

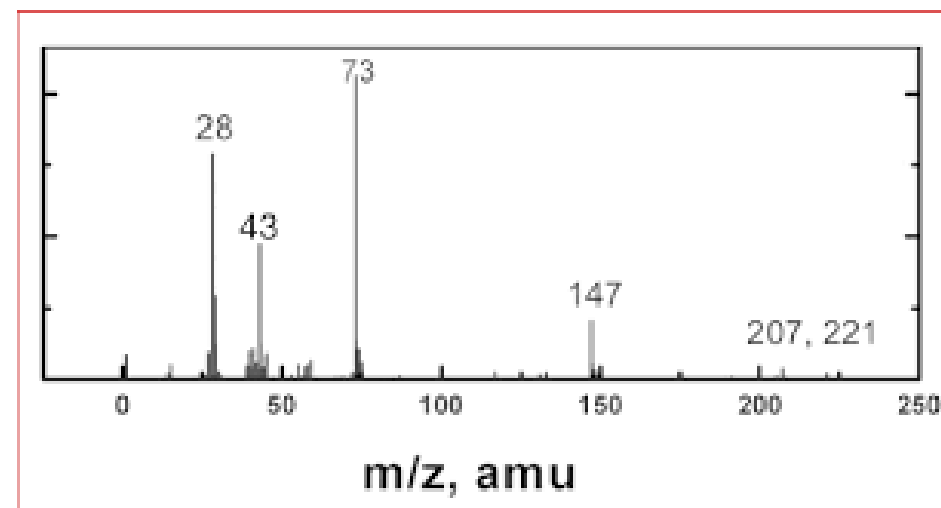
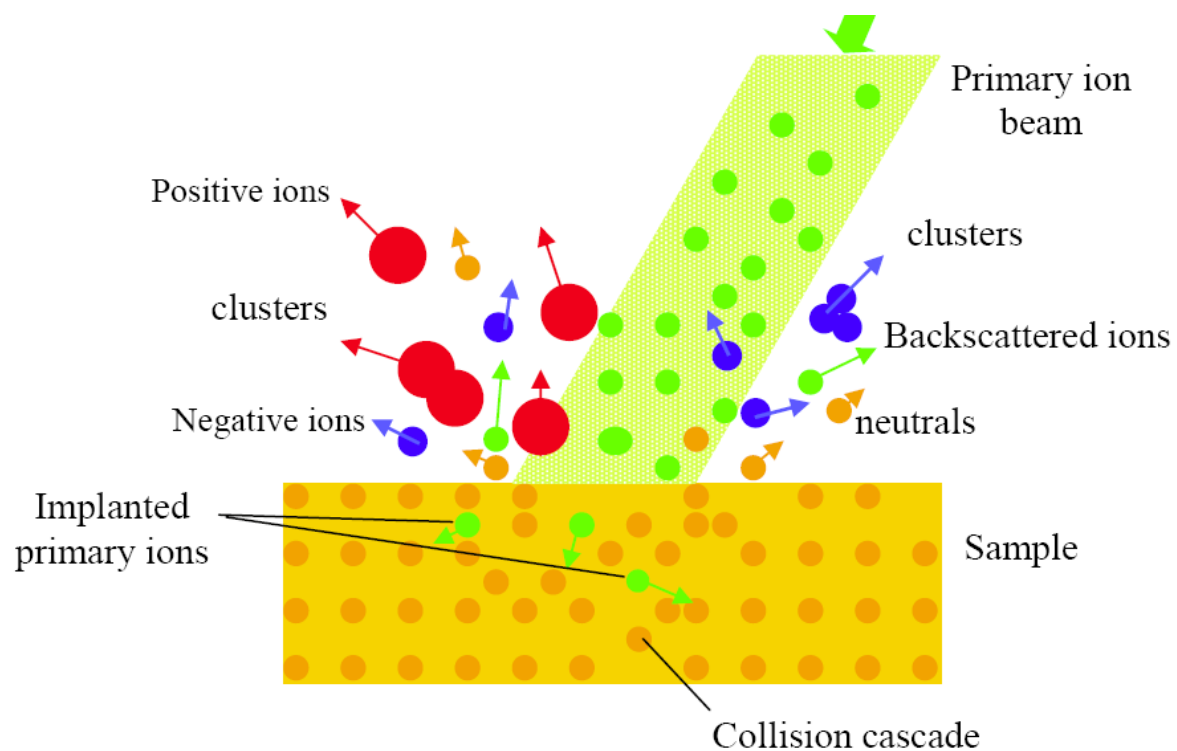
The principle and applications of ToF-SIMS

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Nuance Center
Northwestern University



Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS)

Not ToF MS (laser, solution)

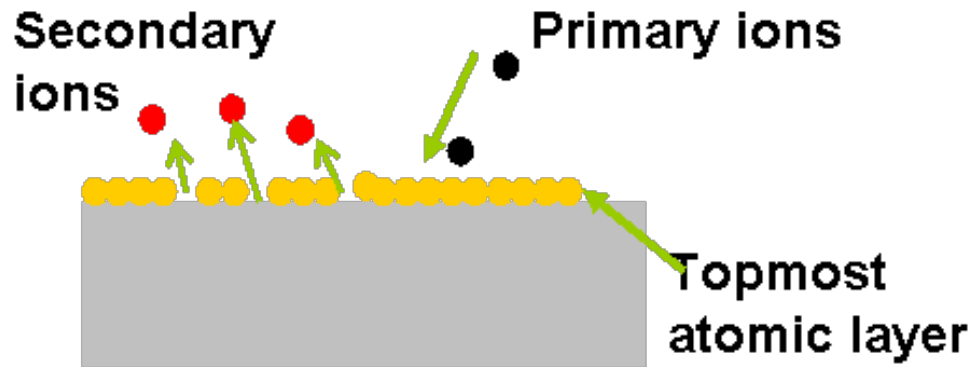


Modes of SIMS



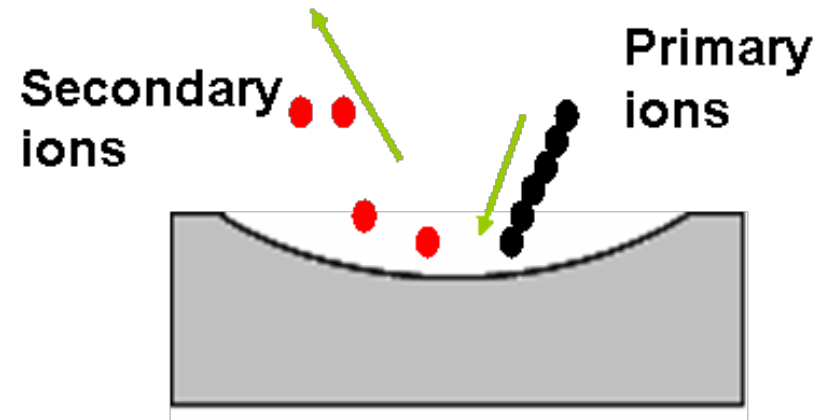
Bi/Ga primary beam

Static



Static SIMS: Secondary ions are ejected only from the topmost atomic layer

Dynamic

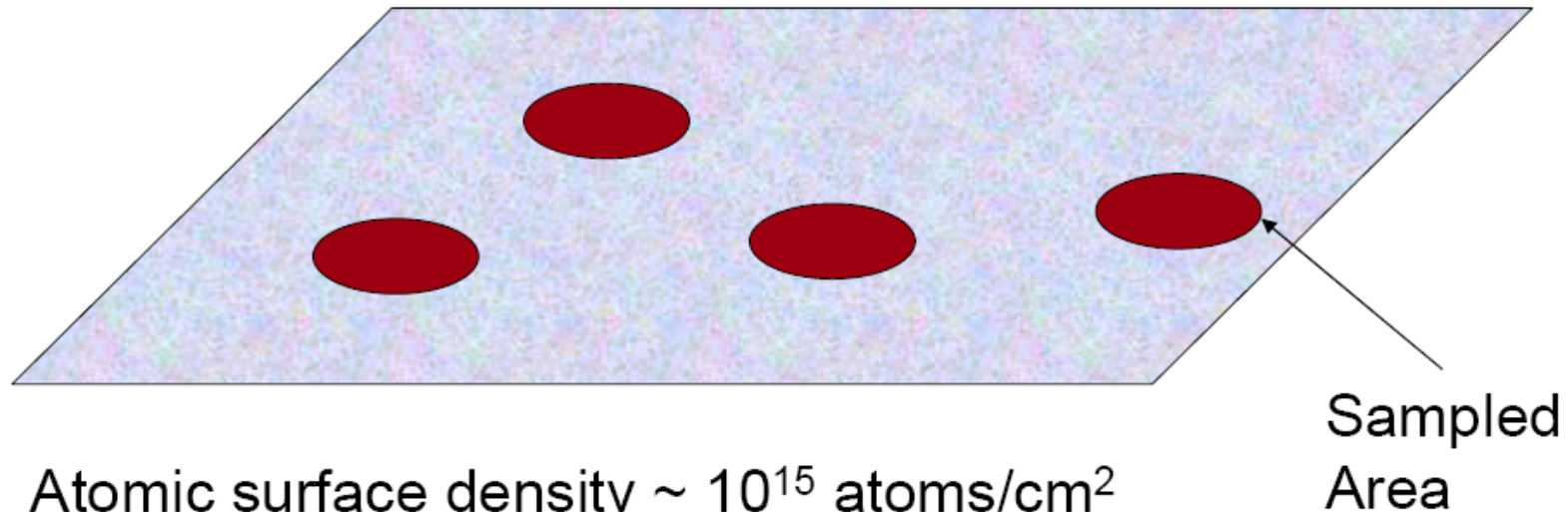


Dynamic SIMS: Top few monolayers are removed because of sputtering caused by the high doses of primary ions

