High Five: UHV SIMS with Plasma Primary & *simultaneous* positive and negative secondary ion detection

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High Five: UHV SIMS with Plasma Primary & *simultaneous* positive and negative secondary ion detection

- Why Simultaneous positive negative ion detection
- Previous work
- Requirements for a new instrument
- Plasma FIB ion source
- SIMS detectors
- *In-operando* measurements

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Why use Simultaneous Detection?

Problems with quasi simultaneous analysis

Changing extractor polarity within an experiment causes deflection of the primary beam and makes image registration and depth profiling difficult – this is especially true for FIB applications where crater sizes are smaller than the shift!

It takes significant time (seconds) to change and stabilise the secondary column potentials

Residual gas deposition – oxygen – may interfere with isotopic diffusion studies

True Simultaneous collection
Allows collection of spatially identical regions for positive and negative ions with accurate image registration.

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Where is this useful?

1) Energy conversion and storage

Understanding and optimisation of the ionic processes taking place in bulk materials surfaces and interfaces of solid oxide fuel cells (SOFC), electrolysers (SOE) and solid state Li batteries (SLIB).

2) Engineering alloys

Study of subsurface oxygen. Evaluation of corrosion cracking with focus on the interaction of H with the surface and H grain boundary migration.

Use isotopically pure deuterium and oxygen-18 and Lithium to understand transport.

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Previous work – FEI FIB 200 with two SIMS detectors

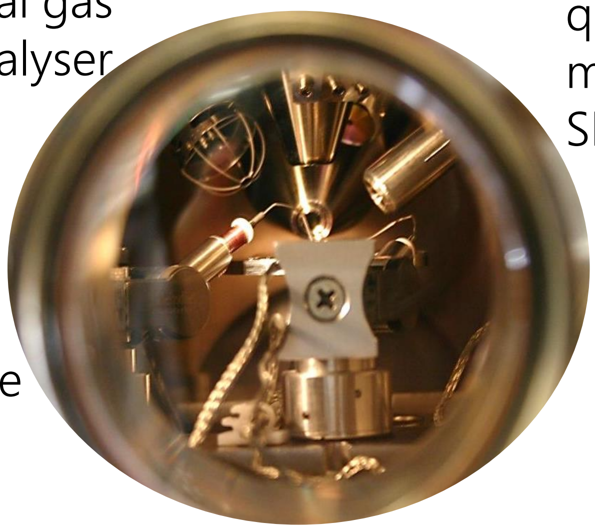
Hiden EQS SIMS detector & Residual gas analyser

Gallium beam

FEI quadrupole mass filter SIMS detector

SED: gridded Channeltron

Micro-probe Needle Connectors

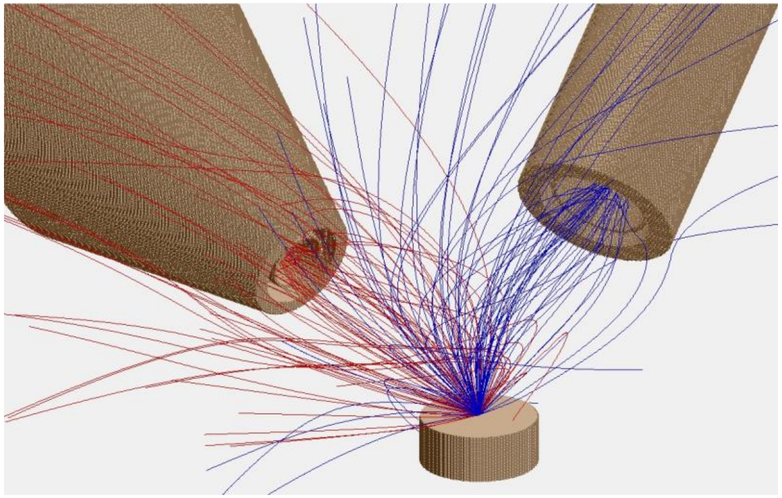


R. J. Chater, B. A. Shollock, D. S. McPhail, A. J. Smith and G. Cooke, *Surf. Interface Anal.*, 2014, 46, 372–374.

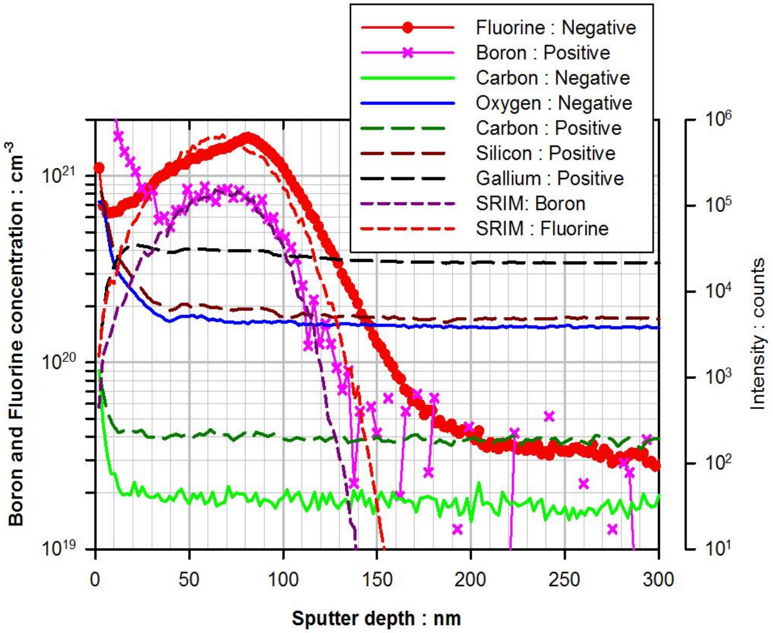
R. J. Chater, A. J. Smith and G. Cooke, J. Vac. *Sci. Technol. B, Nanotechnol. Microelectron. Mater. Process. Meas. Phenom.*, 2016, 34, 03H122.

