IMT Atlantique
Bretagne-Pays de la Loire
École Mines-Télécom

NUCLÉAIRE
& PARTICULES

Subatech

smiles

Time Of Flight Mass Separation coupled to Laser desorption and Laser ionization

Presented by Jean EL KHOUEIRY

PhD Hours

30-04-2026

PRISMA

Physics of Radiation InteractionS with Matter and Applications

Plan

- Introduction
- Our test-bench experiment
- First results
- Next steps in SMILES
- Conclusion

Introduction

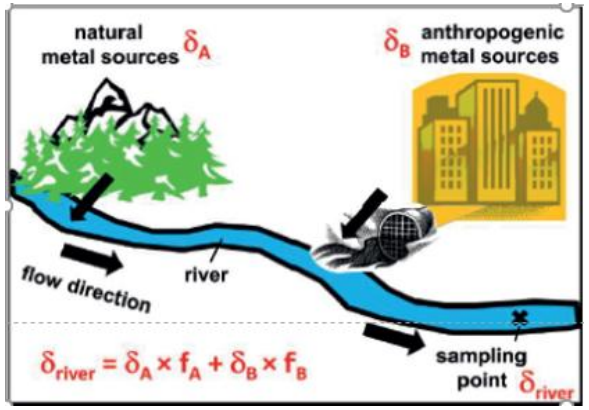
The SMILES project

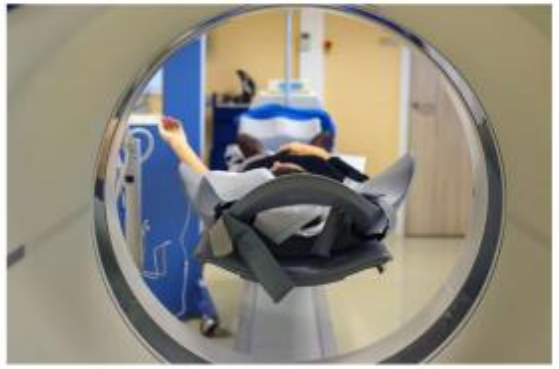
Séparation en **M**asse couplée à l'**I**onisation **L**aser pour des applications **E**nvironnementales et en **S**anté

Need for high-selectivity measurements and separation of trace elements:

1- For identification and quantification: tracking environmentally relevant isotopes. Such as $^{63}Cu/^{65}Cu$ and $^{226}Ra/^{228}Ra$

2- Isotopic purification for targeted applications mostly in nuclear medicine.





Example of an application

Complex sea samples contain many different elements of interest: research study on Cu isotopic ratio with IFREMER*

Contaminants and isobars hinder the purity

Only copper ionized!

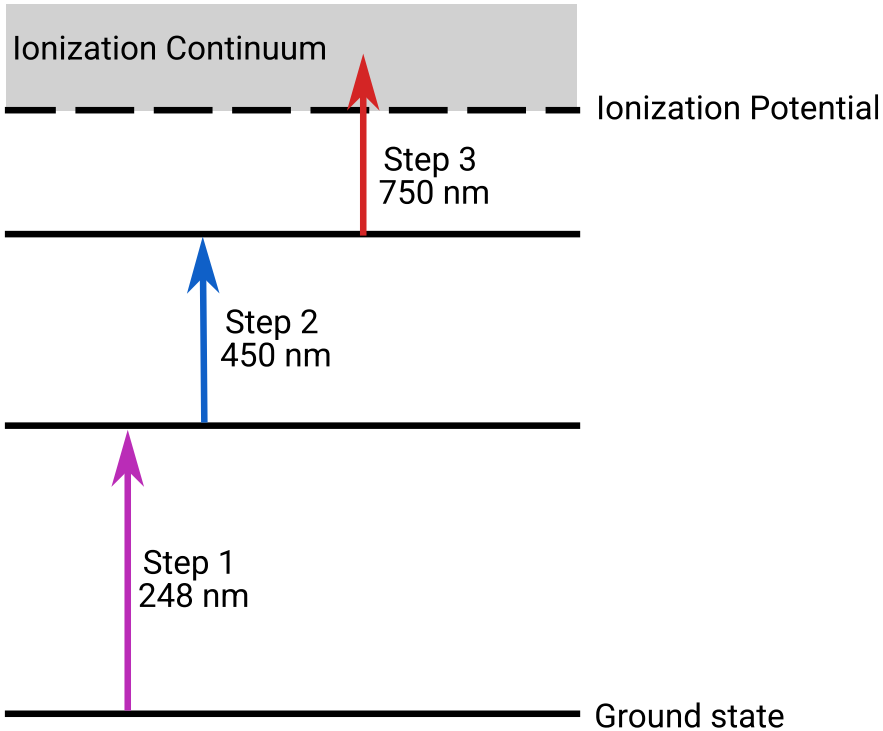


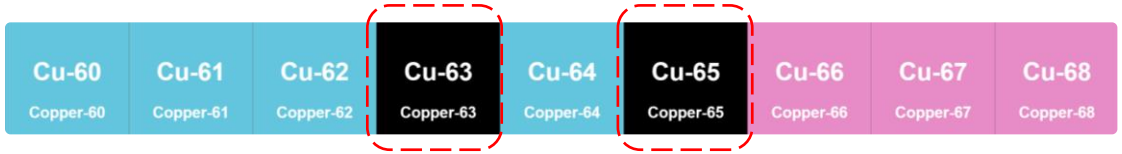
Fig 1 : Schematic of resonant Ionization of Copper

Jean.el-khoueiry@subatech.in2p3.fr

Example of an application

Complex sea samples contain many different elements of interest: research study on Cu isotopic ratio with IFREMER*

Contaminants and isobars hinder the purity



Only copper ionized!

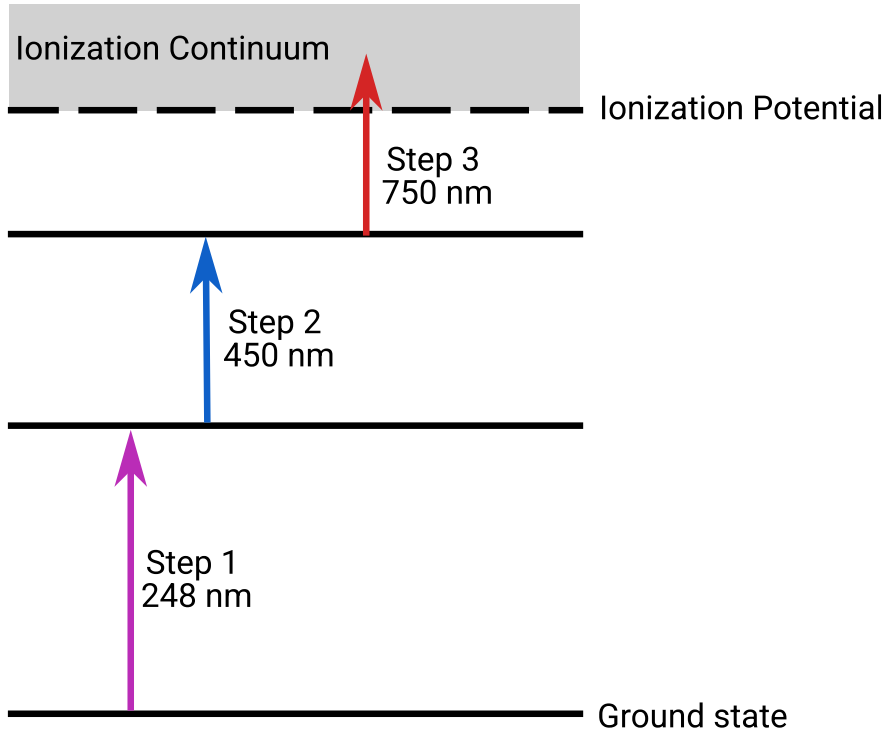


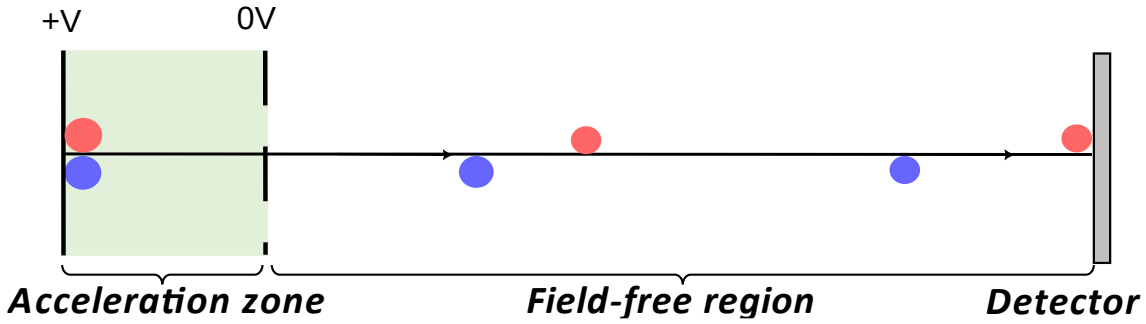
Fig 1 : Schematic of resonant Ionization of Copper

Jean.el-khoueiry@subatech.in2p3.fr

Two Mass Separation techniques

The Time Of Flight method:

- **Electric** fields are used.
- The separation in the flight time of the ions.
- Heavier ions arrive later to the detector.
- Best suited for environmental studies.



m'>m

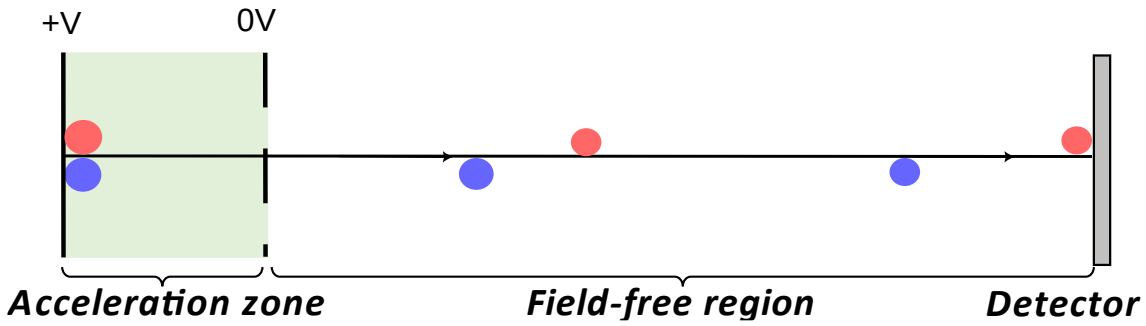
Two Mass Separation techniques

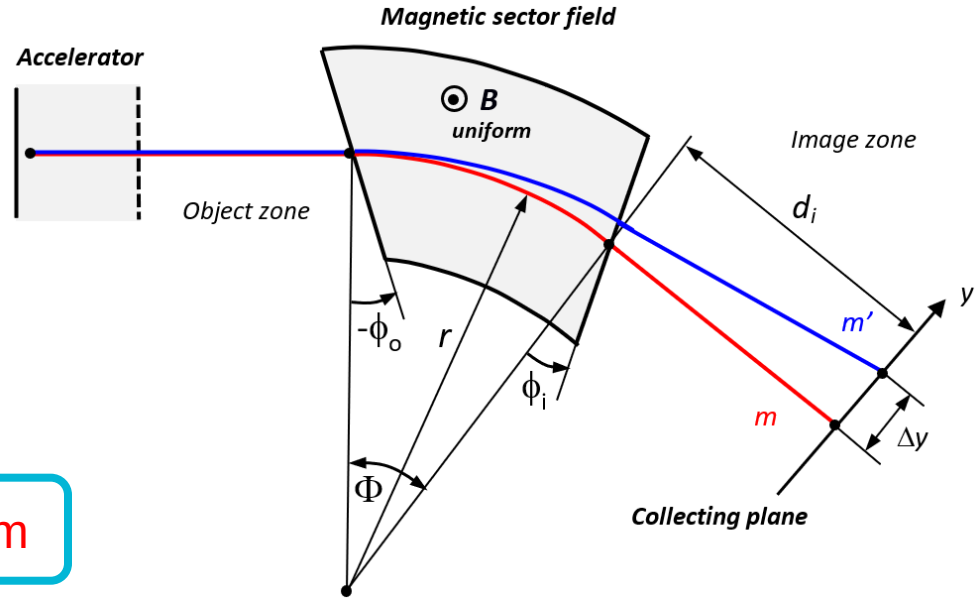
The Time Of Flight method:

- **Electric** fields are used.
- The separation in the flight time of the ions.
- Heavier ions arrive later to the detector.
- Best suited for environmental studies.

