BAM

Bundesanstalt für Materialforschung und -prüfung

Sicherheit in Technik und Chemie

18.10.2020

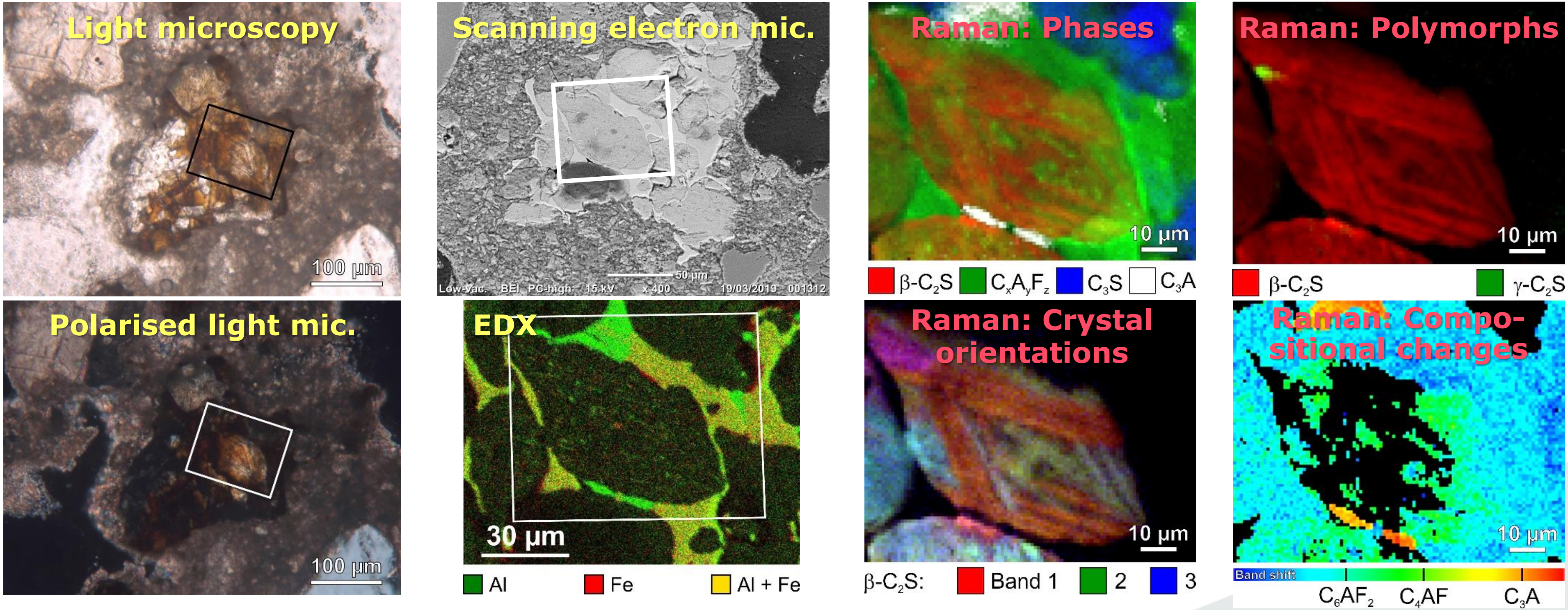
CORRELATIVE ANALYSIS BY RAMAN AND OTHER MICRO & NANOSPECTROSCOPIC IMAGING TECHNIQUES

Thomas Schmid & Dan Hodoroaba

FOCUS AREA
ANALYTICAL SCIENCES

“Spectroscopic eyes” can see more

Example: cement clinker phases (C = CaO, S = SiO_2, F = Fe_2O_3, A = Al_2O_3)

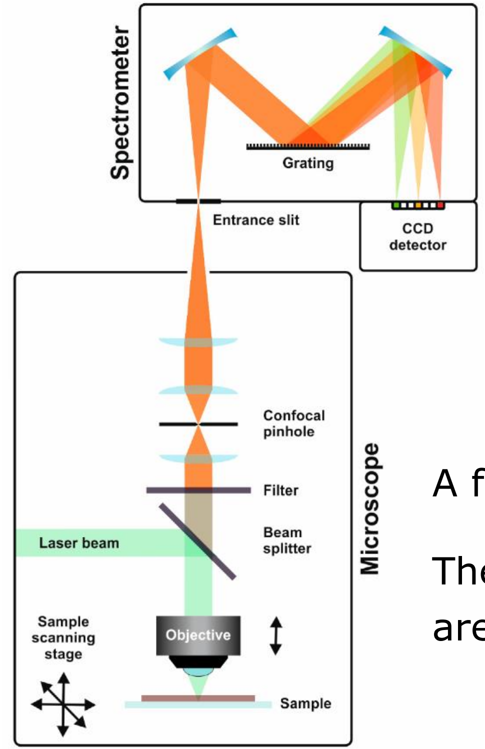


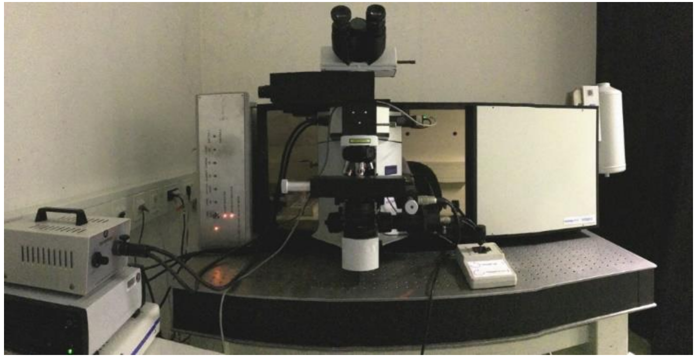
Thomas Schmid, Petra Dariz,
Heritage 2 (2019) 1662-1683.
http://dx.doi.org/10.3390/heritage2020102

Microspectroscopic Imaging or Hyperspectral Imaging

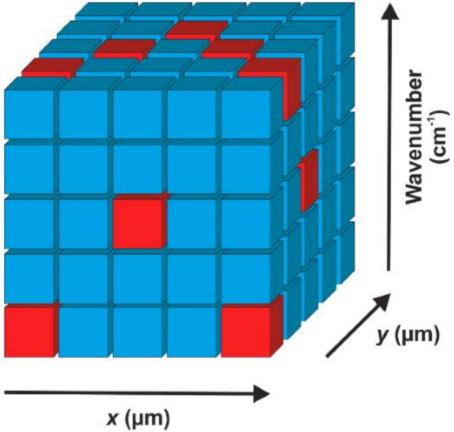
In every pixel of an image
a full spectrum is acquired.

Raman microspectroscopy/Raman microscopy





Horiba JobinYvon Labram HR800
(532 nm, 633 nm, 785 nm)

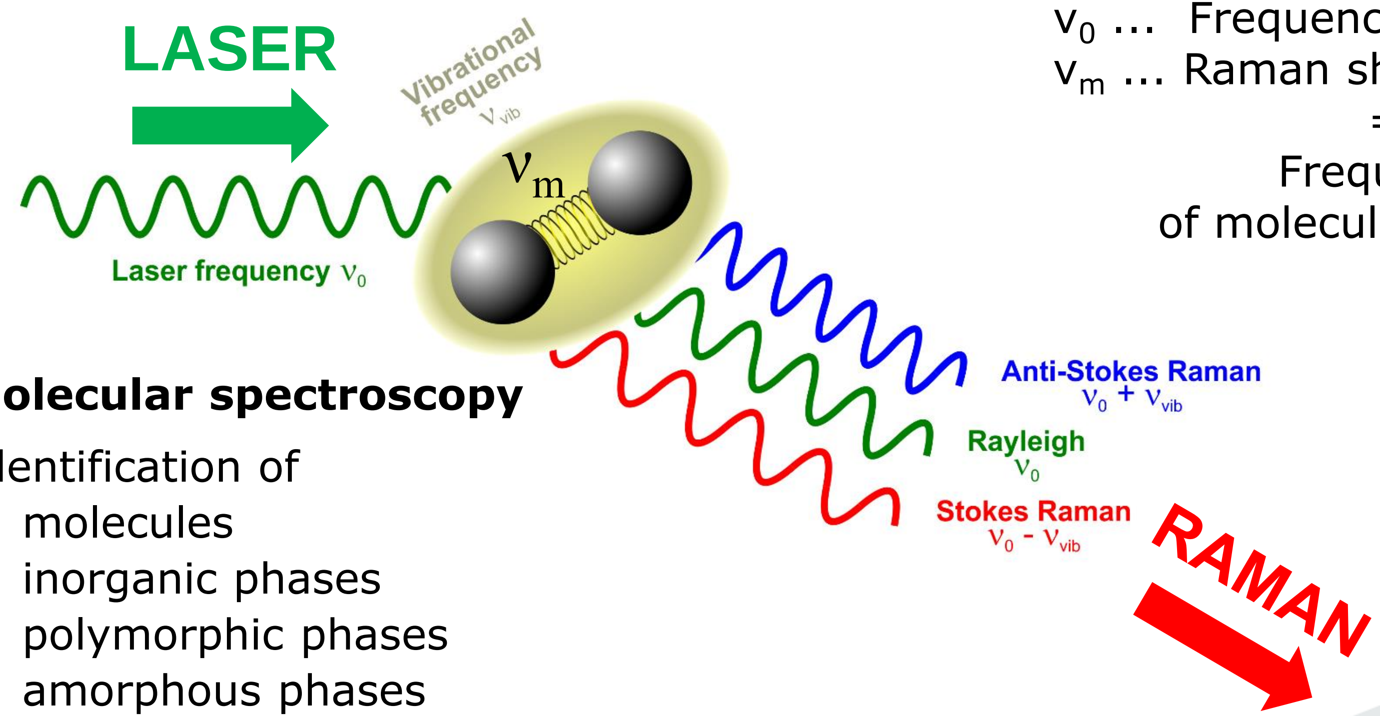


A full-spectroscopic analysis is performed in every pixel of an image.

The resulting 4-dimensional data (2 spatial and 2 spectral axes) are converted into chemical/physical distribution maps.

Thomas Schmid, Petra Dariz, Heritage 2 (2019) 1662-1683.
http://dx.doi.org/10.3390/heritage2020102

Raman spectroscopy



ν_0 … Frequency of laser light
ν_m … Raman shift (cm^{-1})
=
Frequency
of molecular vibration

Molecular spectroscopy

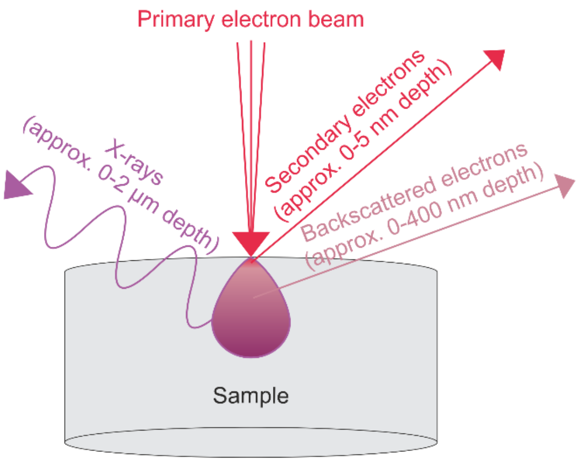
Identification of

- molecules
- inorganic phases
- polymorphic phases
- amorphous phases

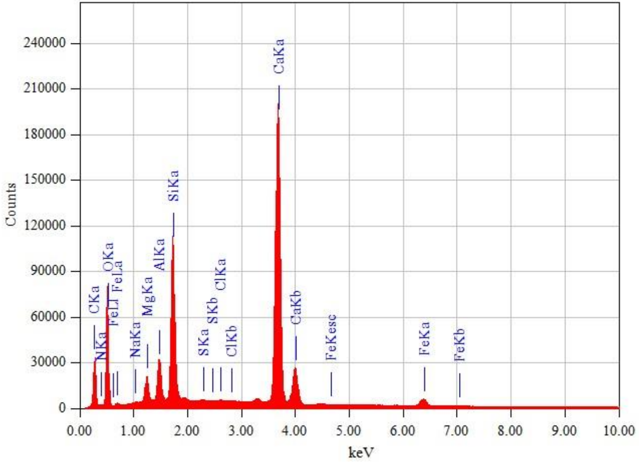
via "fingerprint comparison" of vibrational spectra.

Thomas Schmid, Petra Dariz, Heritage 2 (2019) 1662-1683.

Scanning electron microscopy – Energy dispersive X-ray spectroscopy (SEM-EDX)



JEOL (NikonMetrology) JCM-6000 Neoscope (SALSA ApplicationLab)



Secondary electron imaging: mainly topography contrast

Backscattered e^- imaging: mainly material contrast

EDX: elemental analysis

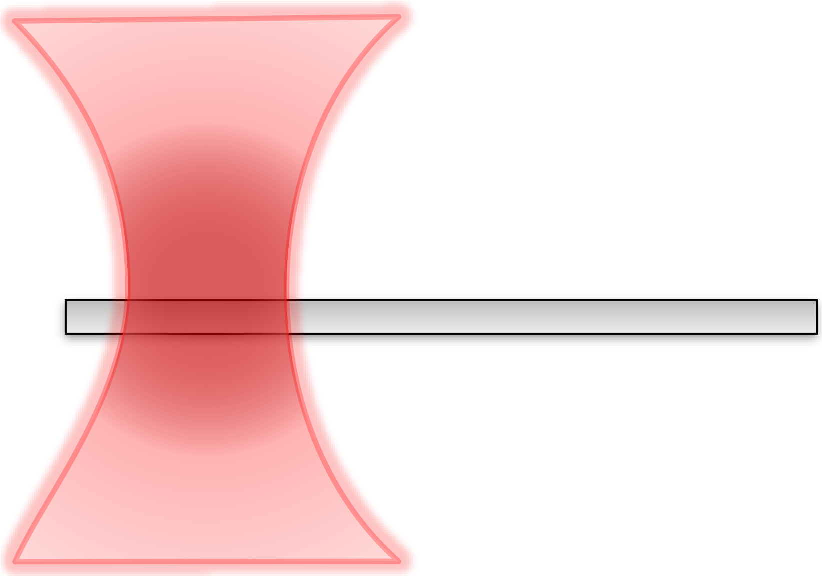
A full-spectroscopic analysis is performed in every pixel of an image.

