Chemical Composition Measurement of Atmospheric Aerosols in Real-Time

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Summary

Utilizing the soft ionization capability of electrospray ionization (ESI), an Aerosol Electrospray Mass Spectrometer Ion Source (AEMS-IS) is developed for collecting aerosols and releasing ions from them for mass spectrometry. This device draws in aerosol, charges them and deposits them electrostatically on the tip of a blunt needle. A conductive solvent is subsequently used to dissolve compounds of interest from the deposited aerosol and ionize them using the electrospray technique. Feasibility of this 2-step process is proven experimentally with a QSTAR XL (AB Sciex, Framingham, MA) quadrupole time-of-flight mass spectrometer, as well as an LTQ Velos Pro ion trap mass spectrometer (Thermo Fisher, Waltham, MA) examining atomizer generated aerosol (of Cesium Iodide and Levoglucosan) as well as secondary organic aerosol (SOA) generated by gas-to-particle conversion. AEMS-IS technology could be used to transition existing atmospheric pressure ion source mass spectrometers into aerosol mass spectrometers, enabling exact mass analysis of parent species (and inference of atomic composition), as well as MS^n analysis, without the need to collect particles onto filters and subsequent extraction.

Instrument Description

Figure 1 shows the schematic diagram of AEMS-IS with three highlighted key components. Particles smaller than 2.5 μm in diameter follow the streamlines of the major flow and are led to a unipolar charger. Inside the charger, positive ions generated via corona discharge readily attach to aerosol particles, which then go into the particle capture/ESI source shown in Figure 2. Figure 3(a) shows the exit end of aerosol delivery tube, located close to the aerosol collection rod (tungsten, 1/16" diameter). The nozzle is electrically grounded; meanwhile, a negative voltage is applied to the collection rod sheathed with a plastic (PEEK) tube, facilitating deposition of particles onto its rounded end. Particle charging and collection proceeds for a predefined period (10-60 min for the results shown here), after which aerosol is no longer sampled, and the polarity of the voltage applied to the Tungsten rod is set to either positive or negative high voltage for ESI. A flow of liquid solvent is driven over the rod, so collected molecules (from aerosol particles) dissolve in it and the high voltage applied relative to the surroundings (the mass spectrometer inlet is grounded) leads to the formation of a Taylor cone at the rod tip, shown in Figure 3(b). The collection of mass spectra with high mass resolving power for generated ions then enables identification of molecules in the collected aerosol.
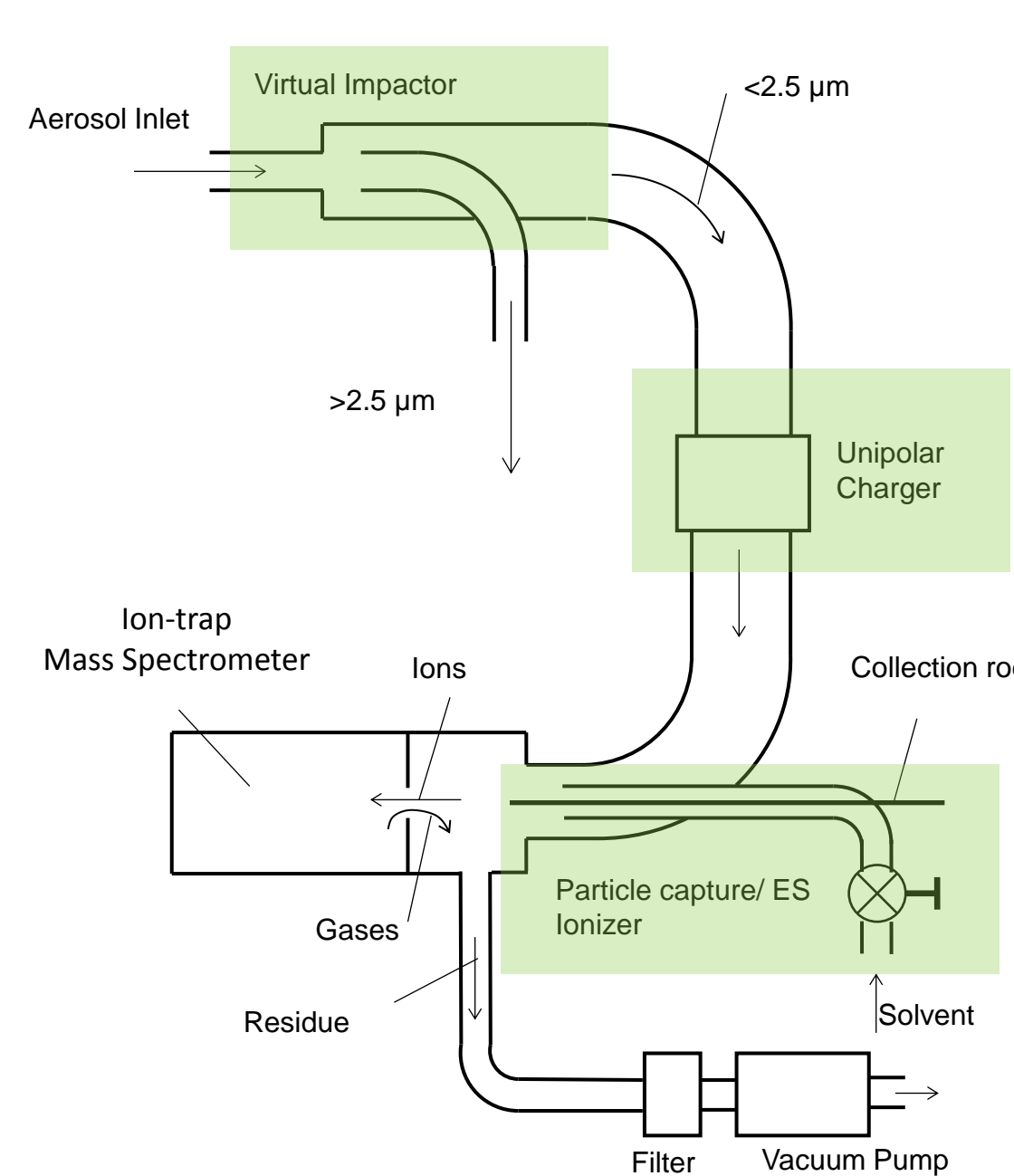

