M. Brüggemann, A.L. Vogel and T. Hoffmann, *Eur. J. Mass Spectrom.* **20,** 31–41 (2014)
Received: 14 August 2013 ■ Accepted: 20 December 2013 ■ Publication: 28 February 2014

EJMS
EUROPEAN
JOURNAL
OF
MASS
SPECTROMETRY

Special Issue dedicated to Professor Michael Linscheid on the Occasion of his 65th Birthday

Analysis of organic aerosols using a micro-orifice volatilization impactor coupled to an atmospheric-pressure chemical ionization mass spectrometer

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We present the development and characterization of a combination of a micro-orifice volatilization impactor (MOVI) and an ion trap mass spectrometer (IT/MS) with an atmospheric-pressure chemical ionization (APCI) source. The MOVI is a multi-jet impactor with 100 nozzles, allowing the collection of aerosol particles by inertial impaction on a deposition plate. The pressure drop behind the nozzles is approximately 5%, resulting in a pressure of 96 kPa on the collection surface for ambient pressures of 101.3 kPa. The cut-point diameter (diameter of 50% collection efficiency) is at 0.13 µm for a sampling flow rate of 10 L min^{-1}. After the collection step, aerosol particles are evaporated by heating the impaction surface and transferred into the APCI-IT/MS for detection of the analytes. APCI was used in the negative ion mode to detect predominantly mono- and dicarboxylic acids, which are major oxidation products of biogenic terpenes. The MOVI-APCI-IT/MS instrument was used for the analysis of laboratory-generated secondary organic aerosol (SOA), which was generated by ozonolysis of α-pinene in a 100 L continuous-flow reactor under dark and dry conditions. The combination of the MOVI with an APCI-IT/MS improved the detection limits for small dicarboxylic acids, such as pinic acid, compared to online measurements by APCI-IT/MS. The limits of detection and quantification for pinic acid were determined by external calibration to 4.4 ng and 13.2 ng, respectively. During a field campaign in the southern Rocky Mountains (USA) in summer 2011 (BEACHON-RoMBAS), the MOVI-APCI-IT/MS was applied for the analysis of ambient organic aerosols and the quantification of individual biogenic SOA marker compounds. Based on a measurement frequency of approximately 5 h, a diurnal cycle for pinic acid in the sampled aerosol particles was found with maximum concentrations at night (median: 10.1 ng m^{-3}) and minimum concentrations during the day (median: 8.2 ng m^{-3}), which is likely due to the partitioning behavior of pinic acid and the changing phase state of the organic aerosol particles with changing relative humidity.

Keywords: secondary organic aerosol, aerosol mass spectrometry, ambient aerosol, particulate organic matter, atmospheric chemistry, instrumentation, BEACHON-RoMBAS, atmospheric-pressure chemical ionization, atmospheric particles, impactor

Introduction

Secondary organic aerosol (SOA) contributes a substantial fraction to atmospheric aerosols and plays a major role in atmospheric chemistry with implications for climate, visibility and human health.[1–3] It is formed when oxidation products of volatile organic compounds (VOCs) undergo gas-to-particle conversion processes, i.e. nucleation, condensation and/or heterogeneous and multiphase chemical reactions. Over the past few decades extensive research has been conducted

ISSN: 1469-0667
doi: 10.1255/ejms.1260

and many sophisticated techniques have been developed to gain detailed knowledge about the formation, properties and transformations of SOA. However, the characterization of the chemical composition and chemical transformations remain a major challenge in aerosol research and are connected to large uncertainties.[4] Recent estimations about the total number of individual compounds are in the range of 10^4–10^5 different organic species present in atmospheric organic aerosols.[5] Additionally, aerosols can undergo further chemical and physical transformations during transport in the atmosphere as a result of coagulation, heterogeneous reactions, gas–particle partitioning and aqueous-phase processing.[1] Providing high sensitivity and the ability to detect a wide molecular mass range, mass spectrometry (MS) is a well-suited technique to analyze this highly complex mixture.[6]

In the past, most SOA measurements were carried out by analyzing aerosol particles collected on quartz filters for several hours up to several days. These methods usually require multistep preparation of the collected samples, such as extraction, concentration and chromatographic separation of the substances, followed by mass spectrometric analysis. They offer an almost complete chemical analysis of the studied aerosol particles, but lack in time resolution and are easily affected by positive artifacts, e.g. gas-phase condensation or reactions on the filter surface, as well as negative artifacts, e.g. evaporation during sampling, degradation on the filter surface and losses or degradation during sample preparation and analysis. Additionally, the preparation of the samples is tedious and time consuming.[4,6] Since the advent of aerosol mass spectrometry (AMS), the application of online measurement methods has become more important. Nowadays, AMS is probably the most common technique used to obtain chemical and size-resolved information about sub-micron particles. However, most AMS techniques rely on electron ionization, which resembles a hard ionization technique, leading to fragmentation of the molecular ions and, thus, demands extensive data analysis, e.g. positive matrix factorization. Furthermore, it is not possible to monitor single organic compounds, which can serve as marker compounds, e.g. anthropogenic activities, wild fires or clean natural atmospheric conditions.[7] Addressing the drawbacks of the AMS, numerous other continuous and semi-continuous methods were developed to provide data on the chemical composition of organic aerosol particles. All of these techniques use low-energy ionization processes, in order to prevent the fragmentation of organic compounds. One possibility to achieve this soft ionization is the use of chemical ionization (CI) techniques, which produce ions through collisions of analyte molecules with primary reagent ions. For example, the aerosol chemical ionization mass spectrometer can utilize several positive ($H^+(H_2O)_2$, $H^+(CH_3OH)_2$, NO^+, O_2^+) and negative (O_2^-, F^-, SF_6^-) primary ions for the analysis of thermally desorbed aerosol particles.[8] Another approach is the use of corona discharge plasmas to produce primary reagent ions. This technique, known as atmospheric-pressure chemical ionization (APCI), is commonly used in MS combined with liquid chromatography. The aerosol particles are evaporated in a first step, and the resulting gas-phase compounds are ionized by primary reagent ions, such as protonated water clusters ($H^+(H_2O)_n$) or $[O_2^+(H_2O)_n]^-$.[9–11] In order to improve sensitivity and the limit of detection, Vogel *et al.* demonstrated that with the APCI technique, in combination with a miniature versatile aerosol concentration enrichment system (mVACES), it was feasible to run the instrument in the field for the real-time analysis of organic acids.[12] However, using semi-continuous methods enables enough material to be sampled for the analysis, even under extreme clean conditions, where the mVACES-APCI-MS technique is not sensitive enough.

