INL/CON-24-81369-Revision-0

Virtual Slit Cycloidal Mass Spectrometry for Isotopic Measurements of Actinide Particles

October 2024

Changing the World's Energy Future

Rafael Bento Serpa

Idaho National Laboratory

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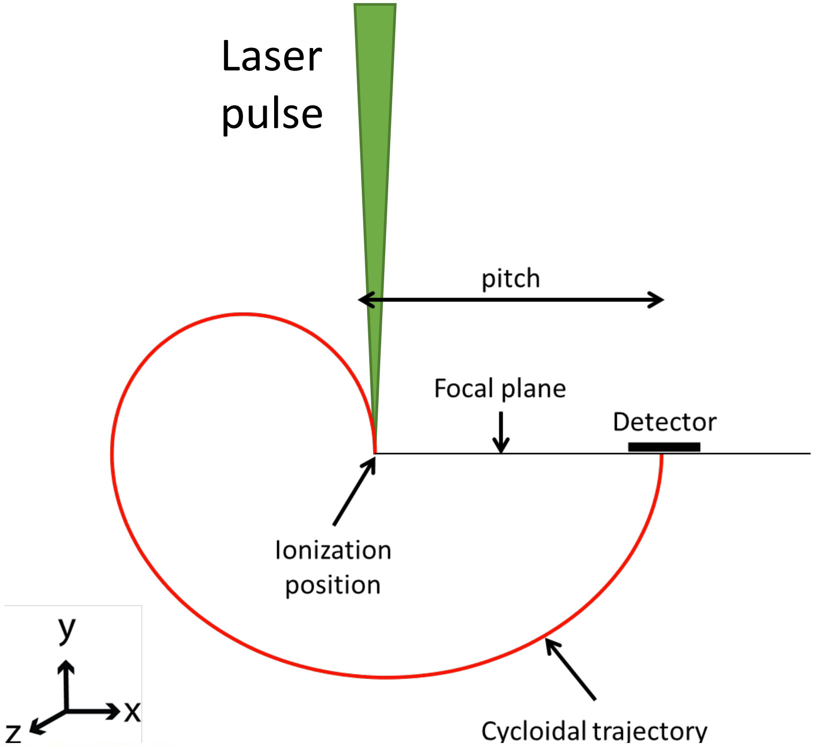
Virtual Slit Cycloidal Mass Spectrometry for Isotopic Measurements of Actinide Particles



Rafael Bento Serpa

SciX 2024
Session ID: 24MASS05
Session: Novel Instrumentation, Analysis Tools, and Chemistry in Mass Spectrometry
Session Date: Wednesday October 23, 2024
Session Time: 10:30 AM - 12:10 PM
Presentation: Virtual Slit Cycloidal Mass Spectrometry for Isotopic Measurements of Actinide Particles
Presentation Time: 11:50 AM - 12:10 PM
Presentation Number: MASS-05.5

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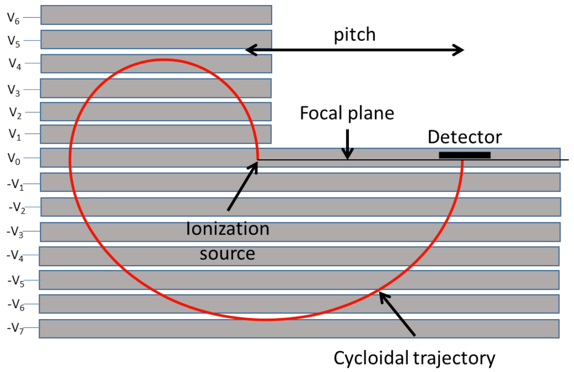
Savannah River National Laboratory

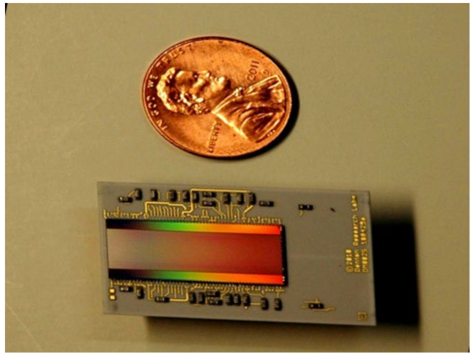
What is VS-CMS?

- The ***Virtual Slit Cycloidal Mass Spectrometer*** is a unique instrument for ***analysis of particles*** with **mass spectrometry.** It combines the unique properties of the **cycloidal mass analyzer** with **capacitive transimpedance amplifier array detectors** to make a portable instrument potentially capable of high sensitivity measurements on single particles, including ***high precision isotope ratios***.

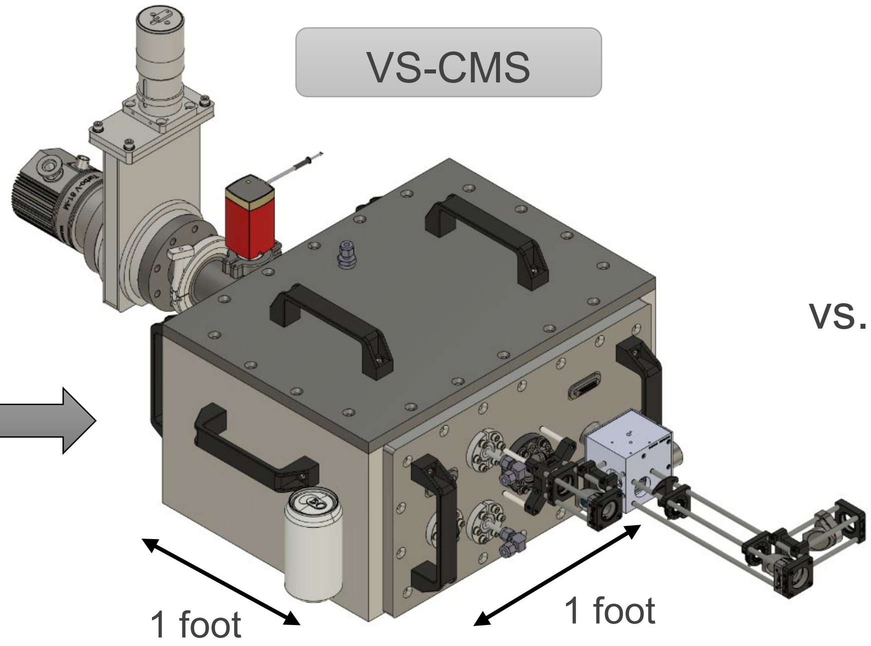
Cycloidal mass analyzer



Ion array detector

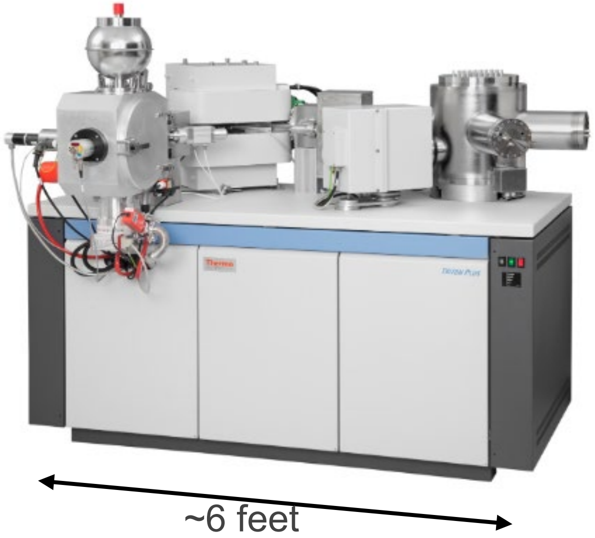


VS-CMS



vs.

Current State of the Art: Thermal Ionization Mass Spec



VS-CMS could result in a small high-performance instrument with improved capabilities over the large and expensive current state of the art for single particle analysis and be revolutionary for nuclear nonproliferation efforts.

ISOTOPIC ANALYSIS OF SINGLE PARTICLES (1-10 μm)

Limitations:

- Extensive sample preparation
  - Requires a nuclear reactor
- Low throughput
  - Only 1-2 particles analyzed per day
  - 6+ months between field collection and analysis
- Large size, weight, power, and cost
  - For isotopic precision

Field sample collection

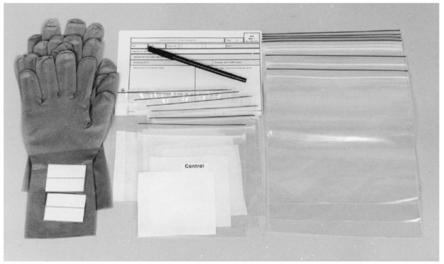
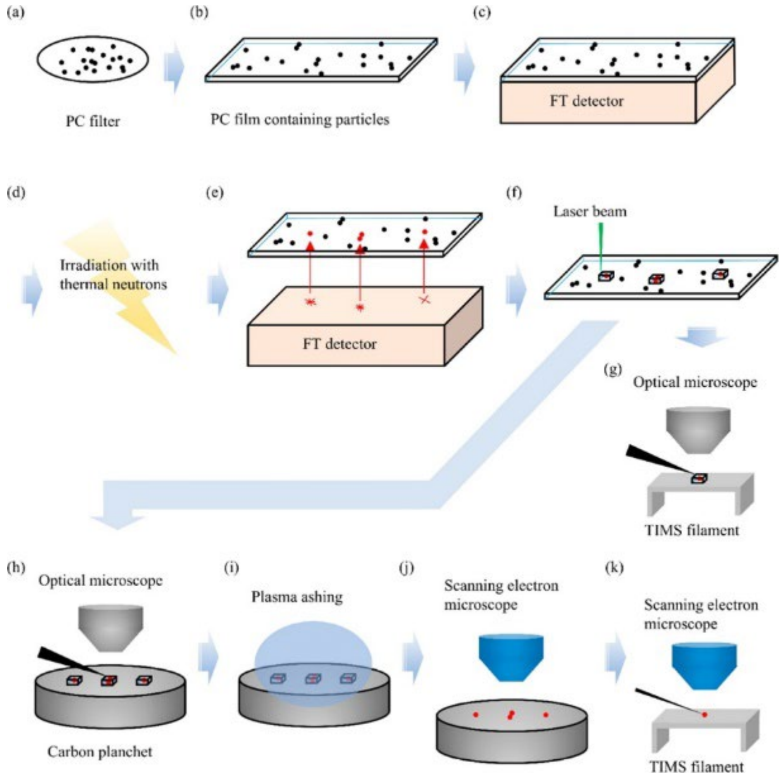


Fig. 1. IAEA cotton swipe sampling kit.

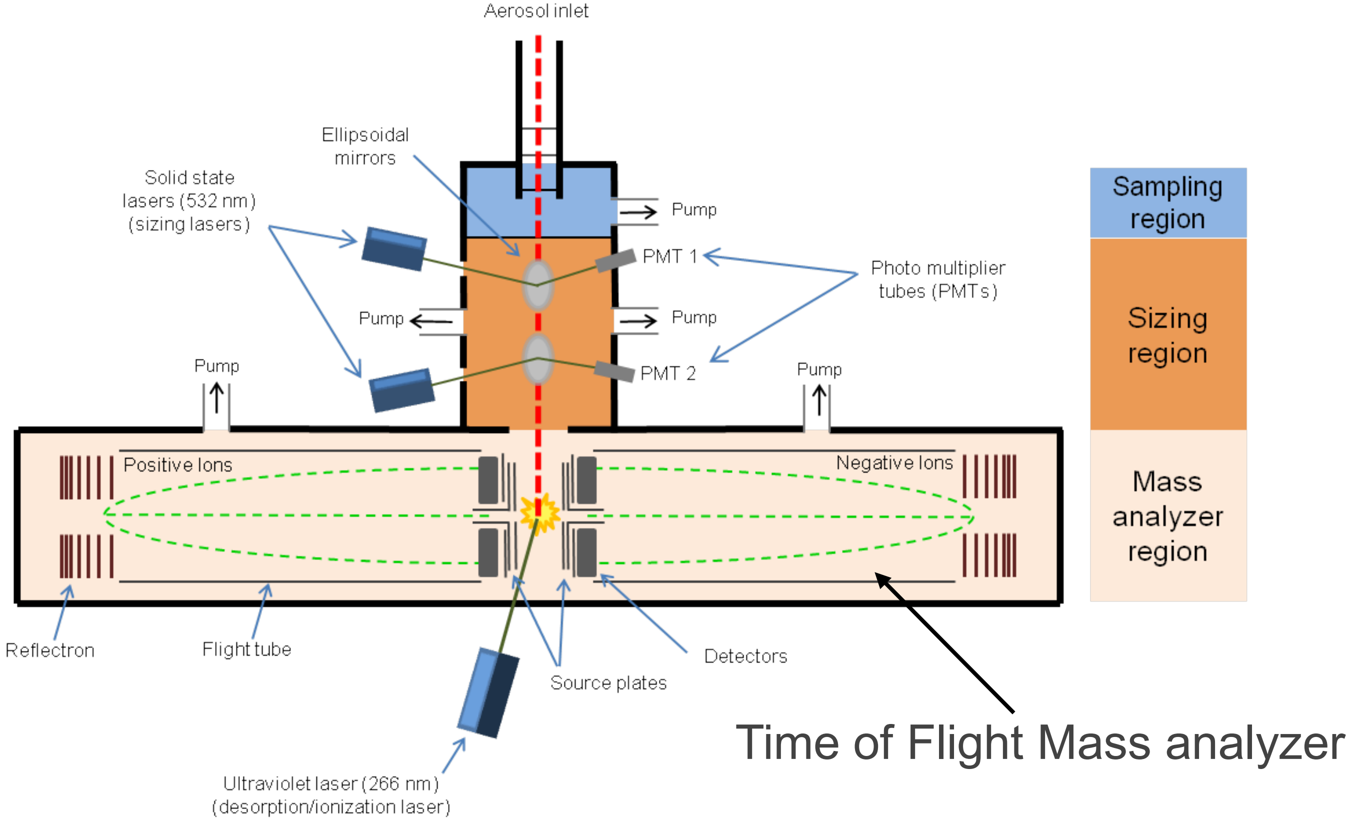
Extensive sample preparation



Large thermo-ionization mass spectrometer

Other Approaches to Single Particle Mass Spectrometry

Schematic and Picture of SPAMS
(single particle aerosol mass spec)