Figure 1. Schematic diagram of AEMS-IS; three key components are highlighted.
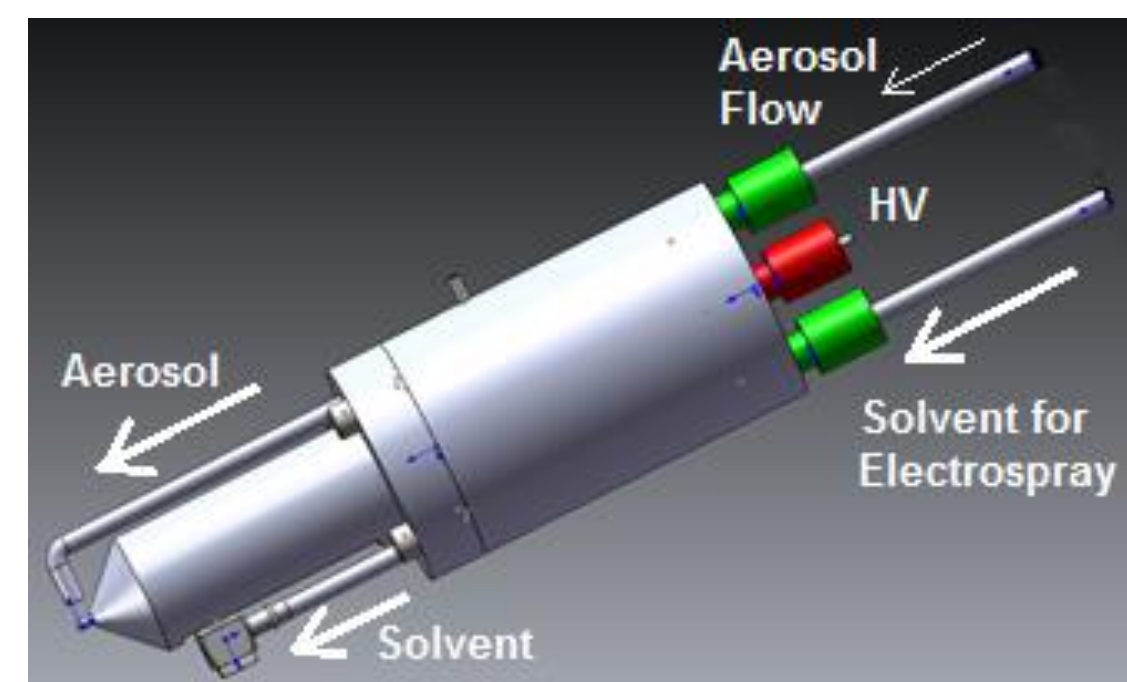

