

## TWO ARE BETTER THAN ONE: WHY TO CONSIDER ESI AND MALDI

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For mass spectrometry-based proteomic analyses, matrix-assisted laser desorption/ionization (MALDI) and electrospray ionization (ESI) are the commonly used ionization techniques. Investigations performed on very large datasets with more than 72000 peptides showed the complementary character of the two methods not only regarding the identified peptides but also with respect to their amino acid composition, hydrophobicity, charge-related parameters and post-translational modifications. Focusing on phosphopeptides enriched by Fe-IMAC chromatography, considerable orthogonality between the two analytical workflows were identified. For instance, laser-based ionization allowed for the identification of an unexpectedly high number and percentage of phosphotyrosine sites. Furthermore, MALDI-TOF MS/MS clearly favored the identification of motif signatures for acidic residue directed kinases. In summary, the investigation of large-scale datasets using both LC-ESI-MS and off-line LC coupled to MALDI-MS allows for the generation of a complete dataset of peptides and post-translational modifications.

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