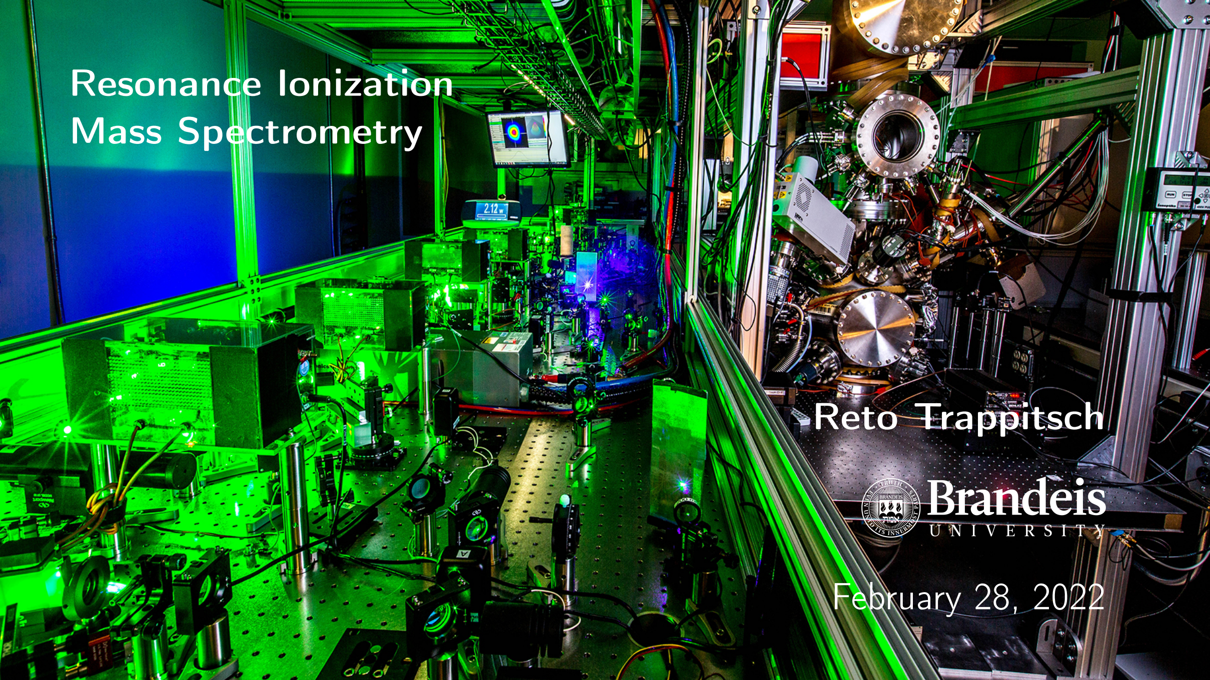
Resonance Ionization Mass Spectrometry



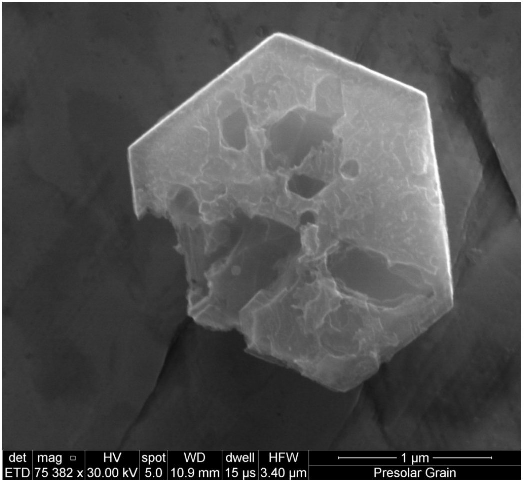
Reto Trappitsch

Brandeis University

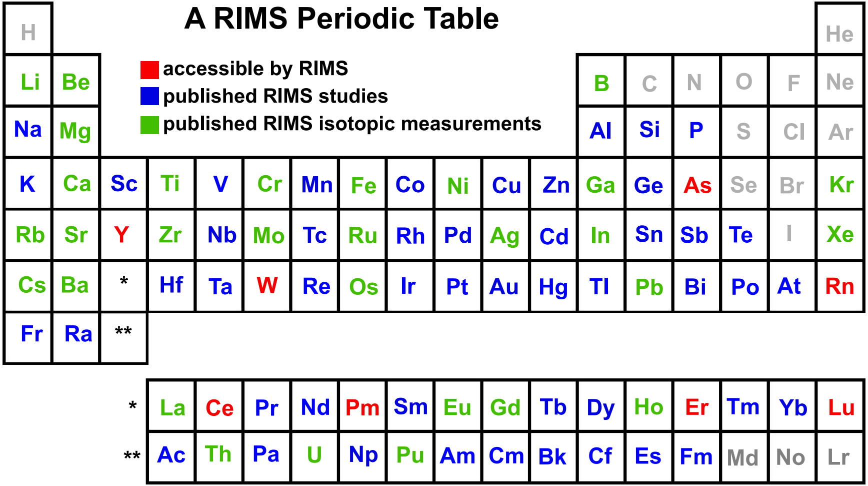
February 28, 2022

RIMS — A Versatile Technique for Trace Element Analyses

- High sensitivity for small, atom-limited samples
- Minimal sample preparation
- Resonance ionization with tunable Ti:Sapphire lasers
- High spatial resolution
  - $\sim 1\,\mu m$ for laser desorption
