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A new aerosol collector for on-line analysis of particulate organic matter: the Aerosol Collection Module (ACM)

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Abstract

In many environments organic matter significantly contributes to the composition of atmospheric aerosol particles influencing its properties. Detailed chemical characterization of ambient aerosols is critical in order to understand the formation process, composition, and properties of aerosols in the atmosphere. However, current analytical methods are far from full speciation of organic aerosols and often require long sampling times. Offline methods are also subjected to artifacts during aerosol collection and storage.

In the present work a new technique for quasi-online compound specific measurements of organic aerosol particles was developed. The Aerosol Collection Module (ACM) is designed to sample, collect and transfer gasified atmospheric aerosol particles. The system focuses particles into a beam which is directed to a cooled sampling surface. The sampling takes place in a high vacuum environment where the gas phase from the sample volume is removed. After collection the particle sample is evaporated from the collection surface through heating and transferred to a detector.

For laboratory characterization the ACM was interfaced with a Gas Chromatograph Mass Spectrometer system (GC-MS). The particle collection efficiency, gas phase transfer efficiency, and linearity of the ACM-GC-MS were determined using laboratory generated octadecane aerosols. The ACM-GC-MS is linear over the investigated mass range of 10 to 100 ng and a recovery rate of 100% was found for octadecane particles. The ACM-GC-MS was applied to investigate secondary organic aerosol (SOA) formed from β-pinene oxidation. Nopinone, myrtanal, myrtenol, 1-hydroxynopinone, 3-oxonopinone, 3,7-dihydroxynopinone, and bicyclo[3,1,1]hept-3-ene-2-one were found as products in the SOA. The ACM results are compared to quartz filter samples taken in parallel to the ACM measurements. First measurements of ambient atmospheric aerosols are presented.
1 Introduction

Numerous techniques for the analysis of the chemical composition of organic aerosols (OA) exist. The complexity of OA and SOA due to the sheer number of individual compounds present (Goldstein and Galbally, 2007) is a major obstacle in the complete speciation of OA.

The most common methods of chemical speciation are filter-based techniques where particles are collected on quartz fiber or teflon filters. After sampling the filter content is analyzed in the laboratory using standard analytical procedures. These include solvent extraction, supercritical fluid extraction or thermal desorption of the filter samples. Pre-treatment of the filters, such as derivatization, can be used to increase the range of measurable compounds. Subsequent analysis with analytical techniques, such as gas chromatography coupled to mass spectrometry (GC-MS, most widely used) and liquid chromatography coupled to MS (LC-MS) (especially for polar compounds) are used for the molecular characterization of the OA. Recent studies showed improvements of the resolution of such techniques by using two-dimensional GC coupled to time-of-flight (TOF) MS (Hamilton et al., 2004). The high quantities needed for laboratory analysis of filter samples often require sampling for several hours or days. Off-line time integrating bulk measurements are often subjected to positive and negative sampling artifacts, such as loss of compounds due to volatilization, gas phase adsorption and reactions during collection that can alter the sample (Turpin et al., 2000). Thus, uncertainties exist as to how representative these samples are for the atmospheric aerosol composition. In a recent study another type of aerosol collector (Thermal Desorption Aerosol GC/MS-FID (TAG)) with 1 h time resolution has been presented by Williams et al. (2006). The TAG system collects aerosols, including both gas and particle phase of the aerosols, on an impaction surface which are subsequently thermally desorbed and analyzed using GC-MS detector.

The types of sampling described before have limitations regarding the spatial and temporal sampling densities. Therefore today an important focus lies on the on-line
measurements of aerosol chemical composition in real time with high time resolution. Two main types of online techniques are widely used, the aerosol mass spectrometer (AMS) and the particle-into-liquid sampling (PILS). For a complete overview the reader is referred to a number of reviews published in the last years (McMurry, 2000; Rudich et al., 2007; Canagaratna et al., 2007; Hallquist et al., 2009).

2 Instrumental description

Within the present work a new technique for online compound specific measurements was developed: the Aerosol Collection Module (ACM). The ACM is designed to sample atmospheric aerosol and transfer the evaporated particle sample to a gas phase detector. In practice, collection is achieved in a high vacuum environment on a cooled collection surface. Subsequently the particles are thermally desorbed by heating the collection surface. The evaporated particles are transferred by a carrier gas through a transfer section and injected into a gas phase detector. Therefore, in difference to similar techniques such as the TAG instrument by Williams et al. (2006), only the particle phase of the aerosols can be analyzed without interference of the gas phase constituents. A schematic of the ACM is shown in Fig. 1. The ACM consists of three main sections: a particle focusing section, a particle collection section and a transfer section. Each section of the ACM is described in detail in the following.

2.1 Particle sampling

The sample introduction system and the vacuum system are of a similar design as for the Aerodyne aerosol mass spectrometer (AMS) (Jayne et al., 2000) and are only briefly summarized here. The particle focusing section consists of two parts, an aerodynamic lens system (Liu et al., 1995a,b) which is coupled to a vacuum system. Aerosols are sampled through a critical orifice with a diameter of 100 µm into an aerodynamic lens. Due to the critical orifice mounted at the aerosol inlet the pressure inside the
lens is fixed approximately at 2.6 hPa. Inside the lens the particles are focused into a narrow beam while gas phase species are removed from the sample volume. The particle transmission efficiency for particles in the size range between 50 and 500 nm in diameter is 100% (Liu et al., 2007). The vacuum system consists of three differentially pumped vacuum chambers. Turbo pump 1 and 2 are separated by a skimmer and turbo pump 2 and 3 are separated by a 0.125” × 0.8” channel aperture. A turbomolecular pump (Varian Turbo-V 301 Navigator Pump) is used to evacuate the first vacuum chamber. The pressure in this chamber is maintained below 10⁻³ hPa which ensures a constant flow through the aerodynamic lens. The second and third vacuum chamber is pumped with two Varian Turbo-V 81 Pumps and is maintained at a pressure below 10⁻⁵ hPa. The vacuum system can be separated from the collector with an automated controlled vacuum isolation valve.

