Time-of-flight methods in ion beam analysis

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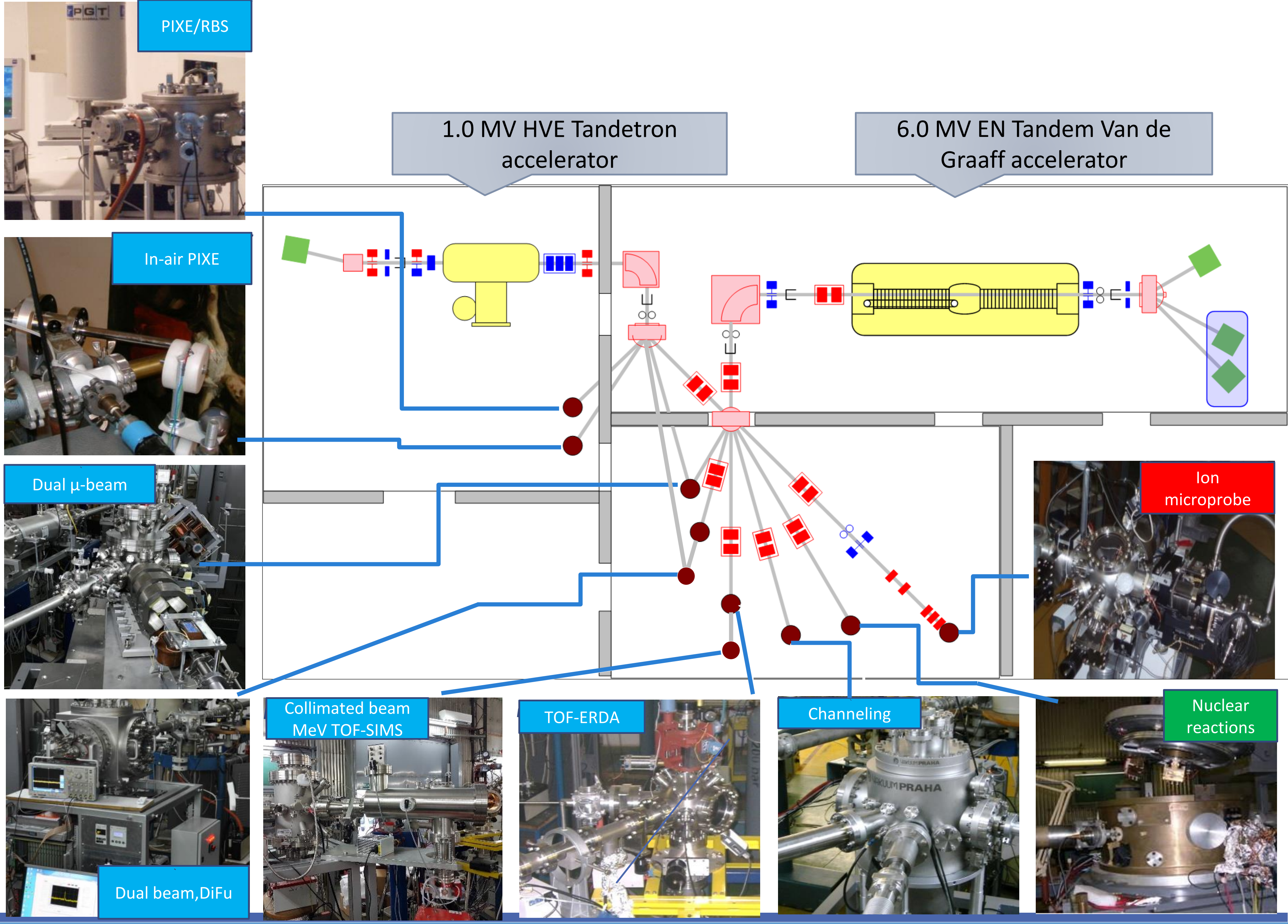
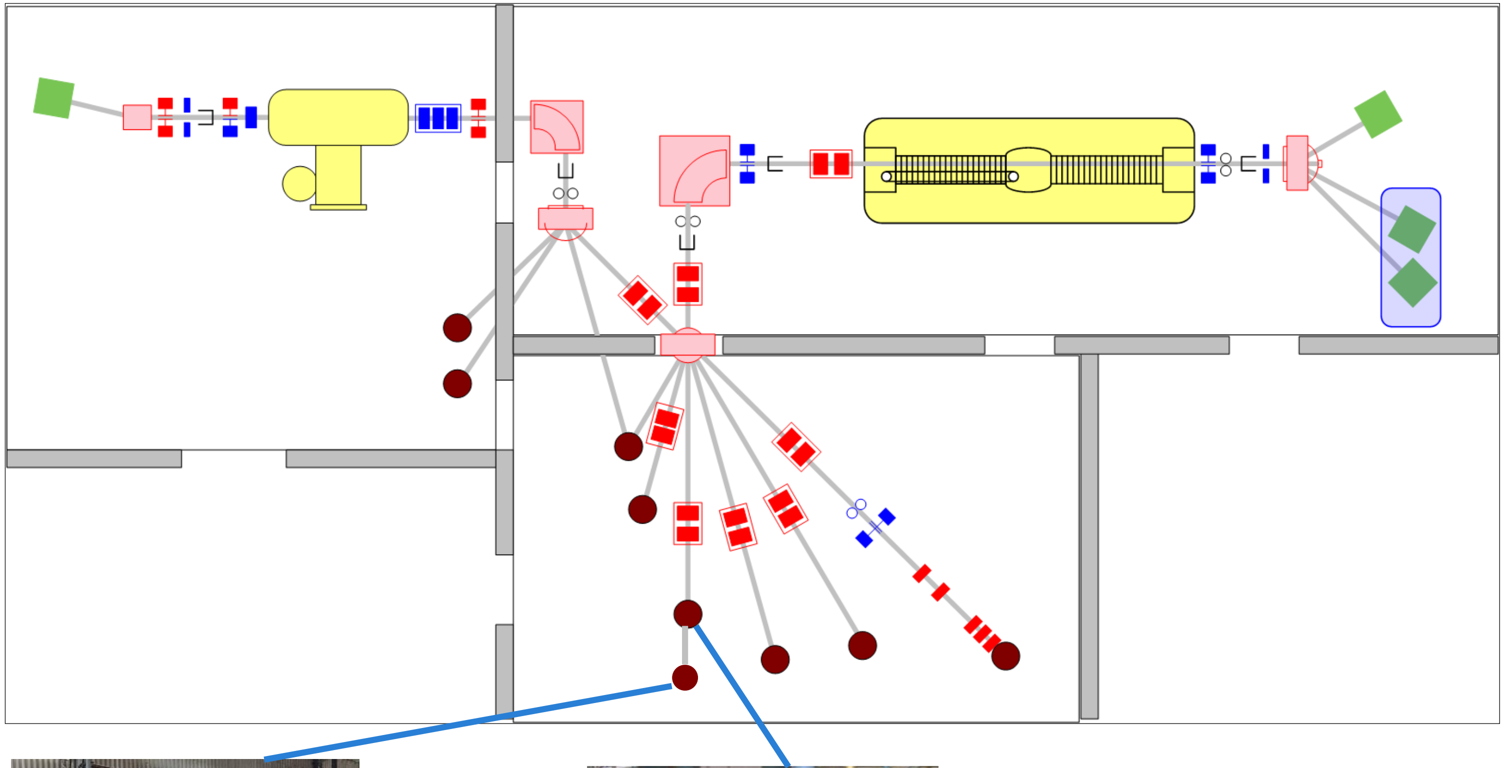
EUNPC22, SANTIAGO DE COMPOSTELA, OCTOBER 2022

RBI ACCELERATOR FACILITY

Currenty: protons up to 8 MeV, and heavy ions up to 30 MeV from the VDG accelerator



HEAVY ION BEAM TECHNIQUES



Most IBA techniques use protons: PIXE, RBS, PIGE, IBIC.

Heavy ions vs protons:

- **Production of recoils and secondary particles**
- **High stopping power**

MeV TOF SIMS
Time-of-Flight Secondary Ion Mass Spectrometry

organic samples

TOF ERDA
Time-of-Flight Elastic Recoil Detection Analysis

inorganic films

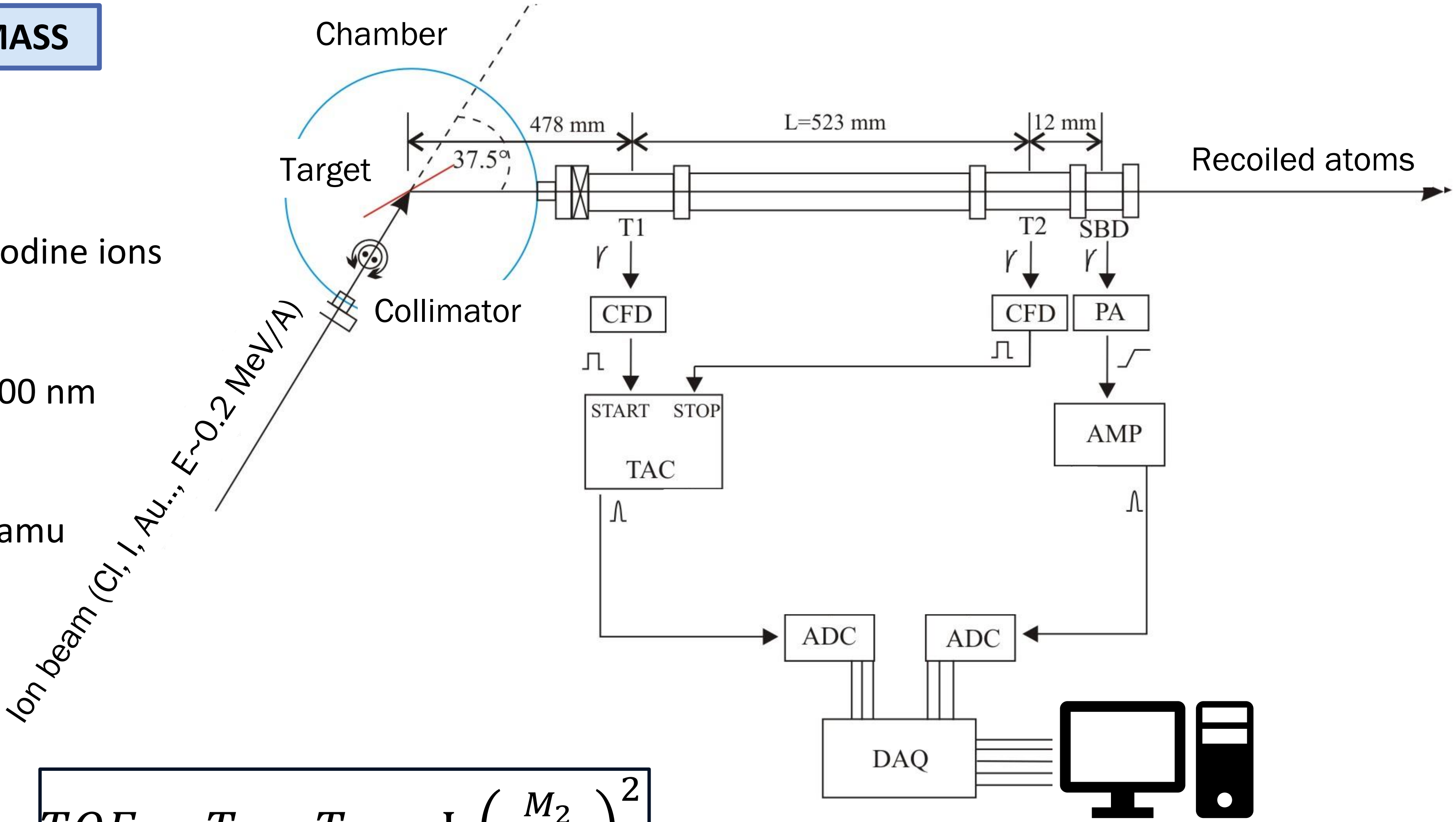
TOF ERDA

Time-of-Flight Elastic Recoil Detection Analysis

SEPARATION OF ELEMENTS BY MASS

Heavy ion beam – e.g. 23 MeV Iodine ions

- sensitivity 10^{15} /cm^2
- 2 nm depth resolution, up to 500 nm probe depth
- all elements are resolved
- Resolution < 1 amu for m < 40 amu



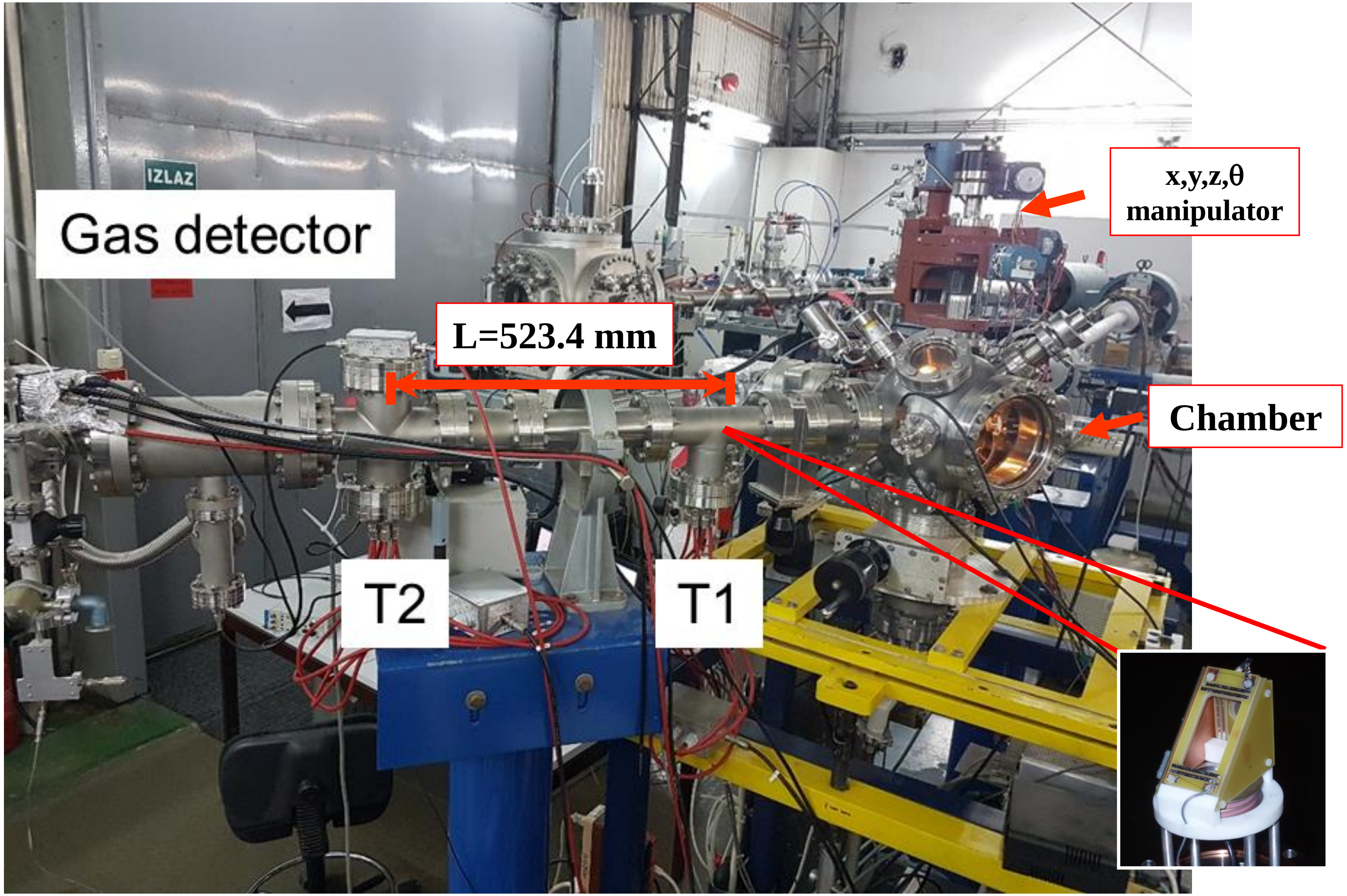
- E and TOF measured
- cross sections, stopping powers known

$$TOF = T_1 - T_2 = \mathrm{L}\left(\frac{M_2}{2KE_0}\right)^2$$

Depth profiling of few 100 nm thick samples
Depth resolution up to ~1 nm at the surface

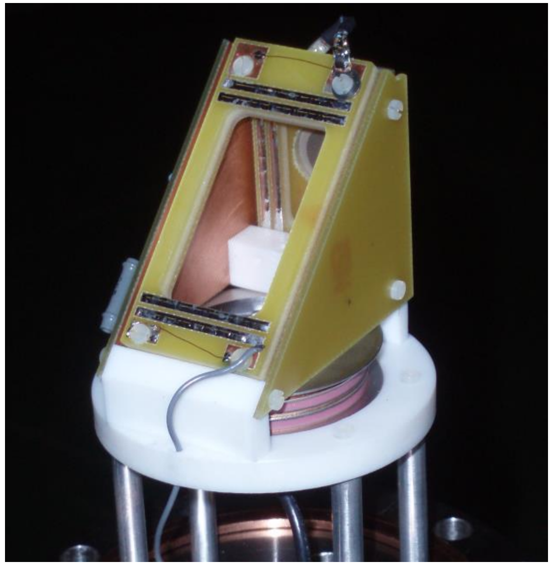
TOF ERDA: SETUP

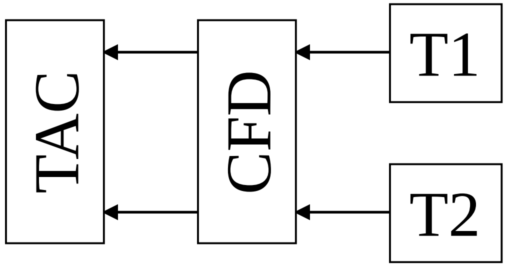
GID: better energy resolution than particle silicon detectors + radiation hardness