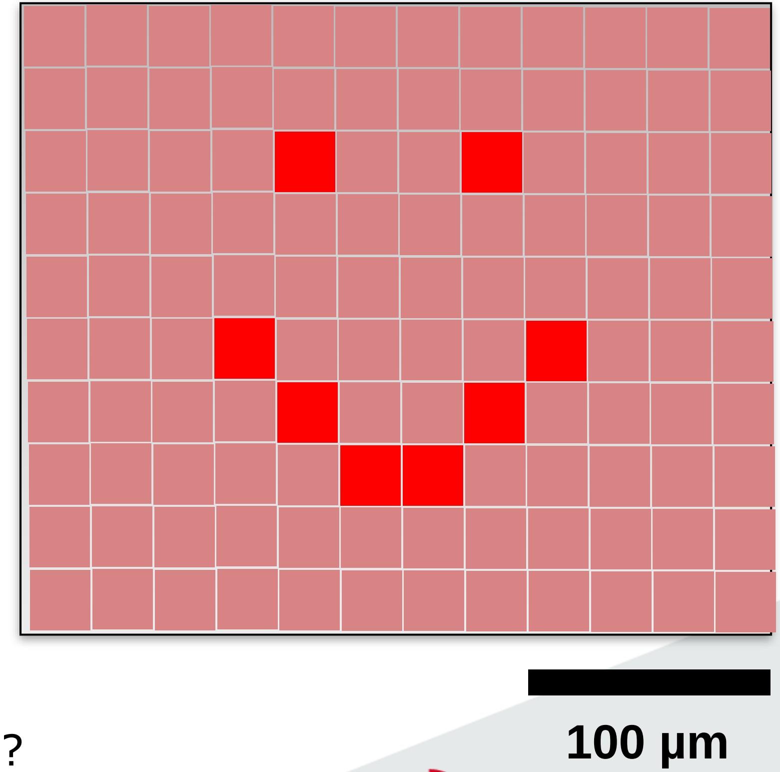
Elemental distribution maps are calculated based on element-specific X-ray emission lines.

Website SALSA AppLab
https://fakultaeten.hu-berlin.de/en/mnf/forschung_internationales/grs/salsa/p-a-labs/application-lab/instrumentation/a-labs-sem/a-labs-scanning-e-microscopy

Spatial resoution of microscopic/microspectroscopic imaging

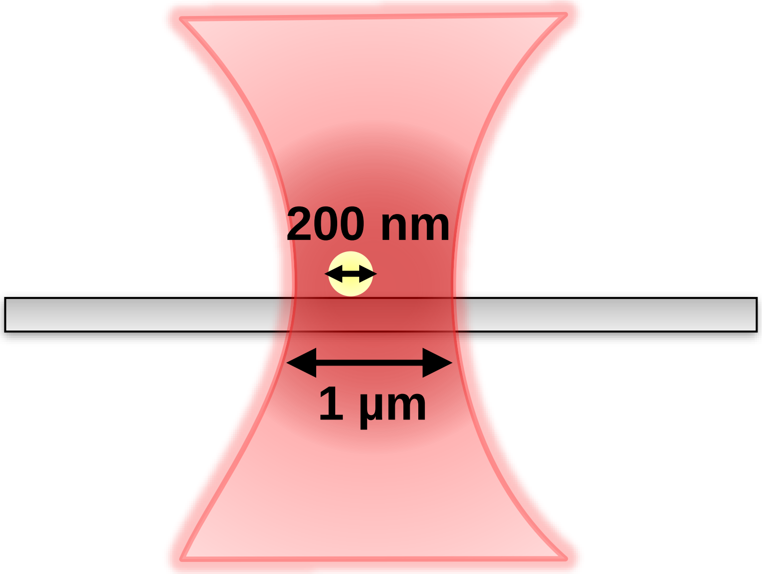
Raman microspectroscopic imaging: Focused laser beam scanning a sample surface

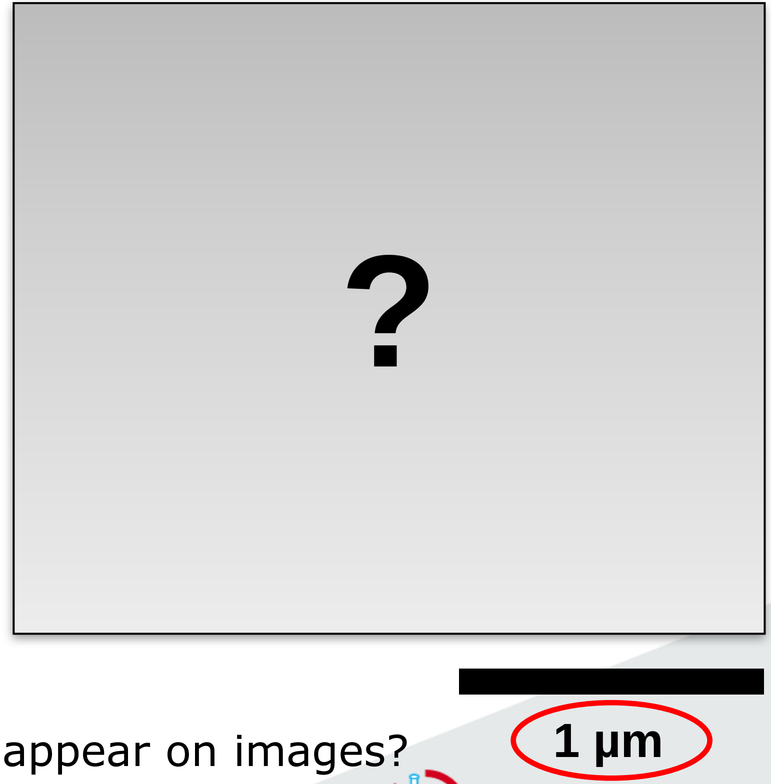




Question 1:
What is the minimum focus size?

Raman microspectroscopic imaging: Focused laser beam scanning a sample surface

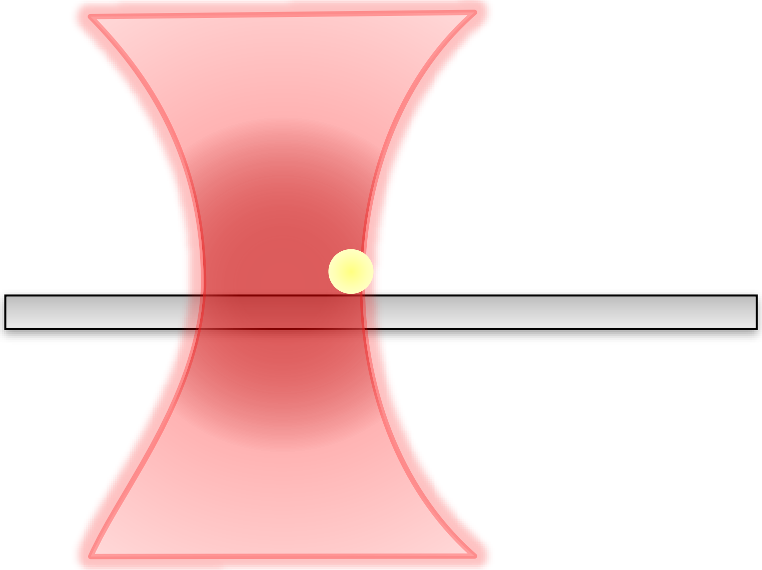


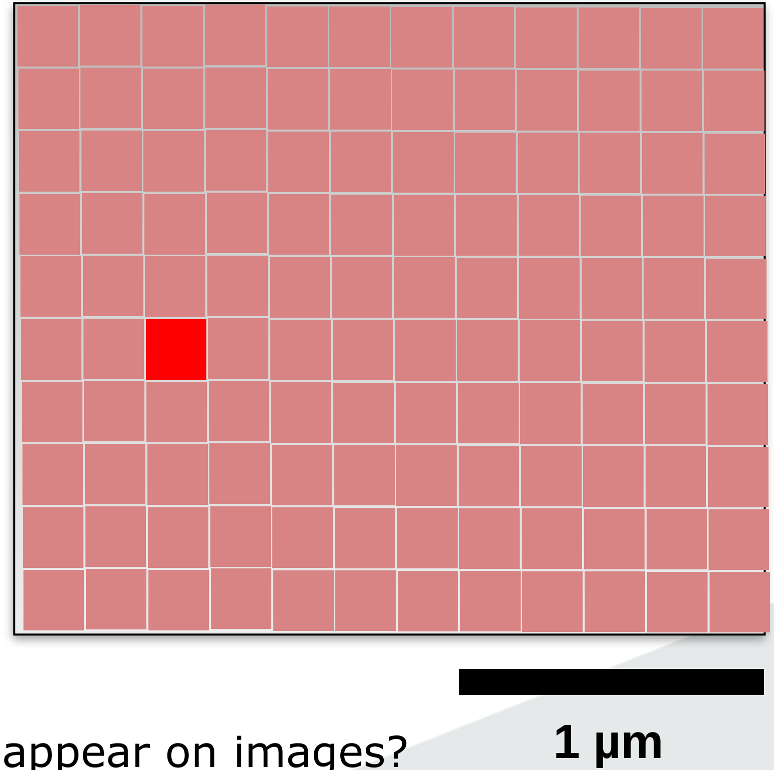


Question 2:

How large do objects smaller than the laser focus appear on images?

Raman microspectroscopic imaging: Focused laser beam scanning a sample surface



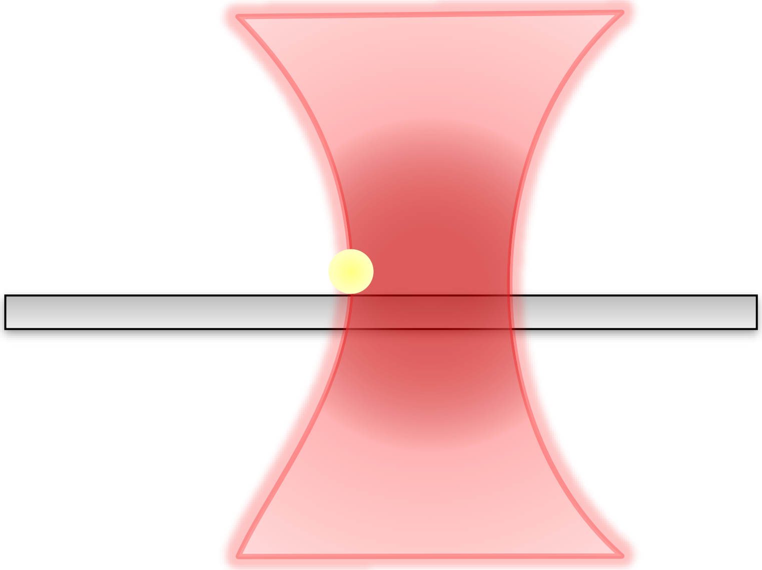


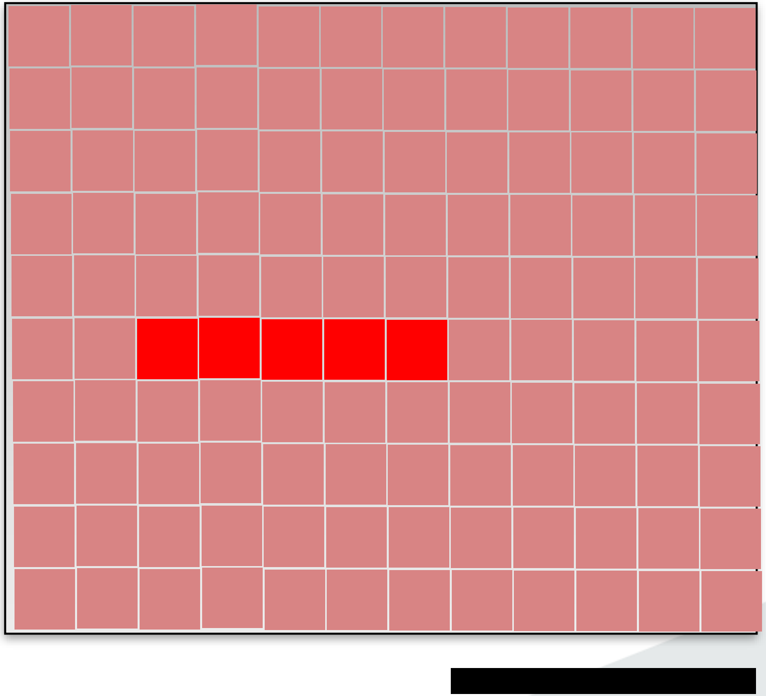
Question 2:

How large do objects smaller than the laser focus appear on images?

