Using atmospheric-pressure glow discharge mass spectrometry for the analysis of secondary organic aerosol

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A

Introduction & Motivation

- the chemical analysis of atmospheric aerosols is still a major challenge and bound to large uncertainties in atmospheric research [1]
- online techniques, such as the Aerosol Mass Spectrometry (AMS, Aerodyne®), offer highly time- and size-resolved information but lack in chemical analysis of single organic compounds due to electron impact ionization [2]
- offline techniques, such as filter-sampling and subsequent analysis by LC-MS, offer almost complete chemical analysis of organic aerosols but have a very low time resolution and additional sample preparation is needed [1]
- here, we present a new online technique for the chemical analysis of secondary organic aerosols (SOA) which uses the flowing atmospheric-pressure afterglow (FAPA) technique, offering highly time-resolved chemical information of sub-micrometer aerosol particles without additional sample preparation [3]

B

The new ion source

- the FAPA ion source consists of a ceramic discharge cell, in which a Helium DC glow discharge plasma is maintained between a tip electrode and a capillary electrode
- exited Helium atoms and primary reagent ions can exit the discharge through the capillary electrode and enter the afterglow region where the desorption/ionization of the aerosol compounds takes place
- the ion source is held in place by a modified Thermo® ESI flange; aerosol is introduced through a 0.25 inch stainless steel tubing
- during operation a negative potential is applied to the inner electrode through a 5 kΩ ballast resistor and the discharge is maintained in current controlled mode; the Helium flow is adjusted to 1 L/min