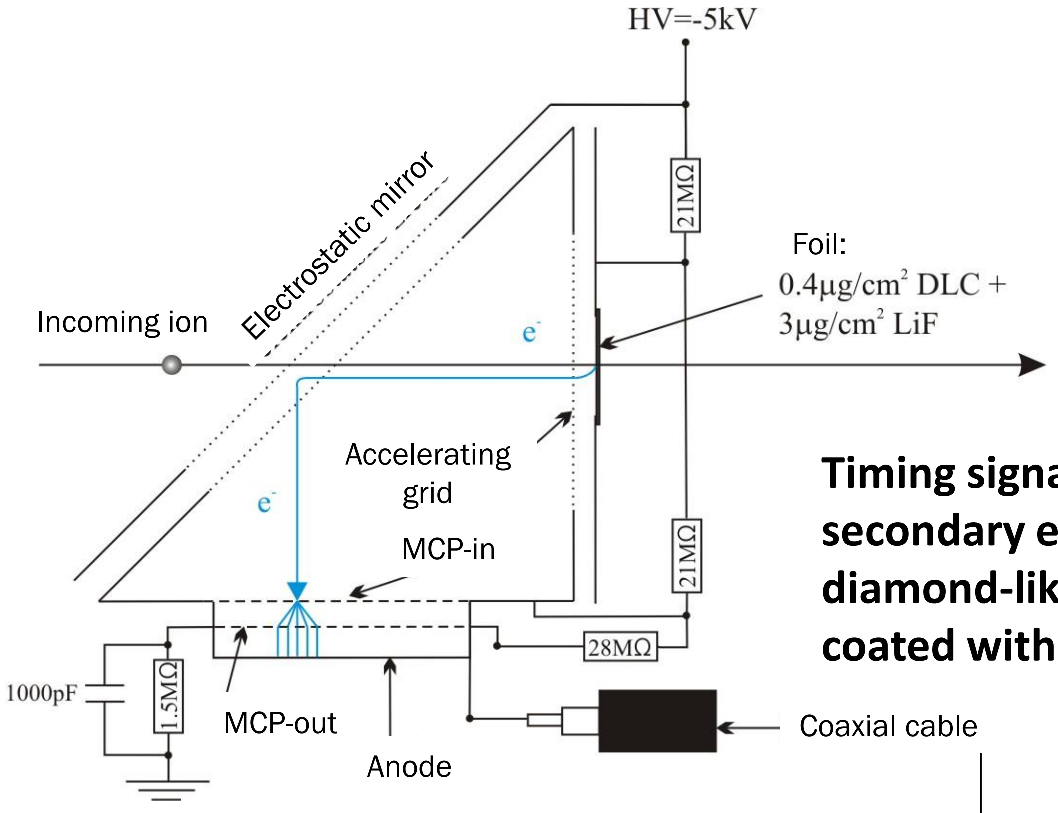


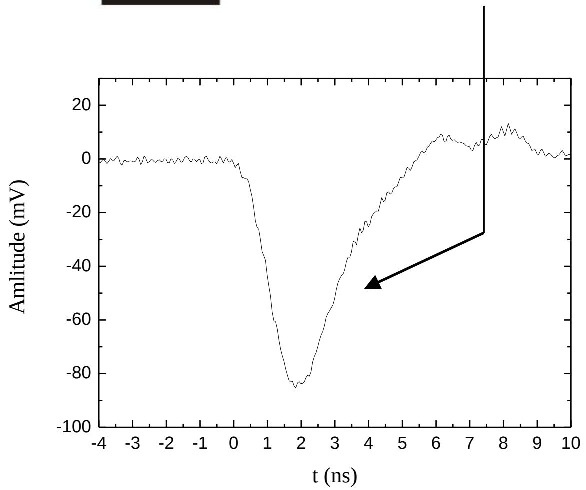
Z. Siketić, N. Skukan and I. Bogdanović Radović "A gas ionisation detector in the axial (Bragg) geometry used for the time-of-flight elastic recoil detection analysis", Review of Scientific Instruments 86, 083301 (2015)

TOF ERDA: SETUP – TIMING GATES



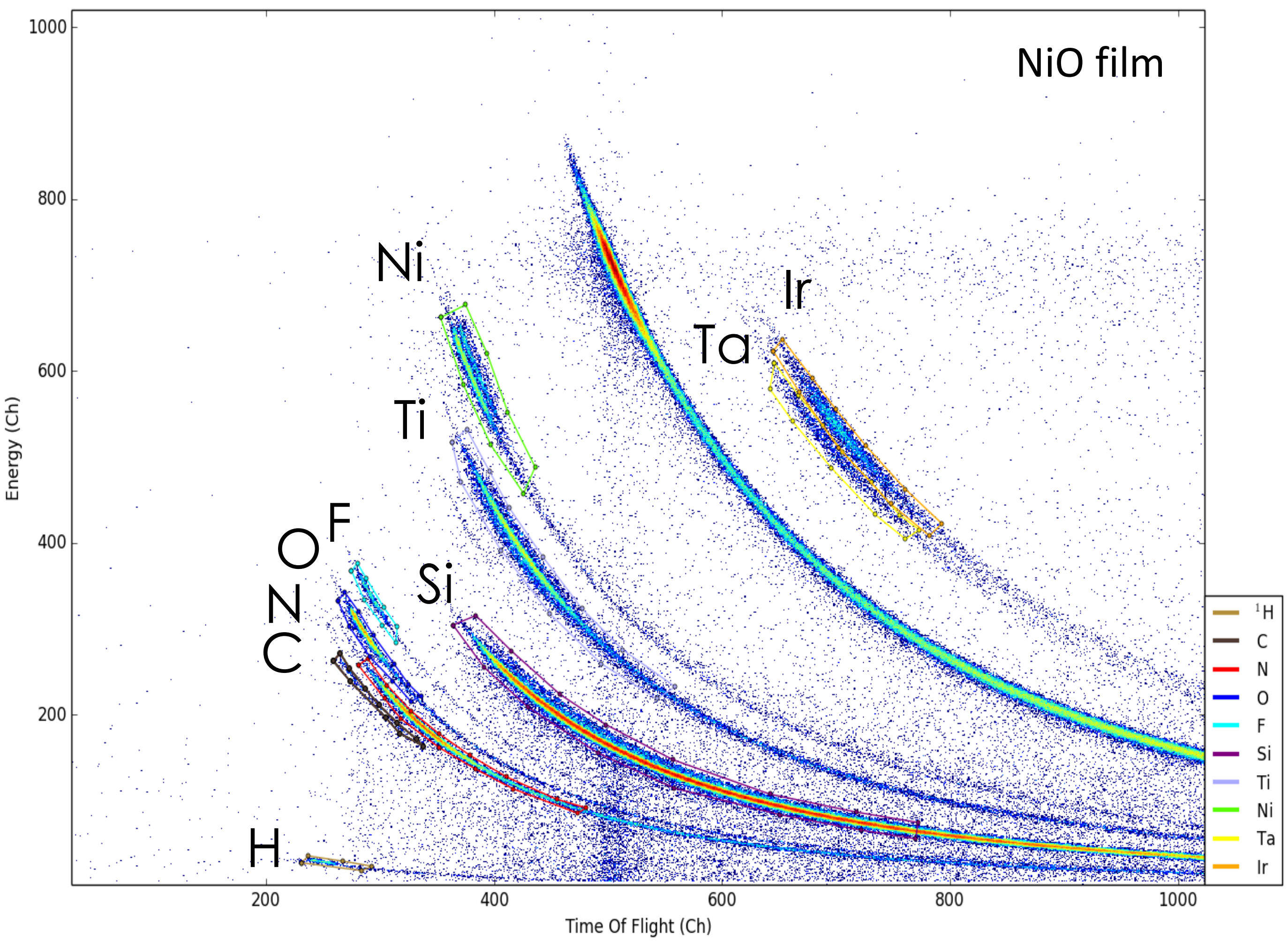


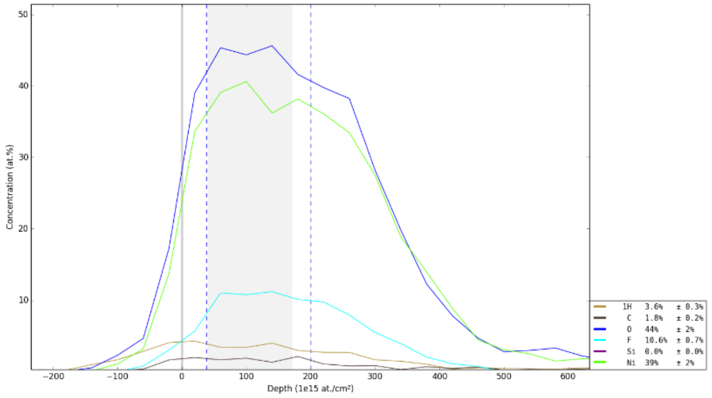




Timing signal: detection of secondary electrons from the diamond-like carbon foil coated with LiF

TOF ERDA APPLICATION – Quality control of production proces





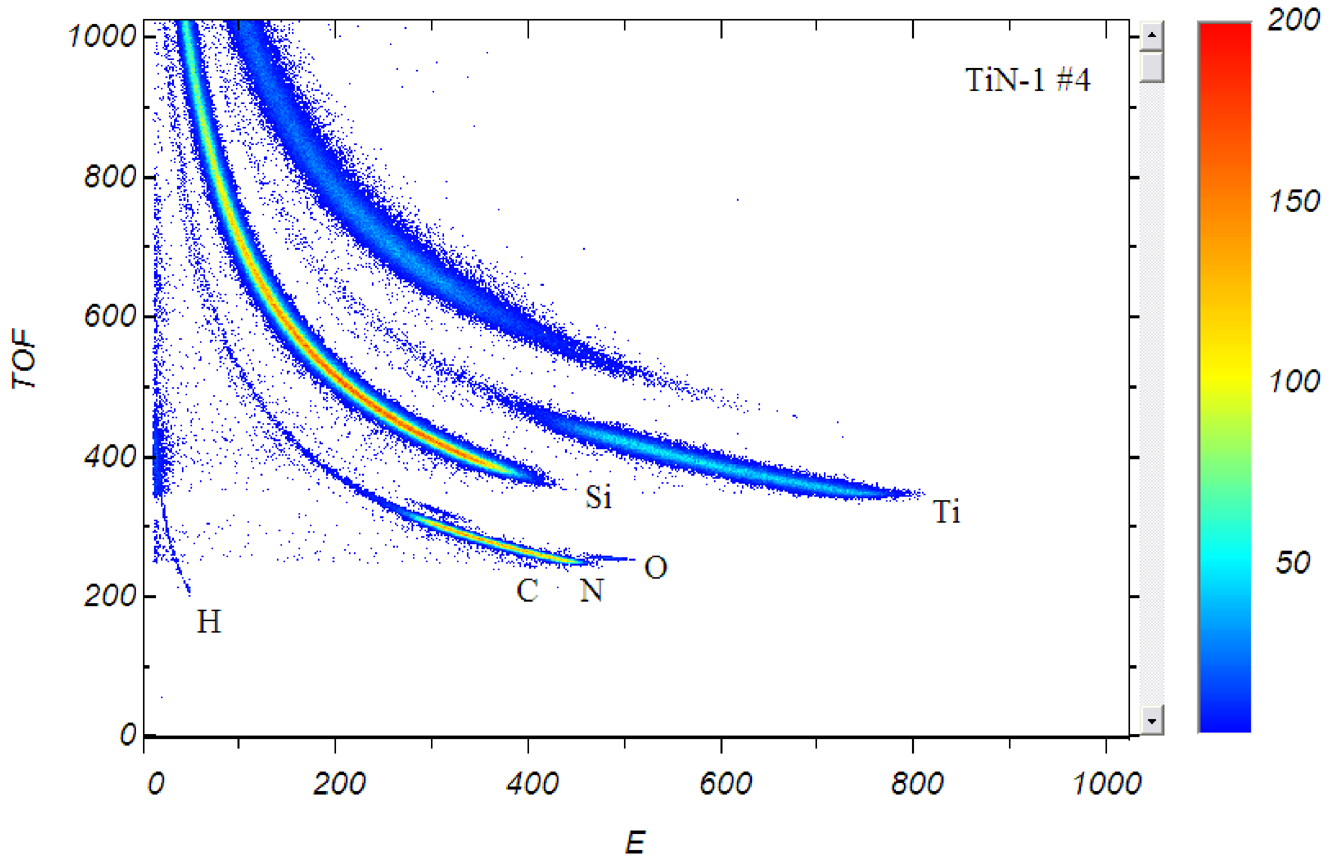
Element	Total Number of 10^{15} at/cm^2
H	15.2
C	6.6
O	158.7
F	33.5
Ni	141.8

