Characterization of novel Gold LMIS delivering projectiles up to nanoparticle sizes for organic SIMS applications

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The development of ion sources capable of delivering large projectiles with defined spot sizes is one of the major research topics in the field of surface characterization under ion beam bombardment (SIMS). These projectiles have been introduced in order to overcome the low sensitivity in organic SIMS and thus to improve the signal of the detected secondary ions.[1] Various approaches have been explored so far, among them gold clusters produced by Liquid Metal Ion Sources (LMIS) are very attractive since their conception by researchers from the "Institut de Physique Nucléaire (IPN) d'Orsay" in France and Texas A&M University in the USA.[2-3] Recently, massive projectiles containing some hundreds of gold atoms each (ex. Au_{400}^{+4}) could be extracted from LMIS and the usefulness of such projectiles has been demonstrated experimentally through a strong ion yield enhancement from various organic samples.[3-5]

The aim of this contribution is to share the recent results regarding, on one hand, the characterization of a novel LMIS capable of delivering gold projectiles with various sizes ranging from small clusters up to massive projectiles of nanoparticle sizes (AuNP). On the other hand, the effect of the gold projectiles implanted as nanoparticles on various organic samples will be investigated through the so-called cationization effect in SIMS.[6]The first part related to the characterization of the LMIS was conducted on a bench test at IPN-Orsay. The source is designed to produce a range of gold projectiles Au_n^{q+} (e.g. Au_1^+, Au_3^+, Au_5^+, and Au_{400}^{+4}) with beam intensities greater than 300pA. Initial tests show that the source is capable of producing more than 900pA of Au_{400}^{+4} with 20qkV impact energy. The impact energy of the selected projectile can be reduced thanks to a decelerating lens which, in addition, has focusing properties. Therefore AuNP projectiles can be focused down to a spot size of ~ 400 μm and implanted into organic samples at depth ranging from the extreme surface (soft landing) to 10-20 nm below the surface. The efficiency of the AuNP implanted into organic samples for ion signal enhancement in SIMS will be evaluated by employing different doses and impact energies.

This experimental study is incorporated within the framework of collaboration between the "Institut de Physique Nucléaire (IPN) d'Orsay" through the "Andromede" project and the "Research Center Gabriel Lippmann" through the "CLUSTERS" project.

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Introduction

ToF-SIMS

Powerful surface analysis technique widely used for different kind of materials such as biomolecules, polymers, metals…

Challenge

Improve the sensitivity (Ion Yield) which can be very useful for various applications such as structural characterization of polymers, SIMS imaging....

Explored routes

Cluster projectiles (C_{60}^+, Bi_n^+, Au_n^+), **Matrix** (cationizing agents metal and alkali salts, molecules, …), **Specific substrate** (Au, Ag, Cu, …) and **Metal evaporation** on sample (noble metal: Au, Ag).

Purpose of work

Source development (Liquid Metal Ion Source)

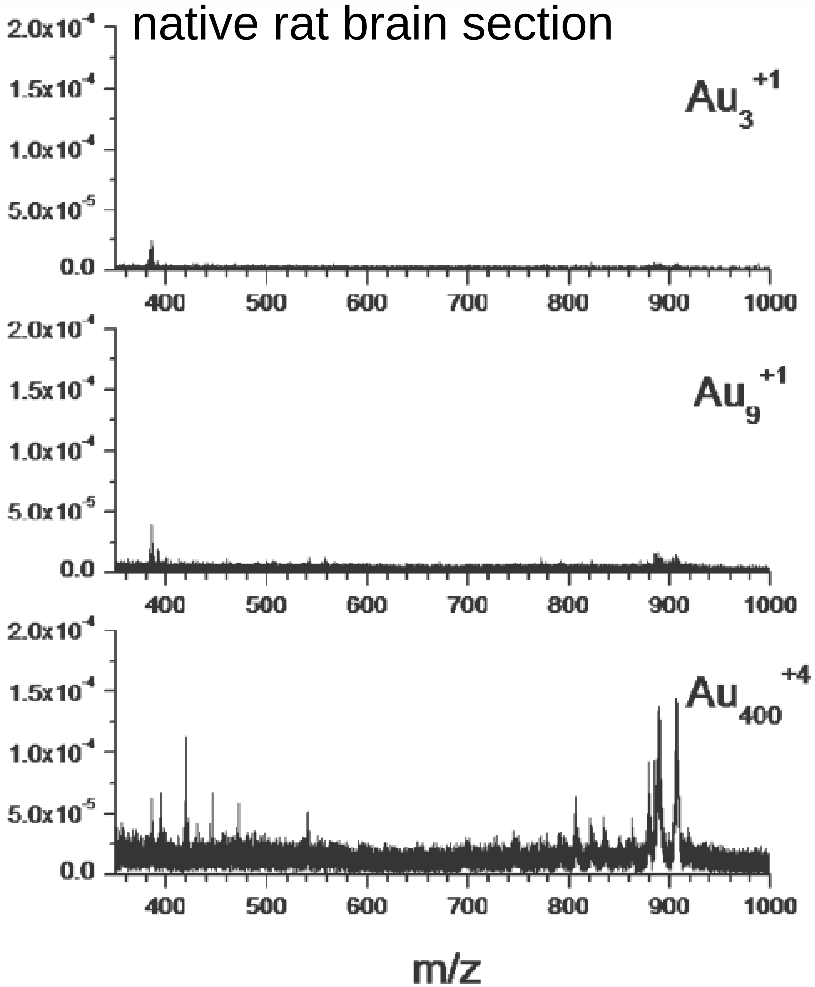
❖ Massive projectile Au_{400}^{+} (Nanoparticle sizes) (operation conditions of the Gold LMIS)

AuNP for SIMS characterization

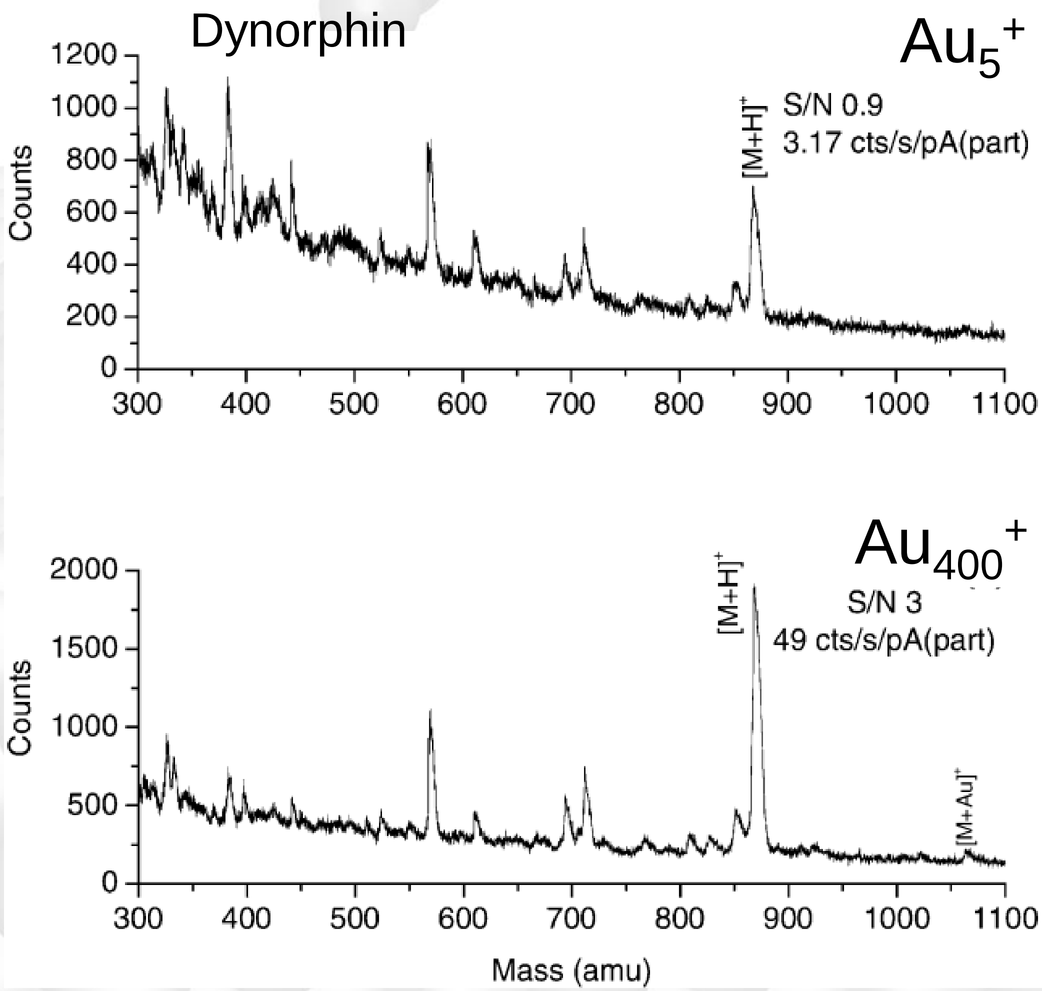
❖ Integrate Gold Liquid Metal ion Source on SIMS instruments at SAM-CRP (Dynamic SIMS)