FOCUS AREA
ANALYTICAL SCIENCES

Raman microspectroscopic imaging:
Focused laser beam scanning a sample surface

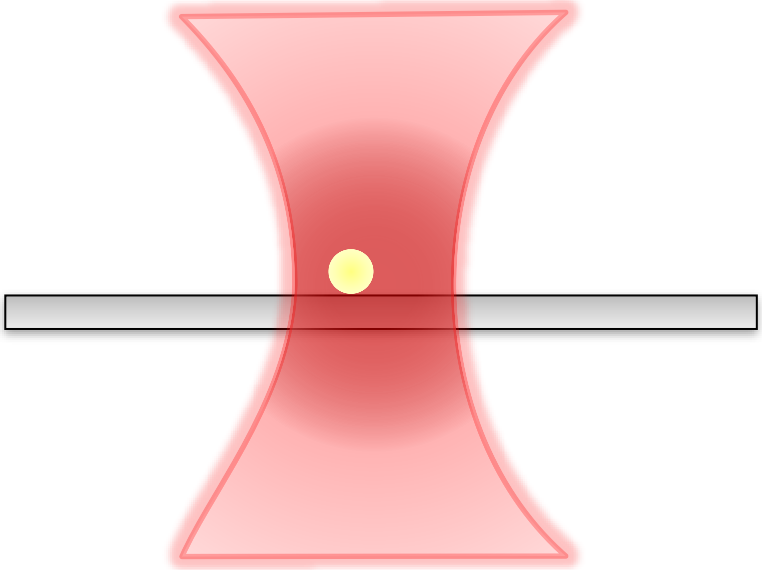


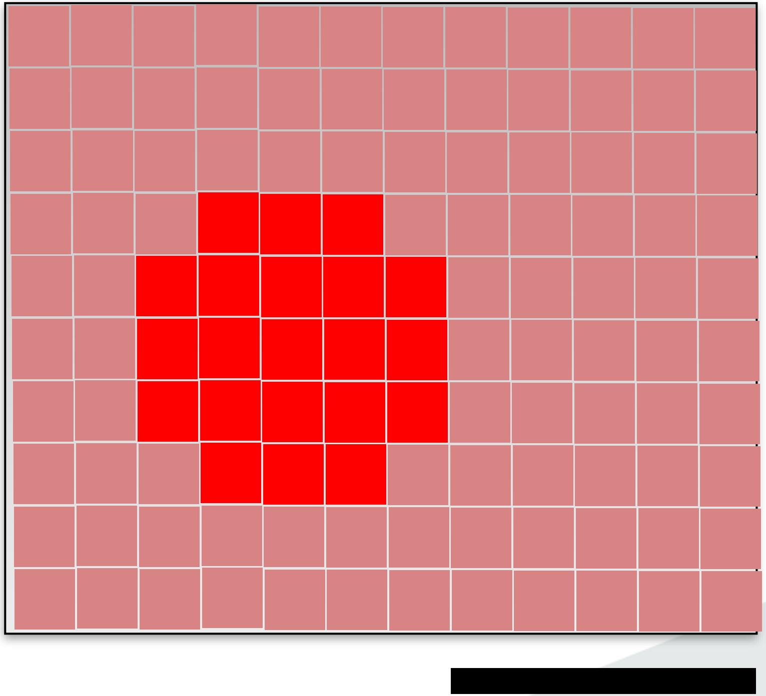


Question 2:

How large do objects smaller than the laser focus appear on images?

Raman microspectroscopic imaging: Focused laser beam scanning a sample surface



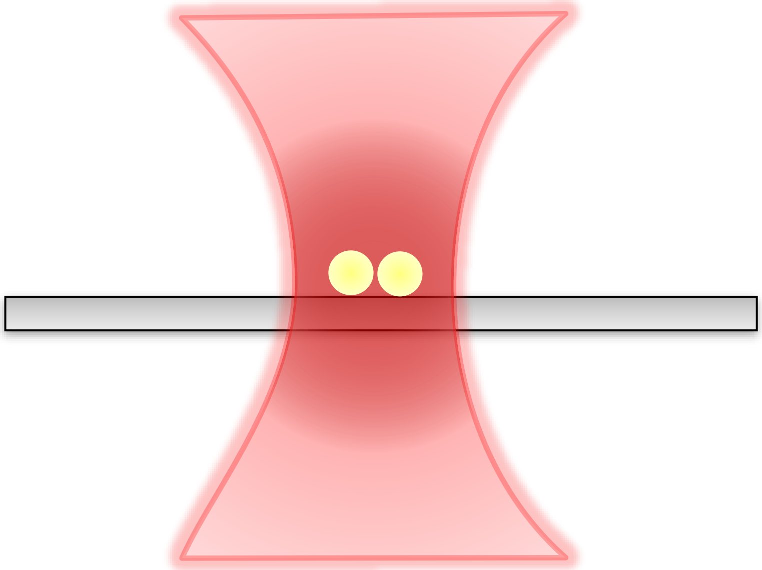


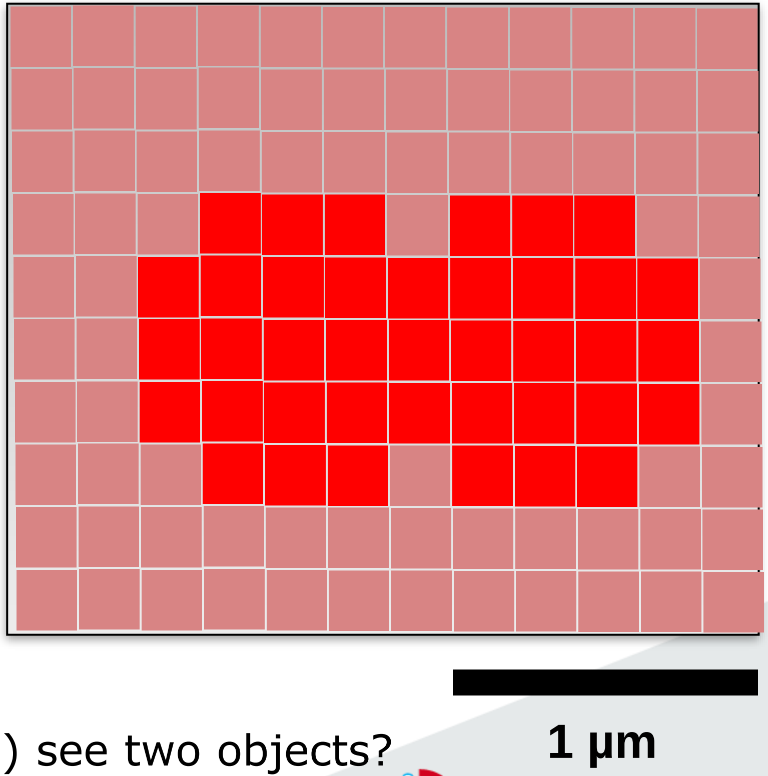
1 µm

Question 2:

How large do objects smaller than the laser focus appear on images?

Raman microspectroscopic imaging:
Focused laser beam scanning a sample surface





Question 3:

What is the minimum distance enabling to (barely) see two objects?

FOCUS AREA ANALYTICAL SCIENCES

Lateral resolution

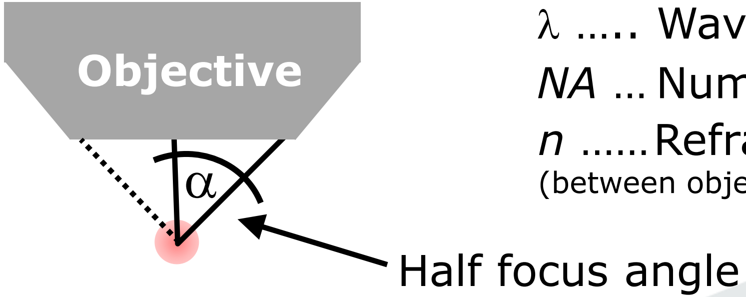
Spencer Bliven: https://en.wikipedia.org/wiki/Angular_resolution

According to the **Rayleigh criterion**, the lateral resolution of a microscope is

$$d = 0.61 \frac{\lambda}{NA}$$

$$NA = n \sin \alpha$$

Focus diameter = 2*d*



λ ….. Wavelength of light

NA … Numerical aperture

n ……Refractive index (between objective lens and sample)

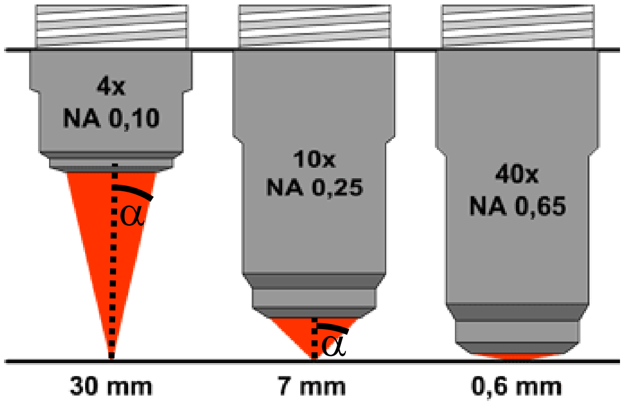
Lateral resolution

Examples: $NA = n \sin\alpha$

10x/*NA*=0.25 (air objective): d(633 nm) = 1.5 µm
d(405 nm) = 990 nm

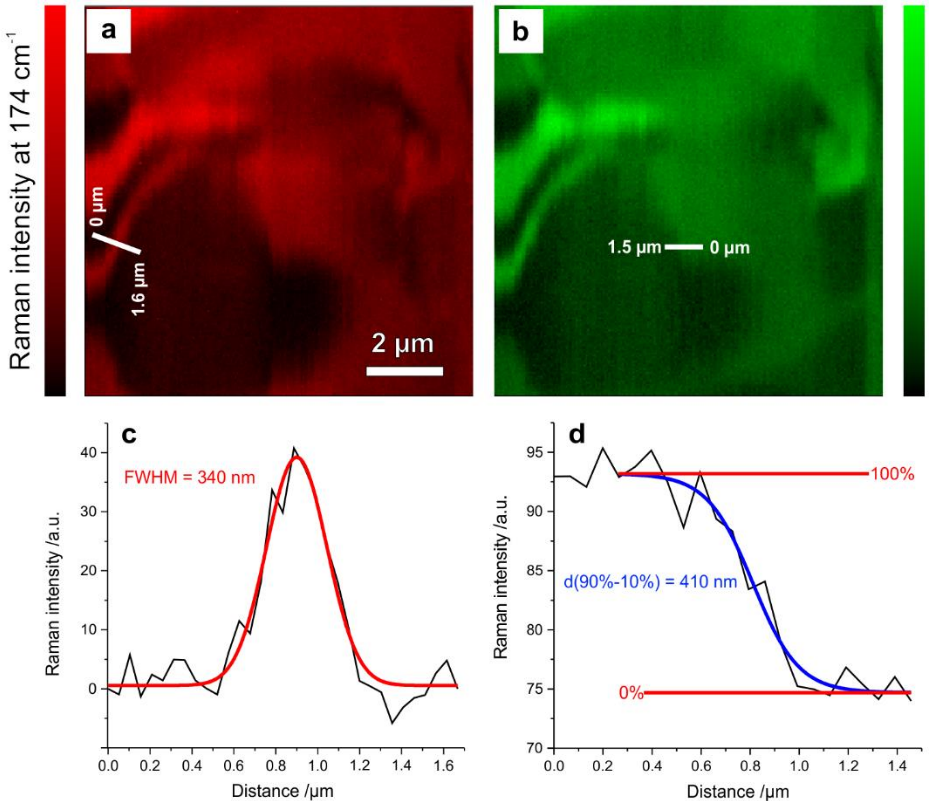
40x/*NA*=0.65 (air objective): d(633 nm) = 590 nm
d(405 nm) = 380 nm