Simultaneous detection on FIB 200

Simion model of
secondary ion collection



BF_2 Implant into Silicon depth
profiled using Ga primary ions



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OREGON PHYSICS High Brightness Ion Beams

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5 Requirements for a New Instrument

Need SIMS for the low mass detection H, Li and O.

1. Simultaneous positive and negative ion detection – two detectors
2. High ion yields and fast analysis time – 30 nm plasma FIB with Oxygen capability
3. In situ processing chamber – cleaning and sample prep
4. In-operando analysis – ability to bias and temperature cycle
5. UHV – Lithium is very sensitive to oxidation!

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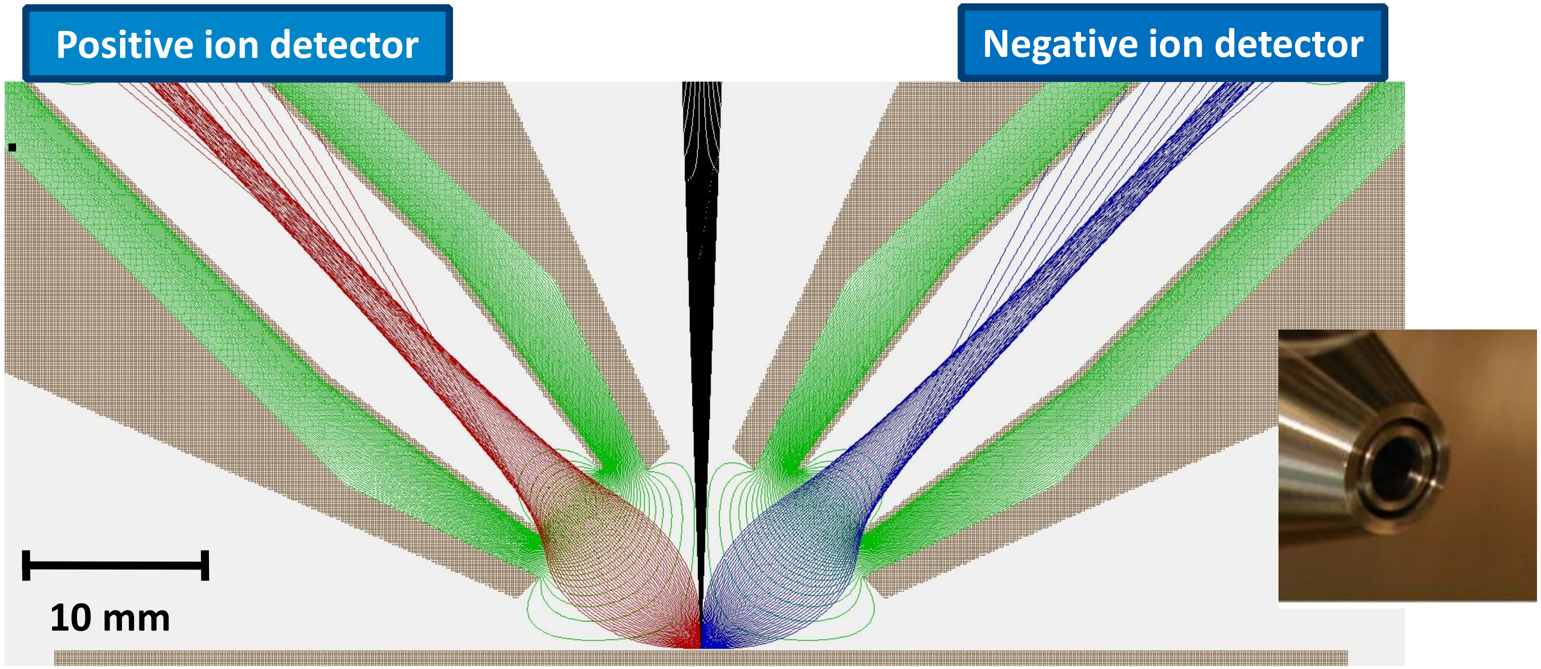

Positive Ions — Negative Ions — Primary Ions — Equipotentials

- SIMION ray-tracing model of a configuration for SPN secondary ion detection with **two Hiden EQS detectors**
- Sputtering by a normally incident primary beam.
- **Opposing balanced symmetrical fields enhance high collection efficiency**

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OREGON PHYSICS
High Brightness Ion Beams

