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Development and applications of the Secondary Ion Mass Spectrometry with MeV ions (MeV SIMS) technique at the RBI accelerator

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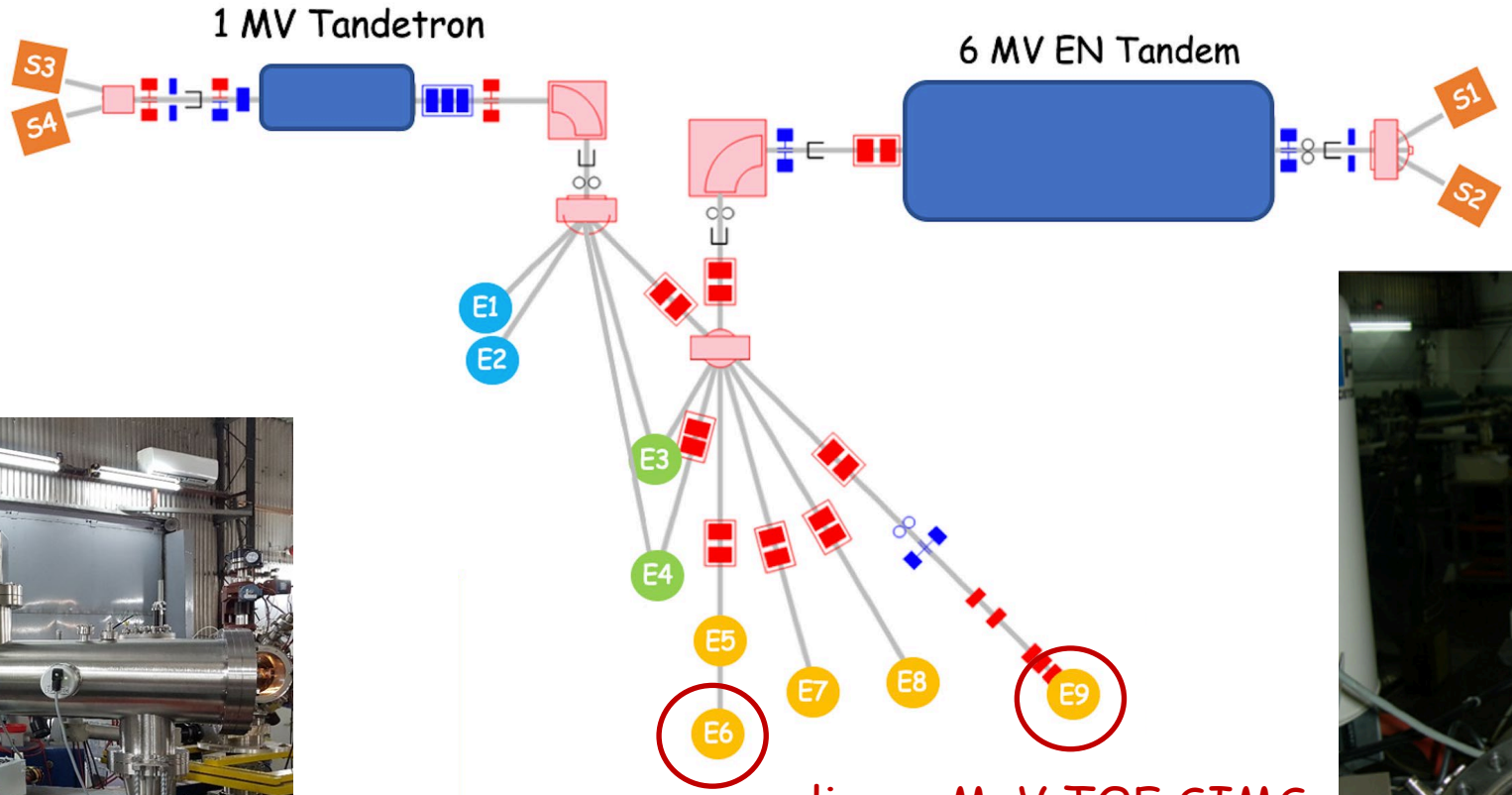
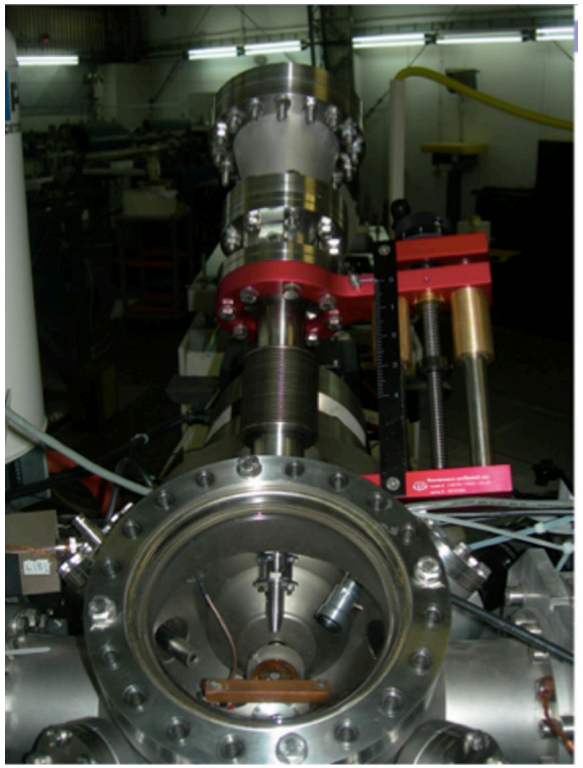
RBI accelerator facility