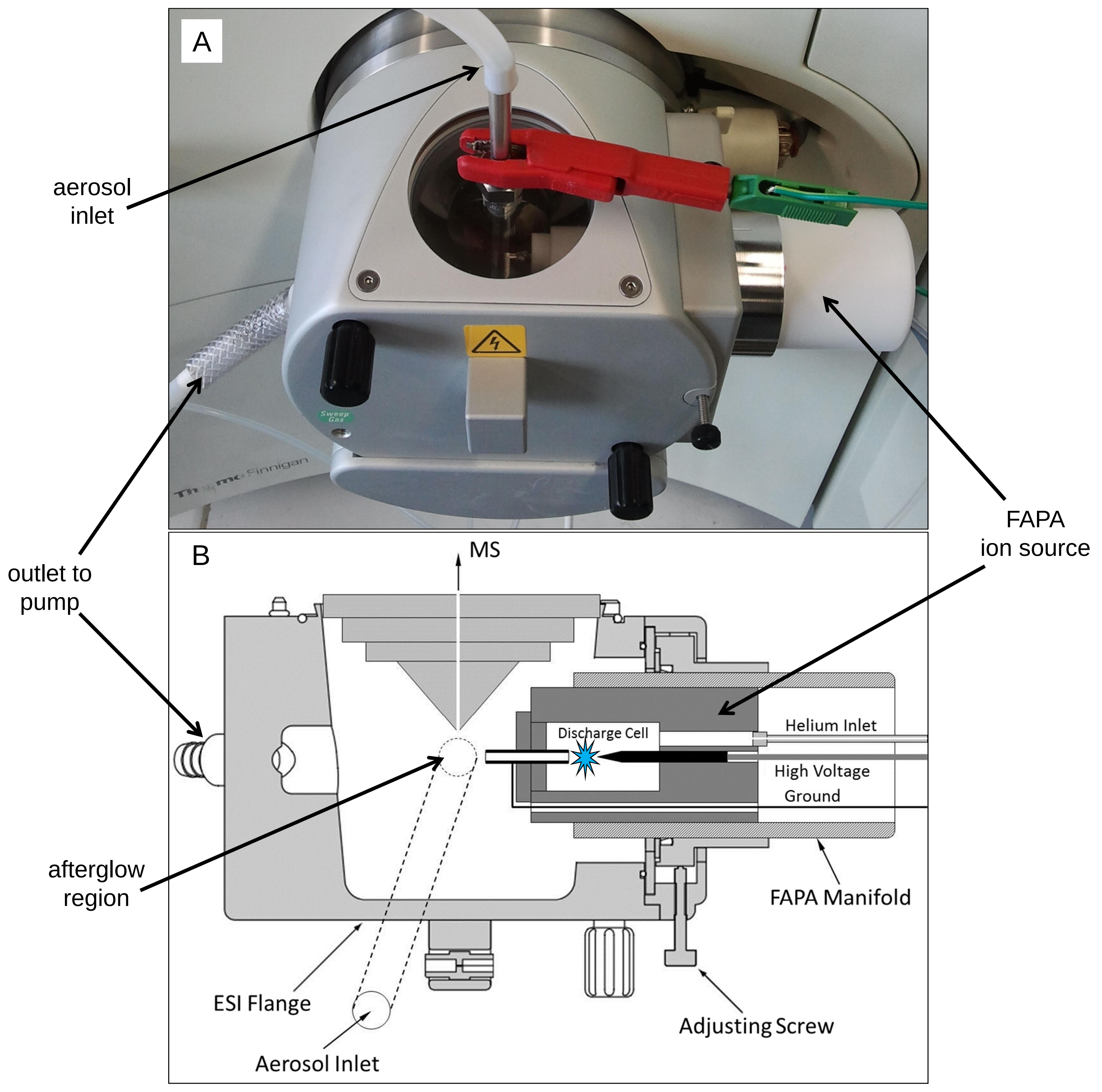


Figure 2: A) Photograph of the FAPA ion source mounted on a LCQ Deca XP Plus (Thermo®) ion trap MS; B) Cross sectional view of the FAPA assembly. The aerosol inlet is arranged orthogonal to the MS inlet and the FAPA exit. While the original Thermo® ESI flange was used the ESI manifold was replaced by a home-built FAPA manifold.

