

Why MALDI works – From Hypotheses to Experimental Evidence

The original conceptual ideas on the MALDI process, i.e. matrix isolation, desorption via disintegration of the matrix-analyte-crystal after laser excitation and ionization via photochemical reactions has recently been revisited and refined. By using molecular probes, such as organic dyes and extremely strong acids, clear evidence is provided that the pH is maintained in the matrix crystals and that typical peptide analytes are incorporated in an ionized, resp. salt state. The desorption process induced by the laser irradiation is now understood as a cluster ablation step substantiated both by numerical calculations as well as by measurements of the ion characteristics, namely their initial ion velocity. Consequently ions do not have to be generated, but are the "lucky survivors" within a random charging and desolvation process which is again evidenced by a chemical approach. Within this frame, connections to the situation in sputtering by ion impact will be drawn and outlooks will be given.