By Benjamin Haywood - Own work, CC BY-SA 4.0, https://commons.wikimedia.org/w/index.php?curid=39073594

Frank M, et al., Single-Particle Aerosol Mass Spectrometry (SPAMS) for High-Throughput and Rapid Analysis of Biological Aerosols and Single Cells. Rapid Characterization of Microorganisms by Mass Spectrometry: American Chemical Society; 2011. p. 161-96. doi:10.1021/bk-2011-1065.ch010

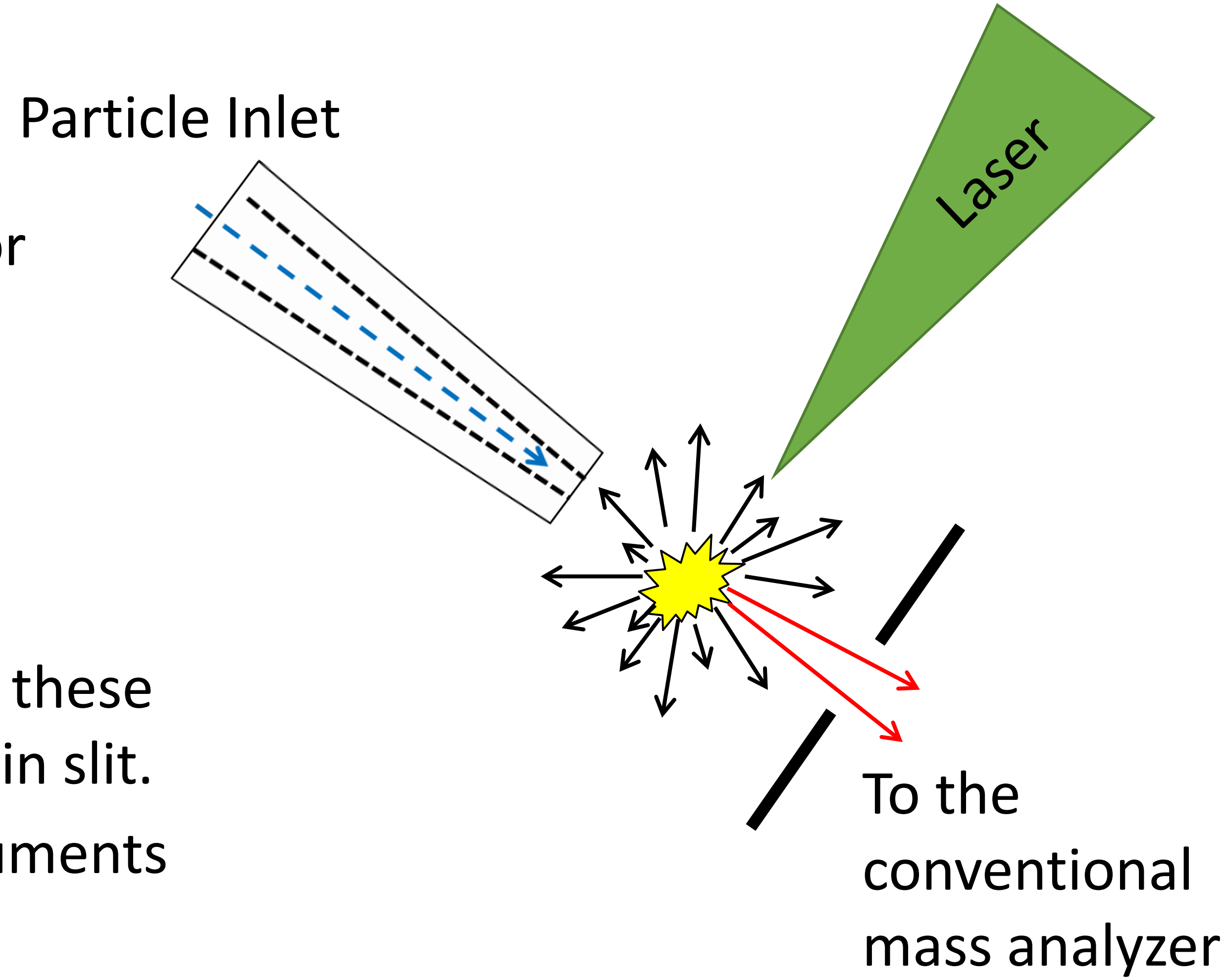
Single particle aerosol mass spectrometer
- Time of flight mass analyzer
- Aerosol inlet
- Particle sizer/selector

Advantages:
- No sample preparation
- Fast

Limitations:
- Large size, weight, power, and cost

Not appropriate for isotope ratio analysis of particles due to:
- Sensitivity and dynamic range of the detectors

- Ideal solution:
  - Particle Inlet +
  - Laser Ionization +
  - Portable high resolution multi-collector magnetic sector mass spectrometer
- Problem:
  - Laser ionization generates ions with a widespread in energy and direction.
  - Traditional instruments cannot handle these characteristics without first use of a thin slit.
  - High energy dispersion requires instruments with a long ion path.



Solution – Virtual Slit Cycloidal Mass Spectrometer (VS-CMS)

Solutions to the equations of motion for an ion in perpendicular electric and magnetic fields

- $x(t) = \frac{E}{B}t + \frac{v_{y0}}{\Omega}\cos(\Omega t) + \frac{1}{\Omega}\left(v_{x0} - \frac{E}{B}\right)\sin(\Omega t) - \frac{v_{y0}}{\Omega} + x_{oi}$
- $y(t) = \frac{1}{\Omega}\left(\frac{E}{B} - v_{x0}\right)\cos(\Omega t) + \frac{v_{y0}}{\Omega}\sin(\Omega t) - \frac{E}{B\Omega} + \frac{v_{x0}}{\Omega} + y_{oi}$
- $z(t) = v_{z0}t + z_{oi},\ \Omega = \frac{qB}{m}$

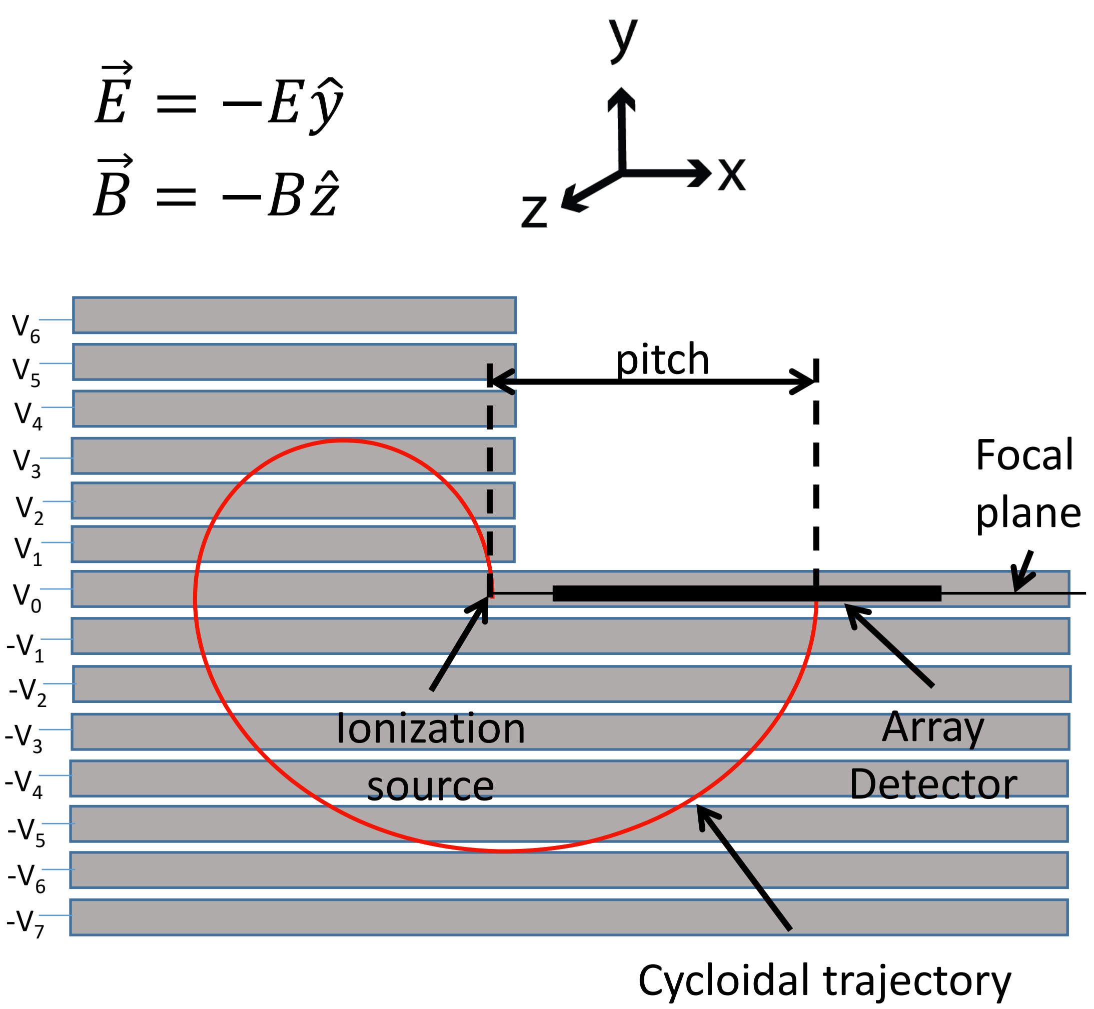
- At $t = \frac{2\pi m}{qB}$ (time for a full cycloidal trajectory)
- $y(t) = y_{oi}$

$$\text{pitch} = a = x(t) = \frac{m}{q}\frac{2\pi E}{B^2} + x_{oi}$$

The focusing does not depend on the initial velocity vector!

$\vec{E} = -E\hat{y}$

$\vec{B} = -B\hat{z}$



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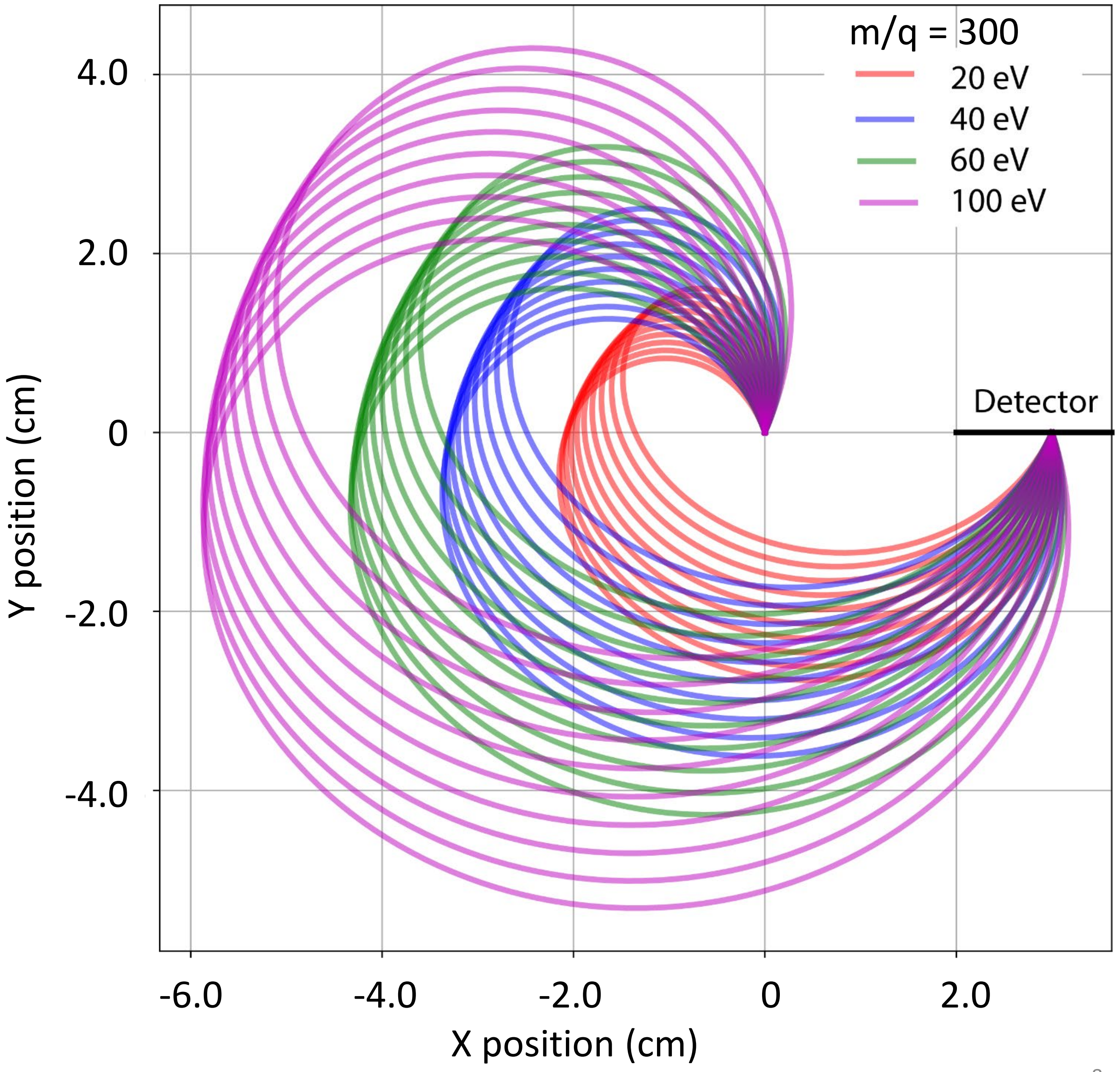
Solution – Virtual Slit Cycloidal Mass Spectrometer (VS-CMS)

- Solution for the cycloidal equation of motion to four values for energies and ten different directions.

