

A Micro-orifice Volatilization Impactor (MOVI) coupled to an ion trap mass spectrometer for the analysis of secondary organic aerosol

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A Introduction

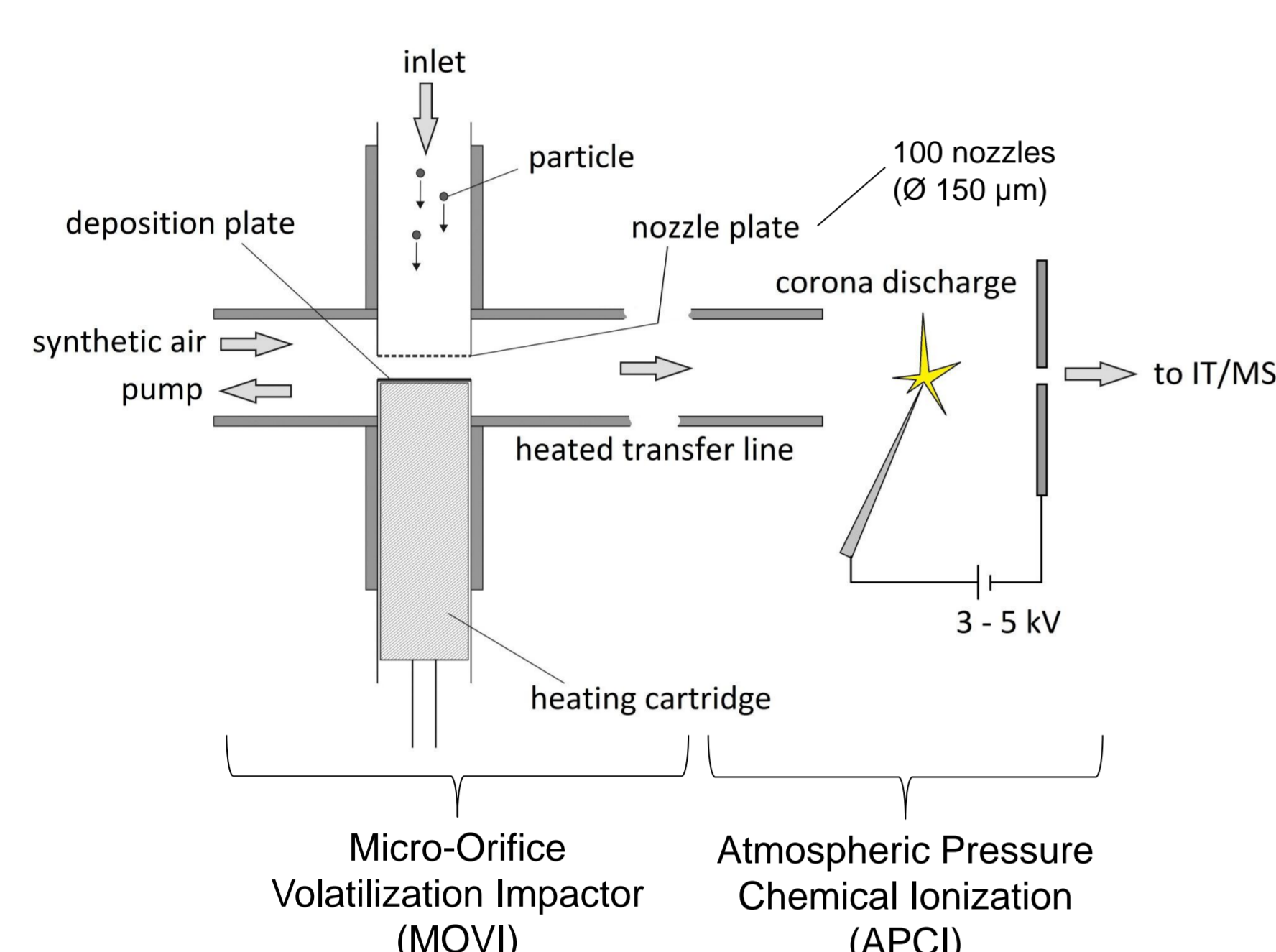
Secondary organic aerosol (SOA) is formed in the atmosphere when oxidation products of volatile organic compounds undergo gas-to-particle conversion. SOA accounts for a substantial fraction of ambient tropospheric aerosol and has implications on the earth's climate and human health. Much research has 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. Yet, without this knowledge it is impossible to predict and evaluate the implications of SOA on atmospheric processes, climate and human health.^[1]

