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.

In prior laboratory studies, we have shown that trace substances can be detected at the ppm level in single micrometer-sized particles by laser ablation mass spectrometry. Tandem mass spectrometry via collision-induced dissociation or ion-molecule reactions can be used for more positive identification of target substances. In addition, the size of each particle can be obtained as a byproduct of the laser triggering, providing additional analytical information. However, in general, charge exchange processes occurring in collisions during laser ablation cause the sensitivity for a particular species to be dependent on the other constituents of the particle. This matrix-dependent sensitivity prevents accurate quantitation of target concentration except in special situations where the particle composition is known a priori and the measurements can be standardized.

We are using two different approaches to eliminate the 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. Resonance ionization offers potentially higher sensitivity over direct ablation/ionization because neutral target species that were not ionized in the ablation process or neutralized by charge exchange can now be ionized by the laser. The ion background signal should be approximately the same for either case. Use of a tuned laser means that the measurement is selective for a particular target and the laser must be retuned for other analytes.

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

In the first nine months of this three-year project, we have made substantial modifications to our airborne particle laser ablation mass spectrometer system for use in the present project. The timing circuit that triggers the ablation and ionization lasers was redesigned so that two-laser ablation and ionization can be optimally performed with a Nd-YAG pumped OPO laser for the resonance ionization step instead of an excimer laser. Timing a YAG laser to fire at the precise time a random particle event is problematic because the flash lamps have to be fired 150 μs before the Q-switch is triggered for optimal output. This was accomplished using a digital comparator circuit to fire the flash lamps at the appropriate time. Now the frequency of the ionization laser can be swept to observe the resonance ionization spectra of the particles.

A Varian 2000 ion trap mass spectrometer has been modified with a differentially pumped atmospheric inlet equipped with ion guides. The front end of the inlet can easily be changed from atmospheric pressure corona discharge ionization to reduced pressure glow discharge ionization. Each ionization source has been designed for optimal performance. The efficacy of each source will be compared. The glow discharge source includes aerodynamic lenses that create a well-collimated beam that passes through the center of the ion source for optimal particle detection efficiency. The corona discharge source has been designed for ionization and ion transport efficiency. Experiments were performed as a function of inlet design to optimize ion transport into vacuum. An adaptable multipole ion guide system has been designed so that transport of the ions into the trap can be optimized. An rf power supply that permits optimization of ion guide frequency has also been built.

Planned Activities

The developments to be explored in the second and third years of the project are designed to alleviate the matrix-dependent sensitivity limitations of the airborne particle mass spectrometer. It is anticipated that the implementation of resonance ionization subsequent to ablation will enhance the sensitivity for the target species and reduce the matrix dependence because the ionization will occur after most of the charge-exchanging collisions in the ablation plume have occurred. Similar sensitivity results are expected for discharge ionization but without the single species selectivity, permitting a wider range of target analytes with a given setup. Discharge ionization should also be especially powerful for negative ion generation.

The research will focus on particular analytes that have been mentioned in several D&D Technical Need Statements. In addition to uranium and other actinides, we will explore methods to analyze for technetium, mercury, and PCB's. It is anticipated that resonance ionization will be more appropriate for elemental analysis while discharge ionization will efficiently generate negative ions from the PCB's with their high electron affinity. Together with particle size measurement and standardization with particles of known composition, the new ionization techniques should make it possible to obtain quantitative results in many cases.