  - $< 100\,nm$ for ion sputtering
- High useful yield
  - 38% for U analysis (Savina+ 2018)
  - $\sim$ 18% for Ti analysis (Trappitsch+ 2018)
- Low backgrounds and high isobar suppression

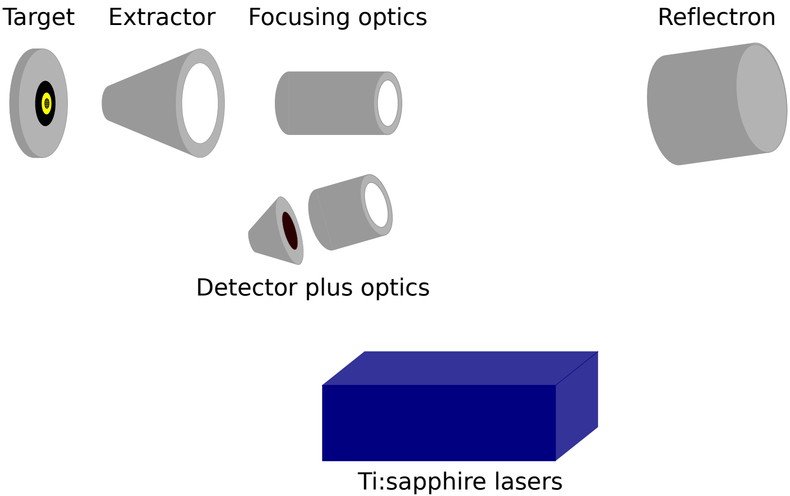


A RIMS Table of Elements



Savina and Trappitsch (2021)

An overview of Resonance Ionization Mass Spectrometry (RIMS)



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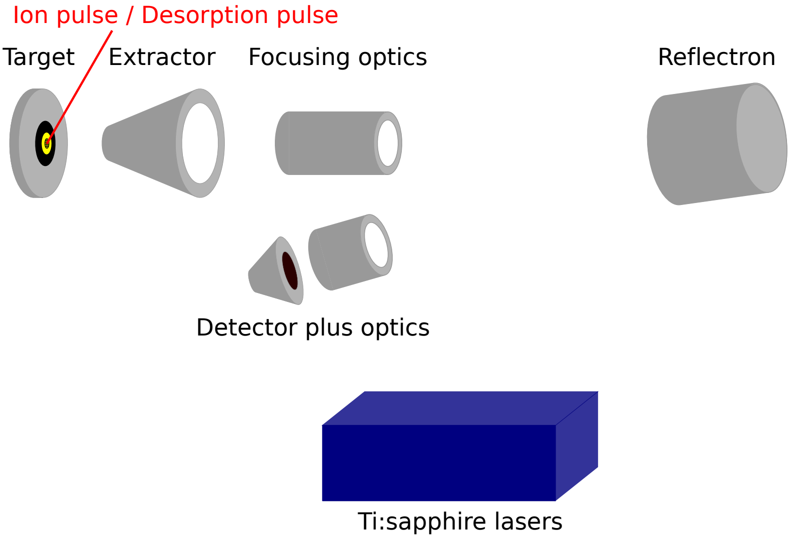

