



Online atmospheric pressure chemical ionization ion trap mass spectrometry (APCI-IT-MSⁿ) for measuring organic acids in concentrated bulk aerosol – a laboratory and field study

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Abstract. The field application of an aerosol concentrator in conjunction with an atmospheric pressure chemical ionization ion trap mass spectrometer (APCI-IT-MS) at the boreal forest station SMEAR II at Hyytiälä, Finland, is demonstrated in this study. APCI is a soft-ionization technique allowing online measurements of organic acids in the gas and particle phase. The detection limit for the acid species in the particle phase was improved by a factor of 7.5 to 11 (e.g. $\sim 40 \text{ ng m}^{-3}$ for pinonic acid) by using the miniature versatile aerosol concentration enrichment system (mVACES) upstream of the mass spectrometer. The APCI-IT-MS was calibrated in the negative ion mode with two biogenic organic acid standards – pinic acid and pinonic acid. Pinic acid was used as a surrogate for the quantification of the total amount of organic acids in the ambient aerosol based on the total signal intensities in the negative ion mode. The results were compared with the total organic signal of a C-ToF-AMS during the HUMPPA-COPEC 2010 field campaign. The campaign average contribution of organic acids measured by APCI-IT-MS to the total submicron organic aerosol mass was estimated to be about 60 %, based on the response of pinic acid. Very good correlation between APCI-IT-MS and C-ToF-AMS (Pearson's $R = 0.94$) demonstrates soft-ionization mass spectrometry as a complimentary technique to AMS with electron impact ionization. MS² studies of specific m/z ratios recorded during the HUMPPA-COPEC 2010 field campaign were compared to MS² studies of se-

lected monoterpene oxidation products formed in simulation chamber experiments. The comparison of the resulting fragments shows that oxidation products of the main VOCs emitted at Hyytiälä (α -pinene and Δ^3 -carene) cannot account for all of the measured fragments. Possible explanations for those unaccounted fragments are the presence of unidentified or underestimated biogenic SOA precursors, or that different products are formed by a different oxidant mixture of the ambient air compared to the chamber ozonolysis.

1 Introduction

It is well known that atmospheric aerosols play an important role in global climate and human health (IPCC, 2007; Pope et al., 2009). Hence, a large scientific community is focussing their research on the physical properties and chemical composition of submicron aerosol particles to understand radiative forcing and air quality (Kulmala et al., 2011). Organic Aerosol (OA) represents the major fraction of non-refractory submicron particle mass (between 18 and 70 %) and in tropical forest regions OA can even account for 90 % of total fine aerosol mass (Zhang et al., 2007; Kanakidou et al., 2005). OA makes up the most abundant but least characterized fraction of atmospheric aerosol particles. This is because OA is a highly complex mixture consisting of thousands of different chemical species at very low concentrations. Goldstein

and Galbally (2007) estimate a number of 10^4 – 10^5 measured organic atmospheric species, which still might be only a fraction of the number actually present. However, a major fraction of OA is believed to consist of organic acids (or multifunctional compounds including organic acid groups) since atmospheric oxidation not only favours the incorporation of oxygen over the atmospheric lifetimes of atmospheric organics, but the low vapour pressure of organic acids also drives these compounds into the particle phase (Kroll et al., 2011).

Common offline techniques for measuring single organic compounds from filter samples are liquid or gas chromatography coupled to mass spectrometry (LC/MS, GC/MS); offline techniques for measuring bulk properties such as functional group contributions are nuclear magnetic resonance spectroscopy (NMR) or direct filter analysis using Fourier transformation infrared spectroscopy (FTIR) (Hallquist et al., 2009; Hoffmann et al., 2011). Unfortunately, offline techniques offer only relatively poor time resolution (several hours to weeks) and can be seriously biased by positive (gas-phase condensation, reactions on the filter surface) and/or negative (evaporation during sampling, degradation on the filter surface, losses or degradation during sample preparation and analysis) sampling artefacts. Turpin et al. (1994) showed that gas-phase adsorption is the dominant artefact in sampling of organic aerosol. The question therefore arises whether filter samples faithfully display the real atmospheric organic aerosol composition (Prather et al., 2008). Warnke et al. (2006) mentioned that more volatile organic compounds (pinonic acid) produce higher artefacts (up to 50 %) than the less-volatile organics. As a consequence, further development and field application of online techniques for directly measuring the chemical composition of the gas and particle phase is required in order to improve our understanding of formation, composition and fate of atmospheric aerosols.

The Aerodyne aerosol mass spectrometer (AMS) enables online chemical composition measurements of aerosol particles by flash vaporization of non-refractory components and subsequent ionization using electron impact ionization (EI) (Jayne et al., 2000). Due to the relatively high energy of the ionizing electrons (70 eV) most organic molecules are fragmented. Selected fragments can then be used for the determination of the oxygen-to-carbon ratio, and indirectly, certain individual sources or the volatility of the organic aerosol components. Using positive matrix factorization (PMF) analysis, the AMS can be used to classify organic aerosol into hydrocarbon-like OA (HOA), biomass burning OA (BBOA), semi-volatile oxygenated OA (SV-OOA) and low-volatility oxygenated OA (LV-OOA) (Zhang et al., 2011; Jimenez et al., 2003, 2009). Based on such an approach also complex processes, such as photochemical ageing of organic aerosols, can be investigated (Ng et al., 2010, 2011). However, identification and quantification of specific molecular tracer compounds is not easily accomplished with EI-AMS (Canagaratna et al., 2007). This goal can only be