The Magnetic Sector method:

- **Electric and magnetic** fields are used.
- Spatial separation: done by the magnetic sector.
- Heavier ions take a bigger radius.
- Purification: collection of separate isotopes independently.





m'>m

Jean.el-khoueiry@subatech.in2p3.fr

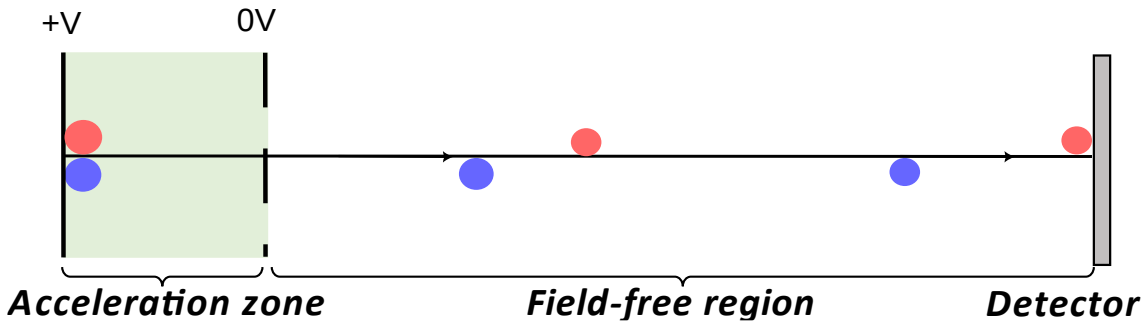
Two Mass Separation techniques

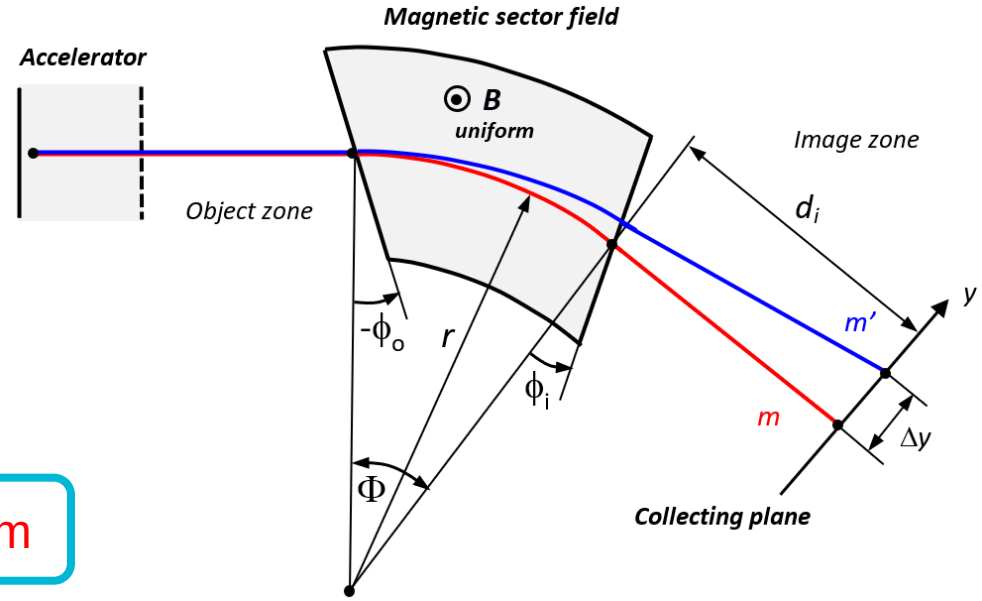
The Time Of Flight method:

- **Electric** fields are used.
- The separation in the flight time of the ions.
- Heavier ions arrive later to the detector.
- Best suited for environmental studies.

The Magnetic Sector method:

- **Electric and magnetic** fields are used.
- Spatial separation: done by the magnetic sector.
- Heavier ions take a bigger radius.
- Purification: collection of separate isotopes independently.

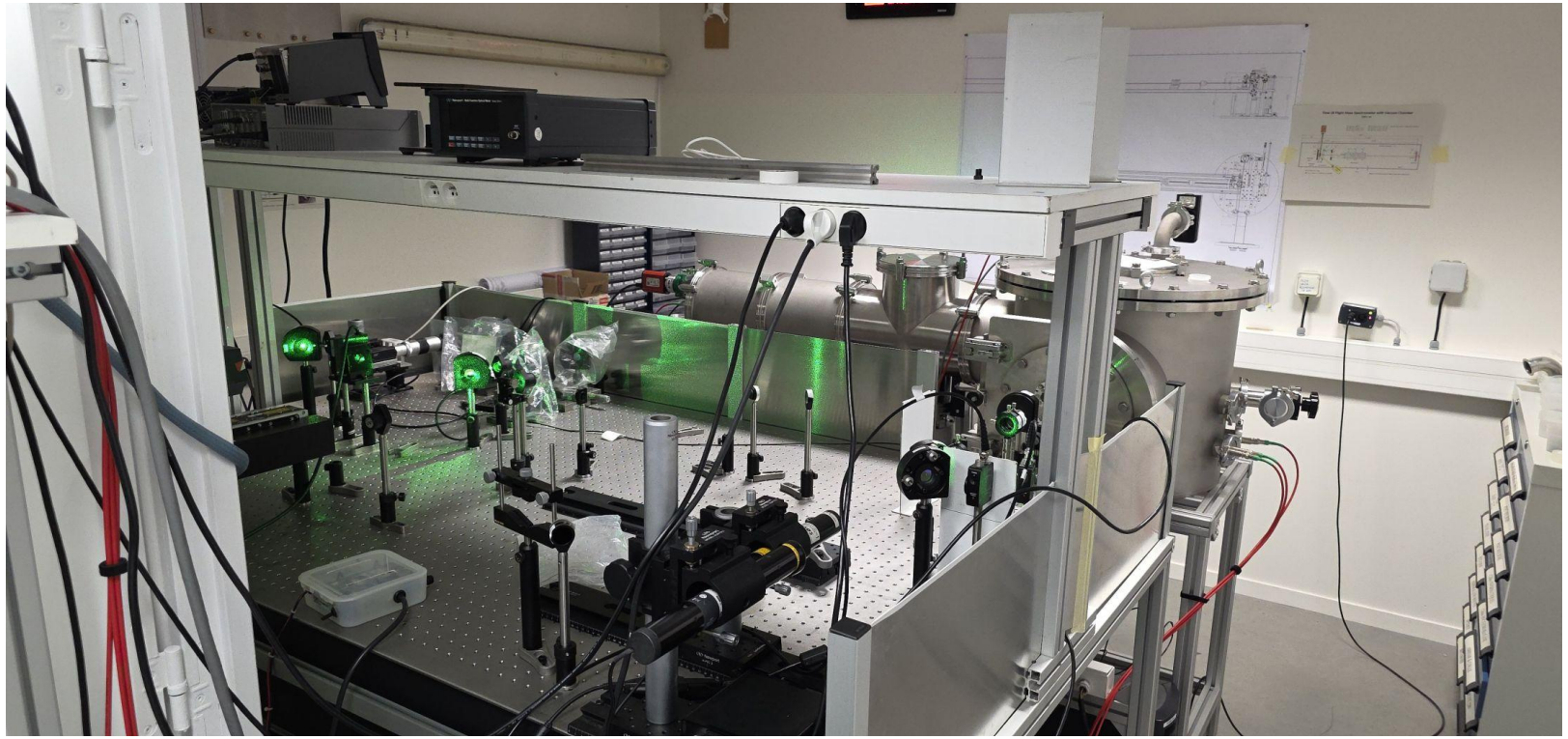




m'>m

Jean.el-khoueiry@subatech.in2p3.fr

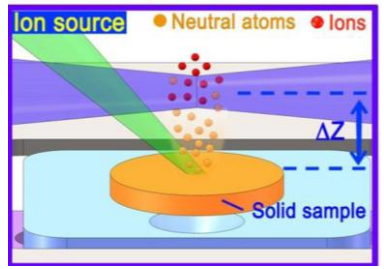
Our test-bench setup



A two laser approach

- LD-LPI-TOF : two separate lasers
- LD : **Laser Desorption** as the way to extract the atoms from the studied sample
- LPI: **Laser Post Ionization** intercepting the neutral atoms

This separation makes it possible to optimize each process



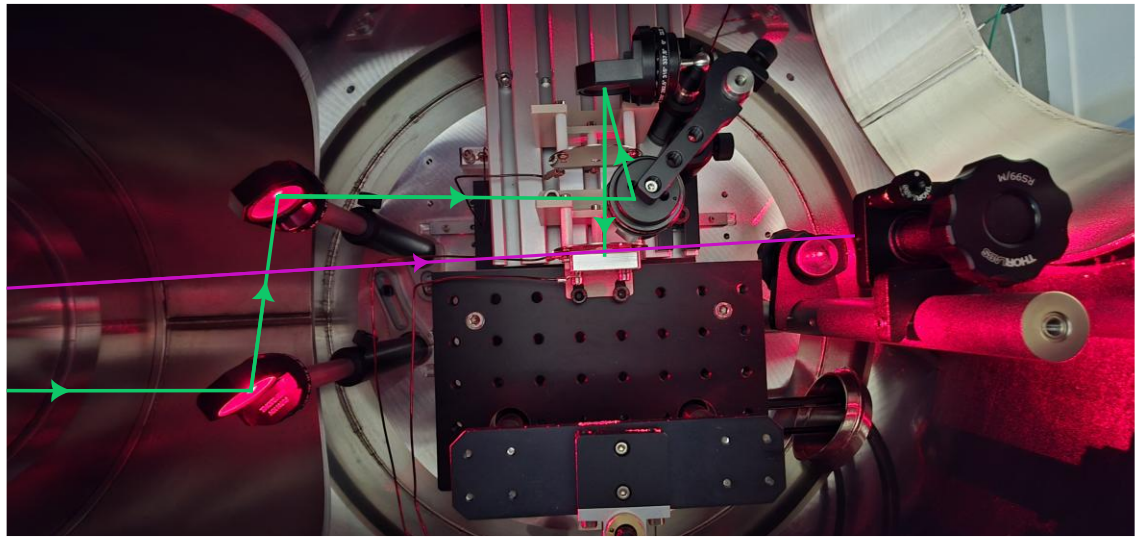


Fig 1 :Schematic diagram of the LD-LPI source [1]

[1] Z. Yin, L. Hang, R. Liu, W. Hang, et B. Huang, « Improved detection sensitivity of elements in solids via laser postionization in laser desorption time-of-flight mass spectrometry », *J. Mass Spectrom.*, vol. 53, nº 5, p. 435-443, mai 2018, doi: 10.1002/jms.4076.