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Hi5 SIMS Instrument

Hyperion II plasma FIB

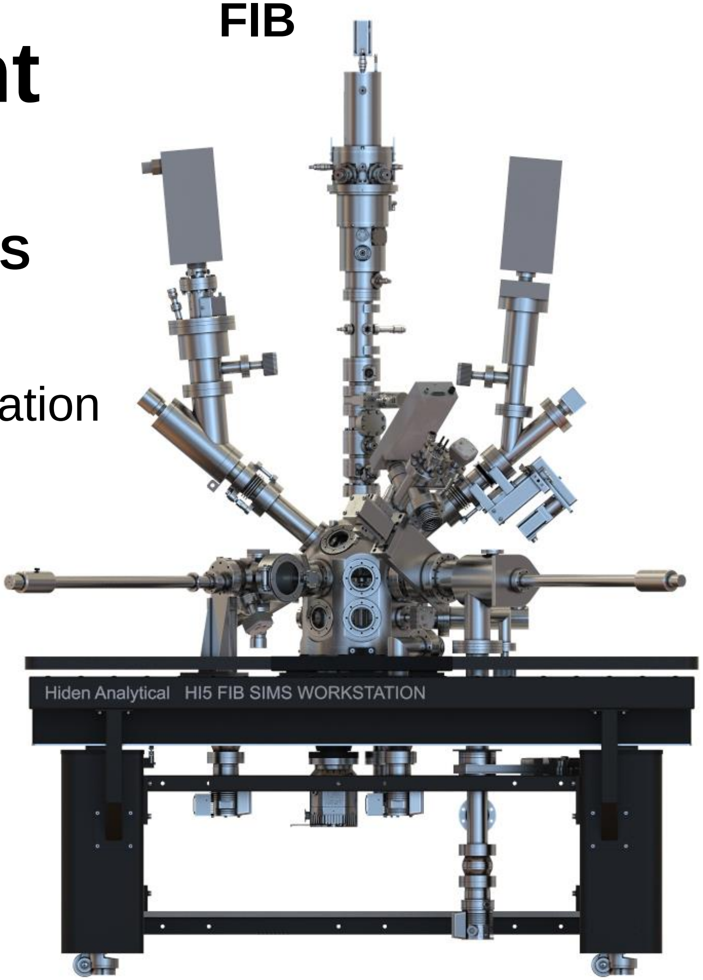
20 mm HMR quadrupole SIMS analyser

Charge compensation electron gun

Loadlock 1

UHV high stability chamber

5 axis stage



9 mm quadrupole SIMS analyser

Secondary Electron detector

IG5C caesium ion gun (Cs flood for –ve ions)

Loadlock 2 and process chamber

Anti-vibration table

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High Brightness Ion Beams

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Hi5 SIMS: Imperial College, Materials Dept., Surface Analysis Facility.
Full primary column build, November 2021. (Noel Smith, Oregon Physics)

Hi5 SIMS: UHV chamber configuration for 10mm working distance
5-Axis stage and Kleindiek piezo probes, base pressure ~5e-9mbar

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High Brightness Ion Beams

Hyperion II – *Plasma source parameters*

- 0 to ±30kV (except Neon & Helium, which is 0-10kV)
- Spot size 30 nm FWHM
- Typically operates with Xenon, Argon, Neon, Helium or Oxygen
- Energy Normalized Brightness
  - + ions - Xenon: $1x10^4$, Oxygen: $4x10^3$, Helium: $6.5x10^3$ $Am^{-2}sr^{-1}V^{-1}$
  - - ions - Oxygen: $3x10^2$ $Am^{-2}sr^{-1}V^{-1}$
- Axial Energy Spread : 5eV (+ ions), 3.5eV (- ions)
- Lifetime > 2 years (+mode), >2000 hours (-mode)
- Stability <1% drift/ hour, <5% drift/24 hours

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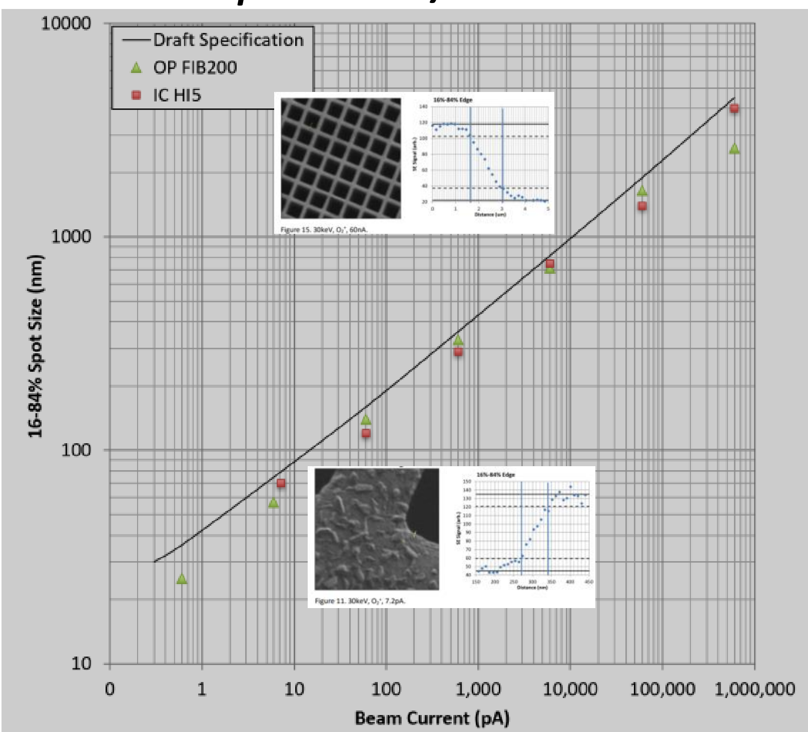
High Brightness Ion Beams

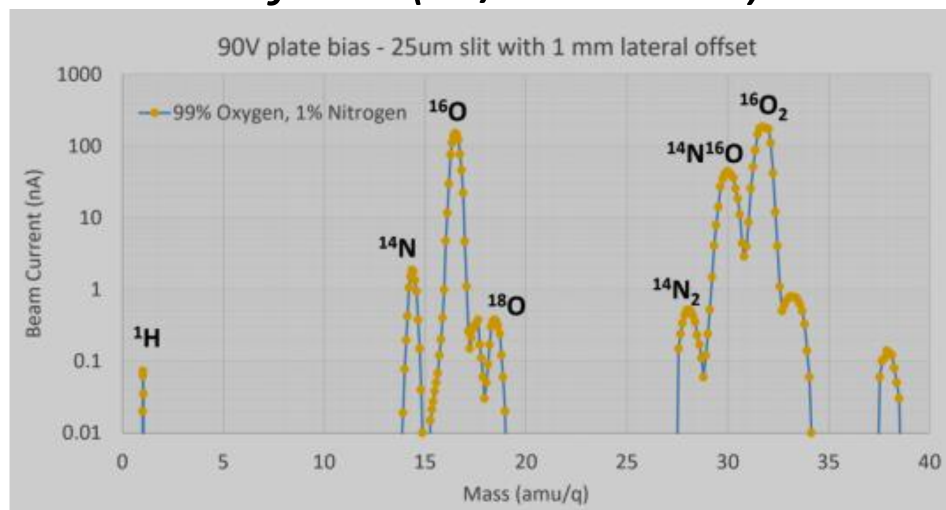
Hyperion II – *Plasma column performance*