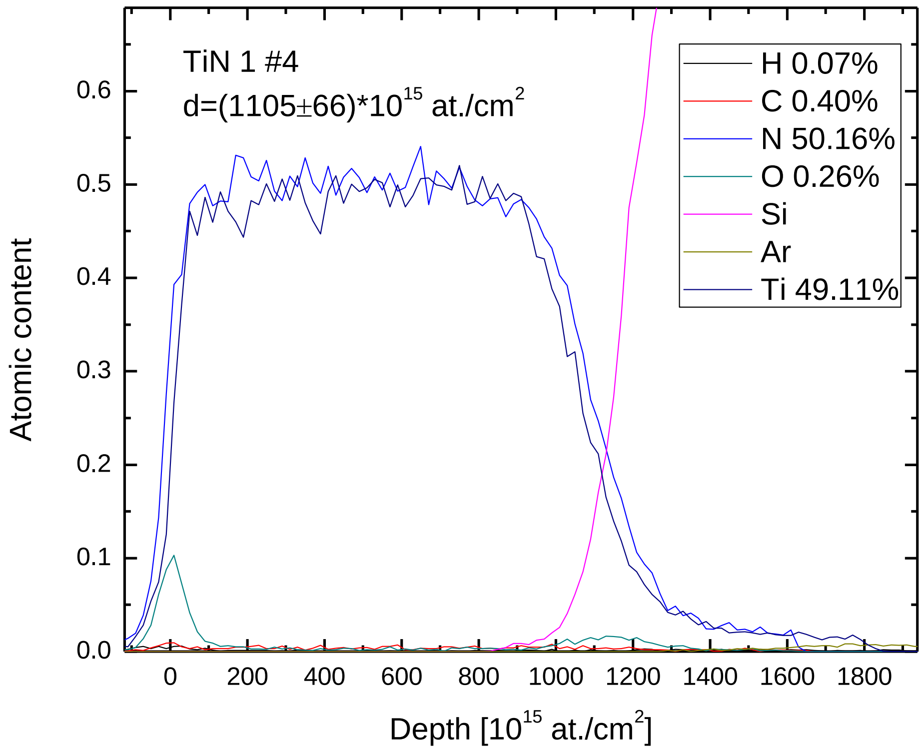
Flourine contamination found

TOF ERDA APPLICATION – Thin film analysis

Sample: TiN

Beam: 20 MeV $^{81}Br^{5+}$

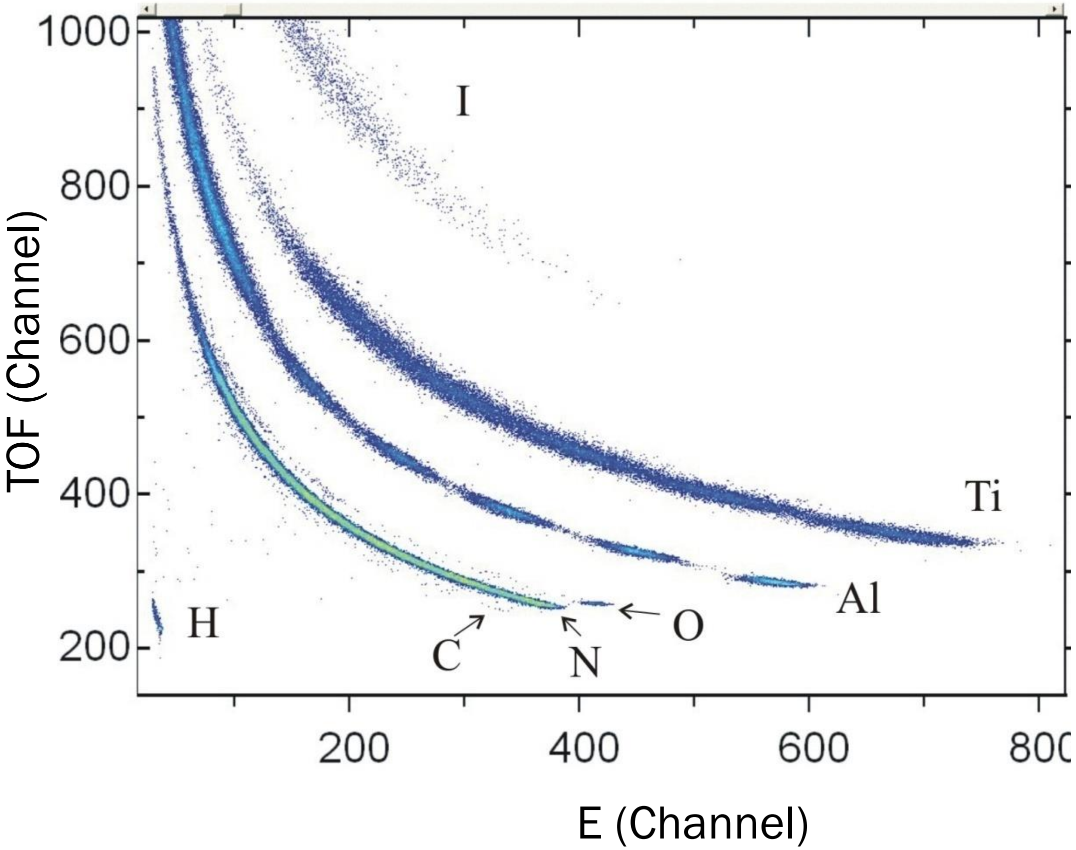




TOF ERDA APPLICATION – Multilayer samples

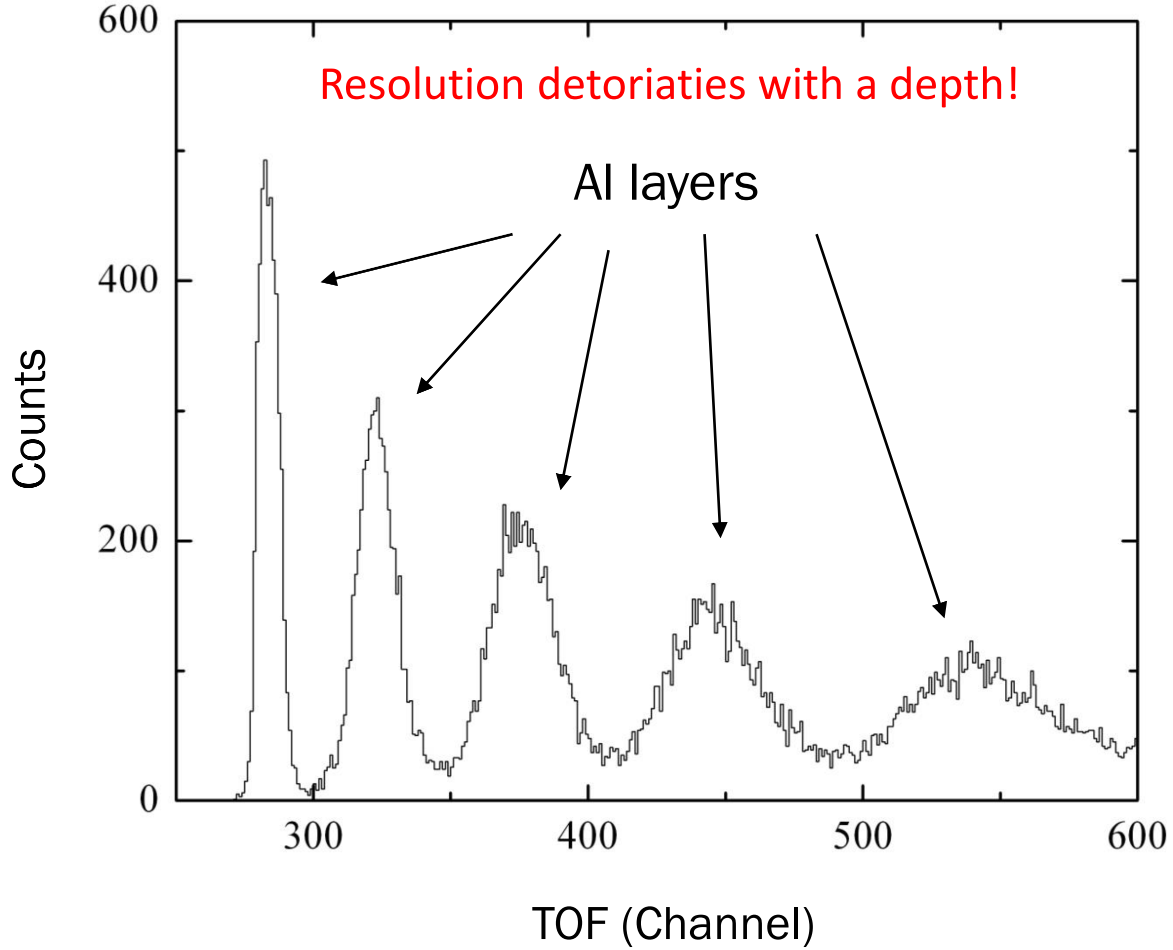
Beam: 25 MeV ^{127}I, θ_{in} = 5°, $\theta_{scatt.}$ = 37.5°

Target: 5x AlN/TiN 20 nm layers



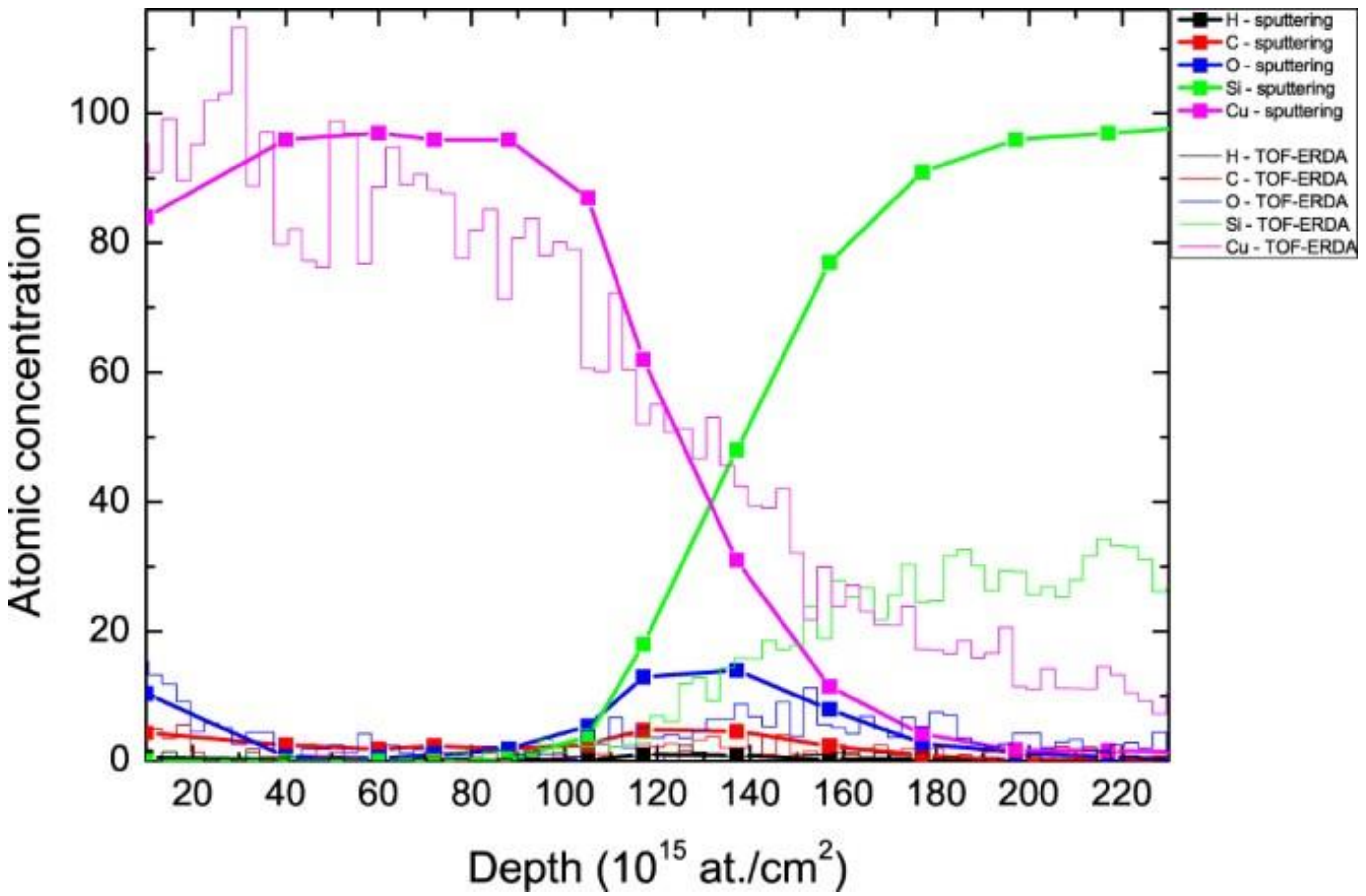
Time spectra of the Al events

Result of the analysis:
Al:N=1:1, d = 24 nm
Ti:N=1:1, d = 40 nm



TOF ERDA + Ar SPUTTERING

- TOF-ERDA used to measure the surface elemental composition, Ar sputtering to extract the depth information
- **best achievable (surface) resolution of 2 nm for the entire layer**



TOF ERDA promoted by argon sputtering (lines + symbols) and TOF-ERDA (lines) depth profile for a 15-nm-thick Cu layer evaporated onto the Si substrate.

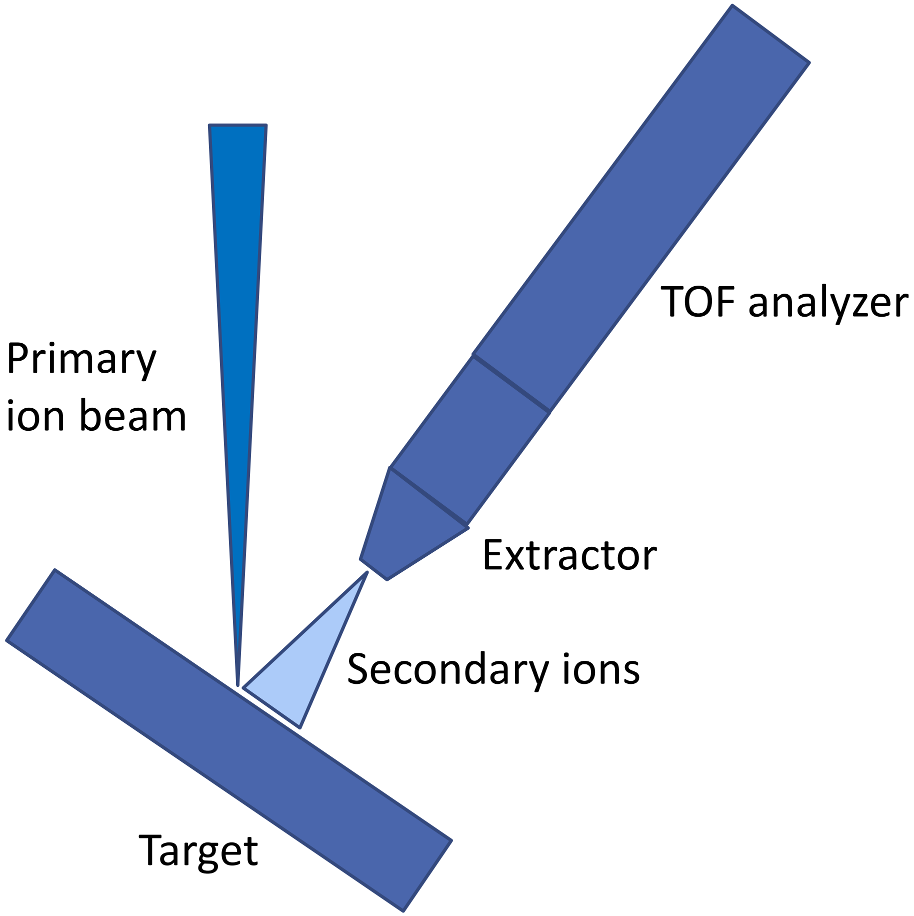
Siketić, Z., Bogdanović Radović, I., Sudić, I. *et al.* Surface analysis and depth profiling using time-of-flight elastic recoil detection analysis with argon sputtering. *Sci Rep* **8**, 10392 (2018).

MeV TOF-SIMS

Time-of-Flight Secondary Ion Mass Spectrometry

MeV SIMS

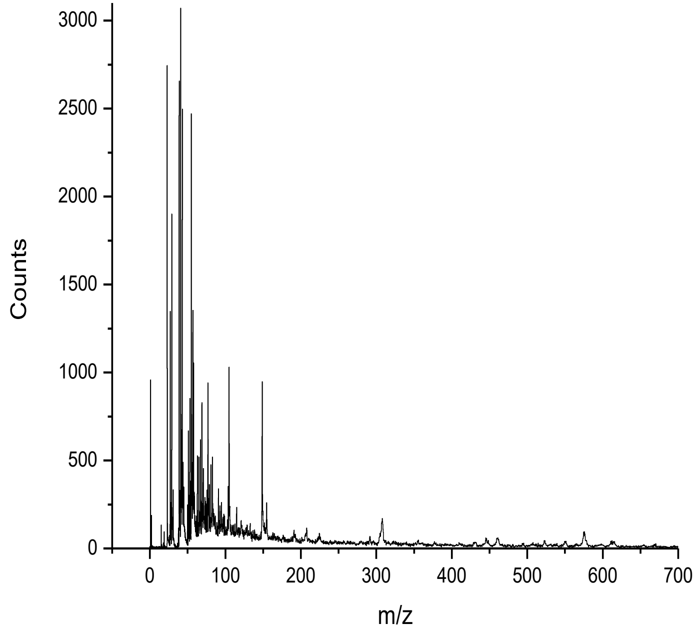
= mass spectrometry technique used for identification of atomic and molecular species by measuring time-of-flight of the secondary ions sputtered from the sample surface



$$E = qV = \frac{m}{2}v^2 = \frac{m}{2}\left(\frac{L}{TOF}\right)^2 \rightarrow \boxed{m/q = 2V\left(\frac{TOF}{L}\right)^2}$$

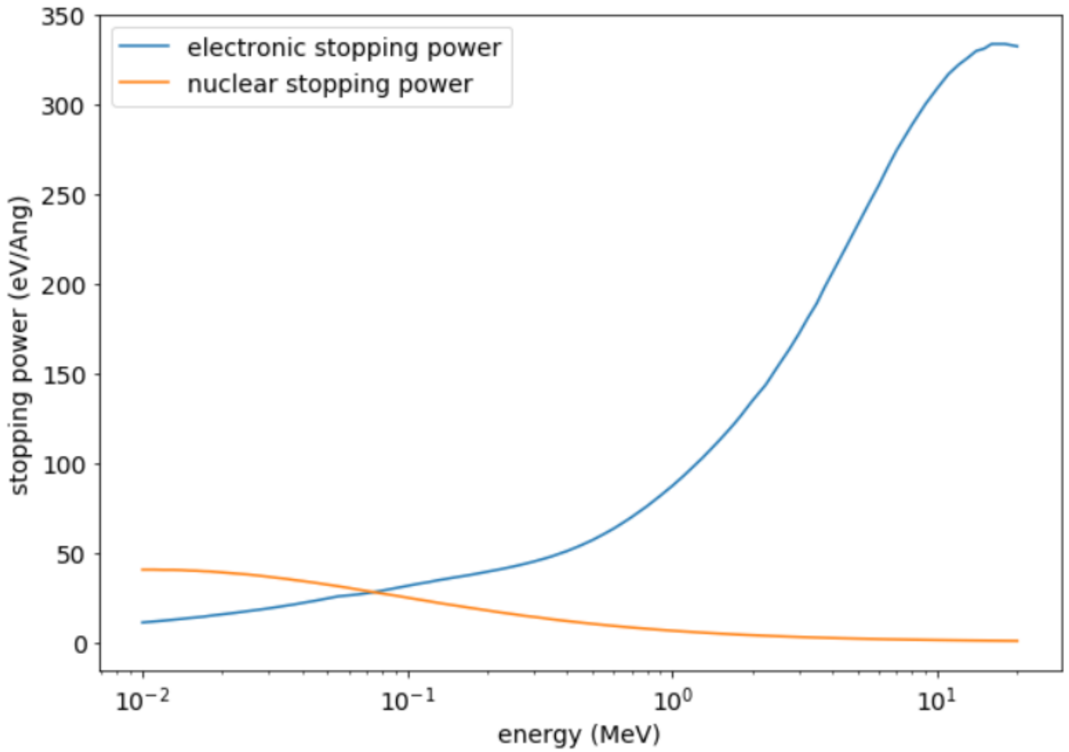
(E_0 few eV)