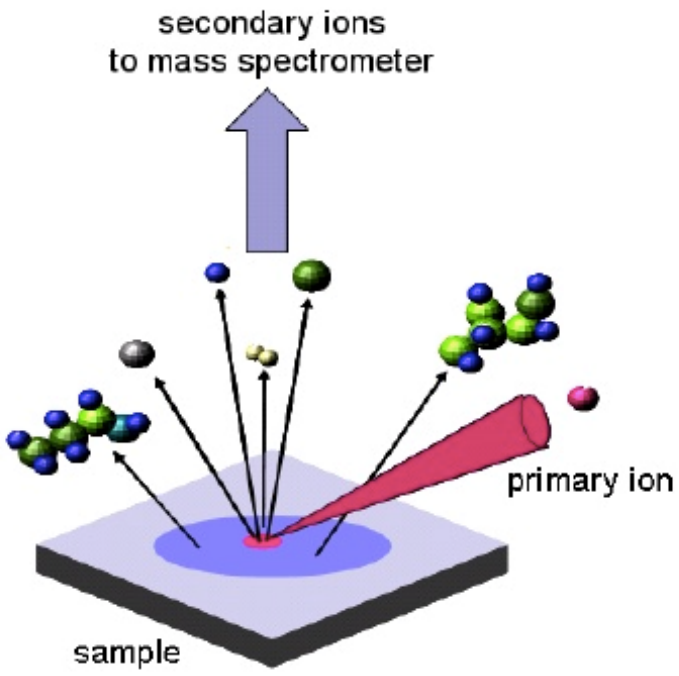


reflectron MeV
TOF SIMS

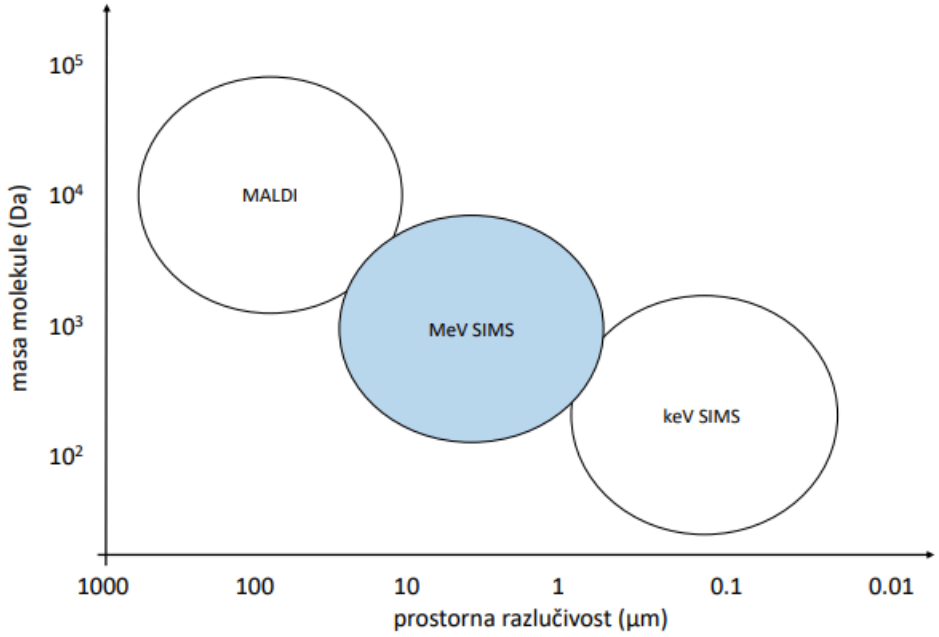
linear MeV TOF SIMS
$ME/q^2<14$
e.g. 8 MeV Si^{4+}



Why Secondary Ion Mass Spectrometry with MeV ions- MeV SIMS?



- first ion beam technique for determining mass composition
- non-destructive – very low currents (fA range)
- detected masses: 1 - 2000 Da
- high efficiency: ~ 1 secondary molecular ion per 100 incident ions
- 10^3 higher yield for heavy molecules than keV



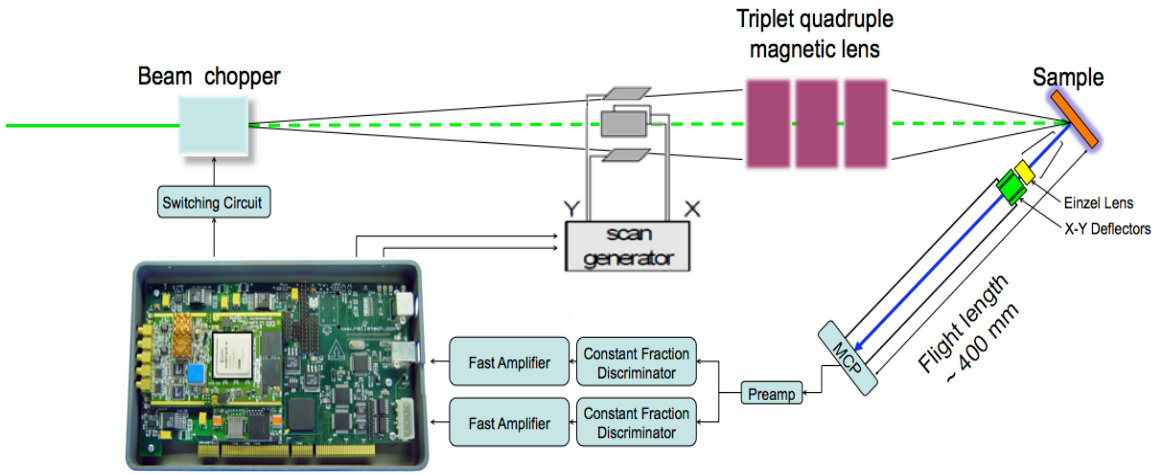
- μ-beam is available – molecular imaging at the micron level