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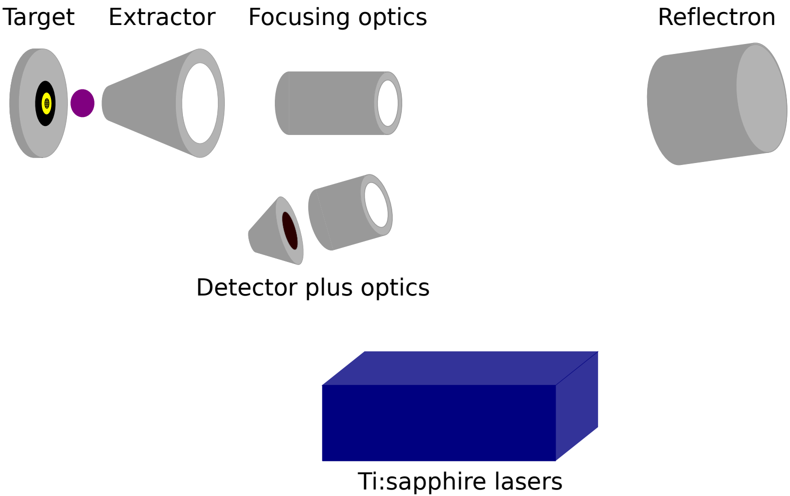

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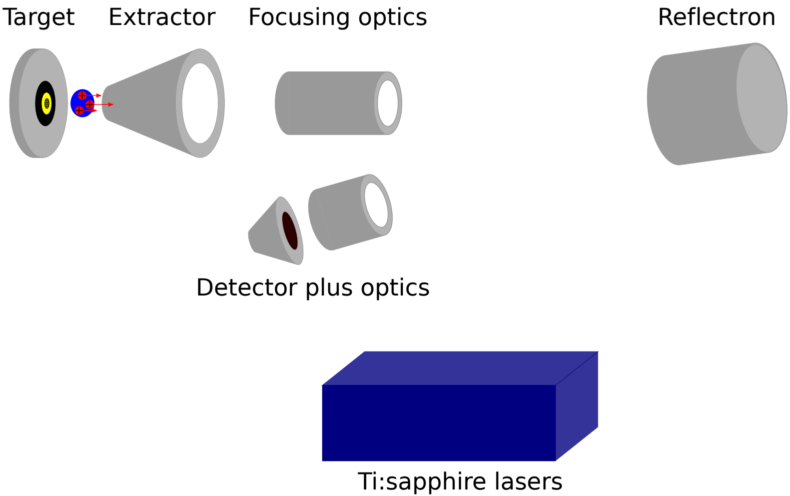

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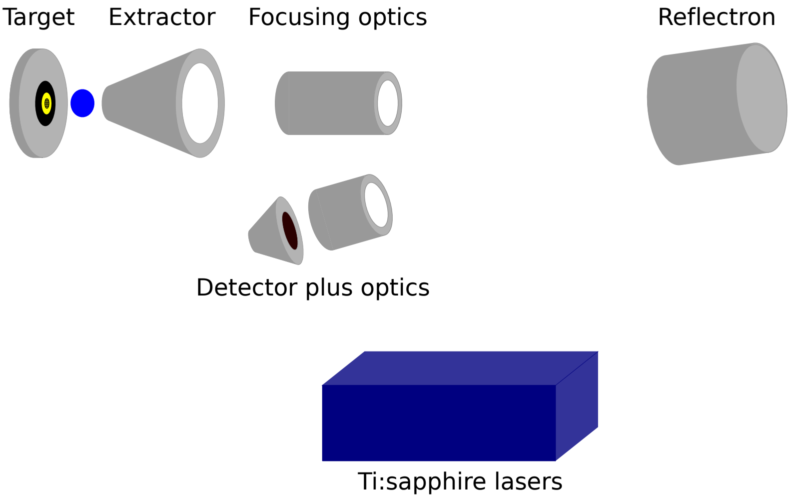

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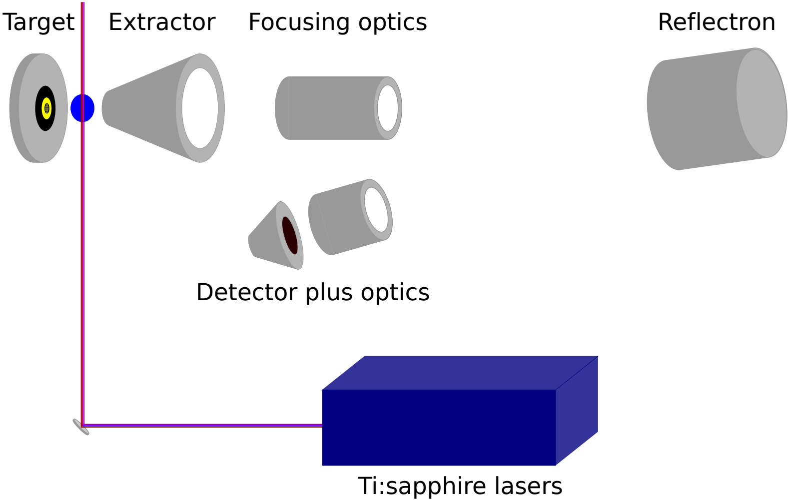