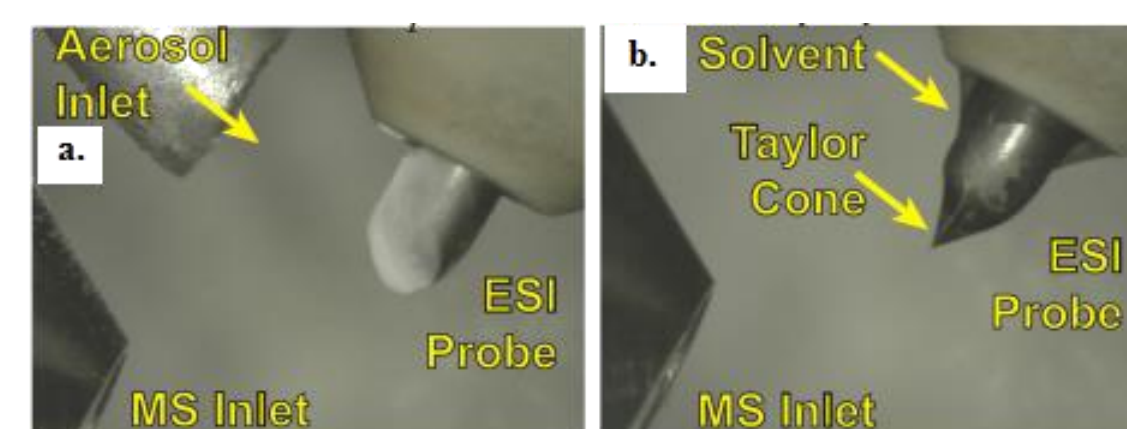**Figure 2.** Particle capture and electrospray ionization device.

Figure 3. Photographs of aerosol delivery tube and ESI tip for (a) Electrostatic precipitation mode and (b) Electrospray ionization mode for generation of ions of the compounds from the captured particles.

Experimental Results

Figures 4 shows the results of levoglucosan particles with 10 minutes of collection. They were subsequently eluted with 95:5 methanol/water containing 10 mM NaCl. At time = 0 minutes, high voltage was applied to the collection rod and the flow of liquid for ESI was initiated. After 1-2 minutes, liquid arrived at the collection rod, leading to the formation of a Taylor cone. Correspondingly, ions were detected in the mass spectrometer after 1-2 minutes. The levoglucosan+Na^+ ion is the dominant species (m/z = 185.1), with the sodiated levoglucosan dimer (m/z = 347.2) also present. No fragment ions of levoglucosan were detected. Figure 5 displays the integrated signal intensity from all ions containing levoglucosan over the entire experiment as a function of exposed levoglucosan mass (particle mass concentration X sample flowrate X collection time) and the deposited levoglucosan mass (which is corrected for charging and deposition efficiencies, but not for transmission and detection in the mass spectrometer). Both plots reveal a power law relationship between detected signal and aerosol particle mass over four orders of magnitude, with less than 10 ng of deposited levoglucosan detectable.