- m/q = 300
- B = 0.7 T
- E = 7.52 V/cm

- Small footprint mass analyzer!
  - > 10 cm X 10 cm

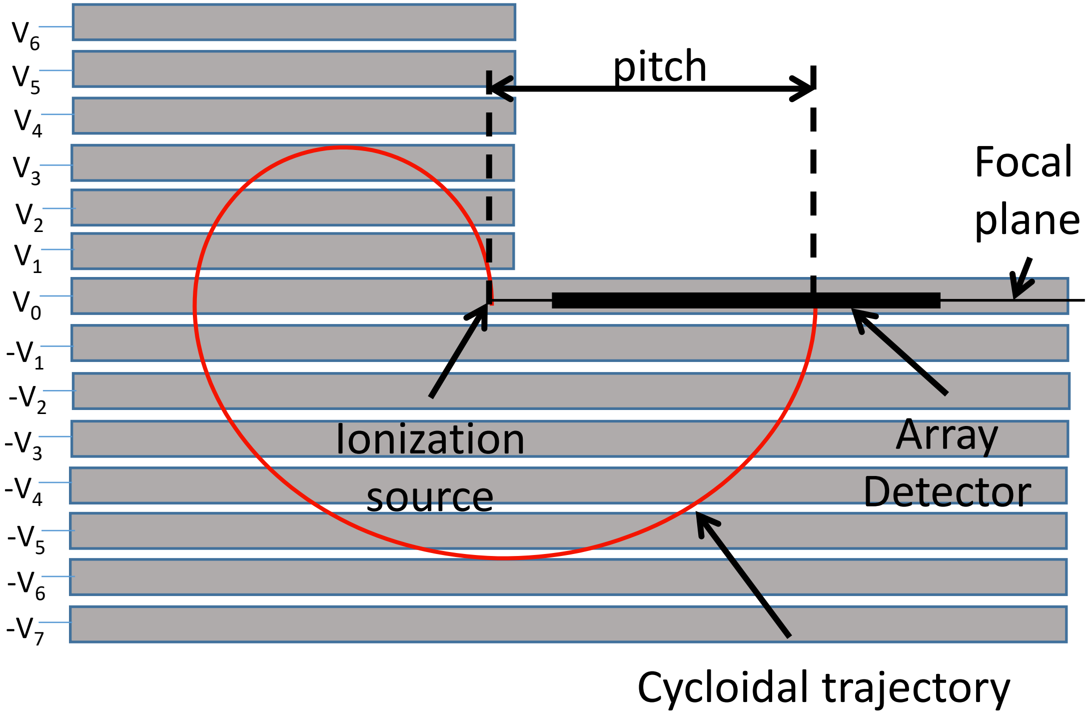
- The area of the cycloidal trajectories increases with the ion energy



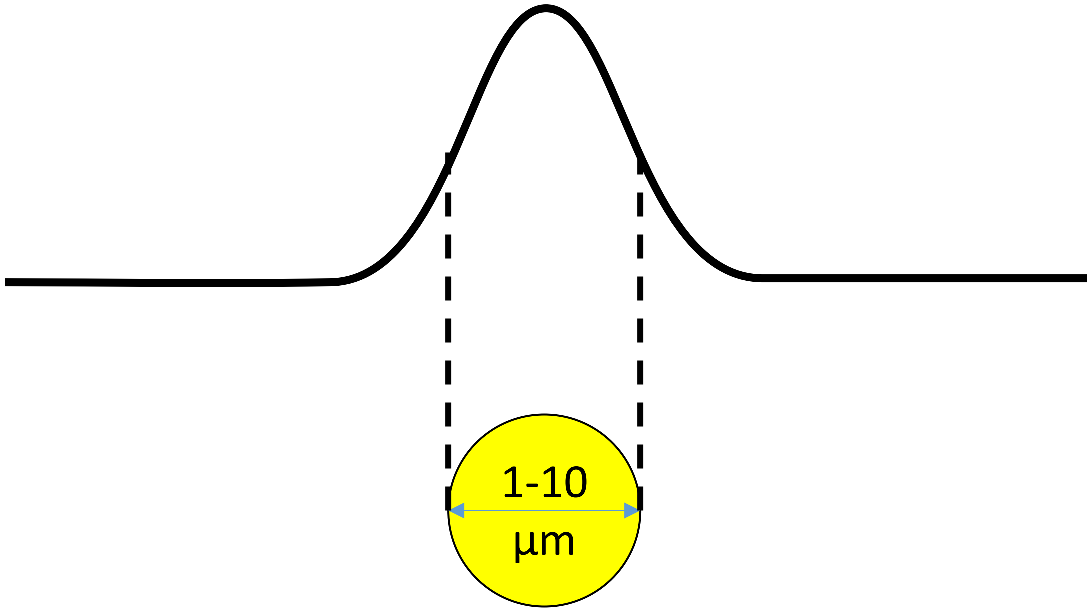
Solution – Virtual Slit Cycloidal Mass Spectrometer (VS-CMS)

- Pitch equation

$$pitch = a = x(t) = \frac{\boldsymbol{m}}{\boldsymbol{q}}\frac{2\pi E}{B^2} + x_{oi}$$



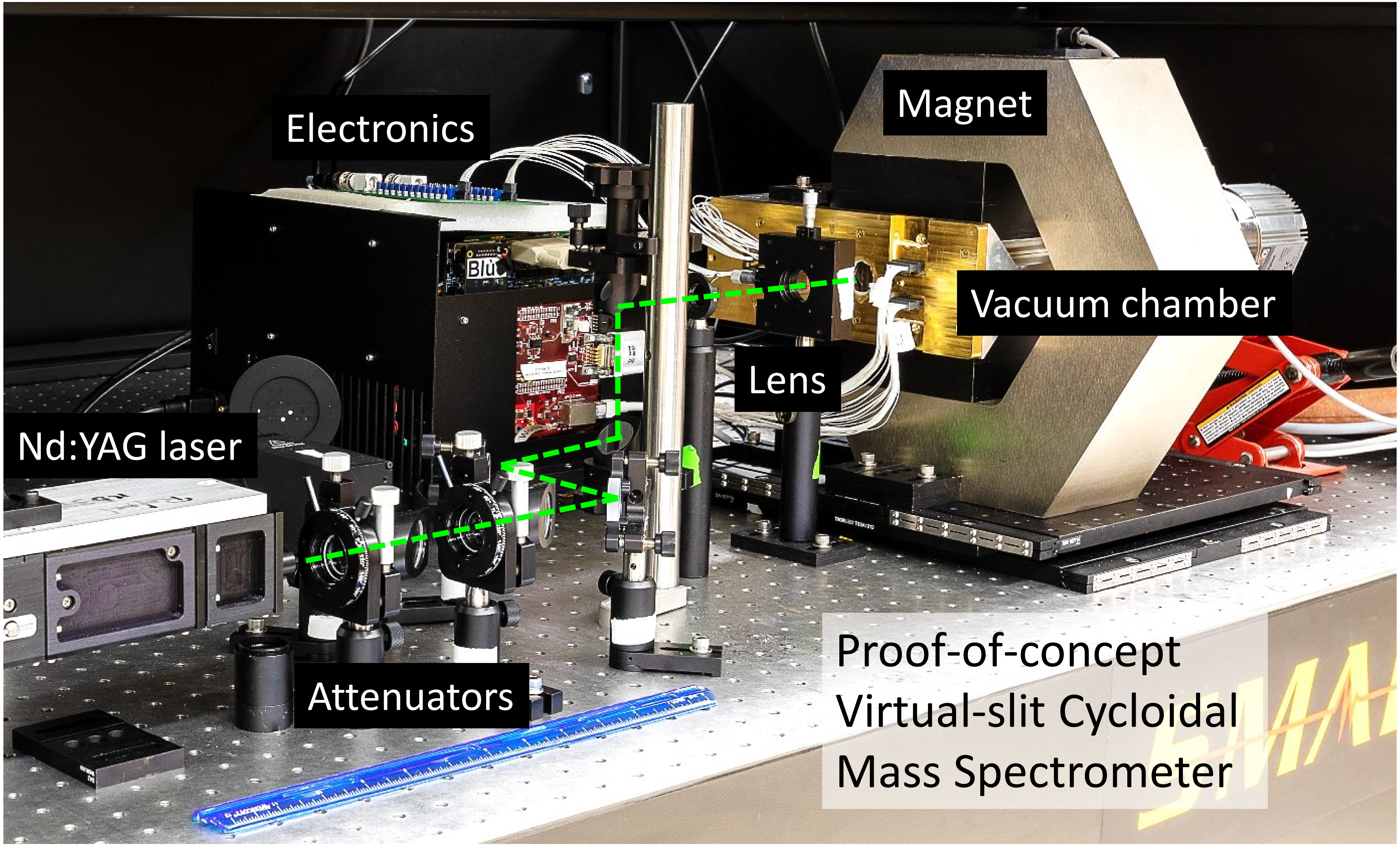
If the source of ions is a 1-10 µm particle



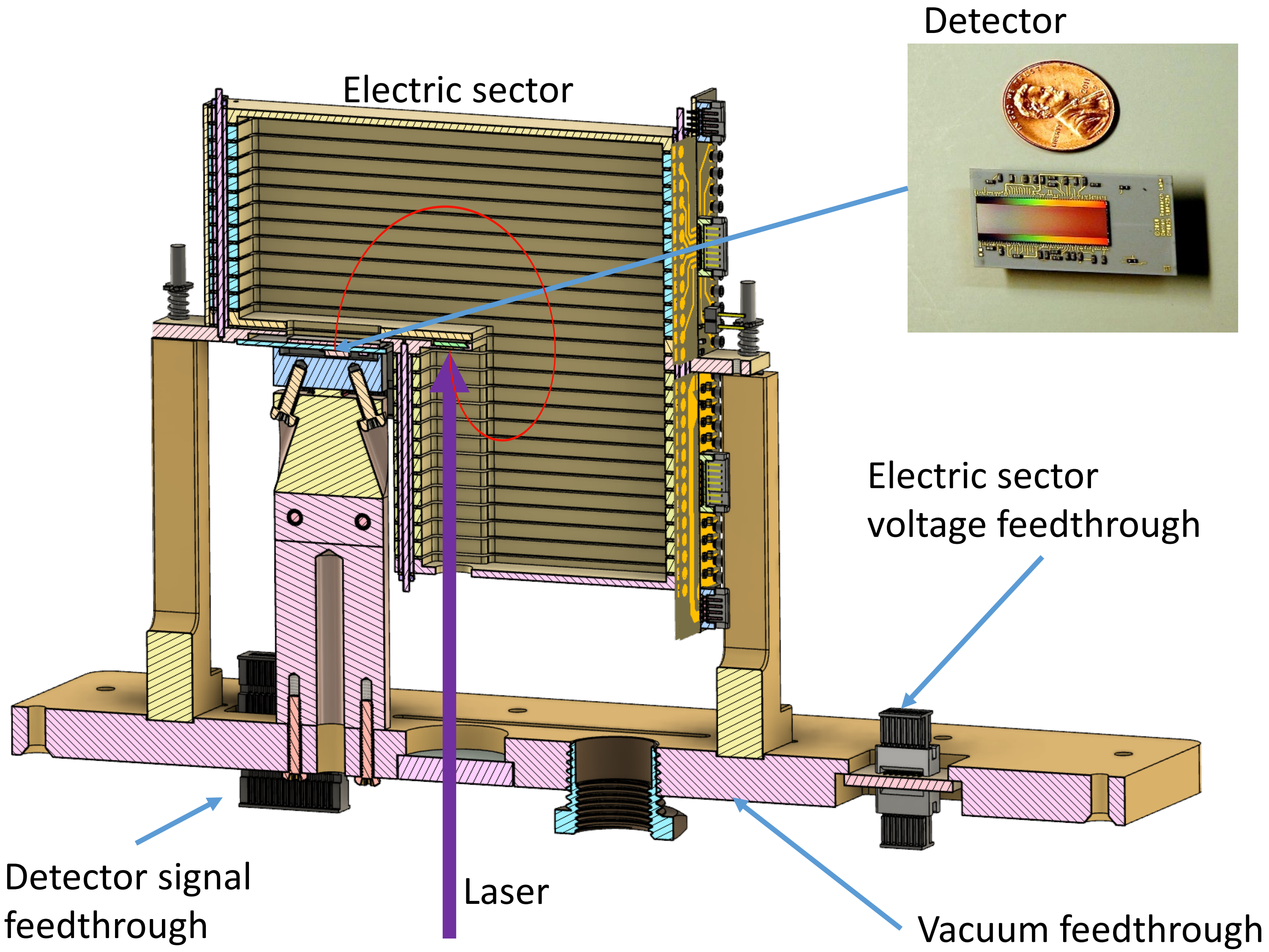
Analyzed particle becomes the "SLIT"
"Virtual Slit" Mass Analyzer

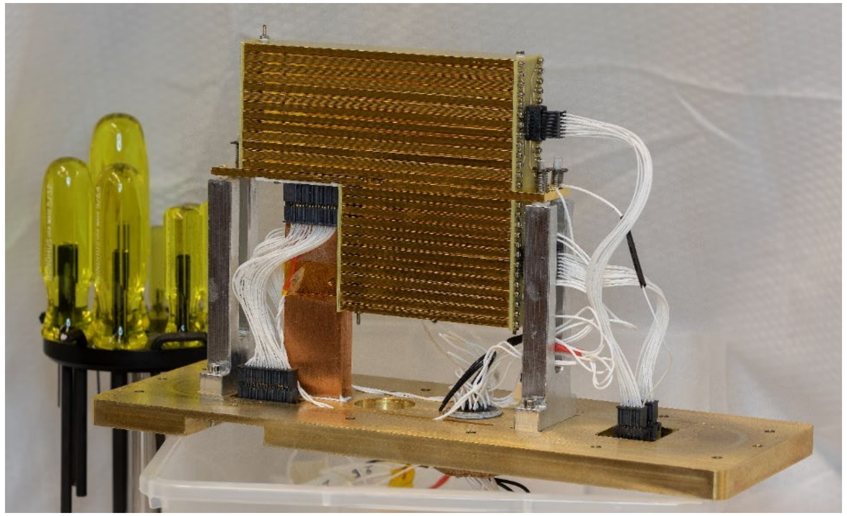
Proof of concept instrument – VS-CMS gen 1

Prototype – Proof-of-concept (previous project)



Prototype – Proof-of-concept (previous project)