2.2 Particle collection

The particle collection system of the ACM consists of a collector and a cooling/heating system. The collector is a 316 stainless steel tubing with an inner diameter of 5.3 mm and a length of 80.8 mm. After 43 mm the tubing tapers for 7 mm and ends at the collection surface which is approximately 3.4 mm in diameter. The particle focusing system is aligned in such a way that the focused particle beam passing the vacuum isolation valve is directed to the center of the sampling surface. The collector is chemically passivated with a Silcosteel® coating (SilcoTek, Bellefonte, PA). During sampling the collector can be cooled with nitrogen from a liquid nitrogen source. The cold nitrogen is sprayed towards the collector. The amount of cold nitrogen can be controlled through an automated solenoid valve. Hence the collection temperature can be kept constant during sampling with a maximum deviation of ±5 °C from the set temperature. To ensure that the deviation of the collection temperature of ±5 °C due to the switching of the solenoid valve doesn’t effect the collection efficiency of the ACM a subzero collection temperature was chosen for all experiment presented in this study. On the back of the collector is a bore hole which holds a cartridge heater. The tip of the heater is centered
6.6 mm behind the collection surface and due to its position rapid heating and evaporation of the collected particle sample are assured. Two additional 1/16” tubings are connected to the collection section which are chemically passivated with Silcosteel® (SilcoTek, Bellefonte, PA). The first tube is located between the vacuum isolation valve and the collection surface. It introduces a carrier gas into the collector. The second tube is located directly below the sampling surface and connects the collector with the transfer section.

2.3 Particle transfer

The valve system used for sample transfer consist of two 4 port valves with 1/16” fittings and 0.75 mm ports (Valco Instruments Company Inc., Houston, TX) which are controlled by a microelectric actuator. A schematic of the valve system is shown in Fig. 2. The valves are connected with the collector and among each other with 1/16” stainless steel tubings. The transfer line is a 60 cm 1/16” tubing which is connected to the valve system at port 4 of valve 2. The valve system and the transfer line can both be heated and kept at constant temperatures up to 300 °C. Both valves and the transfer line are chemically passivated with an Inertium® coating. The 1/16” tubings are passivated with Silcosteel®. In every experiment and set up presented here the carrier gas is helium 6.0. The helium flow is pressure regulated at the entrance to the ACM and held constant at 2400 hPa. The valve settings for standby/backflush mode are shown in Fig. 2a. The carrier gas enters the ACM and is split into two streams. In standby mode stream one flows through valve 1 to the detector. Independent of the valve settings the detector was constantly provided with helium. The second stream flows through valve 2 into the collector, flushes over the collection surface, leaves the collector, passes through the two valves and leaves the system through a vent. A measurement cycle is started by cooling the collector with liquid nitrogen and keeping the collector at the desired collection temperature during the particle collection. As soon as the collector reaches the collection temperature valve 2 is switched. Thereby the collector is separated from the carrier gas. The entrance and the exit of the 1/16” tubing
of the collector are now connected into a loop (Fig. 2b). The vacuum isolation valve opens and the collector and the loop are evacuated. The particle beam is directed to the collection surface where the particles impact upon. After the sampling is completed the vacuum isolation valve closes and valve 1 is switched (Fig. 2c). The carrier gas is introduced again into the collector. The cartridge heater is heated and the particle sample is desorbed from the collection surface. The carrier gas flushes the evaporated particles through valve 1 into the transfer line and to the detector. After the desorption is completed valves 1 and 2 are switched back to their initial positions. The ACM enters the cleaning mode called backflush mode. The cartridge heater remains active and as a general rule is set in this stage to a higher temperature than the desorption temperature previously applied. Due to the higher temperature of the collector and therefore of the collection surface any residuals of the sampling are now desorbed and flushed out of the system through the vent passing both valves. This cleaning of the collector is performed after each measurement. The duration of the backflush mode can be set to meet the actual requirements regarding possible remaining contaminations. After the cleaning is completed the cartridge heater is powered down and the ACM is again in standby and ready for the next cycle.

### 2.4 Detector

The ACM is coupled to a detector where a direct online analysis of the collected gasified particle can be conducted. It is possible to couple the ACM with different types of analytic gas detectors and thereby address different scientific questions without changing the type of sampling. The type of detector can be chosen in regard to the specific analytical abilities of the detectors, for example the chemical speciation of a sample using a gas chromatograph (GC) coupled with a mass spectrometer (MS) or the soft ionization capability of a proton transfer reaction mass spectrometer (PTR-MS). In this study the ACM was coupled with a combination of a gas chromatograph (Fisions GC8060) and a quadrupole mass spectrometer (Fisions MD800) operating with 70 eV electron impact (EI) ionization. The GC-MS system consists of a cryofocusing module (Tekmar 3000)
and an additional flame ionization detector (FID). An Agilent J&W DB-5ms capillary column with 0.25 mm inner diameter, a film thickness of 0.25 µm and a length of 60 m is installed in the gas chromatograph. The coupling of the GC to the transfer line of the ACM was accomplished using a 1/16” Swagelok connector. The cool down of the cryofocusing module (CFM) is started and reaches its final temperature during the ACM sampling. The particle sample desorbed from the ACM is refocused at the beginning of the GC column. One minute after desorption is completed the CFM is rapidly heated and the sample is injected into the GC for chromatographic separation. Compounds eluted from the column are split with a Y-splitter with a constant split ratio of 1:1 to be detected simultaneously with the FID and the MS.