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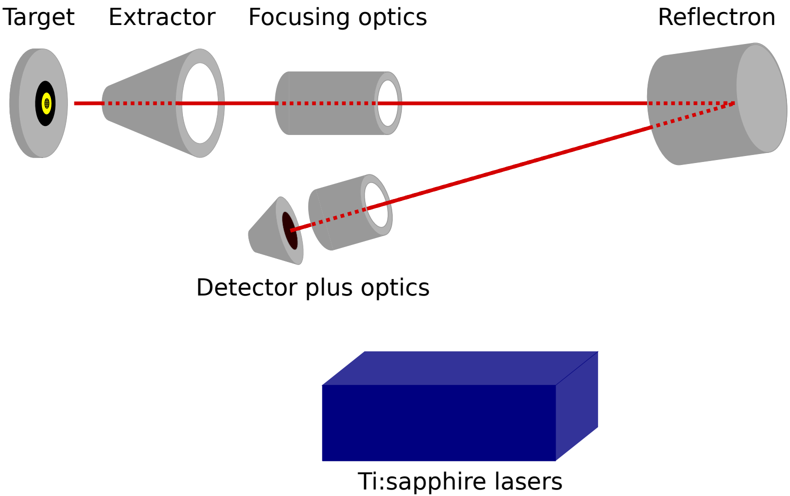
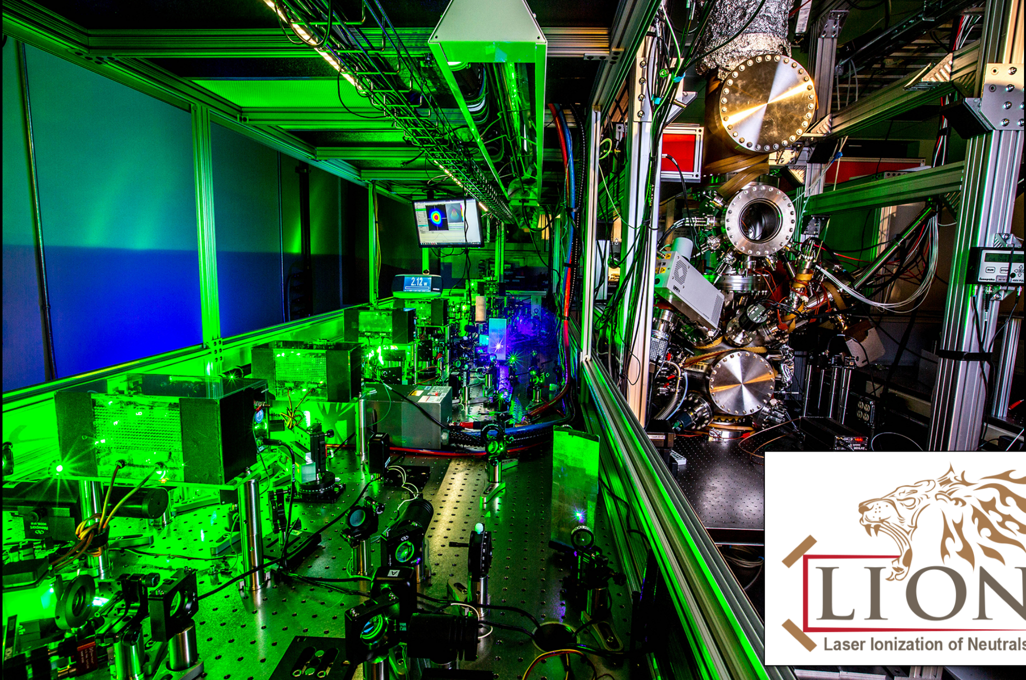
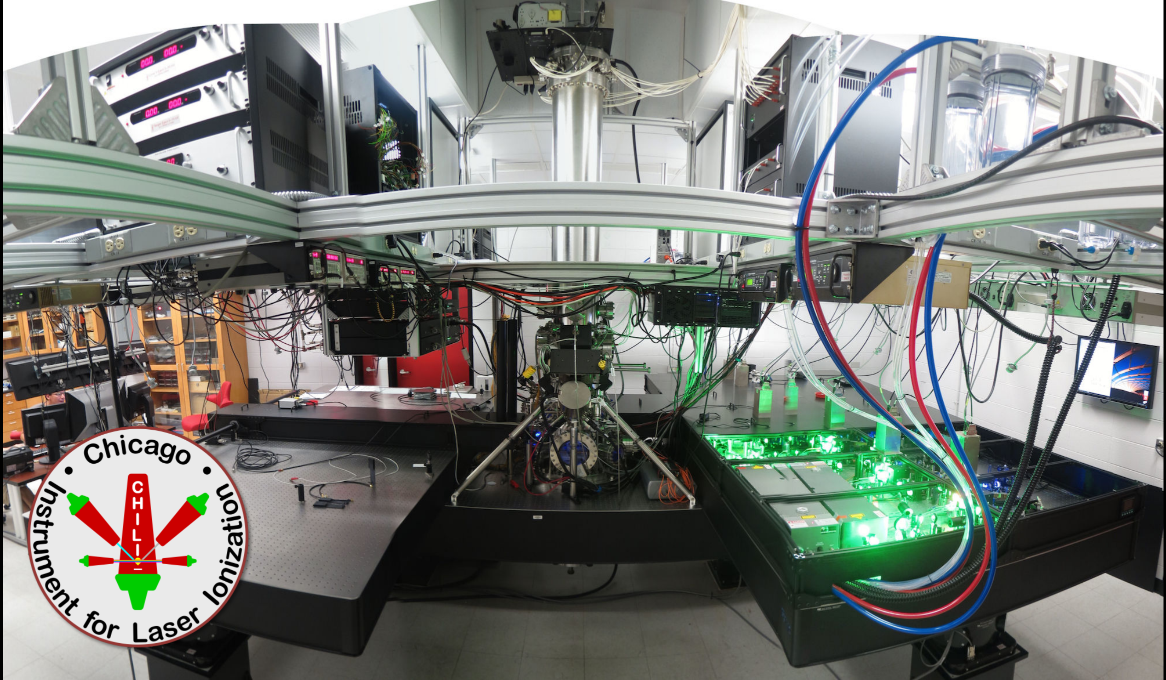