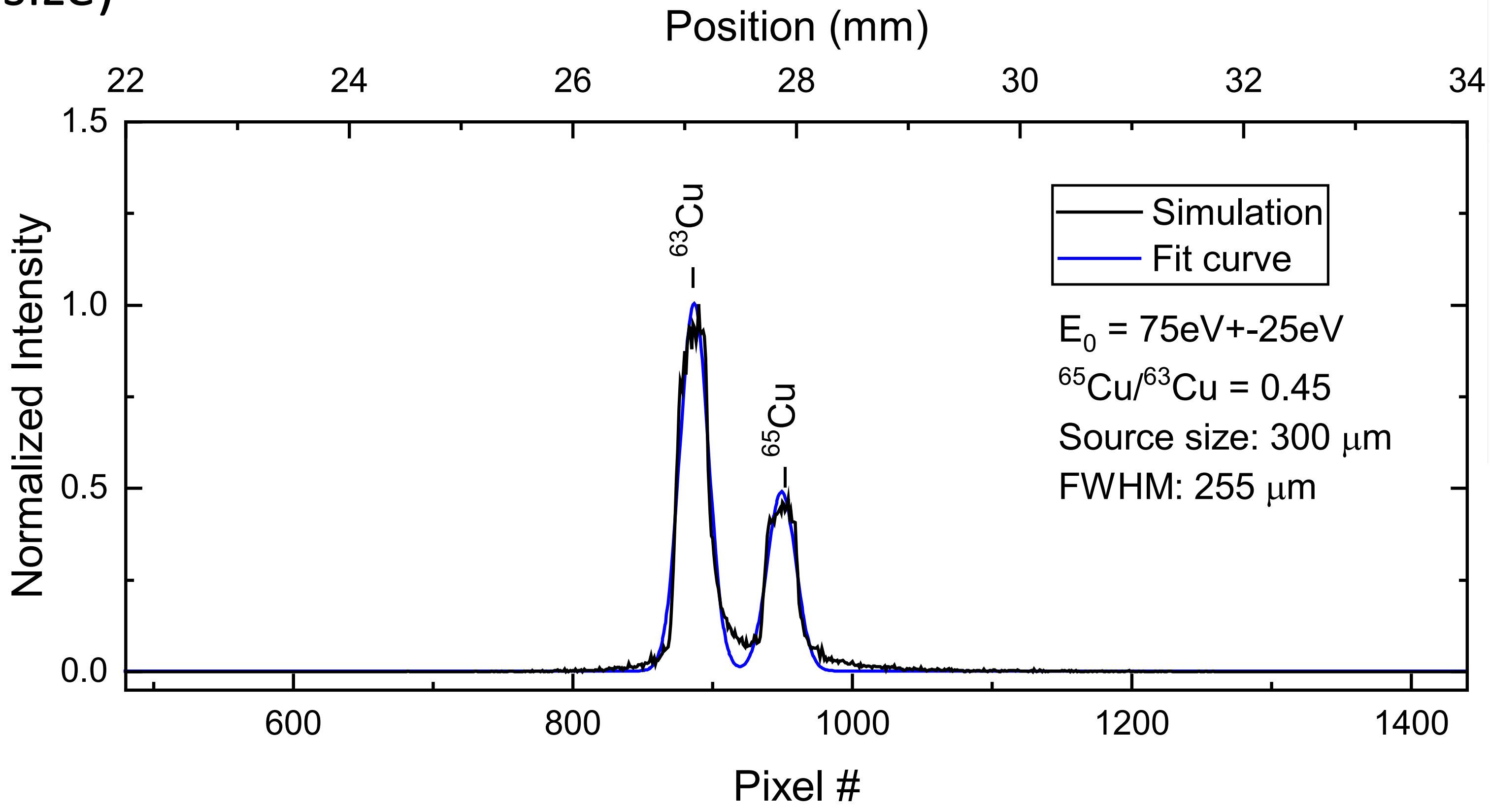


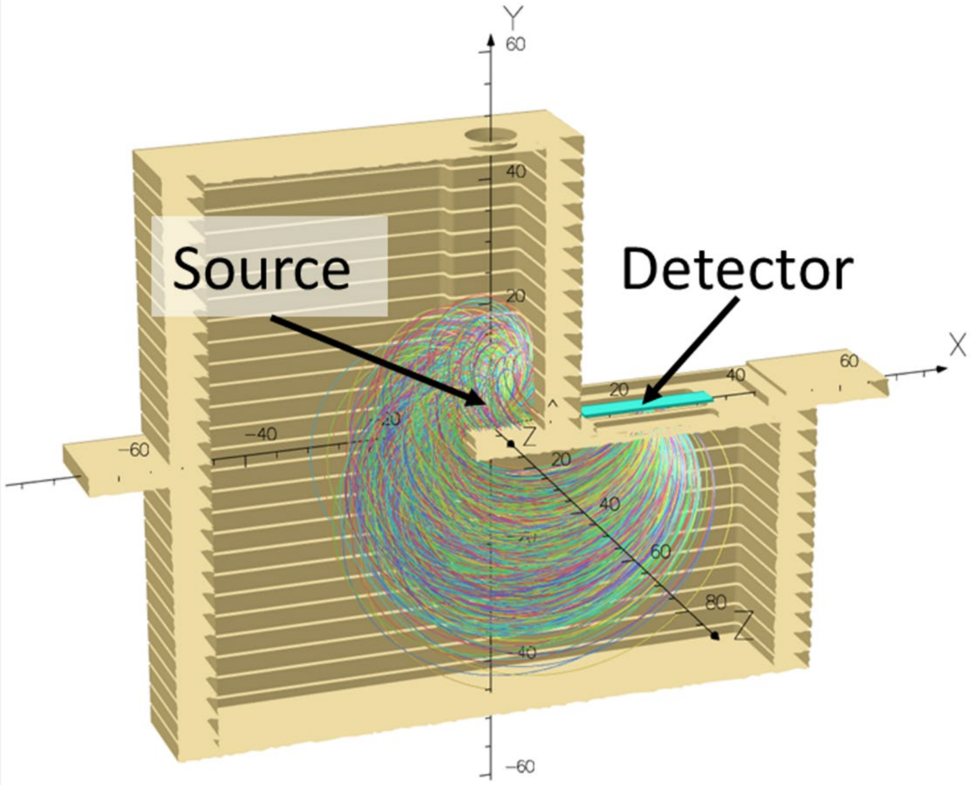


Electric sector compared with a set of screw drivers

Finite element analysis – Proof-of-concept (previous project)

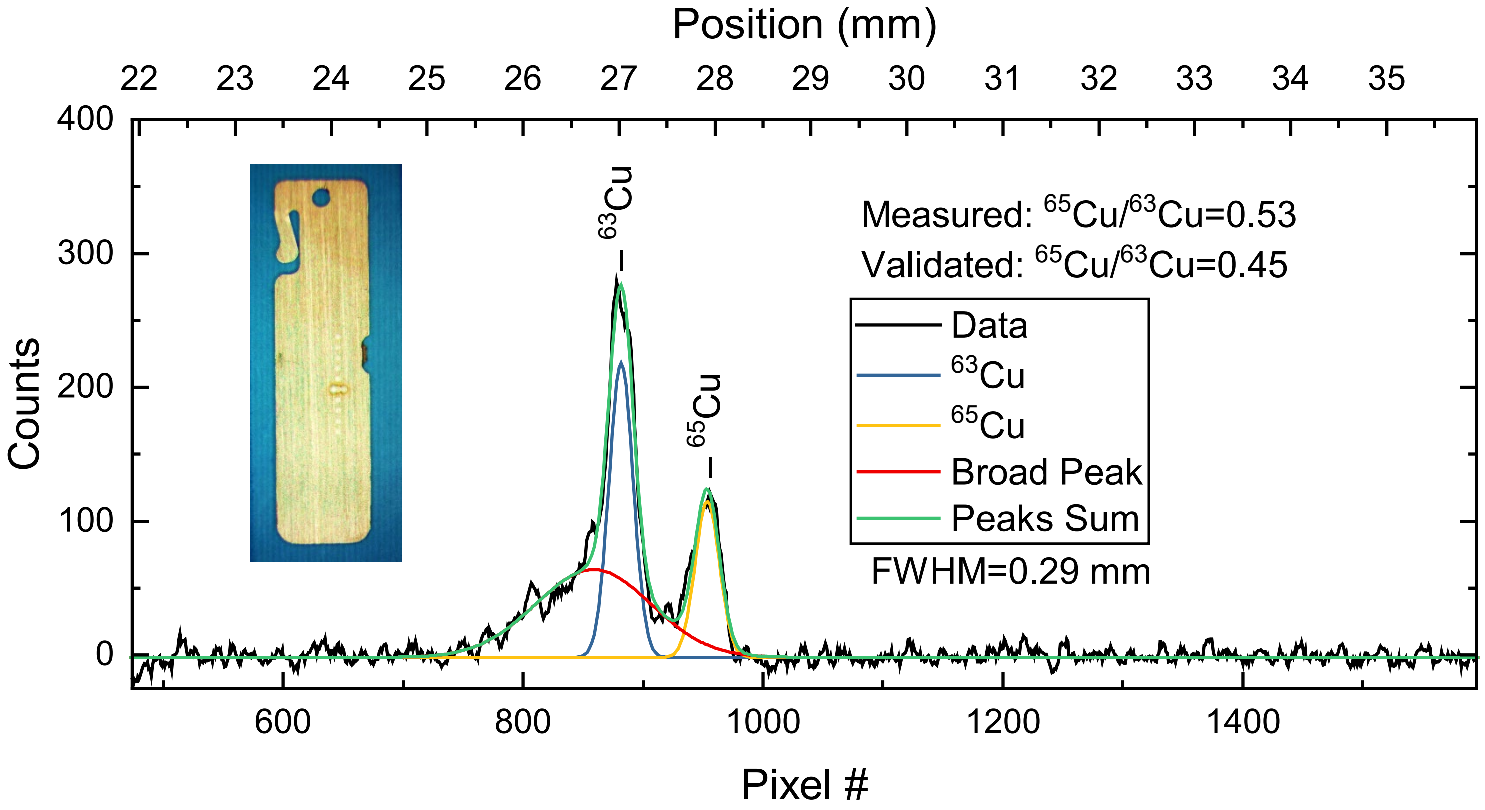
- ${}^{63}_{29}Cu^{1+}$ and ${}^{65}_{29}Cu^{1+}$
- Initial energy: $75 \pm 25\ eV$
- Angle spread: 30°
- Source size: $300\ \mu m$ (based on laser spot size)



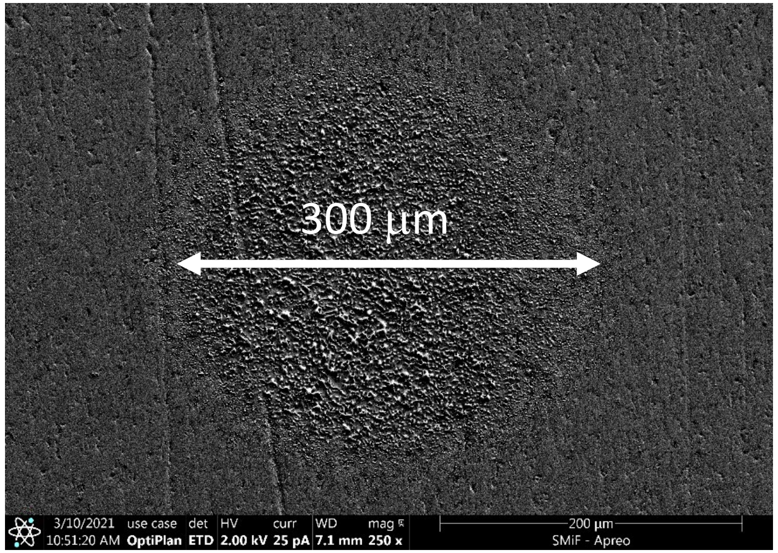


Peak size similar to source size
Source as the "Virtual slit"

VS-CMS Concept Validation with Copper Target



SEM image of Ablation spot



Laser fluence 1.4 J/cm^2

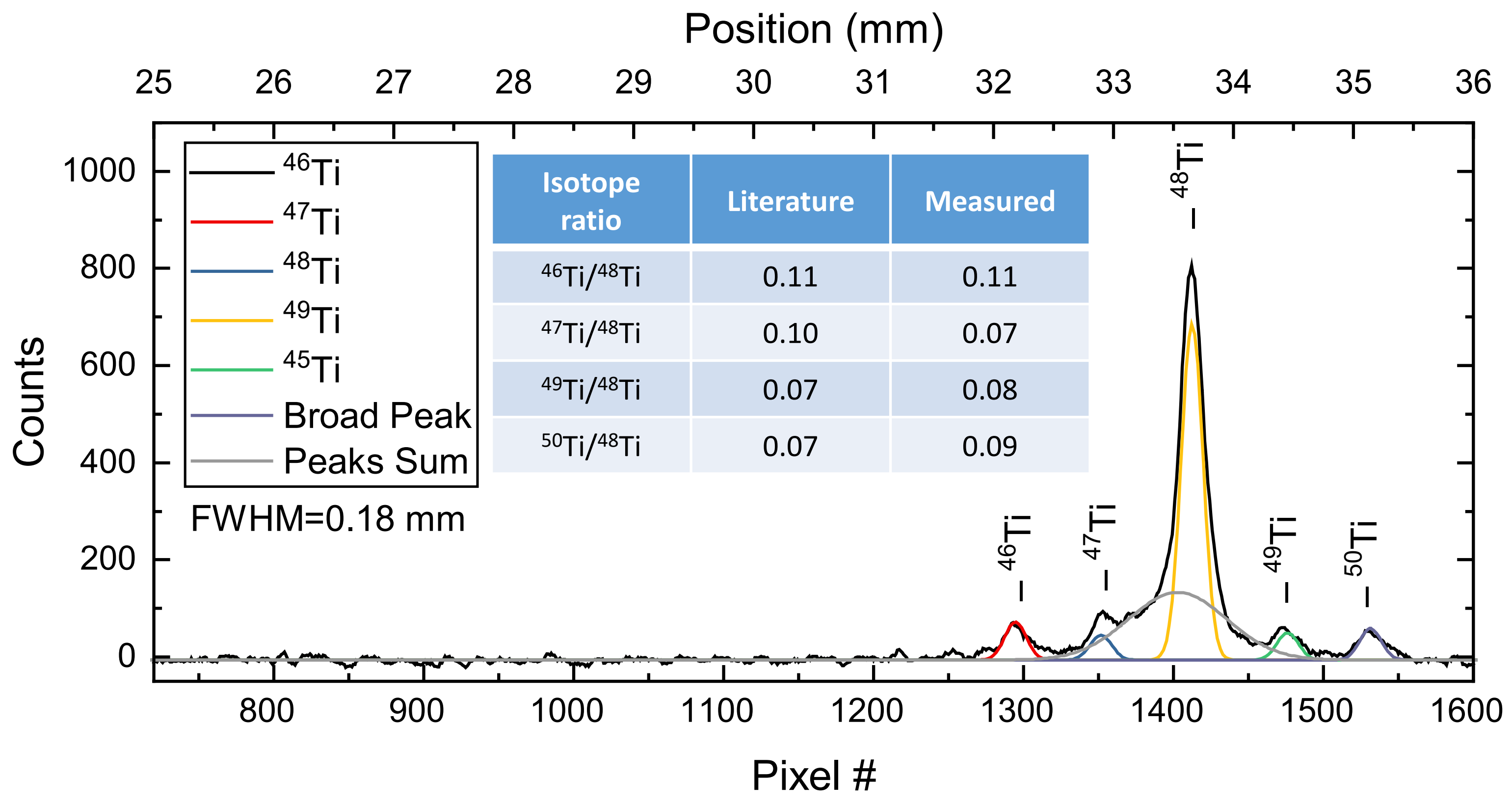
Image taken after 385 laser shots

Mass spectra of Copper with peak width same size as laser spot with isotope ratio close to that made by ICP-MS

*raw data smoothed with a Savitzky-Golay (win=5, pol: 2nd order) to enhance visibility. Fitting was done on unsmoothed data.

