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A fundamental study of small proteins using Gas Cluster Ion Beam Secondary Ion Mass Spectrometry (GCIB-SIMS) – mutliple charging and projectile effects

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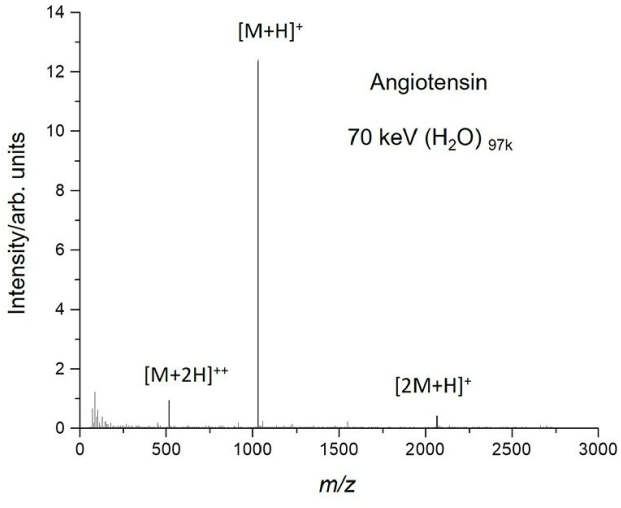
Gas cluster ion beams (GCIBs) are extending the frontiers of SIMS applications in the life sciences, enhancing sensitivity towards intact biomolecules and facilitating 3D cellular imaging [1]. Previously the detection of intact small proteins has been observed using GCIB projectiles. Further study is required to understand and improve the characterisation of bio-macromolecules using SIMS. For example, how should the sample be prepared, which GCIB should be used and using what parameters?
Here we present a study of Angiotensin (1031 Da), Insulin (5730 Da) and Ubiquitin (8565 Da) using GICBs comprised of $(H_2O)_n$ or $(ArCO_2)_n$. A range of primary cluster energies E=9-70 keV and cluster sizes n<100k have been applied with cluster mass up to m~2 MDa to observed secondary ion (SI) yields over a range of E/m ~0.05-0.3 eV/u. We report the yields of diagnostic ions including $[M+H]^+$, $[2M+H]^+$ and $[M+H]^{2+}$. As expected, SI yields scale with the total beam energy E, but importantly show an optimum E/m. We discuss the ion yield dependency on E/m for different SI species as a function of the analyte mass, total beam energy and cluster chemistry. Moreover, we compare SI yield characteristics of dried and frozen-hydrated peptides. Finally, we discuss the implications of this work for extending the mass range of the analysis of biological samples.

References

[1] Hua Tian, Sadia Sheraz, John C. Vickerman, Nicholas Winograd, Multiomics Imaging Using High-Energy Water Gas Cluster Ion Beam Secondary Ion Mass Spectrometry [(H2O)n-GCIB-SIMS] of Frozen-Hydrated Cells and Tissue, *Anal. Chem.* **93**, 7808–7814 (2021)



Angiotensin spectrum using n=97k water GCIB