60x/*NA*=1.4 (oil immersion objective): d(633 nm) = 280 nm
d(405 nm) = 180 nm



Rule of thumb: Lateral resolution ≈ λ/2 … λ

Lateral resolution



Lateral resolution of BAM‘s Horiba JobinYvon LabRam HR800

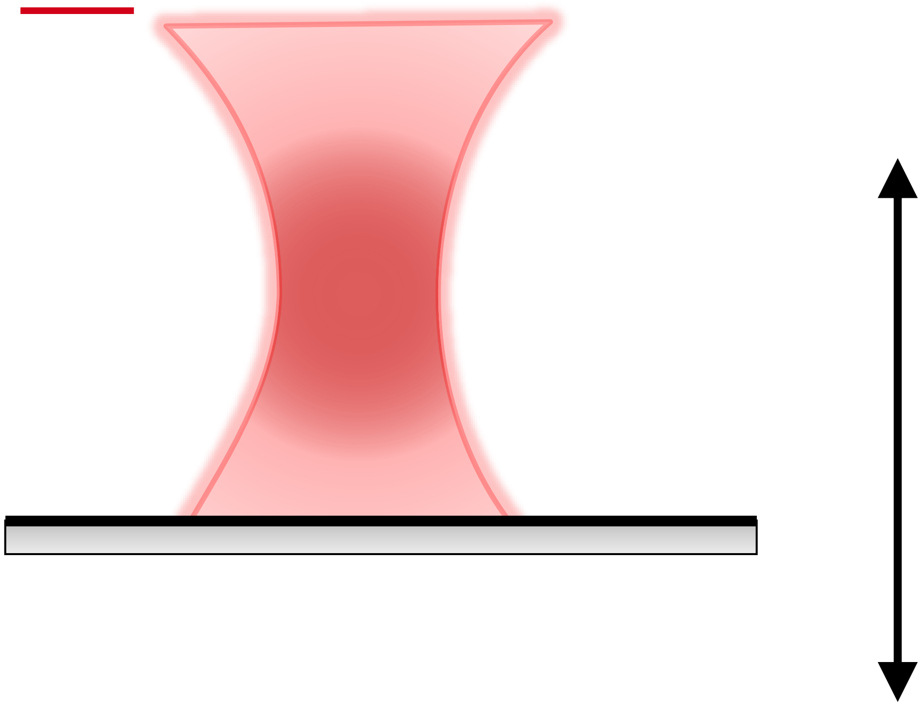
Laser: λ = 632.8 nm

Objective: 100x/*NA*=0.9

Polycrystalline $CuInSe_2$ surface

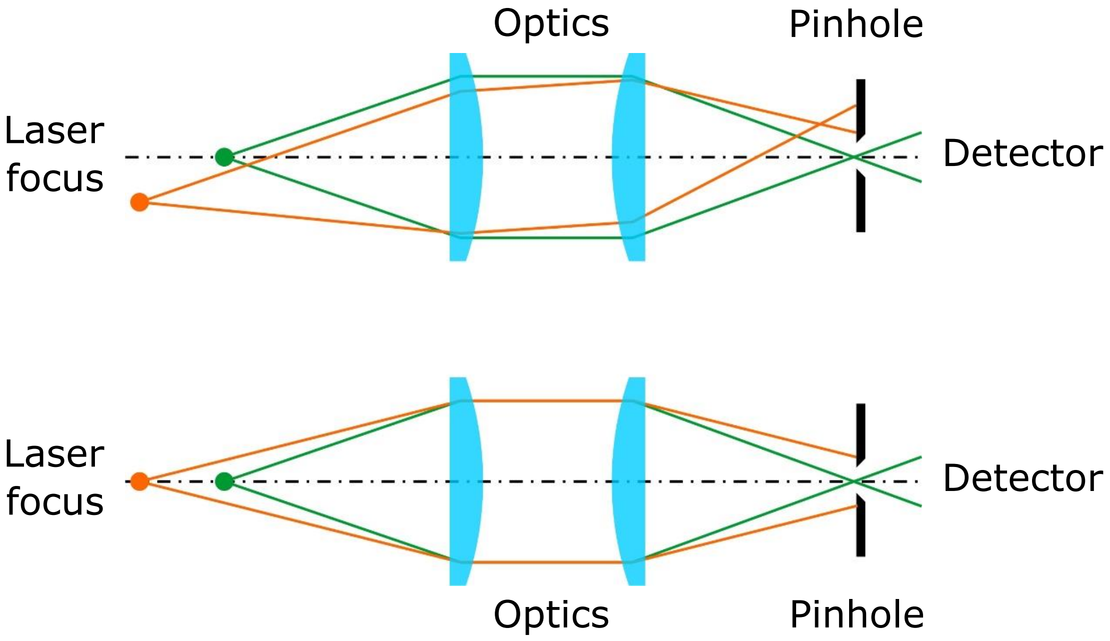
T. Schmid, N. Schäfer, S. Levcenco, T. Rissom, D. Abou-Ras, *Scientific Reports* **5** (2015) 18410.

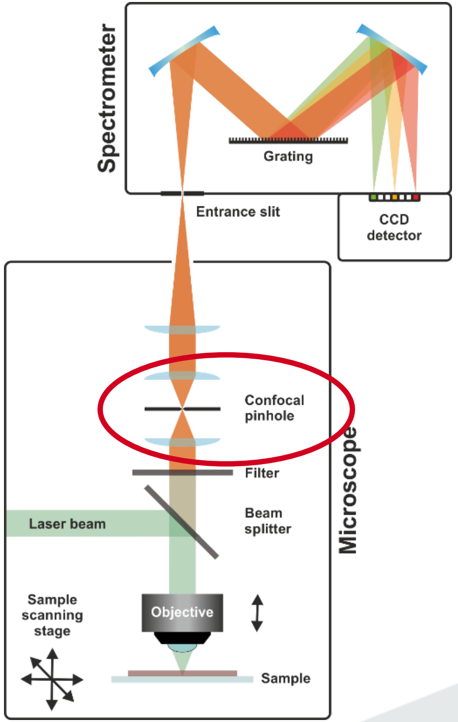
Depth resolution



A thin film or strongly absorbing sample (penetration depth << 1 µm) is scanned through the focus.

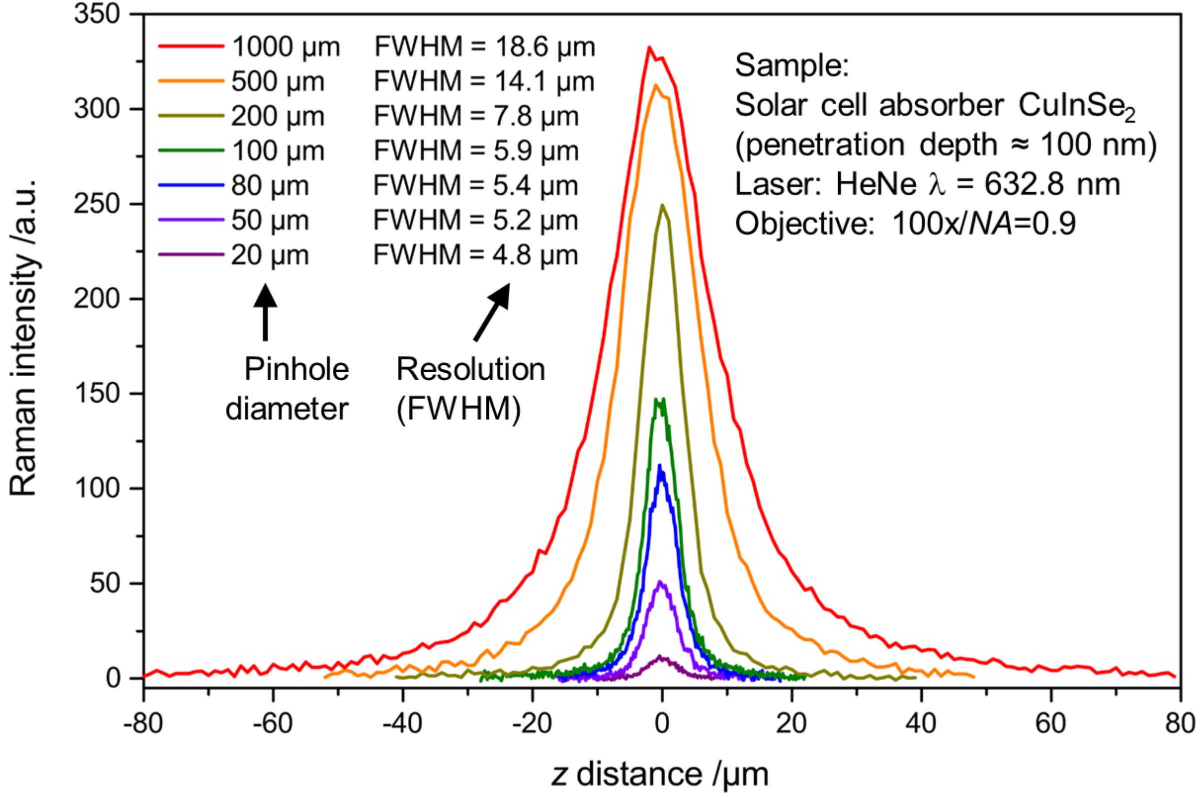
Depth resolution:
Confocal microscopy/spatial filtering





A confocal pinhole aperture rejects out-of-focus light.

Depth resolution

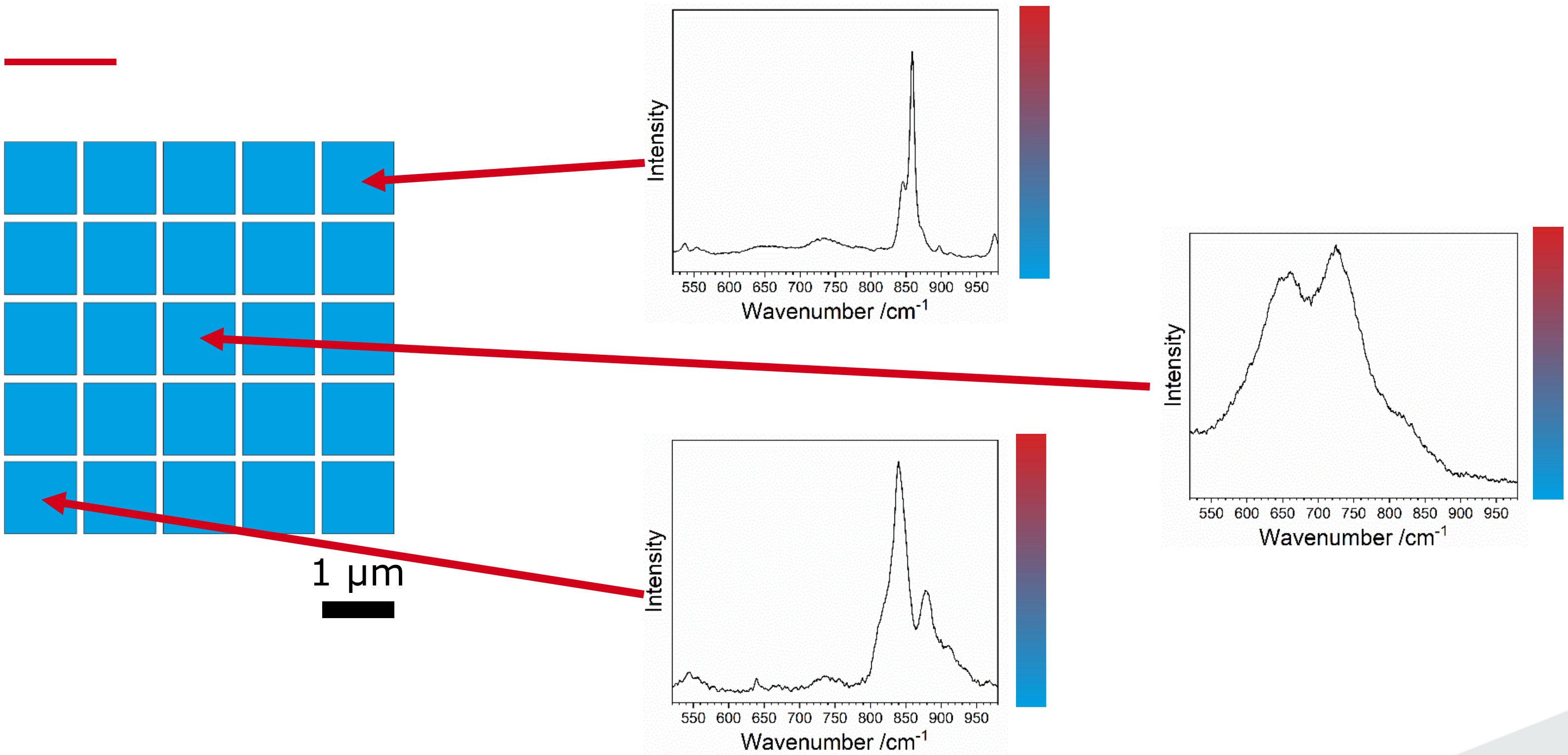


Depth resolution of BAM‘s Horiba JobinYvon LabRam HR800

T. Schmid, N. Schäfer, S. Levcenco, T. Rissom, D. Abou-Ras, *Scientific Reports* **5** (2015) 18410.

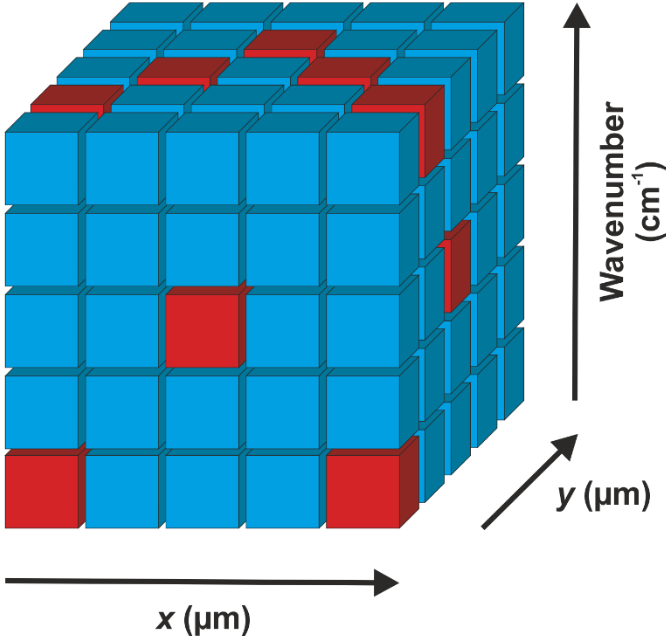
Microspectroscopic Imaging: Analysis of 4D data

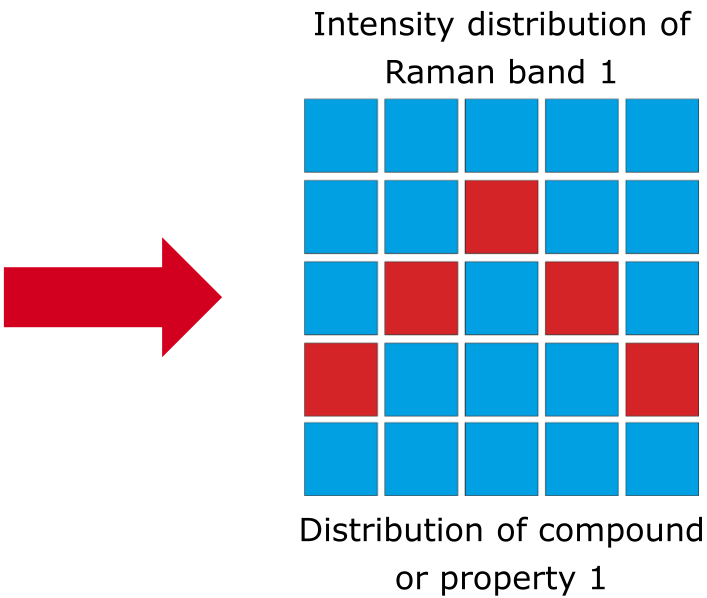
Data analysis: In simple terms …



A full spectrum is acquired in every pixel of an image:
2 spatial and 2 spectral axes.