C

Source characterization

temperature of the afterglow region

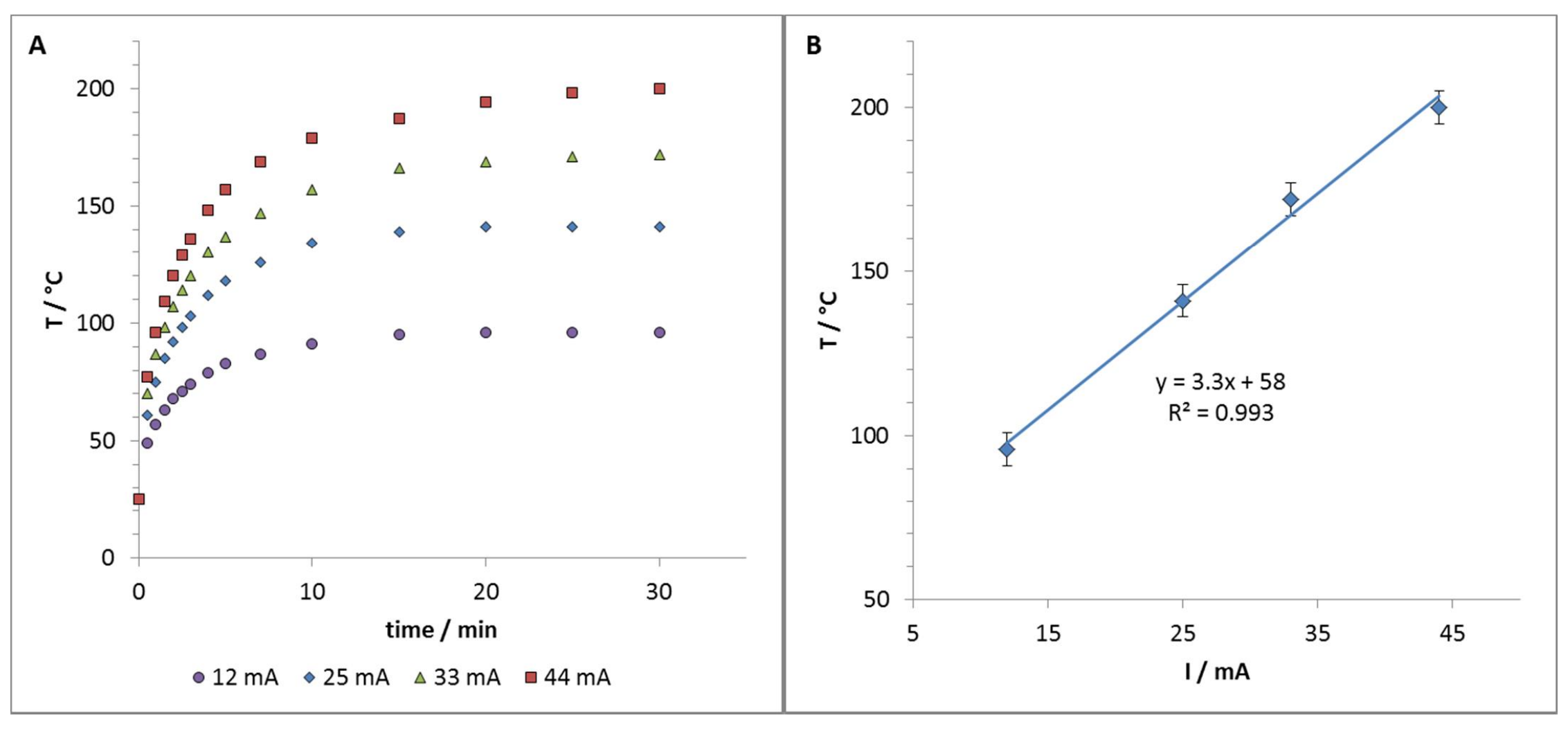


Figure 3: A) Maximum temperature of the afterglow region versus time for different current modes; B) Maximum equilibrium temperature at a chosen current.

- temperature of the gas stream in the afterglow region was measured using a thermocouple (type K), which was placed directly in front of the exit capillary of the ion source
- correlation between the applied current, the time and the maximum equilibrium temperature in the afterglow region was found
- linear correlation between applied current and equilibrium temperature (3.3 °C/mA) covering approximately the range between 100 °C and 200 °C

background mass spectra

The background mass spectra are similar to other common atmospheric-pressure ionization techniques, such as electro spray ionization (ESI) or atmospheric-pressure chemical ionization (APCI). However, much higher signal intensities are achieved due to the higher reagent ion flux.