Coupled with the QSTAR XL mass spectrometer, an AEMS-IS was used to detect the parent molecules within SOA particles generated by a flow tube reactor with α-pinene and toluene as precursors. Figures 6 and 7 display the positive and negative mode spectra for SOA particles obtained with 60 minutes collection (Spectra of ESI Solvent alone contained peaks at nominal
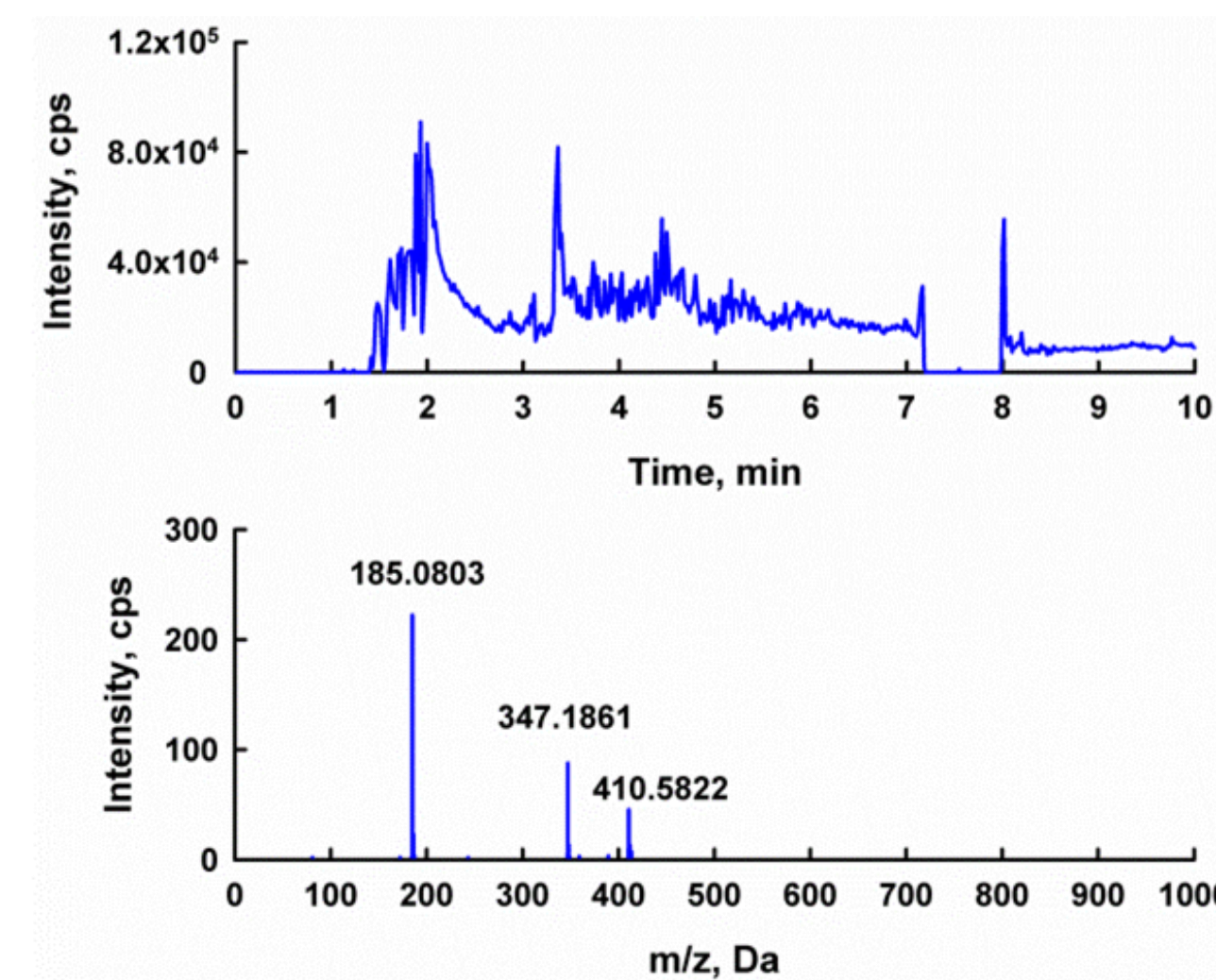
masses of 244 and 303 Da in negative mode, and 536 Da in positive mode). There are a number of species in the 200-900 Da range detected by AEMS. Positive and negative ionization modes enable detection of very different compounds. Higher mass products are formed from reactions involving the lower mass reactants leading to specific families of peaks in the spectra. This is more evident in the negative ion mode. Though not clear on the scales employed in Figures 6 & 7, we do find ions with masses beyond 1000 Da, indicating that there are extremely high mass (and presumably extremely low volatility) compounds present in SOA.