Cs/O₂ primary beam

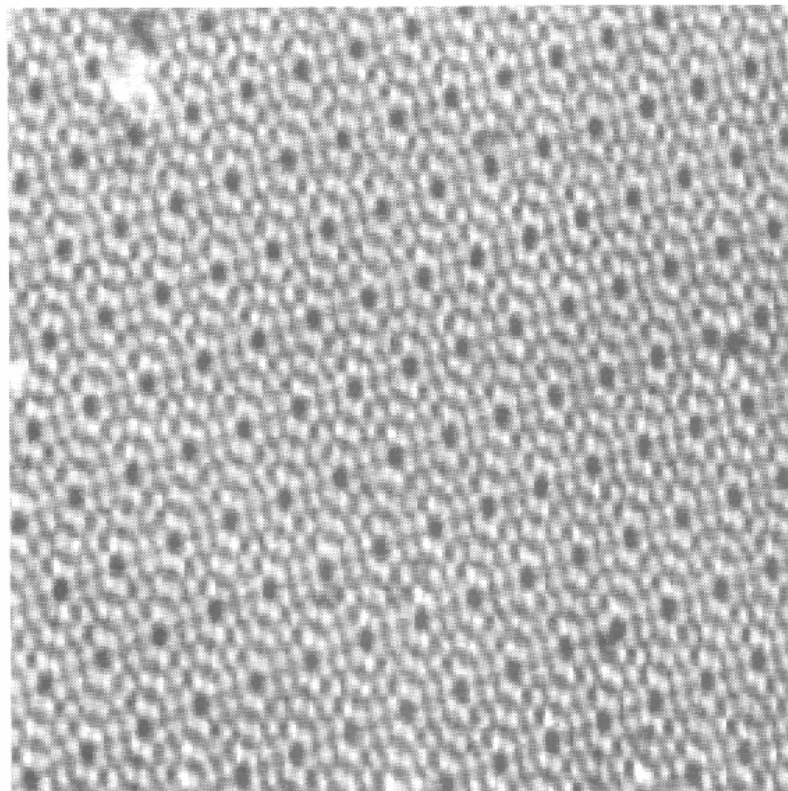
Definition of Static SIMS

When 'dose' of primaries is low: each ion strikes a *new* area of the surface = Static SIMS

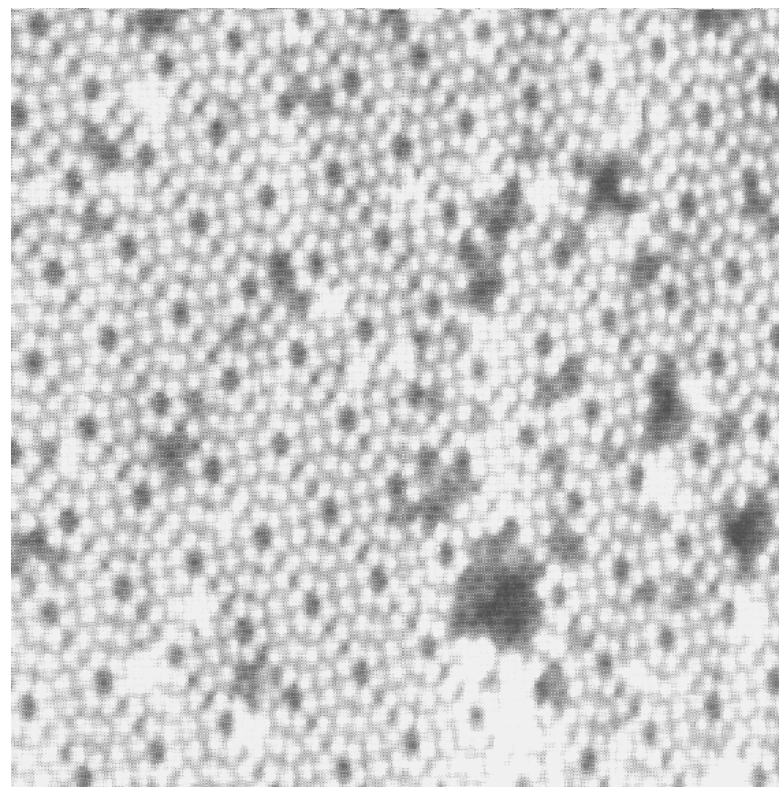


Atomic surface density $\sim 10^{15}$ atoms/cm²
Dose equivalent to $\sim 10^{12} - 10^{13}$ atoms/cm²
TOF-SIMS analysis optimized in this regime

STM Before & After Static SIMS



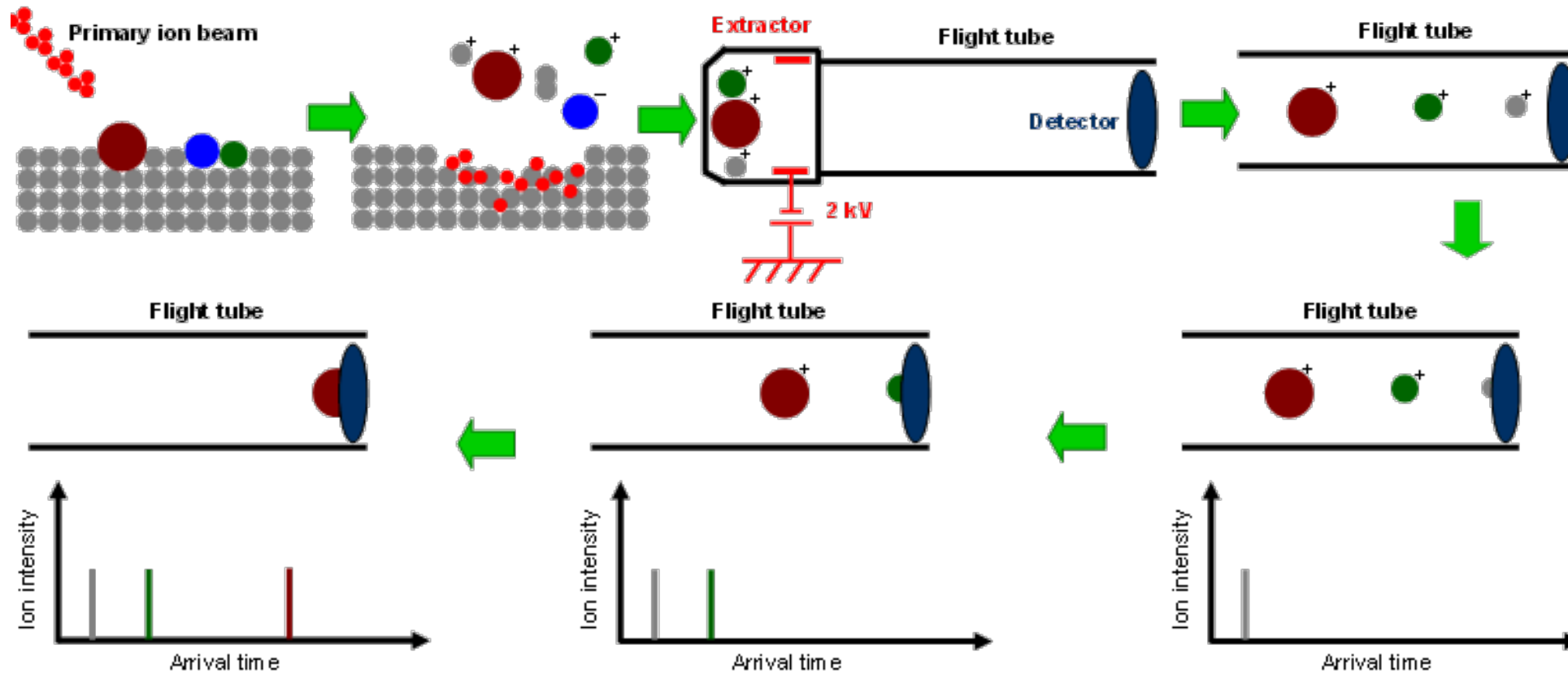
Si surface



Si surface exposed
to 3×10^{12} ions/ cm^2

H.J.W. Zandvliet et al. in *SIMS VIII Proceedings*

Basic Principles

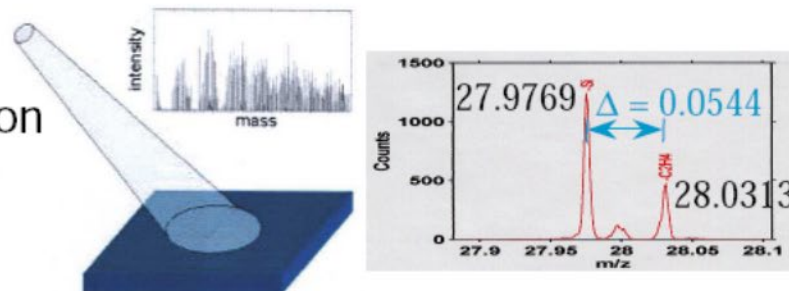


- Each pulse of primary ions create pulse of secondary ions.
- Secondaries of different masses within a single “cycle” arrive at the detector at different times according to the relation: $K.E = \frac{1}{2} * mV^2$

Modes of Operation

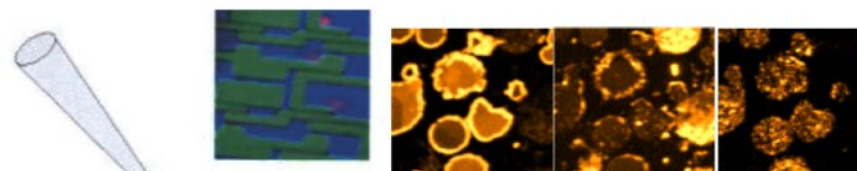
Surface Spectroscopy

Elemental and molecular information
Unlimited mass range
ppm/ppb sensitivity
Mass resolution > 10,000



