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

William A. Harris, Peter T.A. Reilly, and William B. Whitten

Novel Aspect: Ion trap-based MALDI mass spectra and MS^n of individual biomolecule-containing airborne particles were measured in real time with attomole sensitivity on an individual particle basis.

Introduction: Aerodynamic lens systems collimate particles down to less than 0.25 mm in diameter with near unit transmission efficiency making it the most efficient method for delivering analyte into vacuum. Utilizing this delivery system with aerosol mass spectrometry, 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. Coupling the MALDI technique with ion trap-based aerosol mass spectrometry circumvents the resolution issues inherent in time-of-flight-based aerosol MALDI because the resolution in the ion trap is not defined by the laser ablation/ionization process. This technique promises to yield an extremely sensitive method for continuous on-line MALDI MS/MS analysis of biomolecules.

Methods: 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 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.

Preliminary Results: 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. Even higher sensitivity was obtained for particles containing multiple analytes. For bioaerosol coating experiments, the typical matrix-to-analyte ratio was 10:1. 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. 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.

KEYWORDS: Bioaersols, MALDI, Aersosol Mass Spectrometry, Ion Trap, Tandem Mass Spectrometry, Real-Time Analysis

BRIEF: Ion trap-based MALDI mass spectra of individual biomolecule-containing airborne particles were measured in real time with great sensitivity.

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