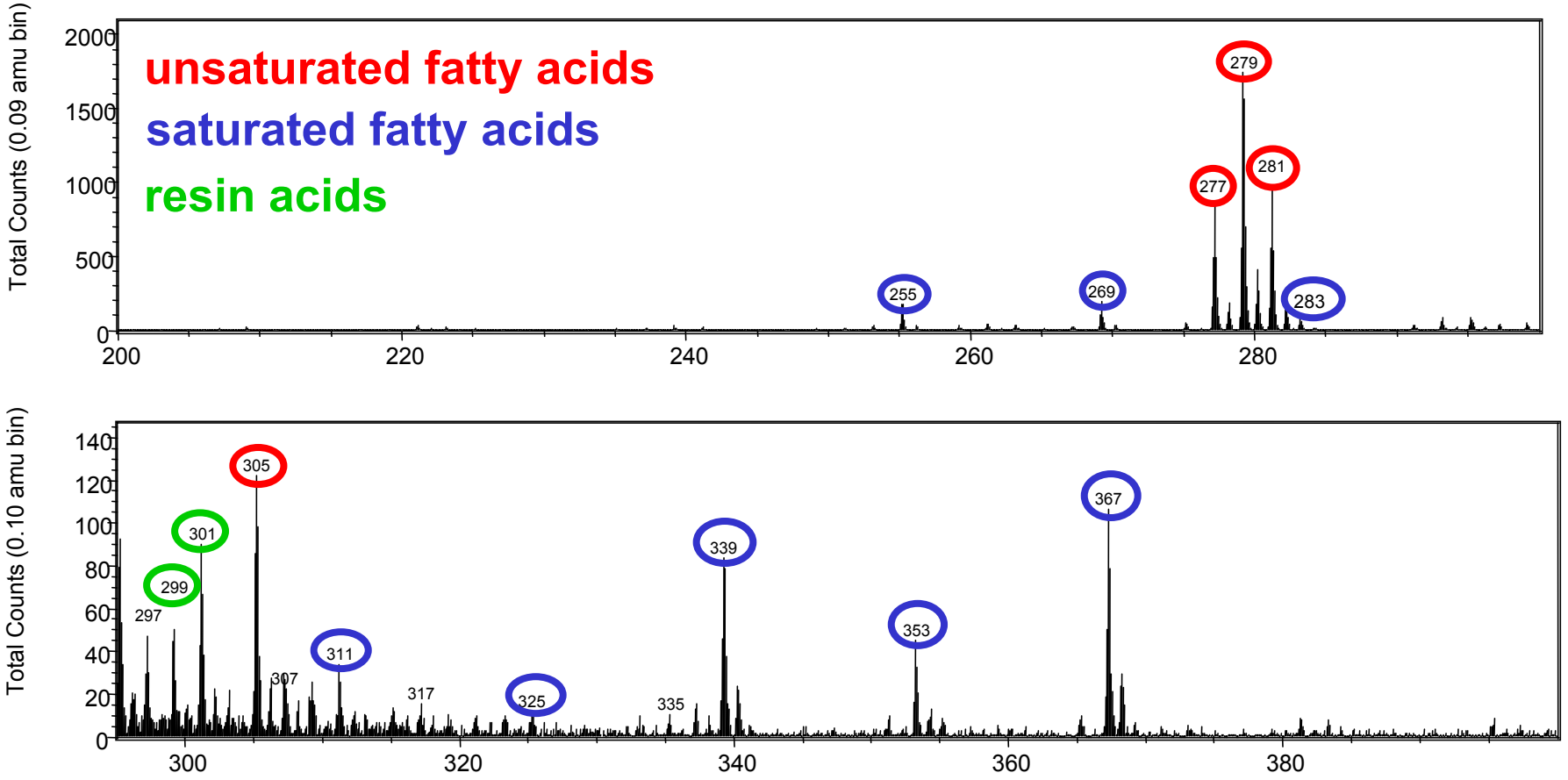


Surface extractives composition by TOF-SIMS

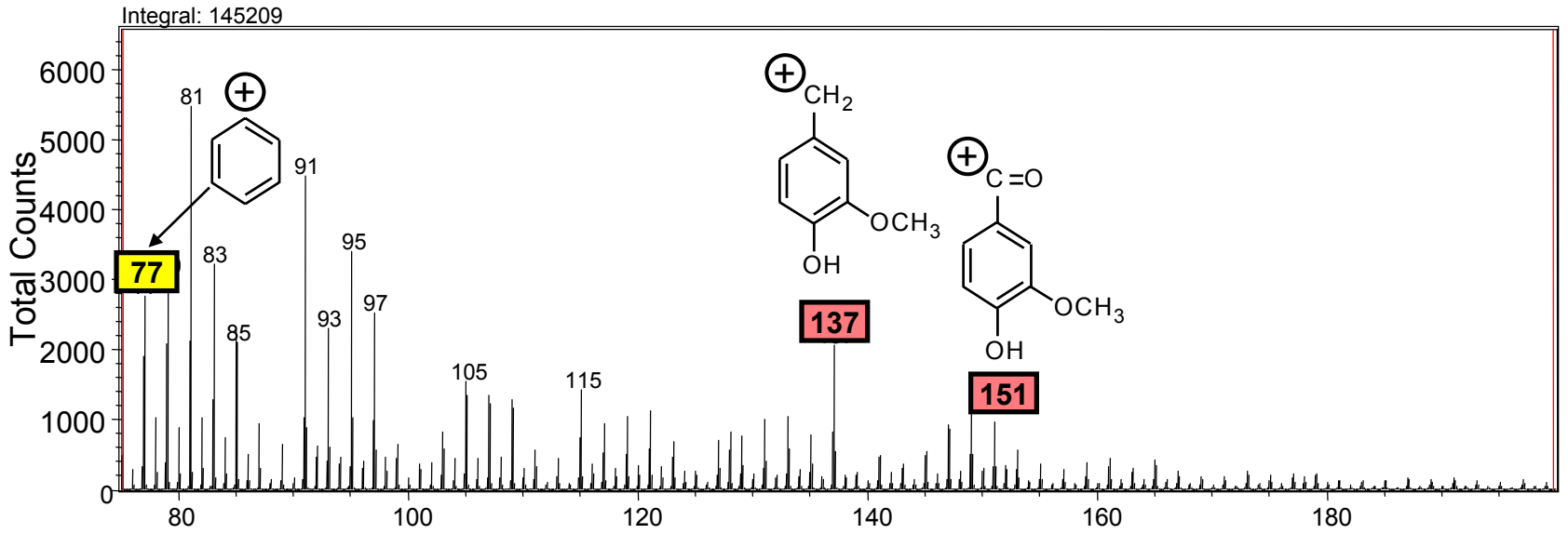


