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MALDI MS Imaging-Molecular Mapping of Biological Samples by MALDI Mass Spectrometry

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Abstract

Matrix-assisted laser desorption/ionization (MALDI) mass spectrometry imaging (MSI) is a label-free method that can determine both identity and distribution of hundreds of molecules on tissue sections, in one single run. Lipids, proteins, peptides, carbohydrates, bacterial colonies, drugs and their metabolites can be analyzed for their distribution and relative concentration, at spatial resolutions down to cellular levels and for sample sizes up to whole body model animals. As such, MALDI MSI has the capability to become a powerful new molecular technology for the biological, clinical, plant and microbiological sciences.

MALDI MSI was first reported in 1994 for inorganic ion distribution [1], but its breakthrough in visualization of peptides and proteins-biomolecules that would normally fragment under harsh sample conditions-directly on tissue surface started 1997 [2]. After these initial imaging experiments, new technological advances and sample preparation protocols have been developed allowing high-spatial resolution images to be produced, with the molecular identity offered by mass spectrometry. Nowadays, MALDI-MSI has been used to image the distribution of a wide range of compounds including proteins, lipids, carbohydrates, pharmaceuticals, metabolites etc. Majority of MALDI MSI application is in the biomedical field [3], where it has provided biomarkers in tissue samples that can be used to identify cancerous regions as well as to monitor drug metabolism in various organs. Moreover, in plant tissues, a range of reports have used MALDI-MSI to assess the spatial distribution of sugars [4], metabolites [5] and lipids [6] to understand metabolical network and processes beyond them. MALDI MSI is also very useful in analysis of microbial colonies ranging from soil bacteria, blood pathogens to fungi, allowing connection of underlying chemistry with specific microbial phenotypes [7,8]. Most of such information cannot be obtained by any other method and advances during last decade suggest that MALDI MSI will have substantial impact on the future of microbiology.

The basic principle of MALDI MSI method relies on the direct application of MALDI time-of-flight (ToF) MS on the biological samples. First, flat surface of biological samples have to be covered with a homogeneous layer of MALDI matrix that has two important roles: (i) extracting molecules from the tissue specimen into the matrix and (ii) facilitating desorption/ionization for the further analysis in the mass spectrometer. The matrix, which is usually aromatic organic acid, absorbs the laser UV energy and transfers it to the analyte, promoting simultaneous analyte ionization and gas transformation in the process. By selecting different matrices, the specific analyte classes can be chosen amongst many analysts present at biological surface. In the mass spectrometer, the biological sample is then raster-scanned (with a spatial resolution ranging from 200 µm down to 20 µm), generating a mass spectrum for each measured spot. The data set can be displayed as an average spectrum, and selected images of individual ion m/z values can be extracted-displaying their spatial distribution based on m/z signal intensities- and superimposed onto a picture of the sample that is analyzed.

The crucial advantage of MS imaging over other imaging techniques is that diverse compounds present at the biological surface can be mapped without the need for prior assumptions of which molecules are likely to be present. As a result, large volumes of data can be generated without excessive investment in sample preparation. Although, the ongoing technological developments in MALDI Imaging mass spectrometry are very promising, scope for improvements – specifically regarding better image resolution, higher sensitivity, optimized sample preparation, and the more rapid acquisition of data and analysis – remained.

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