3 Instrumental evaluation: methods

In the following the methods used to characterize the ACM are presented. The performance of the GC-MS system was determined by direct injection of different compounds into the detector. Also the collection, desorption and transfer efficiency of octadecane test particles of the complete ACM-GC-MS system was evaluated. Reproducibility and recovery rate of the collected particles were determined.

3.1 GC-MS detector calibration

The GC-MS system was calibrated with a homologous series of 14 alkanes from n-Heptane (C_7H_{16}) to n-Eicosane (C_{20}H_{42}), nopinone (C_9H_{14}O, NIST identifier: Bicyclo[3,1,1]heptan-2-one, 6,6-dimethyl-) and acetone. The substances were directly injected into the GC-MS using a 0.5 µl syringe.

3.2 ACM particle collection, desorption and transfer efficiency

In Fig. 3 the experimental setup for producing and measuring octadecane aerosols with the ACM is shown. Aerosols were generated with a TSI constant output aerosol...
generator (TSI 3076) from a solution of 0.5 g octadecane solved in 100 ml ethanol. The aerosols were transferred to a delay tube and dried in an activated carbon drier. Thereafter the aerosols were size selected with a Differential Mobility Analyzer (DMA). The DMA voltage was kept constant so that only particles with a particle diameter of 250 nm were selected. After the size selection the aerosol flow was split to be characterized simultaneously with the ACM-GC-MS and the SMPS (TSI 3934). The time resolution, i.e. one complete scan of the size distribution of the SMPS, was 3 min. The sampling of the ACM was stopped matching the end of a completed scan of the SMPS. For all experiments the collection temperature of the ACM collector was –30 ± 5°C. However the desorption temperature was varied between 150 °C and 270 °C during these experiments to evaluate the temperature dependence of the desorption efficiency of particles from the collector. The temperature of the valve array and the transfer line were always matched with the desorption temperature. The desorption time, i.e. the time the collector was heated and the valve array was in the inject mode, was kept constant at 6 min. The desorbed particles were then concentrated again in the cryofocusing module (CFM) at –120 °C for one more minute after the desorption was completed. Then the CFM was heated in 2 min to a temperature of 220 °C and the sample was injected into the GC-MS for analysis. The GC program for this measurement was: oven temperature held at 50 °C for 5 min; ramped at a rate of 10 °C min⁻¹ to 220 °C; isothermal hold at 220 °C for 8 min.

4 Instrumental evaluation: results

4.1 GC-MS detector calibration

Calibration results for the acetone, nopinone and octadecane are summarized in Table 1. Octadecane is presented as an example for the alkanes because this compound was used further on in the characterization of the ACM-GC-MS system. For all compounds excellent linear responses with $R^2 > 0.93$ were obtained. The direct injection
measurements are also used to verify the capability of the identification of compounds with the quadrupole mass spectrometer. The obtained mass spectra for each compound were compared with the EI spectra of the NIST library database. The comparisons achieve good results and the automatic search and compare algorithm of the MS data acquisition software (Masslab 1.4) identified all compounds with a high probability.

4.2 ACM particle collection, desorption and transfer efficiency

A series of experiments was performed using different sampling times to vary the mass loadings on the ACM collector. The collector loading was calculated using the SMPS distribution. The SMPS number distribution was converted into the volume of the particles. The total volume distribution was derived by integrating each SMPS scan. Since the entire SMPS distribution was used for the calculation of the ACM collector loading the contribution of doubly charged particles was accounted for. Due to the low vapor pressure of octadecane (0.025 Pa at 20°C) it can be assumed that no vaporization losses occurred during the sampling of the octadecane particles. The mass introduced into the ACM was calculated using the following equation:

\[
M_{ACM} = \overline{C_{V_{SMPS}}} \times 10^{-21} \cdot \rho_{C_{18}H_{38}} \cdot f_{ACM} \cdot t_s
\]

where \(M_{ACM}\) is the ACM collector mass loading (µg), \(\overline{C_{V_{SMPS}}}\) the average total particle volume concentration (nm\(^3\) cm\(^{-3}\)), \(\rho_{C_{18}H_{38}}\) the density of octadecane (0.777 g cm\(^{-3}\)), \(f_{ACM}\) the sampling flow into the ACM (1.42 cm\(^3\) s\(^{-1}\)), \(t_s\) the sampling time (s) and \(10^{-21}\) a conversion factor. Note that no impurities or artifacts could be observed in the GC-FID-MS chromatogram for all octadecane particle measurements. The peaks of all octadecane samples measured with the ACM-GC-MS were integrated and the peak areas were converted into octadecane mass using the calibration of the GC-MS measurements. Figure 4 shows the mass measured with the GC-FID versus the calculated mass loading from the SMPS data. The linear fit to the data shows that the slope is one. The recovery rate for octadecane is 100%. Possible losses of octadecane at all
temperatures over the complete pathway of the ACM system were found to be minimal. Additionally the desorption temperature was changed between 150 °C and 270 °C (numbers at each data point). The temperature of the valve array and the transfer line were changed accordingly to match the desorption temperature. Within this temperature range the octadecane is completely desorbed from the collector and transferred without losses to the GC-MS detector. Additionally no thermal degradation, impurities or artifacts resulting from the sampling or desorption of octadecane could be observed. It could be demonstrated that the ACM-GC-MS is linear over a mass range of 10 to 100 ng. The experiments with octadecane represent ideal performance since this compound is easily vaporized and has little thermal degradation. More complex and highly oxidized compounds may not yield transfer efficiencies as has been measured with octadecane.

5 Secondary organic aerosol formation from β-pinene ozonolysis

The ACM-GC-MS was applied to measure secondary organic aerosol (SOA) from the oxidation of β-pinene with ozone in an atmosphere simulation chamber experiment. The SOA was measured and analyzed using SMPS, ACM-GC-MS measurements and filter samples.