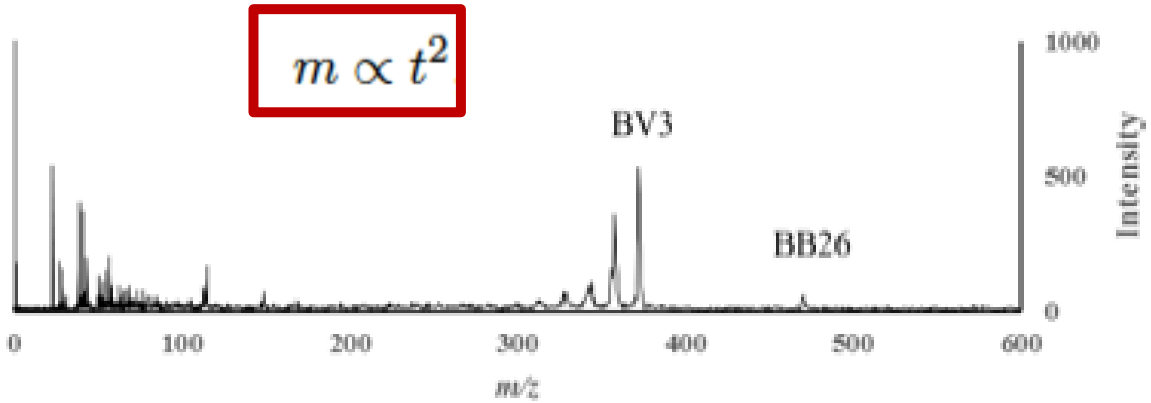
Surface sensitive!

Linear ToF MeV SIMS spectrometer at RBI

MeV-SIMS setup-pulsed mode

In house built FPGA based multi-stop TDC acquisition





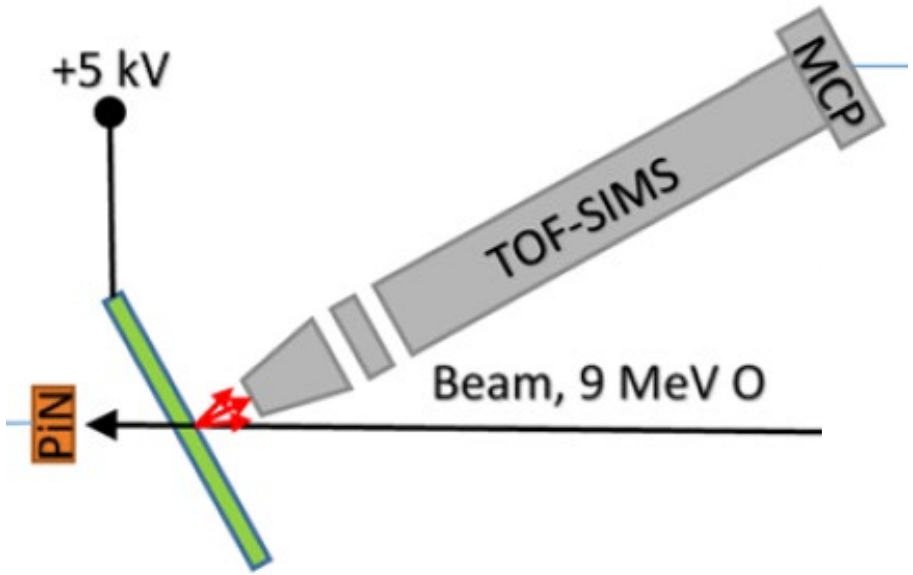
START-beam chopper
STOP-MCP detector

Pulses 2 ns with interval of 100 μs

Mass resolution m/Δm = 370 (for m/q = 132 Da)
Lateral resolution ~ 10 x 10 μm²

T. Tadic et al., NIM B 332 (2014) 234-237

MeV-SIMS setup-continuous mode

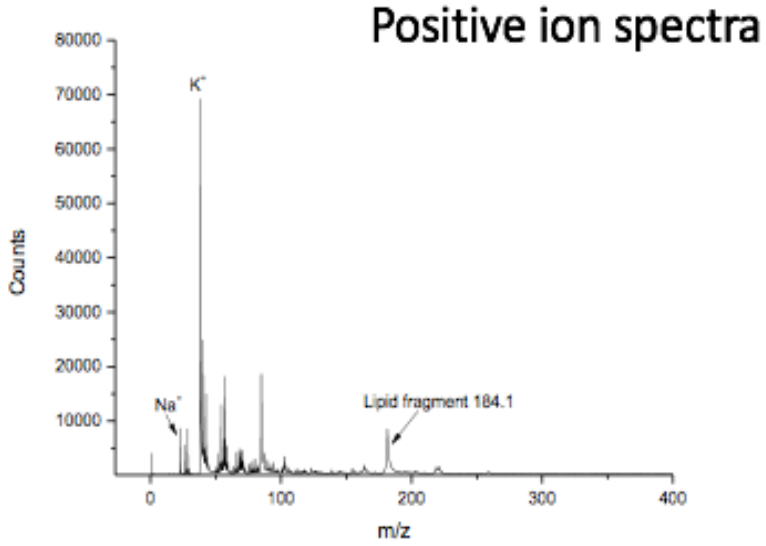


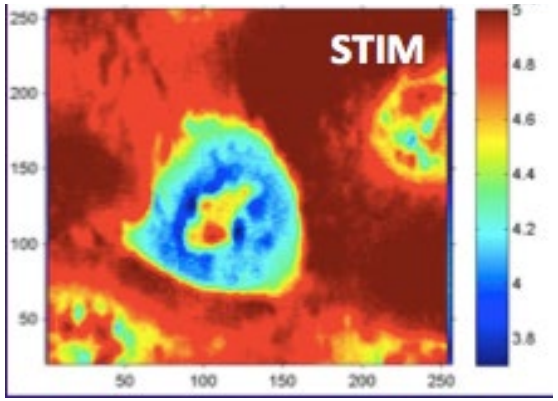
Requirements:

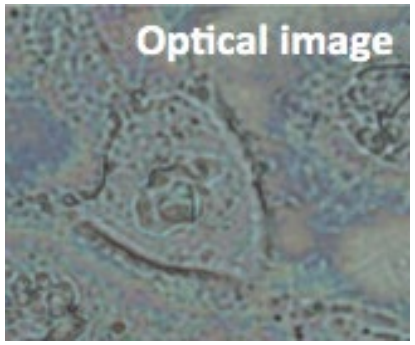
- thin samples
- Cell thickness is ~ 5 μm ☑
- Tissues sections ~5 μm ☑
- Samples are mounted on the thin (100 nm) Si_3N_4 windows

Mass resolution ~ 1/500
Lateral resolution ~ 0.5 x 0.5 μm^2

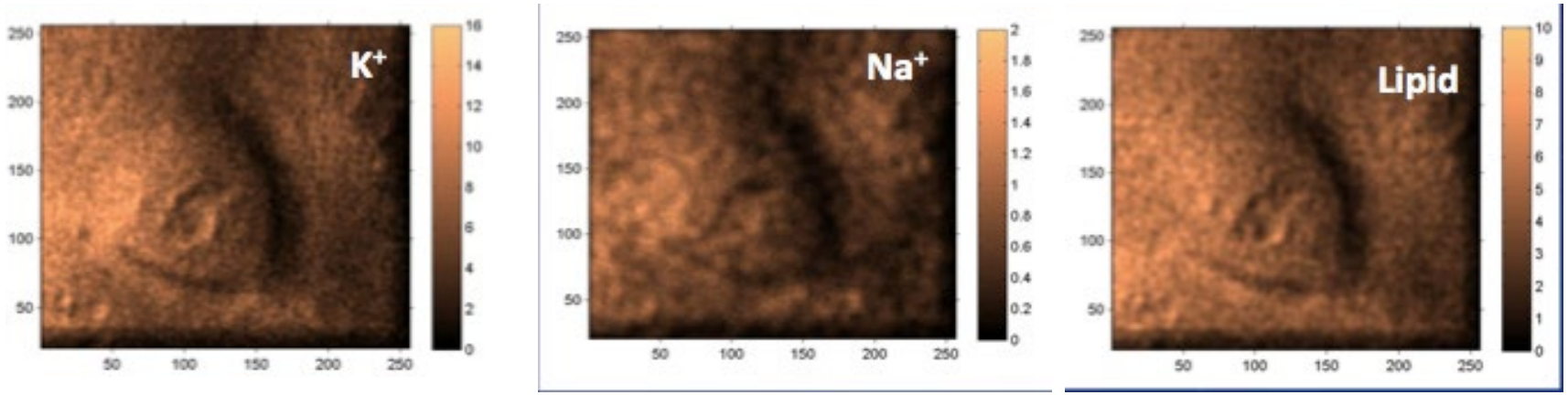
Molecular imaging of single CaCo-2 cells – biological applications







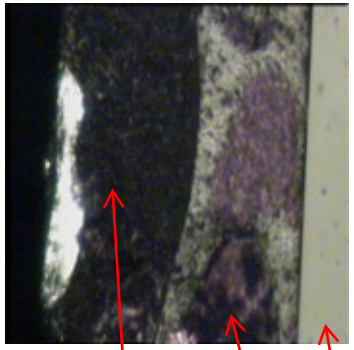
Beam: 9 MeV O^{4+}
Scan size: 85x85 μm^2 (≈300 nm/pixel)

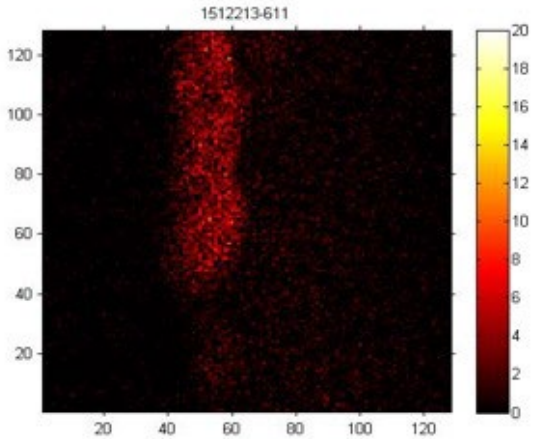


Z. Siketić et al., Apl. Phys. Lett. 107, 093702 (2015)

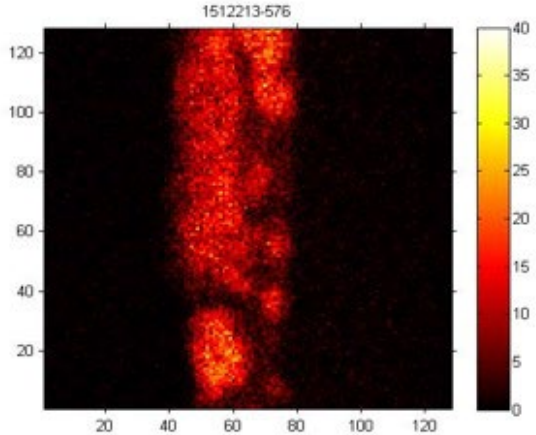
Molecular imaging of modern paint materials for cultural heritage