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-IT/MS). The MOVI-APCI-IT/MS allows the quantification of organic acids and other oxidation products of volatile organic compounds in secondary organic aerosols (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. We present the application of the MOVI-APCI-IT/MS for the quantification of organic acids in sub-micron particles in laboratory experiments and during the "Bio-hydro-atmosphere interactions of Energy, Aerosols, Carbon, H₂O, Organics and Nitrogen - Rocky Mountain Biogenic Aerosol Study" (BEACHON-RoMBAS) which took place in summer 2011 in a ponderosa pine woodland in the southern Rocky Mountains of North America.

C Method

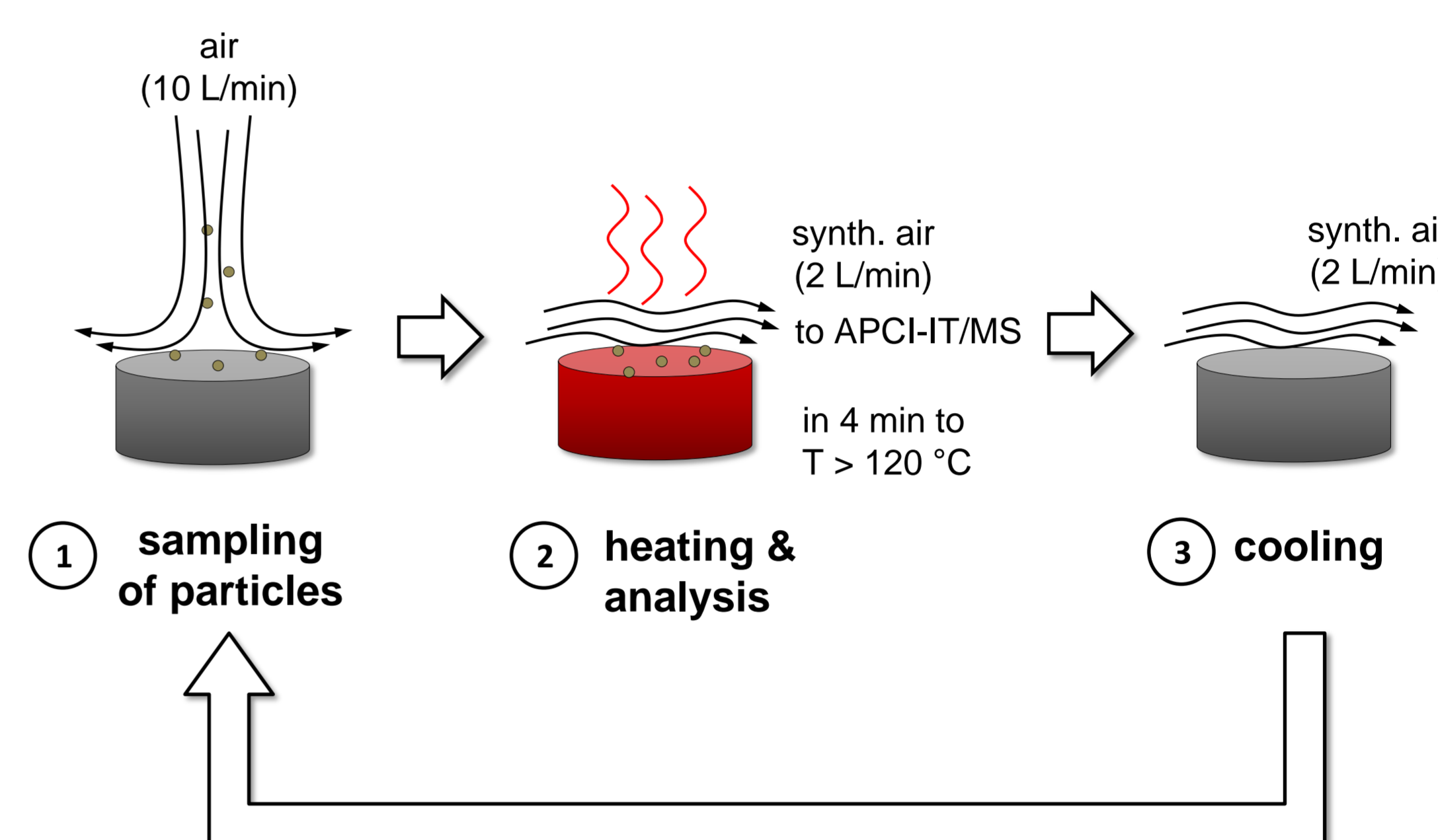
Design of the MOVI



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.^[2] The cut-point diameter (diameter of 50% collection efficiency) is at 130 nm. A low pressure-drop of only 5.3% of atmospheric pressure behind the nozzles allows collecting not only low-volatile but even semi-volatile compounds, which are an important part of SOA.

Ionization mechanism (negative mode):
 $O_2 + e^- \rightarrow O_2^{\cdot-}$
 $O_2^{\cdot-} + n H_2O \rightarrow O_2^{\cdot-} \cdot (H_2O)_n$
Proton abstraction:
 $O_2^{\cdot-} \cdot (H_2O)_n + M \rightarrow [M-H]^- + HO_2 + n H_2O$