5.1 Description of the aerosol chamber of the FZJ

The aerosol chamber of the Forschungszentrum Jülich (FZJ) was used for experiments characterizing SOA with the ACM-GC-MS system and filter samples. The aerosol chamber has been described in detail elsewhere (Mentel and Wahner, 1996). Briefly, the aerosol chamber consists of an aluminium box. The inner walls are lined with chemically inert Fluorinated Ethylene Propylene (FEP) teflon foil. The FEP foil is permeable for gas and the interspace between the aluminium box and the foil is constantly flushed with pure synthetic air (Linde® 6.0) to avoid contamination of the chamber. The
chamber has a volume of 260 m$^3$ and a surface of 250 m$^2$. Thus the chamber has a surface to volume ratio of 0.96 m$^2$ m$^{-3}$. A small surface to volume ratio (<1) minimizes potential wall loss such as deposition of aerosols or trace gases.

Homogenous mixing inside the chamber is achieved by convection. This is provided by a floor heating system which temperature periodically changed in the range of 30 $^\circ$C±4 $^\circ$C over the duration of 2 h. Thus the mixing time inside the chamber is less than 10 min and the change of the gas temperature inside the chamber is approximately 0.25 $^\circ$C.

5.2 Experimental conditions and procedure

In the aerosol chamber experiment the formation of secondary organic aerosol (SOA) from the oxidation of $\beta$-pinene with ozone was studied. The experiment was conducted at ambient pressure and temperature. Prior to the experiment the chamber was flushed with particle free outside air for 16.5 h. The air flow through the chamber during flushing was 25 m$^3$ h$^{-1}$. The humidity of the chamber was determined through the humidity of the outside air used for flushing the chamber. No additional humidification was applied. The initial conditions inside the chamber after flushing were 27% relative humidity, a temperature of 20 $^\circ$C, and an ozone concentration of approximately 20 ppb. CPC measurements were used to check if the aerosol chamber was particle free. The particle concentration was <20 cm$^{-3}$.

Pure $\beta$-pinene (Aldrich, purity of 99%) was introduced into the chamber as a liquid with a microliter syringe. 1 mL of $\beta$-pinene, which is equivalent to 584 ppbv, was injected in 10 steps through an opening in the chamber wall approximately 4 m above the chamber floor. After the content of the chamber was well mixed 1 ppm ozone was injected. The ozone was generated from pure oxygen (Linde, 4.8) through electrical discharges and introduced into the chamber with two inlets, one near a wall and the other at the center of the chamber.

Note that the initial monoterpene and ozone concentrations are orders of magnitude
above ambient levels (Guenther et al., 1995; Kesselmeier and Staudt, 1999). The hydroxyl radical chemistry occurring in the chamber is largely independent of the concentration regarding the chemical mechanism and the products formed (Atkinson, 1997). However, the high concentrations do have an influence on the relative importance of competing reactions of organic species with ozone, OH and NO\textsubscript{x}. Hence the observed yields for products formed in this experiment not necessarily represent ambient yields. In this experiment no scavenger was used so that the oxidation of the precursor and to some extend of the products was due to ozone and OH radicals (Atkinson and Arey, 2003).

The high concentrations of the gas phase precursors were chosen in order to ensure sufficient aerosol mass for the experiment. An excess of ozone was used to ensure that all of the $\beta$-pinene is consumed during the experiment. SOA composition was studied for 57 h in that experiment.

The particle number concentration was measured with a CPC (TSI, 3687) with lower cut off size of 3 nm. The flow of the CPC was 600 mL min\textsuperscript{-1}. The CPC was measuring continuously during the experiment.

The particle size distribution was measured with a SMPS system (TSI 3934). The time resolution of the SMPS system was set to 3 min. The SMPS was measuring the particle diameters between 14 nm and 750 nm. The sample flow of the SMPS system was 300 mL min\textsuperscript{-1}. The SMPS was connected to the ACM with a Y-splitter. The Y-splitter itself was connected to the chamber with a 1 m stainless steel sampling line.

During the experiment aerosol samples were taken regularly with the ACM-GC-MS system. The collection time for each sample was 60 min. The collection temperature of the collector was $-30^\circ$C and the desorption temperature 225$^\circ$C. The particle sample was desorbed for 6 min from the collector. The temperature of the valve array and the transfer line were kept constant at 230$^\circ$C. The gasified particles were focused after desorption in the CFM for 1 min at $-120^\circ$C and injected into the GC-MS at 225$^\circ$C. The temperature program of the GC oven for each sample was as follows: start oven temperature was held at 40$^\circ$C for 5 min; ramped at a rate of 5$^\circ$C min\textsuperscript{-1} to 200$^\circ$C;
isothermal hold at 200 °C for 12 min. The total GC run was 54 min. With the desorption time of 6 min the total ACM-GC-MS measuring cycle was 60 min. After each desorption the ACM was operated in the backflush mode with a temperature of 250 °C for 10 min.

During the experiments aerosol filter samples were taken in parallel to the ACM-GC-MS sampling. The aerosols were sampled on quartz fiber filters (Millipore, 47 mm diameter). The filters were preheated for 10 h at 600 °C before sampling. The filter holders were connected to the chamber with a 1 m long stainless steel tubing. The sampling line of the filters was situated 3 m away from the ACM-GC-MS sampling line. The flow through the filter was 25 l min⁻¹ and was regulated with a mass flow controller (MKS Instruments, Type 579). After sampling the filters were stored in a 55 mm Petri dish, wrapped in aluminium foil, and stored in a freezer at –18 °C for later analysis.