Laser Desorption

- Extraction regime depends on **Laser fluence** (energy/area)

$$Fluence = \frac{Energy}{Area}$$

- Experimental diameter measured at ≈ 70µm
- Pulse energy ≈ 10µJ
- Fluence = 0,52 J/cm^2

Operating close to the ablation threshold 0,50 J/cm^2 [2]

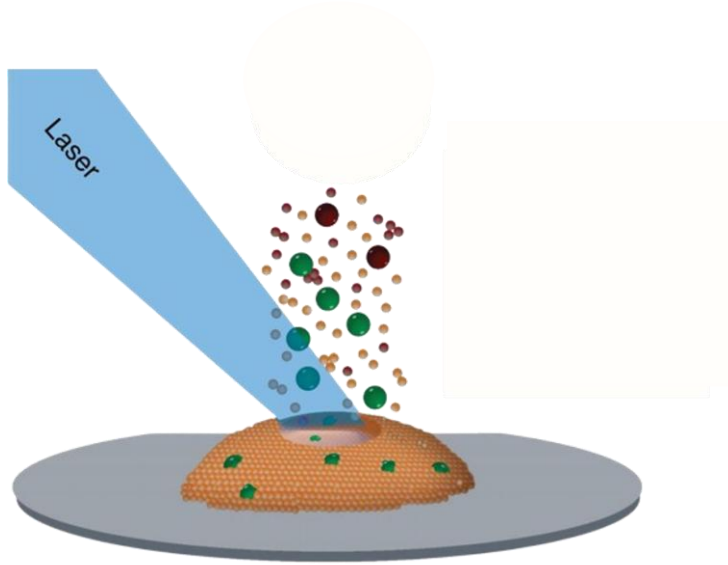


Fig 1: Schematic of laser desorption.
Source:https://www.creative-proteomics.com/support/matrix-assisted-laser-desorption-ionization.htm

[1] S. Prahl, *laserbeamsize: a python module for ISO 11146 analysis of laser beams*. (11 novembre 2025). Zenodo. doi: 10.5281/ZENODO.8346799.
[2] J. Maul *et al.*, « A laser desorption/resonance enhanced photoionisation TOF-system for the spatially resolved trace analysis of elements », *Nucl. Instrum. Methods Phys. Res. Sect. B Beam Interact. Mater. At.*, vol. 226, nº 4, p. 644-650, déc. 2004, doi: 10.1016/j.nimb.2004.08.012

Laser Desorption

- Extraction regime depends on **Laser fluence** (energy/area)

$$Fluence = \frac{Energy}{Area}$$

- Experimental diameter measured at ≈ 70µm
- Pulse energy ≈ 10µJ
- Fluence = 0,52 J/cm^2

Operating close to the ablation threshold 0,50 J/cm^2 [2]

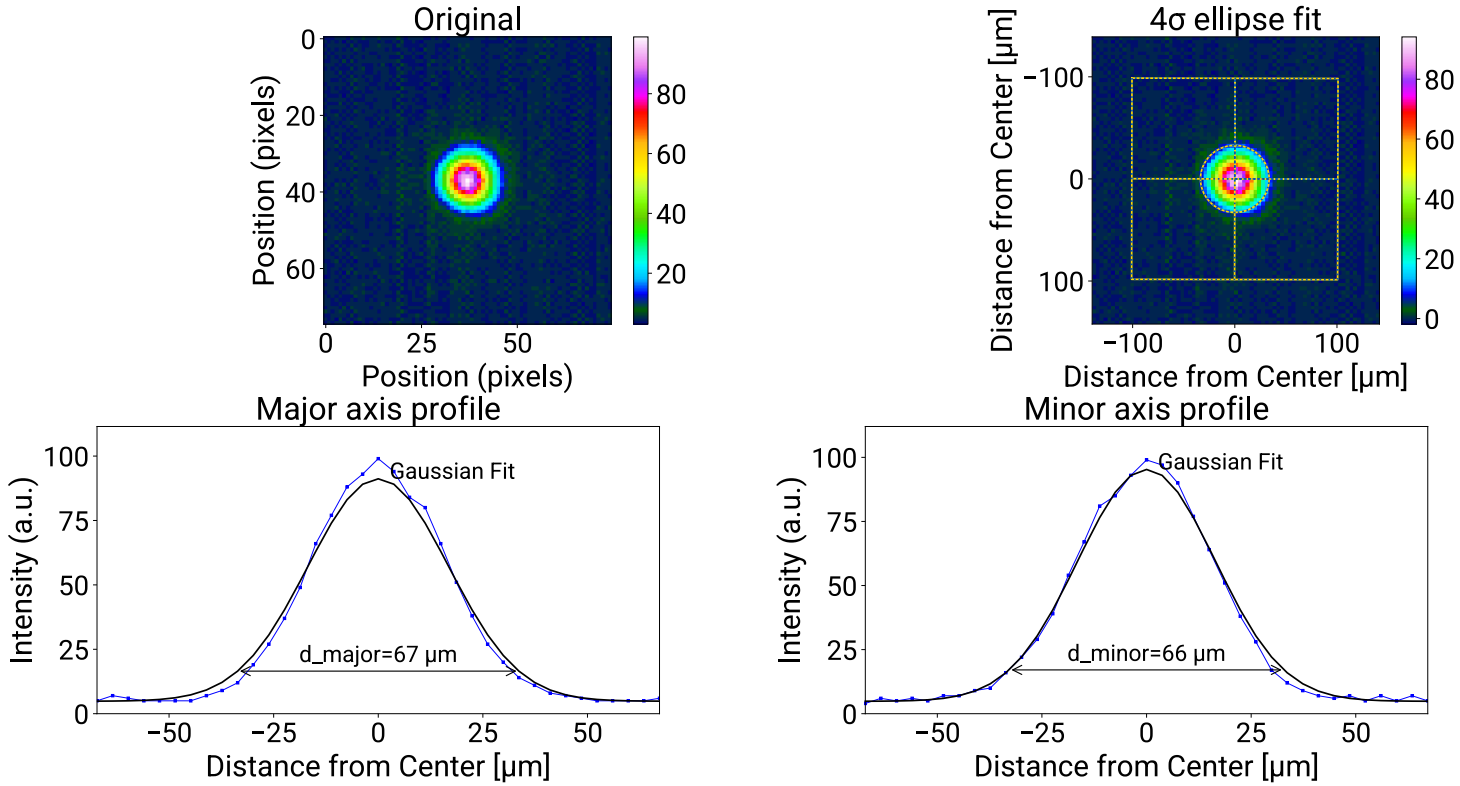


Fig 2 : Measurements of beam dimaeter done by using the library laser beamsize [1]

[1] S. Prahl, *laserbeamsize: a python module for ISO 11146 analysis of laser beams*. (11 novembre 2025). Zenodo. doi: 10.5281/ZENODO.8346799.

[2] J. Maul *et al.*, « A laser desorption/resonance enhanced photoionisation TOF-system for the spatially resolved trace analysis of elements », *Nucl. Instrum. Methods Phys. Res. Sect. B Beam Interact. Mater. At.*, vol. 226, nº 4, p. 644-650, déc. 2004, doi: 10.1016/j.nimb.2004.08.012

Non-resonant Laser Ionization

- Defined delay and distance from the sample.
- Resonant ionization laser cavities were not ready.
- For the testbench we used **non-resonant** ionization.
- Wavelengths emitted: 1064, 532 and 266 nm.

Wavelength (nm)	Energy (eV)
266	4,66
532	2,33
1064	1,16

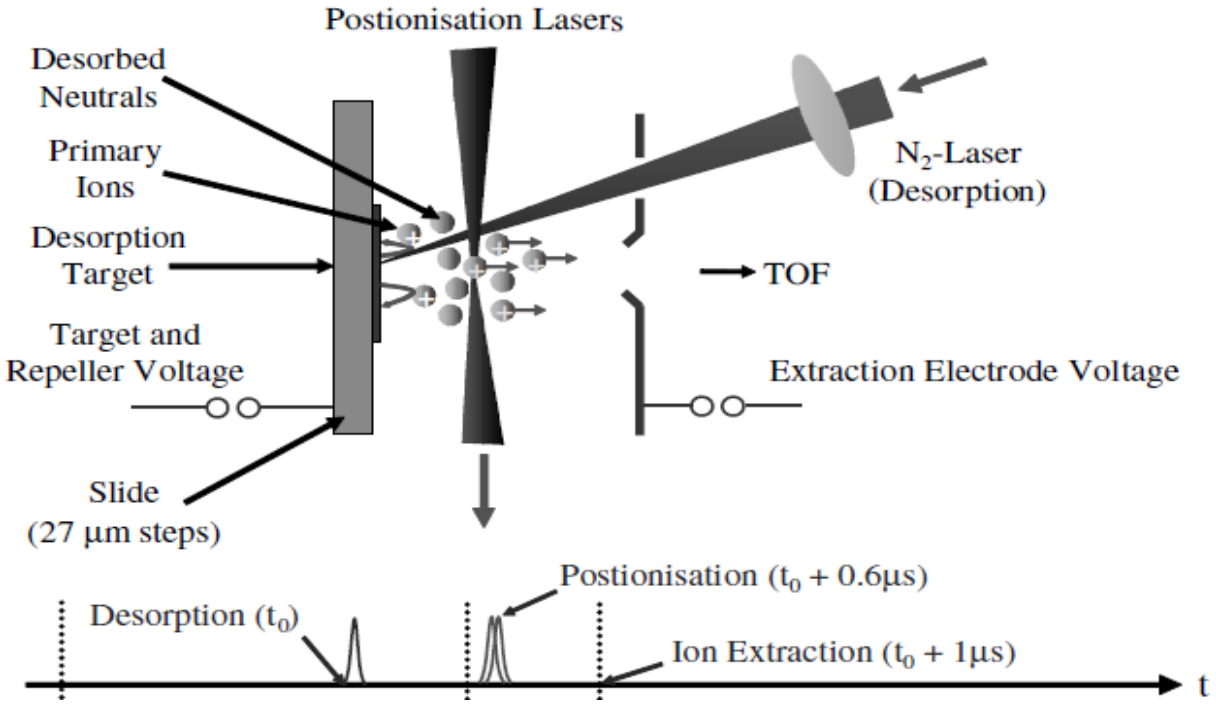


Fig 1: Principle of laser LD-LPI [1]

[1] J. Maul *et al.*, « A laser desorption/resonance enhanced photoionisation TOF-system for the spatially resolved trace analysis of elements », *Nucl. Instrum. Methods Phys. Res. Sect. B Beam Interact. Mater. At.*, vol. 226, nº 4, p. 644-650, déc. 2004, doi: 10.1016/j.nimb.2004.08.012

Ion transport and detection

Ion transport:

- Acceleration: ions accelerated by three electrodes
- Focusing: Einzel lens shapes and focuses the ion beam

Detection:

- Ions are detected using a Magnetof detector
- Signal: Intensity as a function of Time
- Time reference is the desorption Laser pulse.