8 MeV Si^{4+}
1.2 x 1.1 mm^2



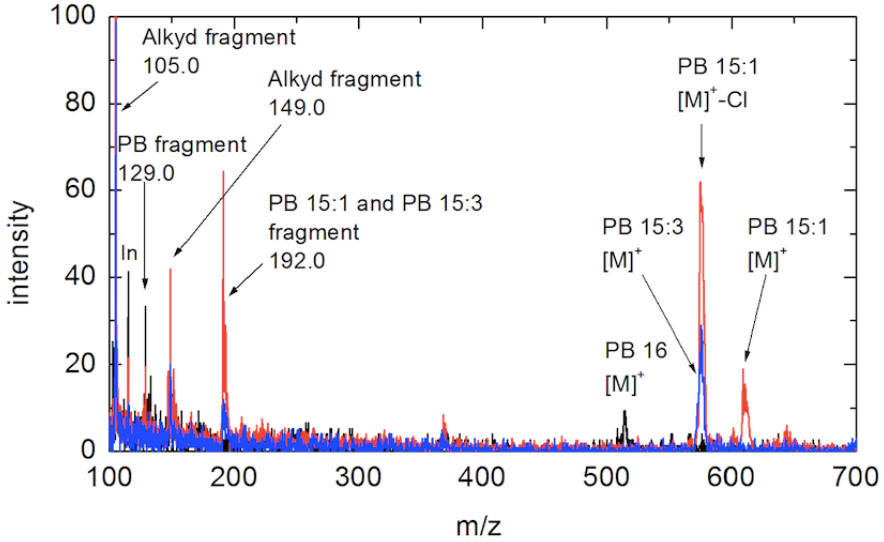


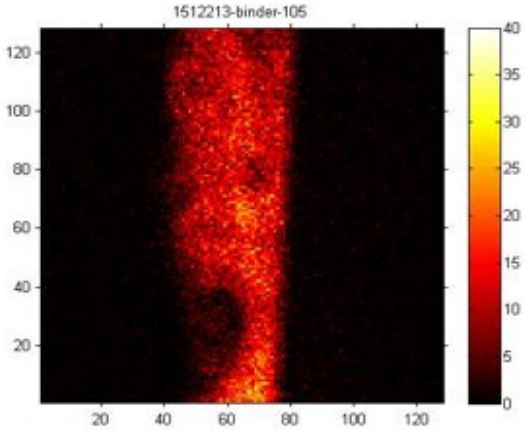
PB 15:1 (m/z=611)



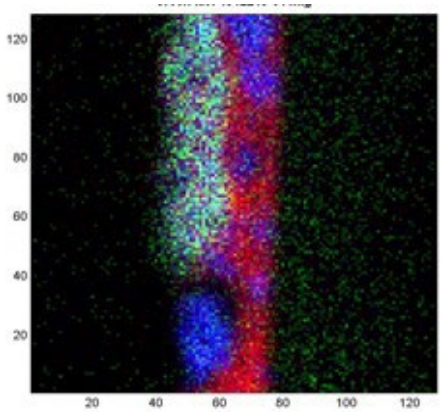
PB 15:1 and PB 15:3 (m/z=576)

Identification of different blue phthalocyanine pigments





Alkyd binder (m/z=105)



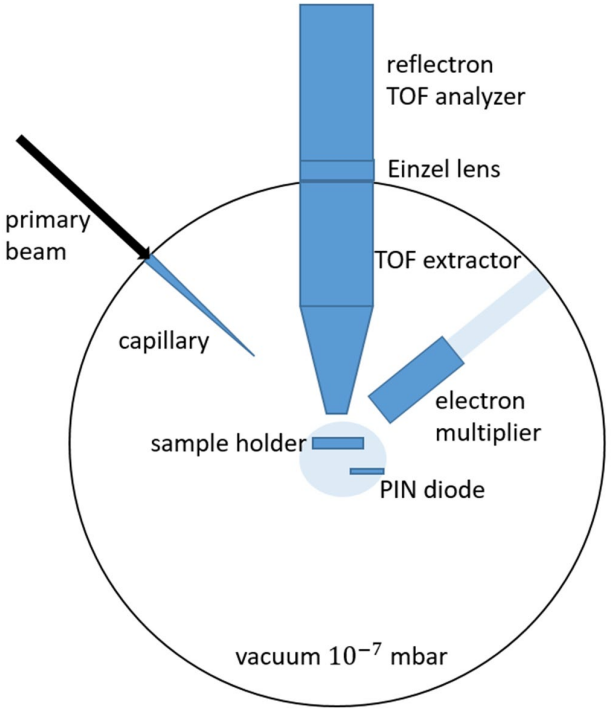
Overlay image:

Green: m/z=611
Blue: m/z=576
Red: m/z=105

I. Bogdanović Radović et al., NIM B 406 (2017)296
M. Krmpotić et al., Analytical chemistry, 92 (2020), 9287-9294
M. Krmpotić et al., Polymer degradation and stability, 195 (2022), 109769, 11

New setup for capillary microprobe for MeV-SIMS

- Capillary instead of quadrupole lenses for focusing ions –cheap alternative to expensive magnetic quadrupoles
- Scanning area 1.5 cm x 1.5 cm instead of 0.1 cm x 0.1 cm that is available on the heavy ion microprobe
- 0 deg beam line - very heavy ions Cl, I, Au – increased yield of secondary molecular ions
- Continuous, not pulsed beam – development of a trigger for START signal
- Reflectron spectrometer – better mass resolution than with a present linear ToF spectrometer



capillaries produced at ETH, Switzerland

M. Brajković et al., *Journal of the American Society for Mass Spectrometry*, **32** (2021), 10; 2567-2572

- primary beam pulsing: NOT an option

TRANSMISSION MODE

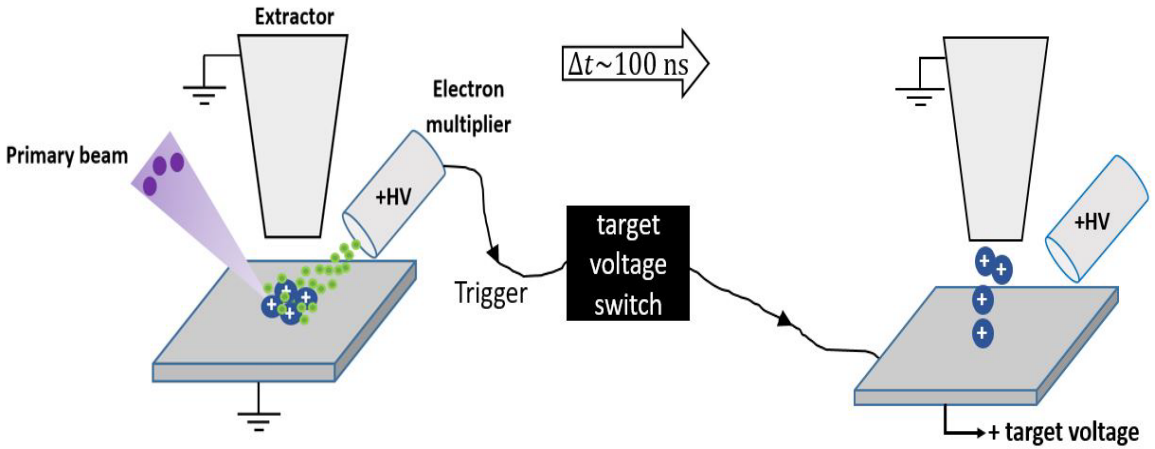
START: primary ion detected in the PIN diode
STOP: secondary ion detected in MCP detector