Here we present a method to analyze SOA particles on a semi-continuous basis by pre-collection and thermal desorption of aerosol particles, followed by mass spectrometry. The technique uses a micro-orifice volatilization impactor (MOVI), first described by Yatavelli and Thornton, for the collection of particles by inertial impaction.[13] The MOVI is directly connected to a quadrupole ion trap mass spectrometer (IT/MS) with an APCI source, allowing the chemical analysis of the sampled particles after thermal desorption. The MOVI-APCI-IT/MS system was used for the analysis of aerosol particles in the laboratory, and in the field during the Bio-hydro-atmosphere interactions of Energy, Aerosols, Carbon, H_2O, Organics & Nitrogen—Rocky Mountain Biogenic Aerosol Study (BEACHON-RoMBAS, http://cires.colorado.edu/jimenez-group/wiki/index.php/BEACHON-RoMBAS) in summer 2011.

Experimental

Materials

Cis-pinic acid was synthesized in our laboratory according to Moglioni *et al.*[14] Methanol (HPLC-grade) and (+)-α-pinene (≥99%) were purchased from Sigma-Aldrich (St. Louis, USA). Synthetic air (hydrocarbon free) was purchased from Westfalen AG (Münster, Germany).

Online-APCI-IT/MS measurements

The online analysis of pinic acid and other carboxylic acids in bulk aerosol was conducted with an LCQ Classic IT/MS (Thermo Scientific, San Jose, USA). The procedure is described in detail for online measurements of gaseous compounds and particulate organic matter elsewhere,[10–12] and therefore only a brief description will be given here. Basically, a modified APCI source is used to volatilize and ionize the sampled aerosol particles. Aerosol particles are drawn into the APCI source by a diaphragm pump at a flow rate of $2.2\,L\,min^{-1}$. Owing to heating in the APCI source, particle components are volatilized. The resulting gas-phase species are ionized and transferred into the MS. The source is operated in the negative mode to produce $[M-H]^-$ ions. At atmospheric pressure several ionic species, e.g. $[O_2 + (H_2O)_n]^-$ and NO_3^-, are formed in the APCI source in a 3–5 kV corona discharge plasma between a needle tip and the MS ion-transfer capillary (Figure 1). All gas-phase compounds with a higher gas-phase acidity than these primary ions are

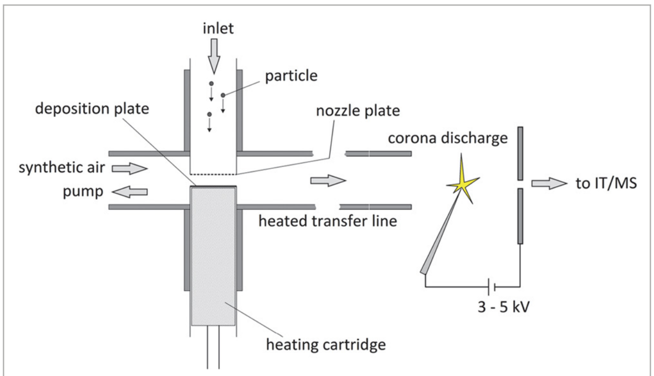

Figure 1. Cross-sectional drawing of the MOVI coupled to an APCI-IT/MS. First, particles are collected by inertial impaction on the deposition plate at a flow rate of 10 L min^{-1}. Then, the deposition plate is heated by the heating cartridge, resulting in evaporation of the sampled particles. Eventually, the volatilized compounds are transferred together with synthetic air into the APCI-IT/MS for ionization and detection.

ionized by proton-transfer reactions. Excess energy remaining from the proton-transfer reaction is transferred by collision to a third neutral molecule. The produced reagent ions are selective toward organic acids, inorganic acids, nitrophenols and combinations between those compound classes (e.g., organosulfates). In order to analyze only particle compounds, gas-phase species are removed prior the APCI-IT/MS by passing the aerosol stream through an activated charcoal denuder.

The MOVI process

The analysis of aerosol particles with the MOVI is divided into three steps: (1) particle collection, (2) particle volatilization and (3) chemical analysis. In the first step, particle-laden air is drawn through the impaction unit of the MOVI and particles exceeding a critical diameter are collected on a collection plate. After a certain amount of time, the aerosol flow is stopped and particle-free synthetic air is led over the collection plate into the APCI region. At the same time, the collection plate is heated and the sampled particles are volatilized. In the third step, the gas-phase compounds are ionized and analyzed using mass spectrometry.