TOF spectrum ⟺ Mass spectrum

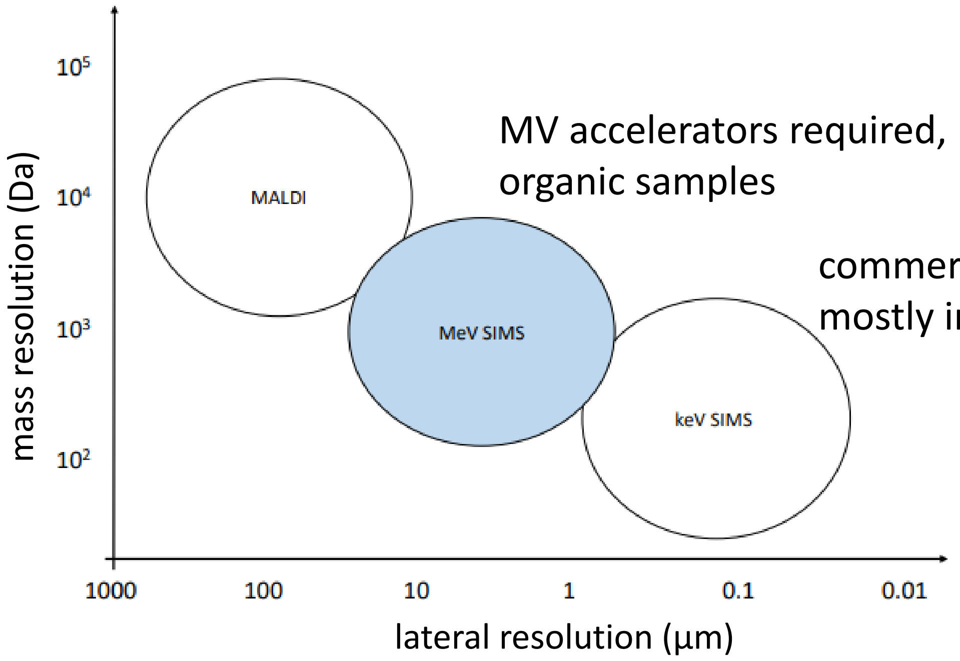


Scanning over the sample → **Imaging** (2D spatial molecular distribution)

- **Higher SI yield** for heavier molecules, and **less fragmentation**, than for keV counterpart



Silicon beam on a leucine target:
electronic stopping dominates for MeV energies



TOF mass spectrometry techniques comparison

MeV SIMS APPLICATIONS @ RBI

Since 2014 we published 16 papers in high IF journals on application of MeV SIMS analysis:

- Biology (identification of lipids and fatty acids in various tissues and single cells, 2 papers published)
- Cultural heritage (identification of pigments and binders of modern paint materials, 3 papers publish
- Forensics (study of deposition order of crossing lines of different writing tools, 3 papers published)
- Simultaneously analysis of organic and inorganic materials (2 papers published)
- Development of MeV SIMS and measurements of fundamental parameters (6 papers published)

analytical chemistry
Article
Cite This: Anal. Chem. 2019, 91, 12997−13005
pubs.acs.org/ac

Determination of Deposition Order of Toners, Inkjet Inks, and Blue Ballpoint Pen Combining MeV-Secondary Ion Mass Spectrometry and Particle Induced X-ray Emission

Katherine Louise Moore,[†,‡] Marko Barac,[†,§] Marko Brajković,[†] Melanie Jane Bailey,[‡] Zdravko Siketić,[†] and Iva Bogdanović Radović*[,†]

Diabetes Research and Clinical Practice
Volume 159, January 2020, 107986
ELSEVIER

Study of the diacylglycerol composition in the liver and serum of mice with prediabetes and diabetes using MeV TOF-SIMS

Marijana Popović Hadžija [a], Zdravko Siketić [b], Mirko Hadžija [a], Marko Barac [b], Iva Bogdanović Radović [b]

scientific reports
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OPEN

Depth profiling of Cr-ITO dual-layer sample with secondary ion mass spectrometry using MeV ions in the low energy region

Marko Barac[1,2], Marko Brajković[1], Zdravko Siketić[1], Jernej Ekar[2,3], Iva Bogdanović Radović[1], Iva Šrut Rakić[4] & Janez Kovač[3]

analytical chemistry
pubs.acs.org/ac
Article

Identification of Synthetic Organic Pigments (SOPs) Used in Modern Artist's Paints with Secondary Ion Mass Spectrometry with MeV Ions

Matea Krmpotić,* Dubravka Jembrih-Simbürger, Zdravko Siketić, Nikola Marković, Marta Anghelone, Tonči Tadić, Dora Plavčić, Mason Malloy, and Iva Bogdanović Radović

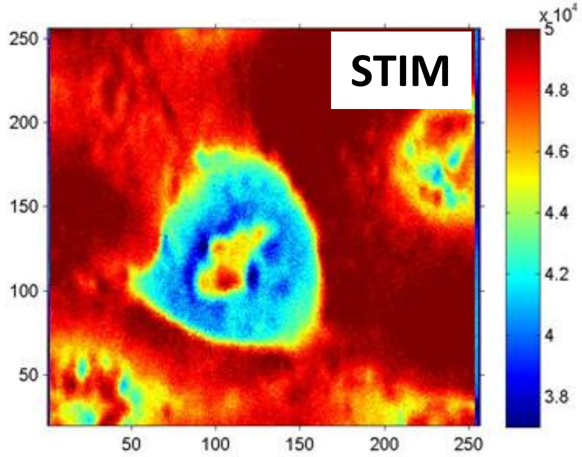
MeV SIMS: APPLICATIONS

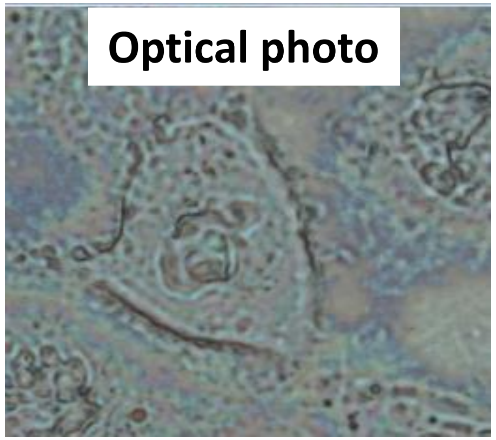
Example #1: Molecular imaging of single CaCo-2 cancer cell

Siketić, Z., Bogdanović Radović, I., Jakšić, M., Popović Hadžija, M., & Hadžija, M. (2015) Applied Physics Letters, 107(9), 093702.

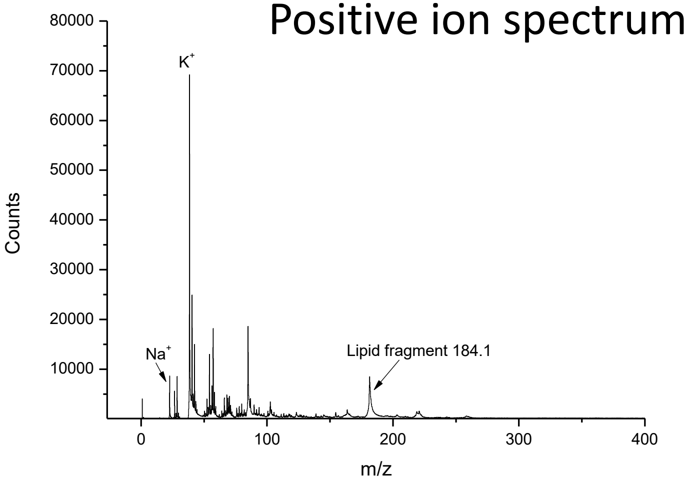
Beam: 9 MeV O^{4+}

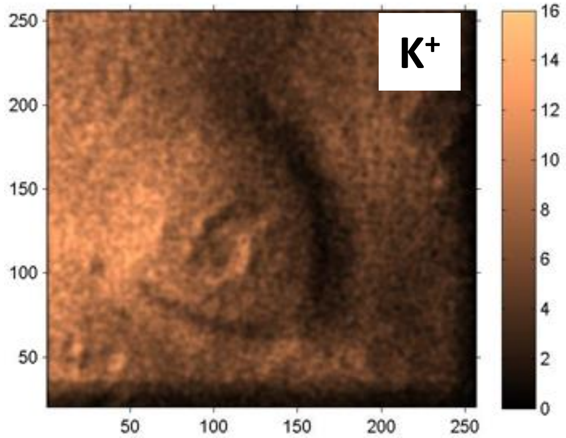
Scan size: 85x85 μm^2 (≈300 nm/pixel)

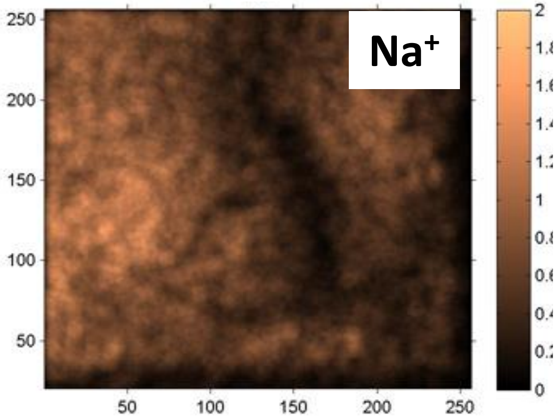


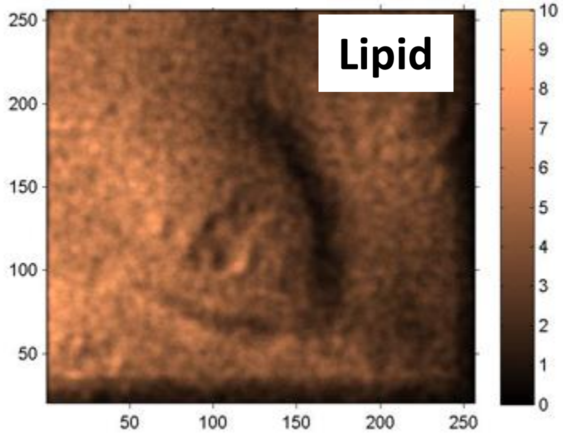


Positive ion spectrum





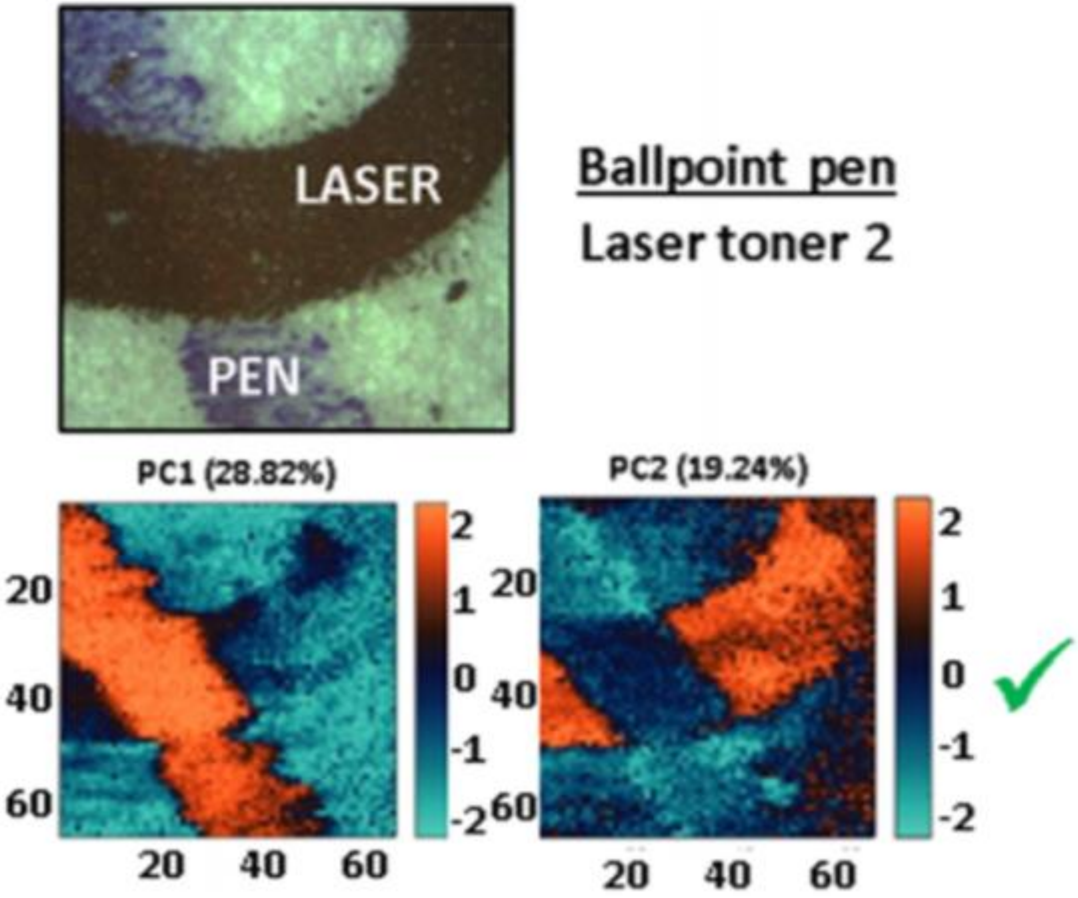




MeV SIMS: APPLICATIONS

Exampple #2: Forensics: determination of depositioning order of inks/toners

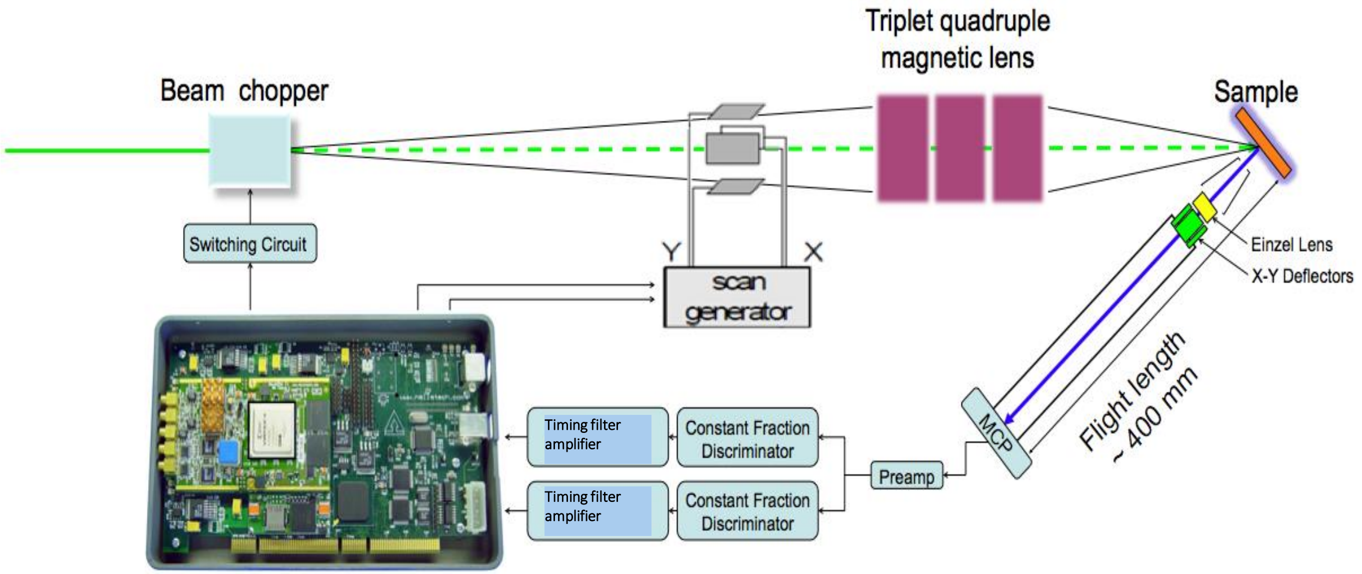
Moore, K. L., Barac, M., Brajković, M., Bailey, M. J., Siketić, Z., &
Bogdanović Radović, I. (2019) Analytical chemistry, 91(20), 12997-13005.

