

## **POSITIVE AND NEGATIVE ANALYTE ION YIELD IN MATRIX-ASSISTED LASER DESORPTION/IONIZATION**

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The most commonly accepted model for the formation of analyte ions in MALDI-MS assumes a primary ionization of matrix e. g. by photoionization, leading to stable protonated and deprotonated matrix ions, respectively. Analyte ions are then formed by secondary proton transfer reactions in the expanding plume. This model had been checked experimentally by comparing the yield of positive to negative ions of three peptides and six matrices, differing in gas phase basicity by about 150 kJ/mole [Int. J. Mass Spectrom. 268(2007)122]. The data have been revisited for a more general and in depth analysis. Model predictions are presented for a wide range of experimental parameters, in particular for ranges of the gas phase basicity and acidity of analyte and matrix and for different molar ratios of analyte to matrix as well as the yield of primary matrix ions. It is shown that the observed ion yields cannot be explained by any single and consistent set of parameters. It is concluded that the existing simple model needs to be modified to fully explain the experimental findings. Such modifications should primarily address the formation of negative matrix and analyte ions.