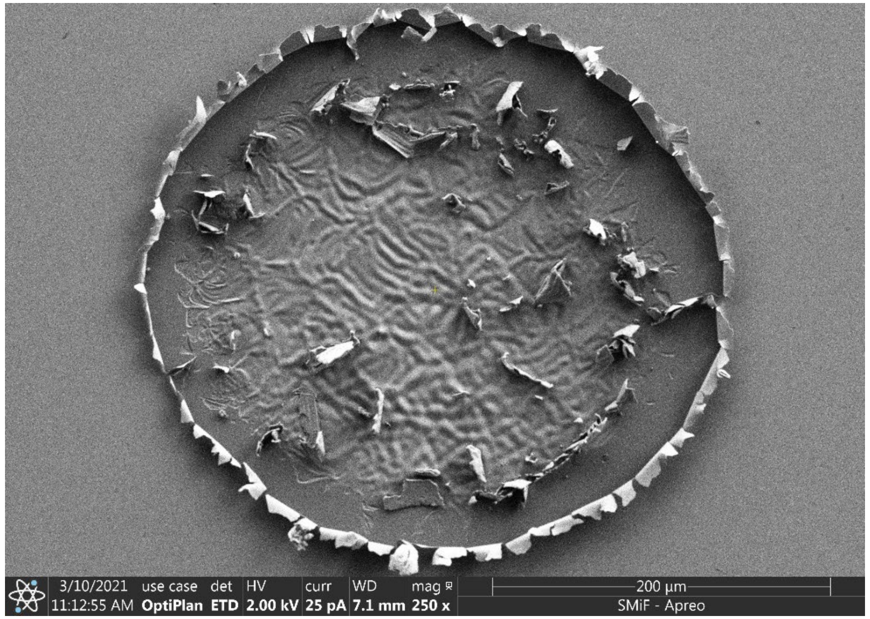
PennState College of Earth and Mineral Sciences | Earth and Environmental Systems Institute | LIME Laboratory for Isotopes and Metals in the Environment

Mass Spectrum of Titanium Isotopes



Isotope ratio	Literature	Measured
$^{46}Ti/^{48}Ti$	0.11	0.11
$^{47}Ti/^{48}Ti$	0.10	0.07
$^{49}Ti/^{48}Ti$	0.07	0.08
$^{50}Ti/^{48}Ti$	0.07	0.09

SEM image of Ablation spot



Laser fluence 1.4 J/cm^2

Image taken after 580 laser shots

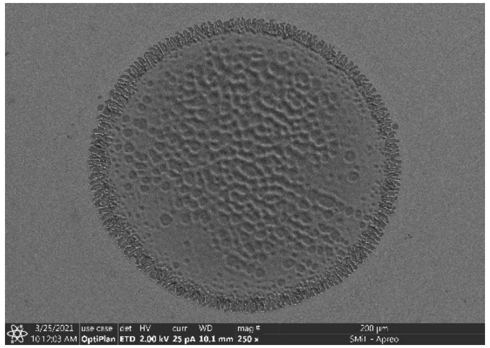
Isotope Abundances Reference – de Laeter, J. R., et al. (2003). "Atomic weights of the elements. Review 2000 (IUPAC Technical Report)." Pure and Applied Chemistry **75**(6): 683-800.

*raw data smoothed with a Savitzky-Golay (win=5, pol: 2nd order) to enhance visibility. Fitting was done on unsmoothed data.

Detection limit estimate

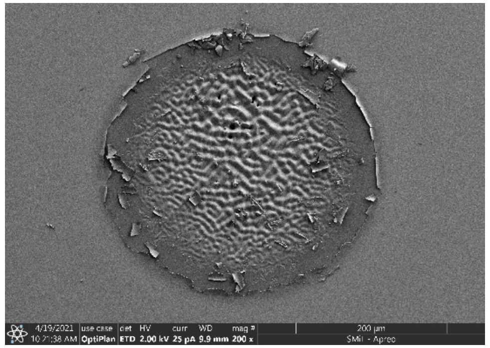
The experiment was carried out by shooting the laser in the same spot until the signal of the sample vanished from the spectra.

- Mass of Cu inside laser spot
  - Radius: 150×10^{-6} m
  - Height: 100×10^{-9} m
  - Volume: 7.07×10^{-15} m^3
  - Cu Density: 8960 kg/m^3
  - Mass: 6.34×10^{-11} kg



  - **Mass removed per laser shot =Mass/450 shots**
  - **<140 fg.**

- Mass of Ti inside laser spot
  - Radius: 150×10^{-6} m
  - Height: 400×10^{-9} m
  - Volume: 2.83×10^{-14} m^3
  - Ti Density: 4507 kg/m^3
  - Mass: 1.27×10^{-10} kg



  - **Mass removed per laser shot =Mass/2000 shots**
  - **<64 fg.**

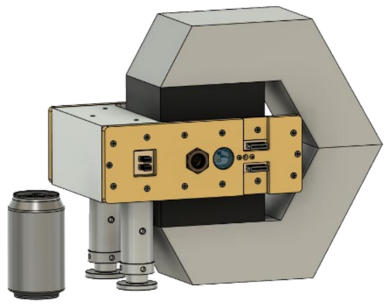
This implies an extremely low detection limit is possible with further development of a next generation prototype

Serpa, R.B., E. Piacentino, K.L. Horvath, T. Aloui, Y. Zhilichev, C. Parker, J.T. Glass, S. Tilden, J.A. Keogh, R. Kingston, R.P. Sperline, M.B. Denton, and J.J. Amsden, *Virtual-Slit Focusing in a Cycloidal Mass Spectrometer – a Proof of Concept*. International Journal of Mass Spectrometry, 2021: p. 116706.

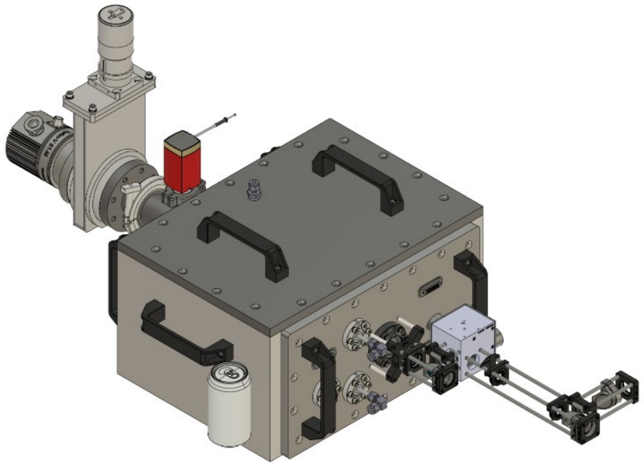
Generation 1 VS-CMS Capabilities and Expected Capabilities of a Generation 2

	VS-CMS Gen 1	VS-CMS Gen 2 (this program)
Sensitivity	**60 fg** Limited by thermal noise from operating detector at high temperature	**<1 fg**
Mass range	**20 – 80 u** Limited by dimensions of the magnetic field	**0 - 300 u**
Resolution	**1 u peak width** limited by laser spot size as the virtual slit, electric field uniformity and magnetic field uniformity	**<0.1 u peak width** **m/Δm = 2000 or better at m/q = 300**
Isotope Ratio precision	**Not measured** Limited by sample throughput	**< 0.002**
Speed of analysis	**5-10 samples per day fixed on a substrate**	**5-10 samples per day fixed on a substrate**
SWAP	**Laboratory based**	**Laboratory based**