achieved through low-energy ionization processes, resulting in no or minor fragmentation of the molecular tracers (soft-ionization techniques). In the extreme case, each ionized organic molecule results in a single signal representative for the molecular ion of the compound of interest. One possibility is the use of corona discharge (CD) at atmospheric pressure; a technique that is well established when liquid chromatography is hyphenated with mass spectrometry (atmospheric pressure chemical ionization (APCI)). The technique represents a soft-ionization method, where fragmentation of the analyte molecules plays a minor role and mostly molecular ions are observed. The application of this technique measuring organic compounds in the particle phase was reported as early as 1998 by Hoffmann et al. (1998) using CD for the generation of O_2^- ions at atmospheric pressure. Prior to the ionization process, the organic compounds are thermally evaporated from the particle phase by a vaporizer within the ion source. Gas-phase compounds are removed upstream of the ion source by an activated charcoal denuder. For higher organic mass loadings, e.g. for measurements in simulation chamber experiments, the atmospheric pressure chemical ionization ion trap mass spectrometer (APCI-IT-MS) is well suited for online measurements of organic acids in the negative ionization mode, providing new insights into product structures (Warscheid and Hoffmann, 2001, 2002) and multiphase chemical mechanism of secondary organic aerosol ageing (Müller et al., 2012). Measuring in the positive ion mode, hydroperoxides and hydroperoxy acids, formed during ozonolysis of biogenic volatile organic compounds (BVOCs), can be identified by a characteristic loss of 34 Da during MS^2 experiments (Reinigg et al., 2009). However, for measuring secondary biogenic organic acids at ambient concentrations below 100 ng m^{-3} , this technique is not sensitive enough.

Other approaches towards soft-ionization AMS are described by Dreyfus and Johnston (2008), Dreyfus et al. (2009), and Geddes et al. (2010). An overview article on soft-ionization mass spectrometry of atmospheric organic aerosols was recently published by Zahardis et al. (2011). Hearn and Smith (2006) describe an aerosol CIMS as an online measurement technique, using a radioactive polonium source (^{210}Po) to generate SF_6^- as primary ions. The reported detection limit of 100 – 200 ng m^{-3} is sufficiently low for sulphate measurements in ambient aerosols; however, it is not sensitive enough for most organic species in the particle phase. By using a cold trap U-tube they were able to measure ambient aerosol organic compounds after sampling for 6 h. Another promising semi-online method for measuring organic acids in the gas and particle phase has recently been reported by Yatavelli and Thornton (2010) using a micro-orifice volatilization impactor (MOVI) in front of a CI-MS. This technique has the advantage of sampling particles by inertial impaction at a relatively high flow rate (10 SLPM) within 15 % of the ambient pressure.

During sampling periods gas-phase concentration can be measured online. An instrumental approach towards measuring nanoparticle composition is the TDCIMS (Thermal Desorption Chemical Ionization Mass Spectrometer, Smith and Rathbone, 2008). The authors use a unipolar charger and a nano-DMA to collect 8–40 nm particles on an electrostatic precipitator. Subsequent thermal desorption and chemical ionization allows measurements of mono- and dicarboxylic acids in nucleation mode particles. Further instrumentation which is based on collection, thermal desorption and ionization of the analytes are the aerosol collection module coupled to GC-MS (Hohaus et al., 2010), the thermal desorption particle beam MS (TD-PBMS, Tobias and Ziemann, 1999) and the thermal desorption PTR-MS (TD-PTR-ITMS, Thornberry et al., 2009). However, these semi-online techniques are all based on thermal desorption of surface-deposited analytes, which increases the hazard of decomposition during desorption. Furthermore, a constant collection efficiency is not guaranteed since particle bounce effects of glassy SOA particles might change with chemical composition, relative humidity and liquid water content of the aerosol particles (Virtanen et al., 2010; Saukko et al., 2012).

In this paper we describe for the first time the coupling of the miniature versatile aerosol concentration enrichment system (mVACES, Geller et al., 2005) with the soft-ionization APCI-IT-MS, allowing online measurements of the composition of laboratory generated OA and ambient OA during the HUMPPA-COPEC2010 field campaign at Hyytiälä, Finland (Williams et al., 2011). The mVACES works by first supersaturating the incoming particles with respect to water vapour and then rapidly cooling the aerosols to force water condensation, followed by enrichment with a virtual impactor. Consequently, the aerosol particles are not enriched by sampling onto a surface but rather the enriched minor flow is measured directly by APCI-IT-MS. Geller et al. (2005) showed that the particle size distribution before and after enrichment and drying is not altered. Khlystov et al. (2005) investigated the VACES technology with focus on artefacts due to repartitioning from gaseous compounds into the particle-phase. They observed significant positive artefacts for semi-volatile nitrate, based on the enrichment factor of sulphate. Artefacts for organic material were less pronounced; however, the artefacts of semi-volatile organics were not investigated by Khlystov et al. (2005) and further fundamental studies are needed in order to clarify those issues. Field applications of the mVACES have been done in combination with online and offline techniques, resulting in a better signal-to-noise ratio of low flow rate instruments or shorter filter sampling time, respectively (Ning et al., 2006). Previously, the mVACES has been demonstrated to measure bulk aerosol composition in a remote region in conjunction with HR-ToF-AMS (Sun et al., 2009) or in an urban environment in conjunction with the soft-ionization PIAMS (photoionization AMS, Dreyfus and Johnston, 2008).

2 Experimental

Online analysis of organic acids in the bulk aerosol was realized by using a Finnigan LCQ ion trap mass spectrometer (IT-MS) (Finnigan MAT, San Jose, USA). The instrument was equipped with a modified atmospheric pressure chemical ionization (APCI) ion source (Kückelmann et al., 2000). It was operated in the negative mode to form $[M-H]^-$ ions. The APCI-IT-MS used has been described in detail by Hoffmann et al. (2002) for online measurements of gaseous and particulate organic compounds in chamber experiments. Briefly, O_2^- ions are formed at atmospheric pressure by a 3 kV corona discharge between a needle and the transfer capillary (Fig. 1). Gaseous analytes, which have a higher gas-phase acidity than O_2^- , become ionized by proton transfer reactions. Remaining excess energy of the proton transfer reaction is transferred by collision to a third neutral molecule. The O_2^- reagent ion is selective towards organic acids, inorganic acids, nitrophenols and combination between those compound classes (e.g. organosulphates). Veres et al. (2008) described a similar CI-MS method using acetic acid as reagent ion. Due to a lower gas-phase acidity of O_2^- compared to acetic acid (Bartmess, 2011), most atmospherically relevant organic acids are detected by the O_2^- -ionization method. Both techniques show limited response on organic acids which rapidly undergo thermal decomposition, e.g. oxalic acid or malonic acid.