30keV Oxygen beam:

spot size/current



mass filter (M/ΔM=37.5)



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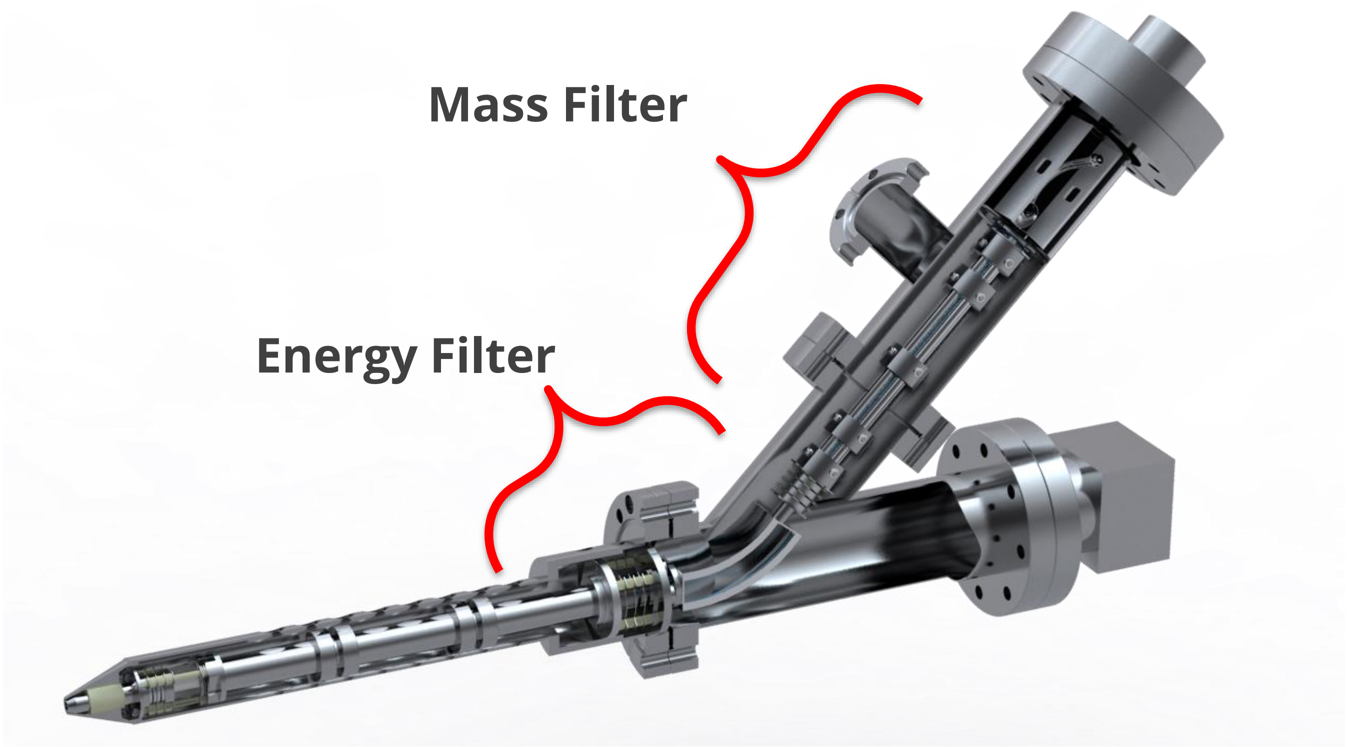
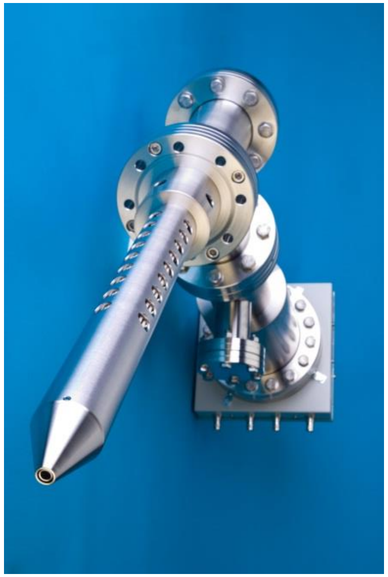
Hiden EQS: – On-axis sampling, energy resolving mass spectrometer for mass spectra with full 10^6 cps dynamic range of channeltron detector





Easily fits to other surface analysis instruments and FIB tools, eg Zeiss Nvision X-beam with EQS