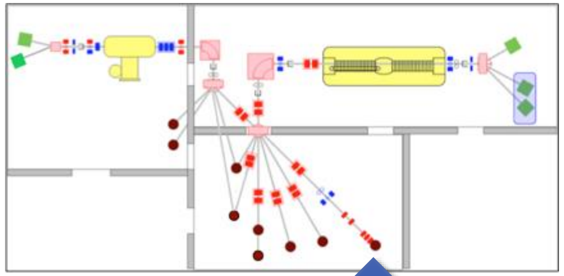


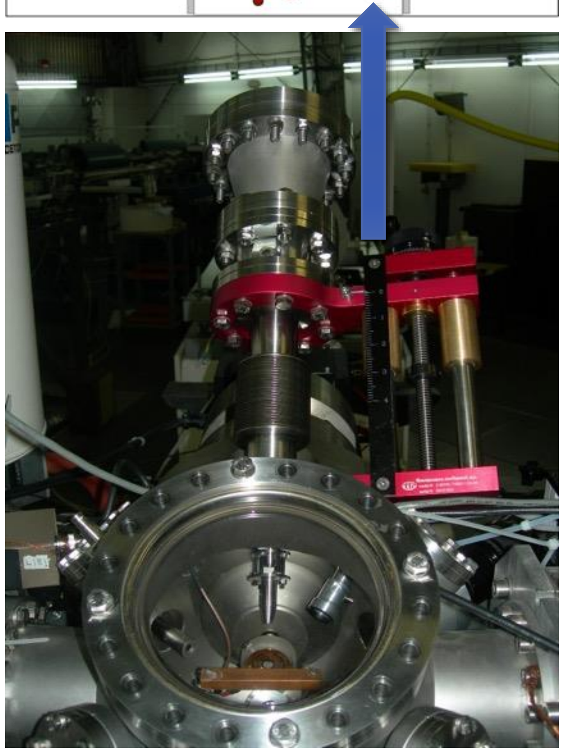
Ink crossing imaging + PCA analysis

MeV SIMS: OLD SETUP

TOF START: Primary beam pulsing
TOF STOP: MCP detector
FOCUSING: magnetic lenses
IMAGING: Primary beam scanning over the sample







Cannot use ions heavier than Silicon!
upper limit: $m \cdot E/q^2 < 14$ MeV amu

ALTERNATIVE: COLLIMATED BEAM

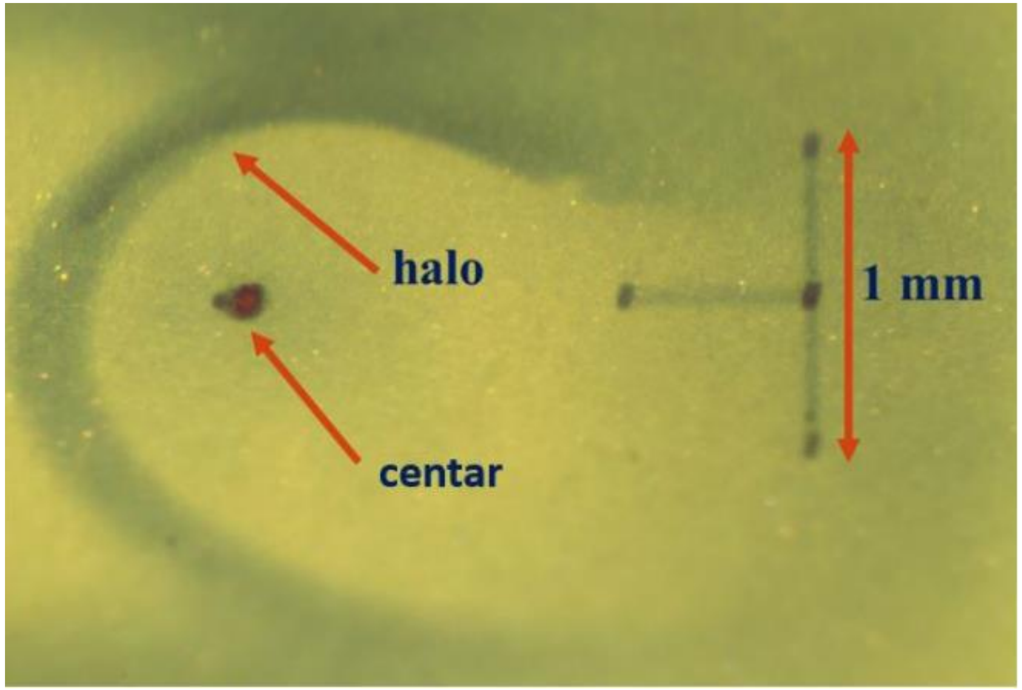
- cheap alternative for magnetic focusing for small current (fA) application
- collimation independent on ion mass and energy = heavy, high energy ion can be used
- in principle, in-air extraction possible

COLLIMATED BEAM:

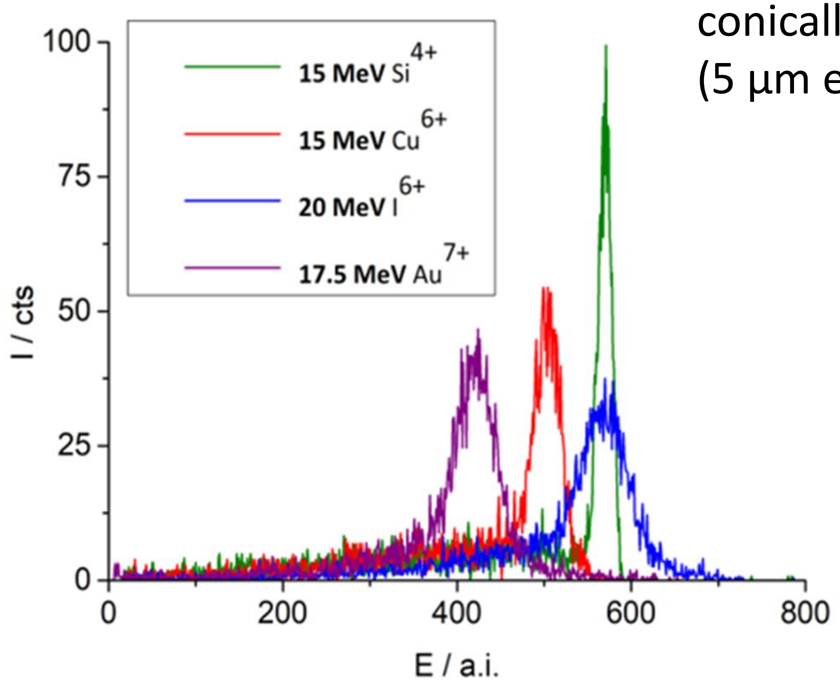
TOF START: ~~Primary beam pulsing~~ **?**
TOF STOP: MCP detector (upgraded with 10 kV postacceleration)
~~FOCUSING~~: **COLLIMATION with micro-capillary/micro-aperture**
IMAGING: sample placed on piezo-stage in front of fixed collimator

MICROCAPILLARY: TRANSMISSION

conically-shaped glass capillary (5 µm exit diameter)



spatial distribution of transmitted beam



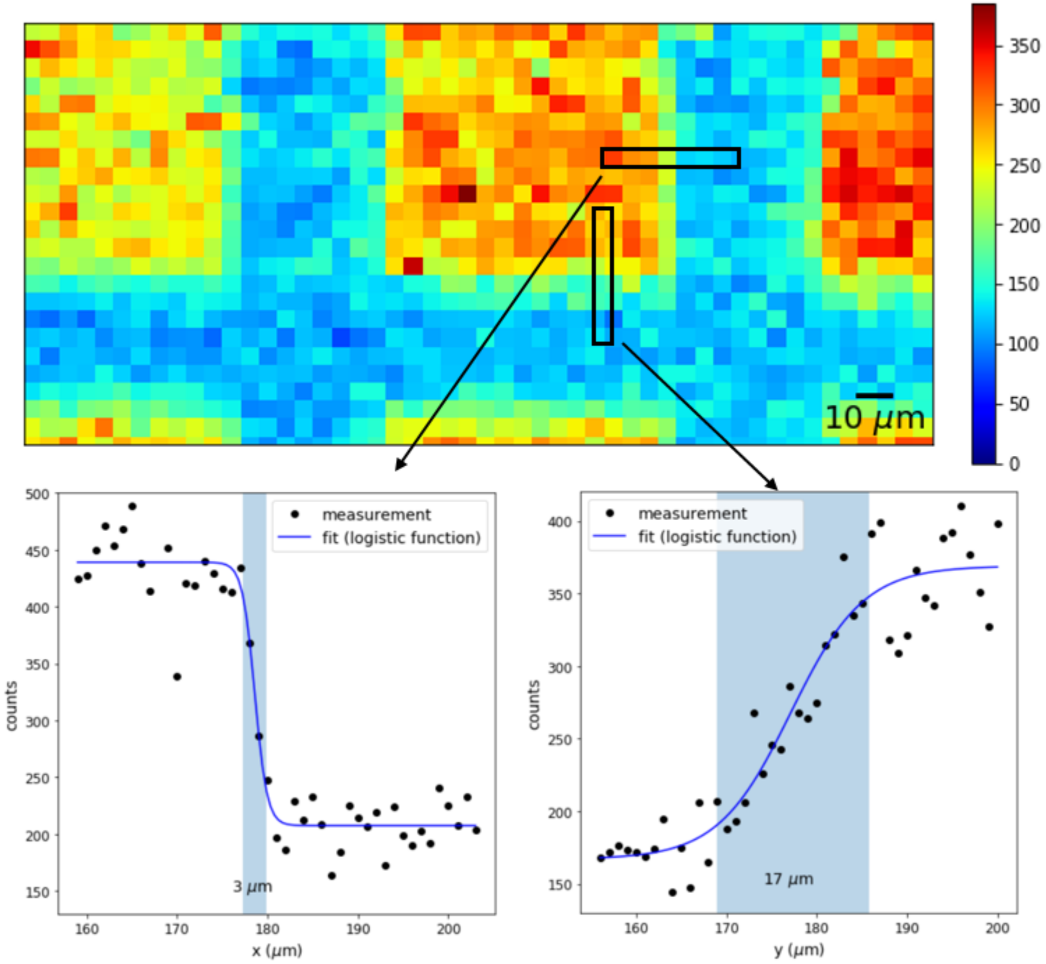
energy spectra of transmitted beams

M. Brajković, M. Barac, D. Cosic, I. Bogdanović Radović, Z. Siketić, Development of MeV TOF-SIMS capillary microprobe at the Ruđer Bošković Institute in Zagreb, Nucl. Instr. and Meth. B 461 (2019) 237-242.

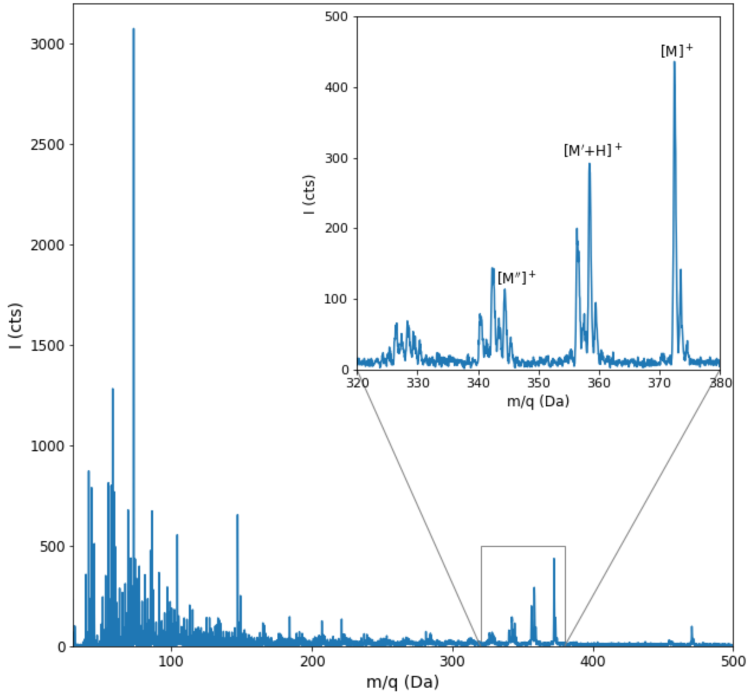
M. Brajković, I. Bogdanović Radović, M. Barac, D. D. Cosic, Z. Siketić, Imaging of Organic Samples with Megaelectron Volt Time-of-Flight Secondary Ion Mass Spectrometry Capillary Microprobe, J. Am. Soc. Mass Spectrom. 2021, 32, 10, 2567–2572.

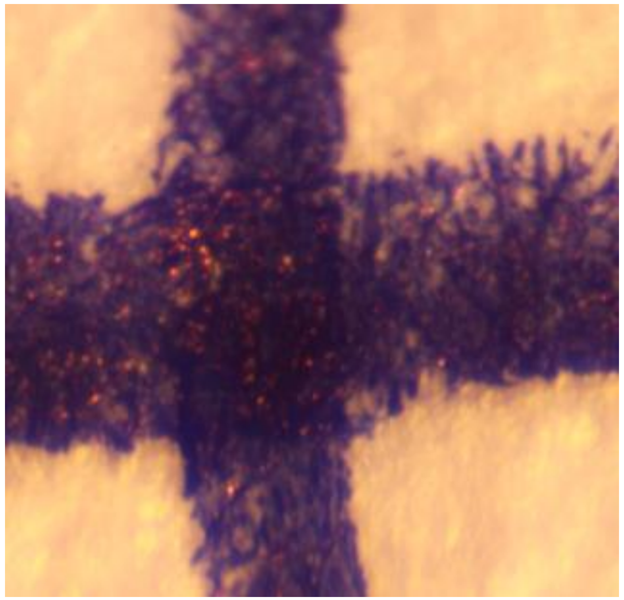
MICROCAPILLARY: IMAGING

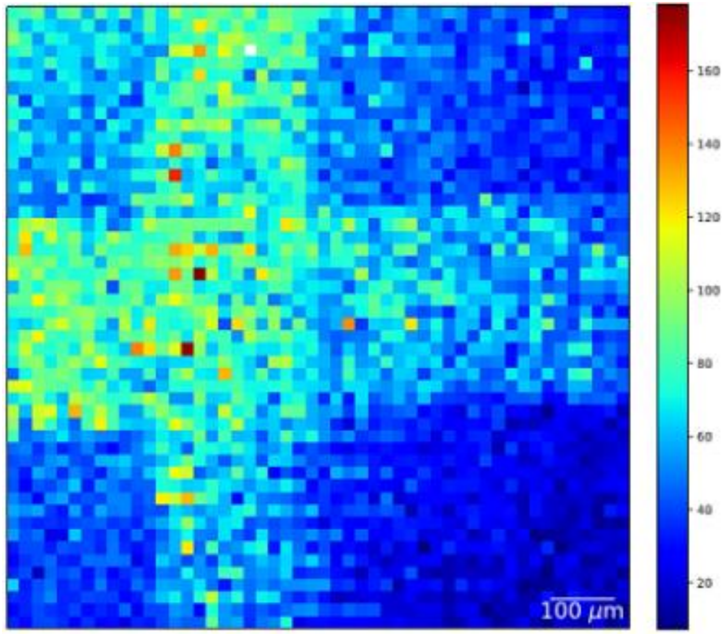
lateral resolution: leucine-evaporated copper mesh