The 3-step MOVI-process



D Organic acids were quantified in smog-chamber & field experiments

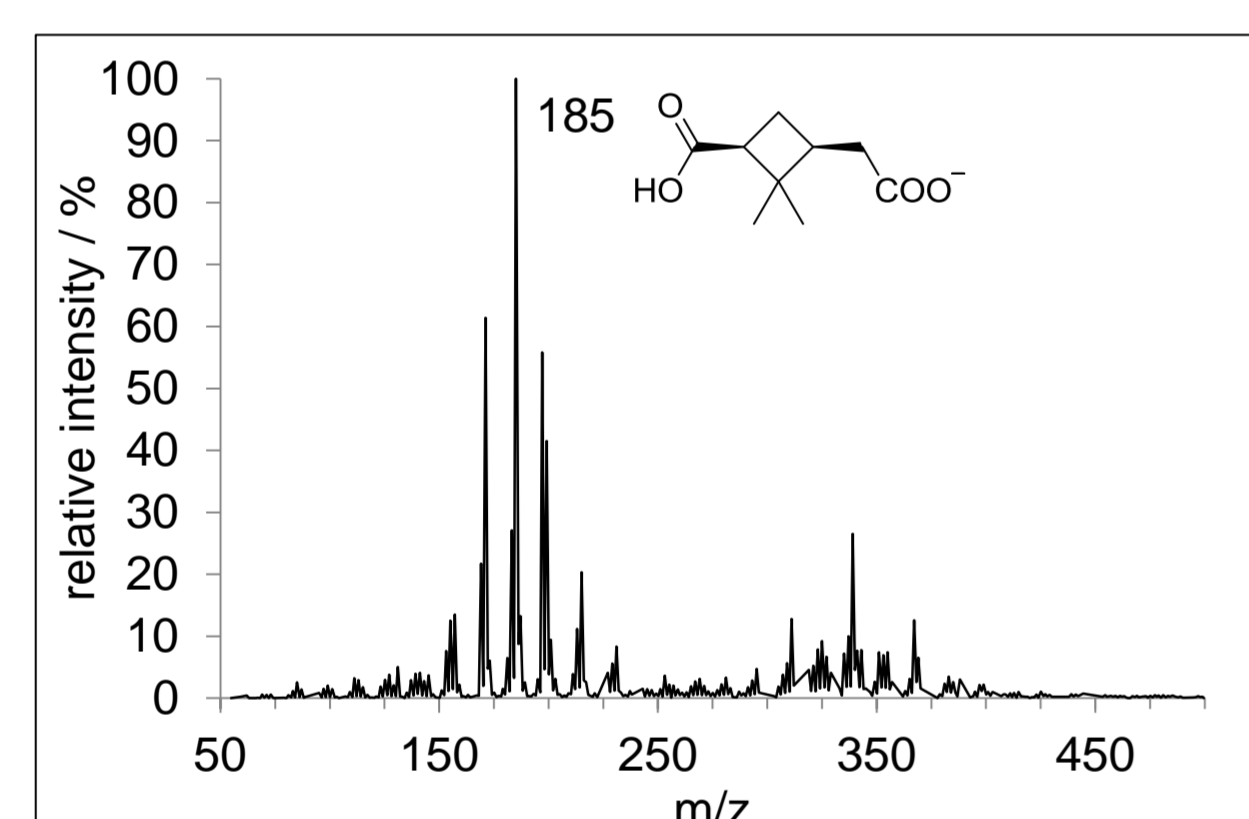


Figure 1: typical mass spectrum of a smog chamber experiment (α-pinene-ozonolysis) recorded