To enhance signal intensities of the particle phase compounds, the APCI-IT-MS was equipped with a miniature versatile aerosol concentration enrichment system (mVACES) in front of the MS (Geller et al., 2005). A scheme of the instrumental setup is shown in Fig. 1.

2.1 mVACES/APCI-IT-MS setup during the HUMPPA-COPEC 2010 field campaign

During July and August 2010, the HUMPPA-COPEC 2010 field campaign was carried out at the SMEAR II station at Hyytiälä, Finland (Hari and Kulmala, 2005). The aim of this campaign was to investigate summertime boreal forest chemistry, mainly focusing on the photochemistry of biogenic emissions. Periods influenced by biomass burning, anthropogenic emissions and sawmill emissions were contrasted to clean natural conditions (Williams et al., 2011).

The measurements described here took place at the main SMEAR II cottage. Ambient air was sampled from canopy level height through a stainless steel tube as the main inlet. The OD of the tube was approx. 5 cm and the flow speed was set to 0.5 m s^{-1} using a fan at the end of the tube. The mVACES/APCI-IT-MS and the Aerodyne C-ToF-AMS were sampling from this tube using Pitot-tube-like sampling ports (Fig. 1). The sampling port and the mVACES/APCI-IT-MS were connected by a 12.0 mm ID and 2.00 m long conductive PTFE tube (Type PTFE EX, Bohlender GmbH, Grünsfeld, Germany). A 2.5 cm ID circular channel was shaped into a

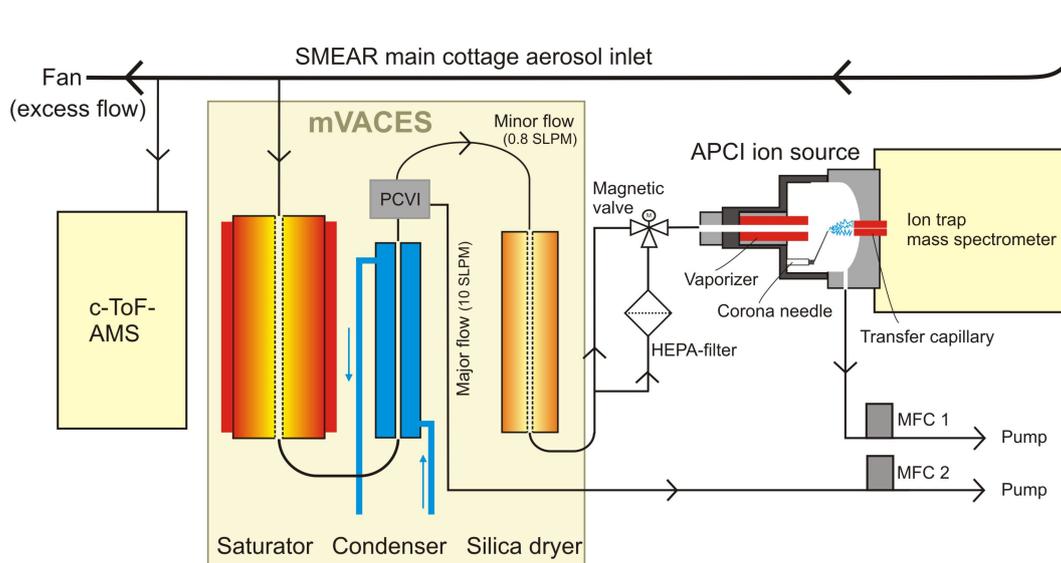


Fig. 1. Scheme of the instrumental setup of mVACES/APCI-IT-MS and C-ToF-AMS during the HUMPPA-COPEC 2010 field campaign (dimensions are not true to scale).

cellulose sponge inside the saturator. The sponge was kept moist using a peristaltic pump which continuously purged water onto the top of the sponge. The water reservoir was exchanged twice a day with ultrapure water to avoid memory effects by absorbed gas-phase species. A heating tape (HBSI, Horst GmbH, Lorsch, Germany) with a temperature regulator (HT30, Horst GmbH, Lorsch, Germany) was adjusted to keep the temperature at the centre of the saturator at 35 °C. The air at the end of the saturator had a relative humidity (RH) above 90 % and a temperature of approximately 30 °C (depending on the conditions of the sampled air). The temperature of the cooling liquid in the condenser (2.0 cm ID, 40 cm length) was kept at -1 °C using a cooling thermostat (Lauda ECO RE 415 S, Lauda Dr. R. Wobser GmbH & Co. KG, Lauda-Königshofen, Germany). A mixture of ethylene glycol and water (1 : 1, v/v) was used as the cooling liquid. Downstream of the condenser a virtual impactor was used to let the grown aerosol particles transit into the minor flow. The virtual impactor used was originally designed as a pumped counterflow virtual impactor (PCVI, Boulter et al., 2006) which separates gas-phase and low-inertia particles from high-inertia particles. In this study the PCVI was operated without counterflow to maximize the transition of low inertia particles into the minor flow. The absolute pressure inside the virtual impactor depends on the input and output flow rates and ranged between 880 and 910 mbar. The major flow was set to 10 standard liters per minute (SLPM) and the minor flow to 0.8 SLPM using two distinct mass flow controllers (MKS Instruments, Andover, USA) resulting in a theoretical enrichment factor of 12.5. A 1/4" stainless steel tube was used to connect the PCVI with a silica gel diffusion dryer (1 cm ID \times 40 cm). Each 72 h the silica gel was

exchanged with dry gel to ensure constant drying. To assess the gas-phase composition, a particle filter (HEPA capsule, Pall Corporation, Port Washington, USA) was switched in line every 2.5 h for half an hour to remove the particle phase signal. A large-orifice magnetic valve (VX3244-02F-5DZ1-B, SMC Corporation, Tokyo, Japan) was chosen to reduce particle losses inside the valve.