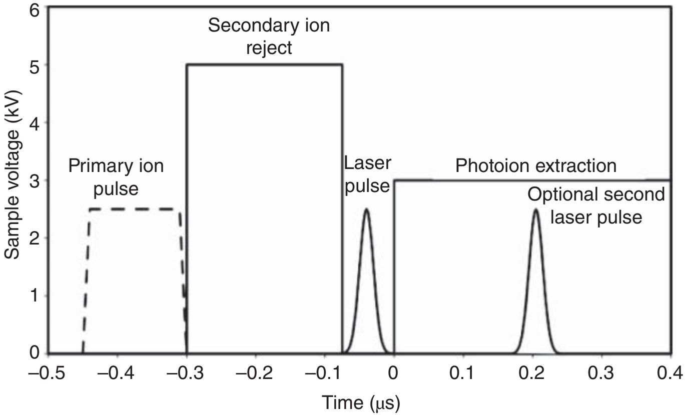
LION
Laser Ionization of Neutrals


Chicago
Instrument for Laser Ionization
CHILI

Measurement Cycles repeat at 1 kHz

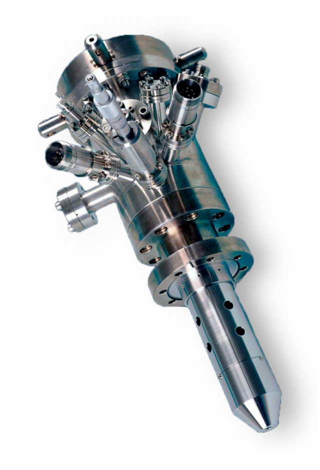
1. Desorption / Sputtering of sample
2. Ejection of secondary ions
3. Resonance ionization of photoions
4. Extraction
5. Mass / Charge separation and detection

Optional second ionization laser pulse allows for separation of isobars



Savina and Trappitsch (2021)

Sample Removal: Sputtering vs. Laser Desorption

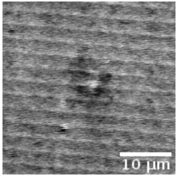


Ionoptica IOG-25Ga

- Sputtering with Ga ion beam
  - $< 50\,\text{nm}$ spatial resolution
  - Motionless blanking required
  - Trade off beteween high current or high spatial resolution
  - Duty cycle compared to SIMS: $\sim 10^{-4}$
- Desorption laser
  - Various wavelength possible to couple with different materials
  - Spot-size down to around $1\,\mu\text{m}$
  - Very low secondary ion backgrounds can be achieved