Imaging: ink crossing on a paper

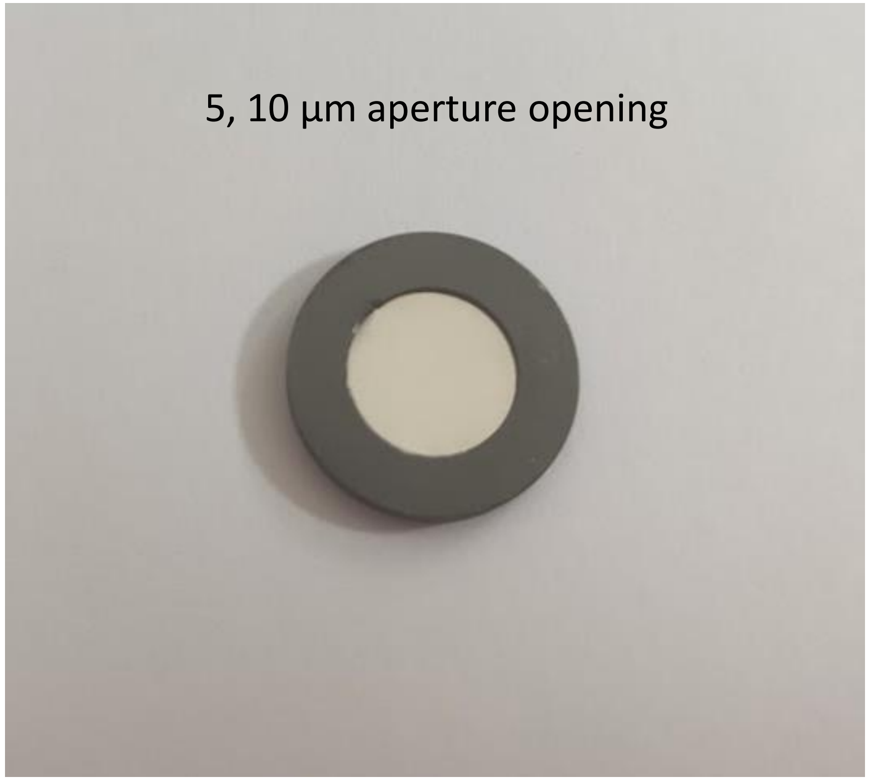




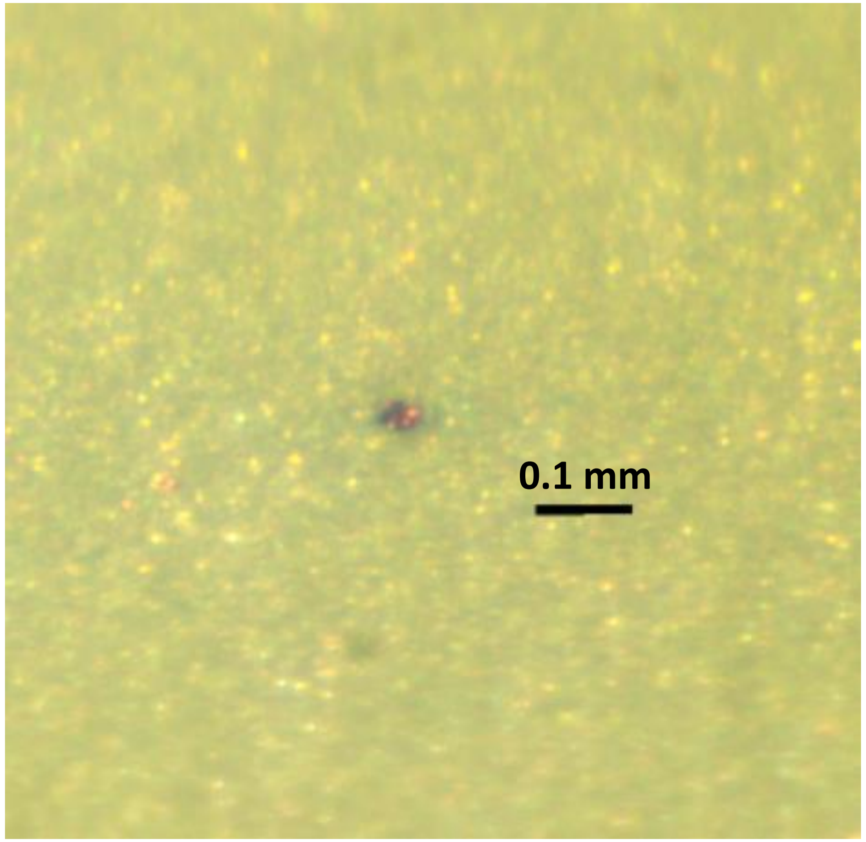


CONS: halo and low contrast

5 µm APERTURE



steel, thickness 12.7 µm, aluminum frame

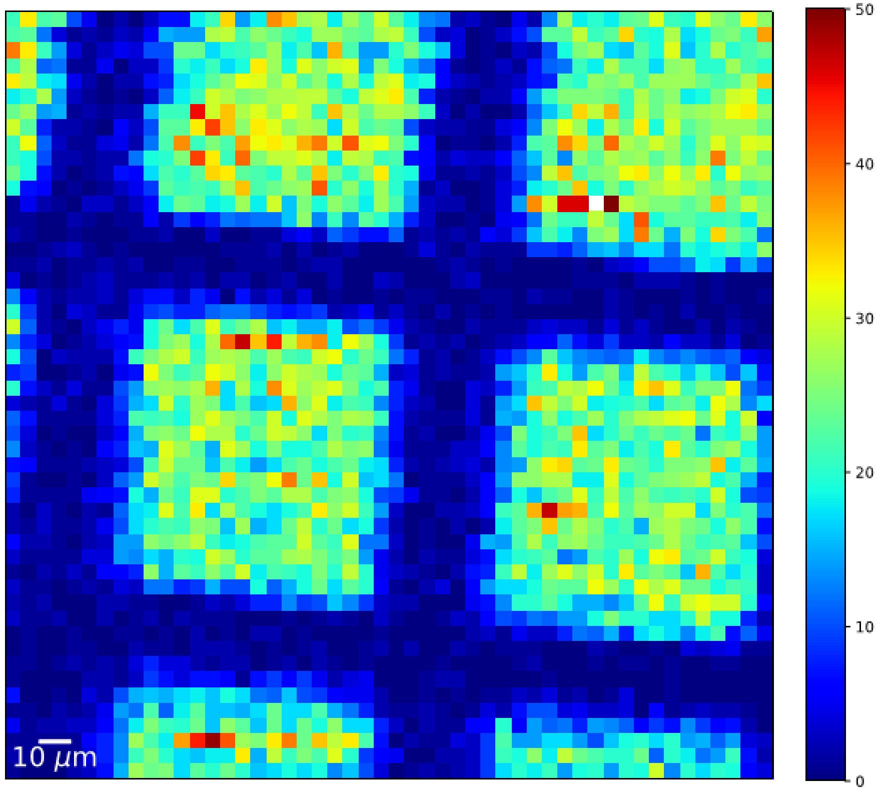


beam through the aperture on Gafchromic EBT3 film

IMAGING #1: MESH

MUCH BETTER CONTRAST COMPARED TO THE CAPILLARY!

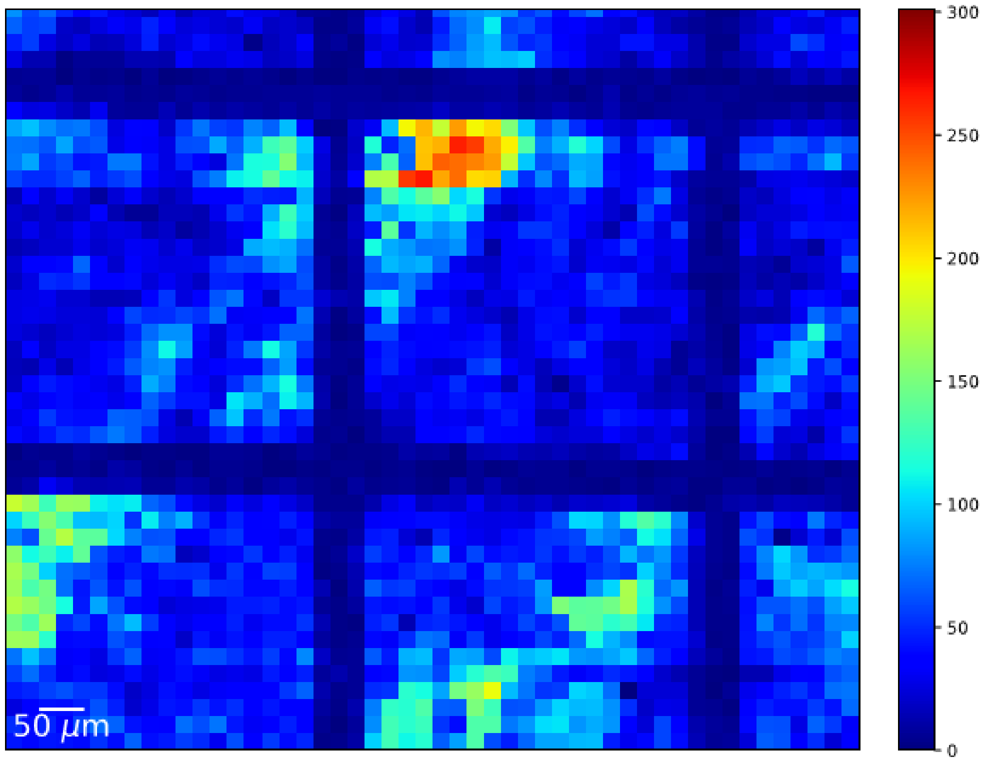
Leucine map, 250 x 250 µm²



transmission: mesh with 127 µm pitch

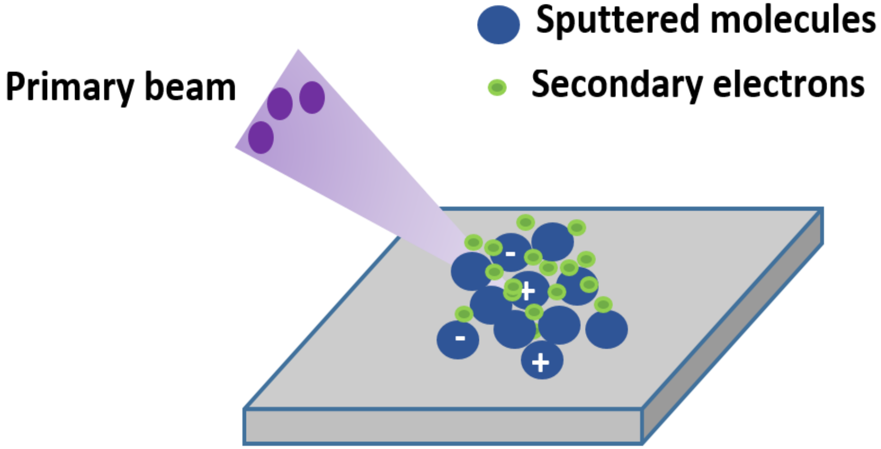
lateral resolution ≈ 10 µm (for 5 µm aperture)

Phthalocyanine map, 1 x 0.9 mm²



electron start: mesh with 440 µm pitch

? TWO TOF START TRIGGER OPTIONS



- Primary ion detection (by a PIN diode)

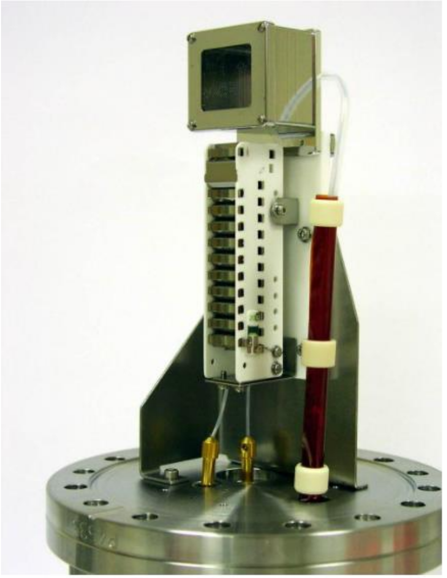
simple setup, good mass resolution
thin targets only, radiation damage

- Detection of secondary electrons

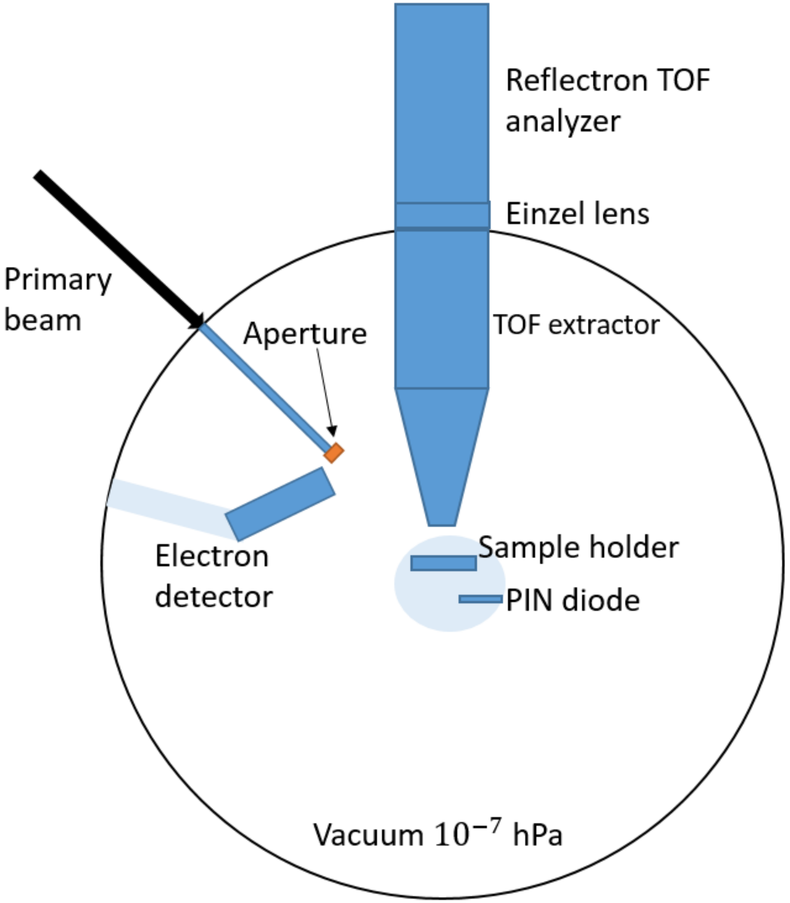
thick targets, radiation hard
complicated setup

STOP signal

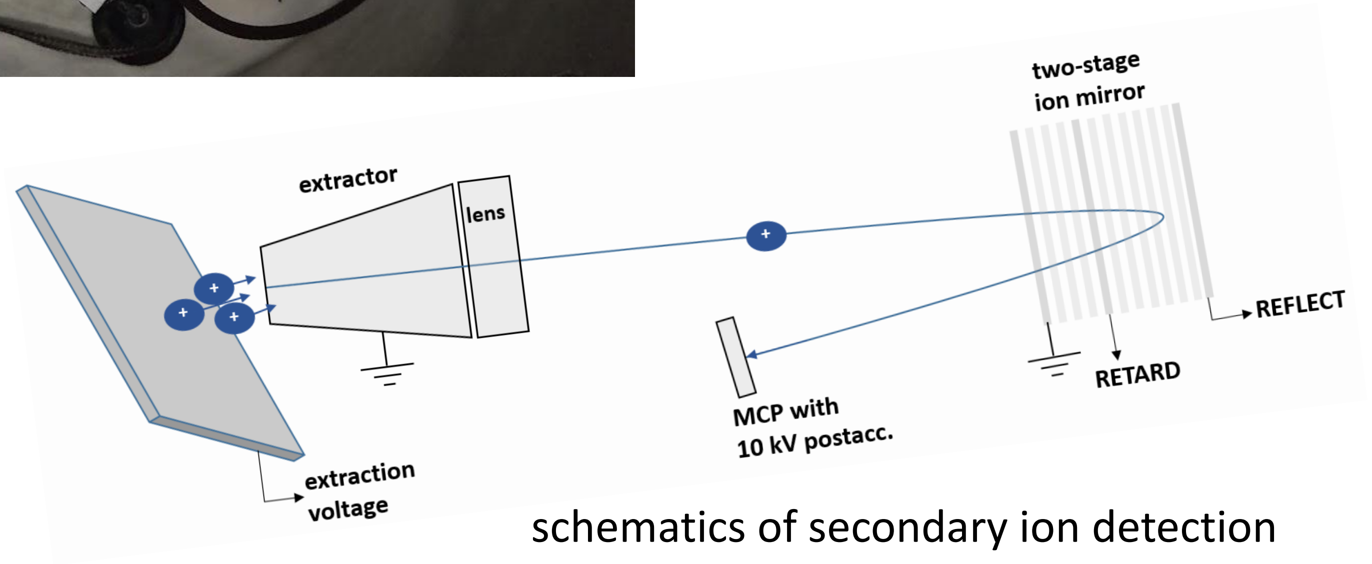
Kore detector with 10 kV postacceleration



THE SETUP



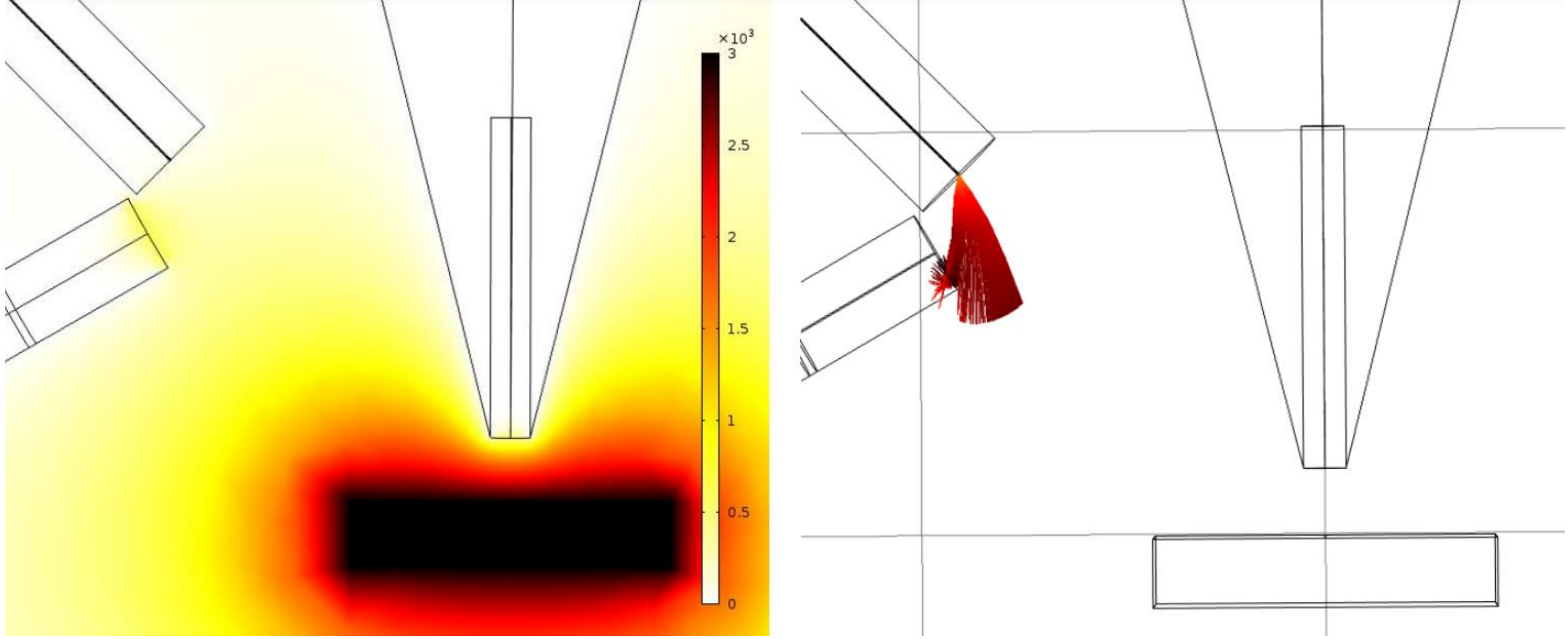
- thin carbon foil (5 nm thickness) over the aperture = **the production of secondary electrons sample-independent** (for example, 7 kHz from a silicon plate but only 1 kHz from a paper