Simple setup, good time/mass resolution
Only thin samples (few μm max), radiation sensitive detector

ELECTRON START MODE (THICK TARGET SETUP)

START: secondary electron detected in electron multiplier
STOP: secondary ion detected in MCP detector

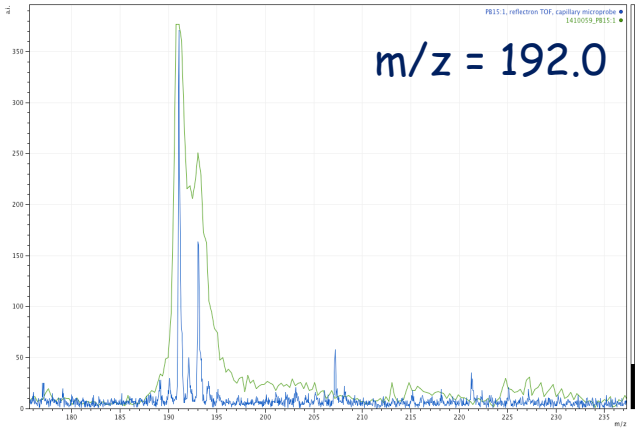
Arbitrary sample thickness, delayed extraction,
radiation hard solution, complicated setup

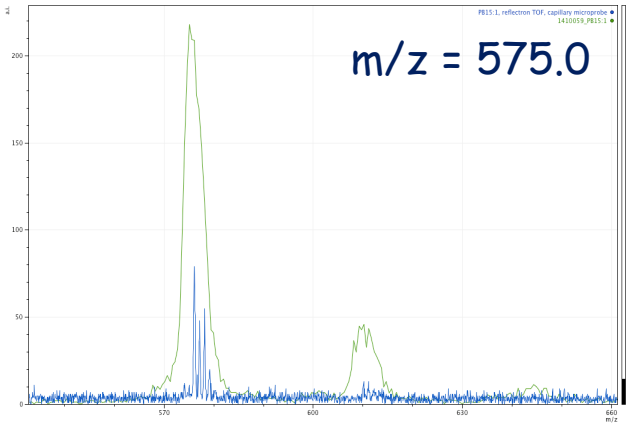


Fast HV switch

Mass resolution Linear TOF vs. Reflektron TOF

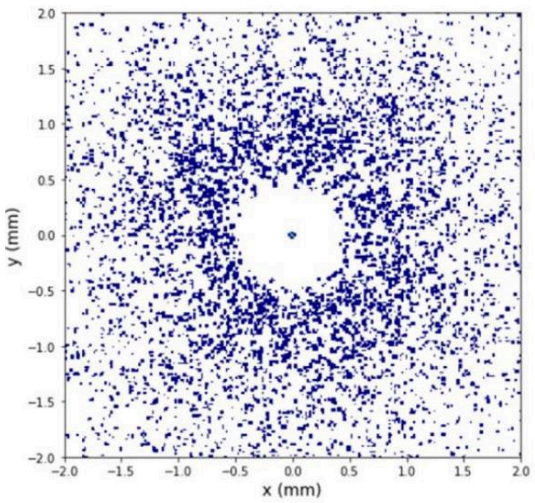
- mass resolution m/Δm = 1250 (for m/q = 132 Da),
- approximately same in both modes of operation
- 3 – 8 μm in x, 17 μm in y direction

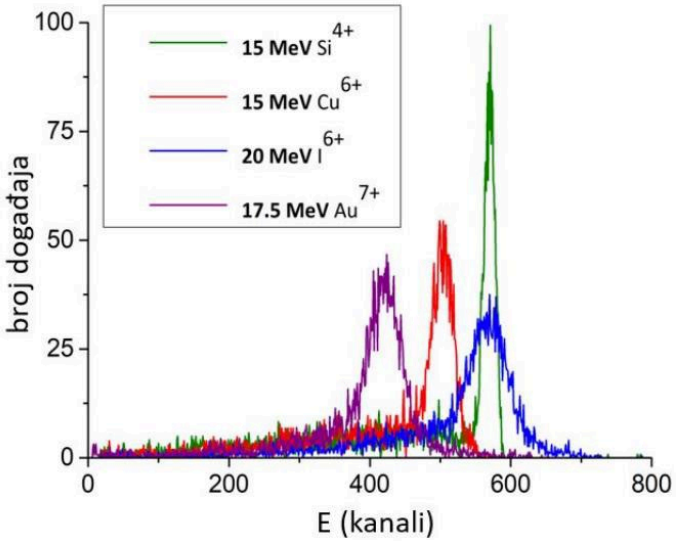




Main constraints of capillary:

- Complicated alignment
- beam halo
- beam divergence
- they stop working after some time for no obvious reason