The micro-orifice volatilization impactor

A schematic of the MOVI is shown in Figure 1. The impaction unit is similar to the one described by Yatavelli *et al.*[13,15] It consists of a stainless-steel nozzle plate with 100 nozzles, each having a diameter of D_n = 150 µm and a length of l_n = 0.76 mm. The outer diameter of the nozzle plate and the aerosol inlet is 12.70 mm. The inner diameter of the aerosol inlet is 10.60 mm. At a distance of approximately 600 µm (= $4D_n$), a stainless-steel impaction plate is held in place by a stainless-steel Swagelok union cross using compression fittings with polytetrafluoroethylene (PTFE) ferrules. The impaction plate is soldered to a stainless-steel tube with the same dimensions as the aerosol inlet. Inside the tube a heating cartridge (250 W, outer diameter 10 mm, length 50 mm, HS Heizelemente, Fridingan an der Donau, Germany) is placed below the impaction plate, which allows rapid heating of the collection surface. Thermal grease (Keratherm KP 92, Kerafol, Germany) is added to the surface of the heating cartridge to improve heat conduction. The heating cartridge is controlled by a proportional, integral, derivative (PID) controller (XMT612, Pohltechnik, Germany) and heats the collection surface during the analysis of sampled aerosol particles. The PID controller is calibrated by measuring the temperature of the impaction surface with a thermocouple (type K) inserted between the nozzle and the impaction plate. Stainless-steel tubings are used to connect one side of the union cross to a diaphragm pump and a synthetic air supply, and the other to the mass spectrometer.

In order to minimize the condensation of organic vapors to the inside surfaces of the MOVI, the connection line to the MS is heated constantly to 140 °C by a resistive heating tape wrapped around the steel tubing. During the sampling of aerosol particles, the pump draws particle-laden air through the impaction unit with a flow rate of 10 L min^{-1}, while the connection to the MS is closed by a ball valve (not shown in Figure 1). The flow rate through the MOVI is monitored and controlled by a mass flow controller (MKS instruments, Andover, USA). The temperature of the collection surface is held at approximately 25–30 °C by the cooling effect of the gas flow and additional cooling of the union cross by an AC-powered fan.

The MOVI was designed with the goal to minimize the pressure drop across the nozzles in order to reduce losses of volatile and semi-volatile species during aerosol sampling.[13] For the design and flow rates mentioned above, the pressure drop across the nozzles is only 5%, resulting in a pressure of approximately 96 kPa on the collection surface for ambient pressures of 101.3 kPa. Using the sample flow rate and the pressure drop, the jet velocity v_n, Reynolds number Re and theoretical cut-point d_{50} are calculated to be v_n = 110 m s^{-1}, Re = 941 and d_{50} = 0.13 µm, respectively. The calculation of d_{50} is done by using the critical Stokes number for round-jet impactors[16] and a density of 1.40×10^3 kg m^{-3} for SOA particles.[3] The calculated d_{50} is in good agreement with measurements conducted by Yatavelli and Thornton who measured a cut-point of d_{50} = 0.13 µm using oleic acid and palmitic acid as model aerosols.[13] For oleic acid the collection efficiency exceeded 90% for particles with a diameter >0.25 µm and for palmitic acid for particles with a diameter >0.4 µm. The cross-flow interferences are estimated to be C = 0.35 using the expression given by Kwon *et al.*[17] and are far below the critical value of C_{crit} = 1.2 given by Fang *et al.*[18]

After a predetermined time of sampling, a needle valve between the MOVI and the diaphragm pump is closed, the ball valve between the MS and the MOVI opened and a stream of synthetic air led over the collection surface. The flow rate of the air stream is monitored by a mass flow meter (MKS Instruments, Andover, USA) and adjusted to 2.2 L min^{-1} by a needle valve. In contrast to the original MOVI design, synthetic air is used because of the need of O_2 for the ionization of the analytes in the APCI source in the negative ion mode.[9–11] Simultaneously, the collection surface is heated by the heating cartridge for 240 s, resulting in a maximum temperature of 127 °C. The sampled aerosol is volatilized and transferred with the carrier gas into the APCI region. It is very likely that very low vapor pressure compounds, e.g. sulfates, remain on the collection plate after the heating step. However, a higher temperature would eventually increase thermal decomposition of fragile substances and complicate the mass spectra obtained. At the end of the volatilization step, the heating cartridge is turned off and the MOVI cooled down to room temperature. Then, the collection plate is heated again to check if all the compounds of interest had volatilized. If the total ion current is high during this blank measurement, the collection plate is cleaned again with methanol before starting a new measurement cycle.

Data analysis

MS data were recorded and background subtracted using Xcalibur (version 1.2, Thermo Scientific, San Jose, USA). Subsequently, the raw files were converted into text files and processed in MATLAB (version 7.11.0, MathWorks, Natick, USA) for the data analysis. For the quantification of pinic acid the following procedure was used. First, the signal of *m*/*z* 185 was fitted and smoothed and the third derivation of the fit was calculated. Using empirically determined values for the intensity of the signal and the third derivation, the signal area between two data points was integrated. The resulting area was converted into a deposited mass by using an external calibration. This procedure was repeated for all heating cycles and allowed a semi-automated data analysis of the obtained MS data. Figure 2 shows the typical signal of *m*/*z* 185 under three different conditions. The observed shoulders in the signals are not integrated, since they are probably due to deposited or adsorbed material on the inside walls of the MOVI.[13,15]

Calibration of the MOVI-APCI-IT/MS

The procedure used for the calibration of the MOVI-APCI-IT/MS for pinic acid was similar to the one described by Vogel *et al.*[12] Briefly, a methanolic solution of pinic acid was prepared with a concentration of 10 ng μL^{-1}. Different amounts of this solution, ranging from 1 μL to 10 μL were deposited on the collection plate and evaporated by heating the surface. The recorded mass spectra were analyzed and an external calibration curve was calculated. All flow rates and temperatures used during the calibration were identical for the laboratory and field measurements.