❖ Usefulness of AuNP implantation on the ion yield for organic layers

Previous studies



Anal. Chem. 2011, 83, 8448–8453



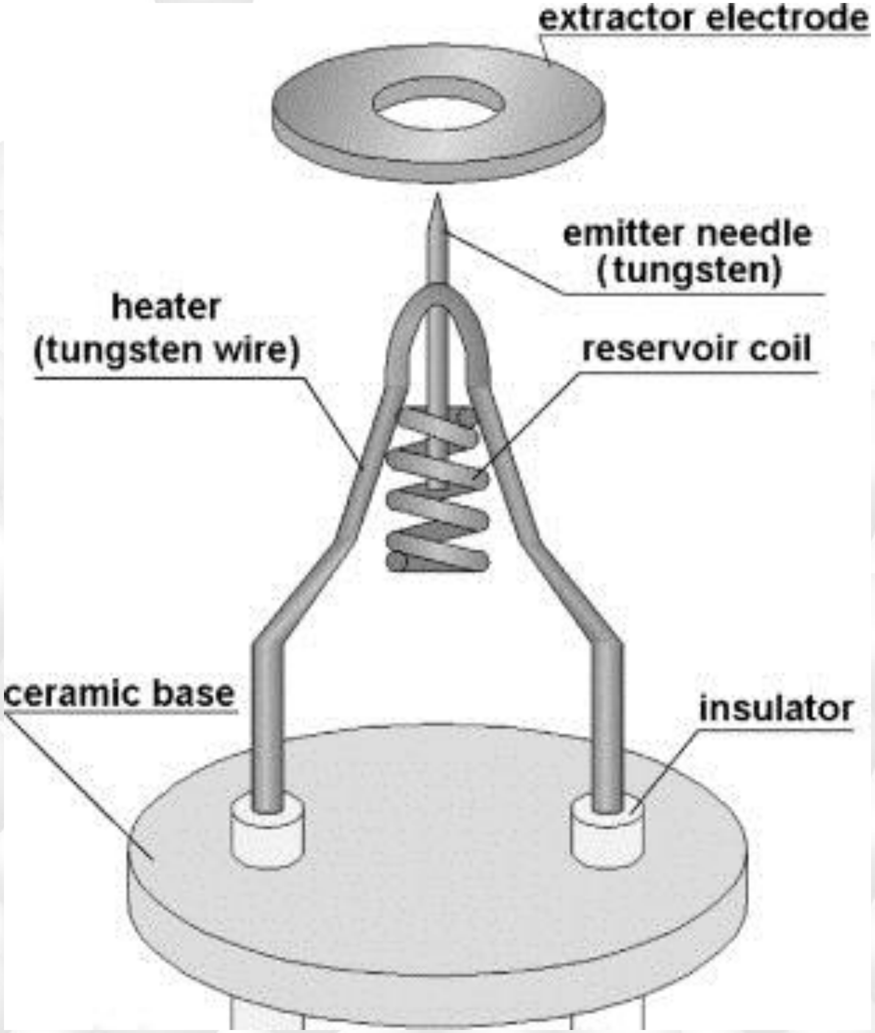
Rapid Commun. Mass Spectrom. 2004; 18: 371–376

Operation conditions of the Gold LMIS

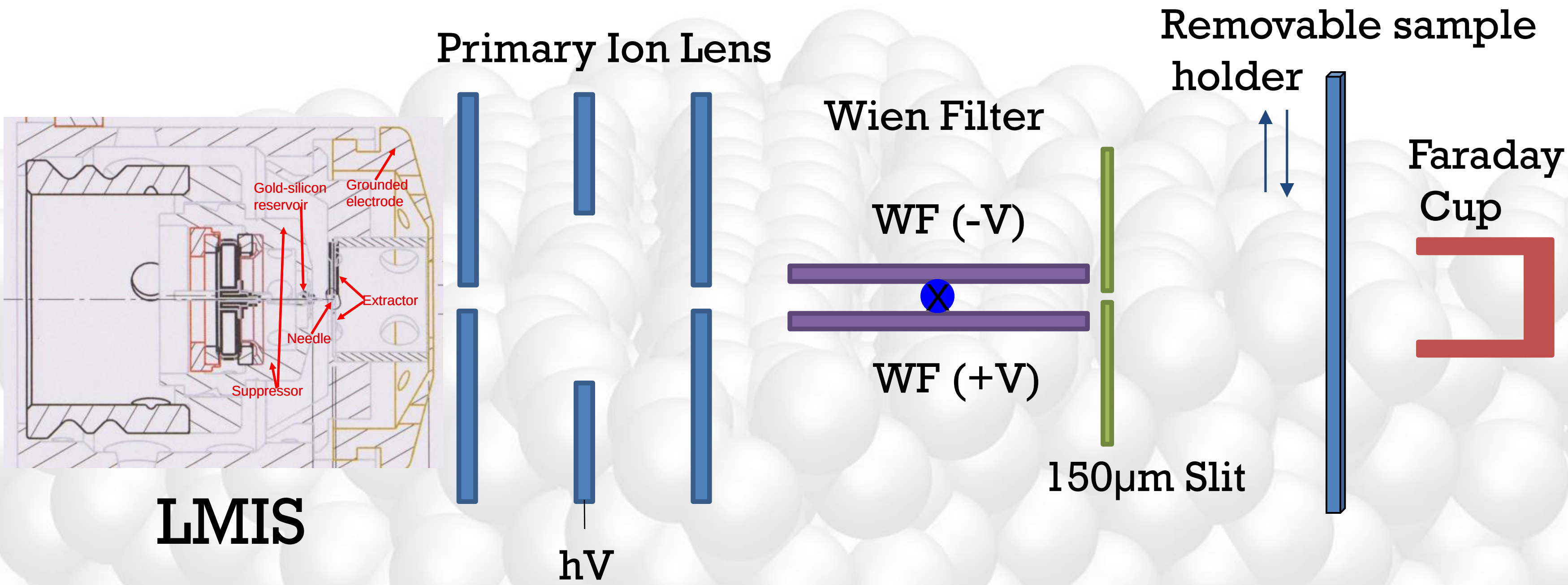
- Heat a reservoir made mainly from gold (Au-Si alloy)