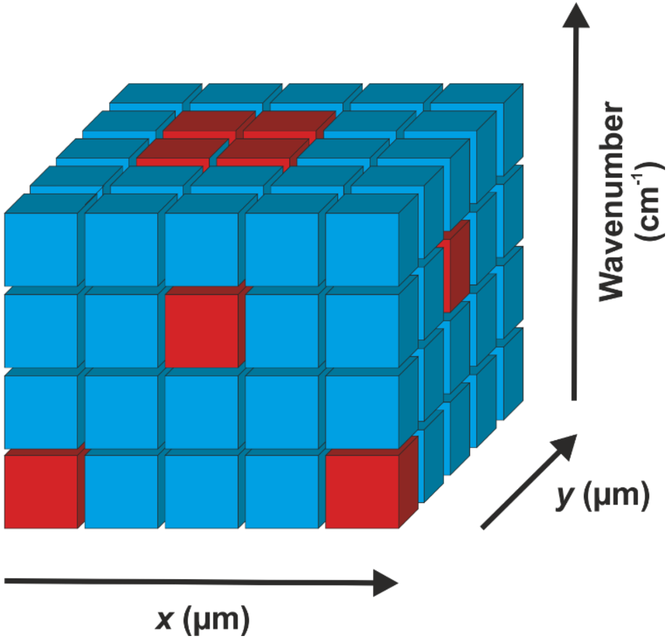
Data analysis: In simple terms …



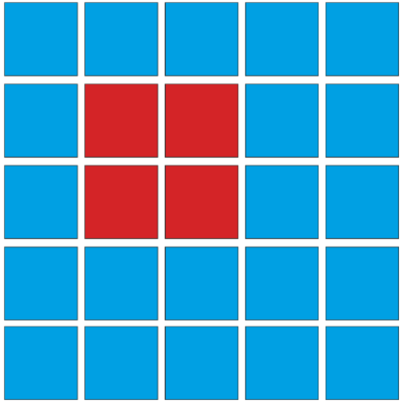


Colours = Spectral intensities

Data analysis: In simple terms …



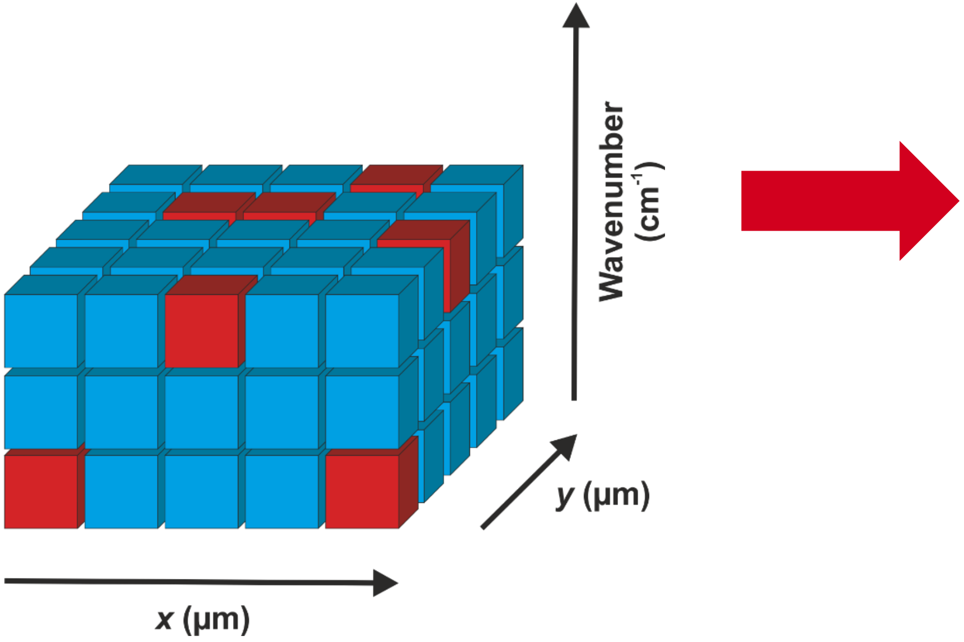
Intensity distribution of Raman band 2



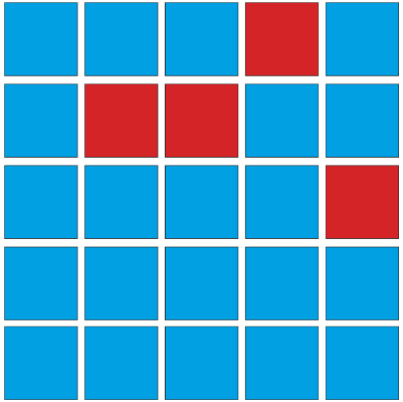
Distribution of compound or property 2

Colours = Spectral intensities

Data analysis: In simple terms …



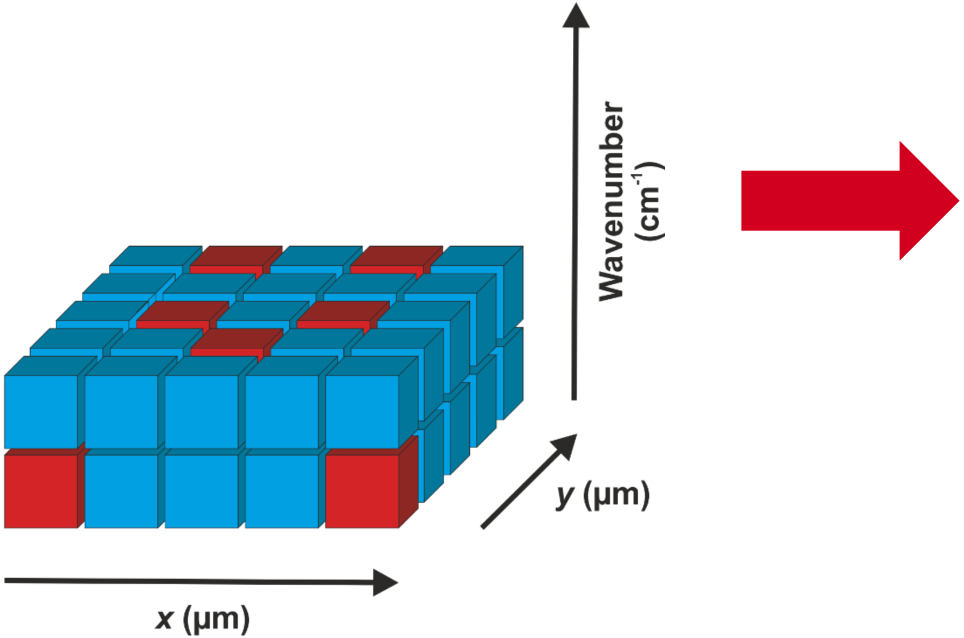
Intensity distribution of
Raman band 3



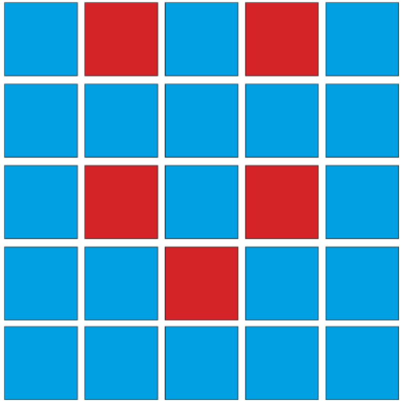
Distribution of compound
or property 3

Colours = Spectral intensities

Data analysis: In simple terms …



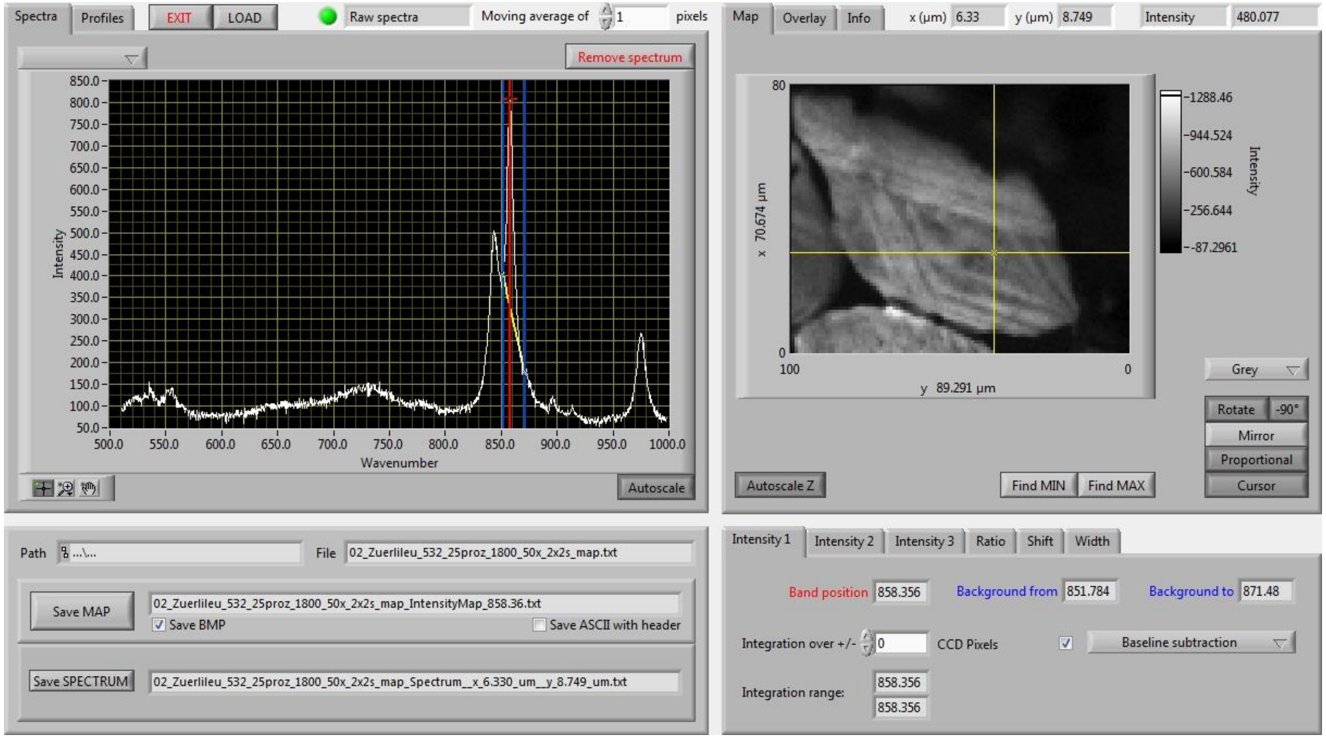
Intensity distribution of Raman band 4



Distribution of compound or property 4

Colours = Spectral intensities

Data analysis: In reality …



In every pixel/spectrum:

- Baseline subtraction
- Band intensity
- Band integral
- Band position
- Peak fitting for:
  - Precise band position
  - Band width
- …

Own LabView (NI™) software for analysis of hyperspectral data.

Raman microspectroscopy

Properties, pros and cons

The full spectroscopic information available in every pixel enables the

- identification of molecules and mineral phases by “fingerprint” comparison
- identification of polymorphs by “fingerprint” comparison
- determination of crystal orientations by evaluating relative band intensities
- determination of stress/strain based on small band shifts
- determination of compositional changes within solid solution series based on large band shifts
- study of crystallinity (crystallite size, lattice defects) by measuring band widths
- …

Raman microspectroscopy

Properties, pros and cons

Which samples can be analysed?