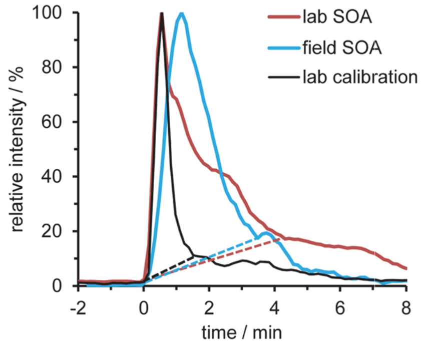

Figure 2. Signal for *m*/*z* 185 during the heating step: (black line) during calibration experiments; (red line) during the analysis of laboratory-generated SOA; (blue) during the BEACHON-RoMBAS field measurements. The dashed lines show the limits for the integration of the area below the signal.

Laboratory setup

SOA was produced under dark and dry conditions (RH <30%) in a 100 L continuous-flow reaction chamber by ozonolysis of α-pinene. Gaseous α-pinene, generated in a thermally controlled diffusion source,[19] was introduced into the chamber and mixed with ozone (1 ppm$_v$) to produce SOA particles. Ozone was generated by an ozone generator (1008-RS, Dasibi Environmental Corp., Glendale, California, USA). The formed SOA particles were measured online using APCI-IT/MS. The particle number concentrations were measured using a condensation particle counter. As soon as the reactants and aerosol concentrations inside the chamber were in a steady state, sampling of aerosol particles with the MOVI was started. Typically, the sampling step lasted for 15 min before the analysis of the collected particles was started.

Field measurements

Atmospheric organic aerosol was sampled and analyzed with the MOVI-APCI-IT/MS during the BEACHON-RoMBAS in the southern Rocky Mountains from July 28th to August 16th, 2011. The site is located in a ponderosa pine forest at an elevation of 2370 m a.s.l. and the vegetation is representative for the Central Rocky Mountains ponderosa pine zone. The dominant biogenic VOCs emitted are 2-methyl-3-butene-2-ol (MBO, 50%) and monoterpenes (33%), such as α-pinene, β-pinene and Δ3carene. Small amounts of aromatics, oxygenated terpenes and sesquiterpenes are also present.[20] During the measurement period, the diurnal variations of MBO and the monoterpenes were anticorrelated. The mixing ratios for MBO showed a maximum during the day (1.5 ppb$_v$), whereas the mixing ratio for monoterpenes was highest during early morning (0.8 ppb$_v$) and lowest during the day.[21] Local aerosol formation is thought to be dominated by monoterpenes.[22]

The MOVI-APCI-IT/MS was set up in a trailer during the campaign period and sample air was drawn from an outer inlet, similar to the one described by Yatavelli *et al.*[22] The inlet comprised a large duct to bring air closer to the MOVI-APCI-IT/MS while minimizing turbulence and wall contact. A smaller-diameter conductive PTFE-tube was used to sample air from the center of the duct to the instrument. The large duct inlet was made of galvanized steel with an outer diameter of 15.2 cm. A stainless-steel bowl was installed above the inlet tube to block rain and debris. A high flow-rate computer fan was installed at the bottom of the duct and adjusted to a flow rate of approximately 330 L min^{-1}. The conductive PTFE-tube (outer diameter 12.7 mm, length ≈ 50 cm) connected to the instrument was inserted 2 m below the top of the duct inlet. During the measurement period, four measurements were conducted per day. The sampling step was run for 5 h and the measurement step took 1 h.

Results and discussion

Calibration of the MOVI-APCI-IT/MS

The limits of detection, linearity and sensitivity of the MOVI-APCI-IT/MS were assessed using pinic acid as a model compound. We chose pinic acid because it is a known major oxidation product of monoterpenes, such as α-pinene and β-pinene.[23] Figure 2 (black line) shows the recorded signal of *m/z* 185 during a calibration experiment after depositing 50 ng of pinic acid in 5.0 µL methanol on the collection surface with a pipette and the subsequent heating step, starting at t = 0 min. As soon as the heating starts, the signal of *m/z* 185 increases very rapidly and reaches its maximum after approximately 30 s. At that point, most of the deposited pinic acid has been vaporized and transferred into the APCI source. The signal decreases rapidly again for approximately another 30–40 s until it reaches a plateau at roughly 10% of the maximum intensity. Afterward, the signal decreases slowly, though the temperature of the surface increases until minute 4. This residual and slowly decreasing signal is likely to be caused by deposited or adsorbed material on the inside walls of the MOVI, the transfer line to the APCI source or the ion-source enclosure. The deposited material is then slowly released into the carrier-gas stream as the temperature increases. Thus, only the first 70 s of the signal were taken into account for the integration of the area under the signal and the calculation of the calibration curve. The residual signal was one of the major limitations during the calibration and compromised the ultimate performance of the instrument. Especially, when going to higher concentrations the reproducibility suffered from this incomplete volatilization, leading to larger variations in the response of the MOVI-APCI-IT/MS. Therefore, future designs of the instrument should decrease the total surface area inside the MOVI and the transfer line to the ion source and eliminate unnecessary dead volume. Additional heating of the ion-source enclosure should also be considered. This is consistent with observations reported by Yatavelli *et al.*[13,15]

Figure 3(a) shows the obtained calibration curve for pinic acid with confidence limits for the laboratory experiments. The measured area under the signal increases linearly with the deposited mass over the range studied. Each mass was measured in triplicate. The detection limit x_{dl} was calculated to be 4.4 ng of pinic acid from the calibration curve with an error of the first kind of 20%. The quantification limit x_{ql} was estimated to 13.2 ng from the detection limit according to equation (1):

$$x_{\mathrm{ql}} = k \cdot x_{\mathrm{dl}} \tag{1}$$

with an uncertainty factor of $k = 3$. This value equals a relative uncertainty of 33%, which is a typical value for this method. Additionally, the upper and lower confidence limits were calculated according to Geiss and Einax[24] and are shown in Figure 3(a) as dashed lines. None of the measured calibration data were outside these confidence limits. However, the variations in the response of the instrument increase with the amount of deposited mass, which is probably because of incomplete volatilization, recondensation and adsorbed mass on the inside walls of the MOVI.