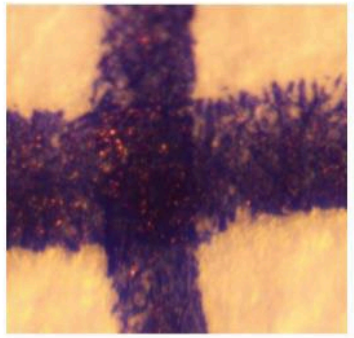


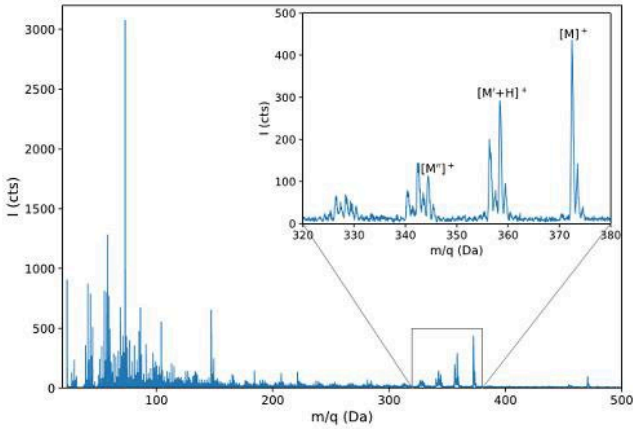
Mapping with capillary MeV SIMS setup

- sample: ink on paper
- scan size: 1 x 1 mm^2(20 μm/pix.)
- strong contribution of halo (10-50%)

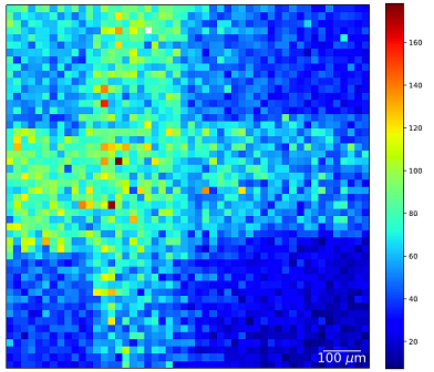
Halo is:

- blurring the picture
- weakening the contrast
- making artefacts

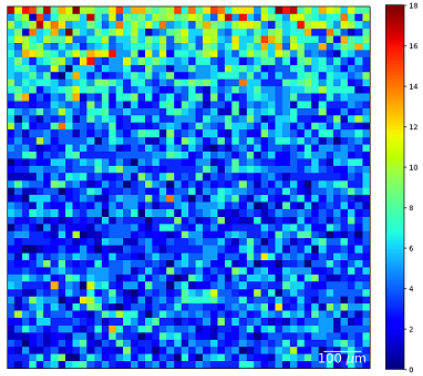




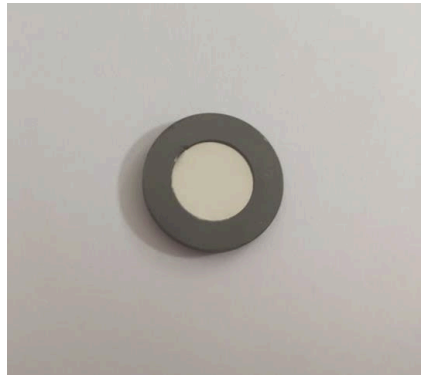
BV3



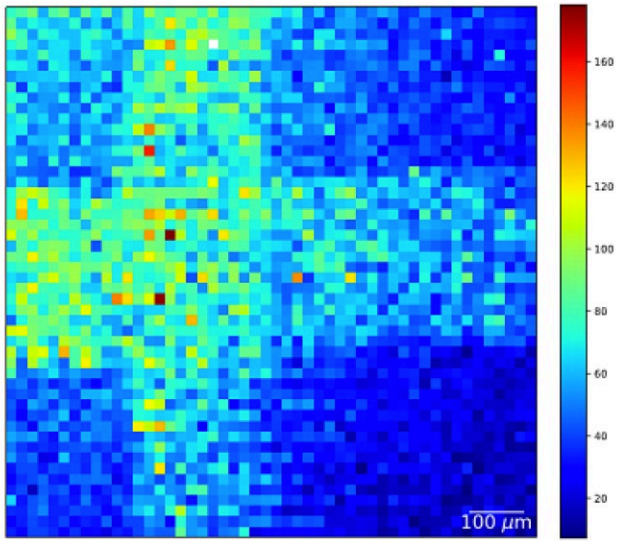
Na

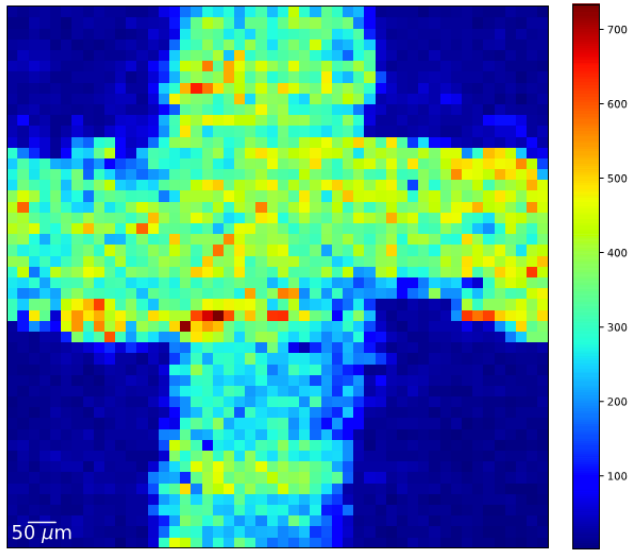


Borosilicate capillary



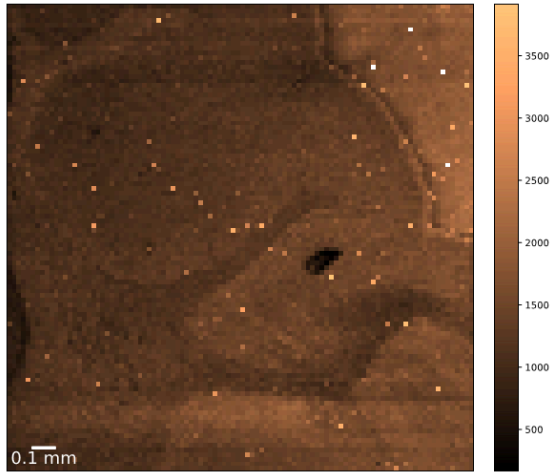
5-10 μm diameter aperture



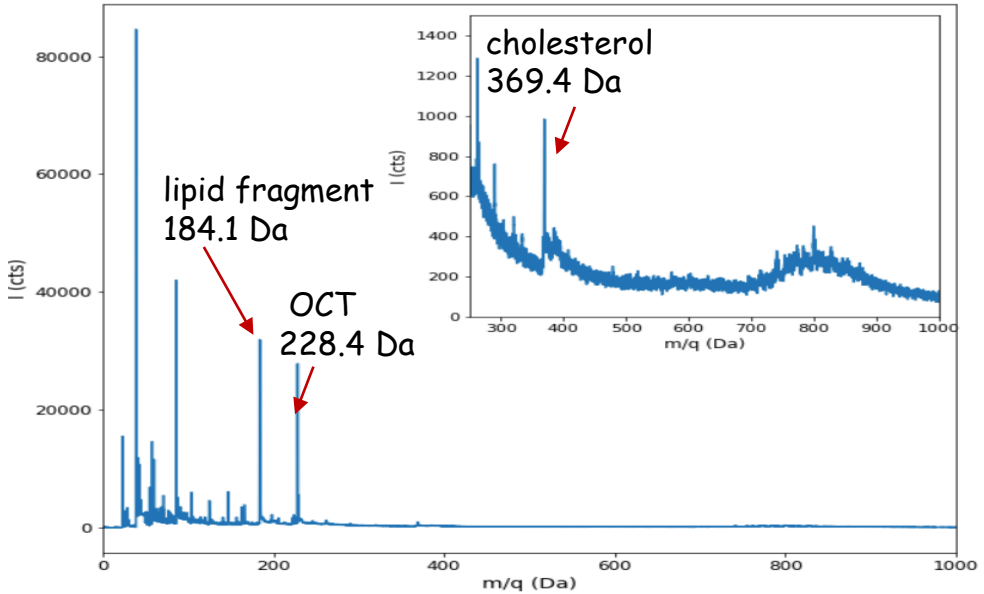


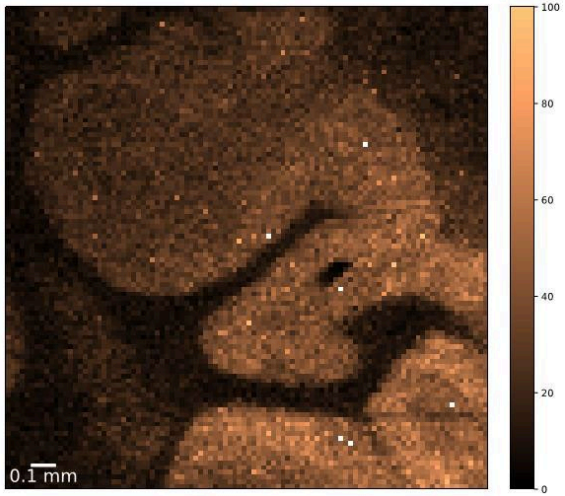
Mouse brain tissue

optical image

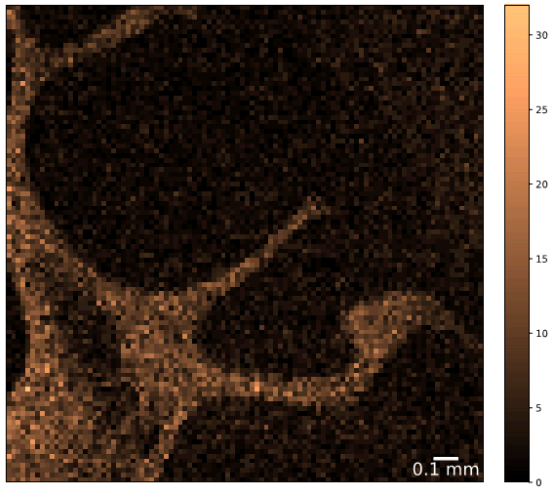


total map

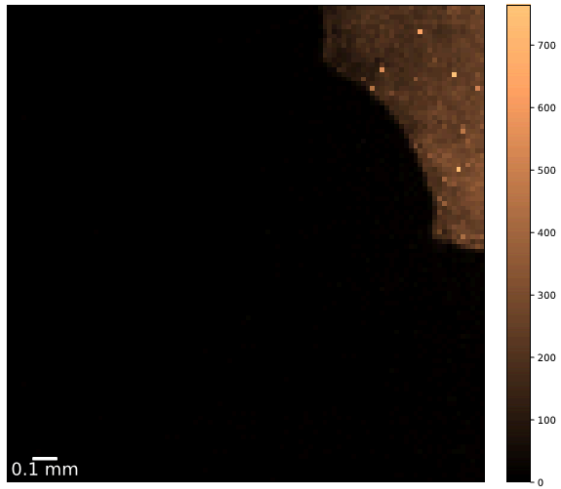




lipid fragment (m = 184.1 Da)



cholesterol (m = 369.4 Da)



OCT (m = 228.4 Da)

14 MeV Cu4

scan size 2 x 2 mm2

t = 3.5 h

Conclusions:

Two setups for MeV SIMS are presently available @ RBI:

1) Linear TOF – lighter ions with lover energy ($ME/q^2<14$), modest mass resolution, smaller samples
2) Reflectron TOF – heavier ions with higher energies, better mass resolution, larger samples

Information about molecular content of organic samples –

- Molecules 1 – 2000 Da
- 2D molecular images
- Surface sensitive
- Very efficient
- Applications in forensics, cultural heritage, biology

Thank you for your attention!

Acknowledgements

Dr. Max Döbeli and Dr. Klaus-Ulrich Miltenberger from ETH Zürich for help with micro-capillary production.

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HRZZ Hrvatska zaklada za znanost

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