with the MOVI-APCI-IT/MS.

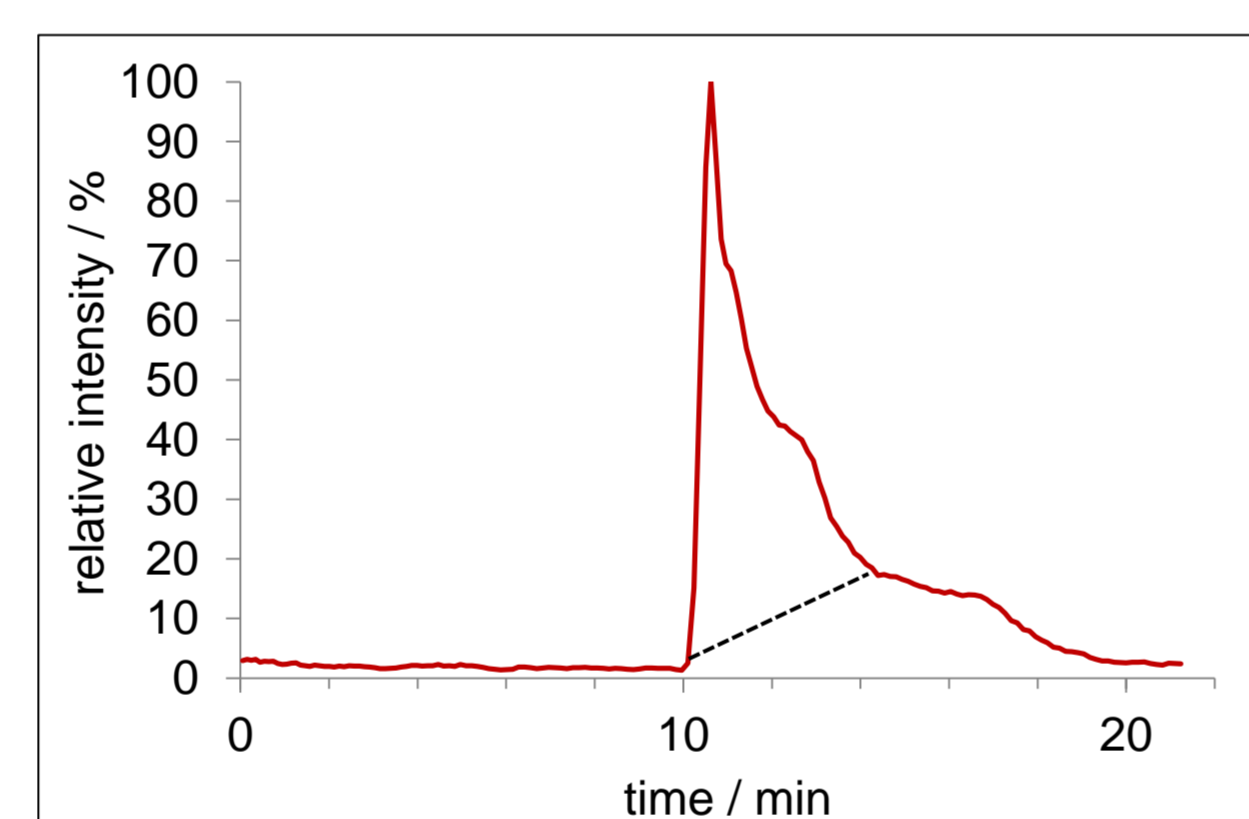


Figure 2: signal of $m/z = 185$ (pinic acid) during the heating step of a smog-chamber experiment. The signal correlates to 55 ng of pinic acid.