In total 16 ACM-GC-MS measurements with a 60 min sampling interval were taken over a time period of 57 h after starting SOA formation. Details of the ACM-GC-MS and filter measurements are shown in Table 2. Prior to the injection of β-pinene a filter and ACM-GC-MS sample were taken from the empty chamber. ACM-GC-MS blank measurements were conducted regularly between the chamber samples. For the blank measurement a High Efficiency Particulate Airfilter (HEPA) was installed between the chamber sampling tubing and the ACM-GC-MS inlet. The same measurement cycle of the ACM-GC-MS was repeated with the installed filter. The blank measurement were used to check for contaminations or residues inside the ACM-GC-MS and for adsorptions from the gas phase onto the collector.

### 5.3 Results of the ACM-GC-MS measurements

Figure 5 shows the first sample (S2) measured with the ACM after the reaction in the chamber was started. The sample was taken 78 min after ozone injection. The FID chromatogram shows a variety of compounds. The majority of peaks are observed between 3 to 8 min and 15 to 33 min retention time. Two peaks, at 3.44 min and 25.3 min respectively, are the major products dominating the aerosol signal at this early stage in the reaction.
For the identification of the chromatographically separated compounds two approaches were used. The first approach was to identify the peaks by comparison of the mass spectra measured with the MS with the content of the NIST database. The two major peaks in the chromatogram could be reliably identified as acetone (3.54 min retention time) and nopinone (25.34 min retention time). The identification of both peaks was also verified by comparison of the mass spectra with the spectra obtained for the calibration of the GC-MS detector.

Nopinone had been previously identified as a major product of the β-pinene ozonolysis (Grosjean et al., 1993; Hakola et al., 1994) in the gas phase (Lee et al., 2006; Winterhalter et al., 2000) and also in the particle phase (Yokouchi and Ambe, 1985; Jaoui and Kamens, 2003a). Also acetone was found as a major product formed in the reaction of β-pinene with ozone (Orlando et al., 2000; Larsen et al., 2001; Wisthaler et al., 2001; Jaoui and Kamens, 2003b). However the acetone in these studies was only measured in the gas phase not in the particle phase. It is unlikely that the acetone partitions from the gas phase into the SOA due to its high vapor pressure. Investigations of the β-pinene SOA with thermal desorption system coupled to a gas chromatograph isotope ratio mass spectrometer (GC-IRMS) show that the acetone found in these studies is a thermal decomposition product of SOA compounds (Fisseha et al., 2009). Based on the δ^{13}C of the acetone Fisseha et al. (2009) conclude that the acetone may be a tracer for higher order oxygenated products or oligomers. Since the samples collected with the ACM were evaporated from the collector at 225 °C it is reasonable to assume that the acetone measured with the ACM-GC-MS is due to a thermal breakdown of higher molecular compounds.

Comparing our results to literature data on the composition of β-pinene SOA formed through both O_3 and OH oxidation we additionally assigned the following substances to peaks in the chromatogram: bicyclo[3,1,1]hept-3-ene-2-one, bicyclo[3,1,1]heptane-2-carboxaldehyde (also known as myrtanal), myrtenol, 1-hydroxinopinone, 3-oxonopinone (also known as 3-oxo-pina ketone) and 3,7-dihydroxynopinone. In Table 3 the structure, molecular weight, the major ion fragments, and the retention time
of these compounds are summarized. To strengthen the identification of myrtenol and myrtanal the retention index (RI) of each compound was calculated and compared to literature data. The linear retention index for the identified compounds were calculated and are summarized in Table 4. The linear retention index for myrtanal and myrtenol reported in the literature correspond well with the index determined in this work. In previous studies myrtenol was only detected in the gas phase. In this work the presence of myrtenol was measured for the first time also in the particle phase. However further studies of the vapor pressure and the partitioning of myrtenol are necessary to clarify if the presence of myrtenol in the particle phase is due to gas-particle-partitioning in the chamber.

5.4 Total mass measured by ACM-GC-MS

In Fig. 6 the total mass measured for each sample with the ACM-GC-MS was normalized to the collector mass loading derived from the SMPS measurements. The collector mass loading was determined using Eq. (1). Note that an average density of 1.2 g cm$^{-3}$ was used for the SOA. The mass fraction measured with the ACM-GC-MS was 11% at the beginning of the experiment and decreased during the first day to 6% and was nearly constant for the next two days. In part the low (6–11%) recovery of SOA mass with the ACM-GC-MS can be explained by the known compound detection limitations of the GC-MS system for higher oxygenated products which are also produced in the $\beta$-pinene ozonolysis. Furthermore the GC-MS technique is limited with regard to measuring high molecular weight compounds. The evidence for oligomer formation in SOA from the photooxidation and ozonolysis of $\alpha$-pinene were measured during different smog chamber studies (Gao et al., 2004; Baltensperger et al., 2005; Müller et al., 2008). Baltensperger et al. (2005) additionally found increasing abundances of high molecular weight compounds (up to 1000 Da) with increasing aging time of the SOA. They also estimated that after 20 h of aging about 50% of the particle mass consisted of oligomers. Under the assumption that in the $\beta$-pinene ozonolysis also oligomerization occurred these high molecular compounds in the SOA would not have been detected.
by the GC-MS system.

As an example also the time series of the fractional abundances of nopinone (green triangles) and 1-hydroxynopinone (red squares) is shown in Fig. 6. While the relative abundances of nopinone decreased continuously over the course of the experiment the relative abundances of 1-hydroxynopinone increased steadily. This shows that the ACM-GC-MS system is also capable of studying changes in aerosol composition.