Data were recorded between mass to charge ratios (m/z) 50 to m/z 500. Each recorded spectrum is an average of 200 microscans, resulting in a measurement frequency of one spectrum per minute. At the beginning of the field measurements the instrument was automatically tuned on m/z 215, resulting in the settings listed in Table 1. The mass calibration of the instrument was carried out by using the recommended mass calibration solution of the manufacturer. The background of the instrument was measured at the beginning, during and at the end of the campaign by connecting zero air (synthetic air, hydrocarbon free, Westfalen, Germany) to the inlet of the saturator.

Data were recorded using XCalibur[®] 1.2 software, the data files were converted to plain text files and then transferred into a matrix with five-minute time resolution using Matlab[®], Mathworks Inc. software. Each recorded m/z ratio was rounded to the nominal mass. Gas-phase measurements, which were recorded in 3-h time intervals, were interpolated linearly and subtracted from the total signal resulting in the particle phase signal.

2.2 C-ToF-AMS setup during the HUMPPA-COPEC 2010 field campaign

During the measurement campaign the C-ToF AMS was operating alongside the APCI-IT-MS, and was sampling from

Table 1. Instrument settings of atmospheric pressure chemical ionization mass spectrometer (APCI-IT-MS).

Vaporizer temperature	350 °C
Sheath gas flow	0 a.u.
Discharge current	3 μ A
Discharge voltage	3 kV (\pm 0.3 kV)
Capillary temperature	200 °C
Capillary voltage	-14 V
Tube lens offset	20 V
Multipole 1 offset	2.5 V
Lens voltage	16 V
Multipole 2 offset	5.5 V
Electron multiplier voltage	-1030 V

the same main inlet. The AMS inlet port was situated approximately 2 m downstream of the APCI-IT-MS inlet and the AMS was connected to the port using 6-mm copper tubing of 1 m length (Fig. 1). For the purpose of intercomparison between the AMS and the APCI-IT-MS, the instruments can be considered co-located and having equivalent inlet losses.

The specifics of the C-ToF have been described in detail by Drewnick et al. (2005), but in short the AMS measures aerosol particle mass and chemical composition. The AMS used in this study features an aerodynamic lens for concentrating the sampled aerosol particles in the size range of roughly 50 to 600 nm into a narrow beam, a particle time-of-flight chamber for particle size distribution measurement, thermal vaporization of the sample at 600 °C using a porous tungsten vaporizer, 70 eV electron impact (EI) ionization of the produced vapour, and a compact time-of-flight mass spectrometer (C-ToF-MS). This particular instrument also features a shorter-than-usual particle time-of-flight chamber, which results in increased transmission of both particles and gas, and therefore also a larger air signal than in most AMS designs. The high air signal was reduced by adding 3.5 mL min⁻¹ of He (AGA, 6.0 grade) to the time of flight chamber. The resulting high He signal at mass 4 Th was removed by a small RF-only quadrupole before the ion lenses and the extraction region of the TOF.

The AMS data were preprocessed using Squirrel (SeQUential Igor data RetRiEvaL) data analysis tool v.1.5. The mass concentration of aerosol particles was quantified and the measured mass was assigned into subgroups of different chemical composition: sulphates, organics, nitrates, ammonia and chlorides. For a thorough description of AMS data analysis, see e.g. Allan et al. (2003, 2004). The measured data were corrected for collection efficiency (CE). A base CE value of 0.43 was selected based on a comparison with the submicron mass concentrations derived from the number size distribution measurements with the differential mobility particle sizer (DMPS) in the size range of 3 to 600 nm. The base CE was estimated for time periods when the aerosol acidity was neutral. For periods with non-neutralized sulphate, im-

plicating elevated aerosol acidity, a higher value was used, based on a linear correction function similar to that of Quinn et al. (2006) and Middlebrook et al. (2012). CE anomalies caused by high mass fraction of nitrates were not observed, and the amount of nitrates remained consistently below 10 %.

The quantitiveness of the AMS results gives a good starting point for more detailed analysis. During the HUMPPA campaign, the ambient aerosol was dominated by organic chemical species with minimum concentrations near zero on a clean day and maximum of 23.1 μ g m⁻³ observed during a long-range transported forest fire smoke episode. On average organic species explained 69 % of the submicron non-refractory mass, sulphates accounted for 20 % of mass, and ammonium compounds and nitrates for 7 % and 4 %, respectively. The amount of chlorides was negligible. The dataset therefore provides a good basis especially for studying the composition of organic species using mVACES/APCI-IT-MS.

2.3 Laboratory setup

To test the coupling of the aerosol concentrator mVACES with APCI-IT-MS in the laboratory, secondary organic aerosol from α -pinene ozonolysis was generated in a 100 L continuous-flow reaction chamber. For this purpose gaseous (+)- α -pinene (Sigma-Aldrich, \geq 99 %), generated in a thermally controlled diffusion source (Thorenz et al., 2012) was mixed with ozone (1 ppm) in the reaction chamber to produce organic aerosol particles. Ozone was generated with an ozone generator (1008-RS, Dasibi Environmental Corp., Glendale, CA, USA) and directly introduced into the reaction chamber. The formed aerosol was measured online using APCI-IT-MS without mVACES. Gas-phase species were removed using an activated charcoal denuder. When the reactant and aerosol concentration in the continuous-flow chamber were in steady state, the online measurement without mVACES was started. After a few minutes the mVACES was switched in between the reaction chamber and the APCI-IT-MS to measure the concentration enrichment factor and to investigate whether the mVACES leads to an alteration of the chemical composition of the particle phase.

For MS² experiments the same experimental setup was used to record online-MS² spectra from ozonolysis products from (+)- α -pinene (Sigma-Aldrich, \geq 99 %), (*R*)-(+)-limonene (Sigma-Aldrich, 97 %) and (+)- Δ^3 -carene (Fluka analytical, \geq 98.5 %). The collision induced dissociation (CID) of an isolated molecular ion inside the ion trap was achieved by using helium (5.0, Westfalen AG) as collision gas. The relative collision energies were adjusted to measure a relative abundance of the molecular ion after fragmentation of 5–20 %. This was achieved by setting CID energy to 26 % for laboratory studies and to 30 % in the field studies. Typically, 30–70 of the recorded MS² spectra were averaged since the intensities during MS² measurements varied significantly.

