Free and immobilized matrix molecules: impairing ionization by quenching secondary ion formation in laser desorption MS

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Résumé en anglais	Within the last 25 years, matrix-assisted laser desorption ionization (MALDI) has become a powerful analytical tool in mass spectrometry (MS). While the method has been successfully applied to characterize large organic molecules such as proteins, sugars and polymers, its utilization for small molecules (≤ 600 Da) is significantly impaired by the coformation of matrix ions. Reducing or eliminating matrix-related signals has been subject of many studies. Some of which propose the enhancement of so-called matrix suppression effects, while others suggest the replacement of matrix molecules by materials such as microporous silicon. Alternatively, the immobilization of matrix molecules by utilizing them as self-assembled monolayers (SAMs) has been discussed. In continuation of this research, the current manuscript focuses on the elucidation of ion formation processes occurring on the surface of light absorbing SAMs. Ion yields obtained by free and immobilized matrix molecules as well as those generated by matrix-free gold film-assisted laser desorption ionization (GF-LDI) were compared. Experiments showed that the formation of strong analyte signals essentially required the presence of free matrix molecules, while the immobilization of the latter severely impaired ionization. The observed effect inversely correlated with the surface coverage of SAMs determined by cyclic voltammetry (CV). Based on these findings, the MS signal generated on light absorbing SAMs could be used supplementary to CV for determining the surface coverage of light absorbing SAMs.
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Liens

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