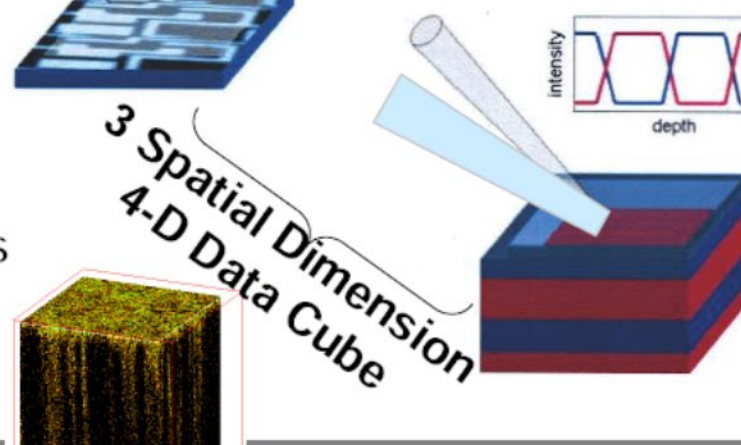
Surface Imaging

Parallel mass detection
Lateral resolution < 100 nm

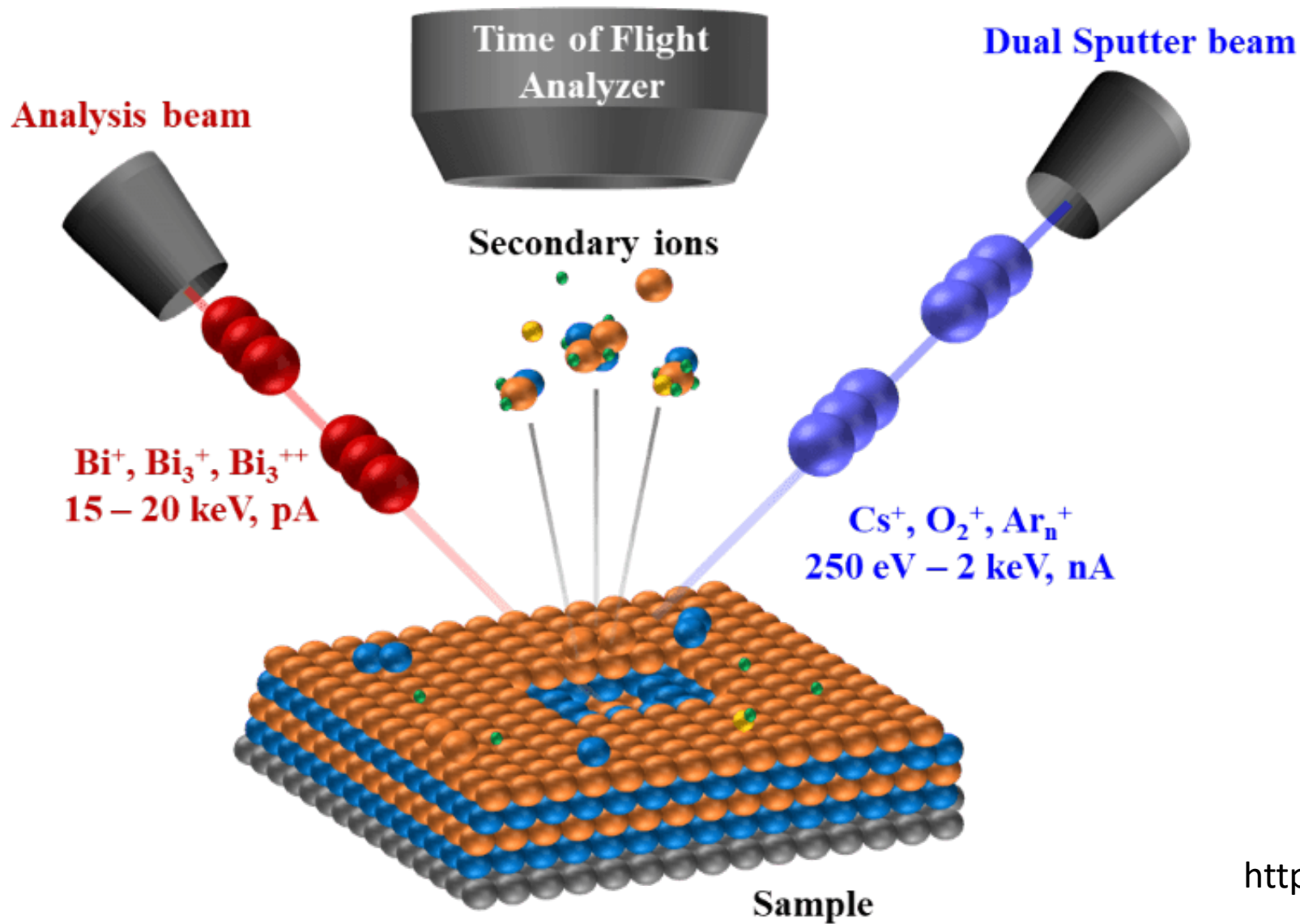


Depth Profiling

Depth resolution < 1 nm
Thin layers from 1 nm to microns
Parallel mass detection

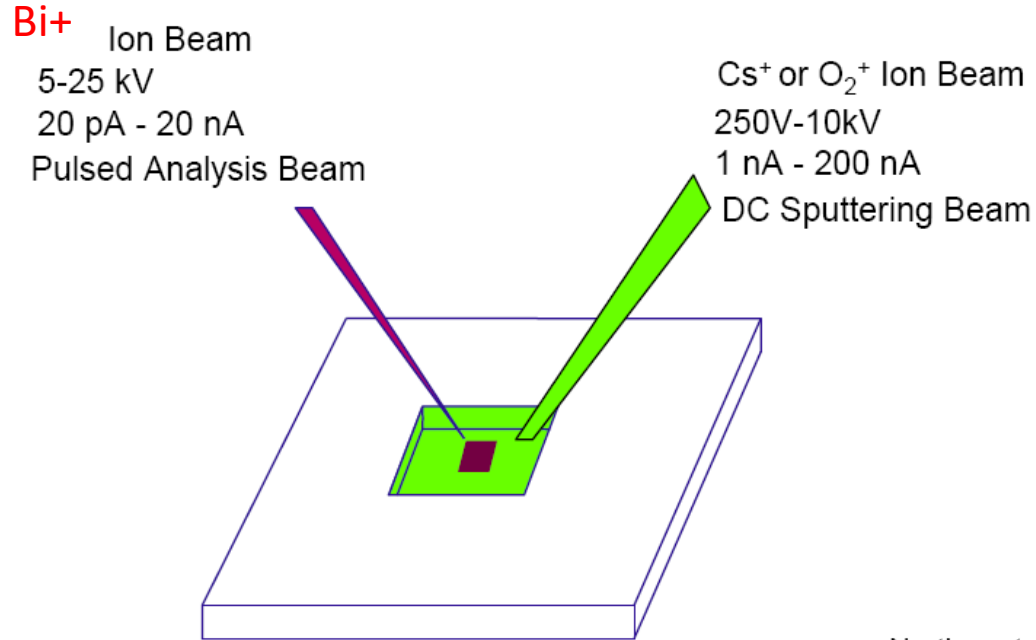


<https://www.osti.gov/servlets/purl/1147222>