### 5.5 Intercomparison of ACM-GC-MS and filter samples

During the chamber experiment filter samples were taken in parallel to the ACM measurements. All filter samples were taken using a front and a back quartz filter. All front and back filter samples were analyzed using a Agilent 6890 (1530A) Gas Chromatograph equipped with a Rtx-1 (105 m × 0.32 mm ID, film thickness 3 µm) (Restek Corporation, Bad Homburg, Germany) fused silica column and a flame ionization detector (FID). The GC was connected to a custom built cryosampling thermal desorption system (GERSTEL GmbH & Co. KG, Mülheim an der Ruhr, Germany) for the preconcentration of VOCs. The setup and its use for filter analysis are described in detail by Iannone et al. (2007) and Fisseha et al. (2009). Note that the temperature of the thermal desorption system was set to 225°C, according to the desorption temperature of the ACM collector. The total amount of nopinone in the SOA sampled with the filters was determined. In Fig. 7 the total nopinone mass measured with the filter samples is compared to the total nopinone mass measured with the ACM-GC-MS. The total nopinone mass measured on the filters was corrected for back filters (BF), particle volume distribution (PVD) and nopinone distribution (ND) on the filter. The BF correction accounts for nopinone gas phase adsorption on the filters. The PVD correction is due to the different size ranges of the particles collected with ACM and filters. During the β-pinene ozonolysis experiment the particles grew such that a significant fraction of the particles had a diameter larger than 500 nm when lens transmission becomes a limiting factor of mass transfer into the ACM. The particles with diameter larger than 500 nm contribute to the total nopinone mass collected with the filters only. Therefore,
the filter nopinone mass corresponding to particles <500 nm was determined by using the SMPS data. Assuming an aerosol composition independent of size, the filter results were thus corrected for the overestimated nopinone mass. For the filter analysis described in detail by Fisseha et al. (2009) 3 mm circular piece were midmost cut out from the whole filter. The total amount of sampled nopinone was derived considering the same concentration on the whole filter. However the distribution of collected particles on the filters is not homogeneous. Profiles of the nopinone concentration on the filters were determined and showed higher values in the center decreasing to the edges of the sampling area. A ND correction owing to the inhomogeneity of particle loading across the filter was done accounting for the overestimated nopinone concentration on the cut out filter piece. In Fig. 7 the total nopinone mass after all above mentioned corrections were applied is represented by the green squares. The amount of nopinone measured with both methods follows a similar temporal trend. The nopinone concentration is highest at the beginning of the experiment and drop continuously over the course of the experiment due to nopinone gas phase loss and aerosol loss in the chamber. Within the margin of error the corrected nopinone mass measured with the filter samples agrees reasonably well with the nopinone mass measured with ACM-GC-MS system during the whole experiment. The agreement of both measurements improves on the second and third day when it can be assumed that the system is in steady state with the chamber walls. Note that on the first day the correction for the gas phase adsorption on the filter is the highest and has therefore a higher uncertainty than on the second and third day.

5.6 Ambient aerosol measurement with the ACM-GC-MS

The first ambient air measurements with the ACM-GC-MS were conducted at the Aerodyne Research, Inc. laboratory in Billerica, MA. The ACM-GC-MS was connected to a sampling line through which ambient atmospheric aerosol could be collected from the roof of the laboratory. In addition an Aerodyne Aerosol Mass Spectrometer (AMS) was measuring in parallel to the ACM-GC-MS sampling from the same sampling line.
Particle samples were taken regularly over the course of several days with the ACM-GC-MS system. The collection time for each sample was 6 h. The collection temperature was −30 °C. Afterwards the collected particles were desorbed at a temperature of 260 °C for 6 min. In total 15 samples were taken over the course of the experiment. An example chromatogram from one of the air samples is shown in Fig. 8. Peaks for individual compounds lie on top of a broad background of unresolved complex mixtures which is indicative of hydrocarbon-like organic aerosol (HOA). Similar chromatograms from urban samplings were also observed by Williams et al. (2006) with the Thermal Desorption Aerosol GC/MS-FID (TAG) system. The blue trace in Fig. 8 shows a typical blank measurement of the ACM-GC-MS which were taken regularly between the ambient air sampling. The blanks were performed with particle-free filtered ambient air entering the ACM.

As a first analysis the ACM-GC-MS total signal measured for the ambient aerosol particle samples was compared to the total organic mass measured with the AMS. The ACM-GC-MS signal was calculated by integrating the total area under the chromatogram. Figure 9 shows the comparison of the ACM-GC-MS signal to the total organic mass measured with the AMS during the same time period. The mass loadings measured with the AMS varied between 10 and 300 µg m⁻³. The correlation between the two sets of data is linear with a high correlation coefficient, indicating that the ACM-GC-MS is capable of linear, quantitative measurements of ambient aerosol mass loadings.

6 Conclusions

A new technique for online compound specific measurements of organic aerosol was developed. The Aerosol Collection Module (ACM) samples, collects and transfers atmospheric aerosol particles to a gas phase detector. Particles are efficiently sampled in the 70–500 nm size range by focusing the particles into a particle beam which passes a vacuum chamber and impacts onto a cooled collection surface. The sampling in a high
vacuum environment allows to study only the particle phase of the aerosols without interference of the gas phase constituents. The organic compounds are then efficiently transferred via thermal desorption into a coupled gas phase detector.

The ACM coupled to a GC-MS (ACM-GC-MS) was used to determine important instrumental characteristics of the ACM. The particle collection, desorption and transfer efficiency of laboratory generated octadecane test aerosols were determined. The total octadecane mass provided for sampling with the ACM-GC-MS was determined with a SMPS measuring in parallel to the ACM-GC-MS. The octadecane particles were collected, desorbed and transferred with an efficiency of 100%. The recovery rate of 100% was confirmed for an interval of desorption and valve array temperatures ranging from 150°C to 270°C. For both characterization experiments the ACM-GC-MS was linear in response to the measured octadecane mass.