- Everything that fits under a microscope.
- For good imaging results, (micrometric) flat surfaces are needed.
- Ideal: Polished cross sections and thin sections embedded in (non-fluorescing!) resins

Drawback 1: Raman scattering is a weak effect

- Relatively long acquisition times
- Easily overwhelmed by fluorescence or other optical emissions

Drawback 2: Microspectroscopic imaging may take a little while …

- 20 x 20 pixels x 1 s acquisition time ≈ 7 min
- 50 x 50 pixels x 1 s acquisition time ≈ 42 min
- 100 x 100 pixels x 1 s acq. time ≈ 2 h 47 min
- 200 x 200 pixels x 1 s acq. time ≈ 11 h 7 min
- 200 x 200 pixels x 5 s acq. time ≈ 2 d 7 h 33 min

Literature for Raman

used in this lecture

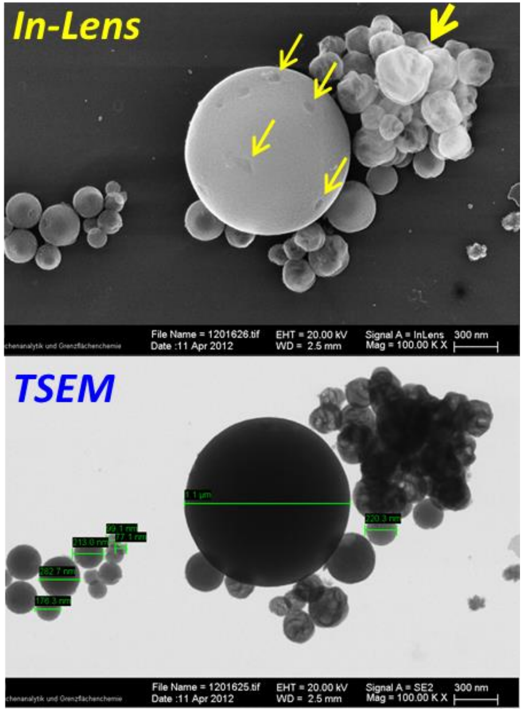
Thomas Schmid, Petra Dariz,
Heritage 2 (2019) 1662-1683.
http://dx.doi.org/10.3390/heritage2020102

Thomas Schmid, Norbert Schäfer, Sergiu Levcenco, Thorsten Rissom, Daniel Abou-Ras,
Scientific Reports 5 (2015) 18410.
http://dx.doi.org/10.1038/srep18410

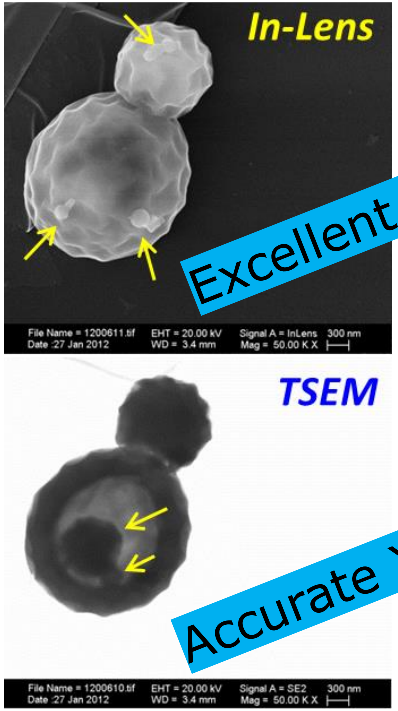
Examples
of Correlative Imaging

Multimodal Imaging with Electron Microscopy

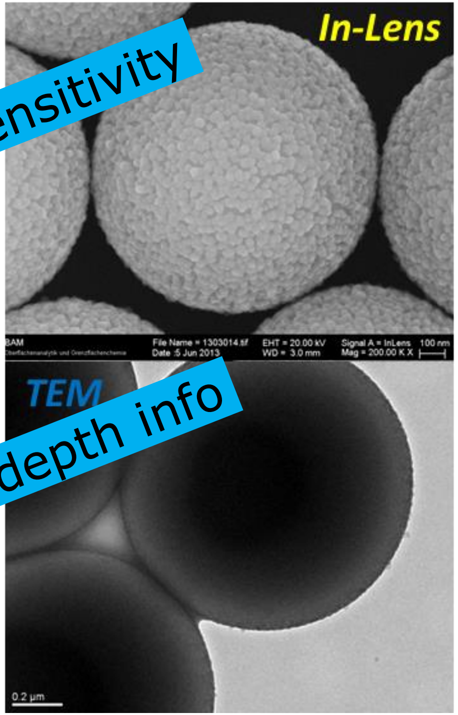
InLens and in-Transmission Detection at nano scale



Hodoroaba & al, *Surf Interf Anal* 2014



Hodoroaba & al, *Analyst* 2014



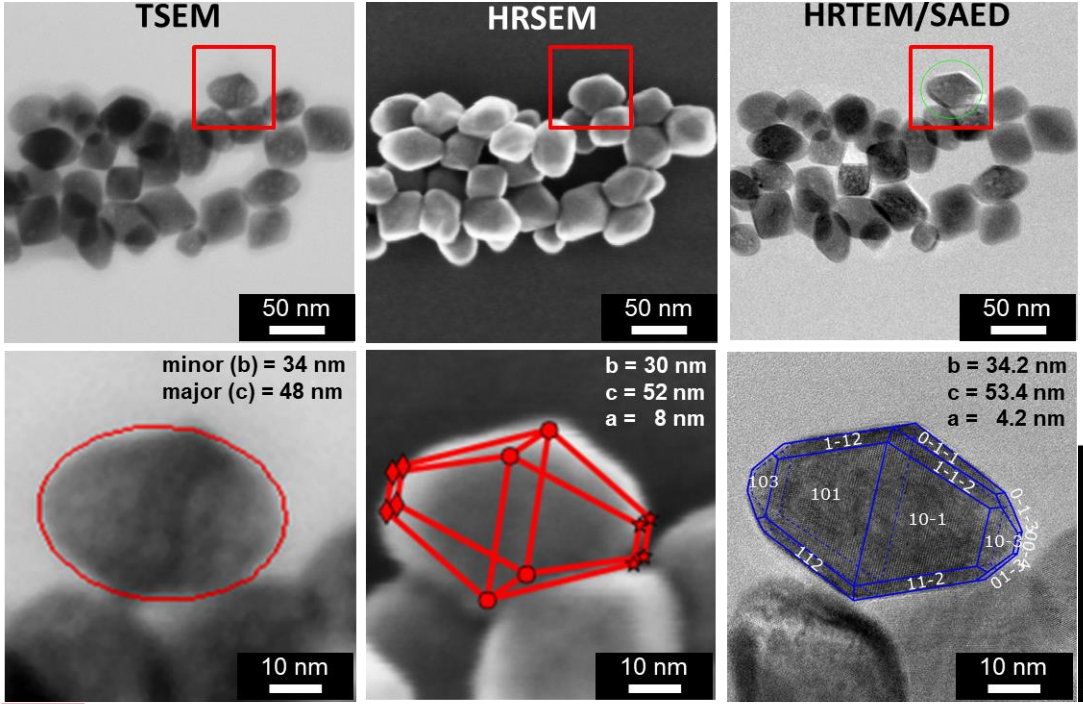
Sarma & al, *Appl Surf Sci* 2017

Excellent surface sensitivity

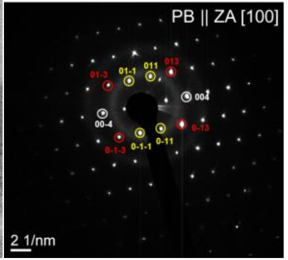
Accurate XY and in-depth info

Correlative Microscopy by SEM & STEM-in-SEM & HRTEM/SAED

Example: **One** (!) TiO_2 nanoparticle examined by three methods



Selected Area Electron Diffraction (SAED)

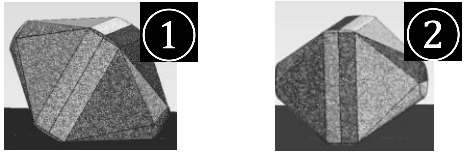


→ SEM: surface morpho
→ TSEM: dimensional projection measurements
→ TEM/SAED: 3D shape

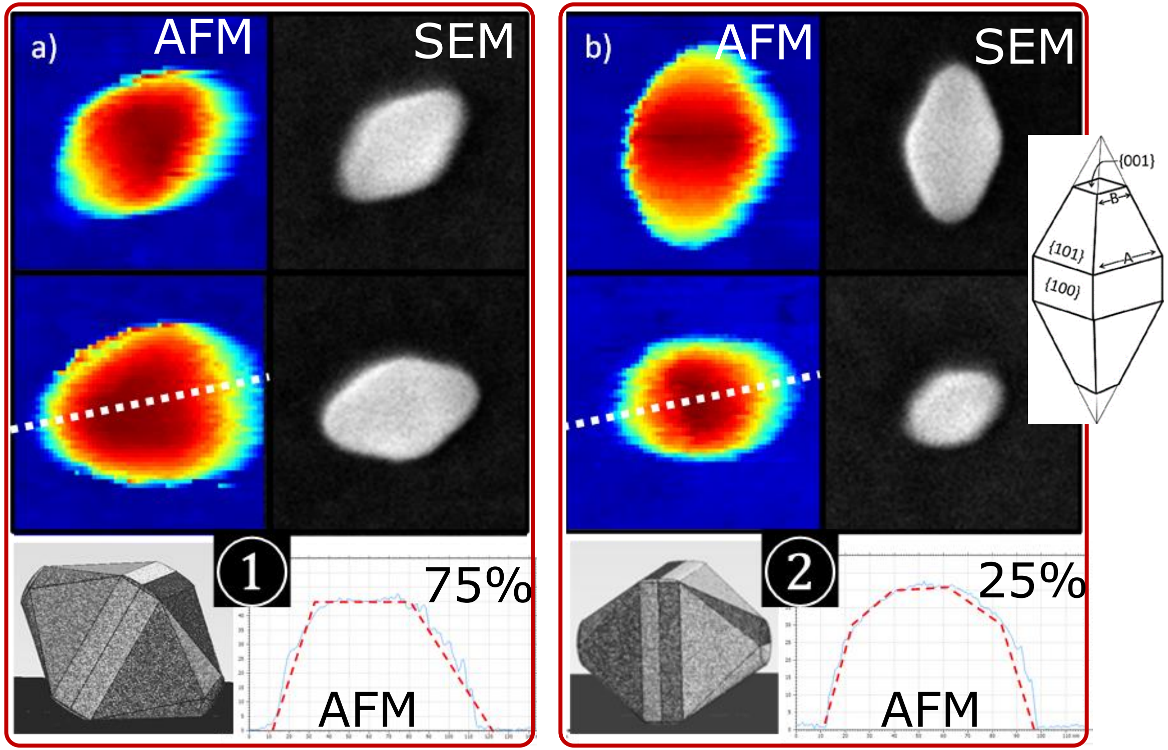
Correlative Microscopy by **AFM** & SEM

The EMPIR initiative is co-funded by the European Union's Horizon 2020 research and innovation programme and the EMPIR Participating States

AFM and SEM image examples of TiO_2 nano-bipyramids with the orientations: a) ① and b) ② on the substrate.

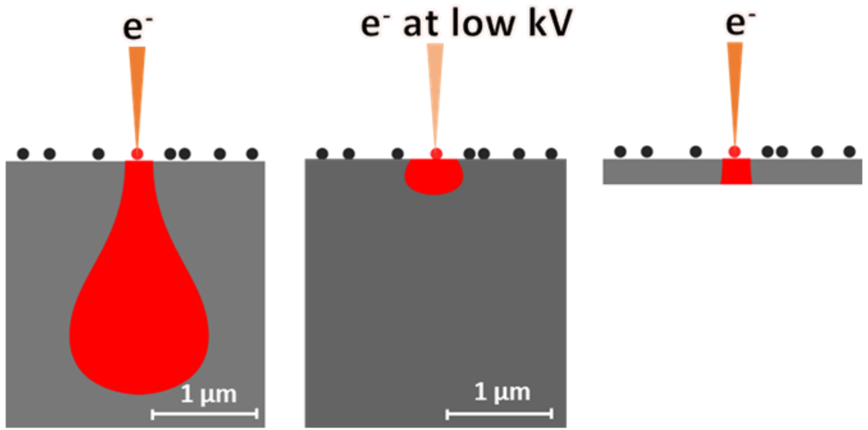


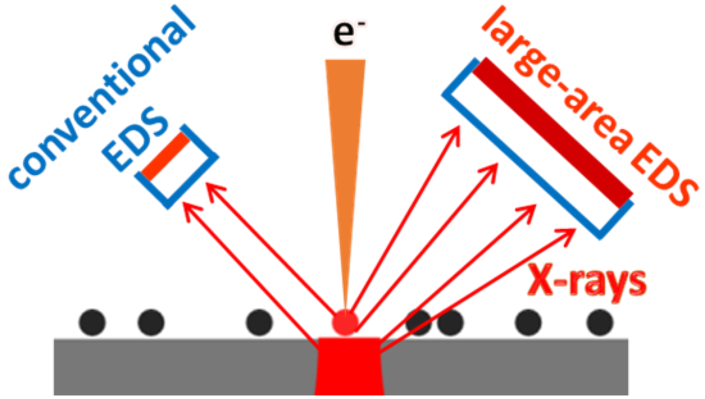
For each orientation, an AFM profile along the long axis is displayed.



Crouzier, ..Cios *et al*, *Nanomaterials* 2021

Multimodal Imaging with Electron Microscopy - TEM in SEM and hi-res (nano) X-ray Imaging
How to catch better the **surface**?