Attaching an AEMS-IS to a LTQ Velos Pro mass spectrometer, similar mass spectra were obtained for α-pinene SOA. Present in both spectra was an ion at a nominal mass of 755 Da, hence we elected to examine the collision induced dissociation products of this ion in MS^n experiments. As shown in Figure 8, the 755 Da parent ions dissociated (25 % relative collision energy) and the resulting ion at m/z = 337, observed in the MS^2 spectrum, is subsequently isolated and dissociated (33 % relative collision energy) to yield the MS^3 spectrum. Although detailed analysis of these results is currently underway (including MS^n analysis of other peaks), they clearly demonstrate that the AEMS-IS enables MS^n analysis of SOA when an appropriate mass spectrometer is employed.

Figure 4. The mass spectrometer total signal chromatograph for levoglucosan (above). The integrated mass spectrum for levoglucosan (below).
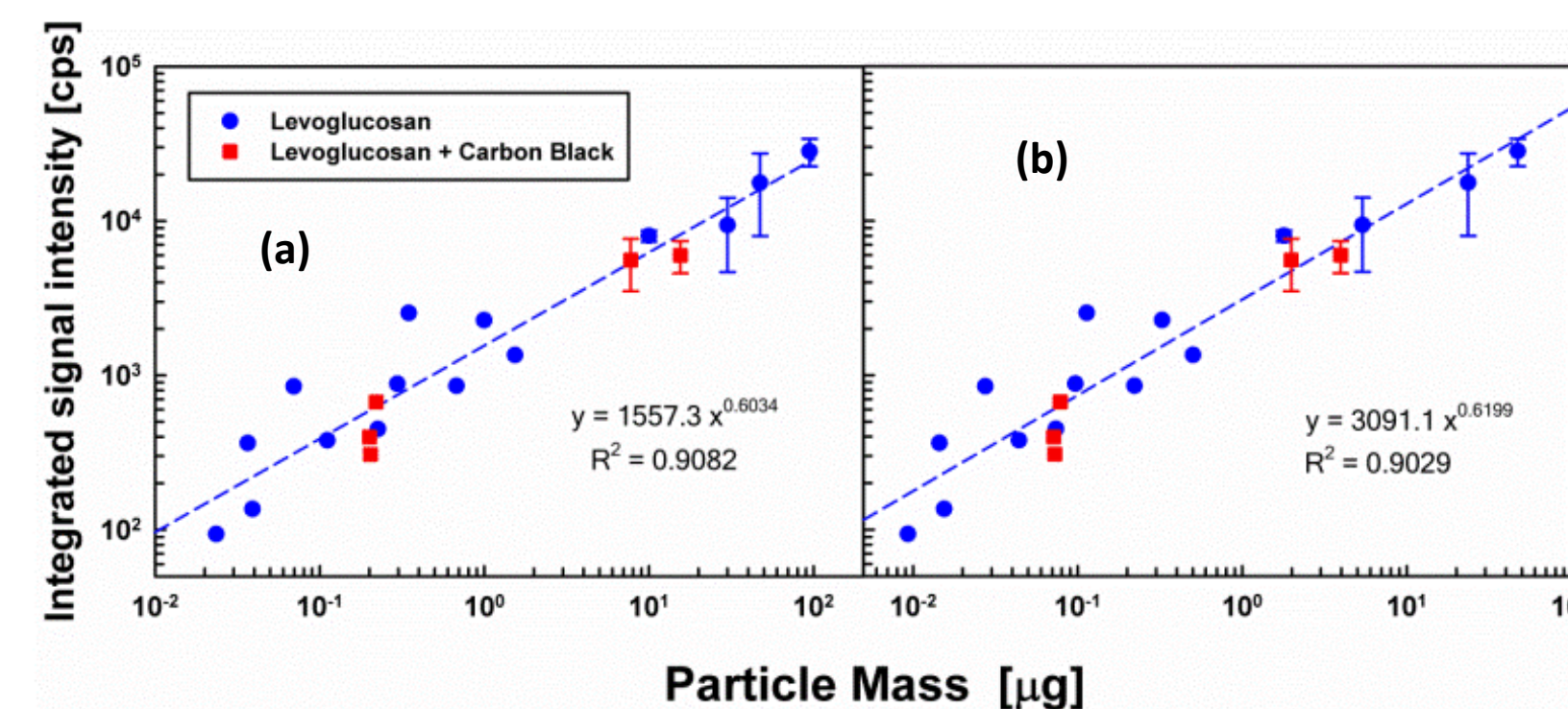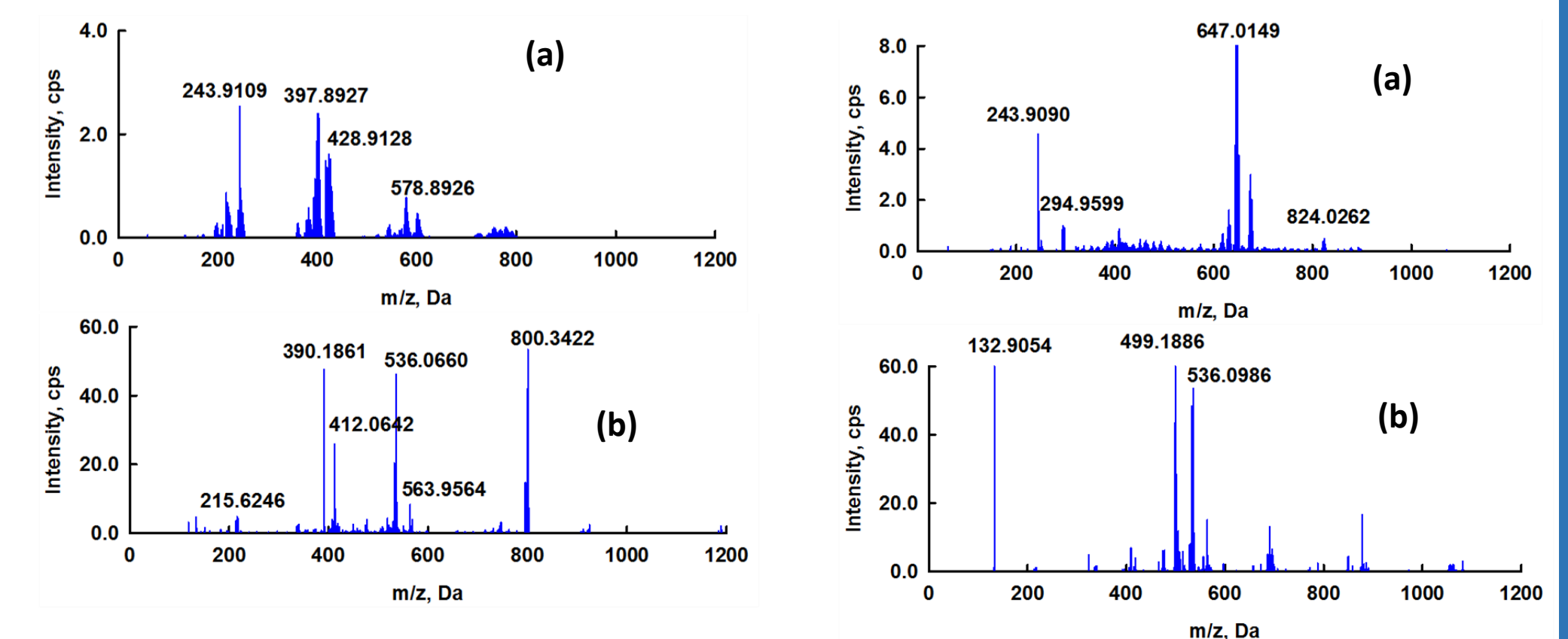

Figure 5. Integrated levoglucosan signal intensity from mass spectrometric measurements as a function of (a) the mass of levoglucosan passed into the ionization chamber and (b) the mass deposited on the collection rod.