The new sampling and characterization technique of the ACM-GC-MS was also used in its first application in a study of the formation of SOA from the ozone oxidation of β-pinene in the Jülich aerosol chamber. During the β-pinene ozonolysis experiment 16 SOA samples over the duration of 57 h were successfully taken and measured with the ACM-GC-MS. Using the ACM-GC-MS several products of the β-pinene ozonolysis could be identified in the particle phase. These compounds were bicyclo[3,1,1]hept-3-ene-2-one, nopinone, myrtanal, myrtenol, 1-hydroxynopinone, 3-oxonopinone, and 3,7-dihydroxynopinone. The presence of myrtenol was observed for the first time also in the particle phase.

Comparison of the total nopinone mass between filter samples and the ACM-GC-MS show a good agreement. The ACM-GC-MS system efficiently collects particles in the size range of 70–500 nm and transfers organic compounds via thermal desorption into a gas phase detector with quantitatively reproducible results.

The first ambient atmospheric aerosol measurement indicates that the ACM-GC-MS system is also capable of linear, quantitative measurements of ambient aerosol mass loadings.

In future works the analytical potential of the ACM will be further explored by cou-
pling the ACM to PTR-MS and GC-IRMS detectors. These set-up will be utilized in chamber and field studies to determine aerosol sources, aerosol transformations, and the identification of organic marker compounds in ambient atmospheric aerosols. Due to its low sampling flow the ACM is especially suited for chamber studies where the sampling volume is limited and high volume collectors can not be used.

Further technical improvements of the ACM including an online derivatization system in the collection section and the aerosol enrichment of the sampling volume using a virtual impactor in front of the ACM inlet will be explored.

**Acknowledgements.** We thank Paul Ziemann and Brent Williams for discussions and helpful suggestions concerning coating materials. Aerodyne and MIT would also like to thank the US EPA (grant number RD-83107701-0) and the US DoE (grant number DE-FG02-05ER84269) for initial instrument development support.

**References**


Jaoui, M. and Kamens, R. M.: Gaseous and particulate oxidation products analysis of a mixture


Mentel, T. and Wahner, A.: A large reaction chamber for nighttime atmospheric chemistry:
Design and characteristics of the reaction chamber, Berichte des Forschungszentrums Jülich GmbH, 3196, 1996. 1371
Yokouchi, Y. and Ambe, Y.: Aerosols formed from the chemical reaction of monoterpenes and ozone, Atmos. Environ., 19(8), 1271–1276, 1985. 1375
Table 1. Fit coefficients of the calibration curves of the direct injection into the GC-MS.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Intercept [pa]a</th>
<th>Slope [pa/ng]a</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>1311 ± 4660</td>
<td>254 ± 54</td>
<td>0.929</td>
</tr>
<tr>
<td>Nopinone</td>
<td>−4354 ± 10 500</td>
<td>629 ± 116</td>
<td>0.955</td>
</tr>
<tr>
<td>Octadecane</td>
<td>−5117 ± 9760</td>
<td>439 ± 35</td>
<td>0.952</td>
</tr>
</tbody>
</table>

a pa = peak area of the GC-MS-FID signal
Table 2. Overview of the course of the $\beta$-pinene experiment and the samples collected with the ACM-GC-MS and filter measurements. $t_{\text{O}_3}$ is the time after ozone was injected into the chamber. $C_{\text{O}_3}$ is the mixing ratio of ozone in the chamber. $M_{\text{SOA}}$ is the total SOA mass inside the chamber. S indicates that a chamber sample is collected with the ACM-GC-MS and in parallel with quartz filters and B indicates that an ACM-GC-MS blank measurement was performed.

<table>
<thead>
<tr>
<th>$t_{\text{O}_3}$ [h]</th>
<th>$C_{\text{O}_3}$ [ppb]</th>
<th>$M_{\text{SOA}}$ [$\mu$m$^{-3}$]</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>-2.12</td>
<td>-</td>
<td>-</td>
<td>chamber blank measurement S1</td>
</tr>
<tr>
<td>-0.93</td>
<td>-</td>
<td>-</td>
<td>injection of 600 ppb $\beta$-pinene</td>
</tr>
<tr>
<td>0</td>
<td>872</td>
<td>0.01</td>
<td>injection of 1 ppm ozone</td>
</tr>
<tr>
<td>1.3</td>
<td>730</td>
<td>650</td>
<td>S2</td>
</tr>
<tr>
<td>3.03</td>
<td>546</td>
<td>870</td>
<td>B1</td>
</tr>
<tr>
<td>4.77</td>
<td>499</td>
<td>827</td>
<td>S3</td>
</tr>
<tr>
<td>6.47</td>
<td>476</td>
<td>821</td>
<td>B2</td>
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<tr>
<td>8.05</td>
<td>465</td>
<td>744</td>
<td>S4</td>
</tr>
<tr>
<td>9.82</td>
<td>449</td>
<td>726</td>
<td>B3</td>
</tr>
<tr>
<td>21.97</td>
<td>390</td>
<td>476</td>
<td>S5</td>
</tr>
<tr>
<td>23.57</td>
<td>385</td>
<td>473</td>
<td>B4</td>
</tr>
<tr>
<td>25.03</td>
<td>382</td>
<td>449</td>
<td>S6</td>
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<tr>
<td>26.55</td>
<td>372</td>
<td>438</td>
<td>S7</td>
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<td>28.12</td>
<td>368</td>
<td>414</td>
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<td>29.72</td>
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<td>391</td>
<td>S9</td>
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<tr>
<td>31.32</td>
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<td>S10</td>
</tr>
<tr>
<td>32.68</td>
<td>346</td>
<td>367</td>
<td>B5</td>
</tr>
<tr>
<td>49.05</td>
<td>307</td>
<td>252</td>
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<td>50.60</td>
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<td>S15</td>
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<td>S16</td>
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<tr>
<td>56.62</td>
<td>282</td>
<td>216</td>
<td>B7</td>
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<tr>
<td>46.03</td>
<td>312</td>
<td>282</td>
<td>S11</td>
</tr>
<tr>
<td>47.52</td>
<td>308</td>
<td>265</td>
<td>B6</td>
</tr>
</tbody>
</table>

$^a$ calculated from the SMPS data using an average SOA density of 1.2 g cm$^{-3}$
Table 3. Retention time, structure, molecular weight, and $m/z$ of the major ion fragments of the identified products in the $\beta$-pinene ozonolysis experiment listed in the order of ascending retention time.