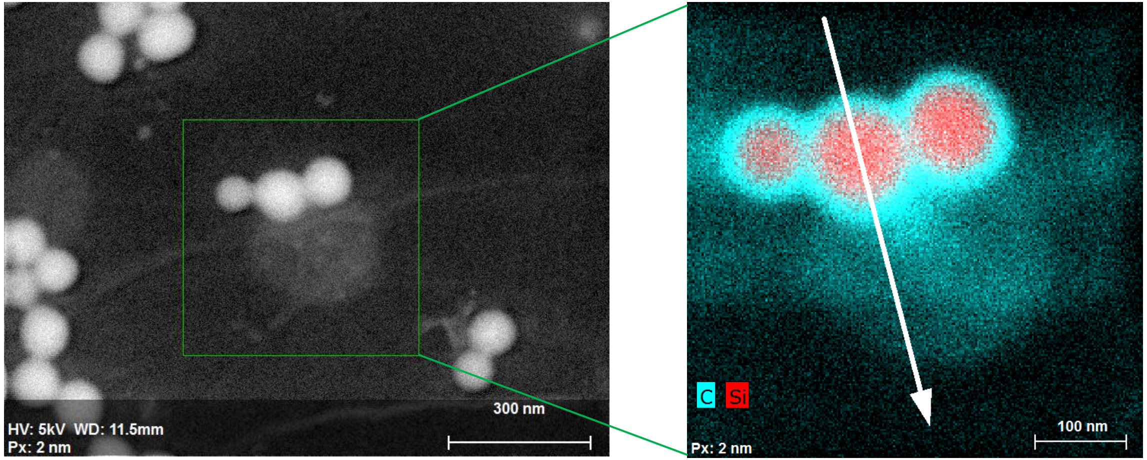


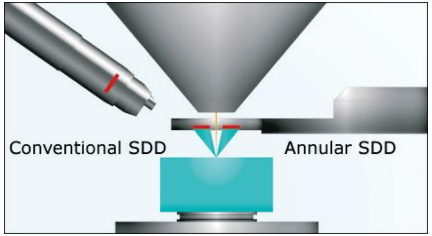
A: get rid of substrate, gentle excitation, sensitive detectors, sample preparation

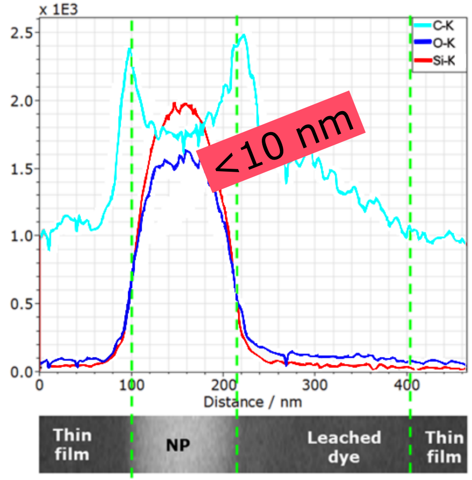
Hodoroaba & al, *Characterization of Nanoparticles*, Elsevier book, 2020

Multimodal Imaging with Electron Microscopy - TEM in SEM and hi-res (nano) X-ray Imaging - Ultimate spatial resolution @BAM: a few nm

Silica NPs coated with Alexa® dye





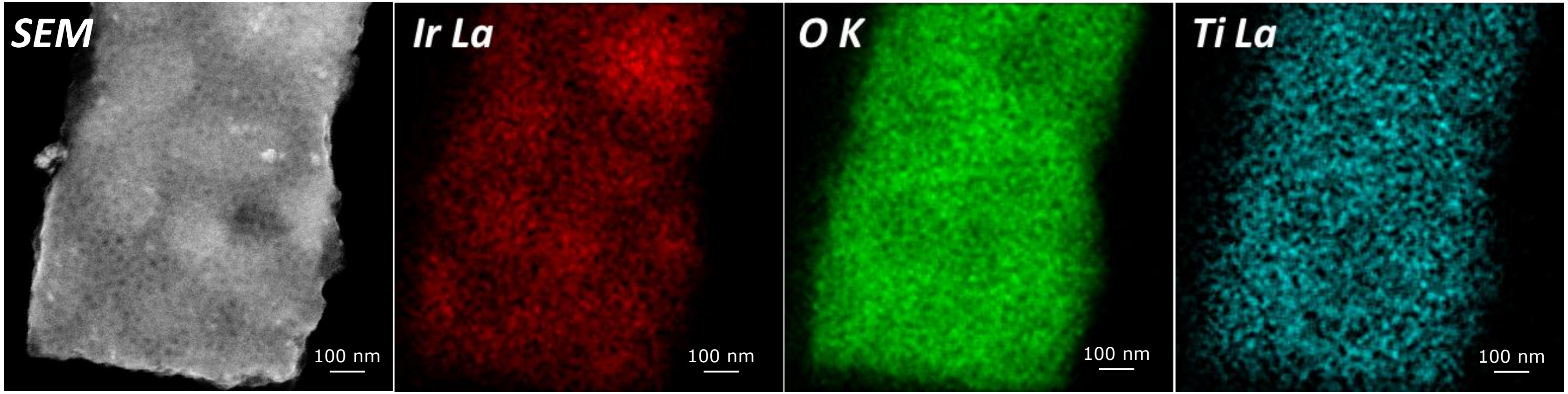


Rades & *al*, *RSC Adv* 2014, Hodoroaba & *al*, *IOP Conf Ser Mat Sci Eng* 2017

Porous IrOx-TiOx thin films for energy appl.
SEM, hi-res elemental imaging by EDS

Thin layer prepared as free standing sample

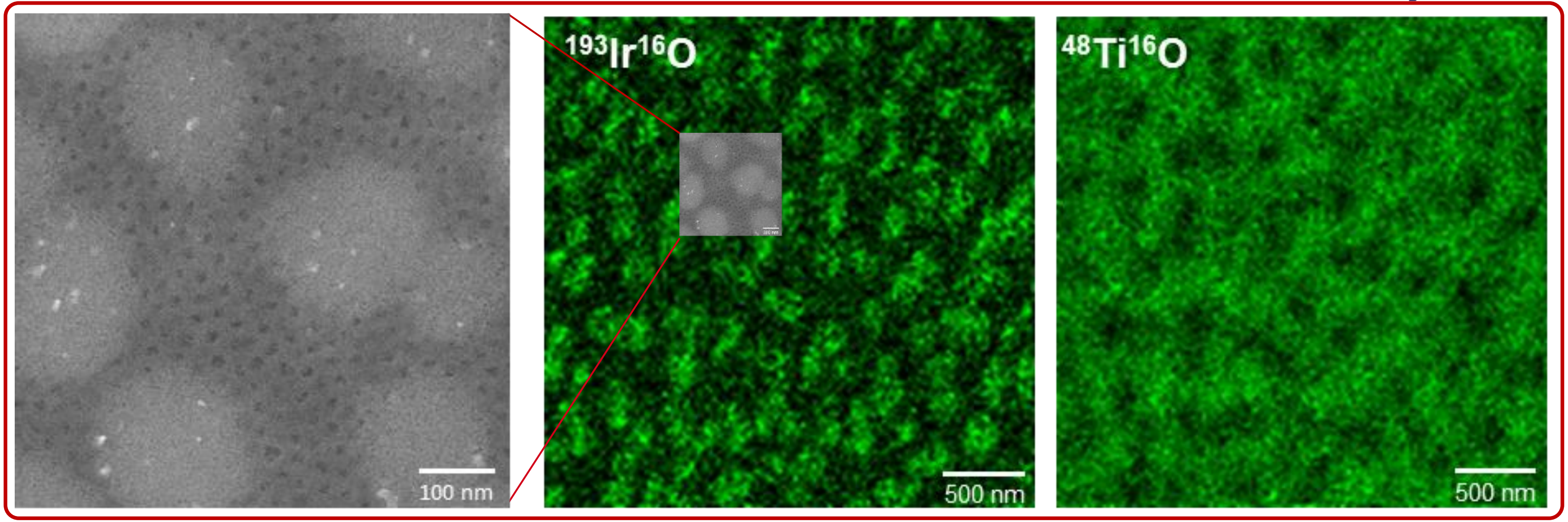
Gentle excitation (5 kV, soft E) + hi-sens EDS ⇒ spatial resol: a few 10 nm



– IrO_x-rich islands within mesoporous TiO_x-rich matrix

Sachse *et al*, *Microsc Microanal* 2019

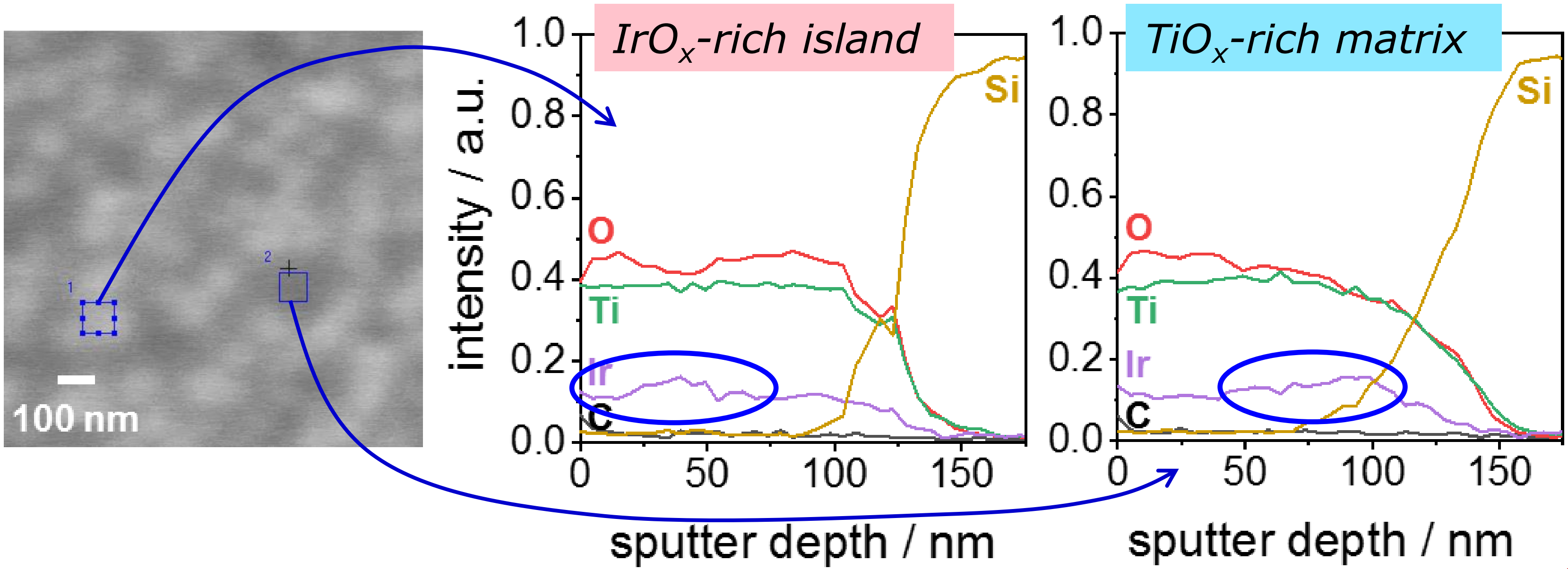
Porous IrOx-TiOx thin films
SEM, EDS & hi-res chemical imaging by nanoSIMS



– IrO_x-rich islands within mesoporous TiO_x-rich matrix at the surface

Sachse *et al*, *Microsc Microanal* 2019

Porous IrOx-TiOx thin films
SEM, EDS & In-depth Auger Electron Spectroscopy

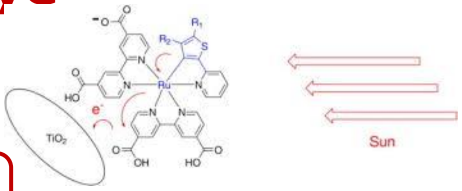


– IrO_x-rich islands in-the-depth of mesoporous TiO_x-rich matrix

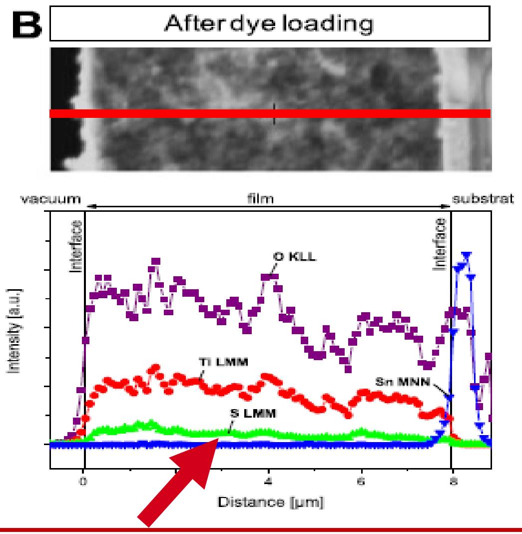
Sachse *et al*, *Microsc Microanal* 2019

Chemistry across-the-layer

Screen-printed TiO_2 NP films loaded with Ru-dye for DSSC applications –

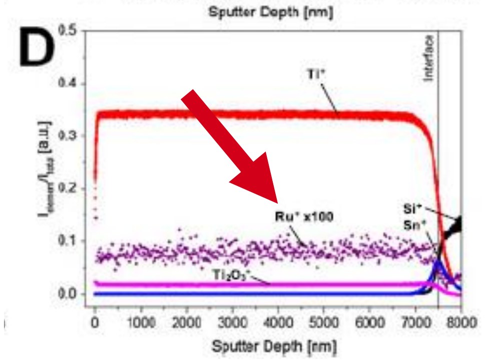


Auger probe **linescan on cross-section** (fractured sample)



ToF-SIMS depth profile by **sputtering**

homogeneous loading ✓



Ortel *et al*, *Surf Interface Anal* 2016

Multimodal Imaging nanoTools -
SEM & Scanning Auger Microprobe
SiO_2 Nanoparticle and the first nm at the surface