Generation 1



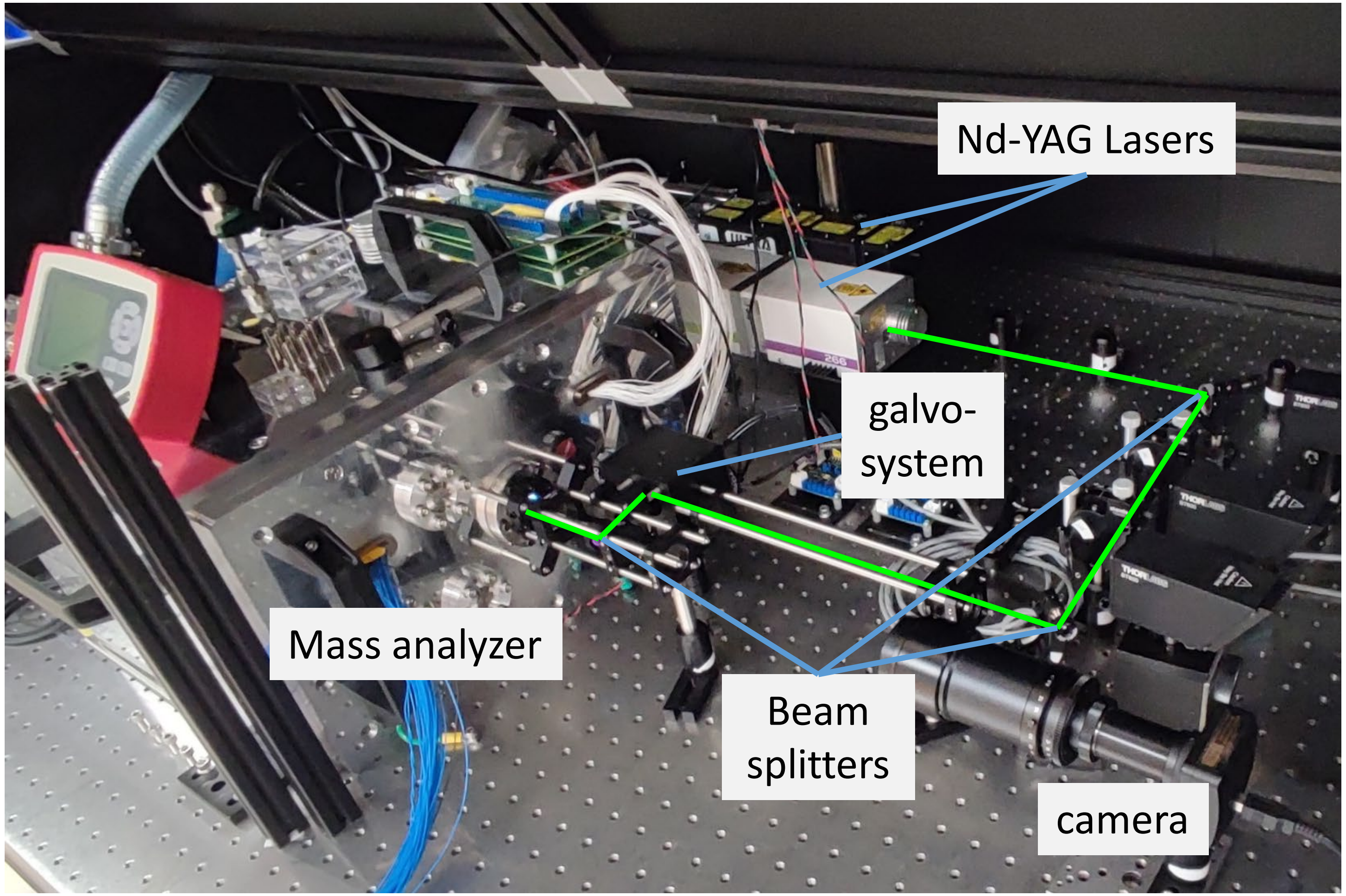
Generation 2



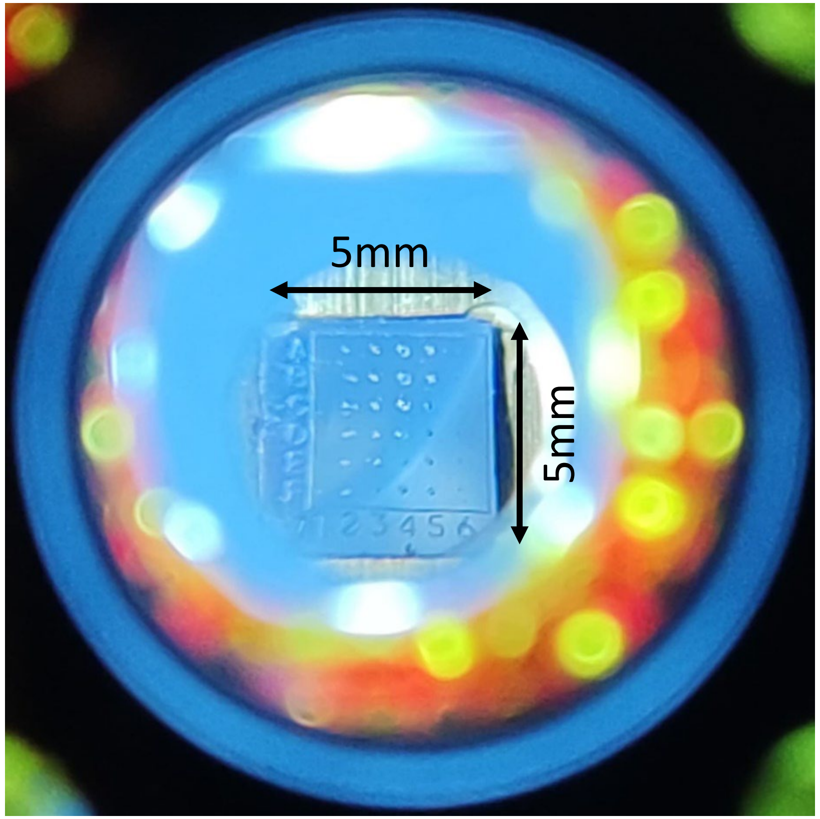
VS-CMS gen2

Installation in optics laboratory

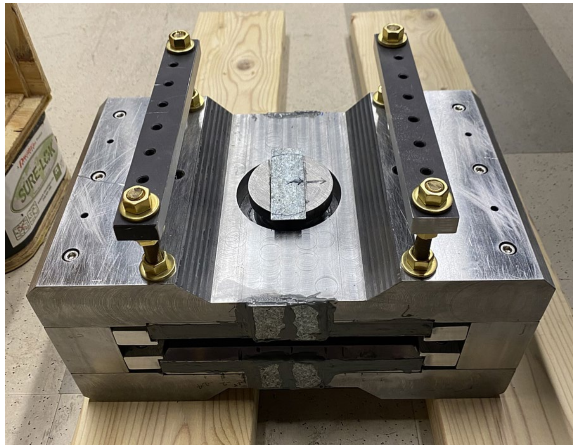
Full system on an optical breadboard



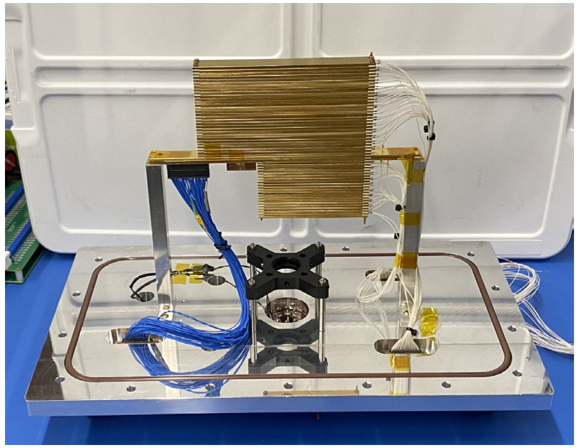
Sample through the laser window



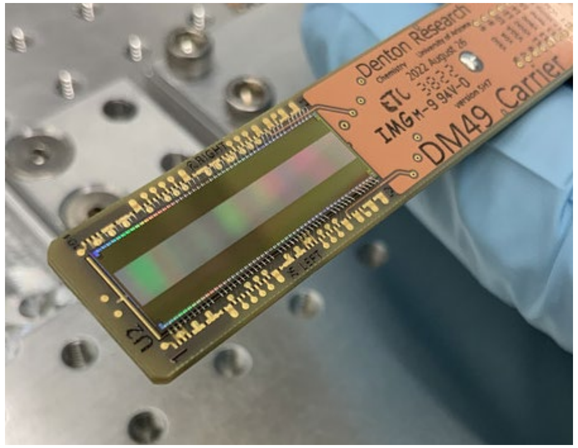
- VS-CMS Gen 2 summary
  - Mass range up to 300 u with resolution of < 0.1.
  - Design considerations paper to obtain constructive parameters[1]
    - Magnetic field of 0.7 T, uniformity <0.02% over 11 x 11 cm
    - Electric field uniformity <0.03% over 11 x 11 cm
    - Detector with 1704 12.5 µm pixels on a 12.8 x 78 mm carrier, cooled to -30C



Magnet



Electric Sector

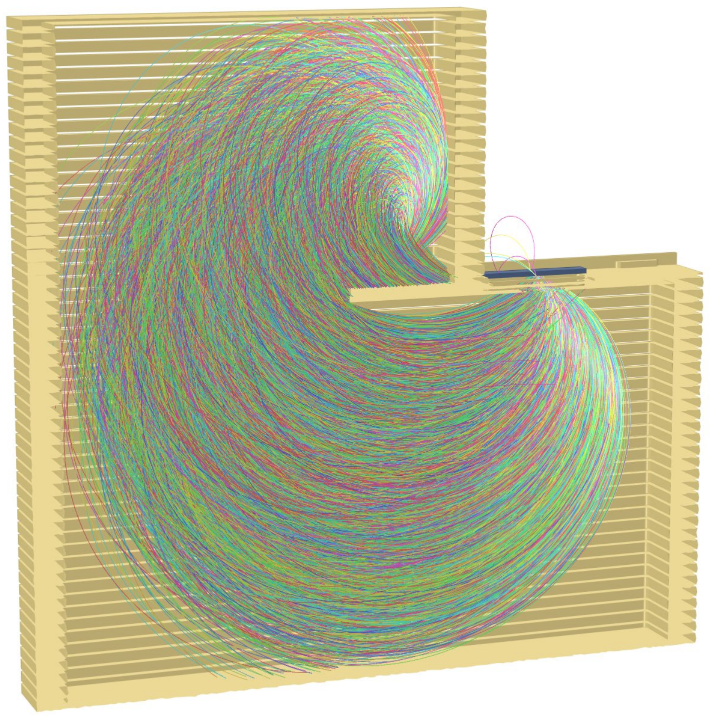


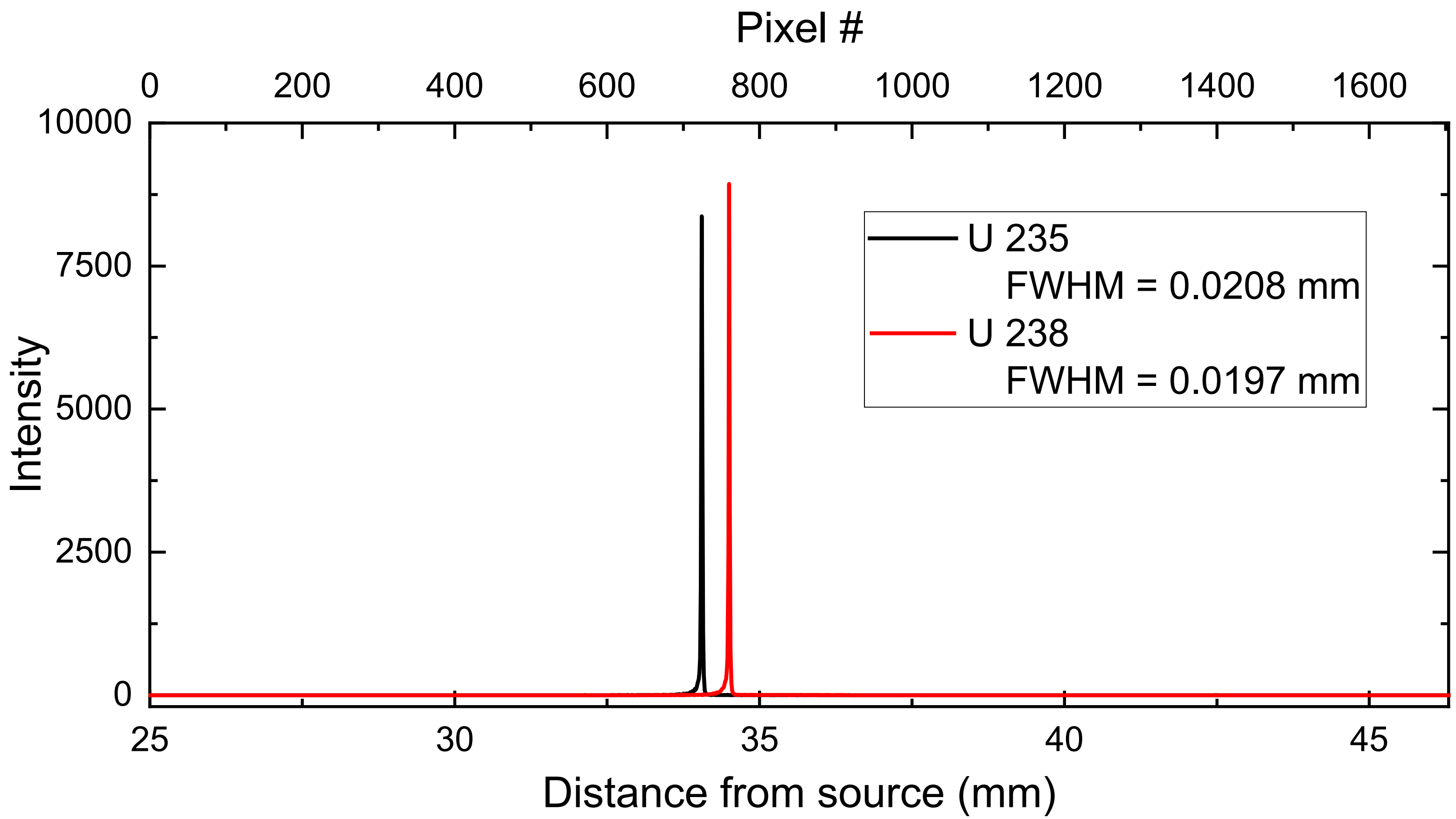
Detector

1. Horvath, K. L., E. L. Piacentino, R. B. Serpa, T. Aloui, R. Vyas, Y. Zhilichev, J. von Windheim, M. L. Sartorelli, C. B. Parker, M. B. Denton, M. E. Gehm, J. T. Glass, and J. J. Amsden. "Design Considerations for a Cycloidal Mass Analyzer Using a Focal Plane Array Detector." J Mass Spectrom 57, no. 7 (Jul 2022): e4874. https://dx.doi.org/http://dx.doi.org/10.1002/jms.4874
2. Code for each step: https://github.com/jasonjamsden/cycloidal_design (private repository, requires invitation, Python, Matlab, and CST Studio Suite with OPERA FEA)

FEA and ion trajectory simulation of VS-CMS Gen 2

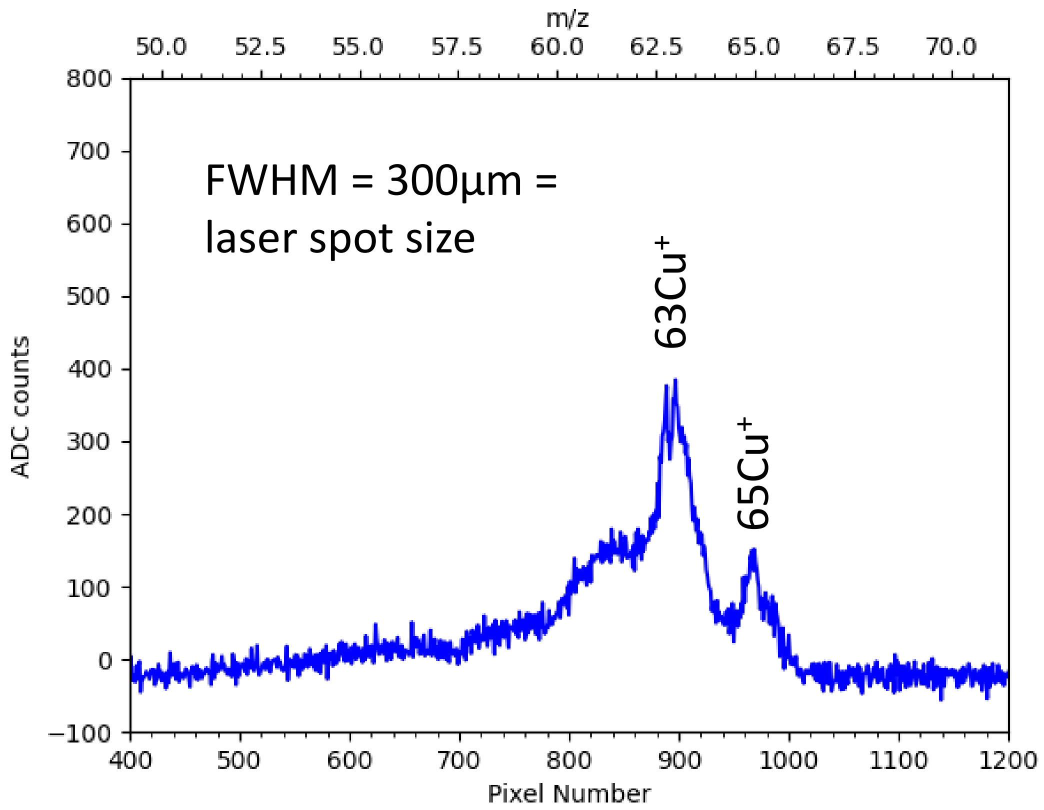
- U 235
  - Distance from source (a): 34.1 mm
  - FWHM (Δa): 0.0208
  - Resolving Power $= \frac{a}{\Delta a} = 1639$ (desired R = 3704)
- U 238
  - Distance from source (a): 34.5 mm
  - FWHM (Δa): 0.0197
  - Resolving Power $= \frac{a}{\Delta a} = 1751$ (desired R = 3704)