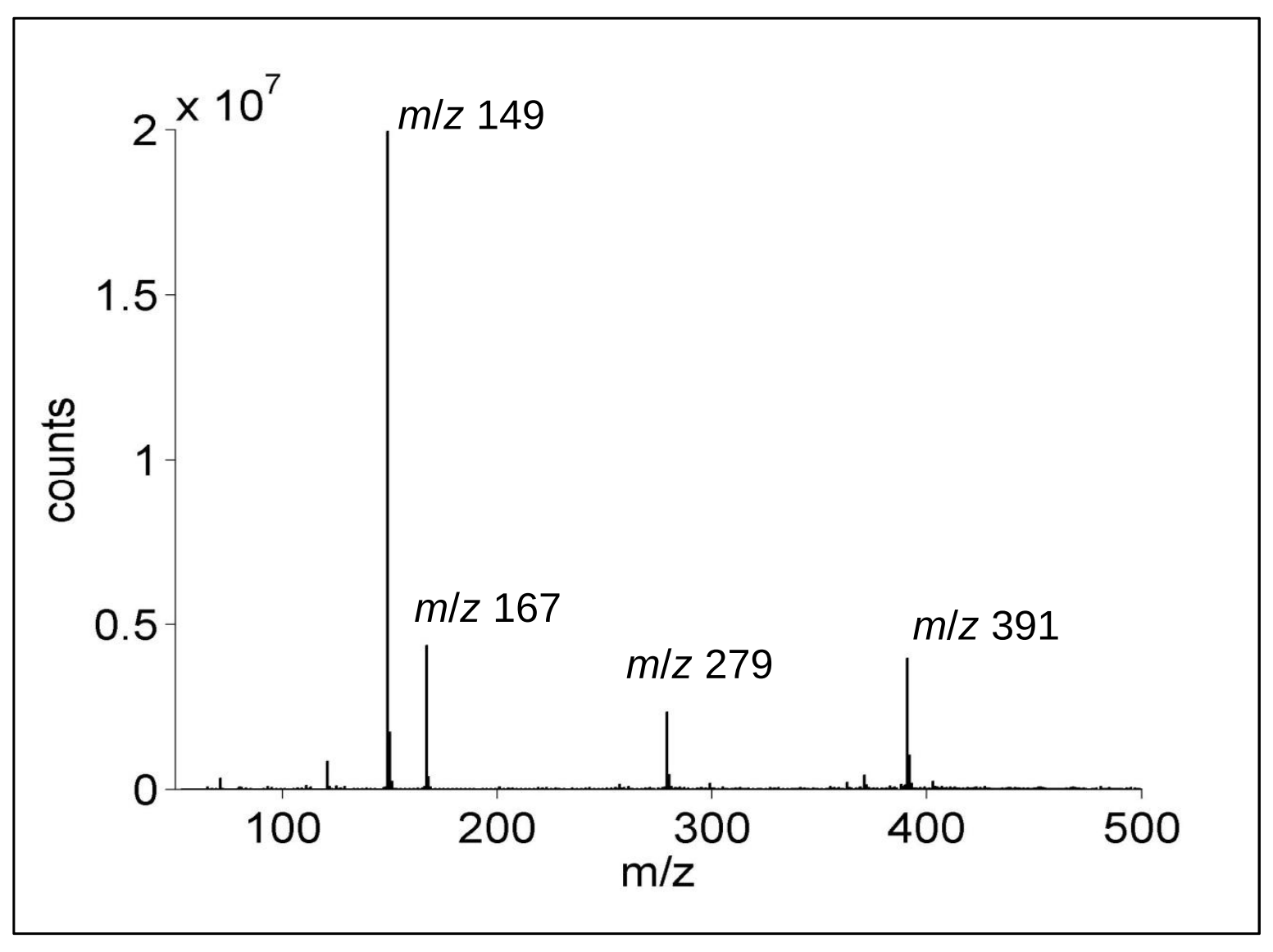


Figure 4: Background mass spectrum in positive ion mode: the four major signals correspond to plasticizers from the laboratory air which are known as common MS contaminants (*m/z* 149 = phtalic anhydride (MH⁺), *m/z* 167 = dimethyl phtalate (MH⁺), *m/z* 279 = dibutyl phtalate (MH⁺), *m/z* 391 = dioctyl phtalate (MH⁺)).