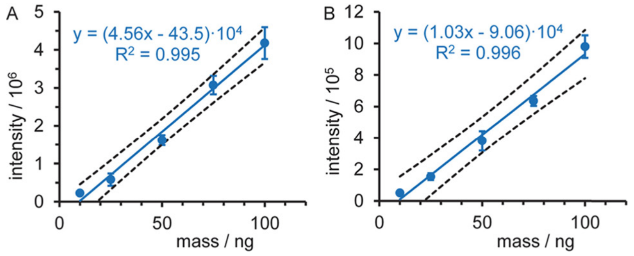

Figure 3. (a) Calibration curve for the MOVI-APCI-IT/MS obtained during the laboratory experiments for solutions of pinic acid in methanol. (b) Calibration curve of the MOVI-APCI-IT/MS for pinic acid obtained during the BEACHON-RoMBAS. The dashed lines show the confidence intervals with an error of first kind α = 20%.

The calibration procedure was also performed during the BEACHON-RoMBAS. Figure 3(b) shows the obtained calibration curve with confidence limits for the instrument. Compared to the laboratory experiments, the calibration curve exhibits much lower intensities and a lower slope for the measured data points. Since the ionization mechanisms occurring in the APCI source are pressure dependent, we assume that this impaired performance and sensitivity is due to the lower ambient pressure of roughly 70–80 kPa at the measurement site. The detection limit was calculated to be x_{dl} = 4.8 ng and the quantification limit, according to equation (1), to be x_{ql} = 14.4 ng of pinic acid.

Analysis of laboratory-generated SOA

SOA was produced in the laboratory by ozonolysis of α-pinene. The resulting aerosol particles were analyzed with two different techniques, online by APCI-IT/MS and semi-continuously by MOVI-APCI-IT/MS. The reaction between α-pinene and ozone gives a wide range of reaction products containing, e.g., aldehydes, ketones and carboxylic acids and has been intensively studied earlier. Some of the major oxidation products, which will be discussed in the following, are shown in Figure 4. Besides the depicted compounds, many other reaction products have been identified and reasonable suggestions about the underlying reaction mechanisms have been published.[3,23,25,26] Figure 5(a) shows a mass spectrum in the negative ion mode of laboratory-generated particles after the reactants and aerosol concentrations had reached a steady state inside the chamber when online APCI-IT/MS was used. The mass spectrum shows two ranges of signals: (1) between *m/z* 150 and *m/z* 250, and (2) between *m/z* 300 and *m/z* 400. The first range represents mainly first-generation products of the ozonolysis of α-pinene and is well characterized. SOA tracer compounds, such as pinic acid (*m/z* 185, $[M{-}H]^- = C_9H_{13}O_4^-$), pinonic acid (*m/z* 183, $[M{-}H]^- = C_{10}H_{15}O_3^-$),

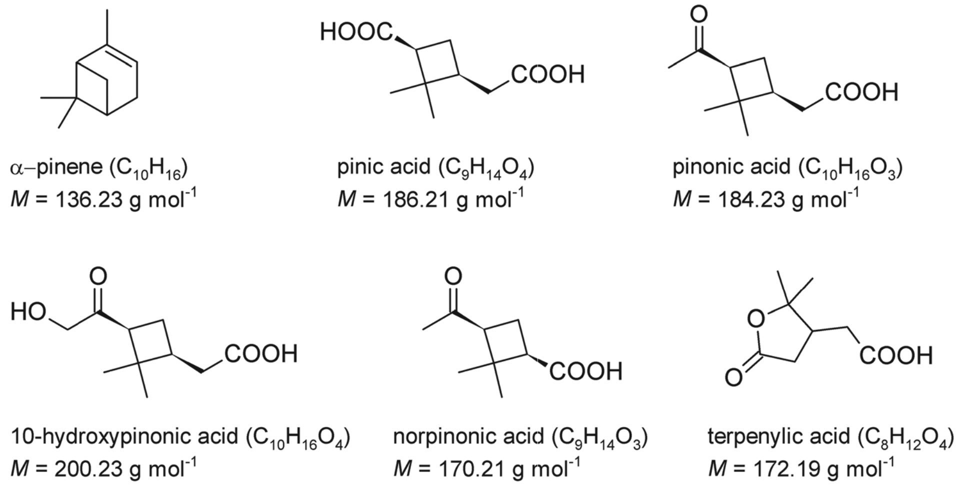

Figure 4. Structures and molecular weights of α-pinene and some major reaction products of its ozonolysis.

norpinonic acid (m/z 169, $[M-H]^- = C_9H_{13}O_3^-$), terpenylic acid (m/z 171, $[M-H]^- = C_8H_{10}O_4^-$), or 10-hydroxypinonic acid (m/z 199, $[M-H]^- = C_{10}H_{15}O_4^-$) were observed in this range.[23,25] The higher m/z range shows signals of second-generation products, also called dimeric oxidation products. These compounds are less-well characterized and still under investigation, though some of them have recently been identified, e.g. m/z 357 and m/z 367.[27,28] Additionally, adduct formation of monomeric oxidation products has to be considered in this range. Although several covalently bonded dimers of biogenic oxidation products have been unambiguously identified in this mass range (Müller *et al.*[27]), additional formation of dimeric adducts in the ion source cannot be excluded (e.g., m/z 169 can result in m/z 338). These ion-source artifacts impede an explicit identification of compounds in the higher m/z range with the APCI-IT/MS and may explain the wide range of these signals.