- 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
- in smog chamber experiments SOA particles were produced by α-pinene-ozonolysis
- the deposition plate of the MOVI was heated up to 120 °C in 4 min and the volatilized components were transferred into the APCI-IT/MS

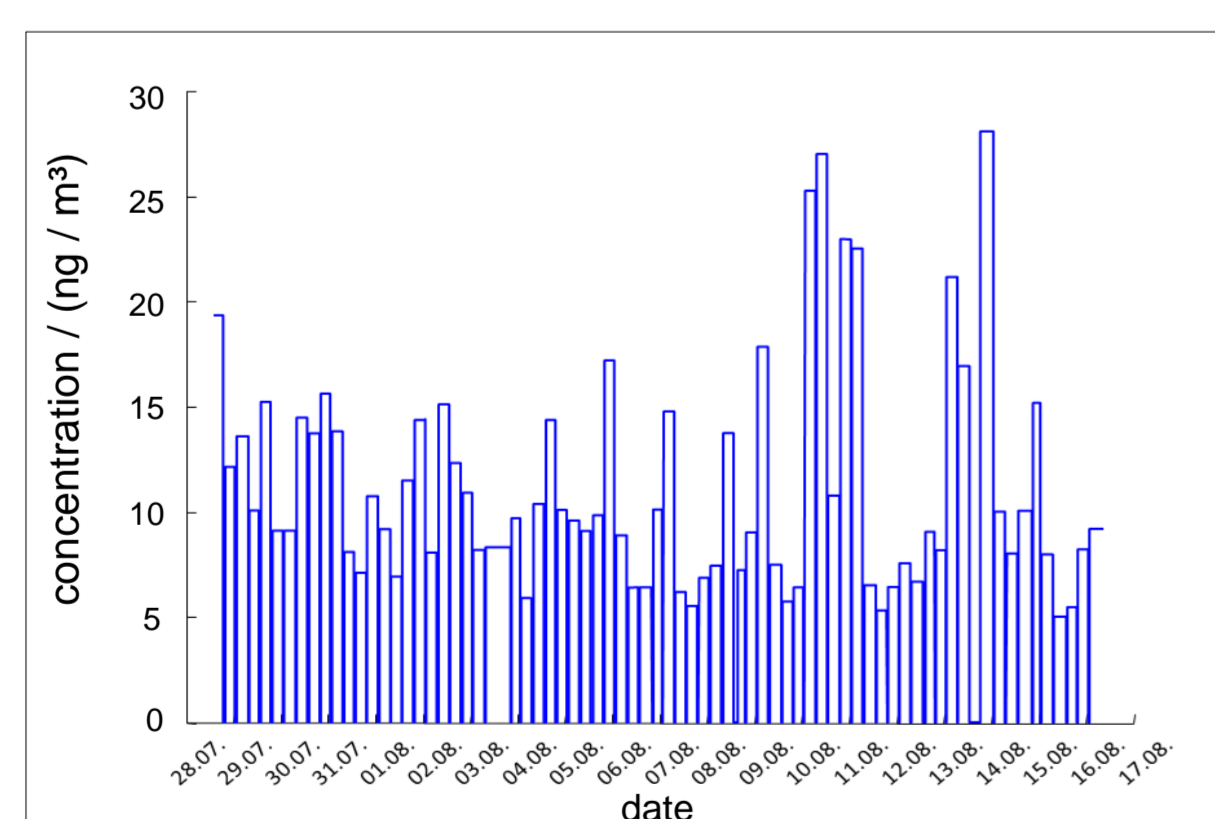


Figure 3: time series of pinic acid ($m/z = 185$) and other isobaric substances in the collected aerosol particles during the BEACHON-RoMBAS.