- Liquid metal diffuse toward the needle

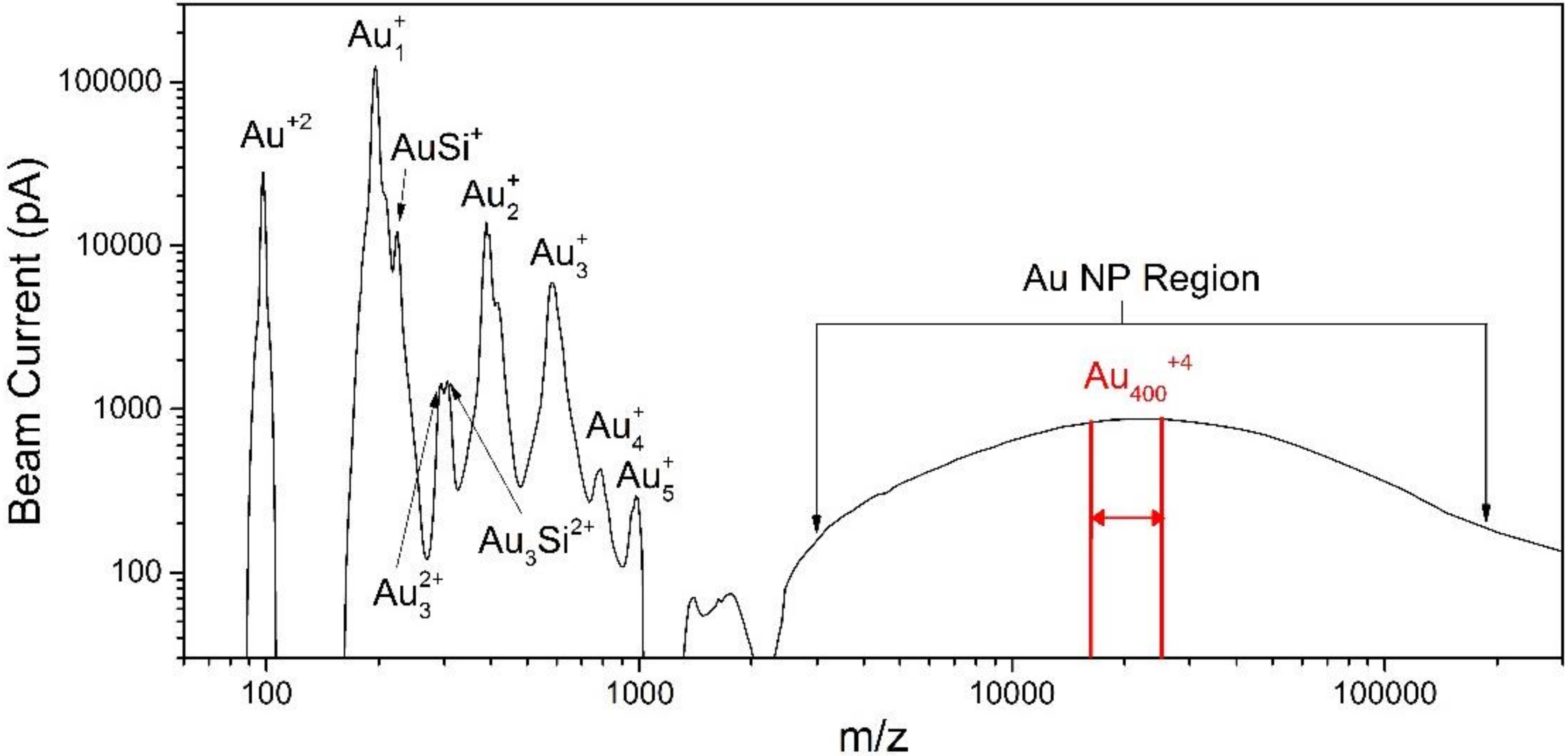
- Ions are ionized and extracted by applying an extraction field