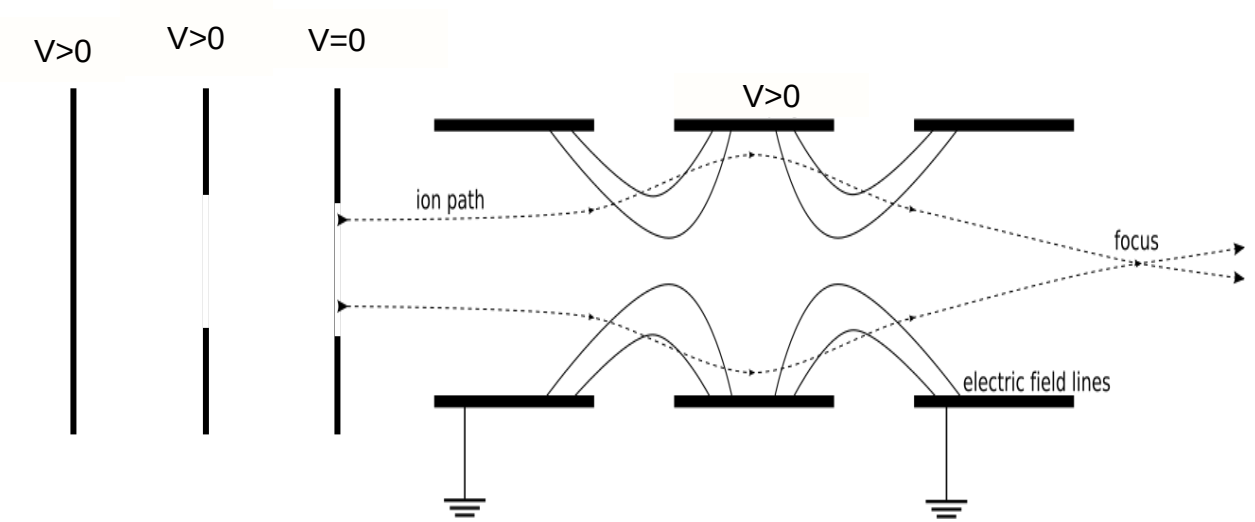
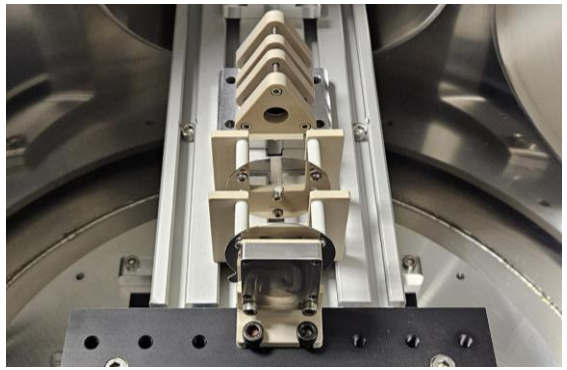
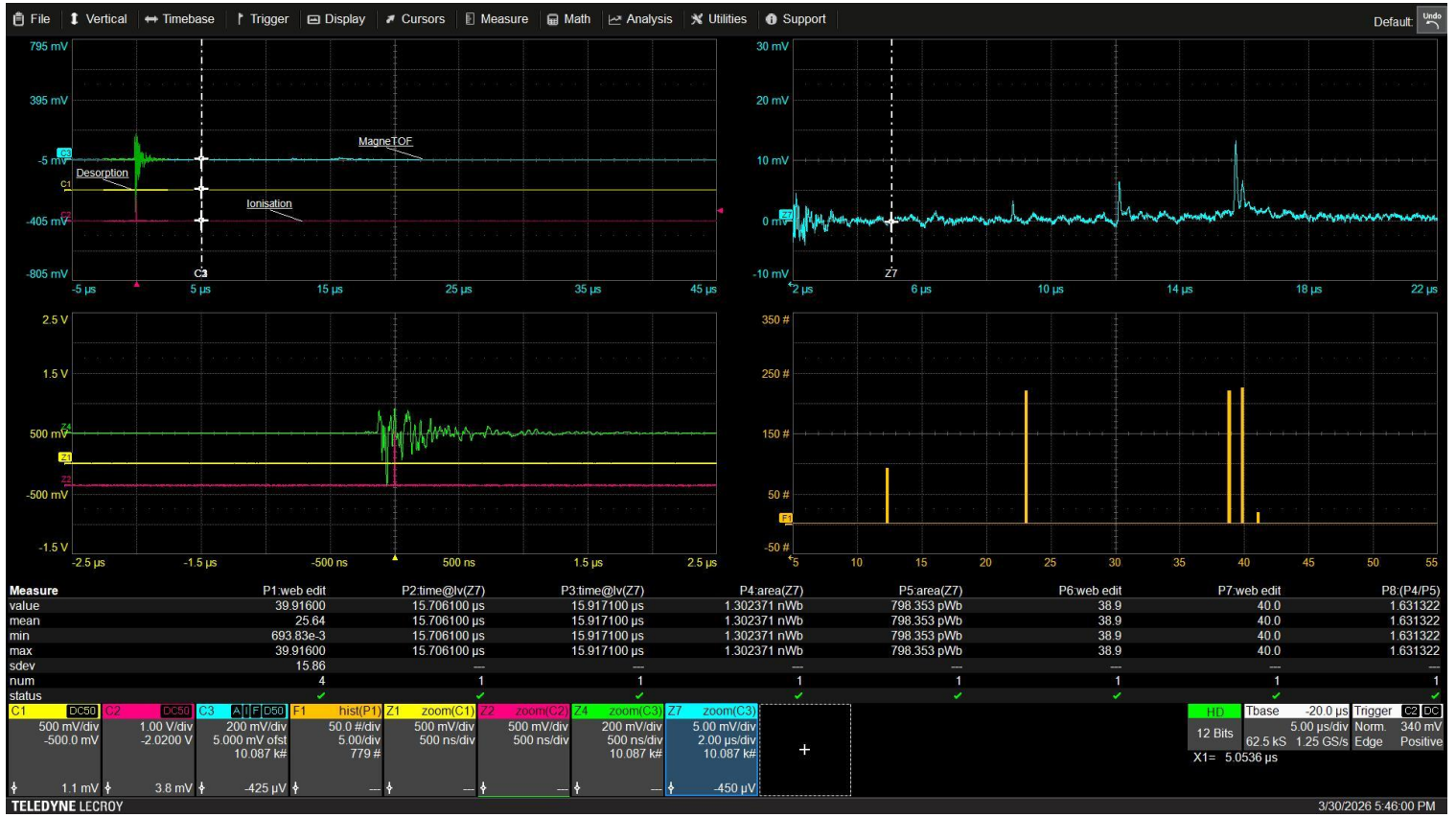


Fig 1: Simplified scheme of Ion transport electrodes



First results



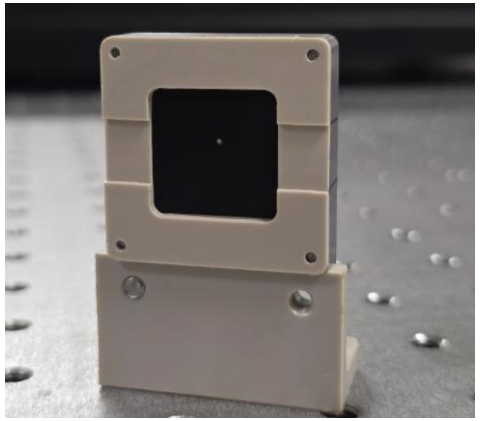
Testing target

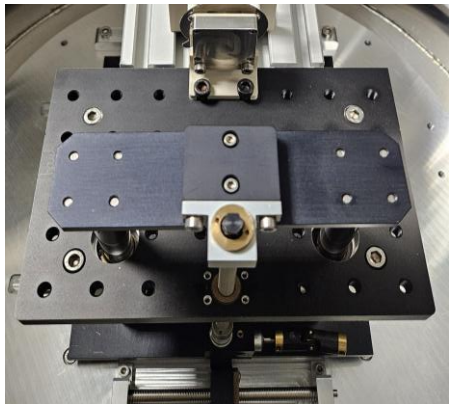
Test sample preparation:

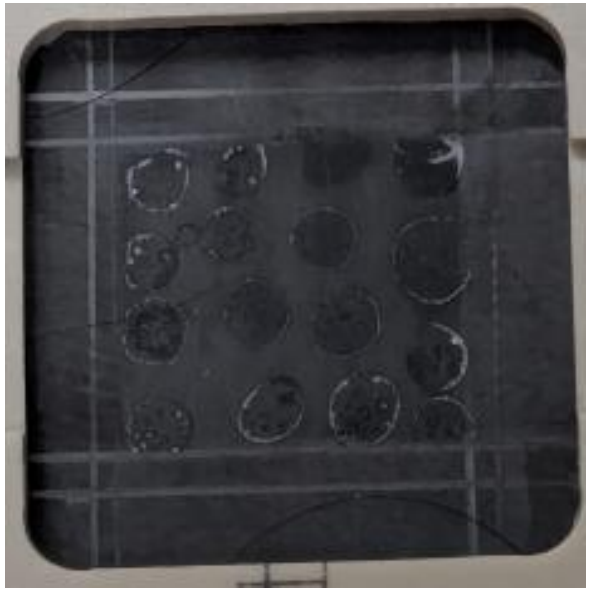
- Solution of **NaCl** and **KCl**
- First demonstration experiment : simple preparation and accessible with non-resonant ionization
- Deposited as droplets on a graphite sheet as test of sample holder
- Left to dry before the experiment.

Positioning:

- Mounted on a two axis motorized stage.
- Automatic, precise movement (sub millimeter)







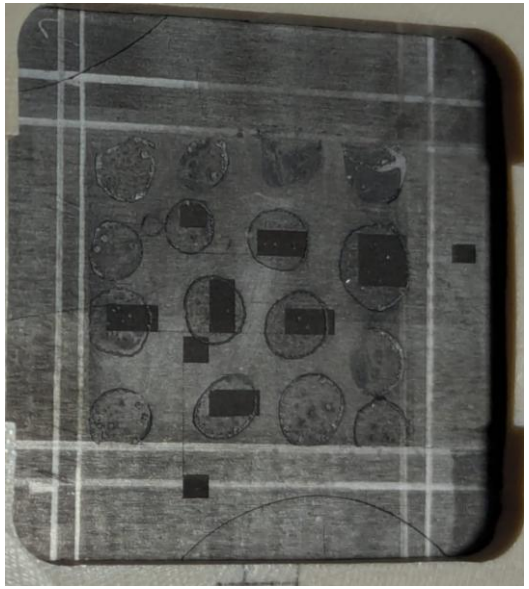
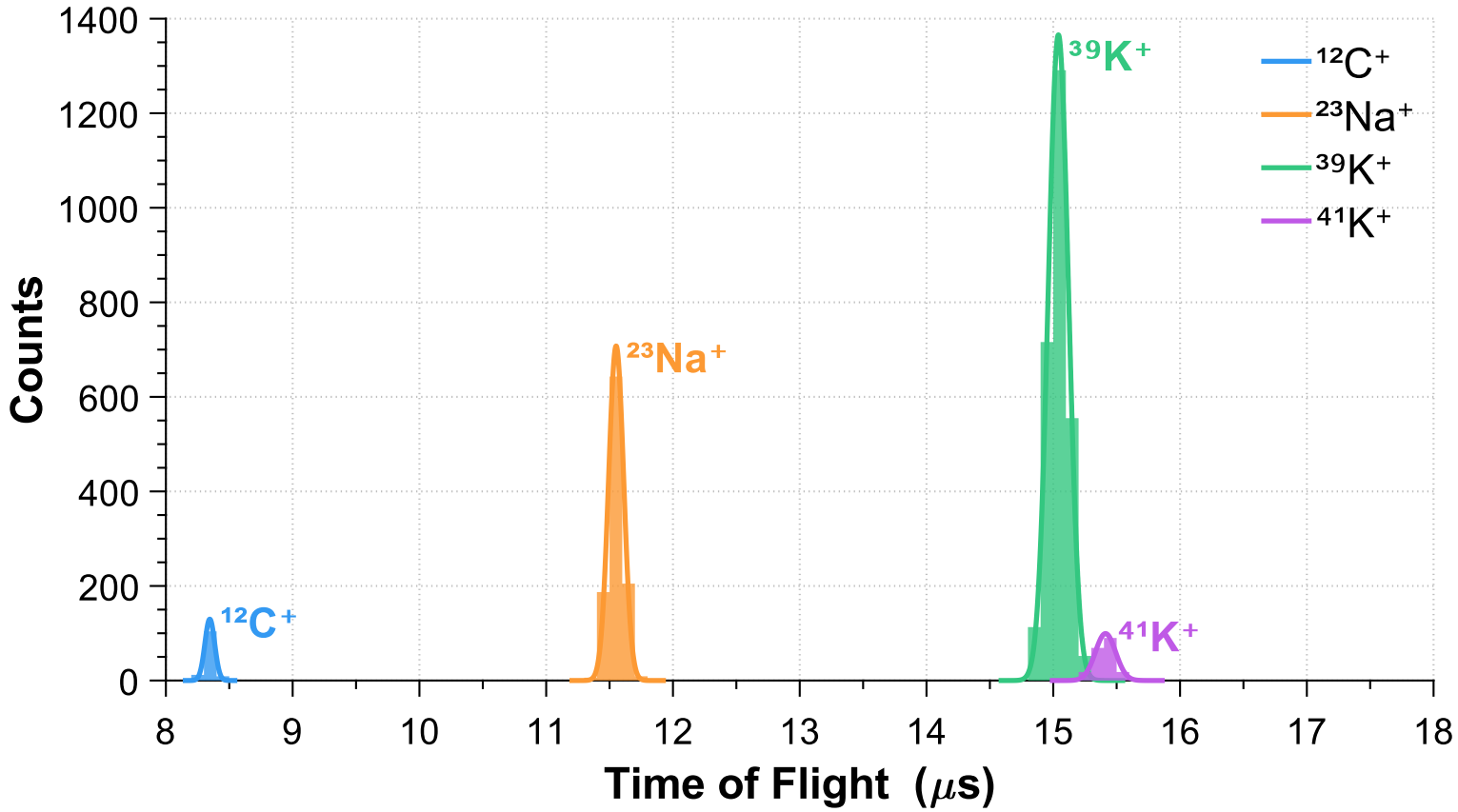


Fig 1 : The sample after drying and after laser desorption

Simulation

SIMION is used to simulate ion trajectories, experimental geometry and voltages were reproduced, along with the expected ions.