Figure 6. Mass spectra of α-pinene ozonolysis products using AEMS with a QSTAR XL mass spectrometer, (a) negative and (b) positive ions.

Figure 7. Mass spectra of toluene ozonolysis products using AEMS with a QSTAR XL mass spectrometer, (a) negative and (b) positive. The peak at 132.9 corresponds to Cs^+ used for instrument calibration.
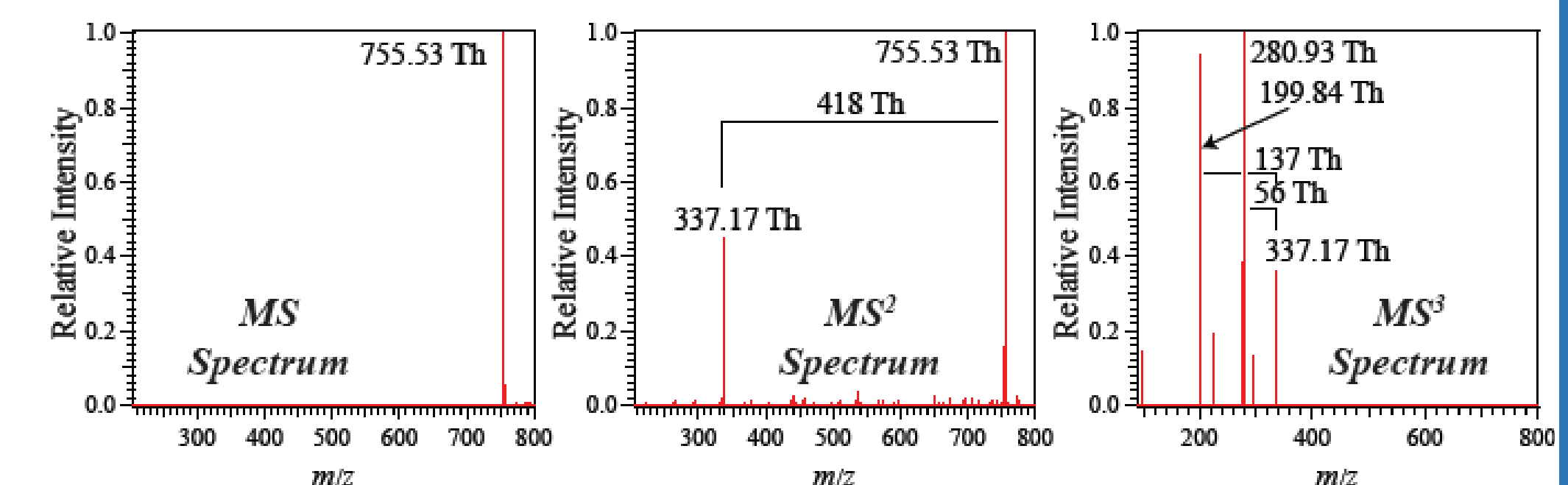

Figure 8. MS^n analysis of the 755 Da ion using AEMS with a LTQ Velos Pro mass spectrometer.

Conclusions

An ion source (AEMS-IS) is developed for collecting aerosols and releasing ions from them using the electrospray technique. Coupled with a quadrupole-time-of-flight mass spectrometer and an ion trap mass spectrometer, this device was proven with several compounds commonly found in atmospheric aerosols, including levoglucosan, levoglucosan mixed with carbon nanoparticles, and secondary organic aerosol generated from α-pinene and toluene ozonolysis. This device is promising for automated measurement of the chemical composition of atmospheric aerosols.