Analysis of secondary organic aerosol using a Micro-Orifice Volatilization Impactor (MOVI) coupled to an Ion Trap Mass Spectrometer with Atmospheric Pressure Chemical Ionization (APCI-IT/MS)

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A Introduction

Secondary organic aerosol (SOA) is formed in the atmosphere when oxidation products of volatile organic compounds undergo gas-to-particle conversion. SOA accounts for a substantial fraction of ambient tropospheric aerosol and has implications on the earth’s climate and human health. Much research has been done over the last few decades to gain detailed knowledge about the formation, properties and transformation of SOA and many sophisticated techniques have been developed to resolve its chemical composition. However, none of these measurement techniques allows a complete chemical analysis of SOA particles and, despite much excellent work on themes such as identifying biogenic and anthropogenic SOA precursors, the knowledge about formation mechanisms, properties and evolution of SOA often remains uncertain.

B Objective

Here we describe the development and application of a Micro-Orifice Volatilization Impactor (MOVI) which is coupled to an ion trap mass spectrometer with atmospheric pressure chemical ionization (APCI-ITMS). The MOVI-APCI-ITMS allows the quantification of organic acids and other oxidation products of volatile organic compounds in secondary organic aerosol (SOA) on a semi-continuous basis. Furthermore, the vapor pressures and saturation concentrations of the particle components can be estimated from the measured desorption temperatures.

C Design of the MOVI

The MOVI is a single stage, multi-nozzle impactor with 100 nozzles, each having a diameter of 150 µm. At a flow-rate of 10 L·min⁻¹ air is drawn through the MOVI and particles are collected on a deposition plate. The outlet diameter (diameter of 50% collection efficiency) is 130 nm. A low pressure drop of only 5.3% of atmospheric pressure behind the nozzles allows collecting not only volatile but even semi-volatile compounds, which are an important part of SOA.

D Organic acids were quantified in smog-chamber experiments ...

Calibration:
- the MOVI-APCI-IT/MS was calibrated by depositing different amounts of a solution of pinic acid in methanol manually on the deposition plate.
- the limit of detection for pinic acid was found at 7.3 ng

Smog chamber experiments:
- in smog chamber experiments SOA particles were produced by α-pinene-ozonolysis
- the particles were collected with the MOVI at 10 L·min⁻¹ for 15 min
- the deposition plate of the MOVI was heated up to 120°C in 4 min and the volatile components were transferred into the APCI-ITMS

E ... and field experiments during the BEACON-RoMBAS 2011

- field campaign in a ponderosa pine woodlands in the southern Rocky Mountains (July 28th – August 16th, 2011)
- study was focused on biosphere-atmosphere interactions
- sampling time: 5 h @ 10 L·min⁻¹
- 4 measurements / day

F Vapor pressures were estimated from desorption temperatures

- laboratory experiments show good agreement with literature data for pinic acid (log pӨ = -5.68 Pa, Pankow et al[4])
- measured vapor pressures during the field campaign are much lower because of:
  - oxidation products from other terpenes
  - oxidation products from non-terpenes
  - anthropogenic contaminations

G Conclusions

The MOVI-APCI-ITMS was successfully tested in laboratory and field measurements:
- quantification of organic acids (e.g. pinic acid) in aerosol particles
- low fragmentation mass spectra due to a soft ionization technique (APCI)
- estimation of vapor pressures of particle components
- quantification of low-volatile compounds not possible
- not suitable for thermolabile substances
- no size-separation of the particles

H Outlook

- quantification of other organic acids (e.g. pinonic acid, 10-hydroxypinic acid, ...) in SOA particles
- method development and further investigations for the measurement of vapor pressures with the MOVI-APCI-IT/MS
- intercomparison studies with other instruments (e.g. Aerosol Mass Spectrometer, online-APCI, ...)
- application of the instrument in field campaigns