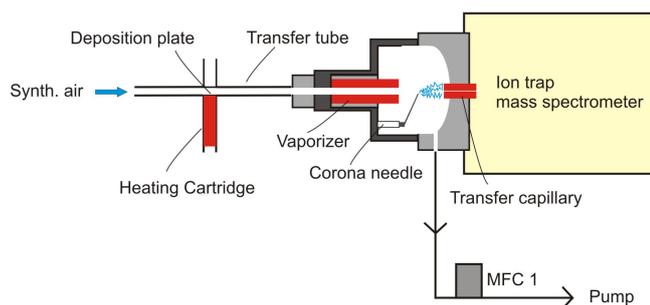


Fig. 2. Setup for the calibration of the APCI-IT-MS.

2.4 Calibration of APCI-IT-MS

The APCI-IT-MS was calibrated for two different biogenic organic acids (pinic acid and pinonic acid) in the laboratory. Both acids are regarded as representative compounds formed from monoterpene oxidation in the boreal forest atmosphere. *Cis*-Pinonic acid (Sigma–Aldrich, 98 % purity) was purchased as a commercially available standard, *cis*-Pinic acid is a self-synthesized standard (Mogliani et al., 2000). Zero air (hydrocarbon free) was purchased from Westfalen AG.

For the calibration of the instrument, the acids were dissolved in methanol (Sigma–Aldrich, HPLC grade) and adjusted to concentrations ranging from 0.25 to 2.5 ng μL^{-1} . 10 μL of the individual solutions were deposited on a stainless steel surface. This deposition surface was installed directly in front of the ion source, a setup similar to the MOVI-CIMS setup described by Yatavelli and Thornton (2010). Figure 2 shows the experimental setup. The deposited compounds were evaporated by heating the deposition surface within 3 min to approx. 120 °C. The zero air flow prior to the ion source was set to 1.0 SLPM using a mass flow controller. The transfer tube to the ion source was heated to 150 °C to avoid condensation of the evaporated acids. The resulting peak height was averaged for 5 and 10 min and related to the sampled volume within these intervals to determine the instruments response of online measurements to a certain concentration of the investigated acids (Fig. 3). It has to be noted that the heated deposition plate was not operative during the field campaign and consequently the calibration procedure was done after the field campaign in the laboratory. As a consequence the calibration procedure is based on the following assumptions:

1. The vaporization of the analytes from the surface takes place in a quantitative manner without decomposition.
2. During online measurements vaporization of the analytes from particles is quantitative.
3. The instrumental performance during field measurements and laboratory calibration did not change significantly.

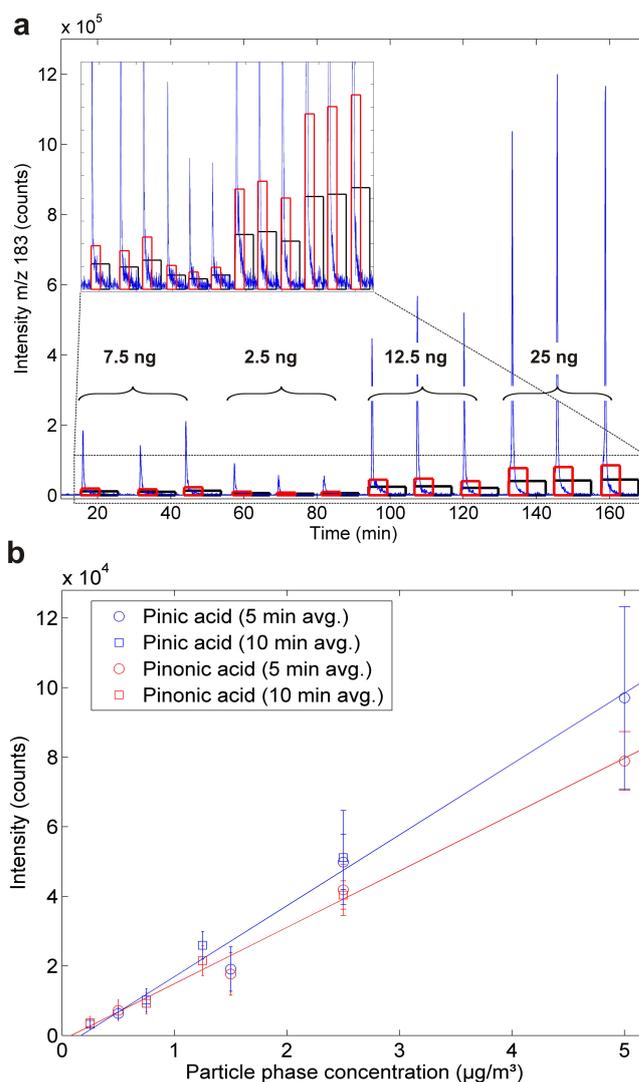


Fig. 3. (a) Mass trace of pinonic acid (m/z 183) during calibration (blue), mean intensity for 5 min (red) and 10 min intervals (black). (b) Linear fit of calibration for pinonic acid (m/z 183, red) and pinic acid (m/z 185, blue).

The recorded mass spectra during the calibration did not actually show any evidence of decomposition of the tested acids. Furthermore, the investigated m/z ratios did not show any significant blank signal such as the observed blank signal of palmitic acid described by Yatavelli and Thornton (2010).