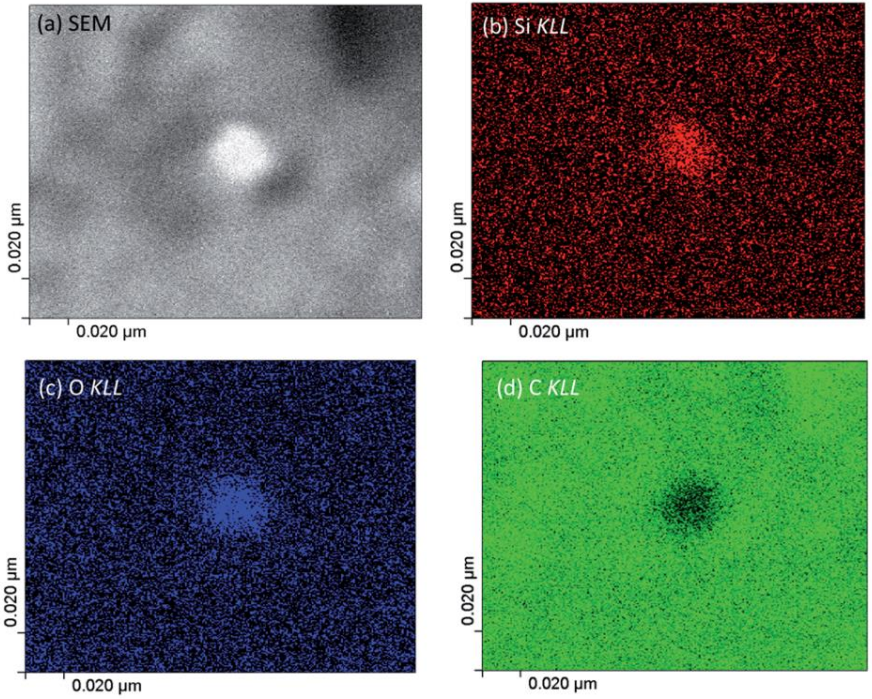
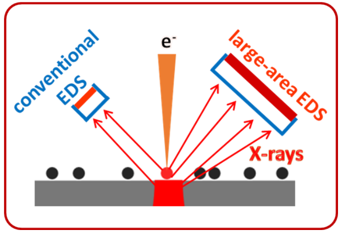


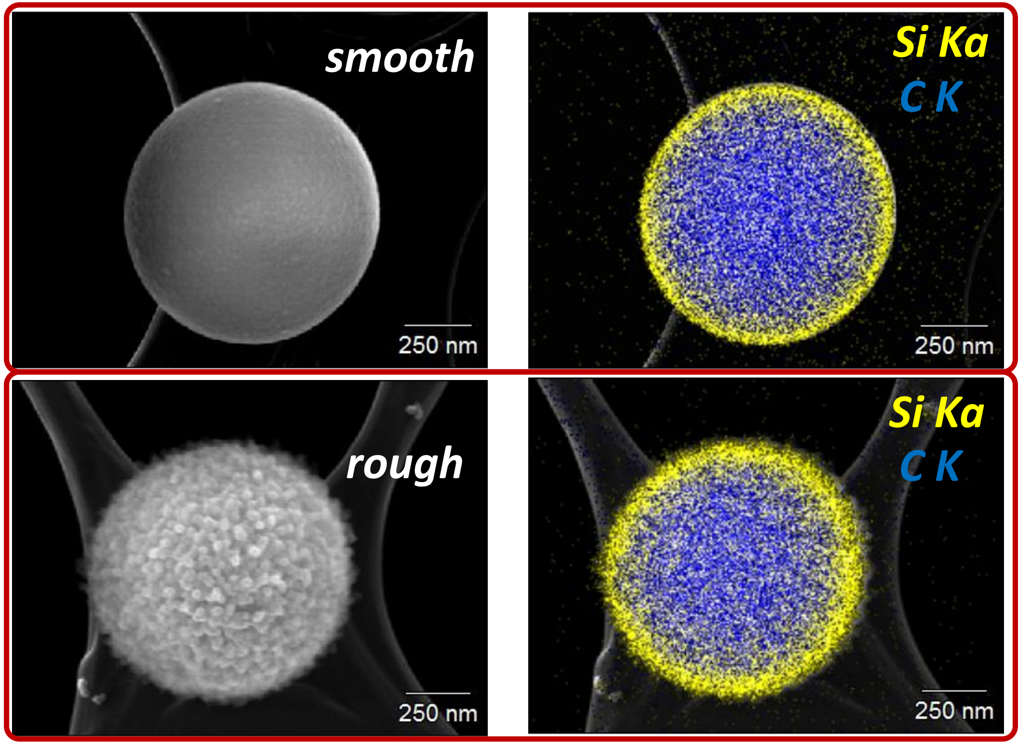
Fig. 7 (a) Image of a silica nanoparticle on a TEM grid taken in the SEM mode of the SAM nano probe applying a 20 keV primary electron beam, (b) Si KLL elemental map, (c) O KLL elemental map and (d) C KLL elemental map.

Rades & *al*, *RSC Advances* 2014

Multimodal Imaging nanoTools - TSEM & hi-res SEM & hi-res EDS Examples

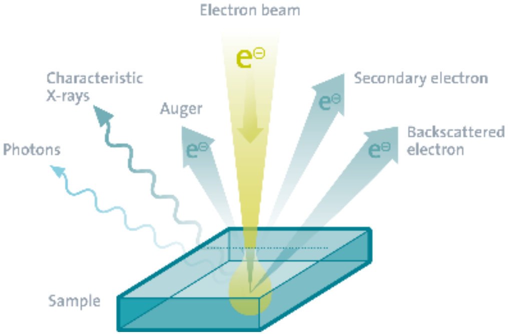
PS core/SiO_2 NP shell



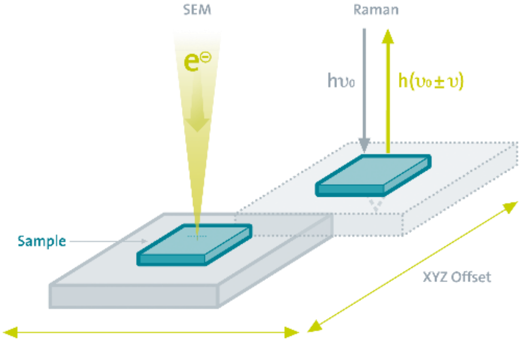


Sarma & *al*, *Appl Surf Sci* 2017

Correlative Surface Imaging on Adv 2D-Materials
An example: Graphene Characterization



WiTec GmbH – 1st integrated AFM & SEM



Schmidt *et al*, *Microsc Microanal* 2019

Accurate characterisation of industrial products:

- **Structural**: thickness and lateral size by SEM & AFM
- **Chemical**: Raman (RISE), XPS, NEXAFS

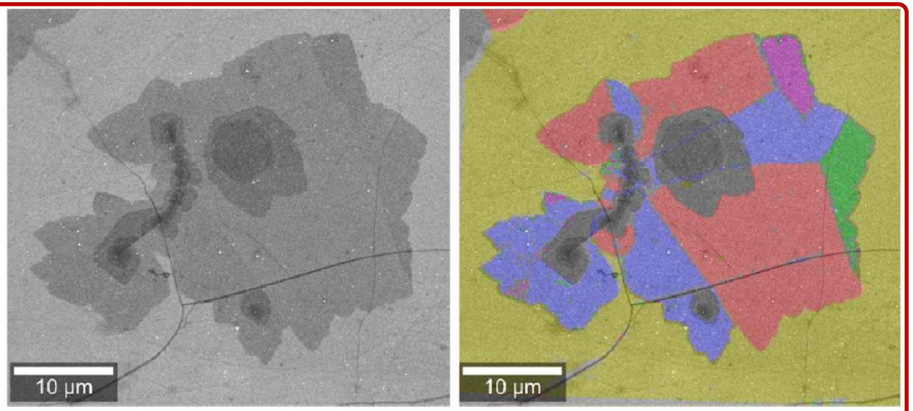


Figure 1. SEM and RISE image of a grain of twisted bilayer of graphene.

Correlative Surface Imaging by ToF-SIMS and SEM for studying deuterium-assisted degradation in duplex steels

HR-SEM + SIMS/PCA/HCA

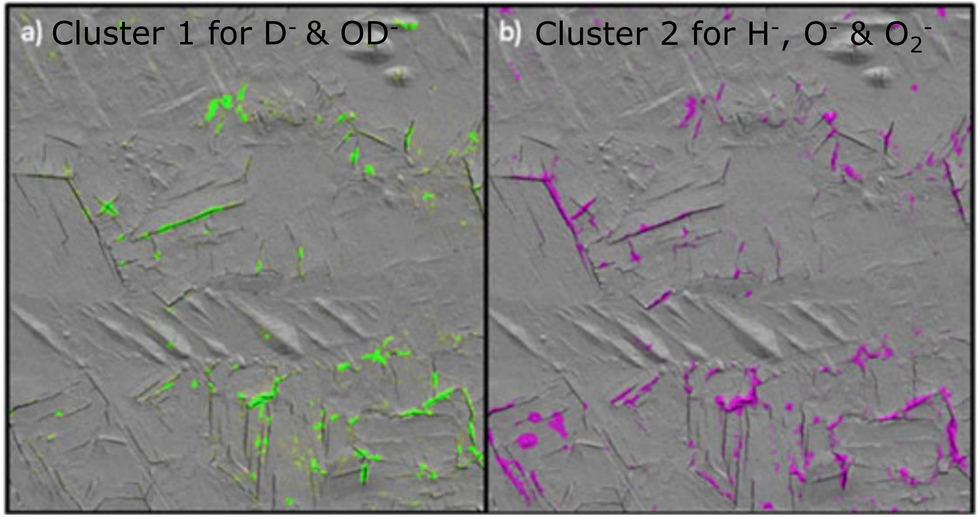
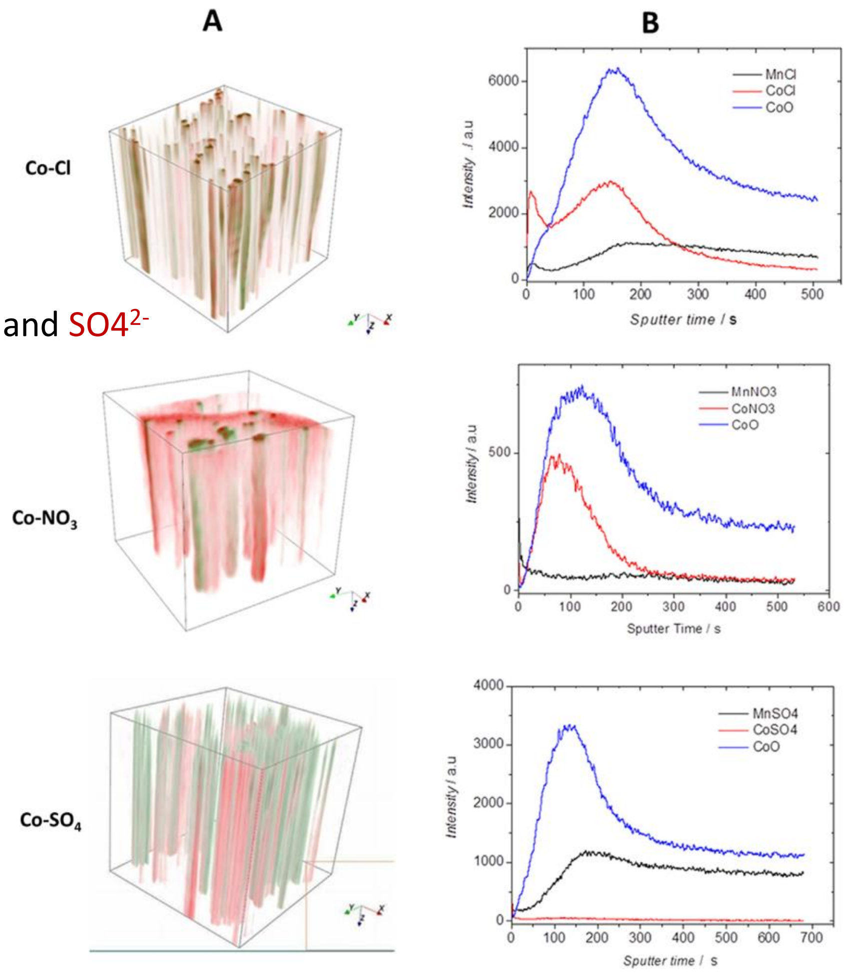


Figure 4. Clusters 1 and 2 (Fig. 3) re-projected to the image domain and finally fused with the high-resolution SEM image. (a) Green areas show regions of high concentrations formed by the cluster 1 (D^- and the OD^-) related to the charging process, and (b) pink areas show regions of high concentrations represented by cluster 2 (H^-, O^-, and O_2^-) related to absorption of hydrogen species via H/D exchange during the transfer of the sample from charging to the analysis chamber. Although both deuterium and hydrogen appear to distribute around crack, it seems that hydrogen is distributed more homogenously around the crack while the deuterium is distributed more in the cracks tips and branches. The high current bunched mode was used to differentiate H_2 and deuterium.

Sobol *et al*, *Surf Interface Anal* 2016

3D SIMS



Co^{+}

Cl^{-}, NO^{3-} and $SO4^{2-}$

(A) ToF-SIMS positive ions 3D data reconstruction on Co@KMO-Cl, Co@KMO-NO and Co@KMO-SO catalysts supported on glassy carbon.

(B) ToF-SIMS negative ions depth profiles

Pu *et al*, *J Catal* 2021

Correlative Surface Imaging
Conclusions

- Use of different working modes = exploitation of different sensitivities, lateral/depth resolutions
- „One method is no method“
- Correlate morphology/structure/chemistry
- Electron Microscopy = gold standard
- Define clearly your analytical task; Imaging makes fun, interpretation, particularly quantitative is mostly difficult
- Many many correlative imaging possibilities, lot of dynamic on the market
- Enjoy it!