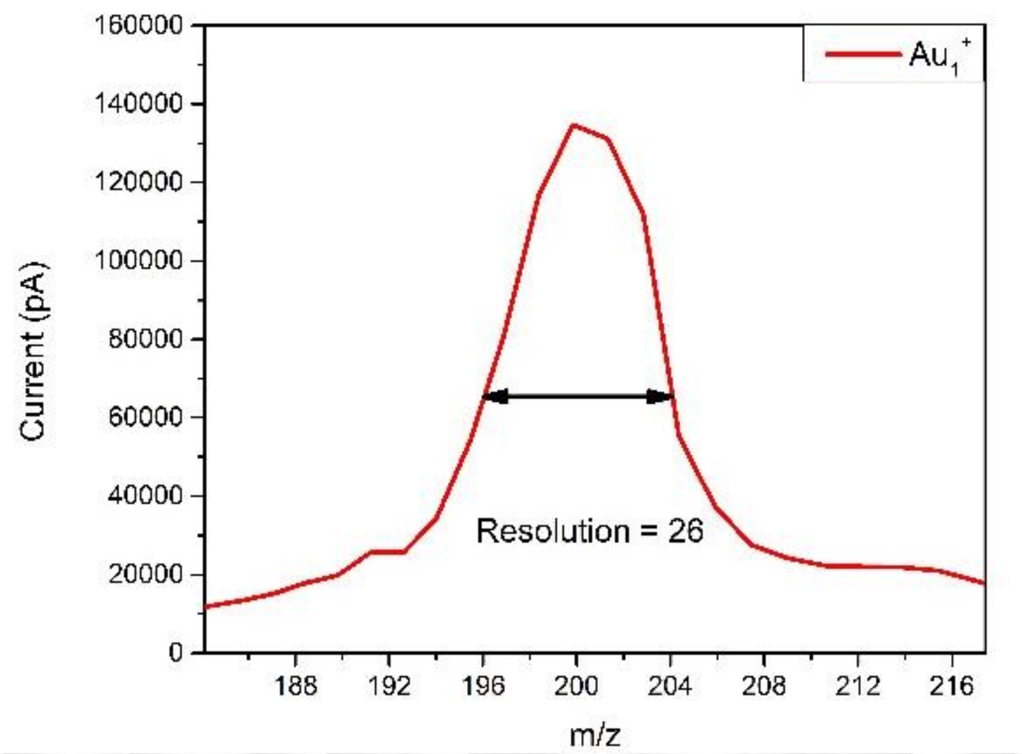
Operation conditions of the Gold LMIS



Mass Spectra of the Extracted Ions

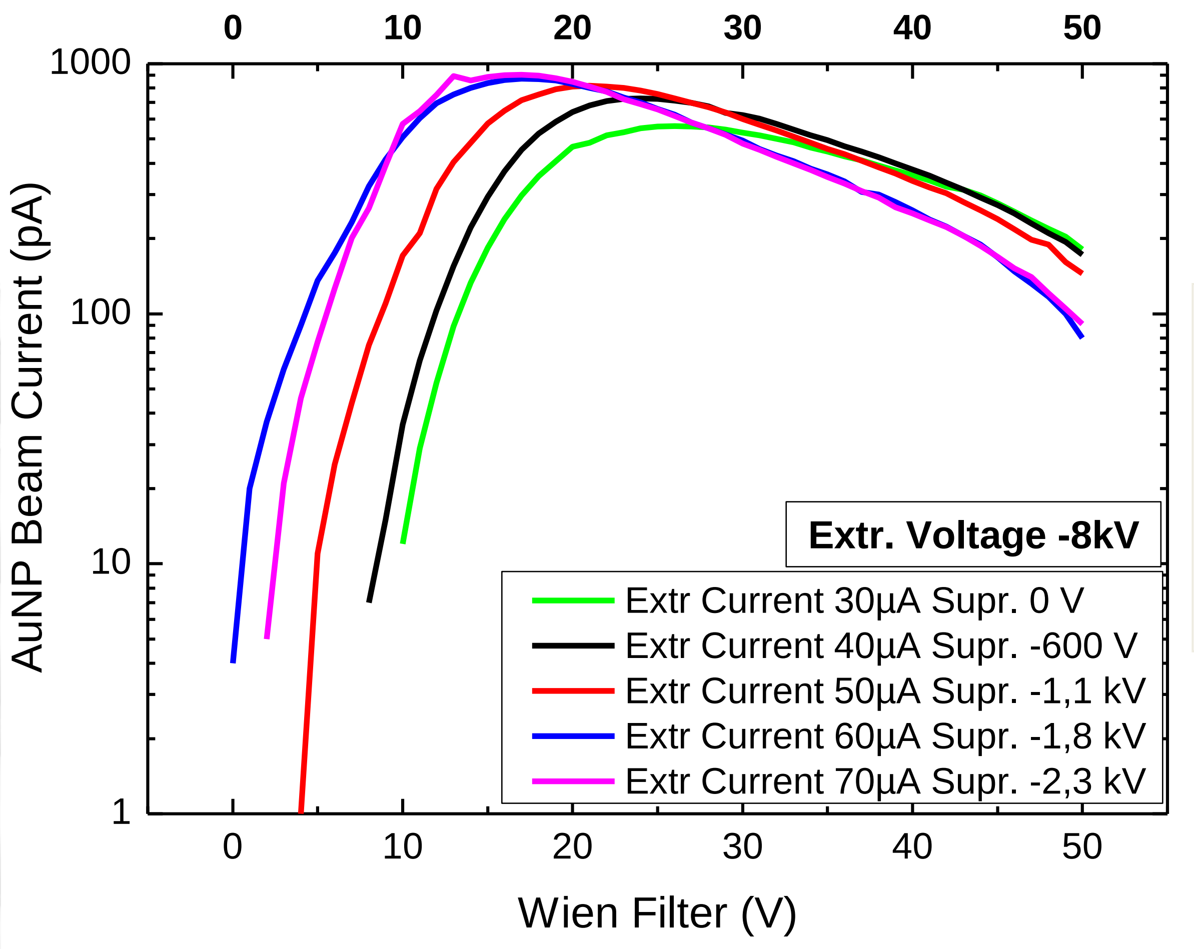


Mass Resolution



Mass Res. is sufficient to resolve Au_1^+ from $AuSi^+$

AuNP Current: Effect of the Source Current

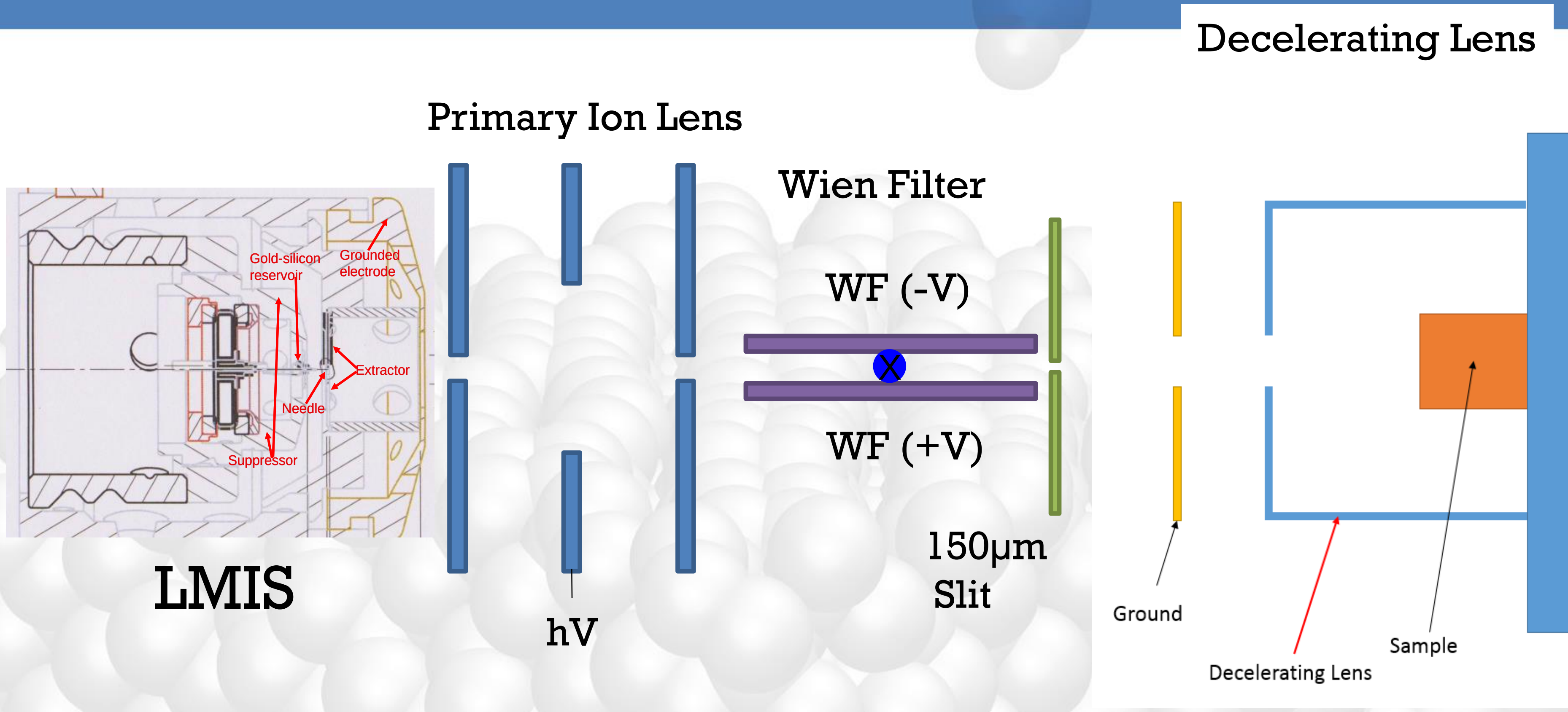


❖ Ext. Curr. Increases AuNP current increases and shift to larger AuNP projectiles

❖ Ext. Curr. 60µA is optimal for AuNP production

Decelerating Lens:

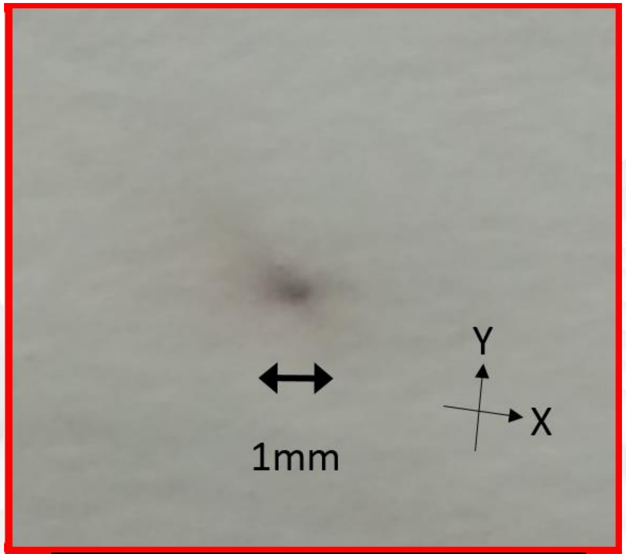
Reduce the impact energy down to few 100 eV (Soft landing)