Surface chemical analysis by TOF-SIMS

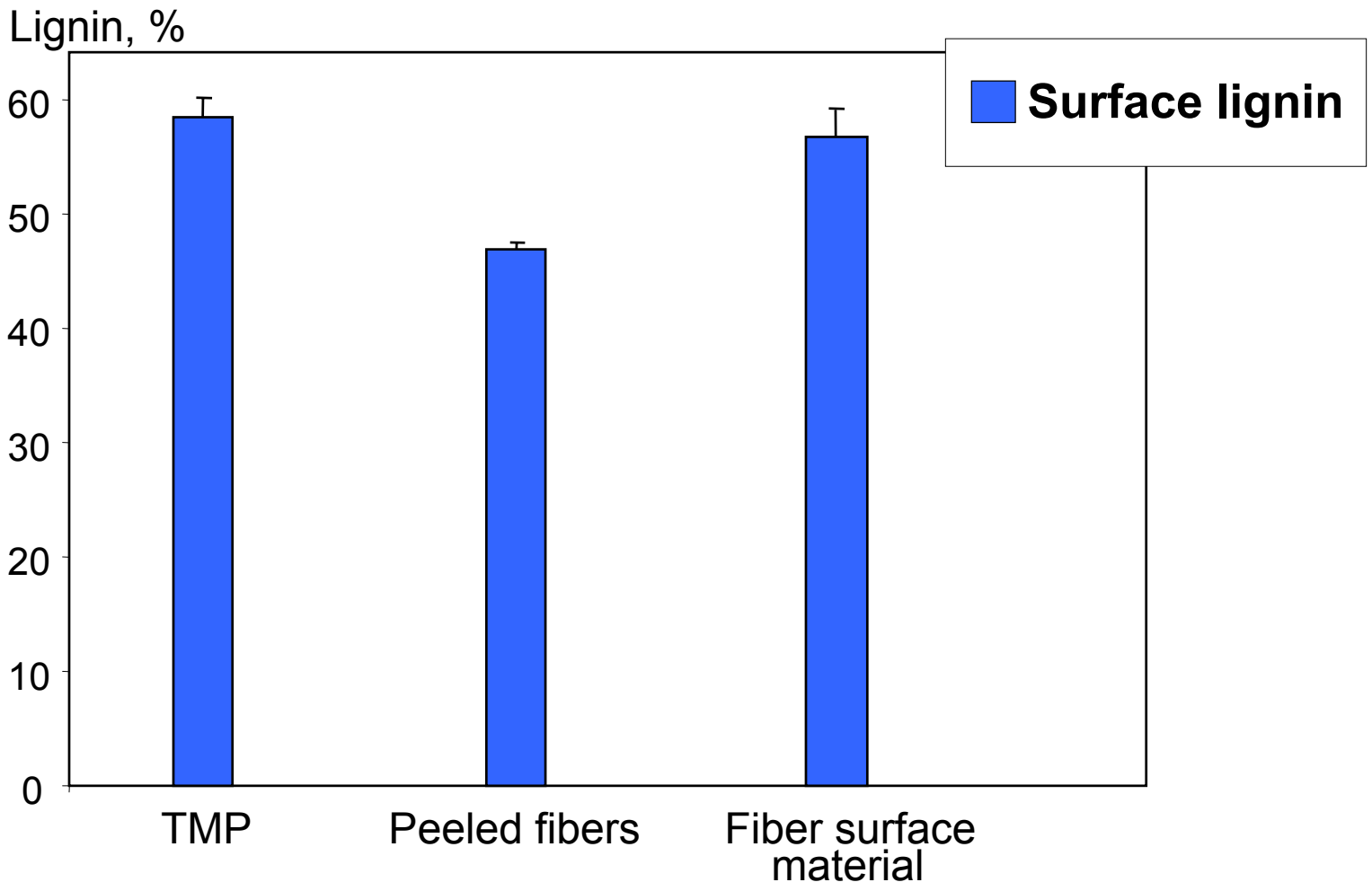
- negative ion mode



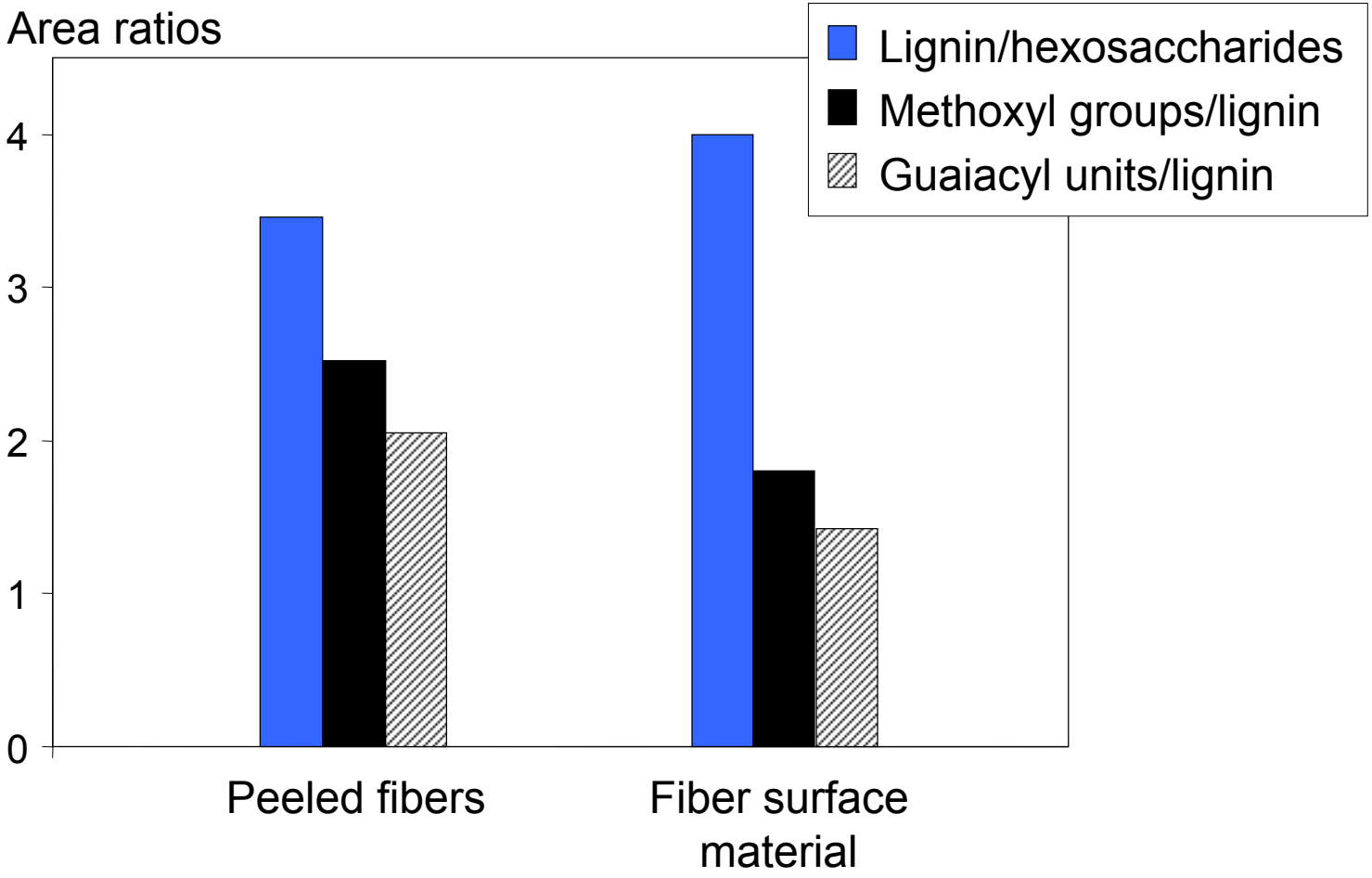