The time of arrival is the key takeaway



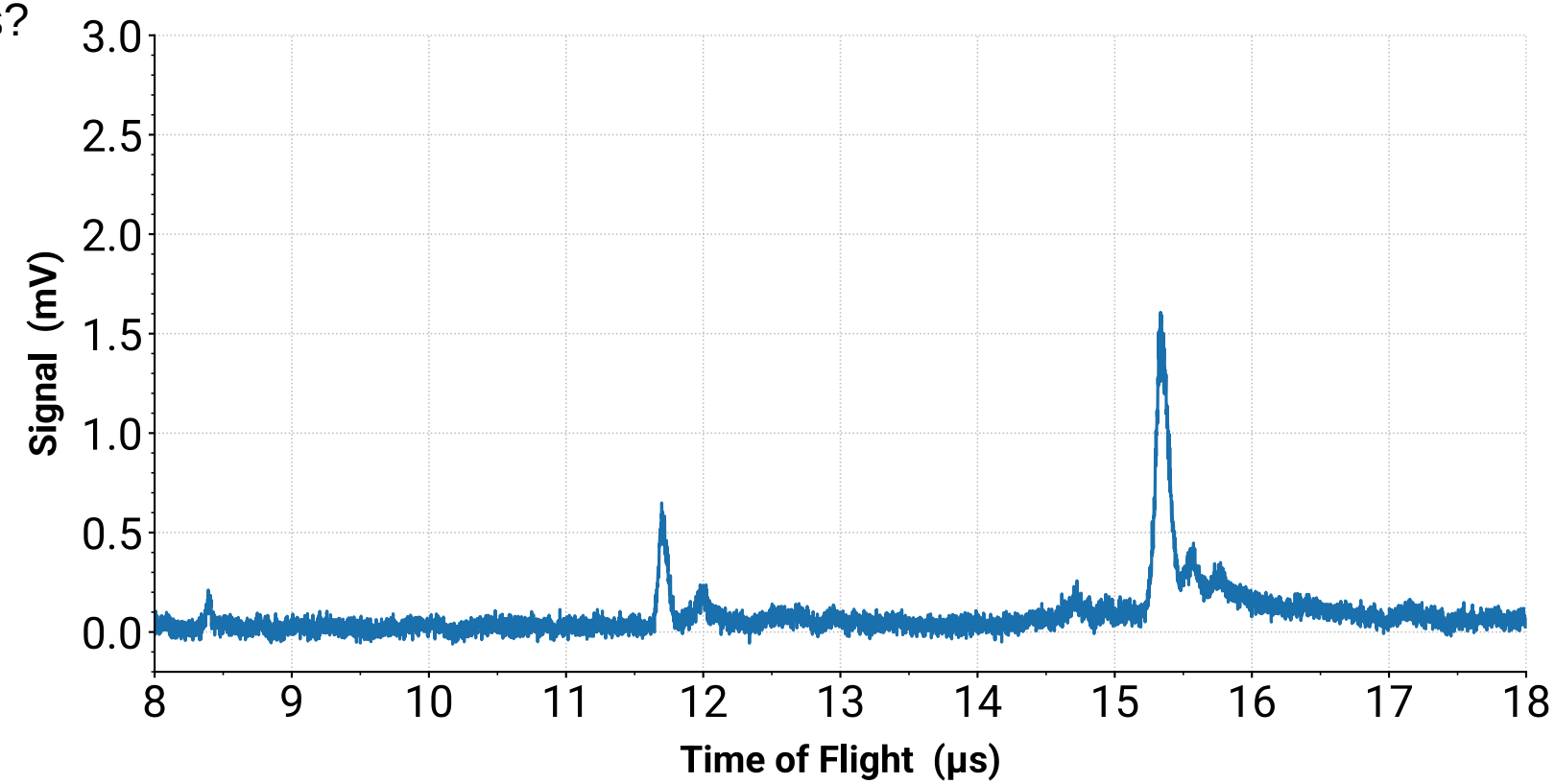
Jean.el-khoueiry@subatech.in2p3.fr

Time Of Flight spectrum

Remember the simulation results?

- ^{12}C at 8,3µs
- ^{23}Na at 11,6µs
- ^{39}K at 15,1µs
- ^{41}K at 15,4µs

- Good agreement with simulations
- Offset due to experimental conditions: initial kinetic energy, space charge effects

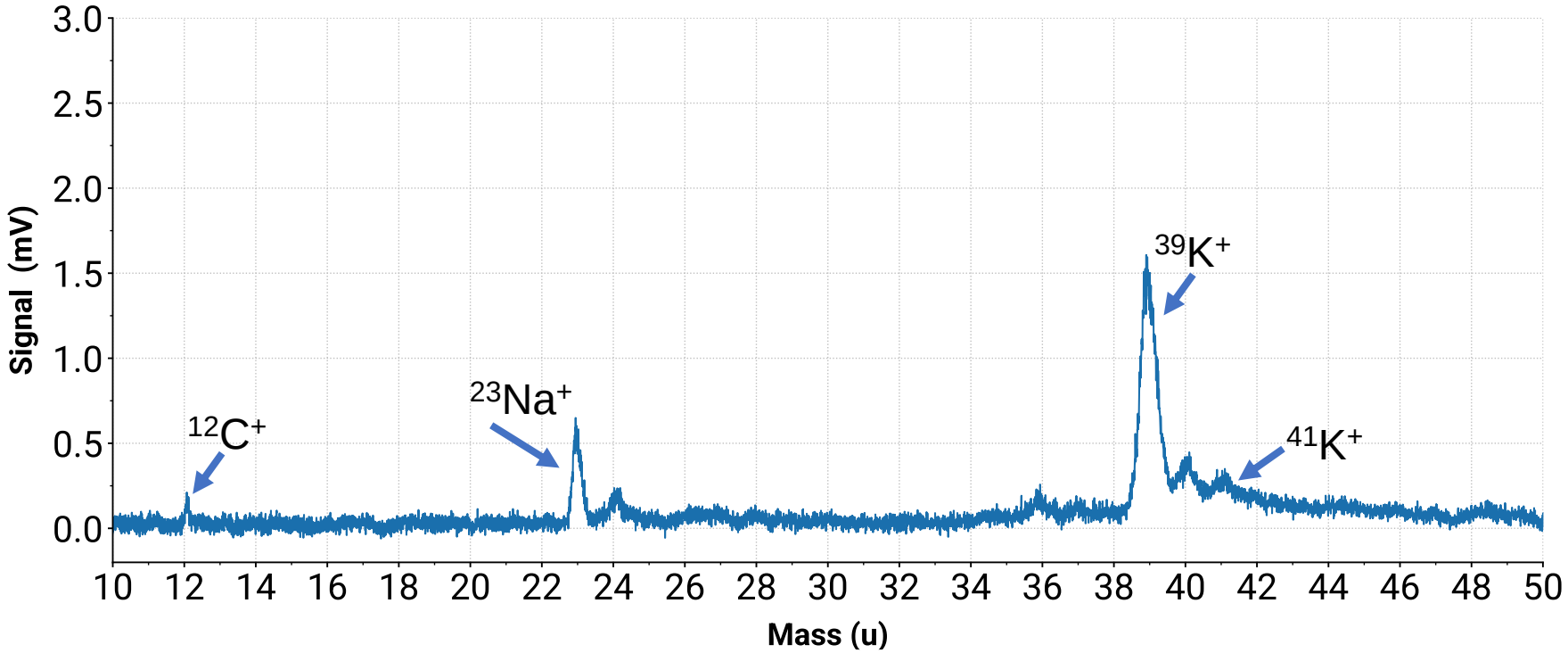


Jean.el-khoueiry@subatech.in2p3.fr

From time to mass

To go from a time to a mass spectra, calibration has to be done, theoretically and/or experimentally
Experimentally “Marker” elements are used

$$TOF = A\sqrt{m}$$

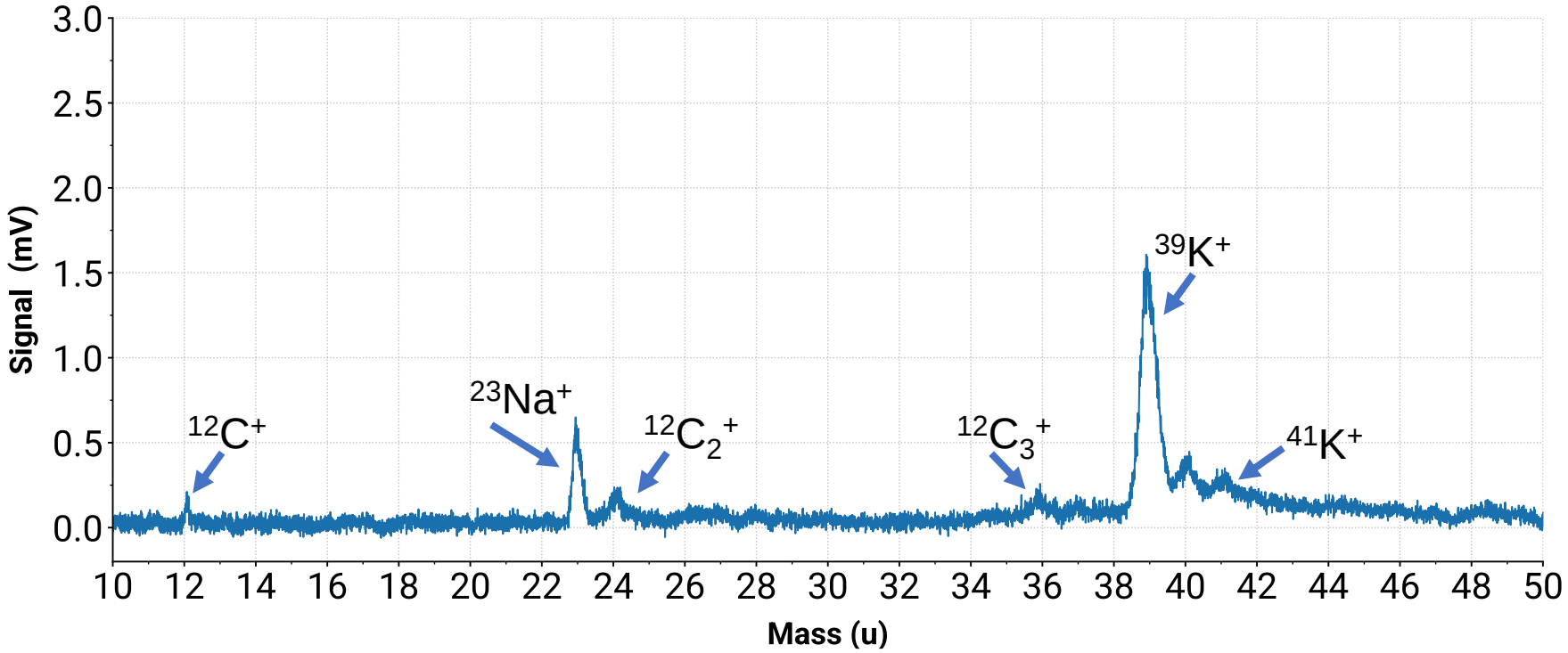


Jean.el-khoueiry@subatech.in2p3.fr

From time to mass

To go from a time to a mass spectra, calibration has to be done, theoretically and/or experimentally
Experimentally “Marker” elements are used

$$TOF = A\sqrt{m}$$

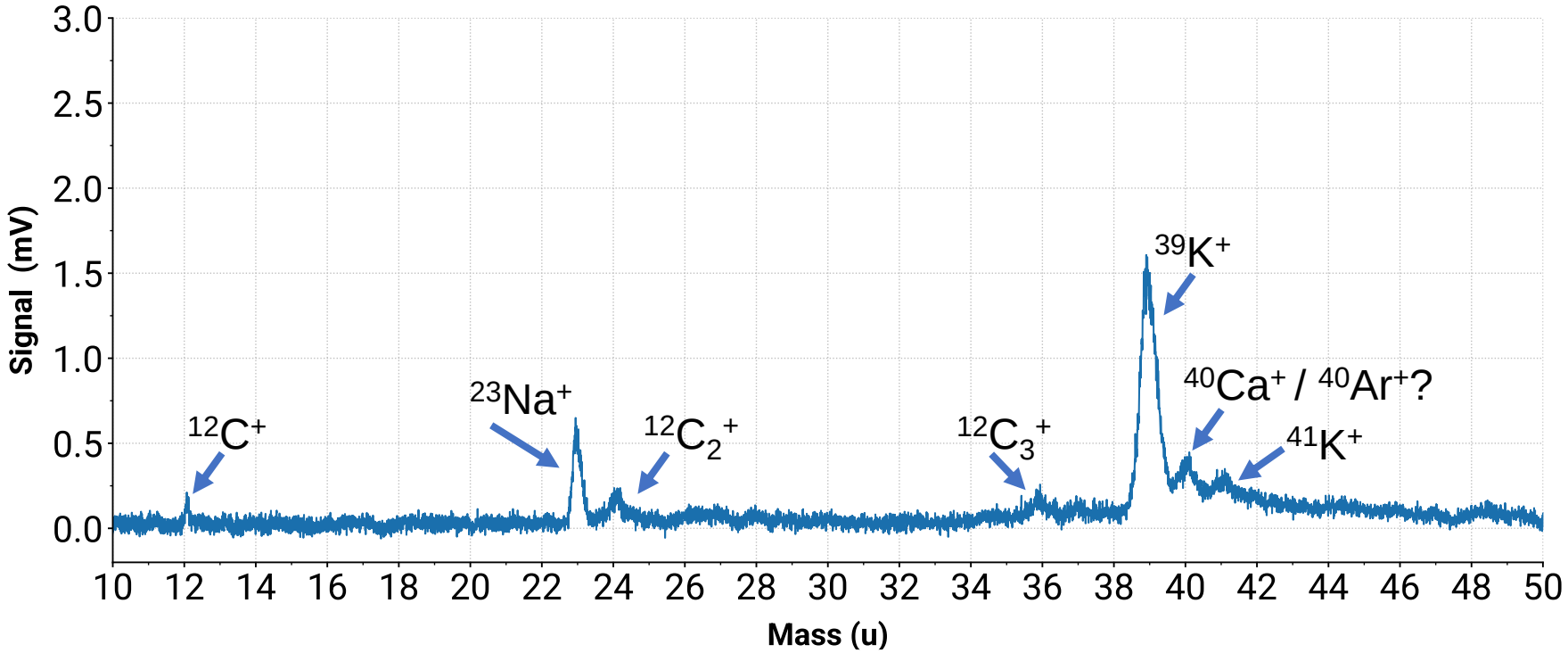


Jean.el-khoueiry@subatech.in2p3.fr

From time to mass

To go from a time to a mass spectra, calibration has to be done, theoretically and/or experimentally
Experimentally “Marker” elements are used