3 Results and discussion

3.1 Calibration and detection limit for biogenic organic acids

Figure 3a shows the results of 12 calibration runs at 4 different concentrations in a laboratory experiment. During heating cycles of the deposition plate, the analytes evaporate into

a controlled flow of 1.0 SLPM carrier gas and produce a characteristic signal peak. The shape of the peak essentially depends on the heating rate and the volatility of the analyte. In order to use this transient signal for calibration of the online APCI-IT-MS measurements, the signals from the calibration experiments were averaged over two intervals: five and ten minutes. Equation (1) is used to determine the instrument's response towards the absolute mass concentration. During the calibration procedure (Fig. 2), the mass of the deposited organic acid on the deposition plate is m (μg), and the denominator expresses the volume (m^3) in which the analyte is evaporated into: the product of flow rate f (SLPM) and average time interval t (min) (red boxes: 5 min; black boxes: 10 min), resulting in the concentration c ($\mu\text{g m}^{-3}$). Based on the assumption that the average intensity I (counts) during the calibration procedure equals the same mass concentration during the online measurement, the linear interpolation (slope s and y-intercept b) was applied on the ambient online intensities to determine the ambient mass concentration.

$$c = \frac{m}{1 \cdot 10^{-3} \cdot f \cdot t} = \left(\frac{I - b}{s} \right) \quad (1)$$

The calibration range was adjusted to match the measured intensity range of gas- and particle-phase measurements of m/z 183 and m/z 185 during the HUMPPA-COPEC10 field campaign, and showed a linear response between deposited organic acid mass and resulting average signal height. Based on the assumptions described above the detection limit (LOD) for pinonic acid in the particle phase was determined to be about 300 ng m^{-3} , and for pinic acid about 410 ng m^{-3} . This LOD calculation was based on the blank signal intensity assuming three times standard deviation of the noise signal. The detection limit of pinonic acid and pinic acid in the gas phase at 25°C would be 41 pptV and 54 pptV, respectively. These detection limits are in the same order of magnitude as the reported sensitivities for oleic acid in the particle phase (LOD: 200 ng m^{-3}) by aerosol CIMS (Hearn and Smith, 2006). However, ambient concentrations of these compounds are expected to be lower than the calculated detection limits. Maximum reported particle phase concentration of pinonic acid and the isobaric overlapping caronic acid in Hyytiälä, Finland are 74 ng m^{-3} and 23 ng m^{-3} , respectively (Warnke et al., 2006). Therefore, the application of the aerosol concentrator mVACES is necessary to detect these species in the ambient air.

3.2 mVACES concentration efficiency

To test the concentration enrichment factor of the mVACES in the laboratory, the setup as described in chapter 2.3 was used. The measured total ion current (TIC) of the products formed from α -pinene ozonolysis was used to calculate the enrichment factor. Figure 4 shows the online mass traces of the TIC (m/z 50–500), a lower molecular weight range (monomeric ozonolysis products, m/z 160–240, hereafter

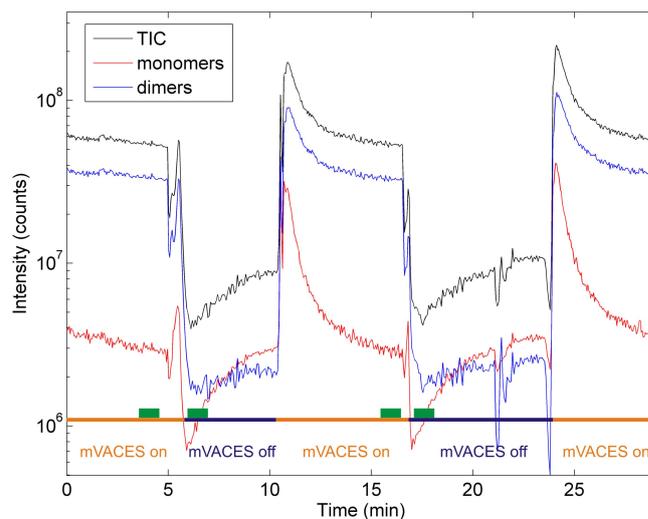


Fig. 4. Performance of mVACES aerosol enrichment during laboratory testing. TIC: total ion current, monomers: sum of signals m/z 160–240, dimers: sum of signals m/z 320–400.

monomers) and a higher molecular weight range (dimeric ozonolysis products, m/z 320–400, hereafter dimers). The green bars in Fig. 4 mark the time interval in which the TIC signal was averaged to determine the enrichment factor in the laboratory. The overall calculated concentration enrichment factor determined in the laboratory as described above was 11.0 ± 2.4 (2^* rel. SD).

It should be noted in Fig. 4 that the signal intensities of the three depicted mass ranges were not constant during the individual measurement periods (i.e. with and without mVACES). This is due to the fact that the product concentration in the continuous-flow chamber changed due to differing flow rates/reaction times when working with or without mVACES. The resulting change of particle concentration (total organic aerosol mass) can affect the gas-to-particle partitioning, especially for the semi- or intermediately volatile compounds (i.e. monomers – resulting in an increased fraction of the monomers in the particle phase with increasing organic particle mass concentration). To avoid potential influences of such concentration changes on the determination of the enrichment factor, the time intervals chosen for the estimation are “end of the mVACES on” vs. “beginning of the mVACES off” (Fig. 4).

Another aspect that should be considered when a VACES system is used are the losses of semi-volatile and at least partly water soluble compounds during the mVACES preconcentration by absorption within the saturator. An estimation of this amount based on the Gormley–Kennedy equation (diffusion coefficient $D = 0.058 \text{ cm}^2 \text{ s}^{-1}$ at a flow rate of 11.0 SLPM) results in a notable loss of 30% of the gas-phase fraction, assuming that the wet sponge acts as a perfect sink for gaseous organic acids. Subsequent re-equilibration between gas and particle phase (evaporation of SV-OOA from

the particle phase) might result in negative artefacts. An indication for negative artefacts of semi-volatile organics can be seen in Fig. 4 at minute 10: before switching the concentrator on, the signal of the monomers is higher than that of the dimers, and vice versa after switching on. Further concerns about possible changes in gas/aerosol partitioning might be raised by multiple temperature changes during the passage through the concentrator. Contrary to negative artefacts, Khlystov et al. (2005) showed that the concentration of water soluble semi-volatile material can be increased at small sizes after passage through the concentrator. Their maximum observed amount of positive nitrate artefacts (relative to sulphate) on a polluted day reached a factor of 2.6; organic material showed significantly less positive artefacts (factor 1.2). These positive artefacts are most probably attenuated due to losses of gas-phase organics in the saturator. Further investigation on artefact formation of the semi-volatile aerosol fraction in a water-based concentrator is needed for a more precise determination of the concentration factor of semi-volatile organic compounds.