Surface lignin structure by TOF-SIMS



Surface lignin by ESCA

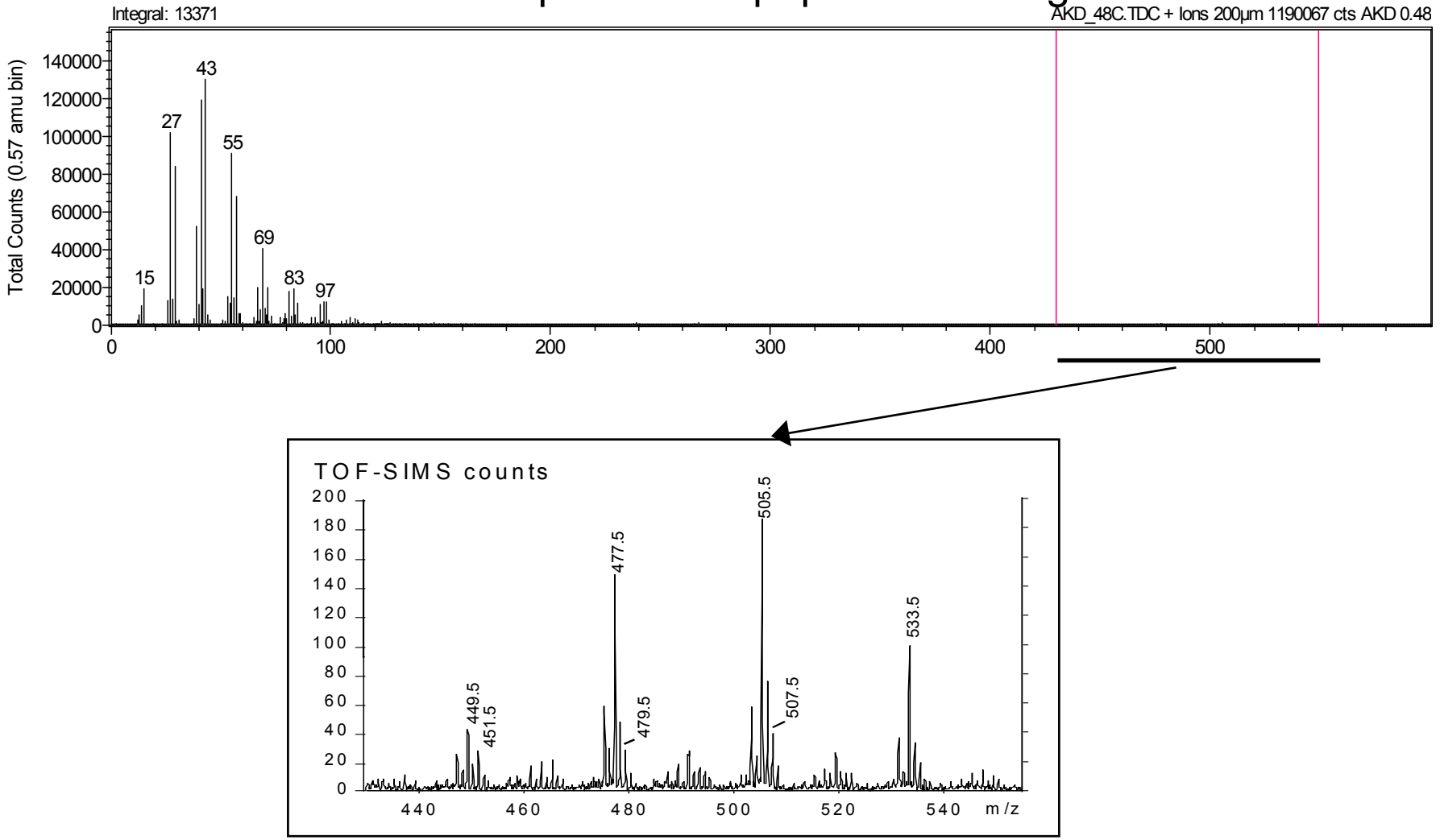