$$TOF = A\sqrt{m}$$

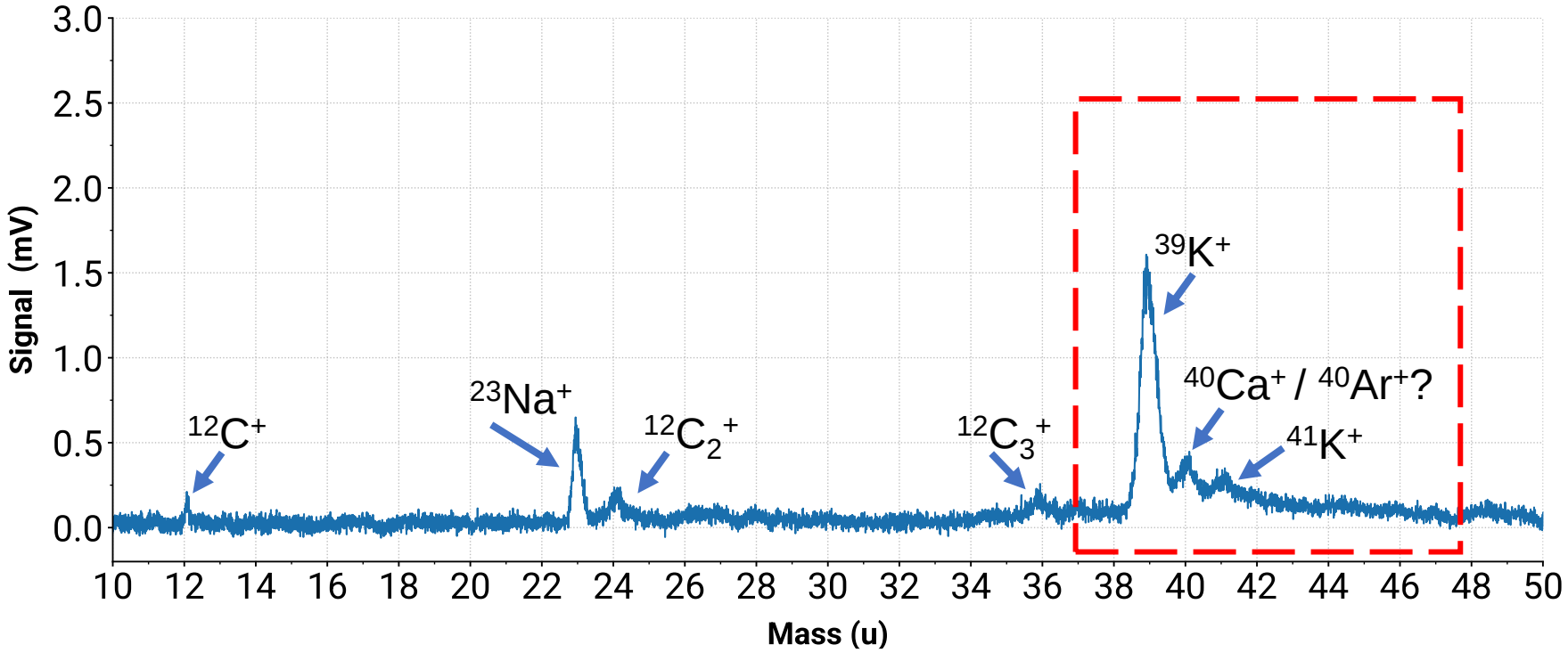


Jean.el-khoueiry@subatech.in2p3.fr

From time to mass

To go from a time to a mass spectra, calibration has to be done, theoretically and/or experimentally
Experimentally “Marker” elements are used

$$TOF = A\sqrt{m}$$



Jean.el-khoueiry@subatech.in2p3.fr

Isotopic ratio of potassium

One of the goals of this experiment is to measure the isotopic ratio of potassium.

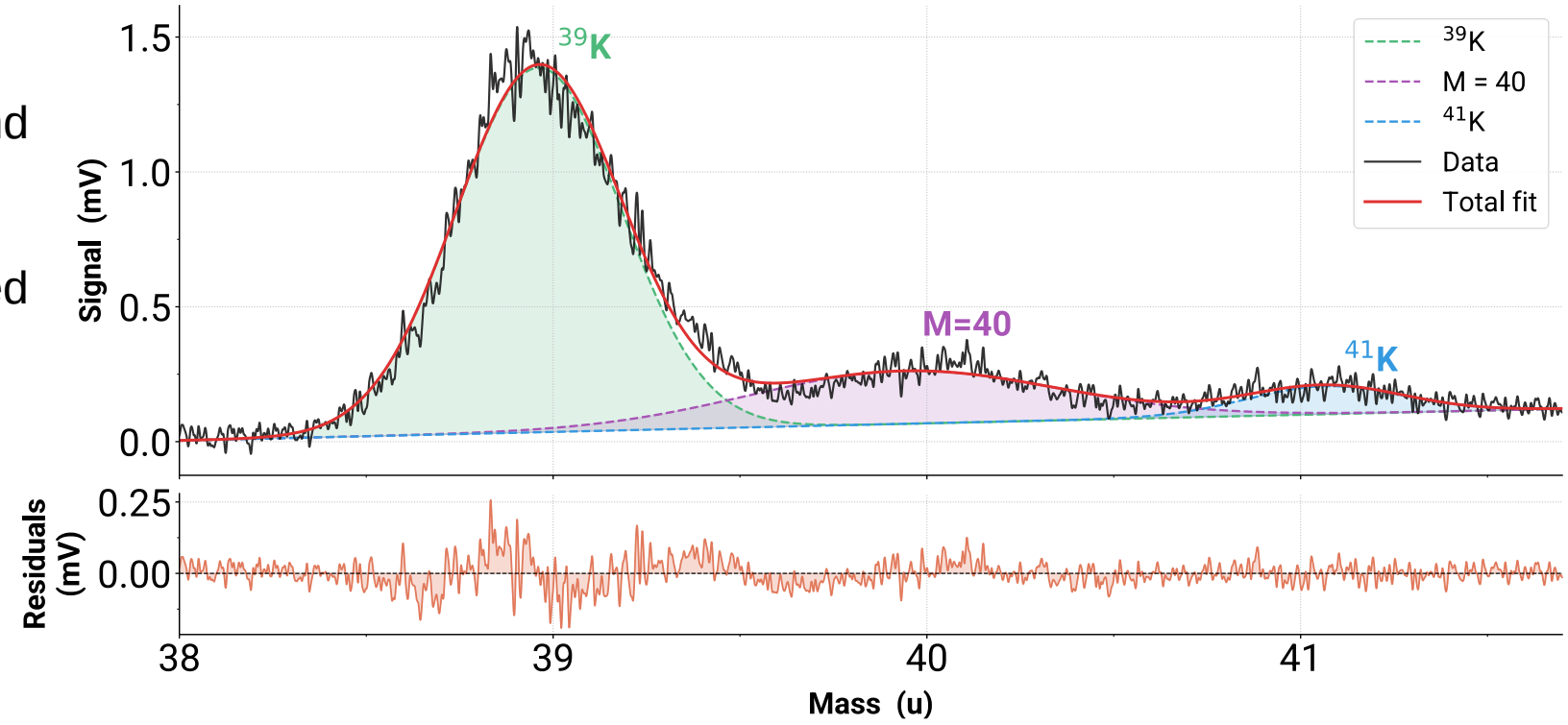
Isotope	Natural Abundance
^{39}K	93,26%
^{41}K	6,73%

For 100 spectra measured

The areas under the ^{39}K and ^{40}K were found

The abundance is calculated by:

$$\mathcal{A}(^{39}\mathrm{K}) = \frac{\mathcal{S}_{39}}{\mathcal{S}_{39} + \mathcal{S}_{41}}$$



Jean.el-khoueiry@subatech.in2p3.fr

Isotopic ratio of potassium

One of the goals of this experiment is to measure the isotopic ratio of potassium.

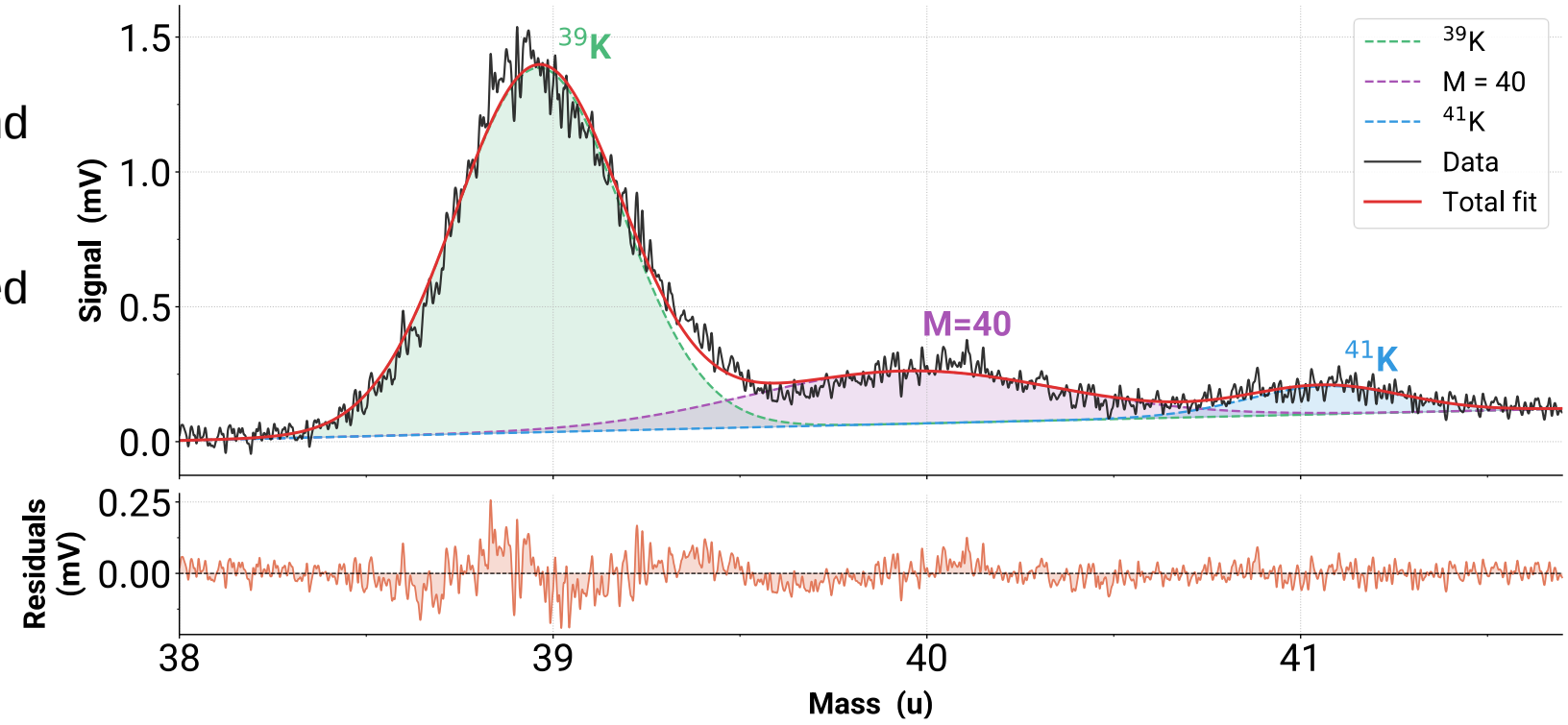
Isotope	Natural Abundance	Experimental Result
^{39}K	93,26%	93,15±0,37%
^{41}K	6,73%	6,85±0,13%

For 100 spectra measured

The areas under the ^{39}K and ^{40}K were found

The abundance is calculated by:

$$\mathcal{A}(^{39}\mathrm{K}) = \frac{\mathcal{S}_{39}}{\mathcal{S}_{39} + \mathcal{S}_{41}}$$



Jean.el-khoueiry@subatech.in2p3.fr

Next steps in SMILES

New Building

- We recently moved to a new building dedicated to SMILES

Implementing resonant ionization

New laser system

- With a collaboration with the LARISSA team at JGU Mainz.
- Four Titanium: Sapphire (Ti:Sa) laser cavities were set up.