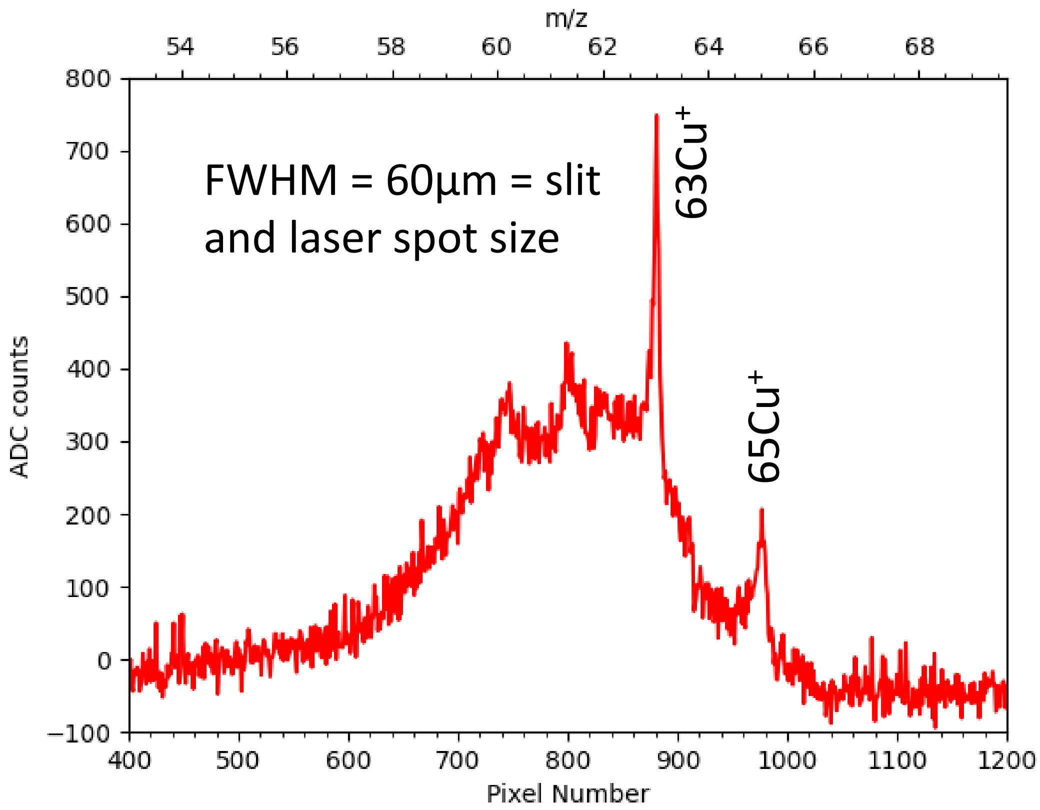


Comparison of VS-CMS Gen 1 with VS-CMS Gen 2 using Copper

- VS-CMS Gen 1



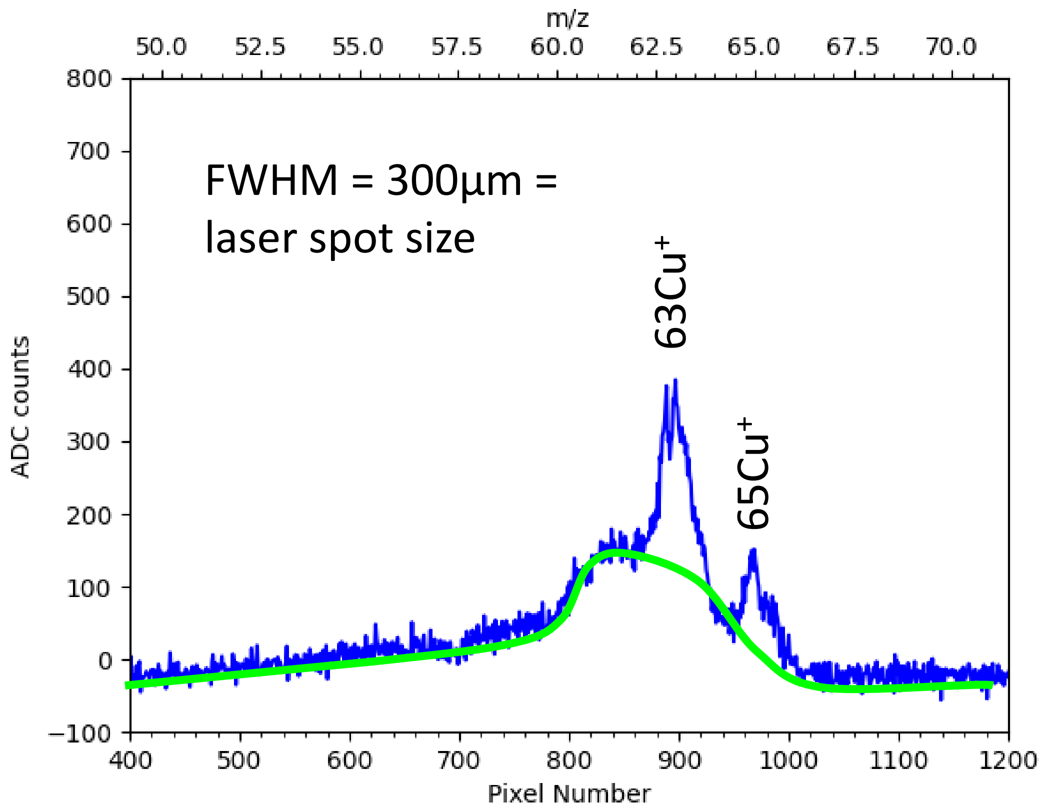
- VS-CMS Gen 2 (current)



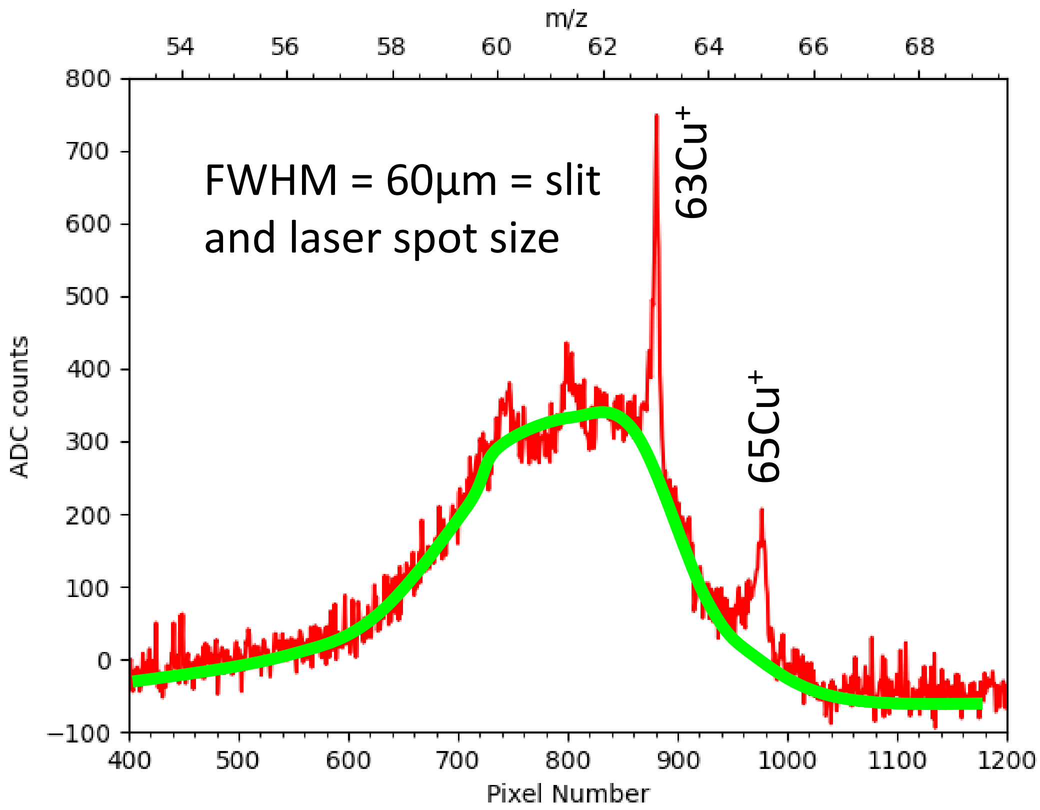
VS-CMS Gen 2 has significantly increased signal strength and reduced peak width

Comparison of VS-CMS Gen 1 with VS-CMS Gen 2 using Copper

- VS-CMS Gen 1



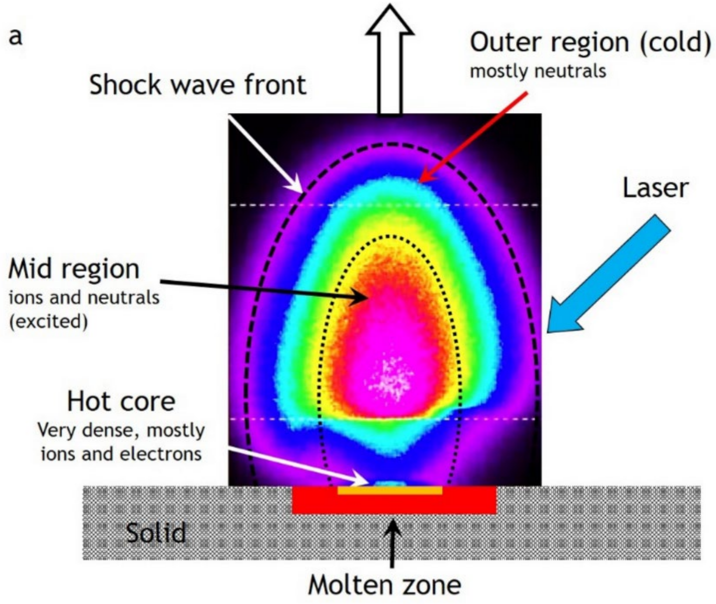
- VS-CMS Gen 2 (current)

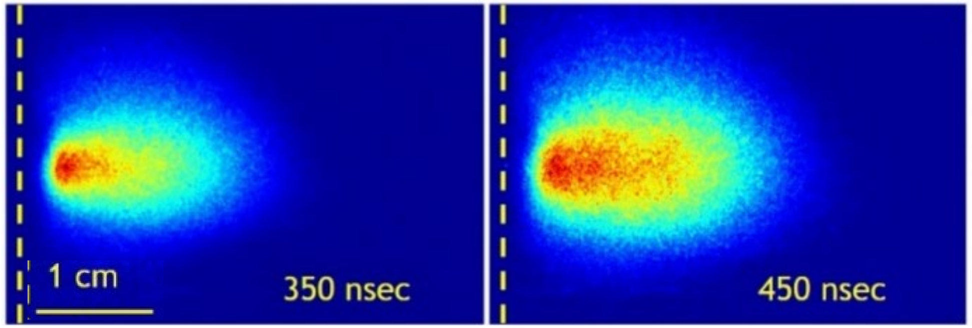


VS-CMS Gen 2 has significantly increased signal strength and reduced peak width

Possible sources for the broad background

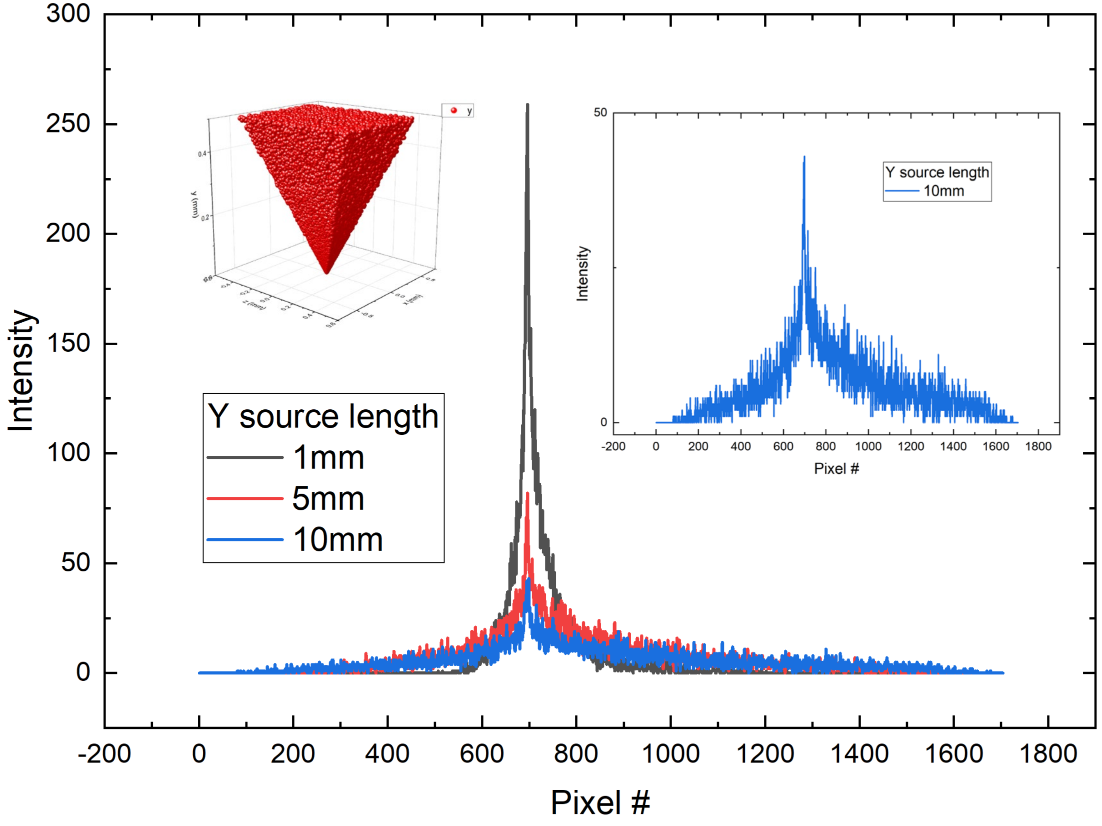
- Ionization of neutrals happening in the hot plume created by the laser.