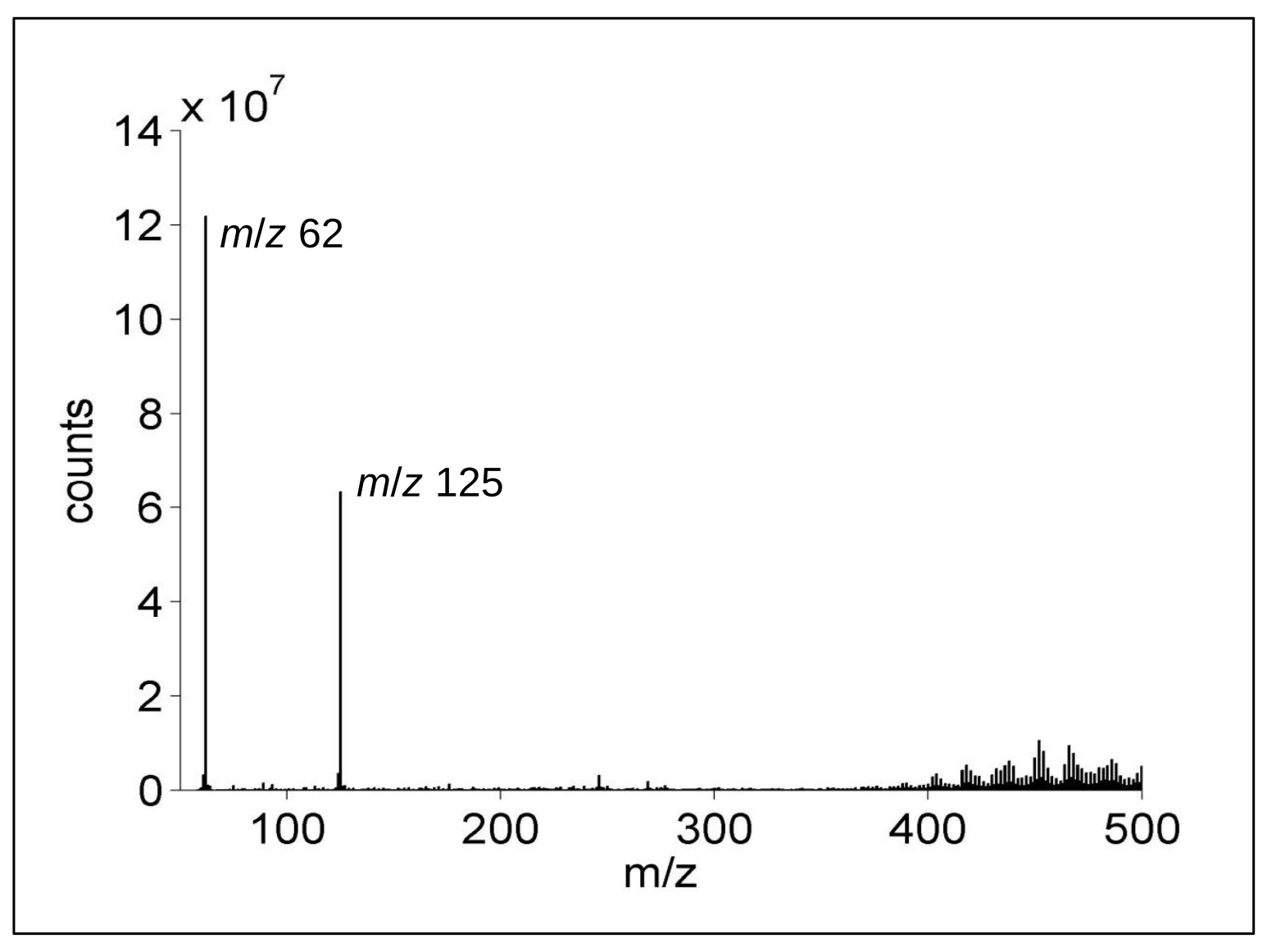


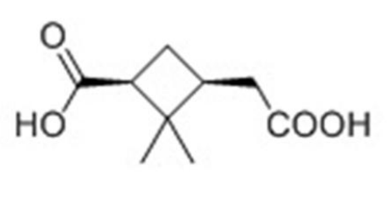
Figure 5: Background mass spectrum in the negative ion mode: the signals at *m/z* 62 and *m/z* 125 correspond to the formation of NO_3^- ions in the afterglow from ambient air. The signals at m/z ratios above 400 are probably caused by polymeric compounds from built-in plastics in the ion source assembly.

D

Analysis of secondary organic aerosol

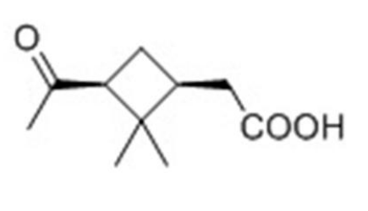
- SOA was generated in the laboratory from α-pinene ozonolysis under dark and dry conditions and introduced into the afterglow region at 2 L/min
- due to the soft ionization processes occurring in the afterglow region, the observed signals correlate mainly with the deprotonated molecular ions
- signals for typical α-pinene oxidation products are observed in the range between *m/z* 150 and *m/z* 200, such as pinic acid (*m/z* 185, [M-H]⁻), pinonic acid (*m/z* 183, [M-H]⁻) and 10-hydroxypinonic acid (*m/z* 199, [M-H]⁻)
- many unidentified signals at higher *m/z* ratios which are possibly dimeric oxidation products of α-pinene