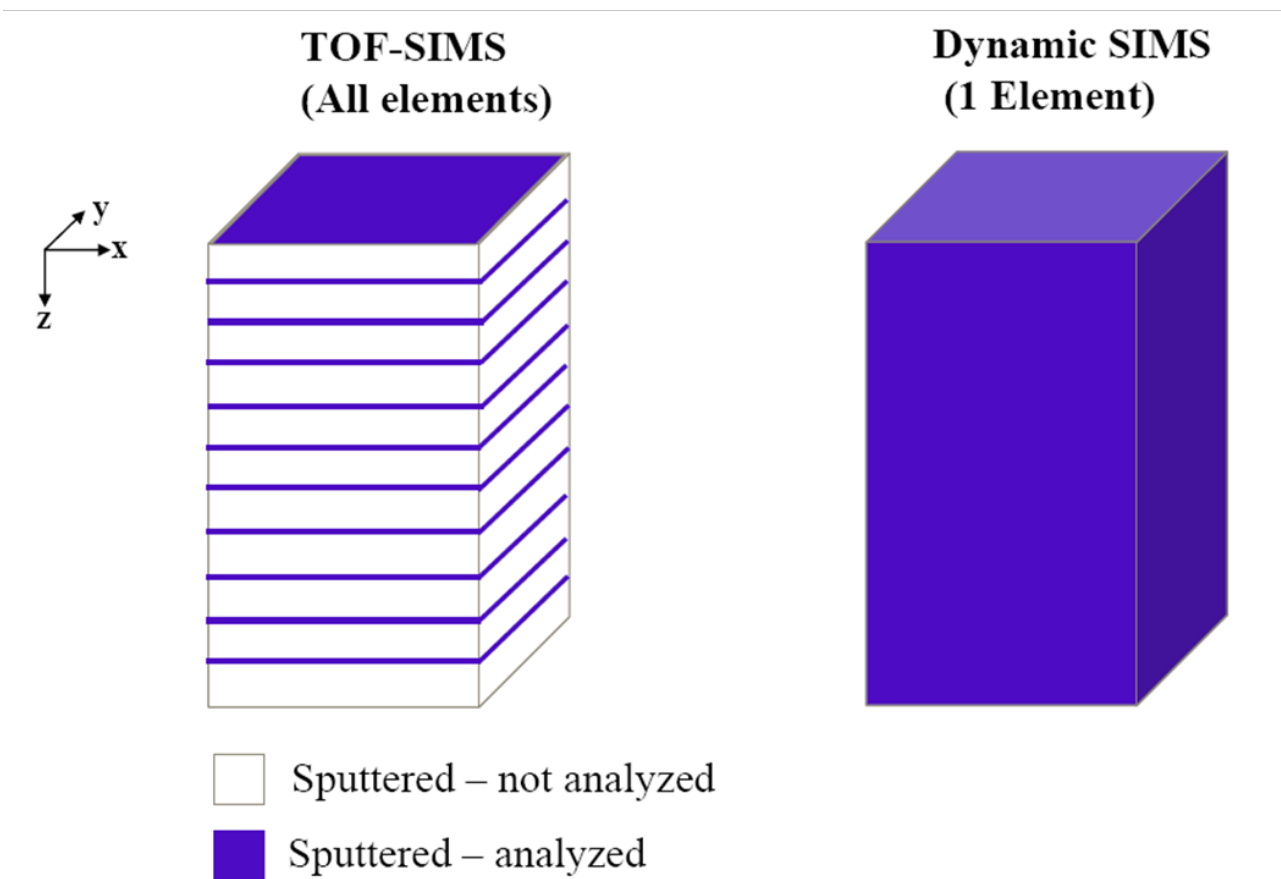


<http://simslab.rice.edu/>

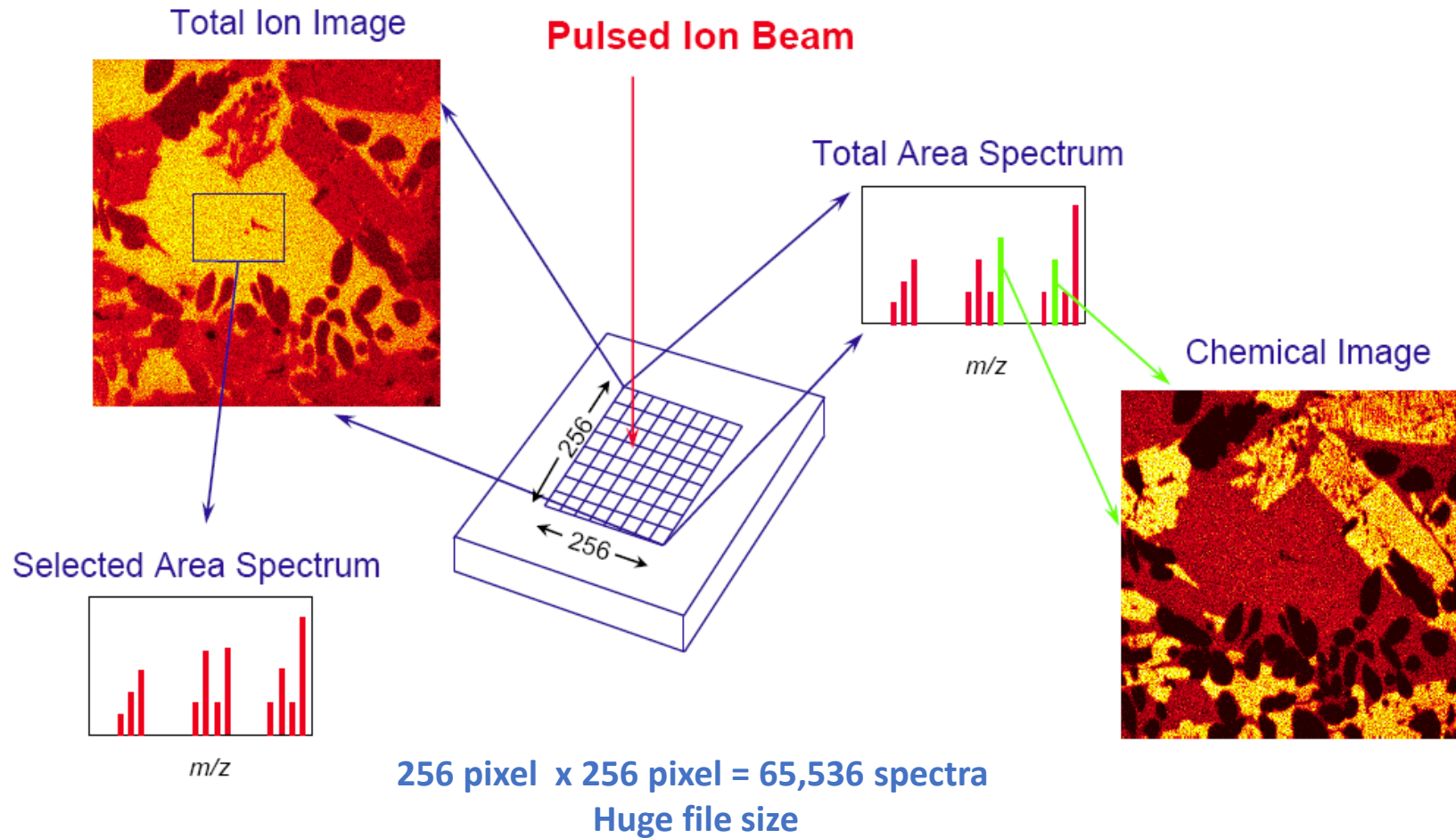
Depth profiling



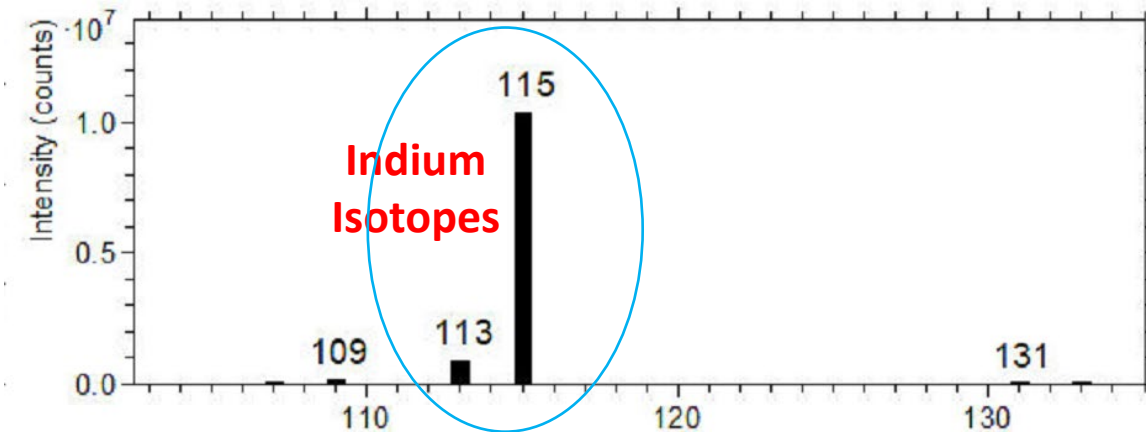
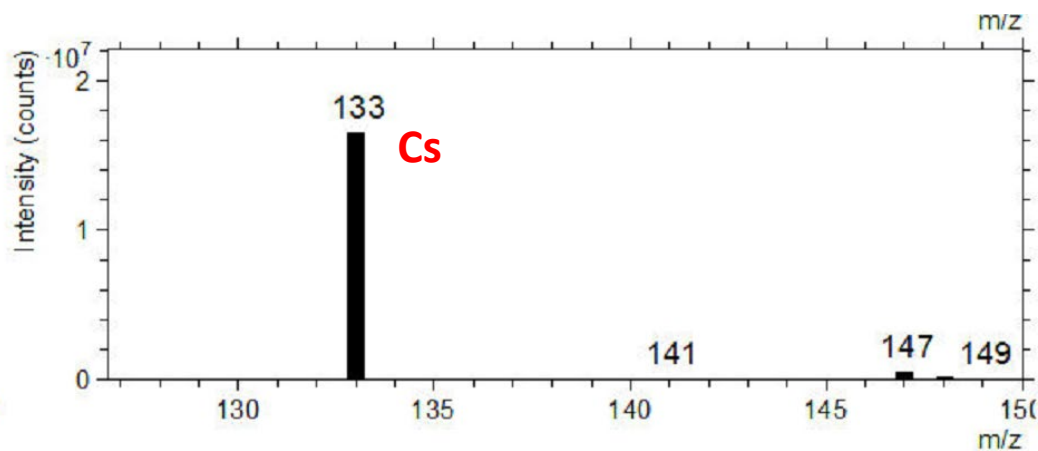
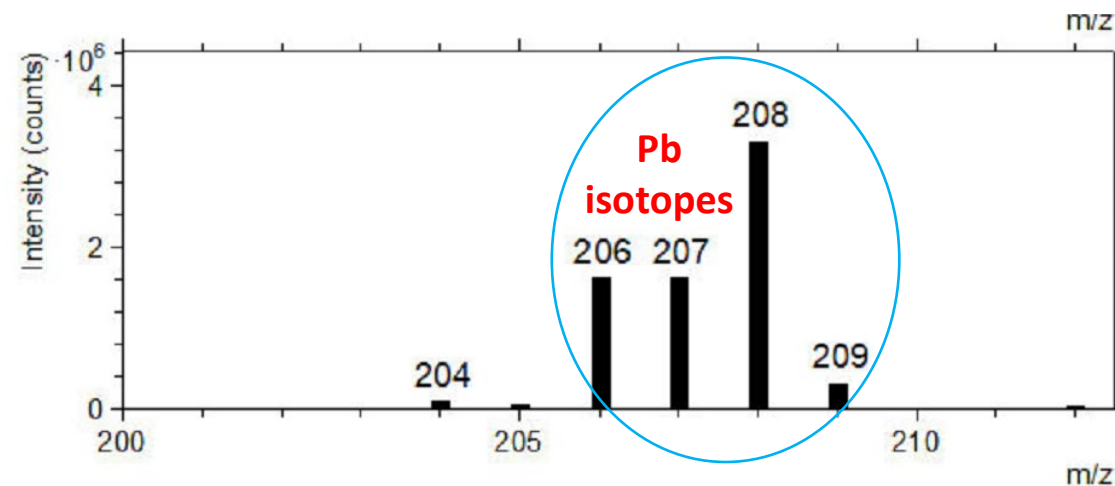
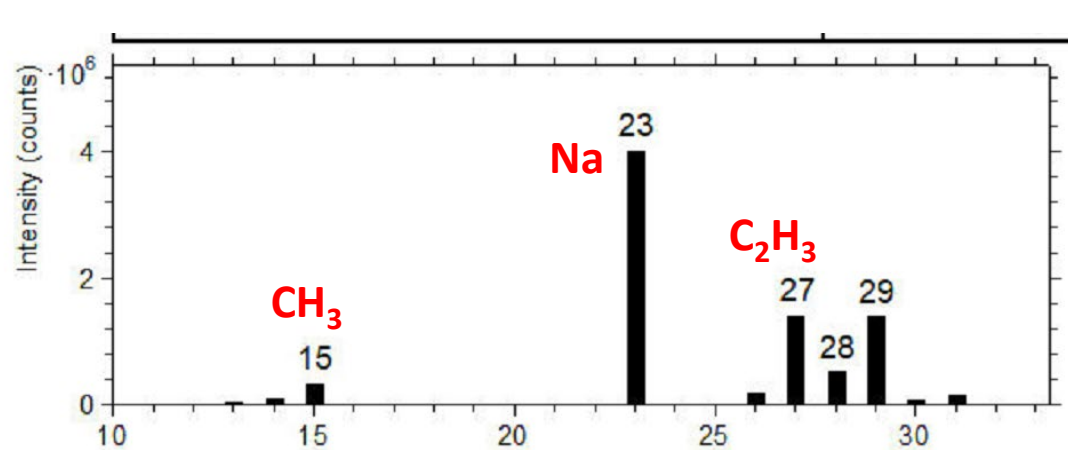
Comparison of Analyzed Volumes