Figure 5(b) shows the mass spectrum in the negative ion mode when the SOA particles were sampled by the MOVI-APCI-IT/MS for 15 min at 10 L min^{-1} and subsequently analyzed. As in the case of the online measurements, signals for typical SOA tracer compounds were observed. Again, the signal for pinic acid (m/z 185) shows the highest intensity. However, during the online measurements the observed intensity was at approximately 1.5×10^5 counts, whereas for the MOVI-APCI-IT/MS measurements it is at roughly 8×10^5 counts. Thus, the MOVI enhances the signal for pinic acid by a factor of five. This enhancement factor can easily be adjusted by increasing and decreasing the sampling times. However, not all signals are enhanced by using the MOVI. The signal for pinonic acid

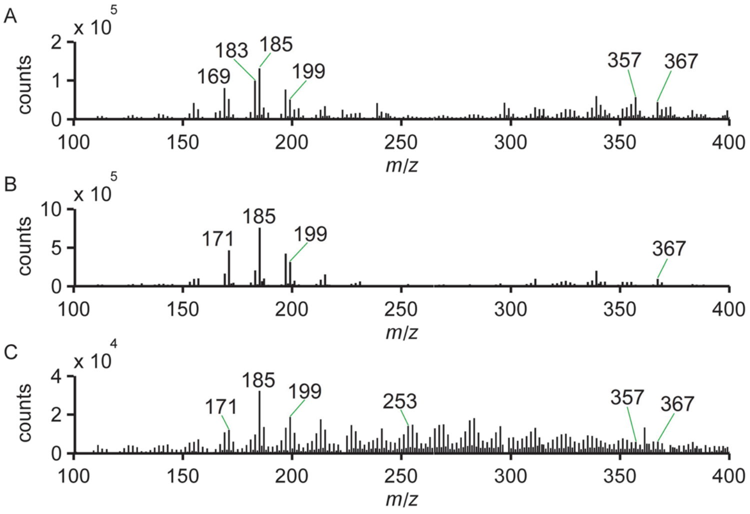

Figure 5. (a) Mass spectrum of the online analysis of laboratory-generated SOA by APCI-IT/MS. (b) Mass spectrum of the analysis of laboratory-generated SOA by MOVI-APCI-IT/MS. (c) Mass spectrum of the analysis of field SOA by MOVI-APCI-IT/MS. All mass spectra are background subtracted.

(*m/z* 183) shows an intensity of approximately 1 × 10^5 counts for both cases. The same is true for the signal of norpinonic acid (*m/z* 169), which shows similar intensities for both experiments, whereas the signal for terpenylic acid (*m/z* 171) is enhanced by almost one order of magnitude. We assume that this behavior can be explained by the different volatility of the compounds. For the lower *m/z* range it is assumed that, due to their high vapor pressure, more volatile compounds are lost during the sampling step, e.g. pinonic acid (*m/z* 183) or norpinonic acid (*m/z* 169). For compounds with a lower vapor pressure, e.g. pinic acid (*m/z* 185) or terpenylic acid (*m/z* 171), the losses play a minor role and the signals are enhanced due to the preconcentration on the collection surface of the MOVI. However, this explanation is not true for the signals of the dimeric oxidation products in the higher mass range (*m/z* 300–400), which show even lower intensities compared to the online APCI-IT/MS measurements. The volatility of these compounds should be lower than that for the monomeric oxidation products because of the much higher molecular weight and additional functional oxygen-containing groups. Thus, losses due to evaporation cannot explain the low abundance. Assuming a very low vapor pressure, an incomplete volatilization of these species during the heating step seems much more likely. Thermal decomposition of these compounds may also play a role, which might lead to an overestimation of lower molecular weight compounds due to the production of isobaric fragments. Yet further experiments are needed to assess the extent of this fragmentation process.

Compared to the online APCI-IT/MS measurements a big advantage of the MOVI-APCI-IT/MS measurements is the possibility of easily quantifying compounds in the sampled aerosol. In contrast to the online APCI-IT/MS, no additional vaporization unit is necessary in order to obtain calibration curves.[12] Figure 2 (red line) shows the temporal behavior of the signal *m/z* 185 for pinic acid ($[M-H]^-$) during the heating step of the instrument. As soon as the heating starts, the signal rapidly increases and reaches its maximum after approximately 40 s, which is similar to the calibration experiments. However, the decrease of the signal is much slower compared to the analysis of pure pinic acid and lasts for almost 200 s until a plateau is reached. In this case, the signal is still at about 17% of the highest observed intensity. The large difference in the decrease of the signal between the calibration experiments and the analysis of SOA particles is likely caused by matrix effects and pinic acid trapped inside the particles. Matrix effects may decrease the vapor pressure of pinic acid by intermolecular interactions, e.g. hydrogen bonds, resulting in an impeded volatilization of the compound. Trapping of pinic acid inside the particles may aid in this process, leading to an even slower release of the analytes from the particle phase into the gas phase. Moreover, owing to thermal decomposition of high molecular weight compounds isobaric substances may be produced, especially at the end of the heating step. This might lead to the observed plateau intensity of the signal. In order to avoid an overestimation only the area above the dashed line from minute 0 to minute 4 was integrated for the quantification of pinic acid. Using the calibration function for the laboratory experiments, the signal represents 55 ng of pinic acid.

Analysis of atmospheric SOA in the field

The MOVI-APCI-IT/MS was used during the BEACHON-RoMBAS 2011 for the analysis of SOA in the southern Rocky Mountains. Figure 2 shows the signal for pinic acid (*m/z* 185, blue line) during the heating step of the MOVI-APCI-IT/MS after collecting aerosol particles for 323 min. The signal rises again as soon as the heating starts. However, in this case the slope is lower than that for the laboratory experiments. The signal reaches its maximum after 60 s and then starts to decrease rapidly. Compared to the SOA experiments in the laboratory, the signal drops much faster and reaches background level after another 70–80 s. For the quantification of pinic acid the signal was integrated between minute 0 and minute 2.5. Using the calibration function for the field experiments the total amount of collected pinic acid was calculated to be 49 ng, which equals a concentration of 15 ng m^{-3} for the sampling period. However, this calculated concentration might be an upper limit for the amount of pinic acid in the sampled aerosol, since a contribution from other isobaric substances cannot be excluded, i.e. oxidation products of other terpenes and non-terpenes as well as anthropogenic VOCs with the same *m/z* ratios. Whether the temporal behavior of the signal can be explained by the contribution of such substances or by various matrix effects, e.g. trapping of pinic acid in aerosol particles, remains uncertain.

