Alternative Ionization Methods for Particle Mass Spectrometry

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Research Objective:
The objective of this project is to enhance the capabilities of a real-time airborne particle mass spectrometer by implementing matrix-independent methods for sample ionization. The enhancements should result in improved sensitivity for trace substances and, more importantly, permit quantitative determination of the presence of target species in microparticle samples on an individual particle basis.

We are using two different approaches to eliminate matrix effects on quantitative accuracy. Both rely on delayed ionization of ablated/desorbed neutral species so that ionization of target substances occurs after most of the expansion collisions have taken place. Resonance ionization by a tunable pulsed laser permits selective ionization of target species, with the laser tuned to a resonance transition from the ground state to an excited state of the target. Additional photons of the same (when possible) or different energy make up the energy required for ionization. The other approach is to perform the laser ablation step within a discharge so that desorbed neutrals are ionized by reactions with the plasma. Electron capture generates negative ions of substances with high electron affinity while electron impact ionization, associative ionization, and Penning ionization from excited metastable species produce positive ions in the discharge. Both atmospheric pressure Corona discharge ionization and glow discharge ionization at reduced pressure are being explored. Discharge ionization is relatively nonselective so that target specificity must be obtained through the mass spectral or MS/MS results.

Research Progress and Implications:
This report summarizes work after year 2 of a 3-year project. We have focused our efforts on two methods of discharge ionization: Corona discharge at atmospheric pressure external to the mass spectrometer, and glow discharge ionization with the discharge occurring in the moderate pressure region after the inlet orifice. An atmospheric pressure inlet system was constructed to guide ions formed outside the vacuum chamber into the ion trap for trapping and mass spectrometry. The ions were formed in a corona discharge between a high-voltage needle and the case. Particles were sampled within the discharge by a pulsed laser. Alternatively, vapor-phase samples could be ionized by collisions with atmospheric ions in the discharge (chemical ionization).

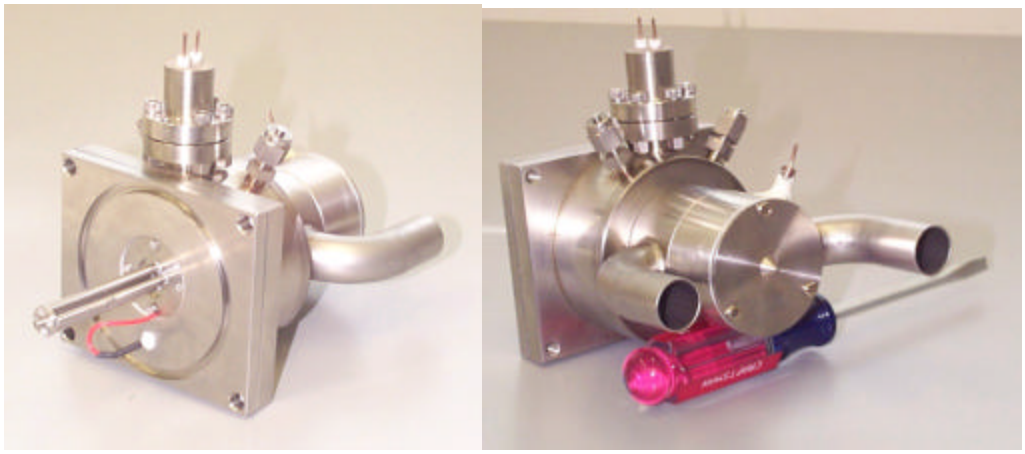

Fig. 1. Views of the atmospheric pressure inlet and ion guides.

A low-pressure discharge was also studied. An input system with glow discharge is shown in Fig. 2. Again, particles were sampled at atmospheric pressure by laser ablation but now neutral species entered the vacuum system through the capillary inlet into a low pressure discharge that causes ionization. The resulting ions were then transmitted by the quadrupole ion guides pictured in Fig. 1 into the ion trap.

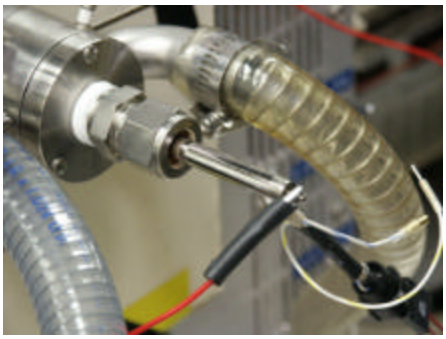

Fig. 2. Glow discharge inlet

We also made some experiments with corona discharge ionization with a Finnigan LCQ DECA XP Plus mass spectrometer. The experimental setup is shown in Fig. 3. The most significant result of these experiments was the observation that laser ablation/chemical ionization of molecular species produced very little fragmentation of the neutrals desorbed in the ablation process. An example of a mass spectrum of tryptophan particles is shown in Fig. 4.

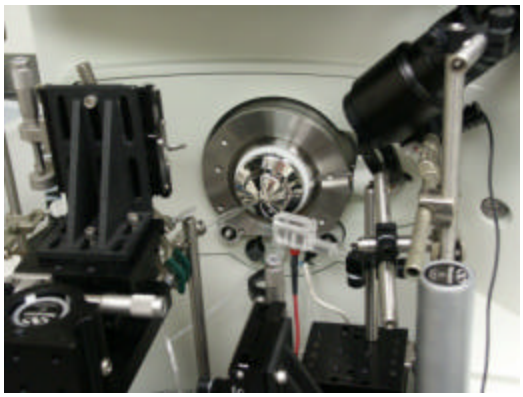

Fig. 3. Setup with Finnigan LCQ

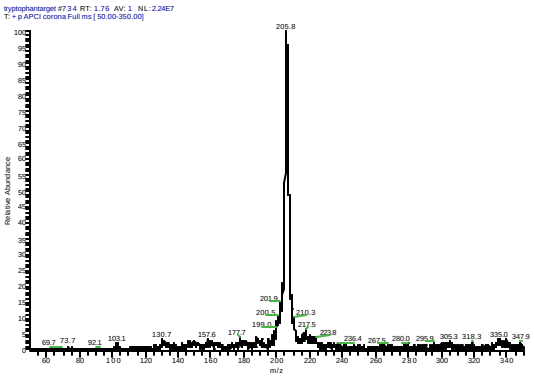

Fig. 4. Tryptophan mass spectrum