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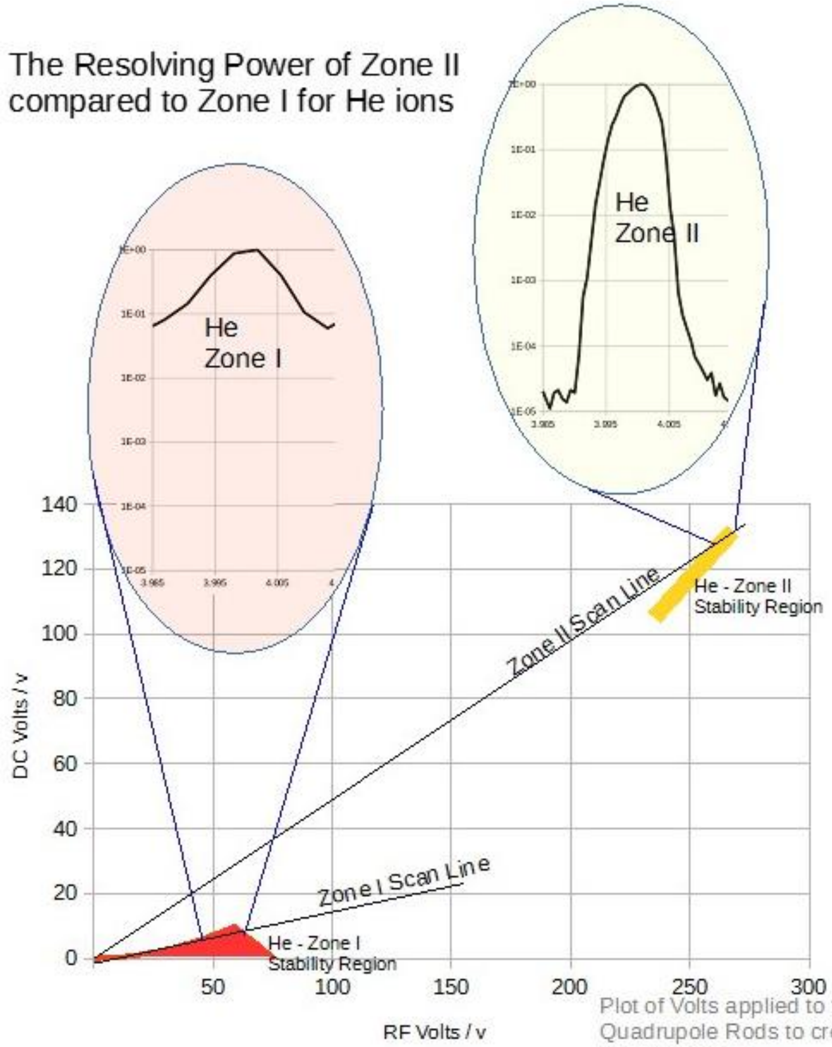
DLS-20 Mass Filter – 20mm pole diameter
Operates in both first and second stability region

Only the Resolving Power of Zone II gives ultimate detection limit for He in D_2

Quadrupoles operate with RF and DC Voltages applied to their rods which then carry ions to the detector
Certain voltage combinations can create 'stability regions' that transmit only ions of a particular m/z
Scanning the Quad's Voltages across the tips of these regions will carry only that ion to the detector
The Zone I region is most often used. However, a second region, Zone II, offers much greater Resolving Power – which helps separate adjacent masses
But only Quadrupole Electronics with both high power and stability can operate in this Zone
Hiden's High Power Electronics is now offered with selectable Zone I and II capability.

Switching time between zones typically 100ms.