schematics of secondary ion detection

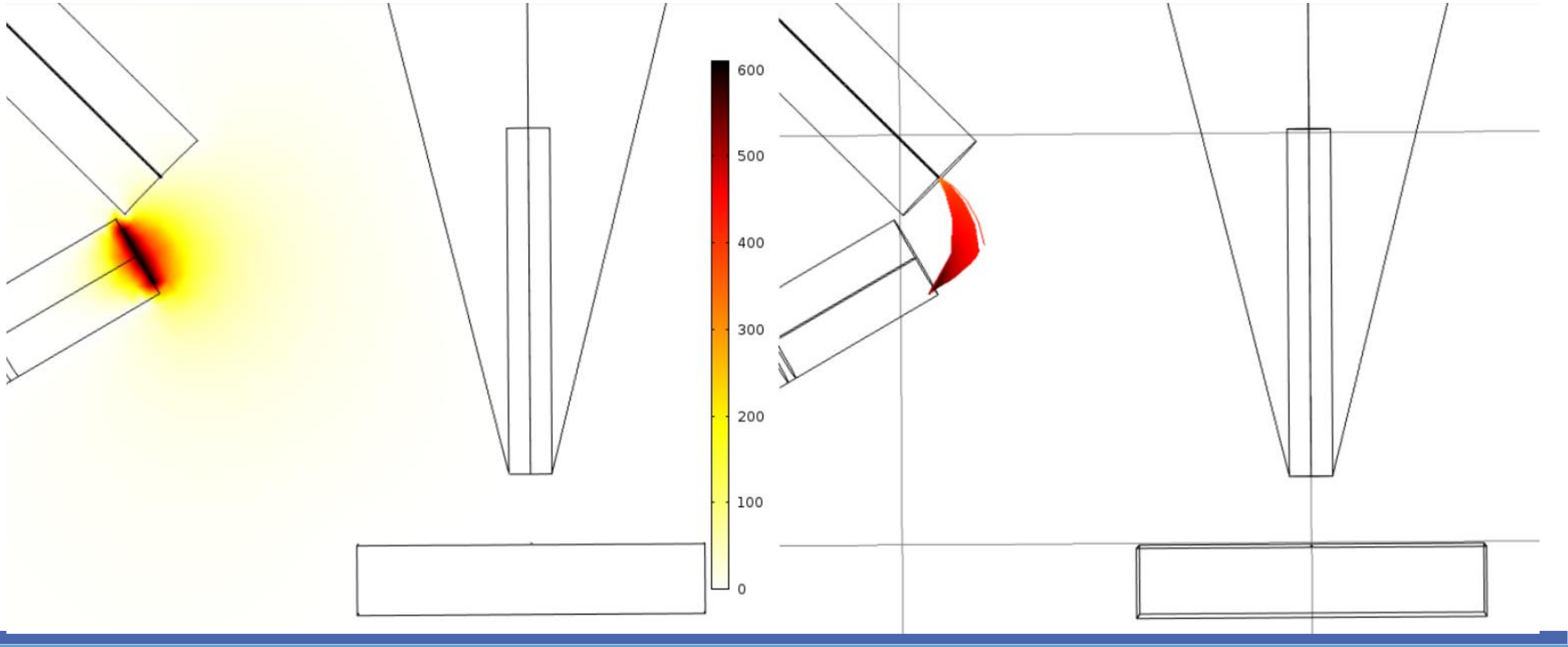
THICK TARGET SETUP: DETECTION OF ELECTRONS

COMSOL simulations



electric potential and electron trajectories with the target at the extraction potential

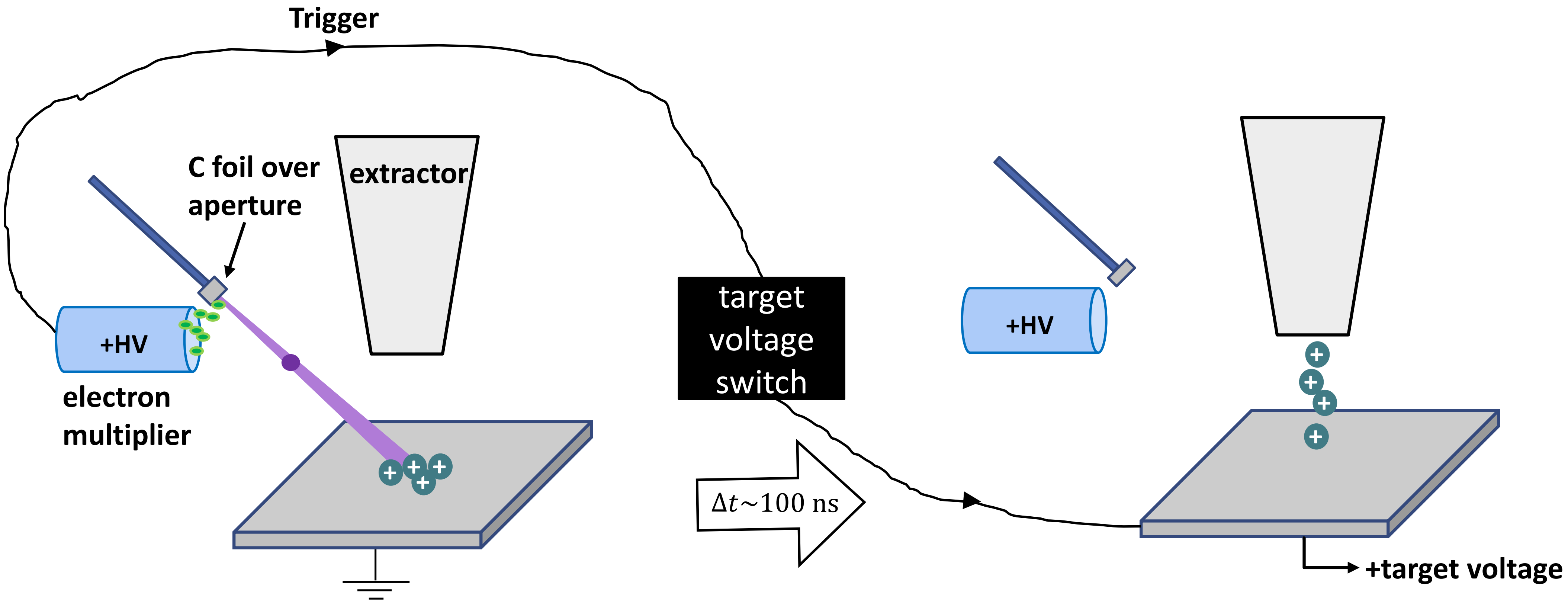
TARGET CANNOT BE HELD AT CONSTANT (EXTRACTION) VOLTAGE!



electric potential distribution and electron detection with the target at zero potential

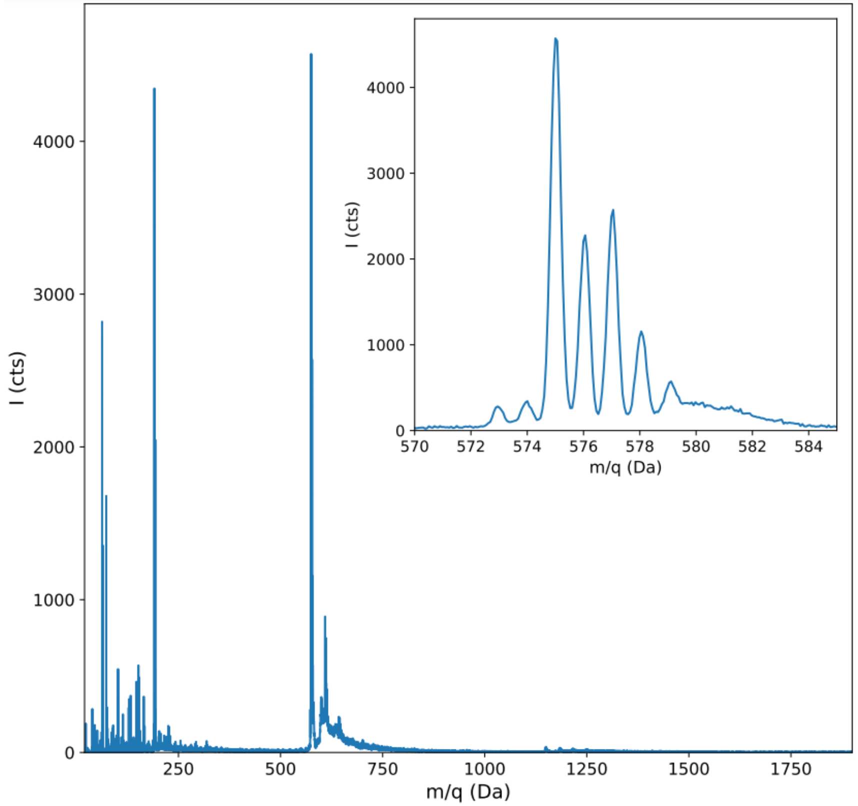
SHEMATIC OVERVIEW OF THE THICK-TARGET SETUP: DETECTION OF SECONDARY ELECTRONS

M. Brajković, I. Bogdanović Radović, M. Barac, D. D. Cosic, Z. Siketić, Imaging of Organic Samples with Megaelectron Volt Time-of-Flight Secondary Ion Mass Spectrometry Capillary Microprobe, J. Am. Soc. Mass Spectrom. 2021, 32, 10, 2567–2572.



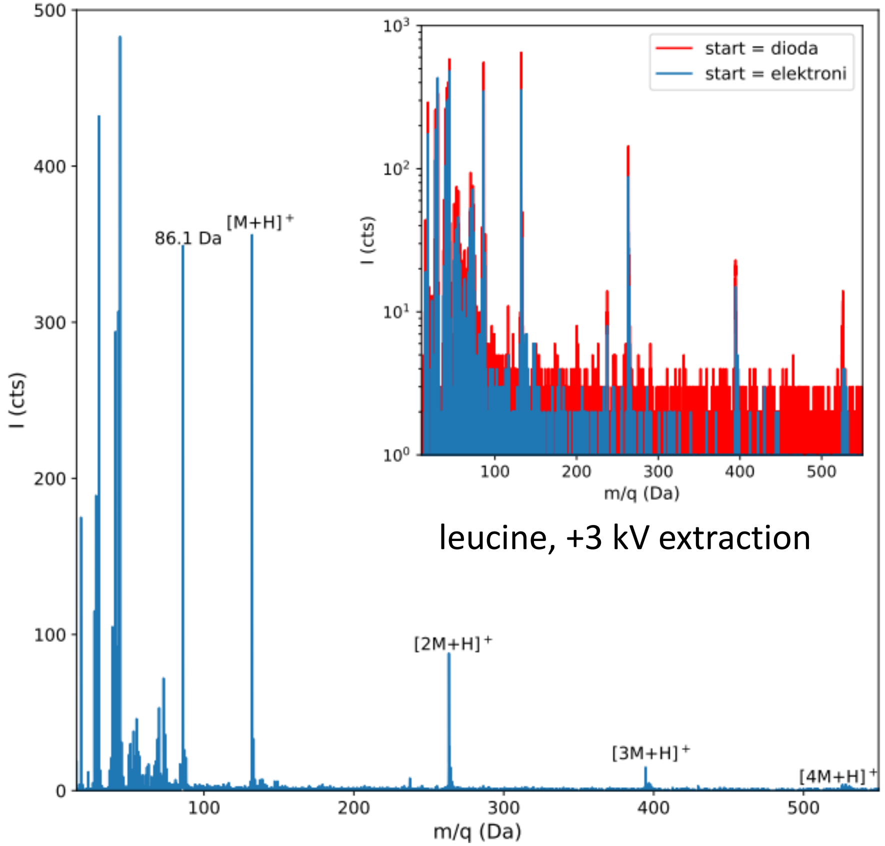
- target voltage applied only for 2 μs
- delayed extraction
- extraction blocked for the remaining part of the acquisiton window(98 μs)

MASS SPECTRUM: TWO MODES



Phthalocyanine blue (m = 576.1 Da) mass spectrum with 10 kV postacc. detector

Comparison of two modes of operation



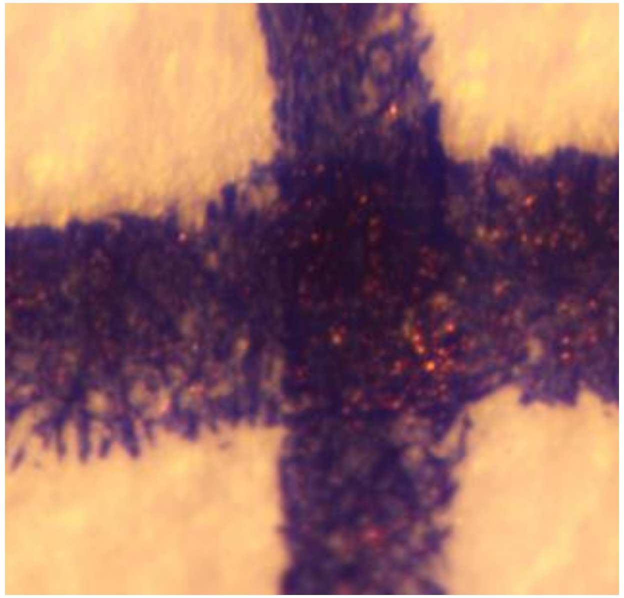
leucine, +3 kV extraction

Mass resolution (for m = 576.1 Da):

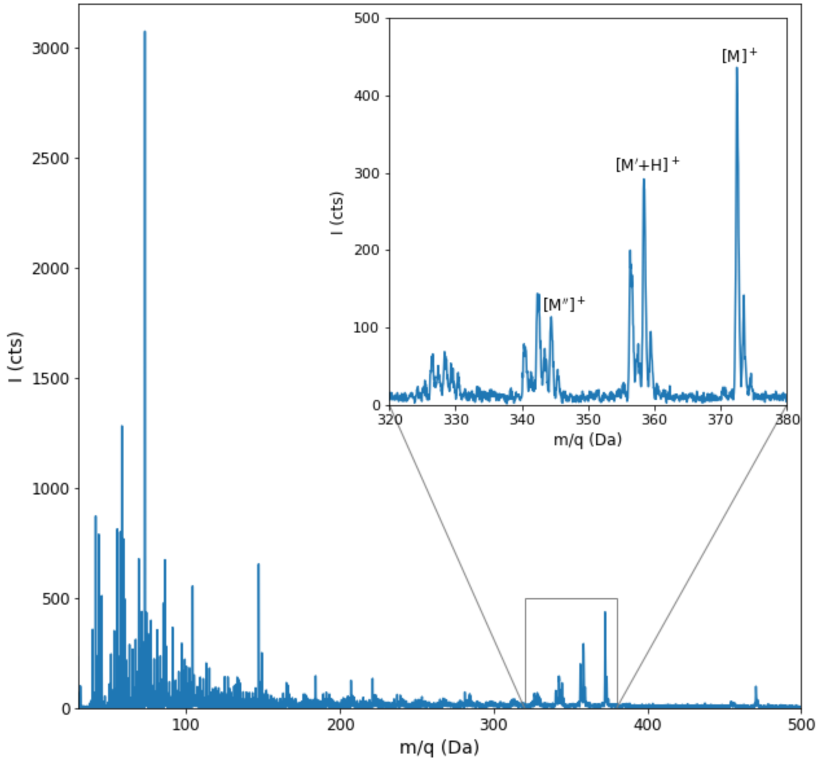
- 2500 in the transmission mode
- 1400 in the electron start mode

but **S/N ration 2 – 5 times better in electron start mode** (random coincidences minimized)