Figure 5(c) shows the mass spectrum in the negative ion mode of the analysis of the collected SOA particles from the field samples. As in the case of the laboratory experiments, the signal for pinic acid shows the highest intensity with approximately 3.8 × 10^4 counts. Again, signals for more volatile species (*m/z* 169, 183) are very low. In the range of the dimeric oxidation products, signals for known products, e.g. *m/z* 357 and *m/z* 367, are observed. However, several additional signals with significant intensities are observed in the range *m/z* 200–300 between the mass ranges of the monomeric (*m/z* 150–250) and dimeric (*m/z* 300–400) oxidation products. Although the origin and structure of these compounds cannot be identified from the measurements performed here due to the unit-mass resolution of the MS, we assume oxidation products of sesquiterpenes, such as β-caryophyllene, to cause a large fraction of these signals, e.g. β-caryophyllinic acid (*m/z* 253, $[M-H]^-$) or β-14-hydroxycaryophyllonic acid (*m/z* 267, $[M\text{-}H]^-$).[29,30] This is consistent with observations made by other groups. An overview of possible compounds correlated to the observed signals can be found elsewhere.[3,29–31] Additionally, signals correlated to anthropogenic activities cannot be excluded for the measurements during the field campaign. Although the identification of single compounds remains difficult without authentic standards, the measurements show that the MOVI-APCI-IT/MS is capable of effectively sampling and analyzing organic compounds in ambient aerosol particles.

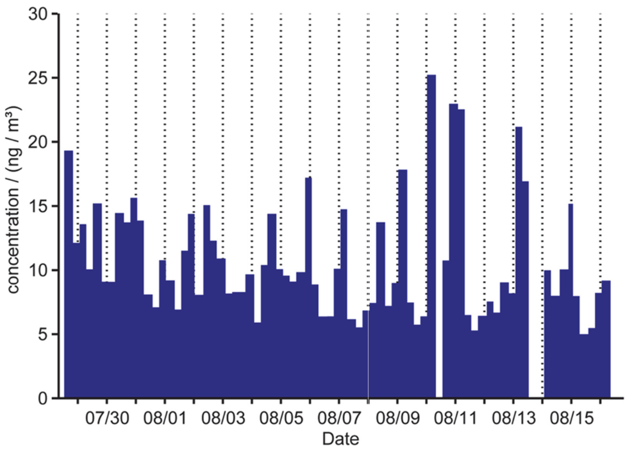

Figure 6. Measured concentrations of pinic acid (*m/z* 185) during the BEACHON-RoMBAS field campaign in summer 2011 (July 28th to August 16th).

Furthermore, it offers the possibility to quantify single organic compounds by external calibration.

Quantification of pinic acid during the BEACHON-RoMBAS

Using the calibration function the amount of collected pinic acid during the field measurements for a period of 20 days was calculated based on four measurements each day. For this calculation it was assumed that the signals at *m/z* 185 derive from pinic acid and no other isobaric substances were present. In order to compensate for small variations in the sampling time, the concentration of pinic acid in the sampled air mass was calculated. The resulting time series is shown in Figure 6. The measured concentrations varied between 5.0 ng m^{-3} and 25.2 ng m^{-3}. The lowest concentration was measured on the 15th of August for the sampling period from 8 am to 1 pm (local time). The highest concentration was measured on the 10th of August for the sampling time from 1 am to 7 am (local time).

The measured concentrations of pinic acid were arranged according to their measurement time. Figure 7 shows the obtained results in a box-and-whisker plot. The whiskers represent the range of measured concentrations for each time period. The values at the end of the whiskers show the measured maximum and minimum concentrations. The bottom and top of the boxes are the first and third quartiles, and the band inside the boxes is the second quartile, i.e. the median. Additionally, a small 'x' shows the arithmetic mean of the data. The red line displays the average ambient temperature at the site during the measurement period, with its standard deviation. The blue line depicts the measured average relative humidity, with its standard deviation. The pinic acid concentrations exhibit a weak diurnal trend for the median and the arithmetic mean values. The median values show a minimum for the measurements between 8 am and 1 pm. For this time period, 50% of the concentrations are in the narrow range between the median at 8.2 ng m^{-3} and 5.0 ng m^{-3}, which is the lowest concentration measured. Additionally, the highest concentration for this sampling period at 16.9 ng m^{-3} is the lowest maximum value of the four measurement periods. On the contrary, the highest median concentration, 10.1 ng m^{-3}, was observed for particles collected in the early evening and night from 8 pm to 1 am. The interquartile range for this period, representing 50% of the values between the first and the third quartile, lies between 8.4 ng m^{-3} and 13.8 ng m^{-3}. Similar values were obtained for the night to morning measurements from 2 am to 7 am (median 9.2 ng m^{-3}, first quartile 8.1 ng m^{-3}, third quartile 14.3 ng m^{-3}), showing that pinic acid concentrations were highest at night. This observation is additionally supported by the fact that the highest values of the entire field campaign were measured during the nighttime. The values for the afternoon measurements from 2 pm to 7 pm are situated between those of the morning and night measurements, though the median value is rather high, with a concentration of 9.8 ng m^{-3} of pinic acid (first quartile 6.4 ng m^{-3}, third quartile 12.3 ng m^{-3}). The arithmetic mean concentrations show a similar behavior and support the diurnal trend observed for