- signal of $m/z = 185$ was monitored and concentration of pinic acid and isobaric substances were calculated (fig. 3)
- concentrations varied between 5 ng·m⁻³ and 27 ng·m⁻³
- the time series shows a weak diurnal trend with a maximum mean value between 2 – 7 am (fig. 4)
- high concentrations at night are probably due to low boundary layer height and high relative humidity

- measurements during the field campaign BEACHON-RoMBAS in a ponderosa pine woodland 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

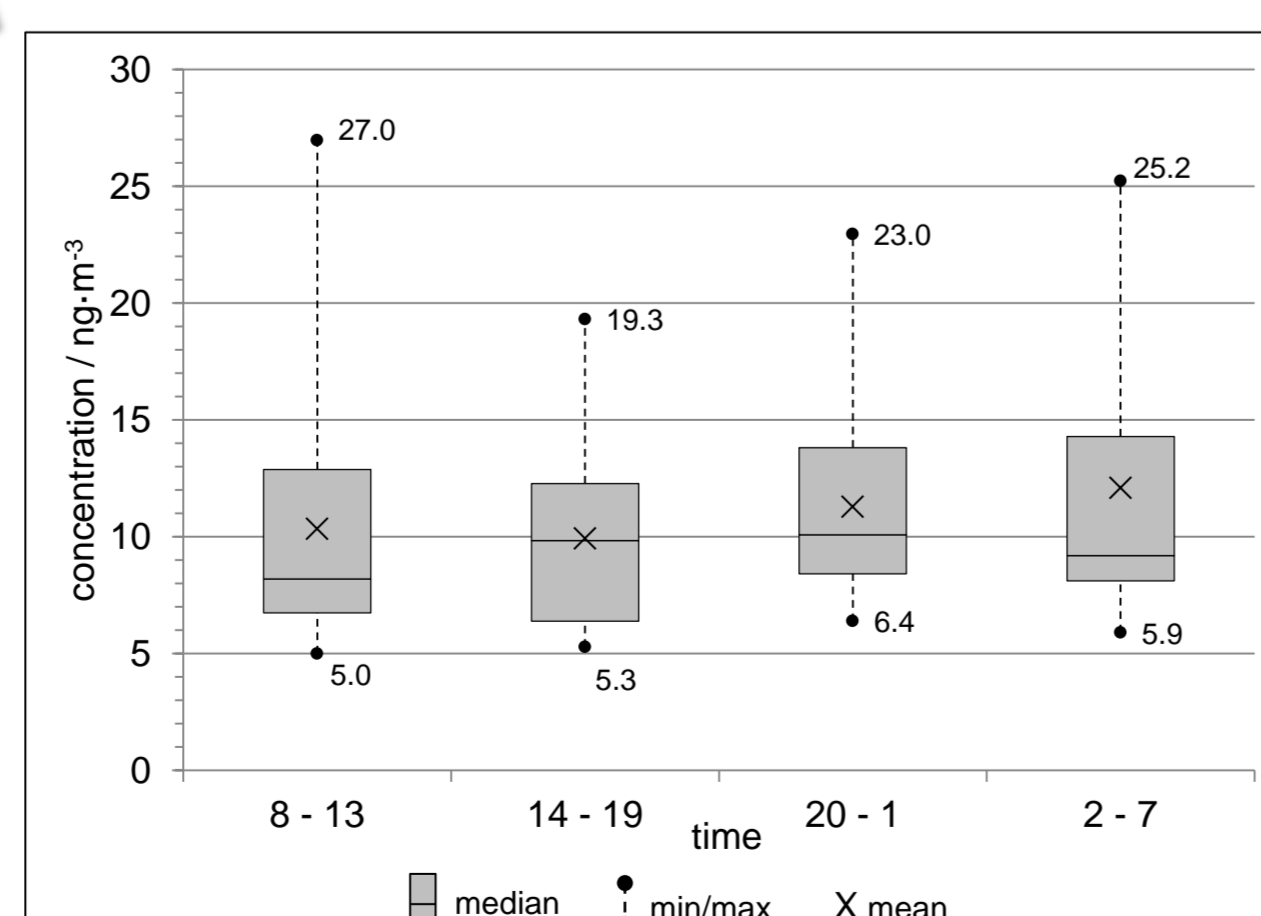


Figure 4: concentrations of pinic acid and isobaric substances correlated to the measurement time.