❒ Lens is held at the same voltage as the source (20kV)
❒ Impact energy is defined by difference between the voltage applied to the sample and the source

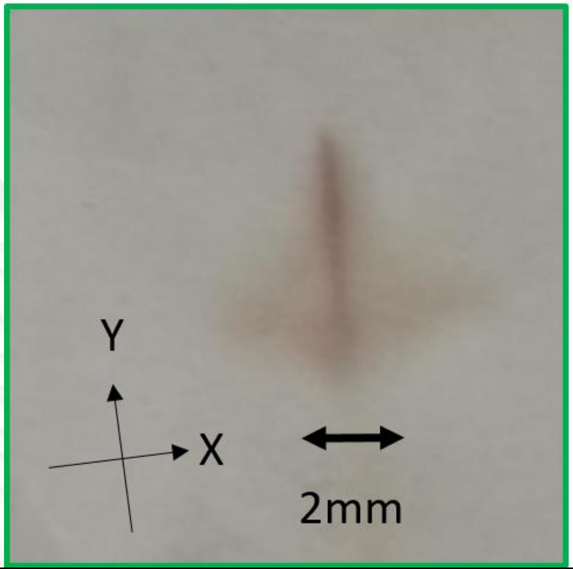
Decelerating Lens:

Effect on the spot size of the Massive Clusters Au_{400}^{+4}



With Decelerating Lens
Impact Energy 2 keV

Au_{400}^{+4}

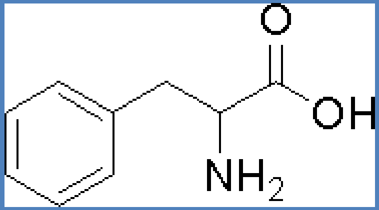


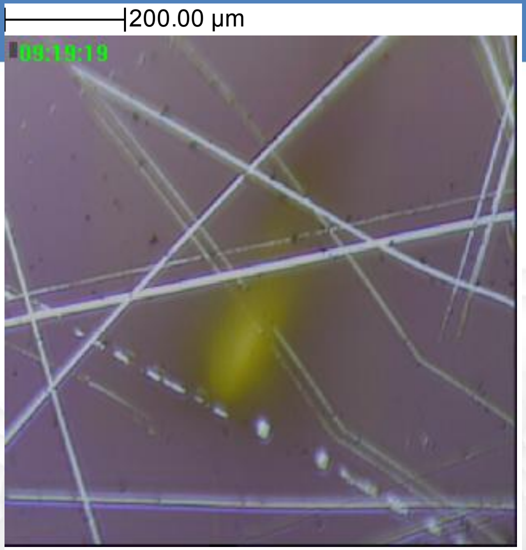
Without Decelerating Lens
Impact Energy 20 keV

- ❒ The decelerating Lens has a focusing properties
- ❒ Beam size drastically reduced to ~ few Hundreds of µm compared to more than 2 mm without the decelerating lens