During the HUMPPA-COPEC 2010 field campaign, the concentration enrichment factor was determined by measuring the sulphate signal at m/z 97 with and without mVACES since (1) sulphate has a lower vapour pressure than most organic compounds and thus the influence of changes in gas/aerosol partitioning due to the mVACES is low, and (2) sulphate was sufficiently high to be measured well above background without mVACES. The concentration enrichment factor during the field measurement was 7.5 ± 2.5 (2^* RSD). Sulphate concentration measured by AMS during this time was around $2 \mu\text{g m}^{-3}$. Furthermore, the total concentration of organic acids in the particle phase during the HUMPPA-COPEC field campaign was approximated by using the average response of pinic acid and applying this response onto the sum of the signals between m/z 150– m/z 500. By doing so, pinic acid is used as a surrogate for the quantification of organic acids based on the total signal intensities in the negative ion mode.

3.3 Instrument comparison

Figure 5 correlates the two online mass spectrometric techniques mVACES/APCI-IT-MS and AMS during the HUMPPA-COPEC 2010 field campaign. Data points are five minute averages between 16 July 2010 and 12 August 2010. Data points for time intervals in which the AMS and/or the APCI-IT-MS did not run due to power cuts or instrumental maintenance were taken out. However, 49 % of the total campaign duration is still covered with simultaneous data from both instruments. The AMS data are corrected using a collection efficiency factor of 0.43. As mentioned above, the APCI-IT-MS data are the sum of the particle phase signal of m/z 150 to m/z 500, quantified by using the average response of pinic acid, regarding this acid as representative for all compounds ionized in the APCI-IT-MS negative mode.

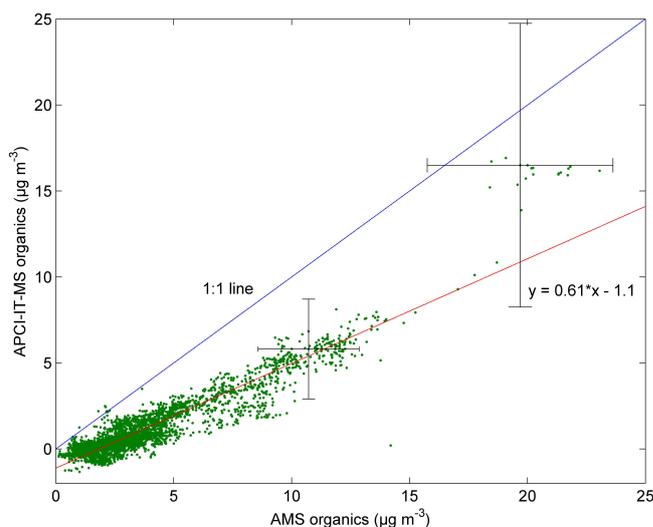


Fig. 5. Correlation plot of organic signals from mVACES/APCI-IT-MS and C-ToF-AMS during the HUMPPA-COPEC 2010 field campaign (APCI-IT-MS signal (sum m/z 150–500) based on instruments response to pinic acid). Estimated errorbars for AMS uncertainty are $\pm 20\%$ and for APCI-IT-MS uncertainty are $\pm 50\%$.

With certainty this is an assumption which does not take into account that higher weight molecular compounds might have a different response factor compared to pinic acid. Unfortunately, to our knowledge there are no literature data available yet on quantitative determination of e.g. sesquiterpene derived acids.

As can be seen in Fig. 5, all data points are well below the 1 : 1 line. This is expected since APCI-IT-MS probably exclusively measures organic acids (or multifunctional organic molecules including carboxylic acid functional groups) and therefore does not include other organics, e.g. alkanes, alcohols, aldehydes or ketones. The campaign bulk average contribution of organic acids measured by APCI-IT-MS to total organic aerosol measured by AMS during HUMPPA-COPEC 2010 was about 60 % (possibly induced by the extreme heat and biomass burning events during summer 2010 (Williams et al., 2011)). Since the sensitivity of the instrument for heat-sensitive acids (e.g. oxalic acid or malonic acid) is almost one order of magnitude lower than for the calibrated acids, the contribution of organic acids might be even higher. However, for the available data the comparison between APCI-IT-MS and AMS shows a very good correlation with a Pearson's R of 0.94 for organics.

On 29 July, at 10:00–14:00 (local time, UTC +2), a plume from strong biomass burning events in central Russia arrived at the station. During this period the AMS measured the campaign maximum of $23.1 \mu\text{g m}^{-3}$ organic aerosol concentration. Also, the concentration of organic acids measured by the APCI-IT-MS was the highest during the whole campaign as well as the relative contribution of acids to the total organic aerosol (see Fig. 5). These observations suggest