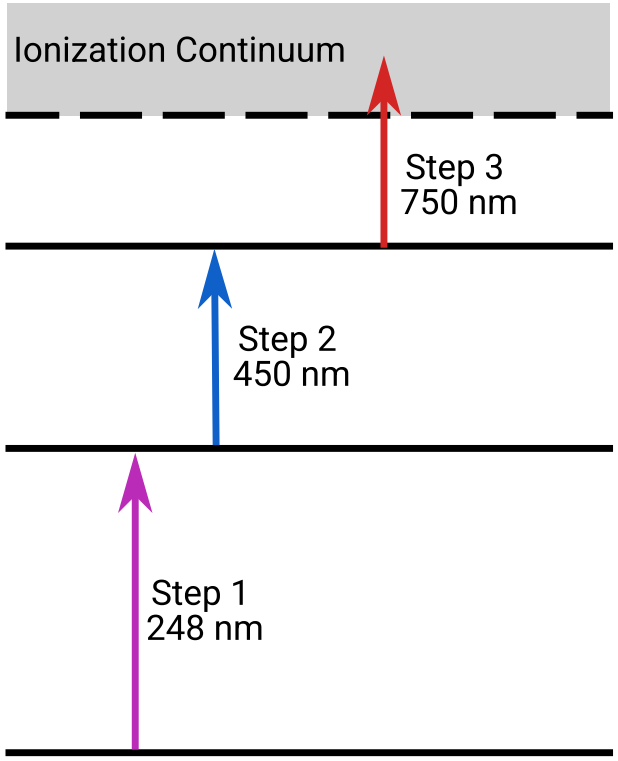
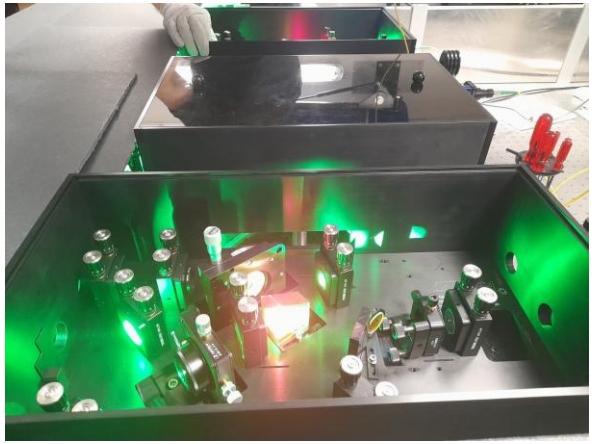


Fig 1 : Schematic of resonant Ionization of Copper



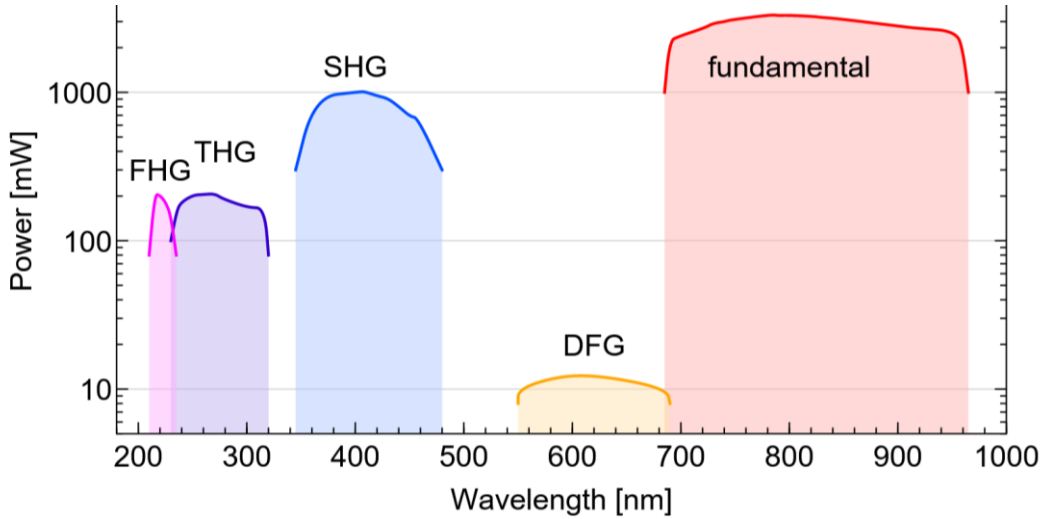
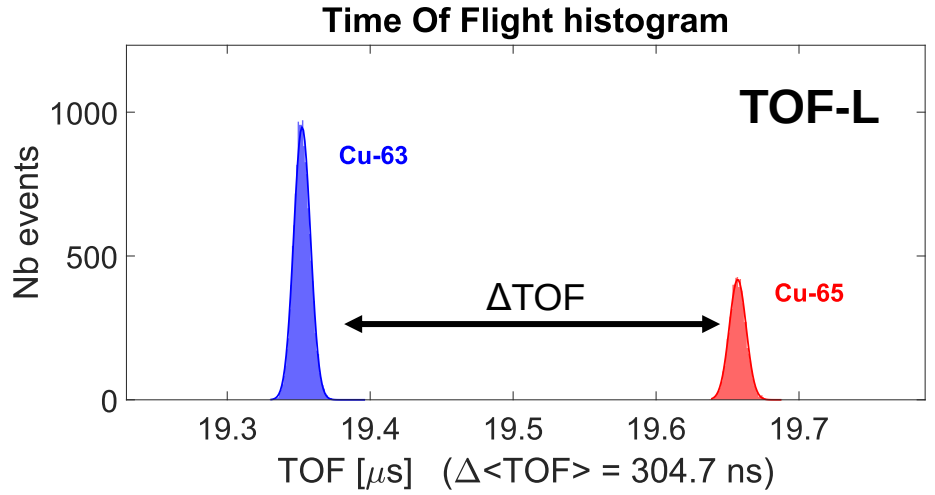


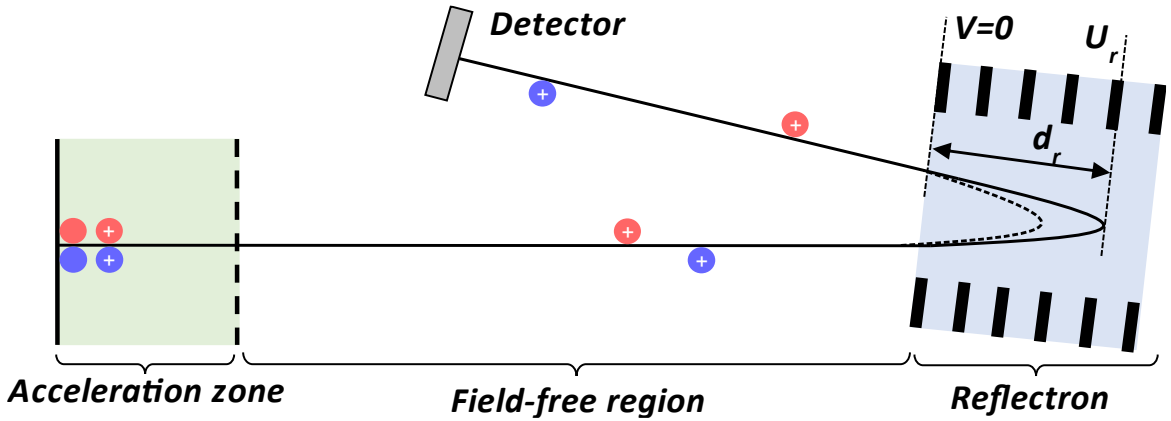
Fig 2 : Wavelengths accessible using TiSa lasers [1]

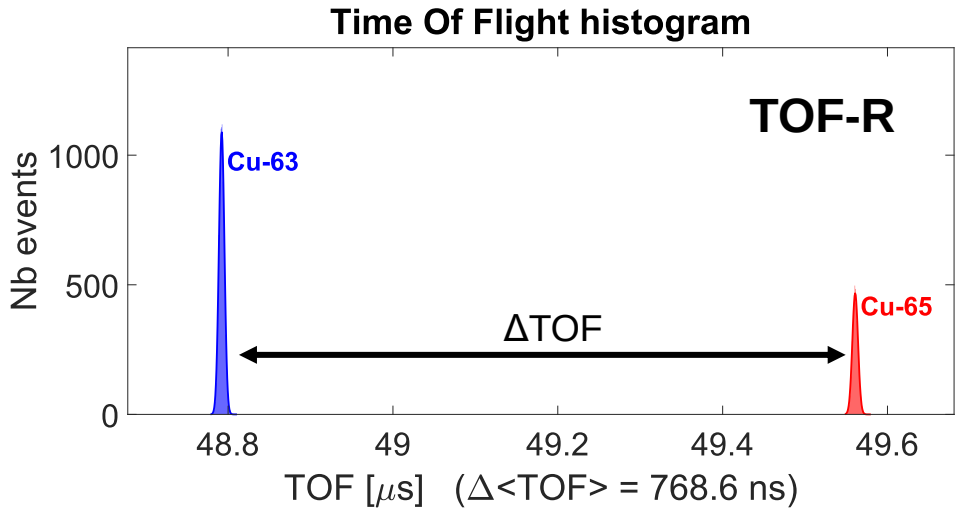
[1] T. Kron, « Pushing the limits of resonance ionization mass spectrometry - ionization efficiency in palladium and spectral resolution in technetium », 2017, doi: 10.25358/openscience-1713.

TOF-Reflectron

- A reflectron is an electrostatic mirror: successively increasing potential electrodes.
- Ions are slowed down then reflected. Compensating initial energy dispersion
- Longer drift region = better separation = better resolution







Jean.el-khoueiry@subatech.in2p3.fr

Conclusion

Conclusion and perspectives

- The initial Linear TOF configuration has been proven to work.
- Results show good correlation in terms of Time of Flight and isotopic ratios.
- The Ti:Sa cavities are in the process of being integrated.
- The Reflectron setup is in its development stage.
- Research for Cu and Ra are planned in the near future.

IMT Atlantique
Bretagne-Pays de la Loire
École Mines-Télécom

NUCLÉAIRE
& PARTICULES

Subatech

smiles

Thank you!

Special Thanks to the SMILES TEAM:

Theo Bigourdan, Arnaud Cadiou, Arnaud Guertin, Ferid Haddad, Keerthana Kamalakannan, Meriadeg Guillamet, Frederic Lefèvre, Antoine Maitrallain, Stéphane Martinez, Vincent Métivier, Nathalie Michel, Ahmad Mortada, Anne Piscitelli, Louis-Marie Rigalleau, Noel Servagent.

As well as the different departments of SUBATECH and IMT Atlantique.