Surface lignin structure by TOF-SIMS

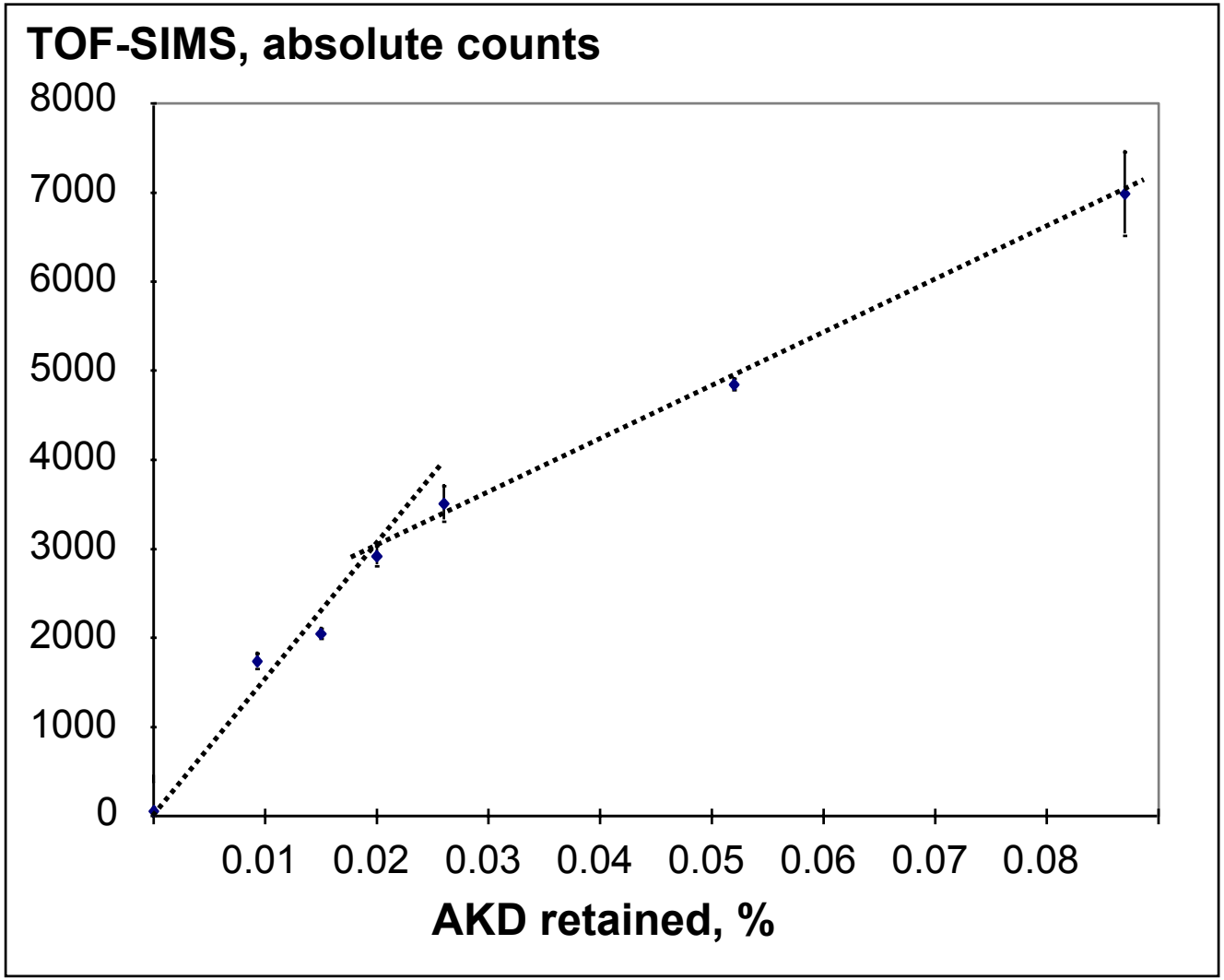


AKD specific ions from 447.5 to 535.5 Da

Positive ion TOF-SIMS