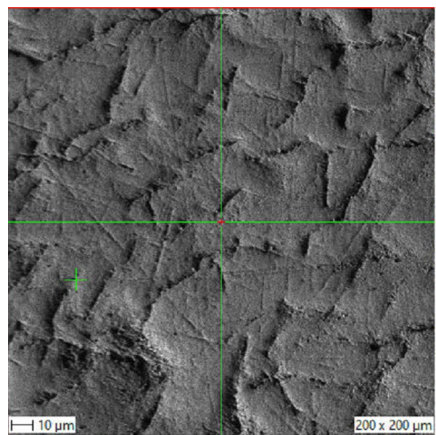
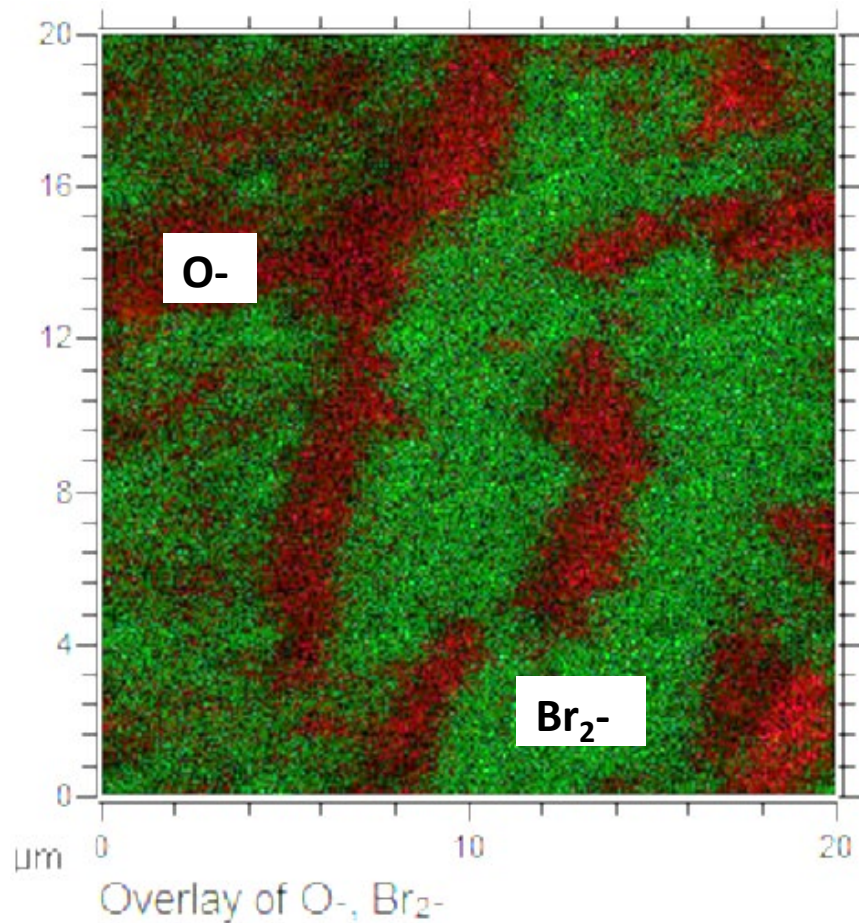
Post analysis with raw data



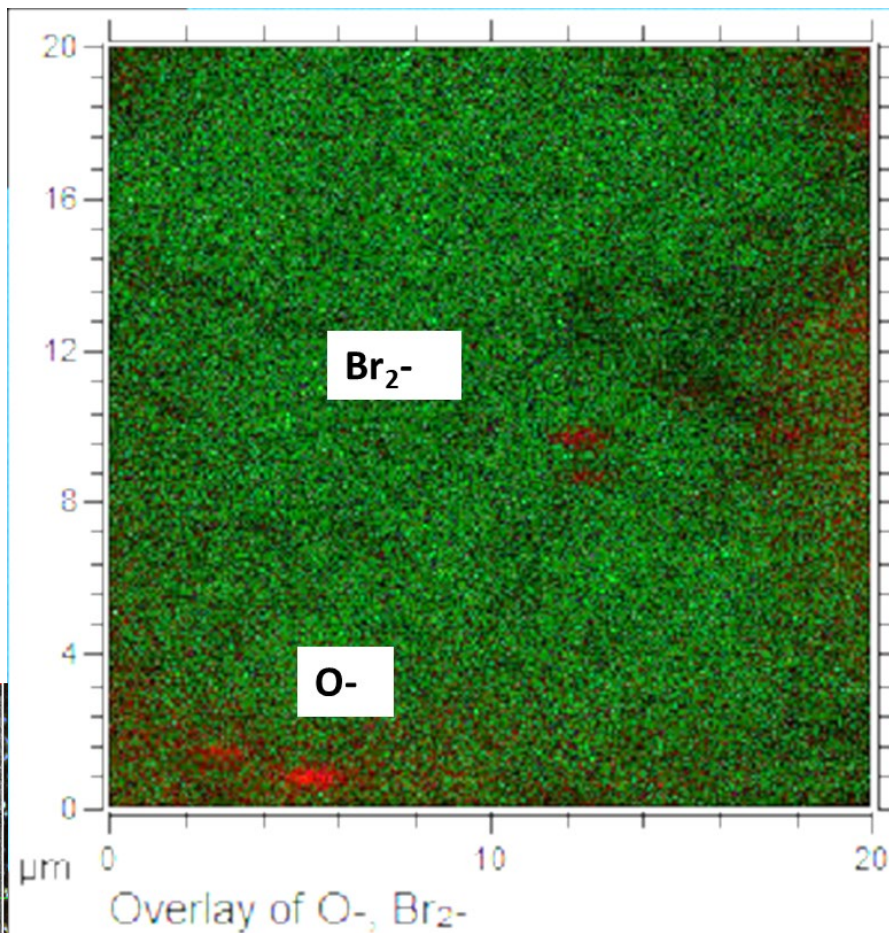
Secondary Ion Mass Spectrum



0.1% oxygen doped CsPbBr₃

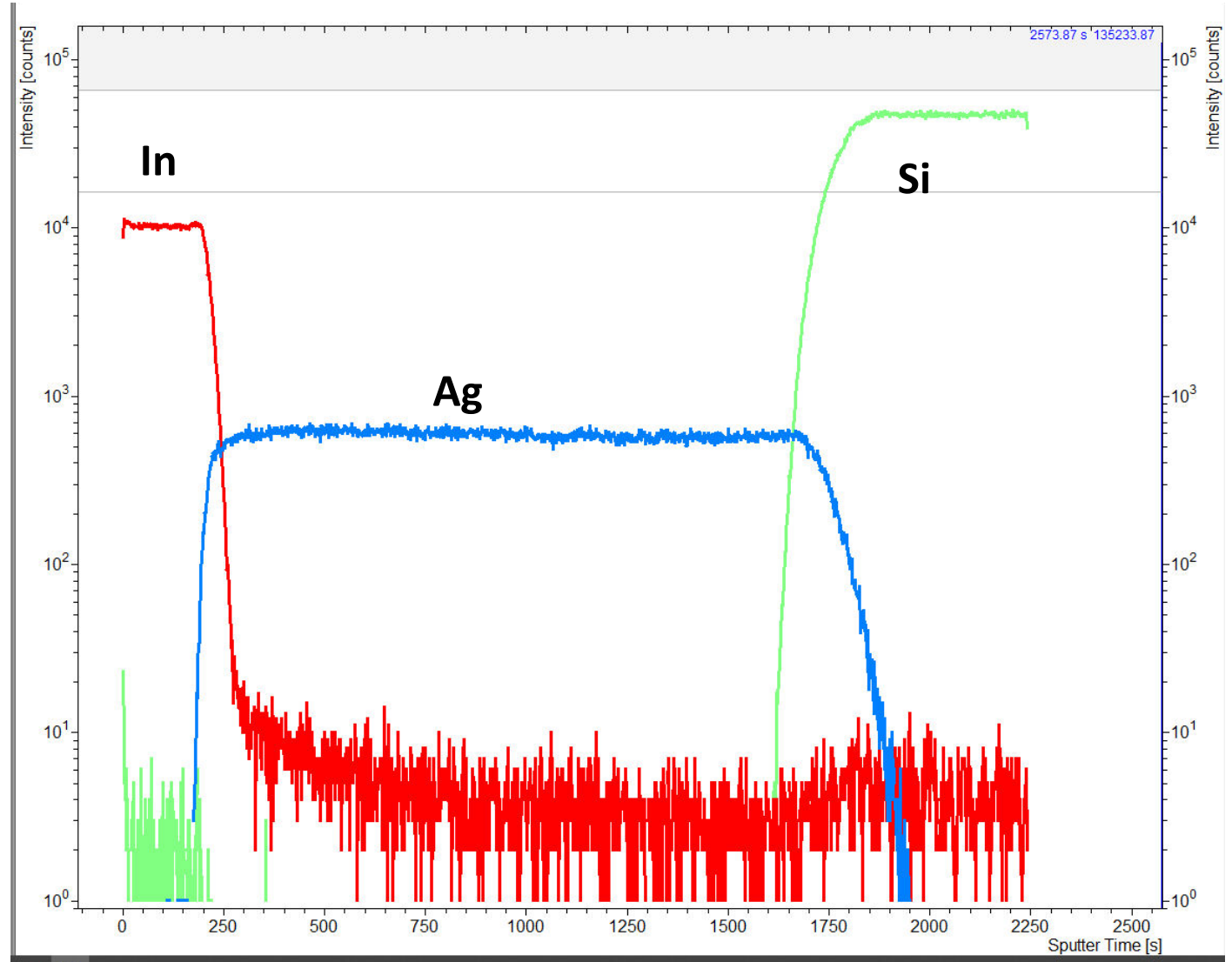
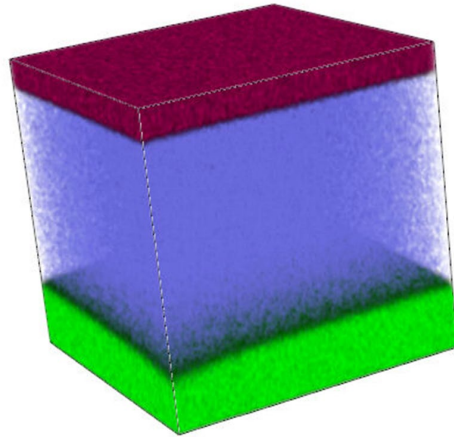
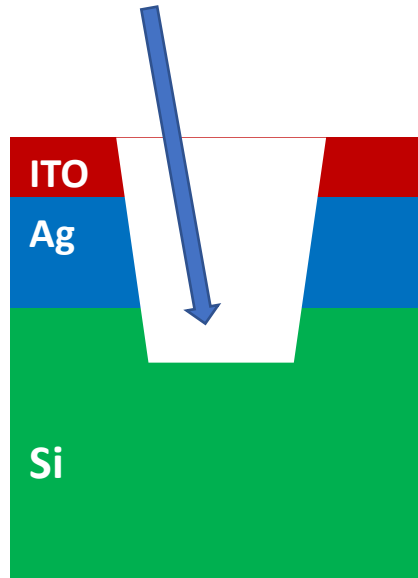