The Resolving Power of Zone II compared to Zone I for He ions



Plot of Volts applied to the Quadrupole Rods to create stabilty regions

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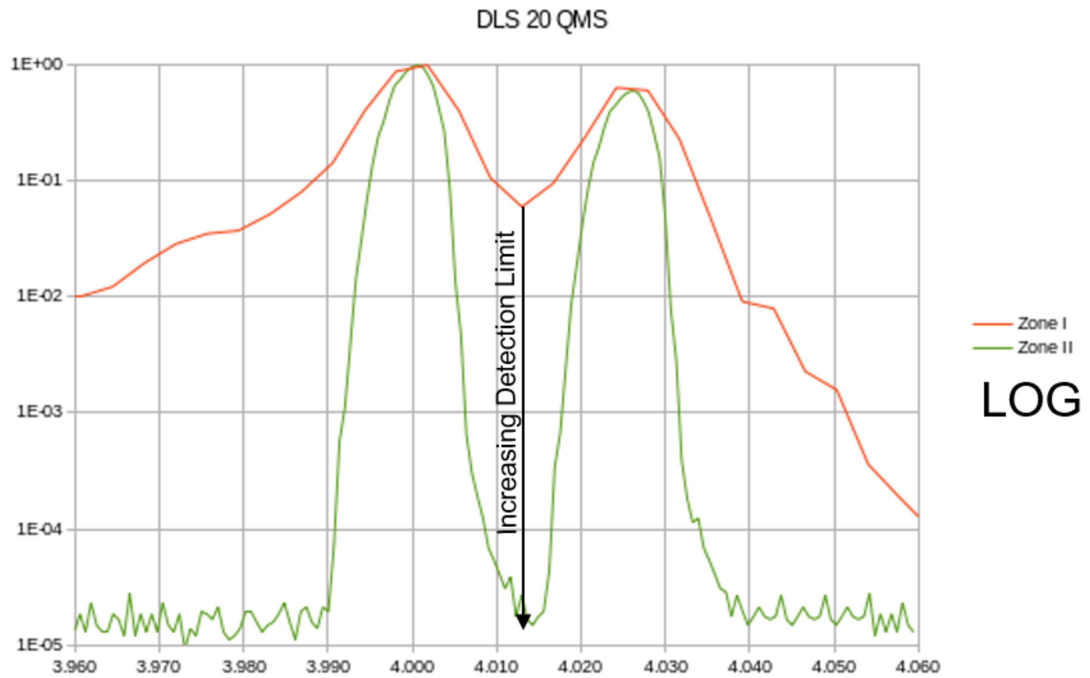
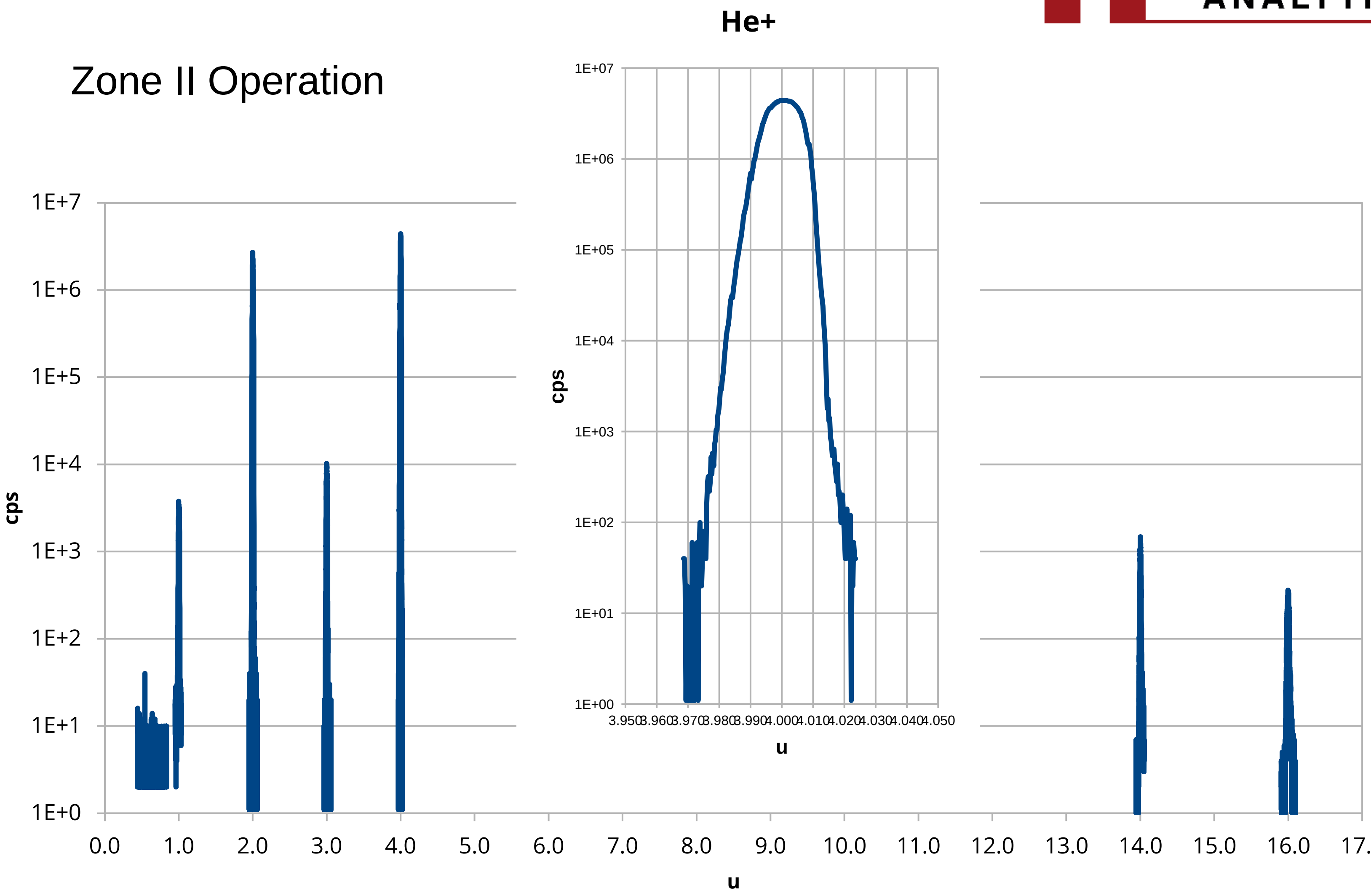
Detection Limits for He in D_2 depend on the Resolving Power of the Quadrupole. The benefits of operation in Zone II are clearly demonstrated – detection limit enhanced by almost four orders of magnitude!



Best FWHM to date

0.002 amu

Zone II Operation



Hi5-SIMS:
Lithium ion solid state battery cathode

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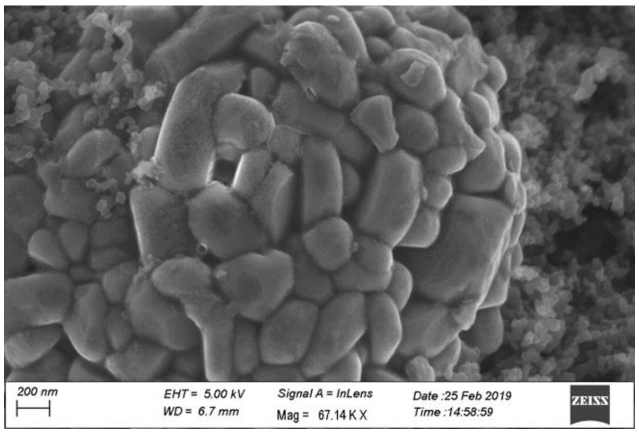
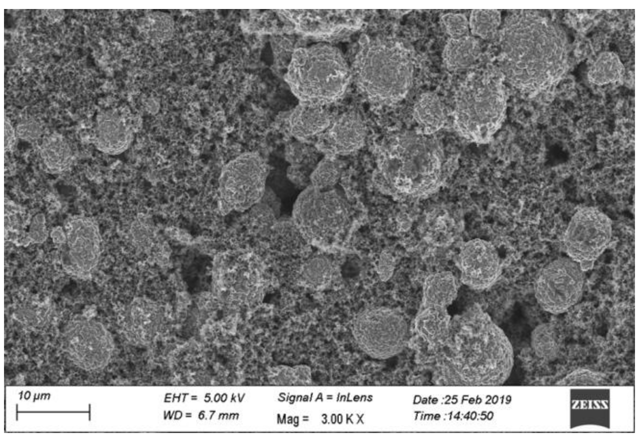
$Li(NiO_{0.8}Mn_{0.1}Co_{0.1})O_2$ + conductive carbon + PVDF binder (NMC)