Sample Removal: Sputtering vs. Laser Desorption

EKSPLA 1064 nm
Desorption Laser



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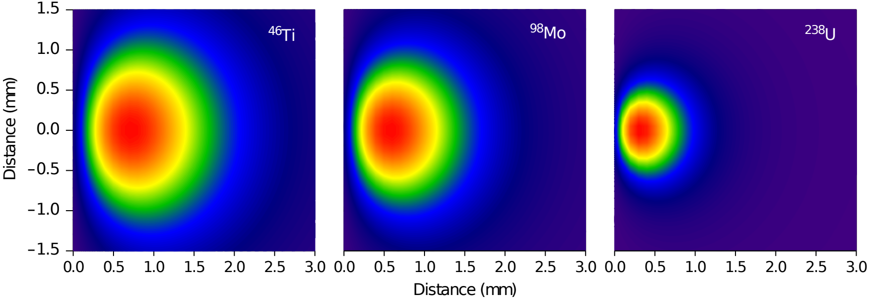
Ionizing of Neutral Atoms: You only get One Chance!

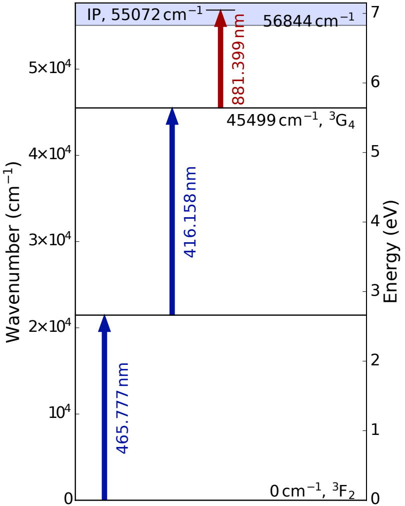


Savina and Trappitsch (2021)

- Ionization laser beam size: $\sim 1.5\,\mathrm{mm}$ diameter cylinder
- Laser intercepts cloud of neutrals above sample surface
- Neutrals that do not get ionized in first shot will be lost due to cloud expansion

Multi-step Laser Ionization of, e.g., Titanium (Trappitsch et. al, 2018)

- Resonance Ionization of Titanium requires three lasers
- Each ionization step is highly selective
- Ionization schemes need to be tested:
  - Spectroscopy of states above ionization potential
  - Saturation: Irradiance counts!
- Ti has low lying states
  - Understand population of these states
  - Scheme specific
  - Here: majority after sputtering in ground state



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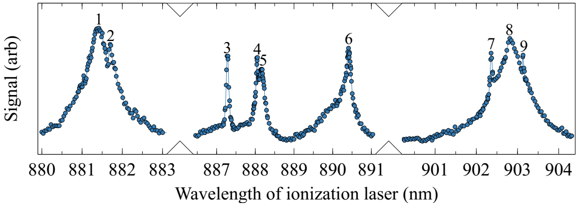

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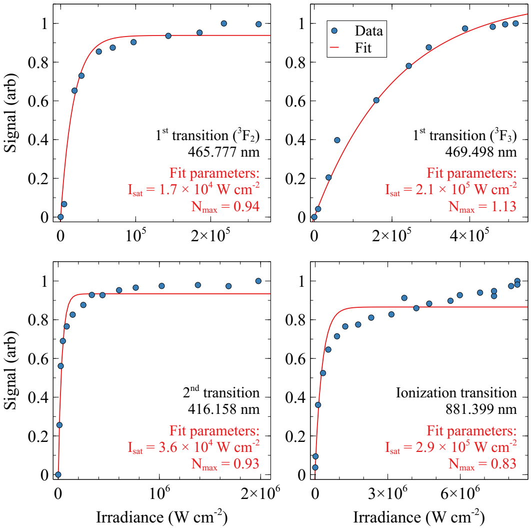

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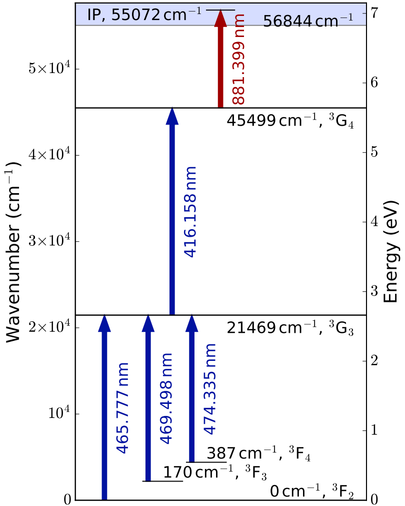
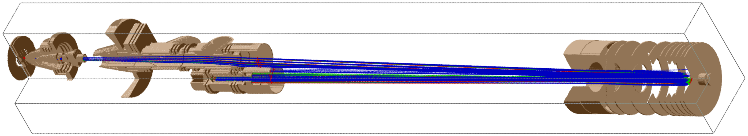
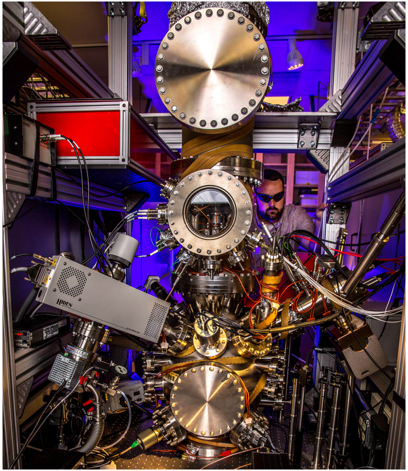


