Enhancing secondary ion yields in ToF-SIMS using water cluster primary beams.

Sadia Sheraz (née Rabbani)[1], Andrew Barber[1,3], John S. Fletcher[2], Nicholas P. Lockyer[1] and John C. Vickerman[1*]

[1]Manchester Institute of Biotechnology, The University of Manchester, Manchester, UK

[2]Department of Chemistry and Molecular Biology, University of Gothenburg, Gothenburg, Sweden

[3] Ionoptika Ltd, Eagle Close, Chandler's Ford, Hampshire, UK

Supporting information

Experimental approach.

Analysis was performed on a J105 ToF-SIMS instrument (Ionoptika Ltd UK) that has been described in detail elsewhere[1]. Briefly the instrument uses a quasi-continuous primary ion beam to generate a stream of secondary ions that is then sampled by a buncher that produces a tight packet of ions at the entrance to a quadratic field ToF-reflectron analyser. The prototype gas cluster ion beam system was designed to enable both argon and water cluster beams to be generated by supersonic expansion through a 100 µm nozzle via a skimmer having an exit aperture diameter of 0.5 mm[2 2]. An alternative method of generating such beams uses an electrospray approach at atmospheric pressure[3], however this is not easily combined with the argon beam capability. The neutral cluster beam passes into an ionisation chamber where the gas clusters are ionized by electron bombardment and mass filtered using a Wien filter arrangement which can be tuned to the species of interest providing a resolving power (m/Δm) of approximately 5. The exiting beam is accelerated to 10 keV, passed through the ion optical column where it is focused and can be rastered over an area of the sample. The source of the pure water clusters is an in line steam generator operated at about 4 bar by controlling the generator temperature. For satisfactory operation the nozzle is heated to prevent water condensation. The present arrangement enables stable clusters of up to $(H_2O)_{1300}$ with beam currents at the sample in excess of 0.5 nA to be routinely generated with a beam diameter at the sample of ~150 µm. The cluster size was monitored by measuring the flight time of the cluster from source extractor to the sample plate. Both the argon cluster and the water cluster flight times were consistent with a singly charged cluster distribution. The system is being developed further with the aim of being able to routinely obtain clusters of 5000 to 10000 water molecules. The experiments reported here focused on the cluster distribution characterised by Ar_{1000} and $(H_2O)_{1000}$.

Solutions of all the samples were spin coated onto cleaned silicon wafers and analysed with an ion dose of 1×10^{11} ions cm^{-2} usually into a 900 x 900 µm area. In some cases sample charging was compensated by a beam of low energy electrons.

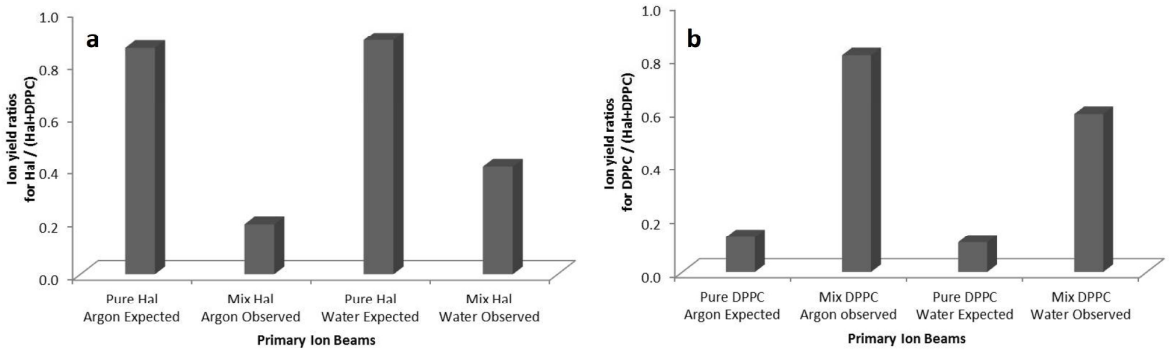

Figure S.1 A study of the matrix effect evident in a 1:10 mixture of haloperidol and DPPC under argon and water cluster primary beams. a) the expected ion yield ratio $\frac{0.09Y_{Hal}}{0.09Y_{Hal}+0.91Y_{DPPC}}$ of haloperidol, and b) $\frac{0.91Y_{DPPC}}{0.09Y_{Hal}+0.91Y_{DPPC}}$ of DPPC calculated from the ion yields of the pure compounds compared to the observed ion yield ratios $\frac{Y_{Halmix}}{Y_{Halmix}+Y_{DPPCmix}}$ and $\frac{Y_{DPPCmix}}{Y_{Halmix}+Y_{DPPCmix}}$ from a 1:10 mixture under 10keV($H_2O)_{1000}^+$ and 10keV Ar_{1000}^+.

1. Fletcher, J. S.; Rabbani, S.; Henderson, A.; Blenkinsopp, P.; Thompson, S. P.; Lockyer, N. P.; Vickerman, J. C. *Anal. Chem.* 2008, *80*. 9058-9064.
2. Rabbani, S.; Barber, A. M.; Fletcher, J. S.; Lockyer, N. P.; Vickerman, J. C. *Anal. Chem.* 2011, *83*. 3793-3800.
3. Beuhler, R. J.; Friedman, L. *J.Chem. Phys* 1982, *77*. 2549-2557.