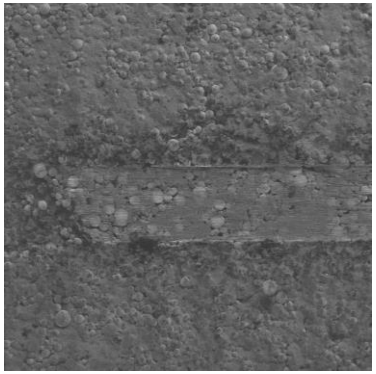
Rough surface prepared by etch and polish with xenon ion beam before SIMS

SEM image of rough surface

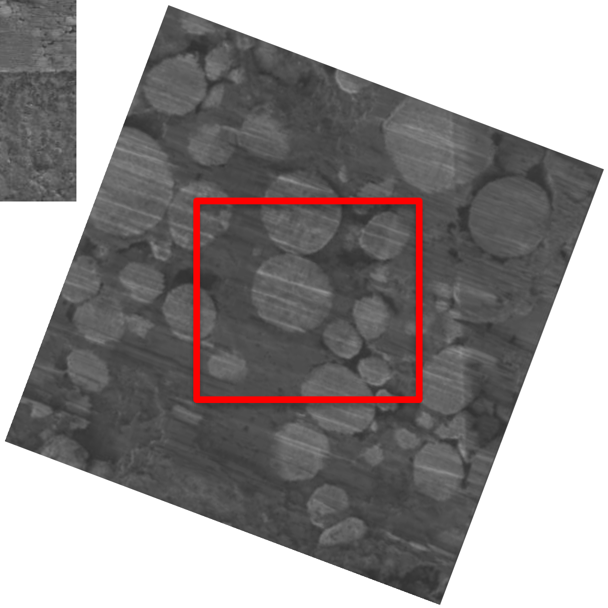




Hi5 SED image of beam polished ramp



Etched and polished ramp



SIMS imaged area on ramp 50um x 50um

<u>Dr Zhonghao Shen</u> & Dr Ainara Aguadero
Partners in the Faraday Institution Degradation Project

ELECTROCERAMIC MATERIALS

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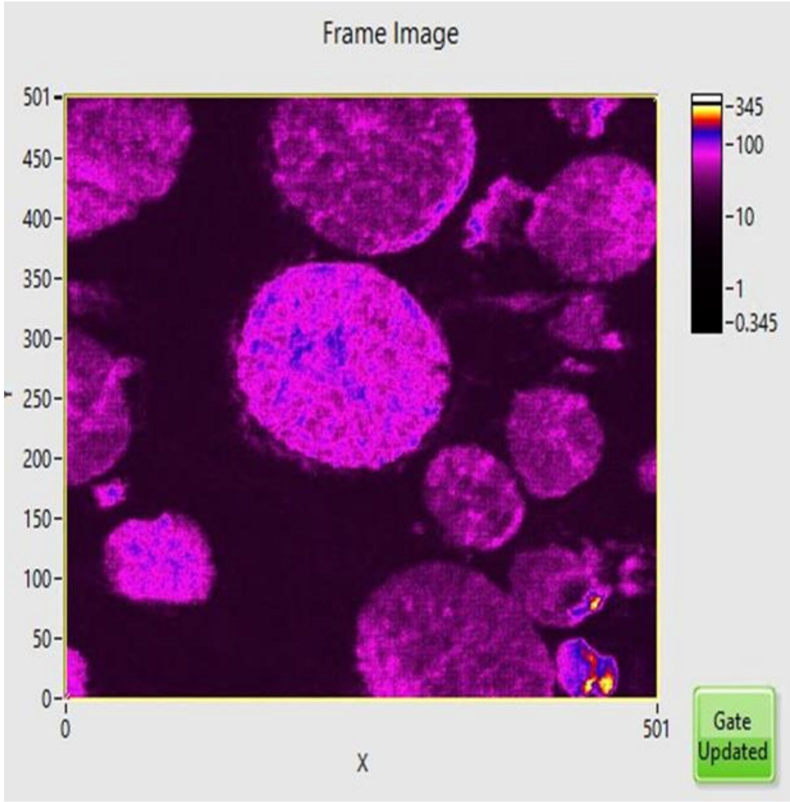
Hi5-SIMS: Lithium ion solid state battery cathode

$Li(NiO_{0.8}Mn_{0.1}Co_{0.1})O_2$ + conductive carbon + PVDF binder (NMC)