Implantation of AuNP in organic layers

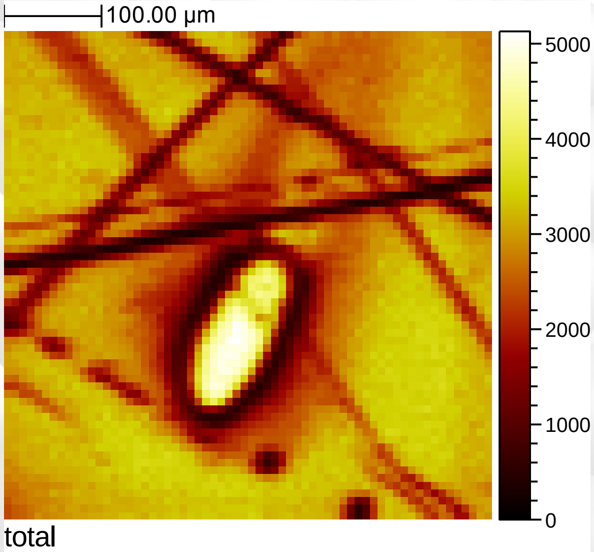
Phenylalanine

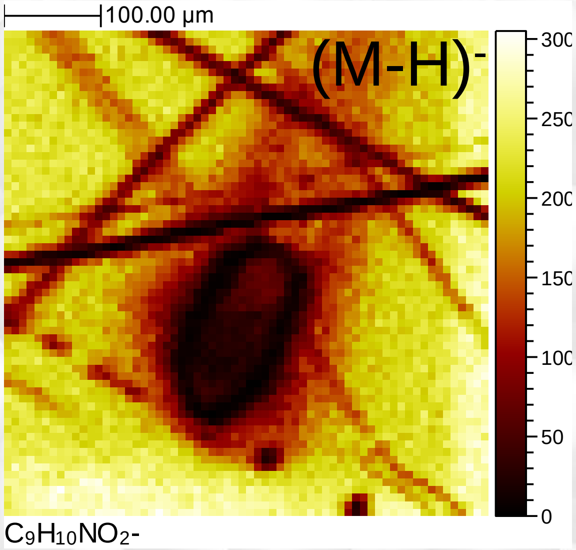


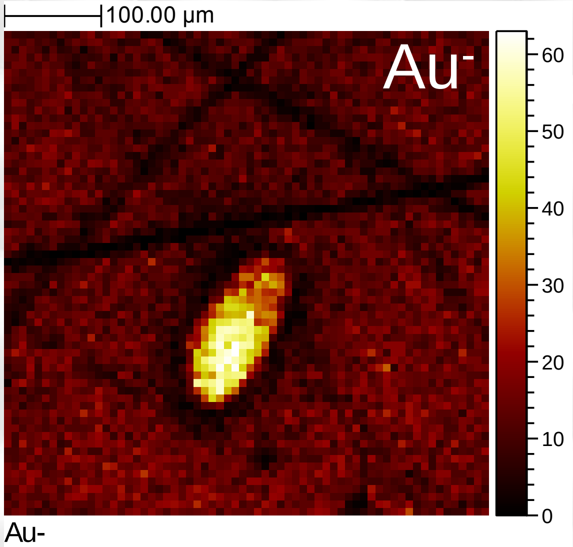


Au_{400}^{+4} Implanted at 80 keV with high dose

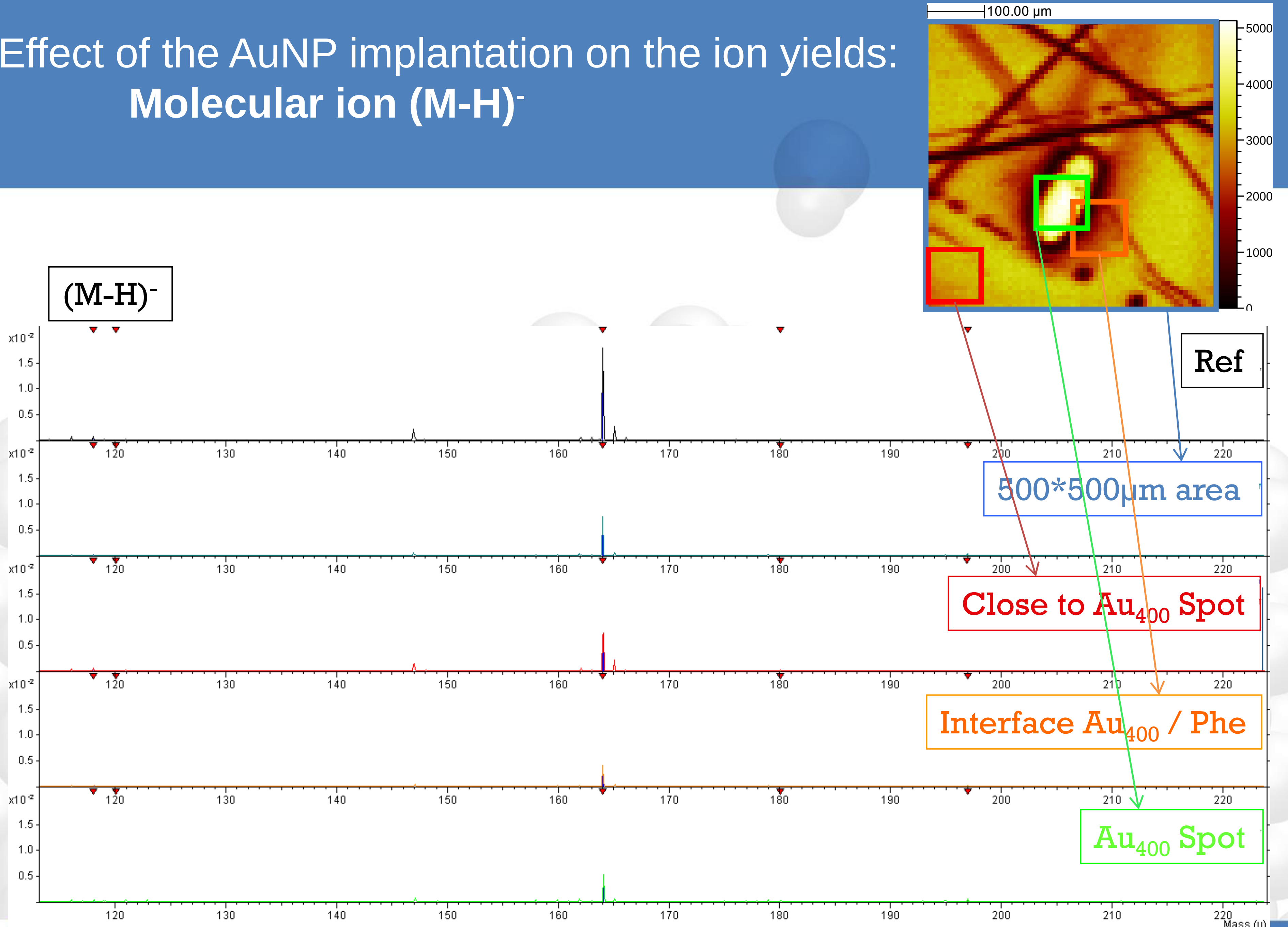
Analysis beam Bi_3^+; 25 keV