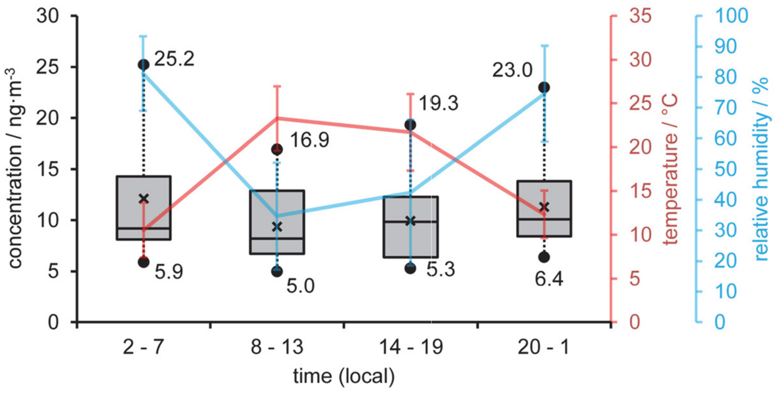

Figure 7. Quantification of pinic acid (*m/z* 185) for different daytimes during the BEACHON-RoMBAS. The dashed lines show the range of measured concentrations. The values at the end of the lines show the maximum and minimum concentrations. Relative humidity and ambient temperatures are shown in blue and red, respectively, with standard deviation during the measurement period.

the median values. A similar diurnal trend for pinic acid during the BEACHON-RoMBAS was also found by Yatavelli *et al.*[22]

In general, SOA production rates are high during daytime and low during the night. This is caused by elevated temperatures during the day leading to higher emission rates of biogenic SOA precursors, such as α-pinene, and by elevated ozone concentrations. However, the observed diurnal cycle shows a minimum for pinic acid during daytime measurements. Several arguments might explain the observations. First, the stronger source term of pinic acid during the day is accompanied by a stronger dilution due to enhanced mixing and a higher boundary layer. Further explanations are the partitioning of pinic acid between the gas and particle phase and the phase state of the sampled aerosol particles. The highest average temperatures were measured between 8 am and 1 pm at roughly 24 °C. These elevated temperatures lead to an enhanced partitioning of pinic acid from the particle phase to the gas phase, resulting in a lower concentration of pinic acid in the remaining aerosol particles. The value of C^*, which is often used as an indicator for the volatility of a compound and its partitioning behavior, is estimated to be $10\,\mu g\,m^{-3}$ for pinic acid.[22,32] Thus, it is considered a semi-volatile organic compound (SVOC, $0.3 < C^* < 300\,\mu g\,m^{-3}$)[33] and should be present in the gas phase as well as the particle phase, strongly depending on ambient temperatures. Additionally to the temperature maxima observed for the time between 8 am and 1 pm, the lowest average relative humidity is observed for that time period. Recently, it has been shown that SOA can have an amorphous solid-phase state that leads to a considerable loss of particles in impactors due to bounce processes. Liquid particles or other easily deformed material tend to adhere to the impaction plate upon collision, whereas solid particles are captured less efficiently owing to bouncing.[34] The behavior of the particles, however, changes with relative humidity. For levoglucosan particles, used as SOA model particles, it was found that the bounce decreases as the relative humidity increases and achieves a minimum at a value around 60%. It is believed that the water uptake acts as a plasticizer, softens the particles and reduces the bounce abilities.[35] Therefore, we assume that besides the enhanced partitioning of pinic acid to the gas phase, the low relative humidity during daytime results in a lower measured concentration, due to an increased bounce behavior of the aerosol particles, and, thus, an impaired collection efficiency of the MOVI. On the other hand, during nighttime measurements the low temperatures around 10 °C result in a decreased vapor pressure of pinic acid, leading to higher concentrations in the condensed phase. Additionally, the high relative humidity enhances the particle collection efficiency of the MOVI and decreases bounce effects by softening the particles.

Conclusions

A MOVI was coupled to a quadrupole IT/MS with an APCI source and used for the analysis of aerosol particles. Ionization in the source was carried out by the production of primary reagent ions reacting with molecules that have higher gas-phase acidity. The APCI technique used here is a soft-ionization technique and mainly gives deprotonated molecular ions ($[M-H]^-$). Aerosol particles were collected for a predetermined time period using the MOVI, volatilized by heating the impaction plate and then analyzed by APCI-IT/MS. The instrument was calibrated for pinic acid by depositing different amounts of a solution of the analyte in methanol directly on the particle-collection surface. The obtained calibration curve exhibited a linear response to the analyte mass and the detection and quantification limits were determined. During laboratory experiments the MOVI-APCI-IT/MS was shown to enhance the detection limit of the MS for small organic acids in the aerosol particle phase by a factor of five or even higher, depending on the sampling time. However, the MOVI-APCI-IT/MS showed significantly lower signals for dimeric oxidation products in the mass range *m*/*z* 300–400, possibly due to incomplete volatilization and thermal decomposition of high molecular weight compounds. Besides the laboratory experiments, the instrument was used in the field during the BEACHON-RoMBAS in the southern Rocky Mountains to analyze organic aerosol particles and to quantify pinic acid in the particle phase. A diurnal cycle for the concentrations of pinic acid in the particle phase with a maximum at night and early morning was found, which may be due to the partitioning behavior of the compound and the phase state of the sampled aerosol particles. In order to assess the contribution of the partitioning and phase state, the partitioning behavior of pinic acid and other compounds has to be studied further and the effect of relative humidity on the phase state of sampled aerosol particles should be measured and taken into account for future field measurements.

Acknowledgements

This work was supported by the Max Planck Graduate Center with the Johannes Gutenberg-Universität Mainz, Mainz, Germany.

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