<table>
<thead>
<tr>
<th>Identification</th>
<th>Retention time</th>
<th>Structure</th>
<th>MW (g mol$^{-1}$)</th>
<th>$m/z$ (EI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>acetone</td>
<td>3.44</td>
<td></td>
<td>58</td>
<td>43, 15, 58</td>
</tr>
<tr>
<td>bicyclo[3,1,1]hept-3-ene-2-one</td>
<td>24.59</td>
<td></td>
<td>136</td>
<td>93, 121, 77</td>
</tr>
<tr>
<td>nopinone</td>
<td>25.34</td>
<td></td>
<td>138</td>
<td>83, 95, 55</td>
</tr>
<tr>
<td>myrtanal</td>
<td>26.81</td>
<td></td>
<td>152</td>
<td>69, 82, 41</td>
</tr>
</tbody>
</table>
### Table 3. Continued.

<table>
<thead>
<tr>
<th>Identification</th>
<th>Retention time</th>
<th>Structure</th>
<th>MW (g mol$^{-1}$)</th>
<th>m/z (EI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>myrtenol</td>
<td>27.18</td>
<td><img src="image.png" alt="Structure" /></td>
<td>152</td>
<td>79, 91, 108</td>
</tr>
<tr>
<td>1-hydroxynopinone</td>
<td>28.35</td>
<td><img src="image.png" alt="Structure" /></td>
<td>154</td>
<td>83, 95, 136</td>
</tr>
<tr>
<td>3-oxonopinone</td>
<td>31.35</td>
<td><img src="image.png" alt="Structure" /></td>
<td>152</td>
<td>83, 55, 152</td>
</tr>
<tr>
<td>3,7-dihydroxynopinone</td>
<td>33.33</td>
<td><img src="image.png" alt="Structure" /></td>
<td>170</td>
<td>83, 111, 55</td>
</tr>
</tbody>
</table>
Table 4. Comparison of determined linear retention indices of the identified products with literature values.

<table>
<thead>
<tr>
<th>Compound name</th>
<th>RI this work</th>
<th>RI other studies (type of column)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>myrtanal</td>
<td>1198</td>
<td>1180 (HP-5MS)</td>
<td>Papandreou et al. (2002)</td>
</tr>
<tr>
<td>myrtenol</td>
<td>1209</td>
<td>1202 (DB-5MS)</td>
<td>Kowalski and Wolski (2005)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1214 (DB-5MS)</td>
<td>Wang et al. (2005)</td>
</tr>
</tbody>
</table>
Fig. 1. Schematic of the ACM instrument. The ACM is composed of three main sections: the particle sampling section consisting of the aerodynamic lens and the vacuum system, the particle collection section including the collector and the cooling/heating system and the gasified particle transfer section which contains the valve system and the transfer line.
Fig. 2. (a) Standby/backflush mode: the collector and detector are supplied with the carrier gas. For cleaning purpose the collector can be heated (backflush mode). (b) Sampling mode: the collector is separated from the carrier gas supply and the particle beam is directed to the collection surface where the particle sample is accumulated. During sampling the collector is cooled with liquid nitrogen. (c) Desorption/injection mode: the vacuum isolation valve is closed and the collector heated. The particle sample is desorbed from the collection surface and transferred with the carrier gas stream to the detector.
Fig. 3. Schematic of the experimental setup for measuring octadecane aerosols simultaneously with the ACM and a SMPS. The aerosols are generated with an aerosol generator, dried, size selected and transferred to the two systems.
Fig. 4. Octadecane mass measured with the GC-FID vs. the collector loading (calculated from SMPS measurements) lie on a line through the origin with slope one. Numbers show the different desorption temperatures for each measurement.
Fig. 5. ACM-GC-MS FID chromatograms measured at the beginning of the experiment. The grey vertical bars indicate the retention times of the homologous series of alkanes from the GC-MS calibration which were used to calculate linear retention indices.
Fig. 6. Time series of the fraction of the particle mass detected by the ACM-GC-MS (black circles). Also as an example the time series of the fractional abundances of nopinone (green triangles) and 1-hydroxynopinone (red squares) are shown. Note that the temporal trend for both compounds are different indicating a change in chemical composition of the SOA.
Fig. 7. Comparison between the corrected (see text) total nopinone mass sampled with filters (green squares) and the total nopinone mass measured with the ACM-GC-MS (black circles).
Fig. 8. ACM-GC-MS chromatogram of ambient aerosol particles sampled at the Aerodyne Research, Inc. laboratory in Billerica, MA.
Fig. 9. Comparison of the signal measured with the ACM to organic mass measured with a co-located AMS.

Linear Fit

- intercept: $2.12 \times 10^5 \pm 8.53 \times 10^5$
- slope: $3.54 \times 10^6 \pm 1.66 \times 10^5$
- $R^2 = 0.972$

$3.5 \times 10^7$ 3.0
2.5
2.0
1.5
1.0
0.5
0.0

AMS Organic Mass [µg]

ACM-GC-MS Peak Area [arb. units]