

Direct analysis of secondary organic aerosol using the flowing atmospheric-pressure afterglow (FAPA) ambient mass spectrometry source



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A Overview

- the chemical analysis of atmospheric aerosols is still a major challenge and bound to big uncertainties in atmospheric research [1]
- online techniques, such as the Aerosol Mass Spectrometer (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 Introduction

- secondary organic aerosol (SOA) accounts for a major fraction of atmospheric aerosol and has big implications for earth's climate and human health
- it is formed when low volatile organic compounds (LVOCs), formed by oxidation of volatile organic compounds (VOCs), undergo gas-to-particle conversion
- to understand the impacts of SOA detailed knowledge about formation, properties and chemical evolution is needed [1]

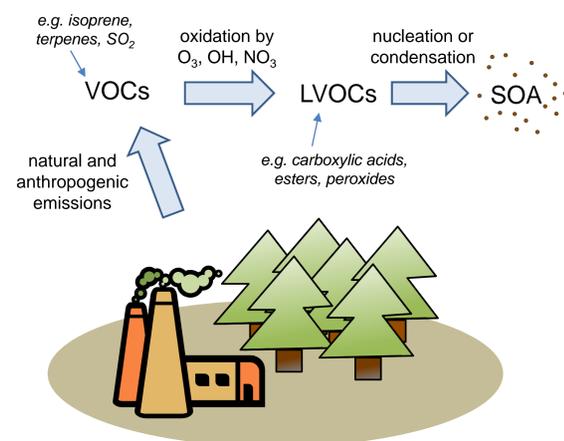


Figure 1: Formation of secondary organic aerosol (SOA) by oxidation of volatile organic compounds (VOCs) and subsequent gas-to-particle conversion.

C Method

- 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 slightly redesigned Thermo® ESI flange; aerosol is introduced through a 1/4" stainless steel tubing

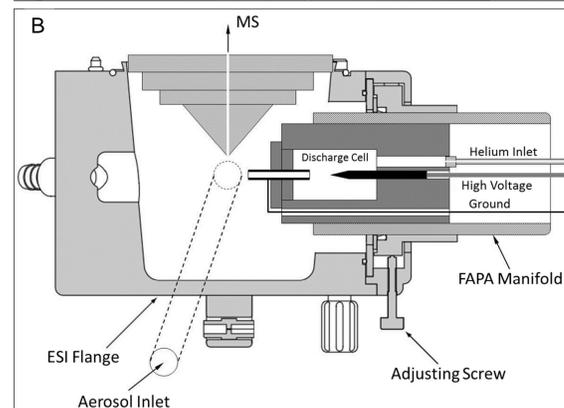


Figure 2: A) photograph of the FAPA ion source mounted on a LCQ Deca XP Plus (Thermo®) ion trap MS; B) Cross sectional view of the FAPA assembly. The aerosol inlet is arranged orthogonal to the MS inlet and the FAPA exit. While the original Thermo® ESI flange was used the ESI manifold was replaced by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

- 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 with a rotameter
- laboratory SOA is produced by α -pinene ozonolysis in a 100 L smog chamber
- SOA gas phase compounds are removed prior to analysis by passing the aerosol stream through an activated charcoal denuder

D Source Characterization

temperature of the afterglow region

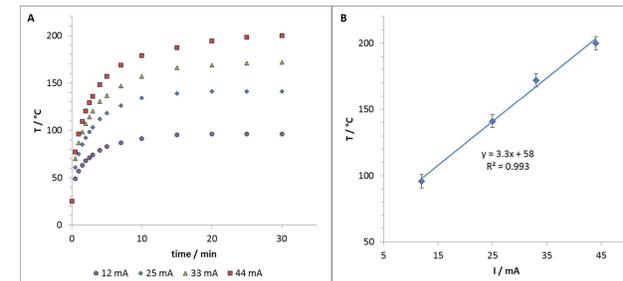


Figure 3: A) maximum temperature of the afterglow region versus time for different current modes; B) maximum equilibrium temperature at a chosen current.

- 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
- temperature shows a logarithmic behavior with time
- 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

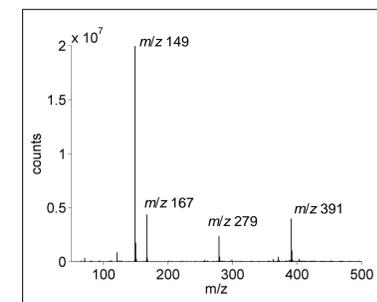
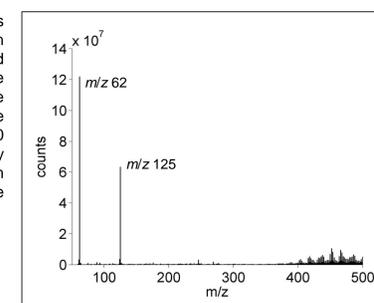


Figure 4: background mass spectrum in positive ion mode: the four major signals correspond to plasticisers from the laboratory air which are known as common MS contaminants (m/z 149 = phthalic anhydride (MH^+), m/z 167 = dimethyl phthalate (MH^+), m/z 279 = dibutyl phthalate (MH^+), m/z 391 = dioctyl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

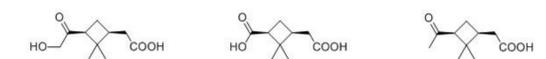
The background mass spectra are similar to other common atmospheric-pressure ionization techniques, such as electro spray ionization (ESI) or atmospheric-pressure chemical ionization (APCI). However, much higher signal intensities are achieved due to the higher reagent ion flux.

Figure 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.



E Analysis of laboratory generated SOA

- SOA was generated in the laboratory from α -pinene ozonolysis under dark and dry conditions
- SOA was introduced into the afterglow region of the FAPA through PTFE tubing with a flow rate of 2 L/min
- 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, $[M-H]^-$)



10-hydroxypinonic acid pinonic acid pinic acid

- many unidentified signals at higher m/z ratios which are possibly dimeric oxidation products of α -pinene

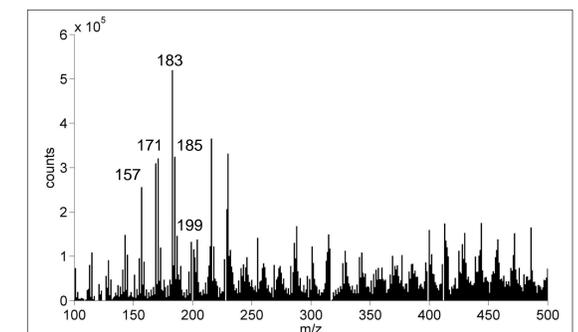


Figure 6: mass spectrum in the negative ion mode (background subtracted) of laboratory-generated SOA.

F Conclusions and 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

Acknowledgements

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