Separation of m/q in Time-of-Flight (TOF) Mass Analyzer

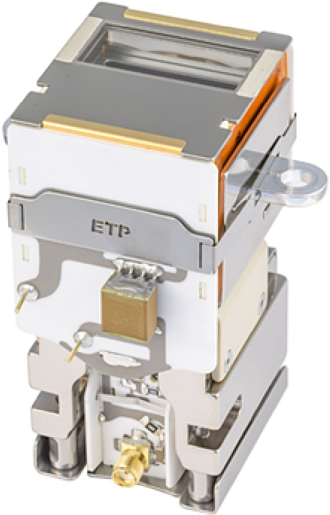
- Time of Flight Mass Analyzer
  - $\sim 3.5\,\mathrm{m}$ flight path
  - Grid-less reflectron to optimize transmission
  - Mass resolution $\frac{m}{\Delta m} > 1000$
- Difficulty: Map a photoion volume in time onto detector
- Lasers however take care of isobars



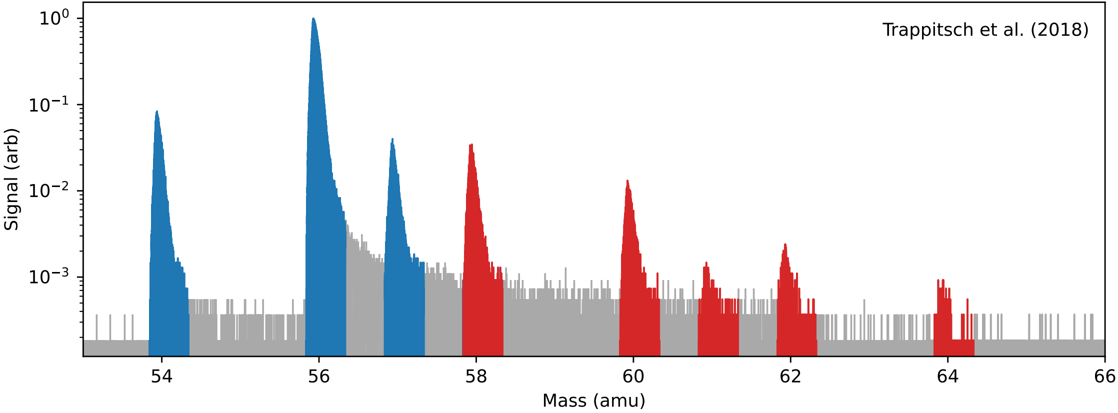


Ion Counting — Record every Arrival Time

- Ion counting detectors
  - Microchannel plate detectors (MCPs)
  - TOF Electron Multipliers
- Time-to-Digital Conversion: 80 ps time resolution
- Overall system dead-time: $\sim 700\,\text{ns}$
- Reasonable count rates: $\sim 2,000\,\text{cps}$