spectrum of paper containing AKD as internal size

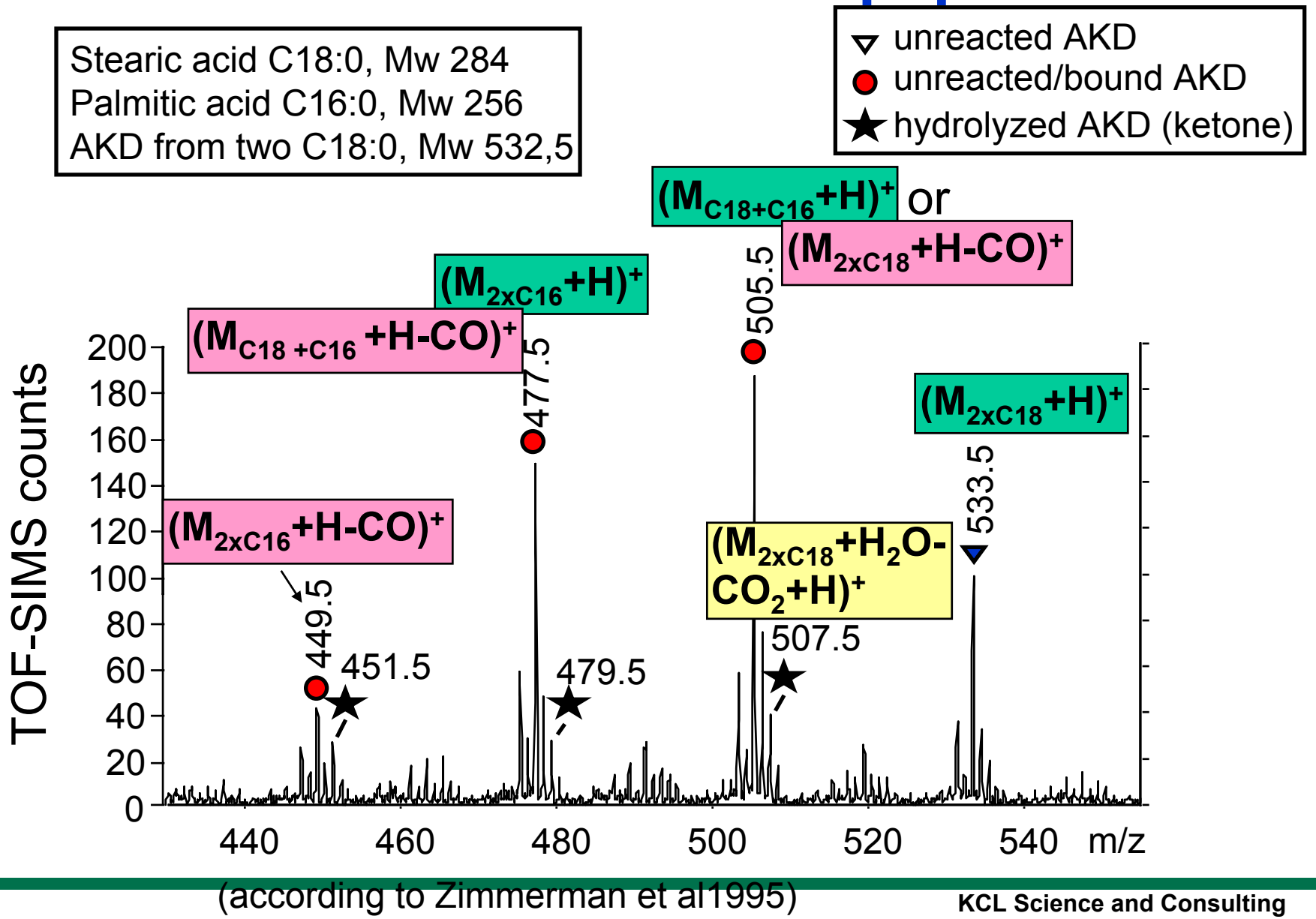


AKD sized paper



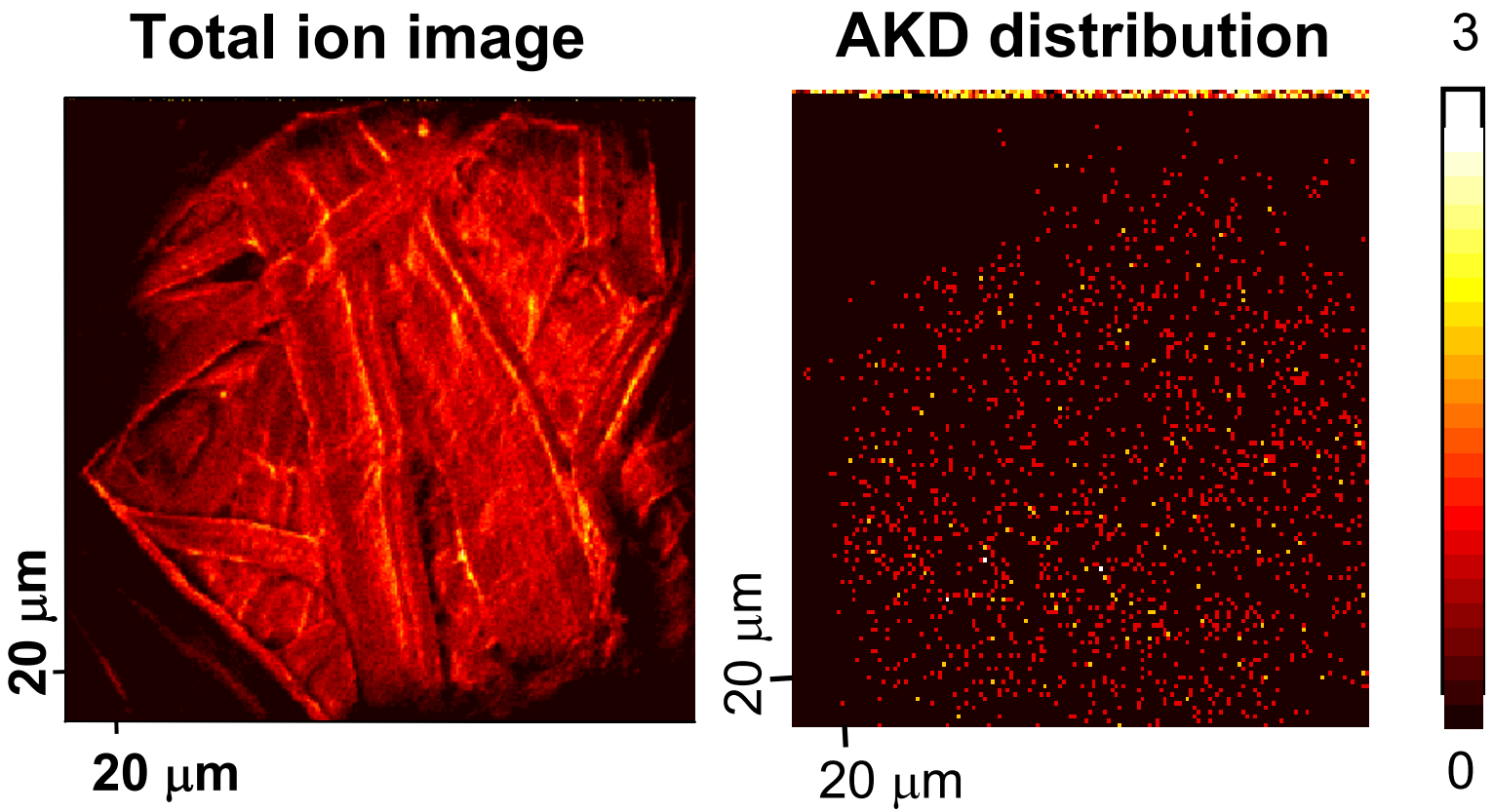
Different forms of AKD on paper surface

Stearic acid C18:0, Mw 284
Palmitic acid C16:0, Mw 256
AKD from two C18:0, Mw 532,5



(according to Zimmerman et al1995)

AKD sized paper by imaging TOF-SIMS



Summary

- **Advanced surface analytical instruments available**
  - **ESCA, quantitative**
  - **TOF-SIMS, qualitative**

- **Identification of surface molecules by TOF-SIMS**