m/z 183



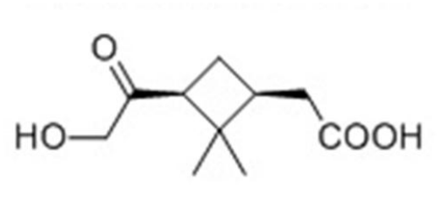
pinonic acid

m/z 185



pinic acid

m/z 199



10-hydroxypinonic acid

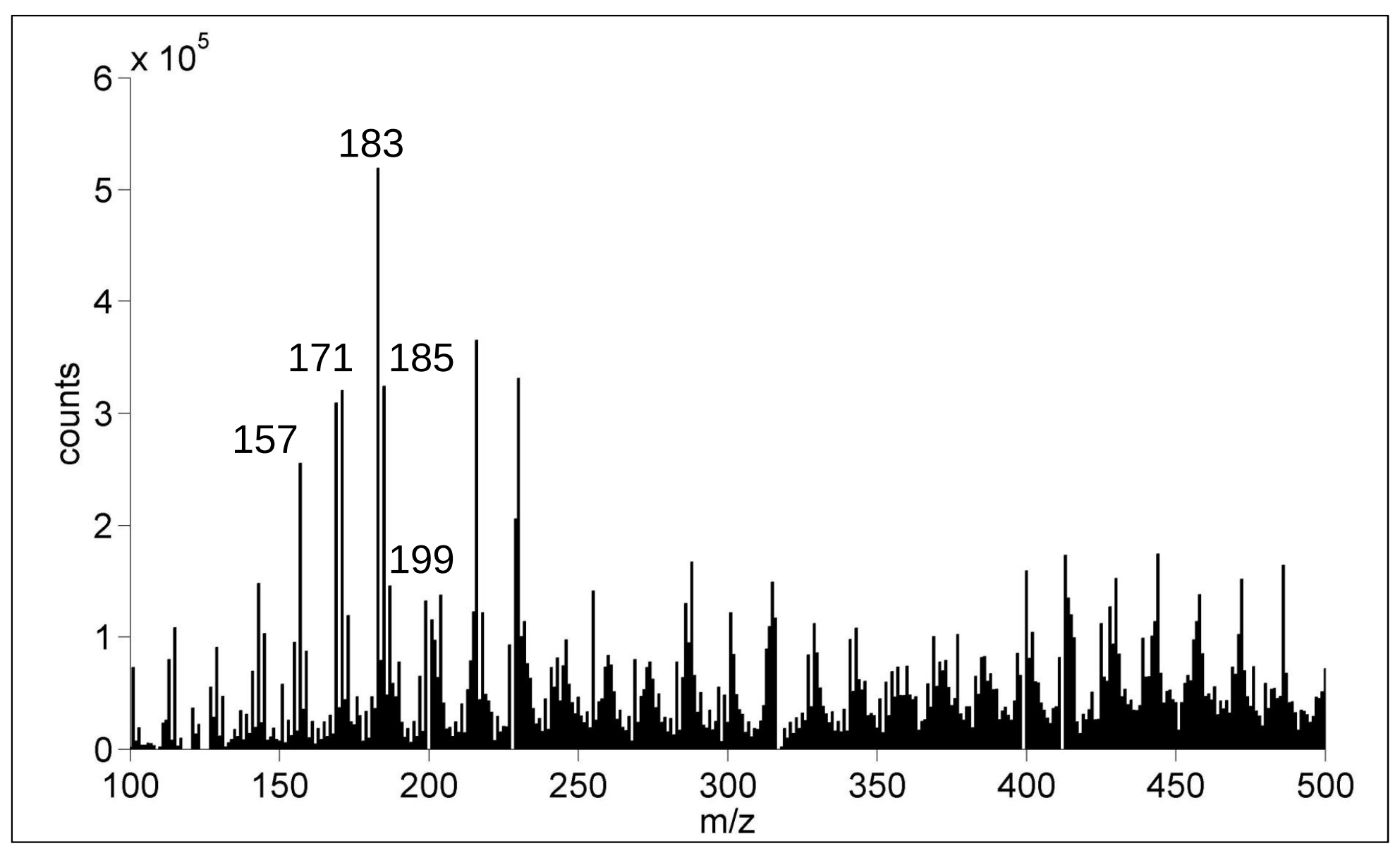


Figure 6: Mass spectrum in the negative ion mode of laboratory-generated SOA (background subtracted).

E

Conclusions & Outlook

- ✓ a new ion source for the online analysis of secondary organic aerosols based on the flowing atmospheric-pressure afterglow technique was developed and characterized
- ✓ first measurements with laboratory-generated aerosol were conducted
- ☐ further experiments are needed to improve the analysis of higher molecular weight compounds
- ☐ intercomparison studies with other aerosol instruments to evaluate the obtained data
- ☐ experiments for calibration of the ion source and measurement of detection limits for different substances
- ☐ application of the instrument in field measurements

This poster can be downloaded at tiny.cc/aerosol-FAPA or by scanning the QR code on the right-hand side.

Acknowledgements

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References: [1] T. Hoffmann, R.-J. Huang, M. Kalberer, *Anal. Chem.*, **2011**, *83* (12), 4649–4664. [2] V. A. Lanz *et al.*, *Atmos. Chem. Phys.* **2010**, *10*, 10453-10471.
[3] J. T. Shelley, J. S. Wiley, G. M. Hieftje, *Anal. Chem.* **2011**, *83*, 5741-5748.