Abstract
Secondary ion mass spectrometry, matrix assisted laser desorption ionization mass spectrometry (MS), electrospray-based MS and other strategies are widely used for the analysis of intact bacterial biofilms, mammalian tissue, cell cultures, and their interfaces with biomaterials [Bhardwaj & Hanley, Nat. Prod. Rev. 31 (2014) 756]. The combination of these desorption / ionization methods with high resolution MS and tandem MS capabilities permit metabolomic and proteomic imaging of such samples. While these ion sources can detect many analyte classes within intact biological samples, they can also display low sensitivity, selective ionization, and/or poor lateral or depth resolution. Laser ablation with femtosecond laser pulses (fs-LA) can remove material from a solid with minimal damage to the remaining sample, potentially allowing both depth profiling and additionally, higher lateral resolution [Cui, *et al.*, Anal. Chem 87 (2015) 367]. Recent work has also shown that fs-LA can, under the proper experimental conditions, lead to no more molecular fragmentation that from other popular ion sources operating at similar background pressures. Furthermore, postionization of gaseous neutrals formed by fs-LA, either under vacuum or at atmospheric pressure can further enhance subsequent detection by MS. Laser postionization under vacuum has the additional advantage that proper selection of the delay time between the ablation and postionization pulse controls the extent of molecular fragmentation. The molecular imaging capability of fs-LA combined with laser postionization is demonstrated on intact biological samples and other complex organic thin films. A pseudo-continuous laser desorption-based strategy is also described that allows solid sampling with any portable MS instrument equipped with an atmospheric pressure interface.

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