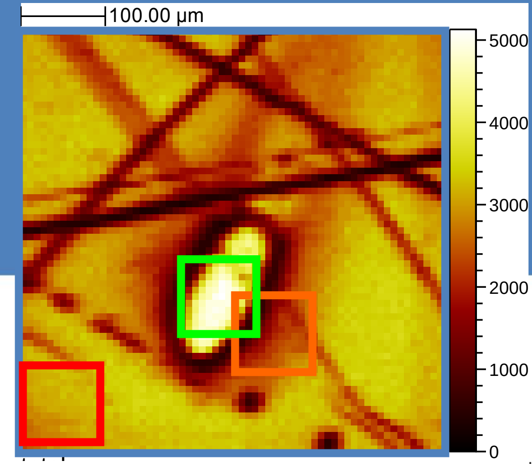


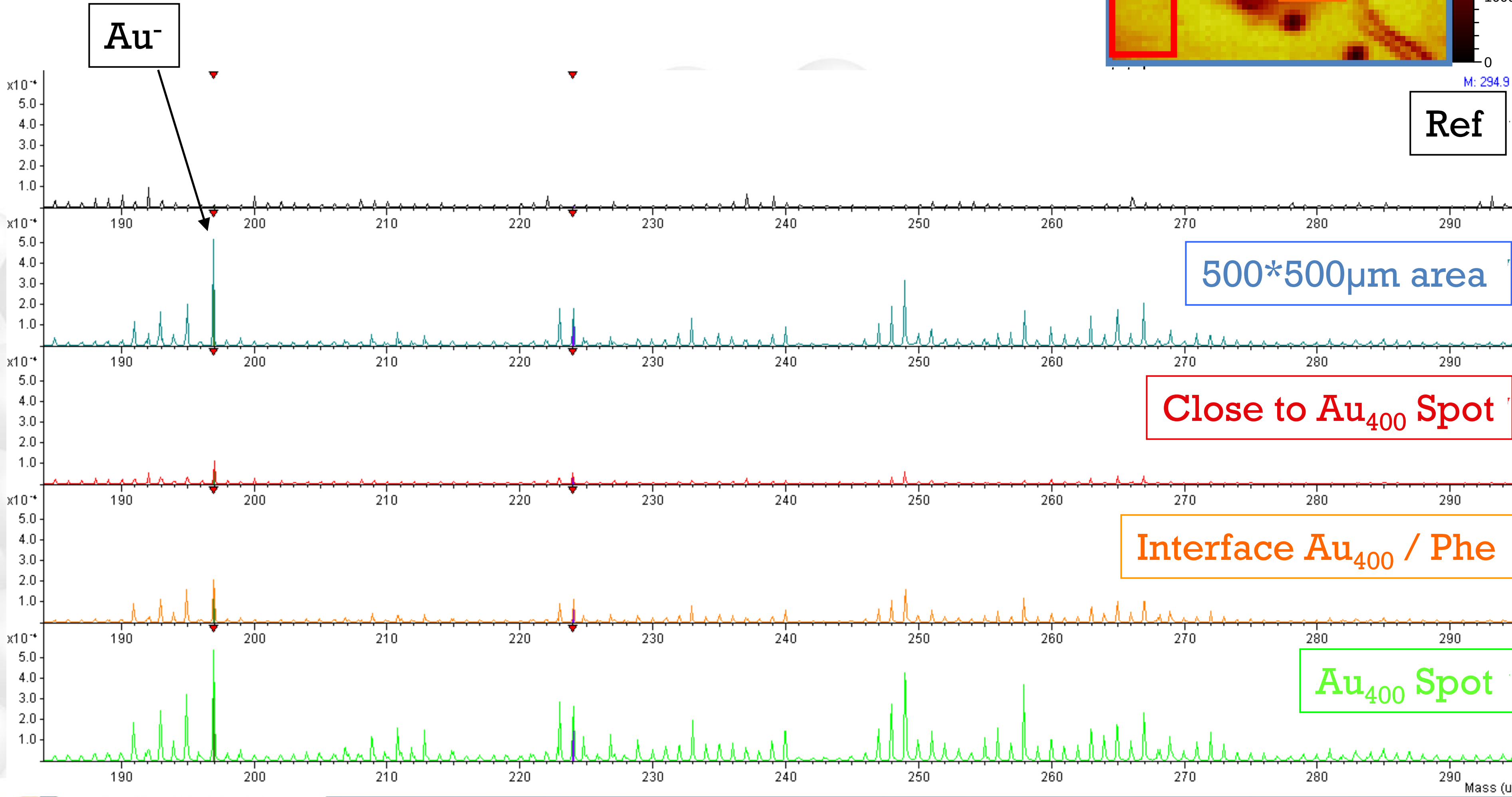


Effect of the AuNP implantation on the ion yields:
Molecular ion (M-H)$^-$

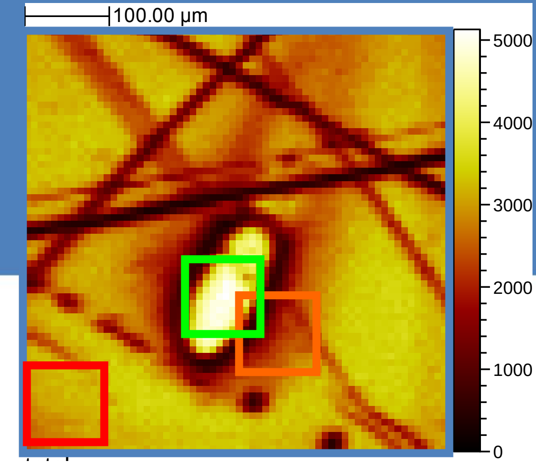


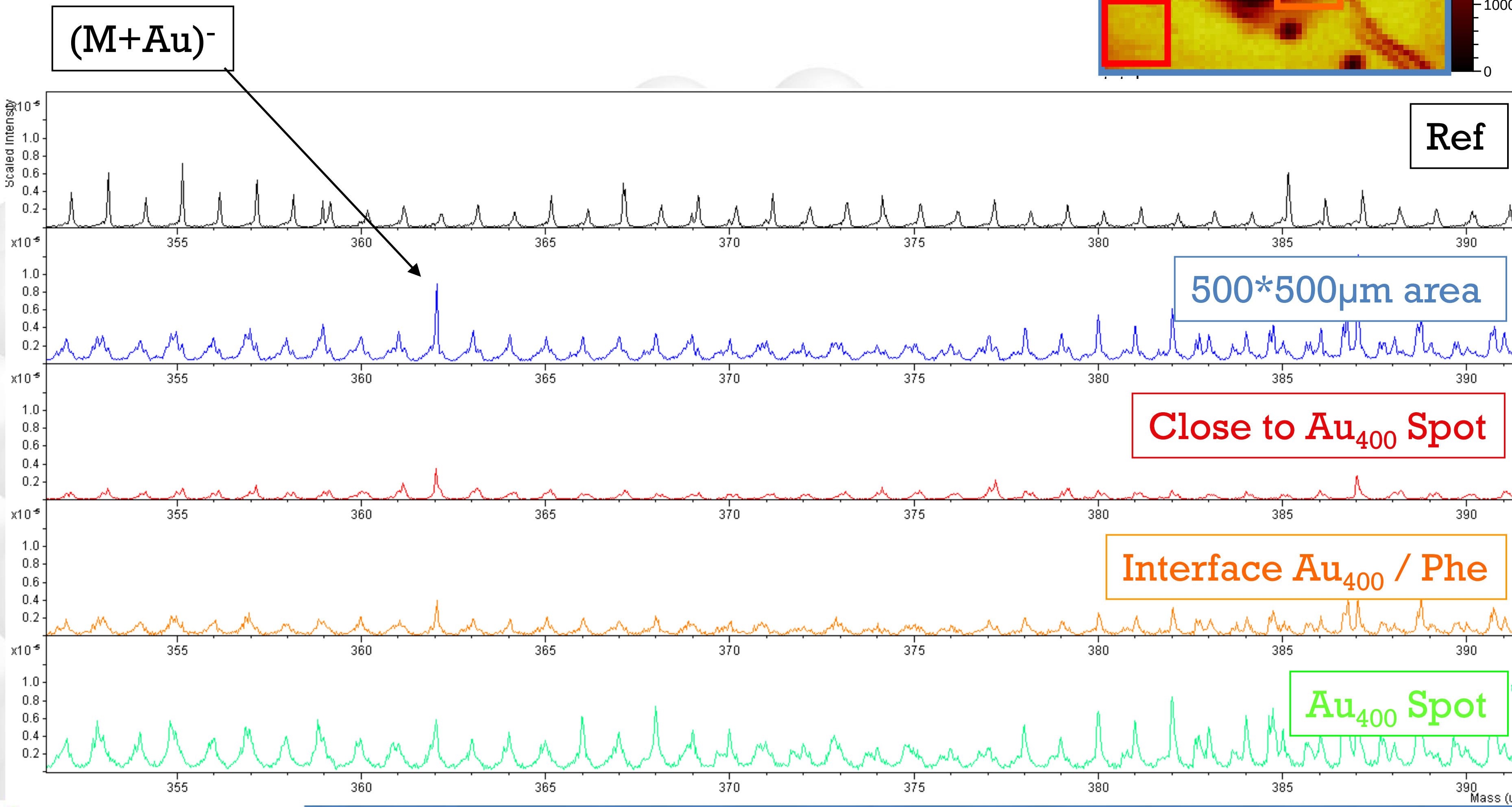
Effect of the AuNP implantation on the ion yields: **The gold signal Au^-**