Simultaneous Measurements of Iron and Nickel



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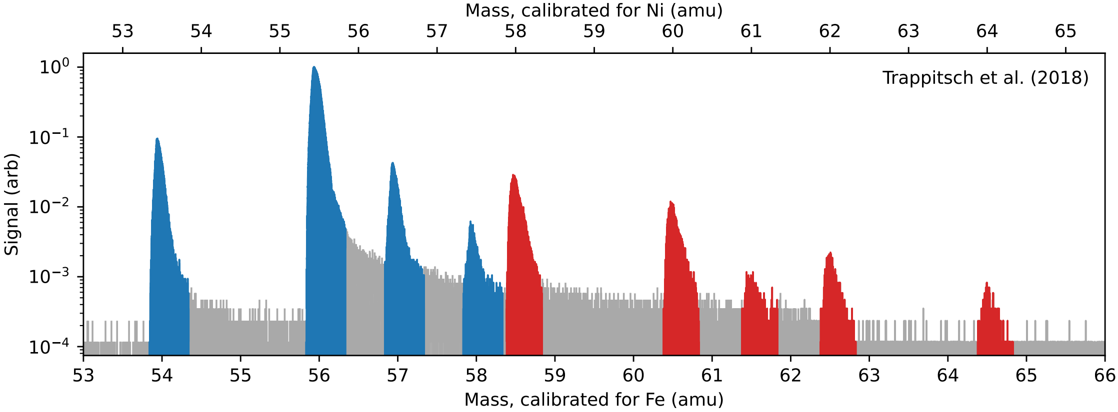
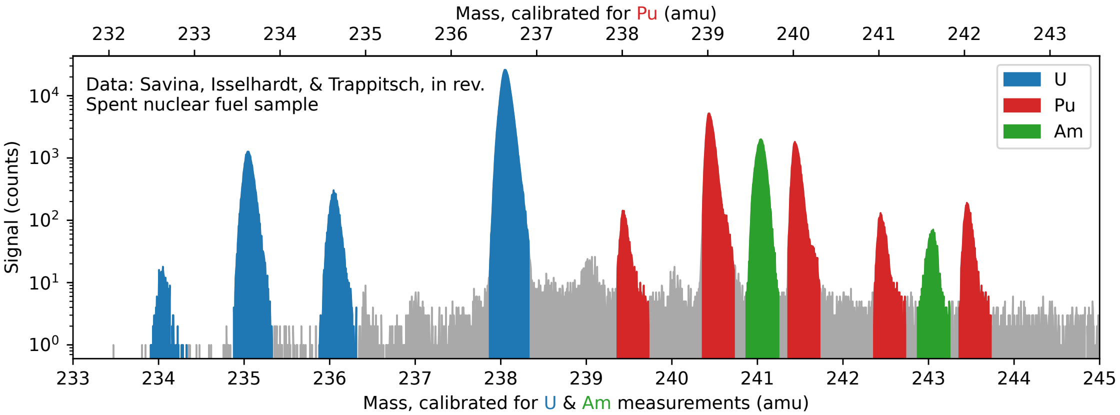
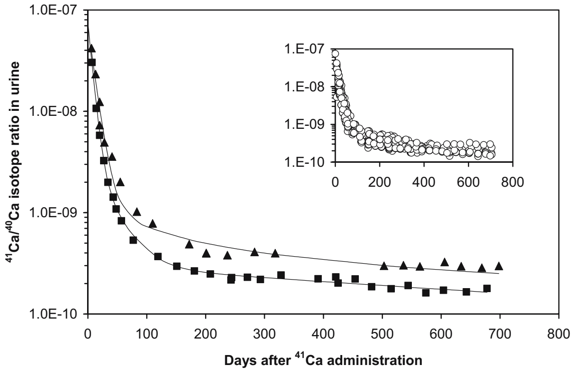


Multi-Element Analysis avoiding isobaric overlap



Full Disclosure — Limitations of RIMS

- Count rate limitations significantly limits the dynamic range
  - Narrowband lasers can be used in special cases to increase dynamic range
  - Example: $^{41}Ca/^{40}Ca$ analysis
- Ionization laser pulse width $\sim 20\,\mathrm{ns}$: $\rightarrow$ Duty cycle $\sim 10^{-5}$
- Desorption laser coupling depends on material and wavelength
  - Choose the right wavelength and pulse width
- Sample material is removed as molecule
  - In-vacuo surface chemistry



Denk et al. (2006)

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Hiden Analytical IG20

The Next Generation RIMS Instrument

- TOF Mass Spectrometer Optimization
  - Commercial TOF?
  - Optimized home-built TOF?
- Improved laser design and automation
- Ion Imaging
- Cryo-capability to handle biological samples
  - Trace isotopes in tissues, ...
  - Medical labeling with radioactive isotopes

New capabilities, research areas, and higher instrument up-time

Kore Technology SurfaceSeer

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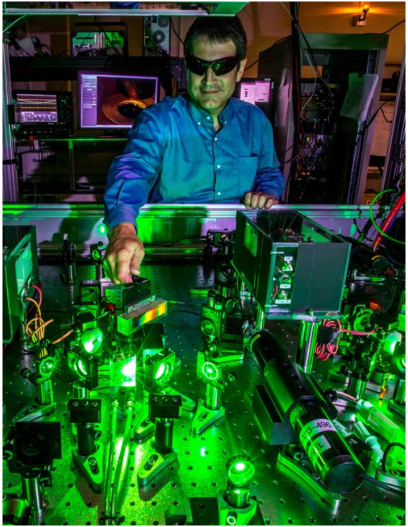

Thank you!

Acknowledgement

Lawrence Livermore National Laboratory

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