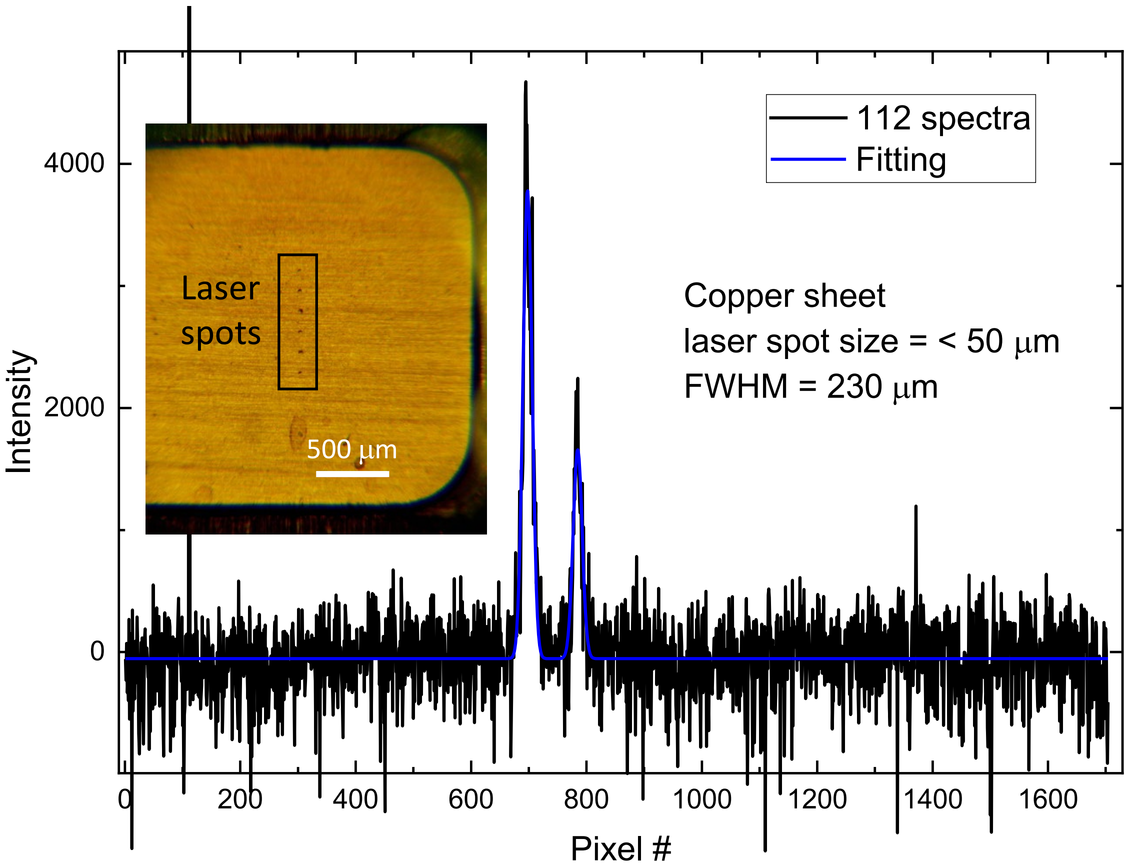
Schneider, C.W., Lippert, T. PLD plasma plume analysis: a summary of the PSI contribution. *Appl. Phys. A* **129**, 138 (2023). https://doi.org/10.1007/s00339-023-06408-4

- FEA simulation using a source as a trapezoid instead of a plane.

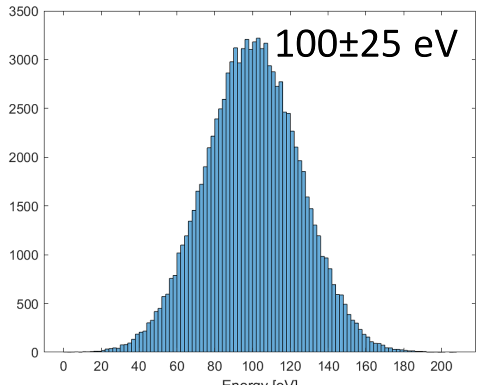


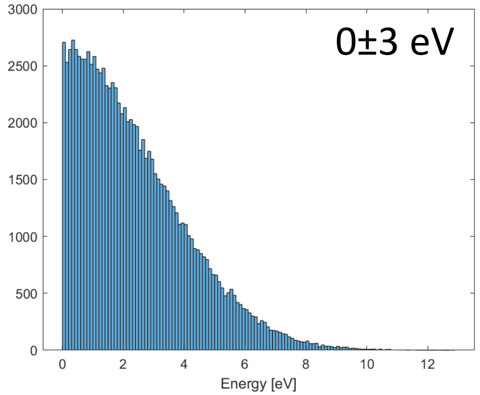
Possible sources for the broad background

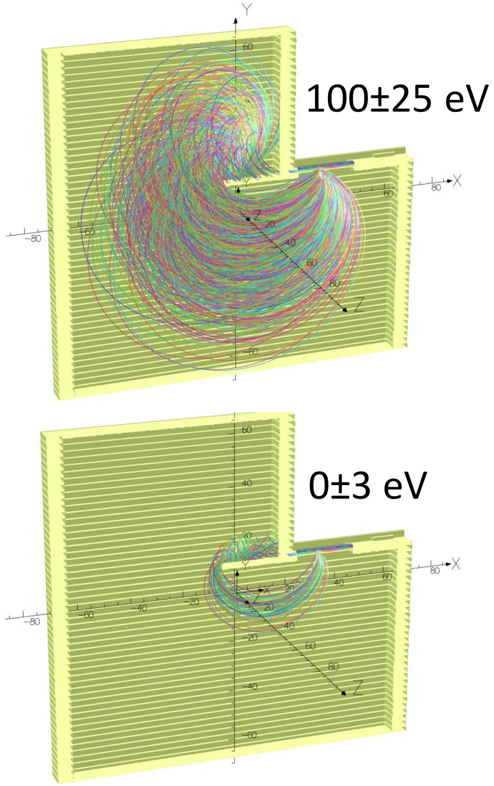
- Decreasing the laser power decreases thermal effects, but also the ionization and the energy of ions.

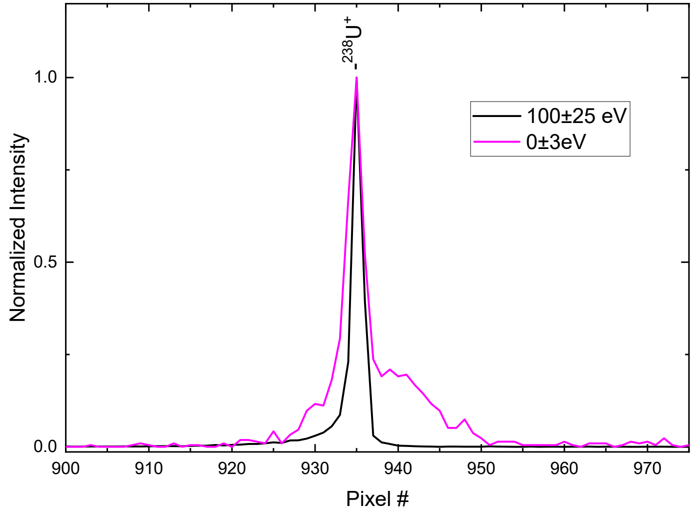


FEA simulation for ions with different energies



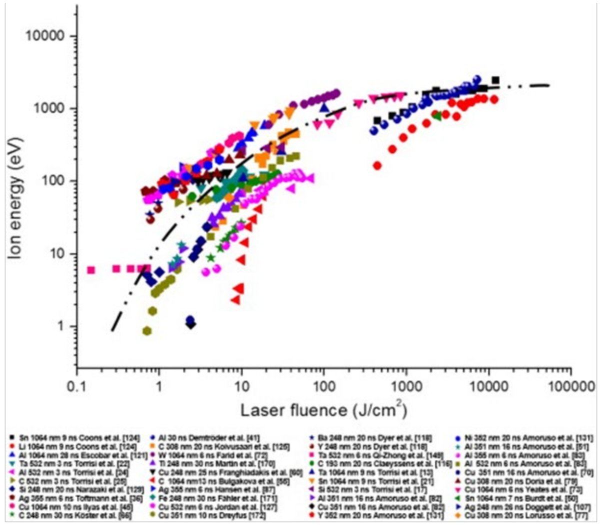






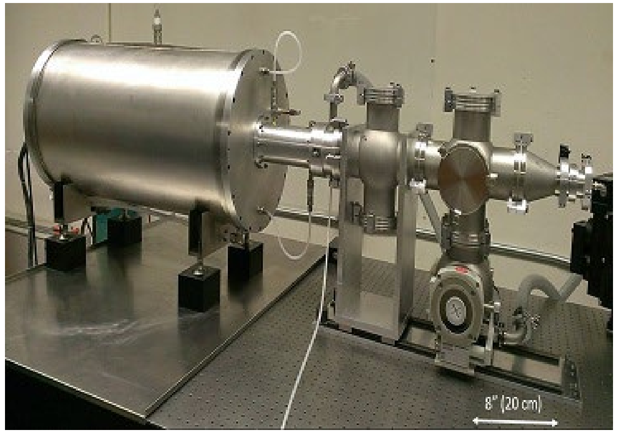
Investigate different laser sources for ionization

- Extreme UV/soft x-ray (46.9 nm)
  - Single photon process
  - Higher ionization efficiency
  - Smaller spot size
- Femtosecond laser
  - Decrease contribution of thermal effects
- Alternative localized ionization techniques
  - Spark ionization
  - Two step process – ablation laser followed by laser ionization



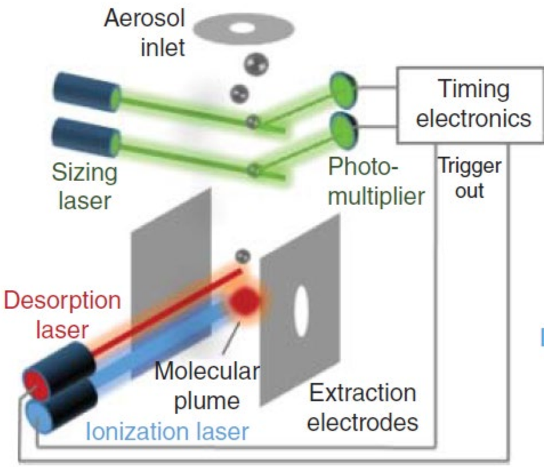
Wang, X.; Zhang, S.; Cheng, X.; Zhu, E.; Hang, W.; Huang, B., Ion kinetic energy distributions in laser-induced plasma. *Spectrochimica Acta Part B: Atomic Spectroscopy* **2014,** *99*, 101-114.

XUV laser source



http://www.xuvlasers.com/welcome.html

Two step process



Photoionization and Photo-Induced Processes in Mass Spectrometry. 2021. p. 359-411.

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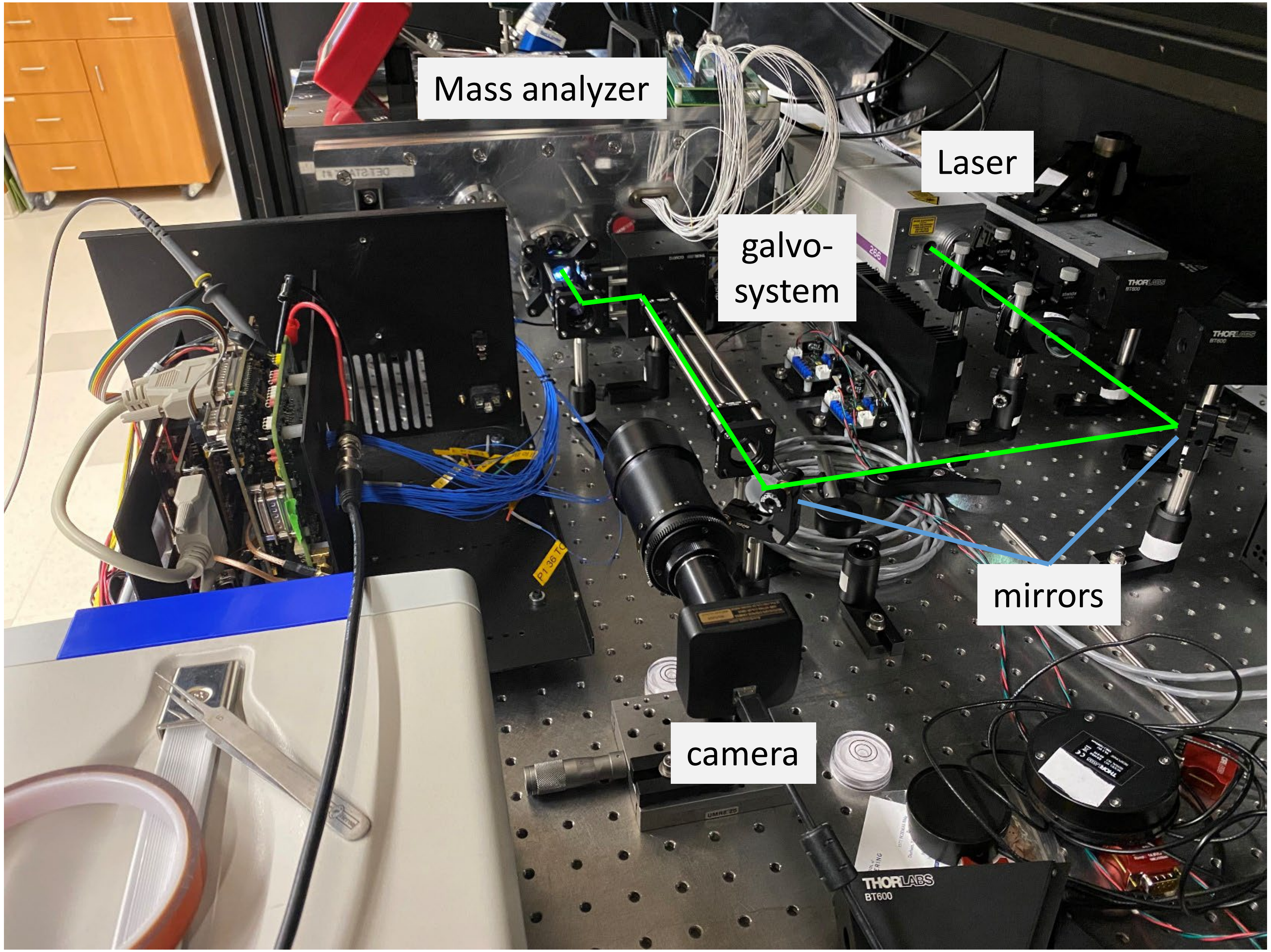
- Backup slides

Installation in optics laboratory

Full system on an optical breadboard



Sample through the laser window