Undoped CsPbBr₃

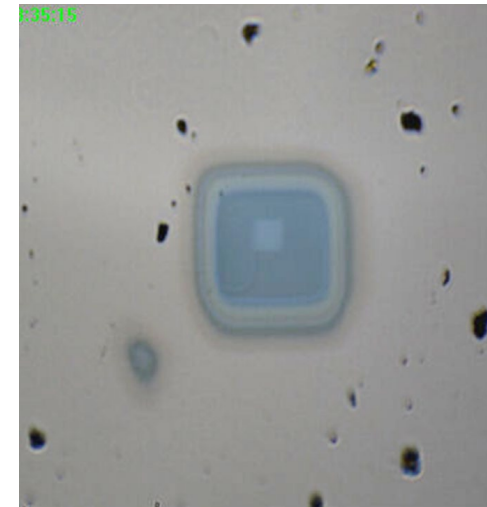
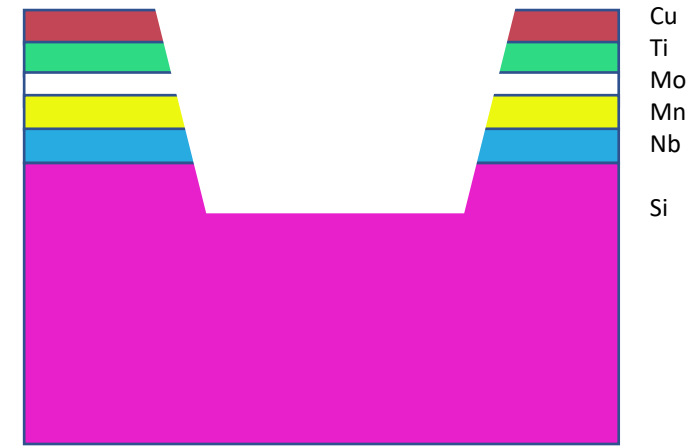
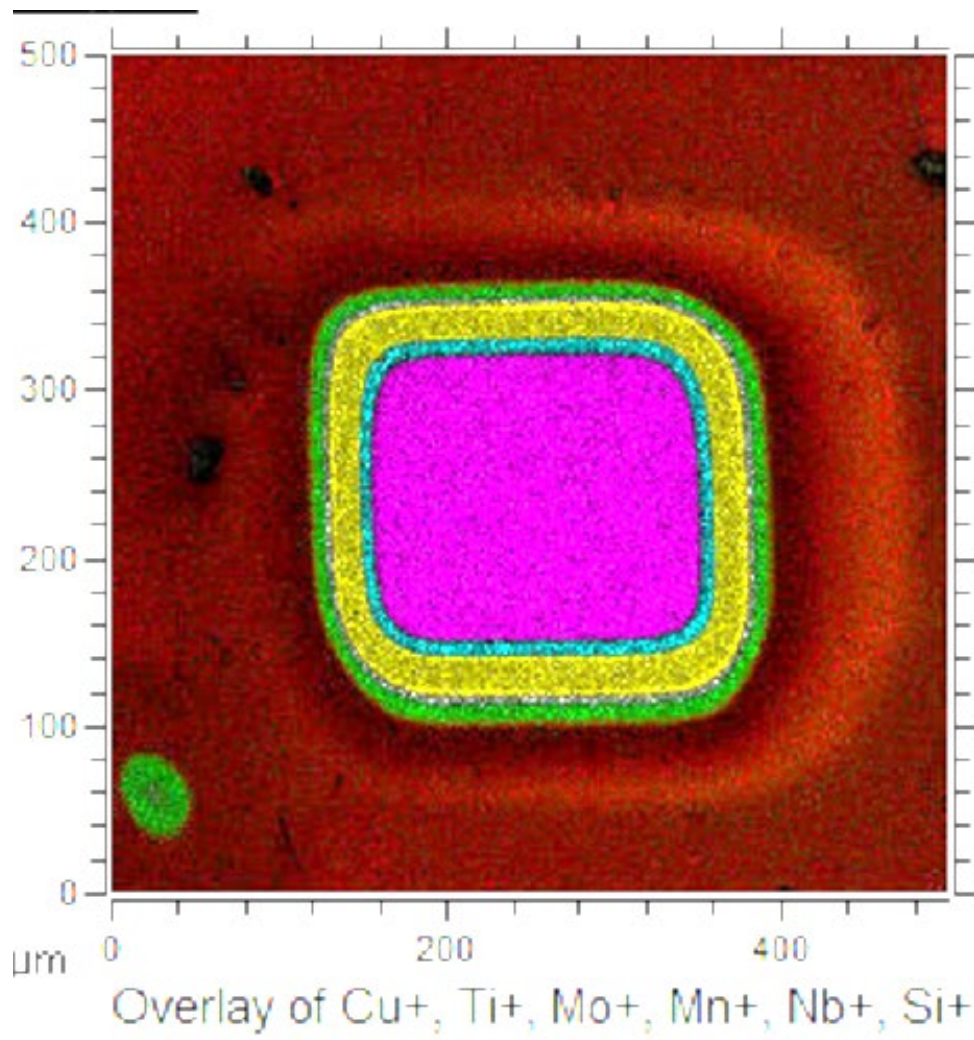