E Vapor pressures were estimated from desorption temperatures

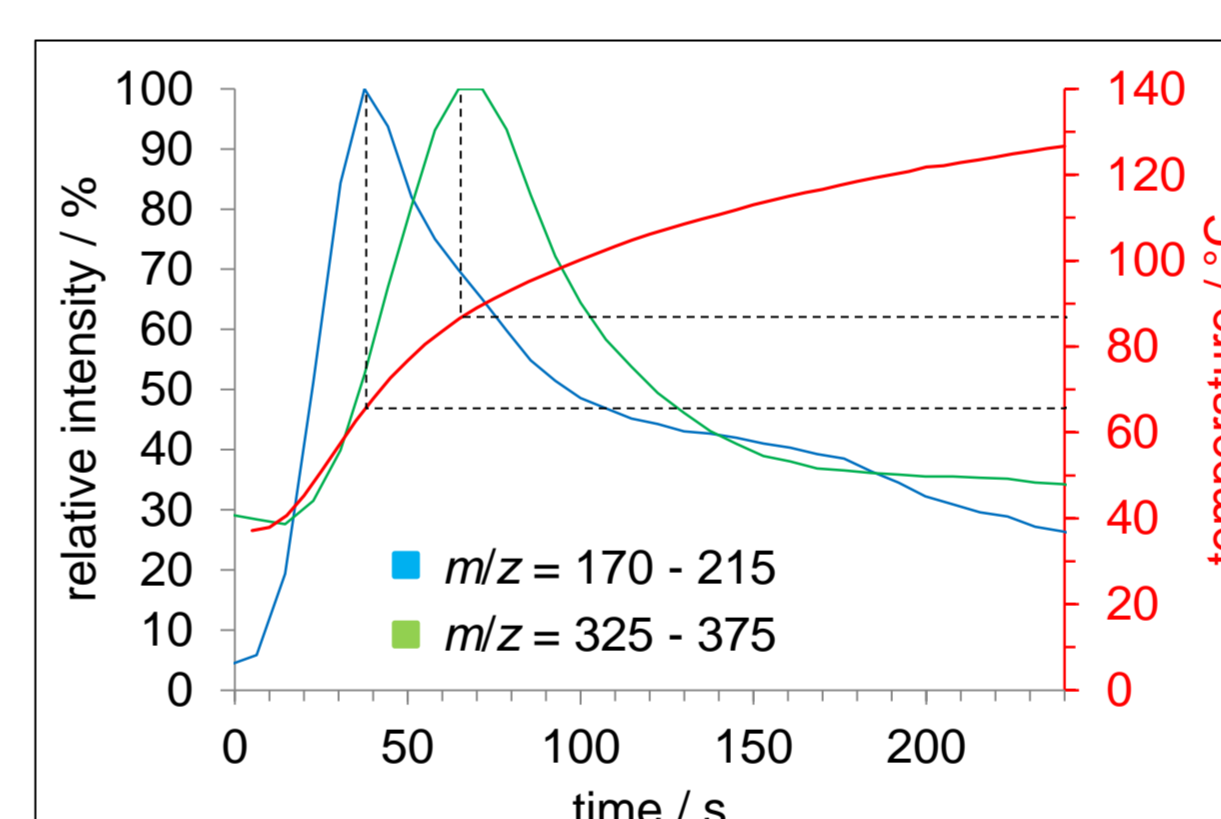


Figure 5: signal for low and high molecular weight compounds and the temperature of the deposition plate during the heating step.

- laboratory experiments show good agreement with literature data for pinic acid ($\log p^0 = -5.68$ 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

- high molecular weight compounds are less volatile (fig. 5)
- vapor pressures p^0 were calculated according to an empirical method which was developed by Faulhaber *et al.* (2009) for a thermodesorber system^[3]
- assumption: at the maximum of the signal (T_{TD}) 50% of the monitored compound are volatilized

	m/z	$T_{TD} / ^\circ C$	$\log p^0_{25} / Pa$
laboratory	185	68 ± 2	-5,66 ± 0,14
	325 - 375	87 ± 5	-6,92 ± 0,31
field	185	90 ± 3	-7,11 ± 0,51
	325 - 375	94 ± 9	-7,35 ± 0,56

Figure 6: comparison between the volatility of the particle components during the laboratory and field measurements.

F Conclusions & Outlook

The MOVI-APCI-IT/MS 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 other organic acids (e.g. pinonic acid, 10-hydroxypinonic 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, ...)