PRISMA
Physics of Radiation InteractionS with Matter and Applications

Appendix – Simulation vs Experimental

Element	$TOF_{simulation}$	$TOF_{experimental}$	Δ
^{12}C	8,34	8,46	0,12
^{23}Na	11,54	11,77	0,23
^{39}K	15,05	15,42	0,37
^{41}K	15,41	15,85	0,44

Many reasons can lead to this increasing difference with the mass:

1. Initial kinetic energy of the neutral plume
2. Space charge effects
3. Disruptions in electric fields

$$TOF \propto \sqrt{\frac{m}{qV}}$$

Appendix - Ablation threshold

Definition

- The ablation threshold is the minimum laser fluence required to eject material from the sample surface.
- Measured threshold for our NaCl/KCl on graphite sample: 0.52 J/cm²

Experimental significance

- Below threshold: laser energy heats the surface only, no material ejected → no signal.
- Above threshold: atoms and clusters desorb as a neutral plume → available for post-ionization.
- Far from threshold unwanted ions are created hindering resolution
- Operating fluence: 0.52 J/cm² (pulse energy 20 µJ, beam diameter ~70 µm)

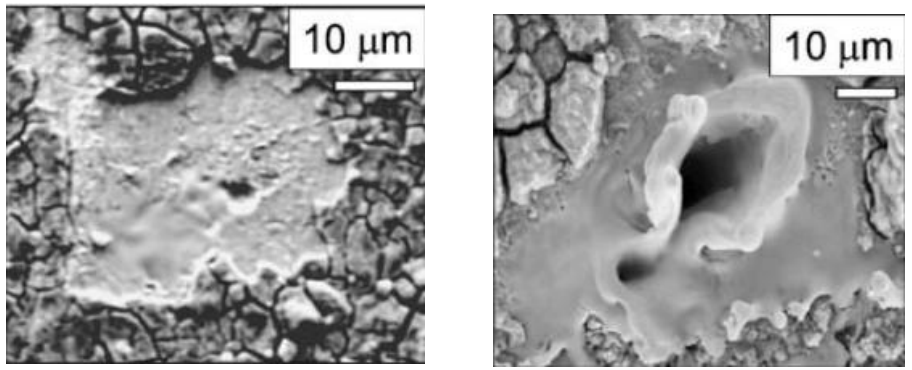


Fig 1: Topology of a gadolinium sample after 100 laser hits at different fluences [2]

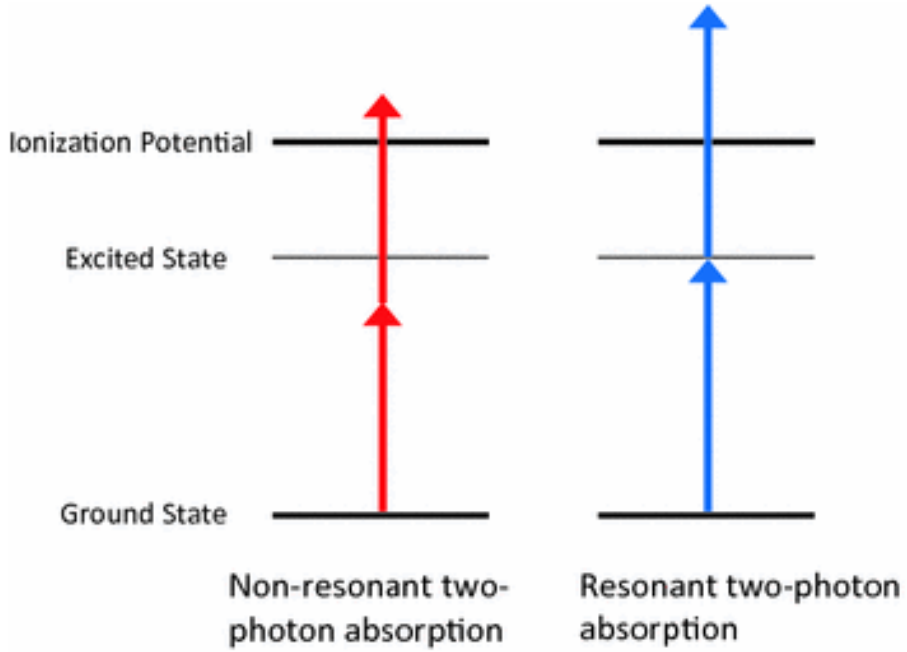
Appendix - resonant vs non resonant ionization

Non-resonant post-ionization (current setup)

Uses 266 nm photons (4.66 eV each) multi-photon absorption to exceed ionization energy.
Can ionizes elements in the plume (non-selective).
532 and 1064nm can also contribute to multi-photon ionization
Laser intensity formula: $I = \frac{E}{A * \tau}$ must be high enough for multi-photon process.

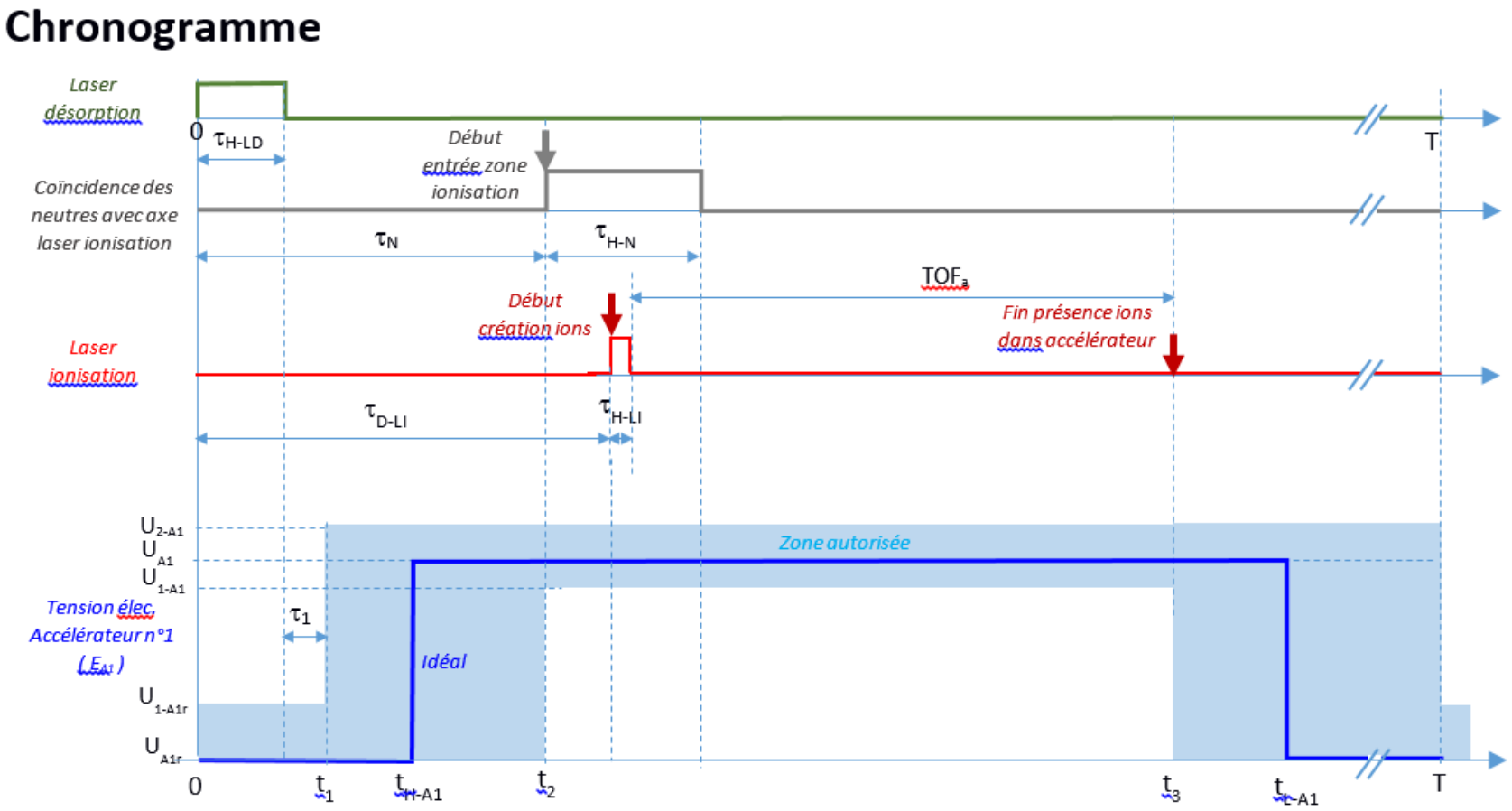
Resonant laser ionization (next step)

Uses sequential photon absorption through real atomic energy levels specific to one element.
Only the target element is excited and ionized isobars are suppressed by orders of magnitude.
Requires tunable lasers (Ti:Sa) matched to the target element's electronic transitions.



Appendix - Timings + Eliminating unwanted ions

- Ions created by the desorption are hindering the resolution of the setup,
- A voltage switch is put in place and modulated in order to be reflective during the process of desorption and the flight of the neutral atoms and to be acceleration just before the ionization process



Appendix - Sample specifications

- The sample consists of many droplets of a NaCl and KCl solution.
- 5% of mass in Na and 2,5% of mass in K , in a total of 100µl of solution
- The droplet deposition showed better stability in measurements : stable ion signal

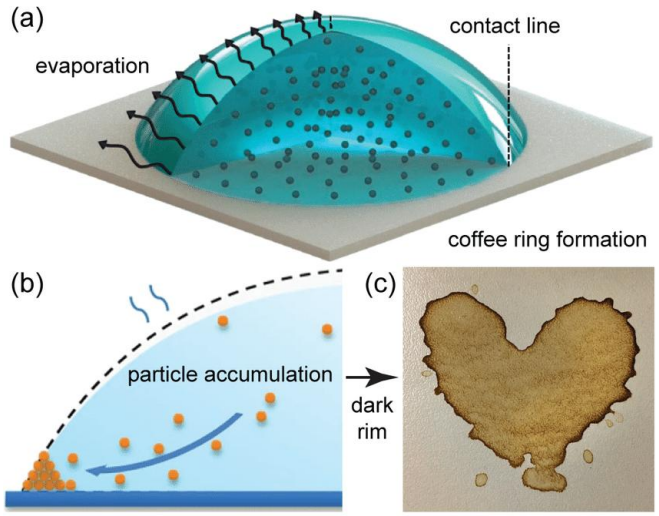


Fig 2: The Coffee ring effect : (a) evaporating droplet (b) accumulation of particles ©heart shaped coffee ring [1]

Fig 1: Two types of deposition: (a) one big drop (b) multiple smaller drops

Evaporation is stronger on the edges, internal flux heading outwards to compensate
This leads to more material accumulating on the edges

[1] Mathijssen, Arnold & Lisicki, Maciej & Prakash, Vivek & Mossige, Endre. (2022). Culinary fluid mechanics and other currents in food science. 10.48550/arXiv.2201.12128.

Appendix - Ti:Sa Laser

- The active medium is a solid sapphire crystal doped with Titanium ($Ti3^{+}:Al_2O_3$)

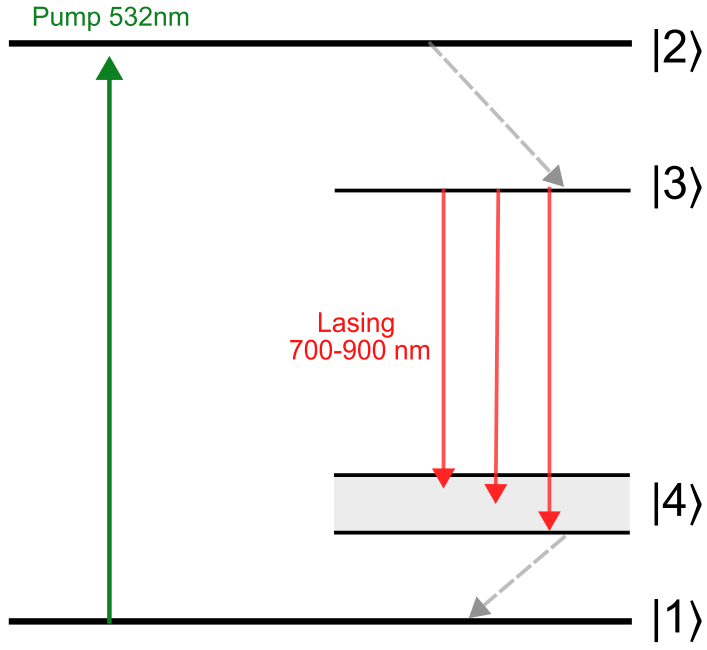
Why the broad emission spectrum?

Broad electronic energy levels → broad absorption and emission bands.

4-level laser scheme

Wavelength extension via non-linear crystals

SHG (÷2) and THG (÷3) extend coverage to 230-450 nm reaching UV transitions of many elements.



Appendix - Magnetof vs other types of detectors

- **Magnetof used in our setup**
- Micro-channel plate (MCP) detector combined with a permanent magnetic field that focuses secondary electrons onto the impact plate.
- Advantages: very fast timing resolution (<1 ns), high detection efficiency, compact, suitable for TOF mass spectrometry.

- **Standard MCP** Similar timing performance but lower detection efficiency at high ion energies, easily saturated.