Depth profiling with oxygen gun

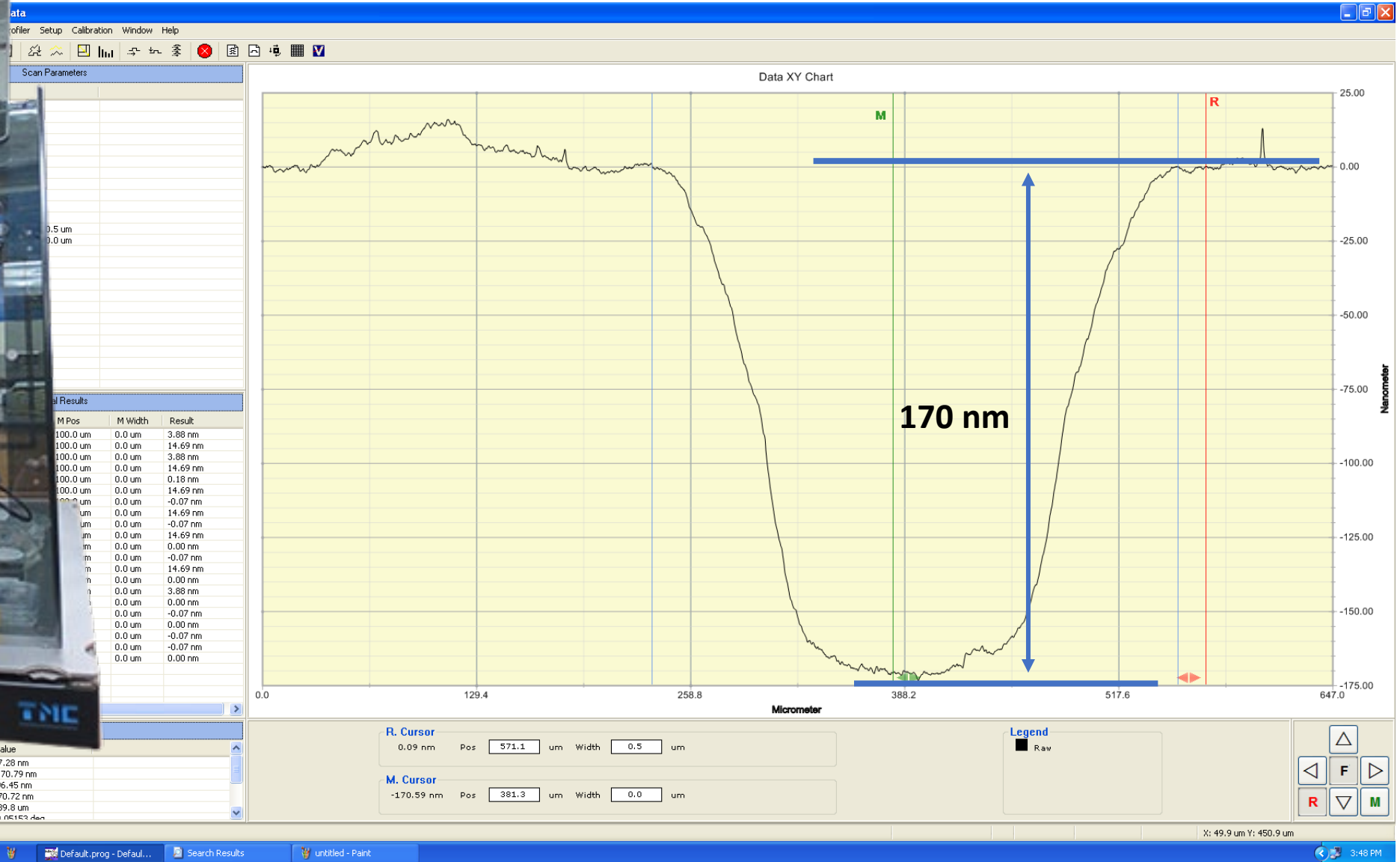
O₂, Cs, Ar



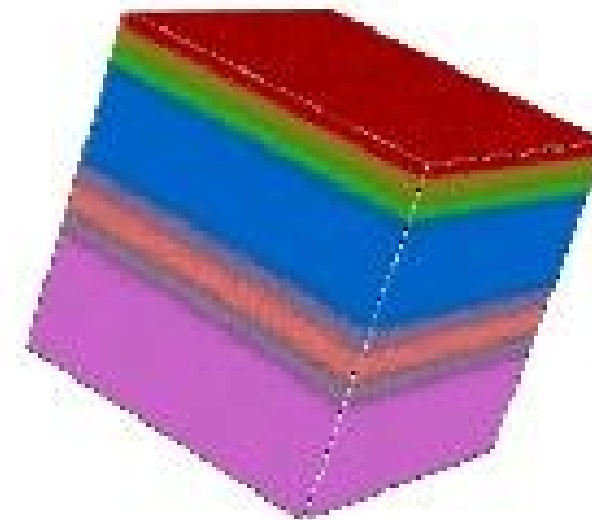
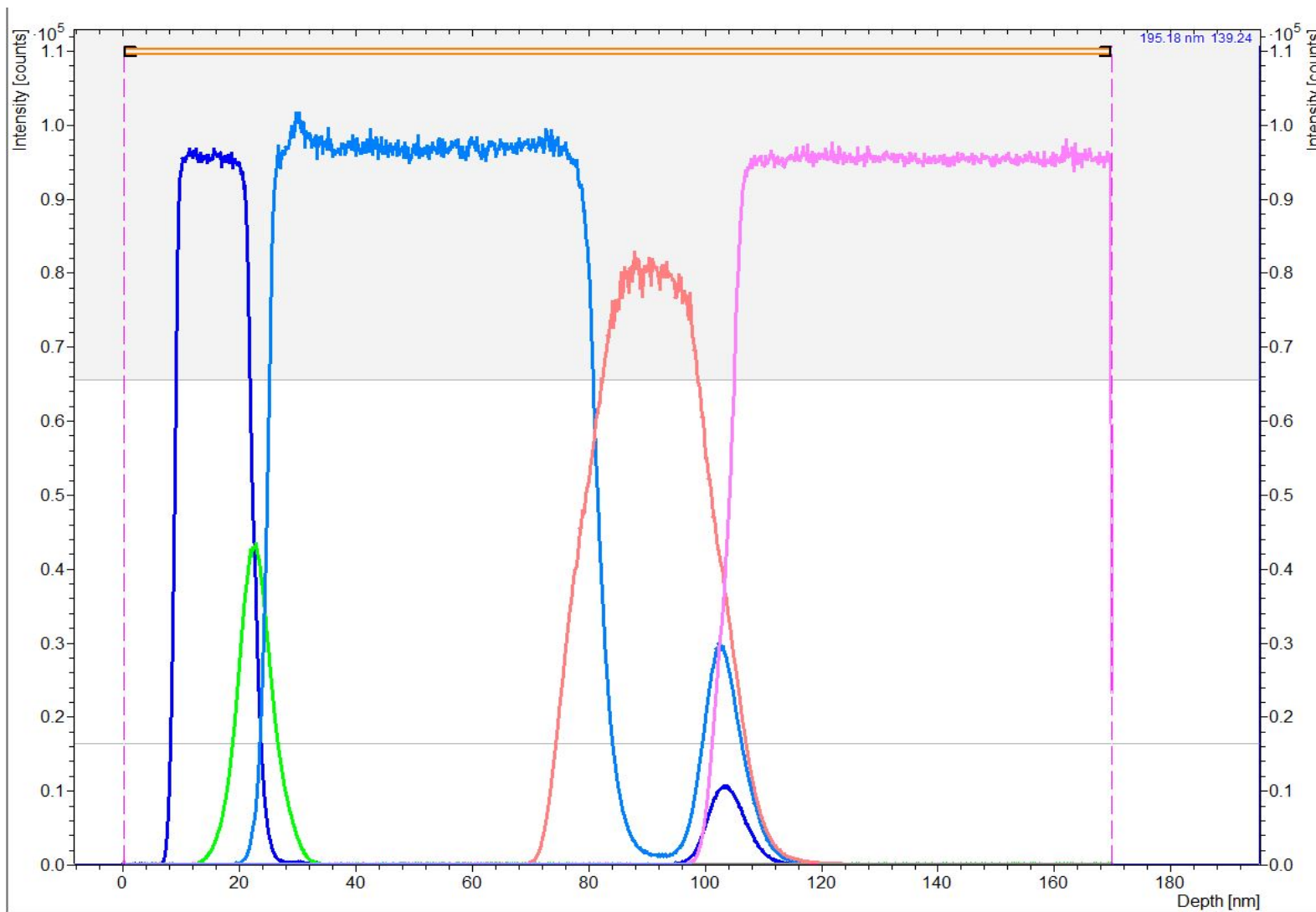
Depth Profiling on Cu/Ti/Mo/Mn/Nb on Si Wafer



Stylus Profilometer

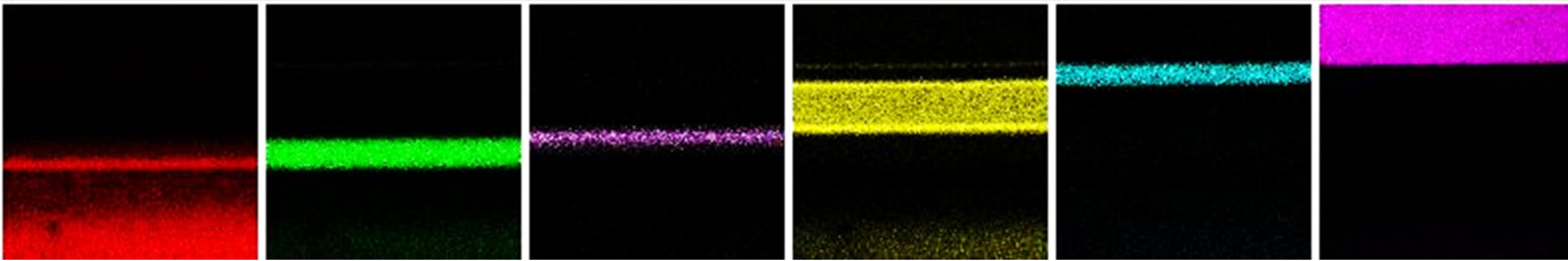


Depth profiling with oxygen sputter gun



3D reconstruction of the sputter crater

Mass Intervals					
<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	2		47.94	Ti+
<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	3		97.88	Mo+
<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	4		54.92	Mn+
<input type="checkbox"/>	<input checked="" type="checkbox"/>	5		92.90	Nb+
<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	6		27.97	Si+
<input type="checkbox"/>	<input checked="" type="checkbox"/>	7		15.99	O+
<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	8		28.97	$^{29}\text{Si}^+$
<input type="checkbox"/>	<input checked="" type="checkbox"/>	9		249.74	Nb_2O_4^+
<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	10		108.87	NbO+
<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	11		206.74	$\text{Cu}_2^{65}\text{CuO}^+$
Special Intervals					
<input type="checkbox"/>	<input checked="" type="checkbox"/>	1			total



