

MALDI of Individual Biomolecule-Containing Airborne Particles with an Ion Trap Mass Spectrometer

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We have demonstrated ion trap-based MALDI of individual biomolecule-containing particles in near real time by on-line coating of the particles with matrix. Biomolecule-containing particles were laboratory generated and passed through a heated region containing a solution of matrix in equilibrium with the gas phase. Passage into a cooler region created a supersaturation resulting in rapid deposition of the matrix vapor onto the biomolecule-containing particles whereupon they were sampled into the inlet of our spectrometer. The coated particles were collimated with an aerodynamic lens and individually sized by light scattering-based time-of-flight. When the sized particle reached the center of the ion trap, it was irradiated with a focused 266-nm or 355 nm laser and the resulting ions were mass analyzed.

Mass spectra of leucine enkephalin, bradykinin, substance P, polylysine, melittin, and insulin chain b-containing particles were demonstrated with attomole sensitivity. For example, a MALDI mass spectrum from a 730 nm particle containing substance P resulted from only 43 amol of analyte. Isotopic structure was displayed in the mass spectra for peptides. As little as 30 amol were observed for higher mass analytes, such as insulin chain b. Even higher sensitivity was obtained for particles containing multiple analytes. For bioaerosol coating experiments, the typical matrix-to-analyte ratio could range from 10:1 to 100:1. To obtain higher matrix-to-analyte ratios, the matrix and analyte were premixed in solution. With premixing, zeptomole sensitivity was observed for bradykinin. Structural information of the peptides contained in an individual particle was obtained by tandem mass spectrometry. Collision-induced dissociation of peptides typically yielded b- and y-type fragments. Analysis of the results yields insights into the aerosol laser ablation ionization process that suggests an optically limited mechanism for ion production that has interesting ramifications on the utility of aerosol-based MALDI as an analytical technique. This technique promises to yield an extremely sensitive method for continuous on-line MALDI MS/MS analysis of biomolecules.

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