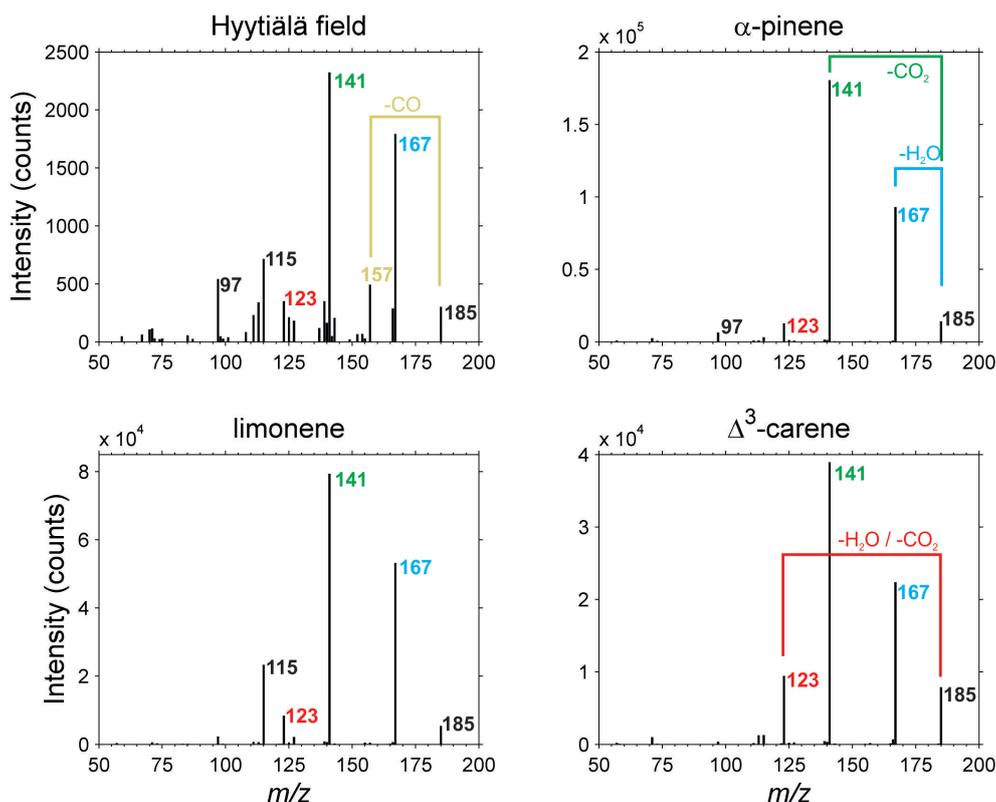


Fig. 6. Online MS² experiments at Hyytiälä (CID energy 30 %) and from laboratory ozonolysis using α -pinene, limonene and Δ^3 -carene (CID energy 26 %).

that the biomass burning aerosol during this event was extremely oxidized and photochemically aged – a suggestion also supported by the observed ratio of AMS organic signals on m/z 43 and m/z 44, which are commonly used as a qualitative indicator of the degree of aerosol oxidation. Unfortunately, the C-ToF-AMS was not capable to determine a reliable O : C ratio to further corroborate these findings.

3.4 Online MS² experiments from field and laboratory experiments

On 22 July 2010, at 13:20–15:20 h (UTC +2), during the HUMPPA-COPEC 2010 campaign, MS² spectra of the total organic signal (gas and particle phase) were recorded. Several individual m/z ratios between m/z 150 to m/z 250 were isolated (isolation width ± 0.5 amu) in the ion trap, and by subsequent addition of RF energy, collision induced dissociation caused specific fragmentation of the isolated ions. Figure 6 shows the resulting MS² spectrum of m/z 185, measured at the boreal field site together with the online MS² spectrum on m/z 185 of α -pinene, limonene and Δ^3 -carene ozonolysis products in the laboratory. The main compound at this m/z ratio is supposed to be pinic acid and isobaric acids originating from other monoterpenes, e.g. 3-caric acid. Although the field MS² mass spectrum is similar to the spectra

from the reaction chamber experiments, some fragments actually appear only in the field MS² spectrum, indicating that several other compounds might contribute to the signal on the same m/z ratio.

All of these spectra show that m/z 167 and m/z 141 are the most prominent ion signals. These fragments are the result of water loss (18 Da) and of CO₂ (44 Da) – characteristic loss and evidence for carboxylic acid functional groups. Furthermore, the limonene spectrum shows a loss of 70 Da (potentially C₄H₆O), resulting in the fragment m/z 115, which is not present in the spectrum of α -pinene and Δ^3 -carene ozonolysis but clearly detectable in the Hyytiälä spectrum. The m/z 115 signal was also described as a fragment of ketolimononic acid measured by offline ambient filter measurements from K-pusztá and analysis by HPLC/ESI-MSⁿ (Yasmeen et al., 2011). The abundance of the MS² fragment m/z 115 at Hyytiälä seems surprising since the main monoterpene emissions at Hyytiälä measured by GC-MS are α -pinene and Δ^3 -carene (Yassaa et al., 2012). An explanation might be that limonene is emitted in larger amounts than derived from ambient measurements or cuvette studies – possibly induced by the very high reactivity of the double unsaturated monoterpene. Due to the diversity of biogenic emissions at the Hyytiälä station, oxidation products from other volatile organic precursor molecules might also contribute to

the m/z 115 fragment, e.g. myrcene-, camphene-, sabinene- or sesquiterpene-derived acids. The loss of CO or C₂H₄ (28 Da), resulting in m/z 157 cannot be found in chamber experiments with the tested monoterpenes (β -pinene also tested but not shown). The fragment m/z 97 can originate from the dissociation of the sulphate group from organosulphates (detachment of HSO₄⁻) or, more likely, from the dissociation of two CO₂ molecules from the molecular ion. Since pinic acid and 3-caric acid are both dicarboxylic acids, the dissociation of two CO₂ is very likely. In conclusion, we would like to speculate that the oxidation of fast reacting (e.g. myrcene) or unknown VOCs (DiCarlo et al., 2004) can form products which might explain the non-assignable fragments measured during the MS² experiments.

4 Conclusions

We have demonstrated for the first time the application of an online mass spectrometric technique with the ability to perform MS² experiments from biogenic organic acids in the field. To record the MS² spectra, it is essential to use soft ionization to preserve the structural information of the molecular ion before entering the detector – in our case a quadrupole ion trap. The soft-ionization technique adopted here was chemical ionization at atmospheric pressure using O₂⁻ ions as primary ions reacting with molecules that have higher gas-phase acidity. To improve the detection limit in the field, an mVACES was operated in front of the MS system. The APCI-IT-MS data were compared to C-ToF-AMS data, revealing that the two techniques are complementary mass spectrometric techniques which can lead to an improved understanding of organic aerosol formation and composition. MS² studies did indicate the abundance of several compounds on one nominal mass in the boreal forest environment. The overall AMS/APCI-IT-MS comparison suggests that organic acids formed a major part of organic aerosol mass during the HUMPPA-COPEC2010 campaign. Furthermore, the APCI-IT-MS technique is in principle suited to measure quantitatively rarely measured species (i.e. the suite of organic acids) in the gas phase, which can be of great help in assessing the significant missing reactivity observed in the boreal forest (Nölscher et al., 2012). For upcoming ecosystem or megacity studies, the capability to perform online high-resolution mass spectrometry for more detailed observation of molecular tracer compounds would be a very valuable asset.

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