Simultaneously mapped area with 100 nm pixel resolution

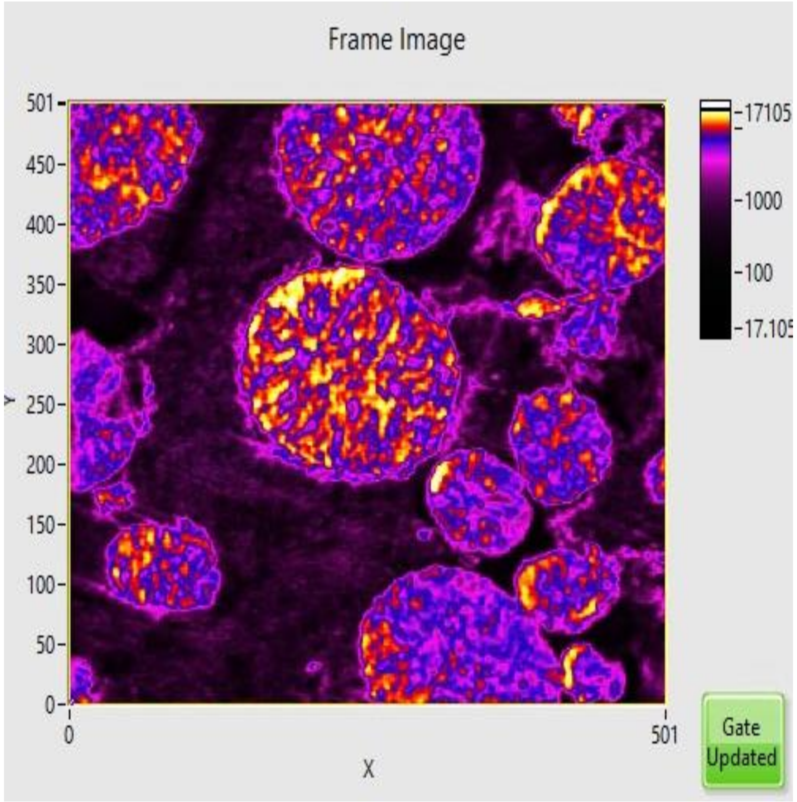
Negative SIMS image

$O16^-$, 50um area, 500 x 500 pixels, 0.1um resolution, countrate scale



Positive SIMS image

Li7+, 50um area, 500 x 500 pixels, 0.1um resolution, countrate scale



Dr Zhongao Shen & Dr Ainara Aguadero

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Hi5-SIMS:
Lithium ion solid state battery cathode

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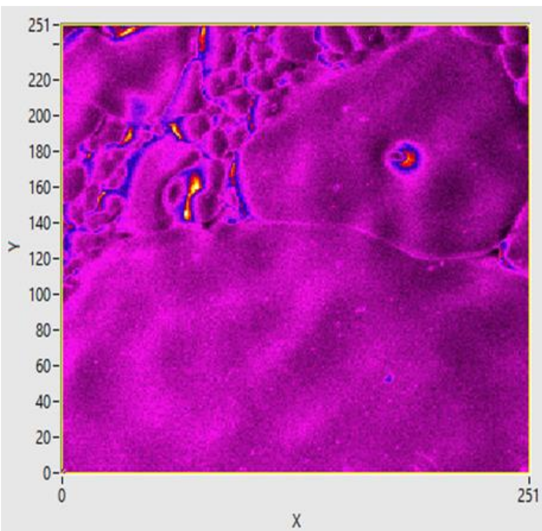
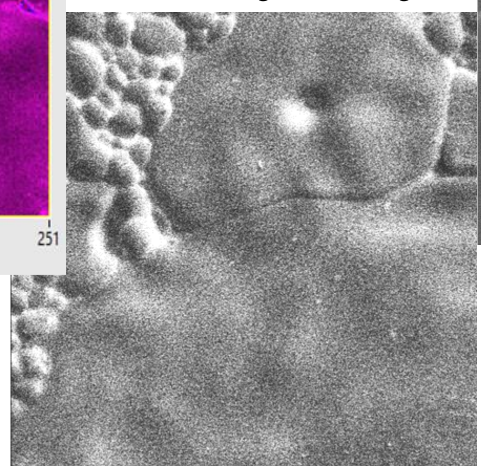
Lithium-stuffed garnet, $(NiO_{0.8}Mn_{0.1}Co_{0.1})O_2$ (LLZO)

Grain boundary selection for in-situ electrochemical analysis

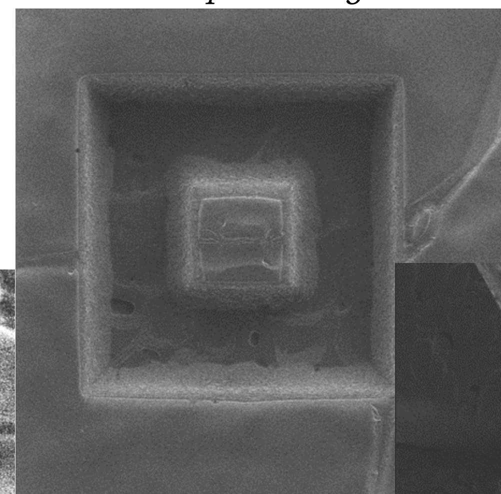
Negative SIMS image
$O16^-$, 250um area, 250 x 250 pixels



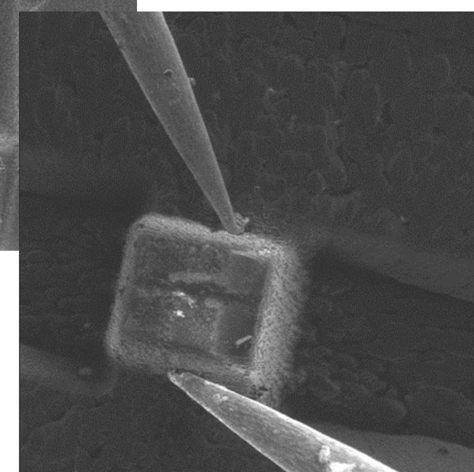
Total positive secondary ion image



Pillar structure using Xenon beam patterning with Raith Nanosuite patterning



Microprobe contacts to pillar for Electrochem analysis of grain boundary



Dr Nomaan Nabi, Dr Ainara Aguadero & Prof Stephen Skinner, CDT-ACM, Materials Department.

Conclusion

Hi5 is a simultaneous positive and negative UHV plasma FIB-SIMS instrument specifically aimed energy storage, corrosion and fuel cell applications.

It also has micro-machining capability for sample preparation and chambers for isotopic diffusion studies.

A High mass resolution Quadrupole operating in first AND second stability regions reduces the effects of mass intereference.

Heating, cooling and electrical contacts enables In-operando analysis for real time evaluation of the sample.