Cu+

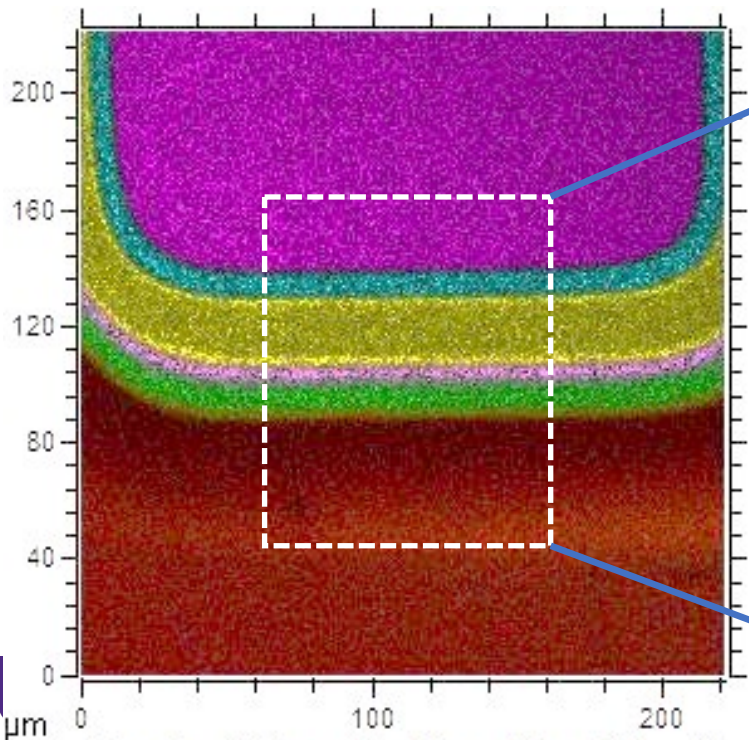
Ti+

Mo+

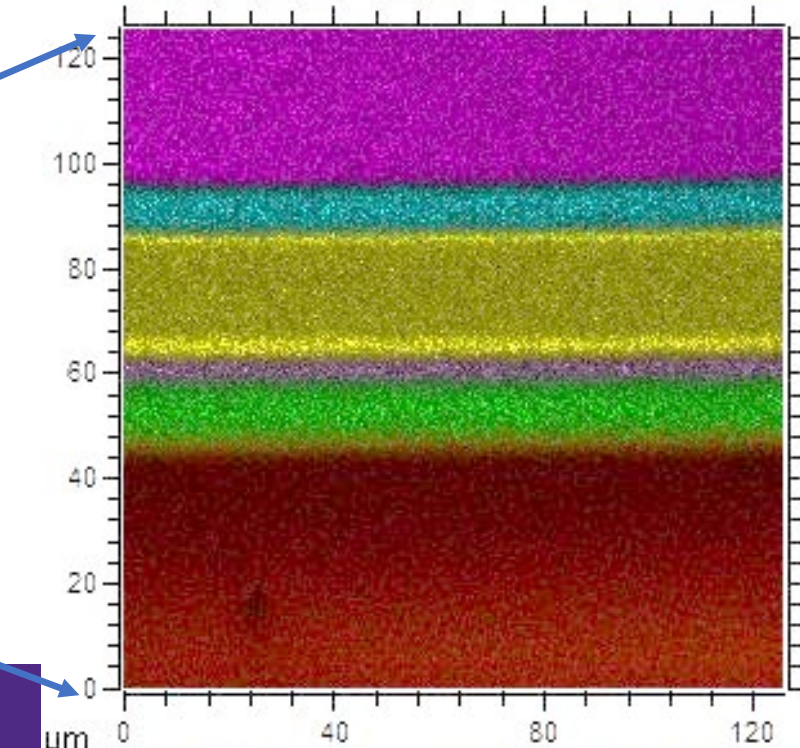
Mn+

Nb+

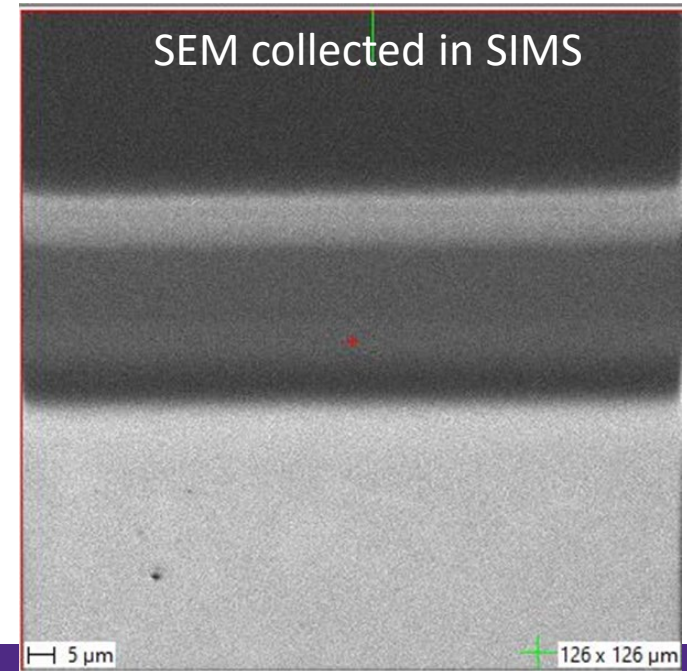
Si+



Overlay of Cu+, Ti+, Mo+, Mn+, Nb+, Si+



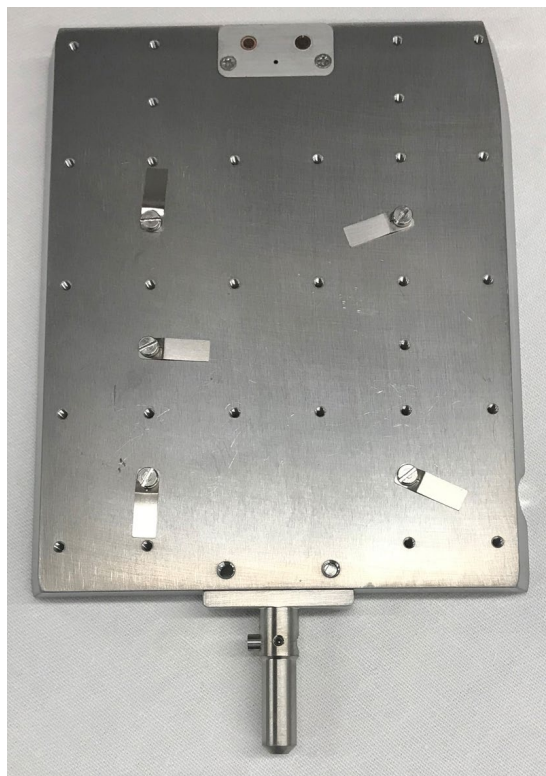
Overlay of Cu+, Ti+, Mo+, Mn+, Nb+, Si+



Northwestern

EXPLORING INNER SPACE

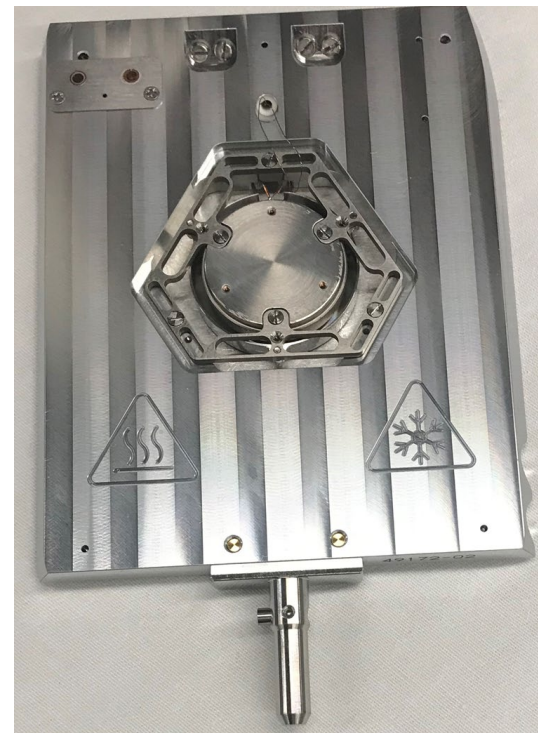
Various Sample Holders



Top mount holder



Back mount holder

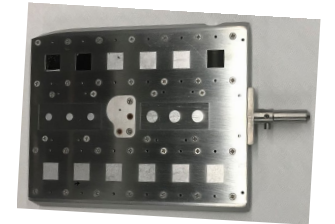


**Heating/cooling stage
-180C to 600C**



Air-free sample transfer holder

Air free sample transfer



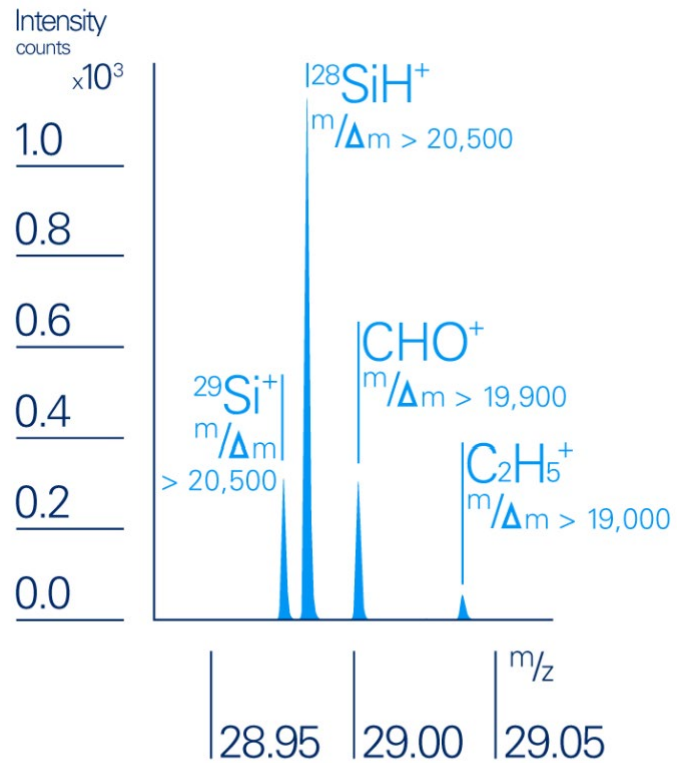
Advantage of ToF-SIMS

- Detection of **All Elements** – H, He, Li, etc.
- Isotopic Detection – 2H , 3H , 18O , 13C , etc.
- Trace Sensitivity – ppm to **ppb** range
- **High Spatial Resolution Mapping**
 - –Typical Lateral Resolution < 100nm
- Parallel Detection of All Masses
- Detailed Molecular Information – organic or inorganic
- Molecular Imaging
- **3D profiling**
- Analysis of **All Materials** – conductor, semiconductor, insulator

Disadvantages

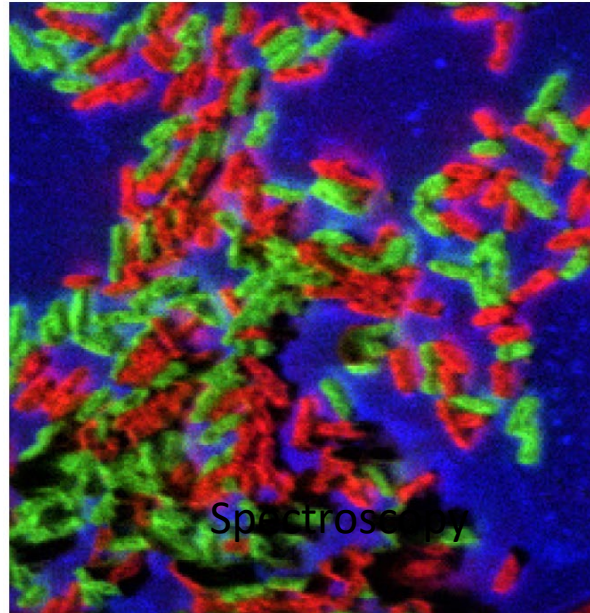
- Secondary ion yields are often highly dependent on the **matrix**
- Secondary ion yields vary by more than six orders of magnitude across the elements
- **Destructive**
- Well-characterized reference standards that are as close as possible to the matrix of the samples of interest are needed for quantification
- **Qualitative**
- Data interpretation could be difficult.

Summary



High resolution mass spectra demonstrating the new level of mass resolution in the low and high mass range.

Spectroscopy

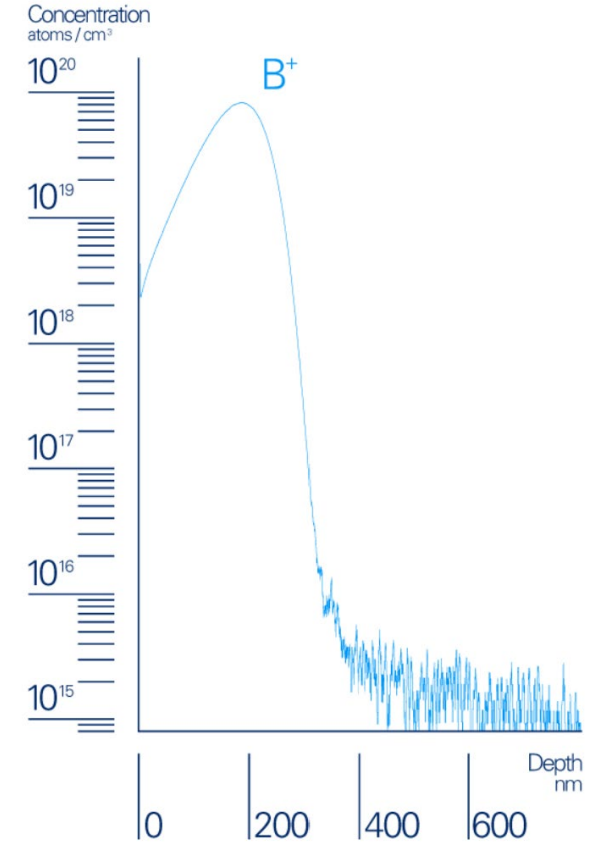


Overlay: $^{12}\text{C}^-$ (red), $^{13}\text{C}^-$ (green), Si^- (blue)

Surface image of ^{12}C and ^{13}C labelled Escherichia Coli Cells on silicon showing the surface distribution of $^{12}\text{C}^-$, $^{13}\text{C}^-$ and Si^- . For the analysis the delayed extraction mode of the M6 TOF analyser was used to combine ultimate imaging resolution with a mass resolution above 10,000.

Primary ion: Bi_3^{++} , Field of view: $15 \times 15 \mu\text{m}^2$, Pixel size: 60 nm

Secondary Ion Mapping



Depth profile of a boron NIST implant standard (SRM 2137).

Depth Profiling

Thanks for your attention

Questions?

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