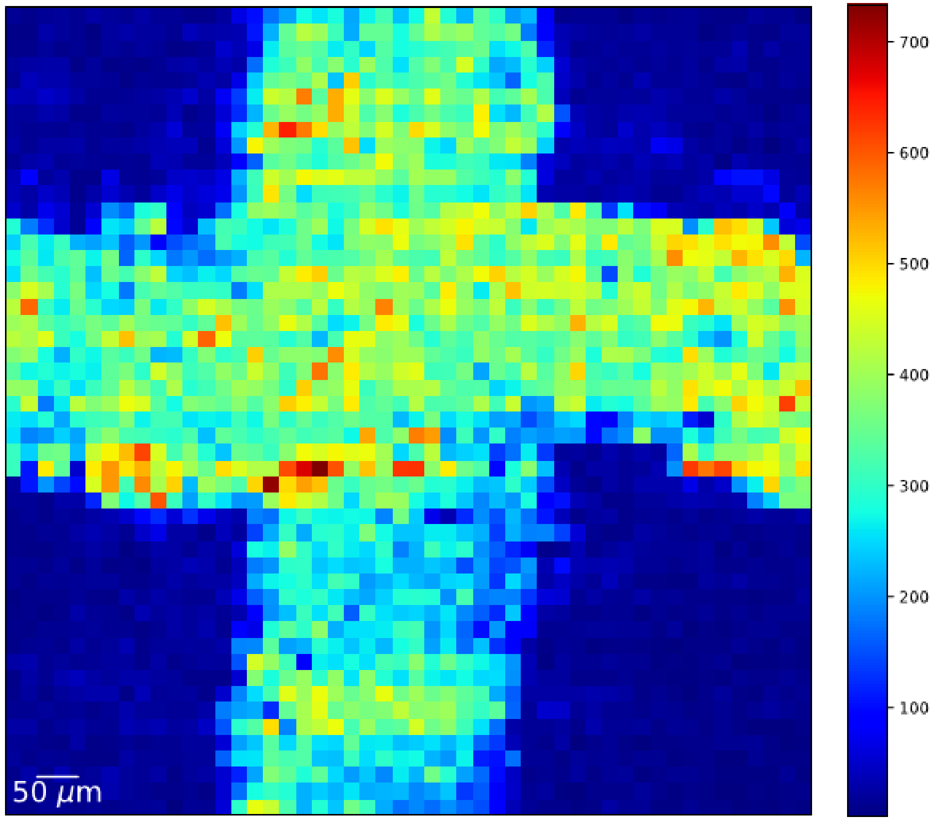
IMAGING #2: INK CROSSING ON A PAPER



optical photo of ink crossing on a paper

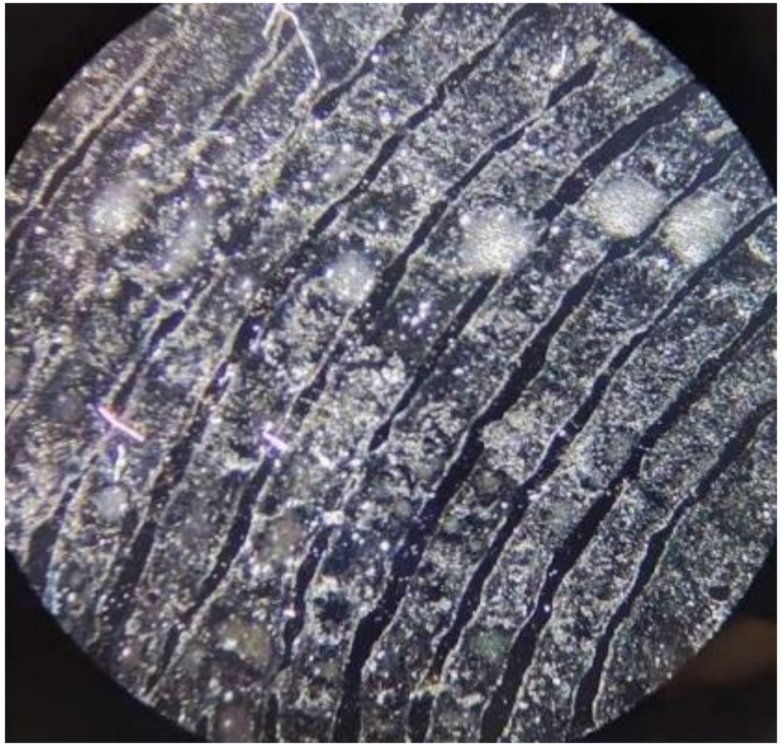


mass spectrum from the ink crossing area

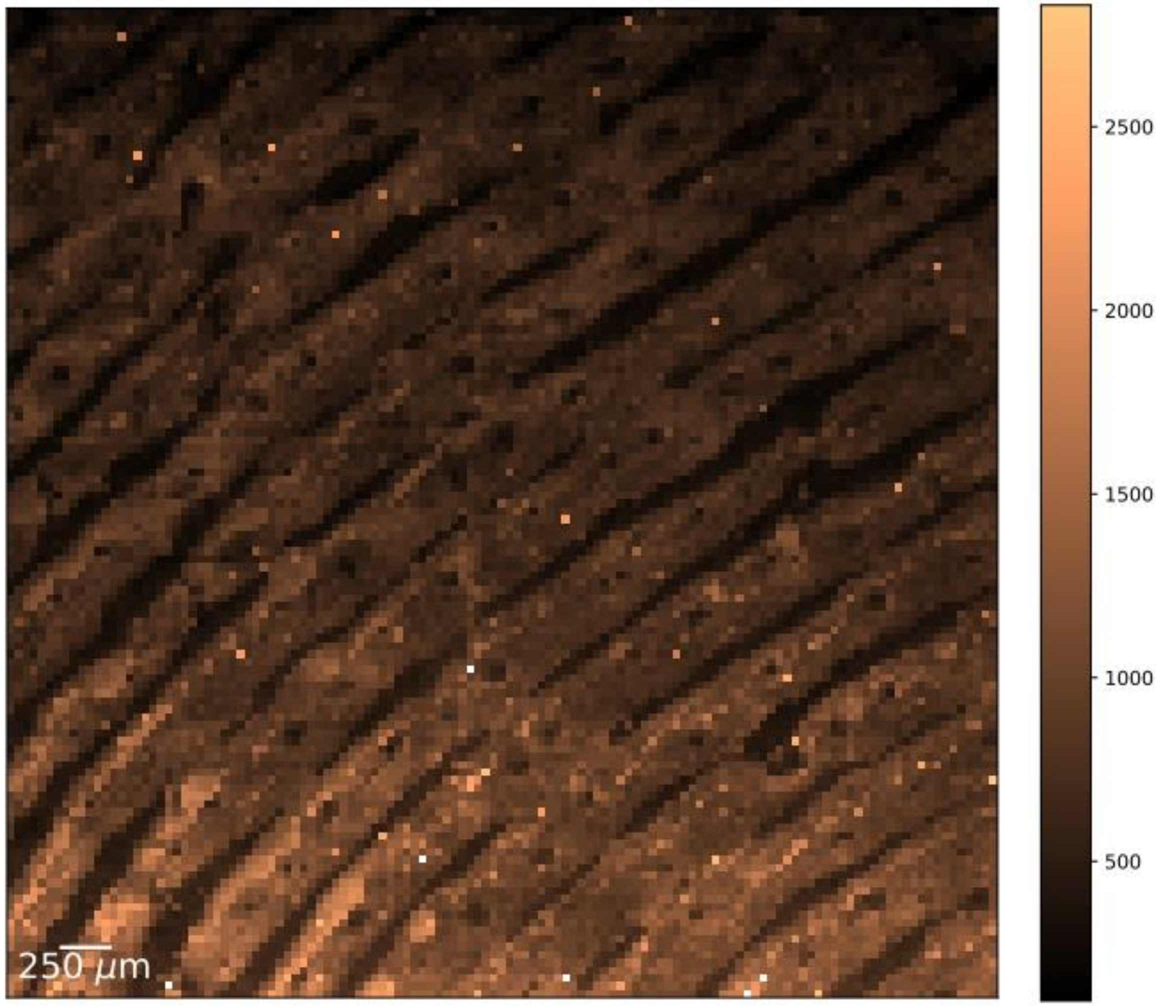


map of signature ink molecules (358-372 Da), ink crossing on a paper, 1 x 1 mm^2

IMAGING #3: FINGERMARK

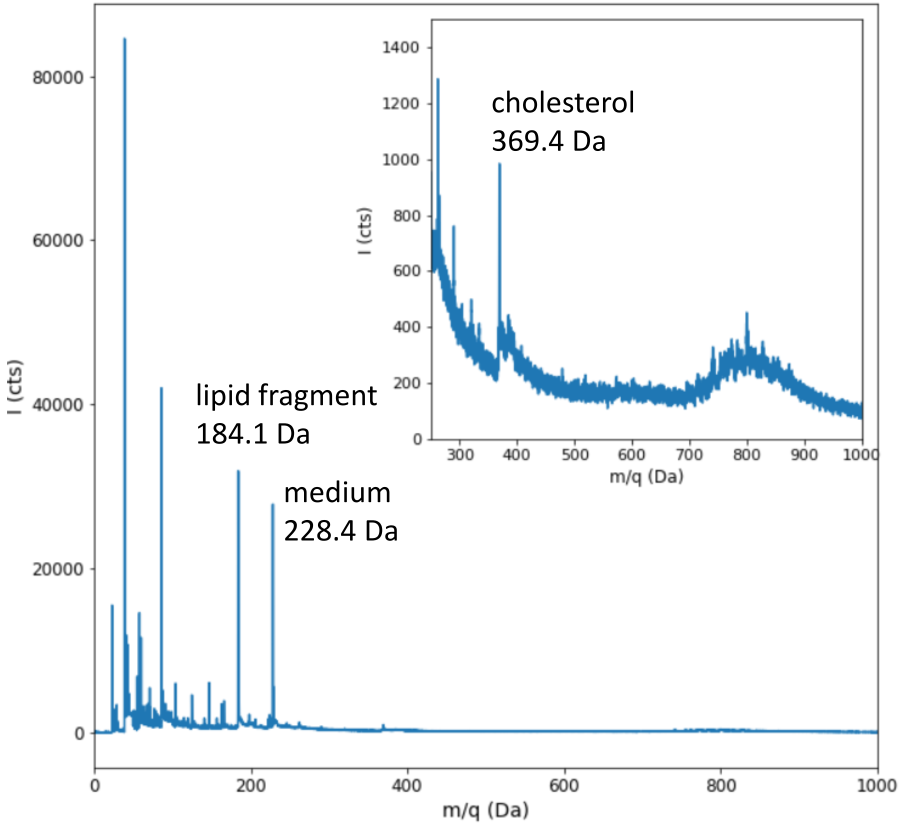


fingermark on a silicon plate
under optical microscope

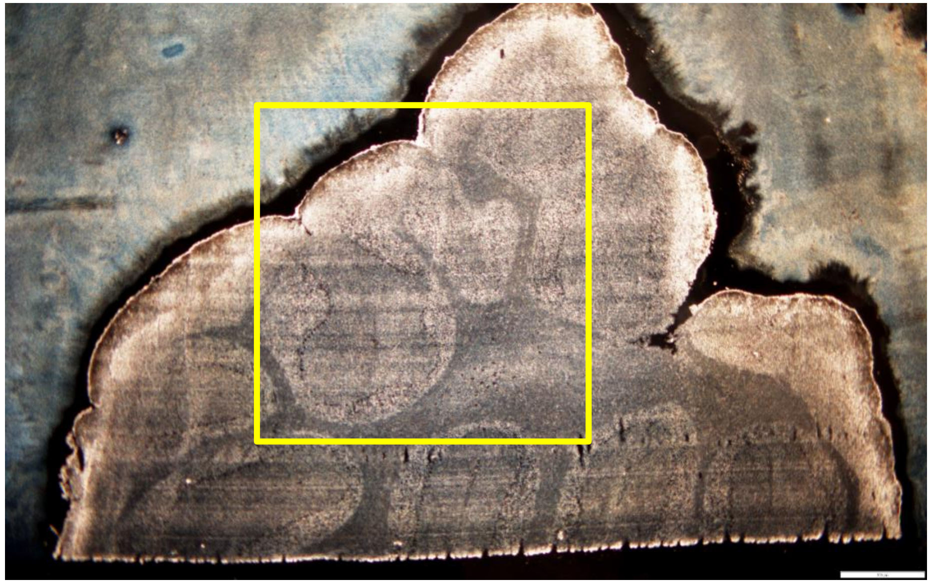


total map, fingermark on a silicon plate, 5 x 5 mm^2

IMAGING #4: MOUSE TISSUE

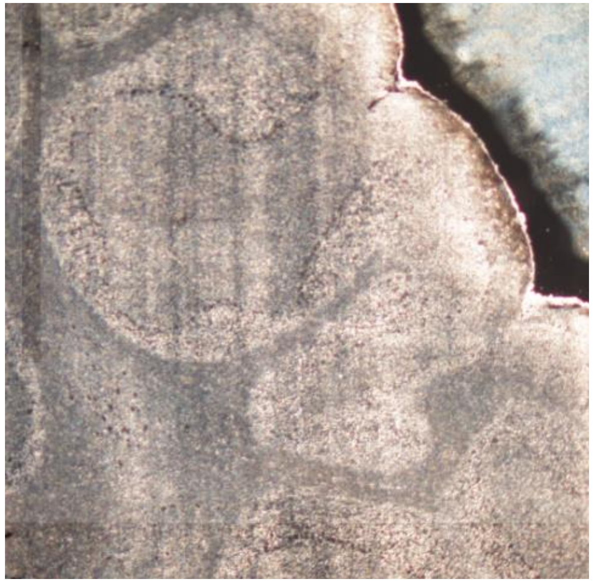


2 x 2 mm^2 scan,
t = 3.5 hours

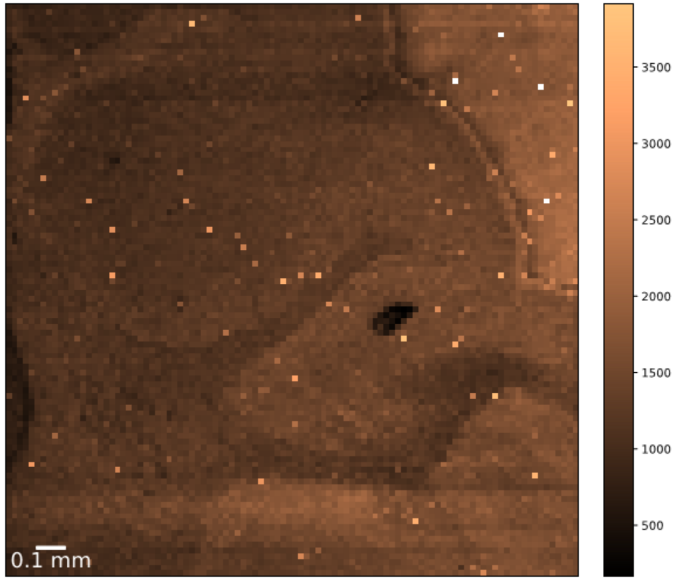


primary beam 14 MeV Cu^{4+}

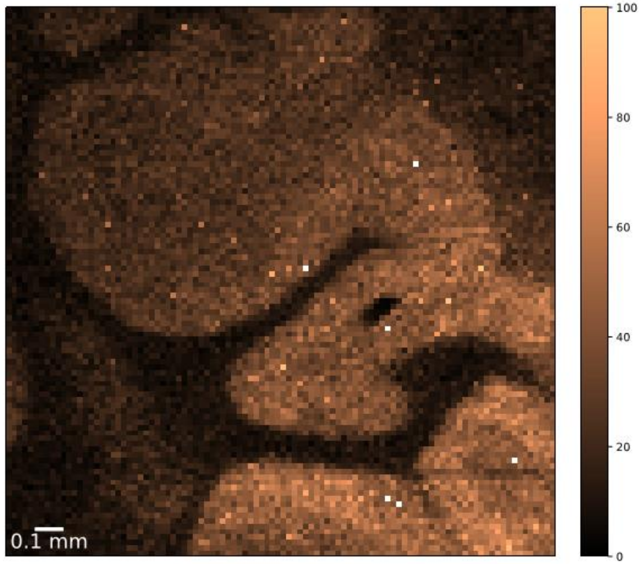
IMAGING #4: MOUSE TISSUE



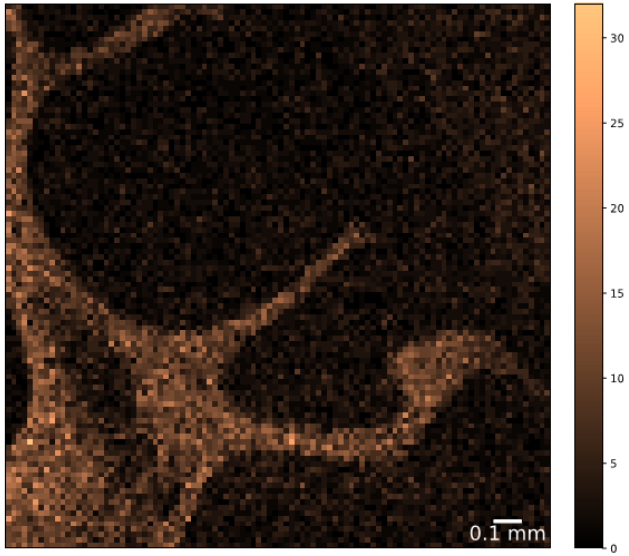
sample photo on an optical microscope



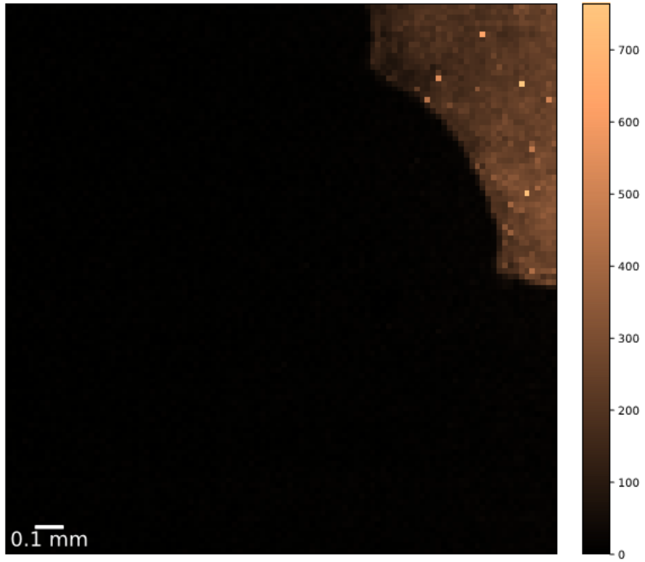
total map



lipid fragment (m = 184.1 Da)



cholesterol (m = 369.4 Da)



medium (m = 228.4 Da)

CONCLUSIONS

- Two techniques (heavy MeV ions + TOF measurements): inorganic films and organic samples
- Different applications: thin film analysis, biomedicine, forensics, ...

THANK YOU FOR LISTENING!

Acknowledgments

Hrzz Hrvatska zaklada za znanost

CEMS

RADIATE