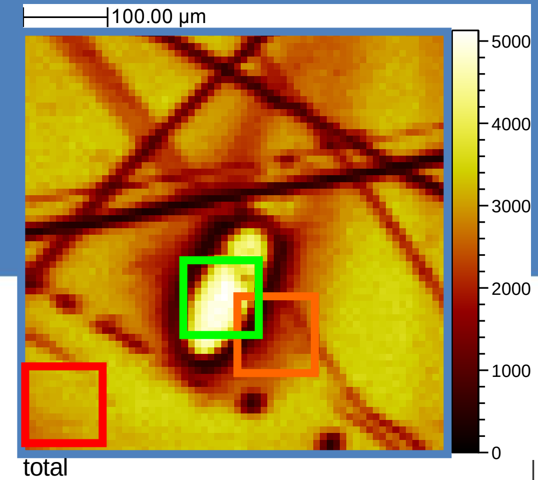


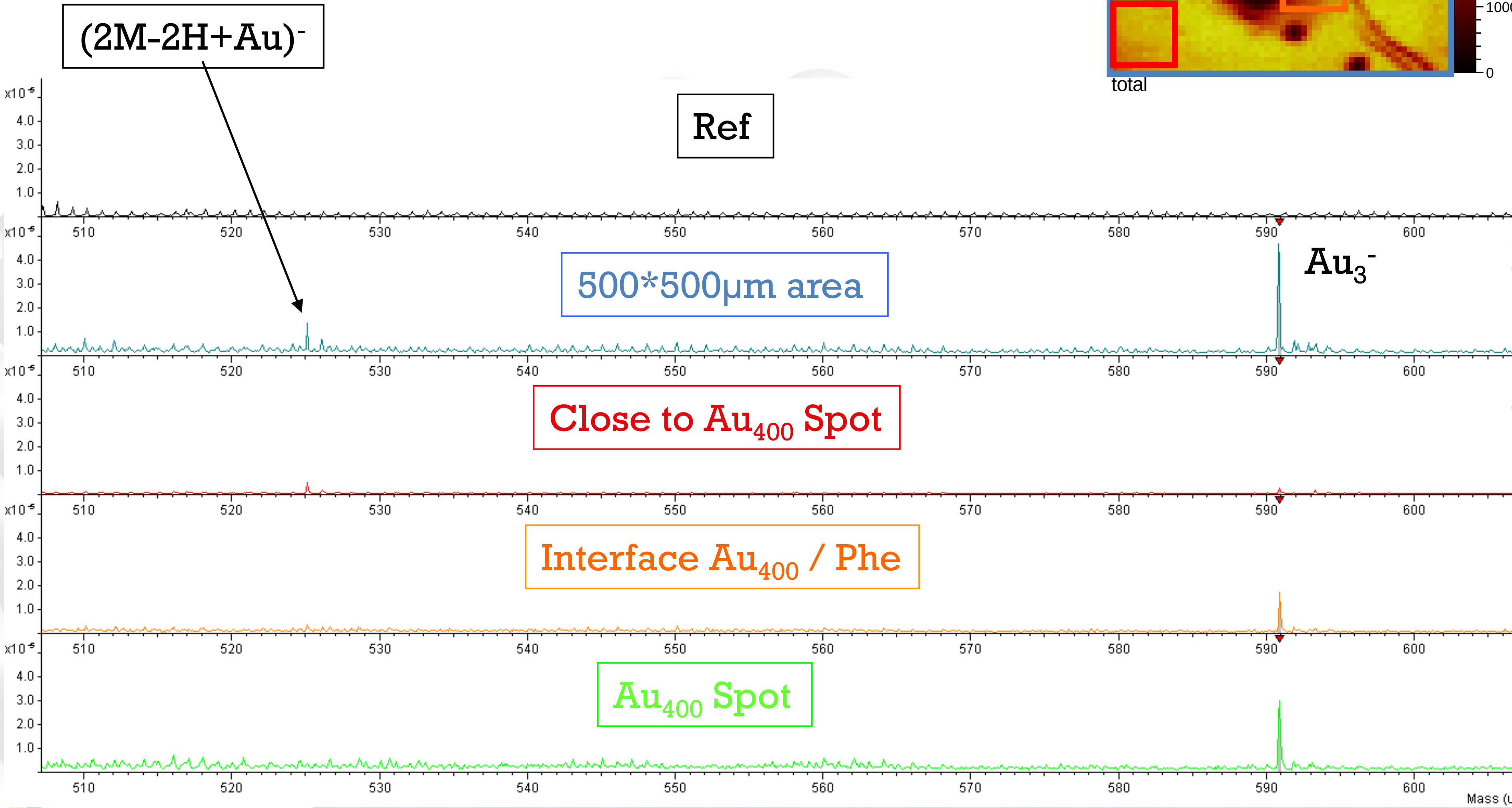
Effect of the AuNP implantation on the ion yields: The cationized **molecular ion**



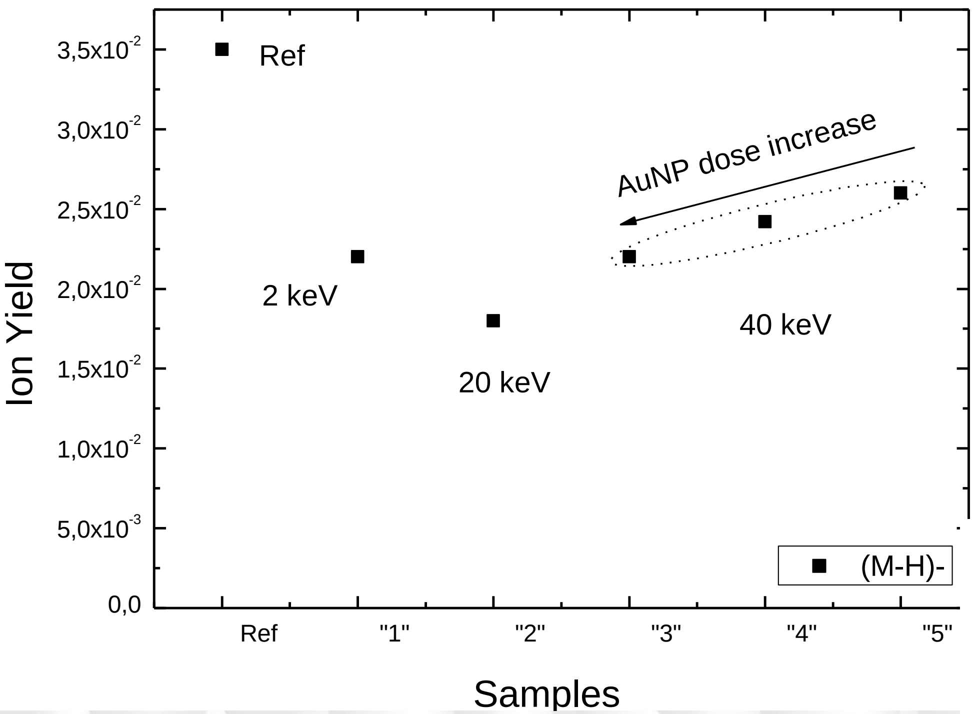


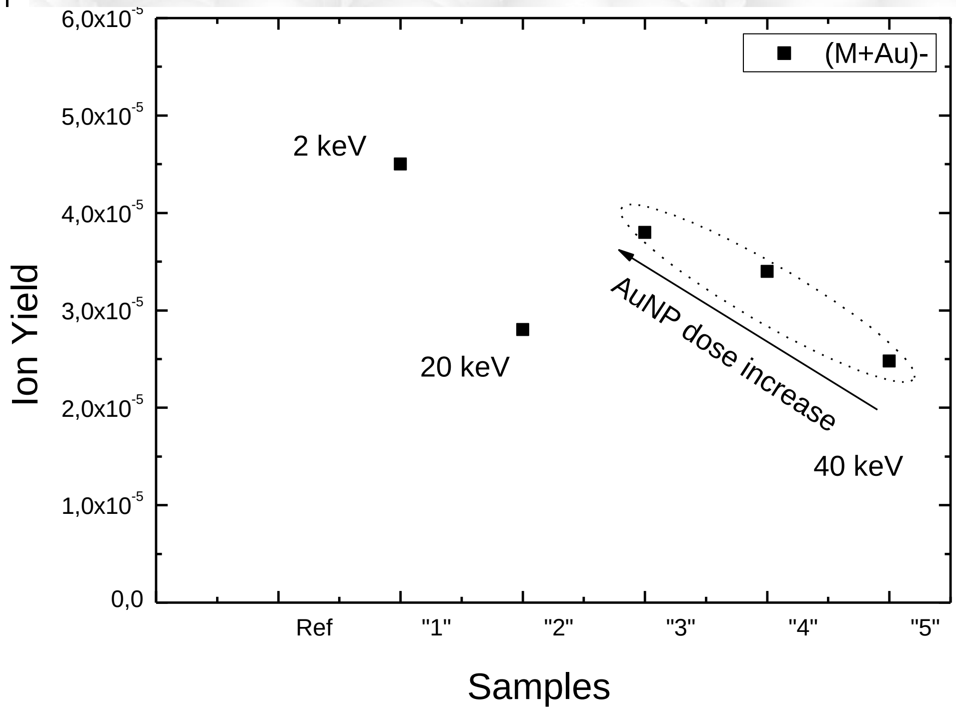
Effect of the AuNP implantation on the ion yields: The cationized **molecular ion**





Effect of the AuNP dose ad energy on the ion yields





Conclusions

Extraction of Au_{400}^{+} from LMIS

- We have determined the optimized parameters to generate various gold cluster beams, in particular the AuNP and are able to obtain 900pA of Au_{400}^{+4}.
- We have mass resolution capable to separate Au_1 from Au_1Si.
- The decelerating lens has a focusing properties so that the AuNP size is strongly reduced and much well defined (few hundreds of µm)

Implantation of Au_{400}^{+} into organic layer

❖ The molecular ion signal is preserved although some damage is present around the AuNP spot.

❖ New peaks ascribed to cationized molecular ions $(M+Au)^-$ are detected

❖ The $(M-H)^-$ yield seems to decrease for higher AuNP doses whereas the $(M+Au)^-$ yield increases as the AuNP dose.

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