

Responses to Referee #2

A chemical analyzer for charged ultrafine particles

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The review is in general positive. We greatly appreciate Jim Smith's insightful comments that helped improve the manuscript. Thank you very much for your time and effort! We trust that all suggestions have been addressed accordingly in the revised manuscript. We respond to the specific comments as follows:

1: 3861, 5: Nucleated particles can grow by condensation and by coagulation with particles of similar size. Coagulation is especially important when considering the "growth" of the nucleation mode of a size distribution as it seems the authors are describing here.

We agree with the referee. The corresponding sentence has been changed to:

Typically, particle nucleation events begin after sunrise and the nucleated particles grow for several hours to a few days by coagulation and condensation, reaching diameters in the order of 100 nm.

2: 3862, 9: Both here and in the concluding remarks (3872, 5), the authors state that a unique feature of CACHUP has something to do with being "commercially available." In this sentence (pg 3862), it seems that the message is that this instrument is commercially available. Please correct or provide more details about what is meant by this statement. Was the intention here to state that this inlet can be used with a commercially-available ion source and mass spectrometer? Even most custom instruments use commercially-available mass spectrometers.

The indication that no such instrument is commercially available was meant to underline the necessity to develop our instrument. However, the sentence on page 3862 is somewhat misleading and was changed to the following:

Both instruments are custom-built. Considering the scarcity of available instrumentation to measure the molecular composition of sub-30 nm particles, we present the design and first measurement results of an additional aerosol mass spectrometer for this size range.

The sentence on page 3872 was changed to:

We have developed an aerosol mass spectrometer for the chemical analysis of particles with diameters below 30 nm.

3: 3864,20: The extrinsic charging efficiency is the same as the overall charging efficiency if the only flow that enters the charger is the sample flow, and the only flow that exits the charger is the flow containing the charged particles. Please clarify if this is the case for the charger used here. In Fig. 2, I am surprised by the low charging efficiency of this charger. For the unipolar chargers used in the TDCIMS and NAMS, and described in detail in McMurry et al. (2009), charging efficiency was 100% for particles larger than 30 nm.

Our charger is not equipped with a sheath flow, the only flow entering and exiting the charger is the aerosol flow. We used the definition for the extrinsic charging efficiency by (Han et al., 2008), equation (15), which is the number of charged particles exiting the charger divided by the total

number of particles entering the charger. This is, as the referee mentions, the same as the overall charging efficiency.

The charging efficiency of our charger is slightly below that of the original design by Han et al. (2008). Optimizing the number and diameter of the carbon fiber bundles may help to improve the charging efficiency. Other than the charger described by Chen and Pui (1999) and McMurry et al. (2009) our charger is not equipped with an electrostatic field enhancing the charging efficiency.

The corresponding paragraph has been revised:

The extrinsic charging efficiency is defined as the number of charged particles exiting the charger divided by the total number of particles entering the charger. Since no sheath flow is used in our charger the extrinsic charging efficiency is the same as the overall charging efficiency.

4: 3864, 29 (and 3872, 26): *I am not aware of a pre-separator that can operate at atmospheric pressure with a cut-off at 30 nm. Can the authors provide an example of a technique that could be used for this?*

A conventional pre-impactor with a high pressure drop, e.g. a low pressure impactor with a lower cut-off at 50 nm and a pressure drop of 900 hPa, is not recommended due to the potential evaporation of volatile compounds under the reduced pressure conditions of 100 hPa. Therefore, we suggest using a metal fiber filter designed to have a high penetration efficiency in the size range between 5 nm and 50 nm. For example, Otani et al. (2007) report a 50 % cut-off diameter at 50 nm particle diameter for a fiber diameter of 8 μm , a filter length of 8 mm, a filtration nozzle diameter of 4 mm, and a flow velocity of 30 m s^{-1} . This configuration exhibits a pressure drop of about 130 hPa, i.e. the pressure is reduced from 1000 hPa to about 870 hPa. With this relatively small pressure drop, we expect that evaporation of volatile compounds will be negligible in this pre-separator, while particles larger than 50 nm diameter will be efficiently removed.

The corresponding paragraph was extended to:

The perturbing influence of doubly charged particles could be minimized by applying a pre-separator prior to the unipolar charger, preventing particles with diameters above 50 nm to enter the charger. Otani et al. (2007) report of a metal fiber filter having a high penetration efficiency in the size range between 5 nm and 50 nm exhibiting only a small pressure drop of 130 hPa.

5: 3865, top paragraph: *In your discussion of multiple charging, it would be good to reference the 2009 McMurry et al. characterization of their charger (mentioned above), and in particular Fig 2 which quantifies the charge distribution using that technique.*

The paragraph on page 3864, line 27 was extended to:

In fact, under certain experimental conditions we observed considerable double charging of sub-30 nm particles with the unipolar corona charger. This observation is consistent with the size dependent charge distribution of a unipolar charger (Chen and Pui, 1999) shown in McMurry et al. (2009) (Fig. 2).

6: 3865, 25 and Fig 3: *Are the distributions shown in Fig 3 transfer functions for the RDMA's? This would require the use of a TDMA inversion routine (e.g., TDMAFit by Stolzenburg or TDMAinv by Gysel (2009)).*

The curves in Fig. 3 are not transfer functions of the rDMA, but are observed particle distributions selected by our rDMA, measured with an SMPS at the exit of the rDMA to characterize the performance of the instrument. In addition to the measured distributions in Fig. 3 (a) we now show

the calculated theoretical transmission curves (b) for the tandem DMA system. The curves are calculated according to Stolzenburg and McMurry (2008) and Zhang and Flagan (1996) including diffusional broadening.

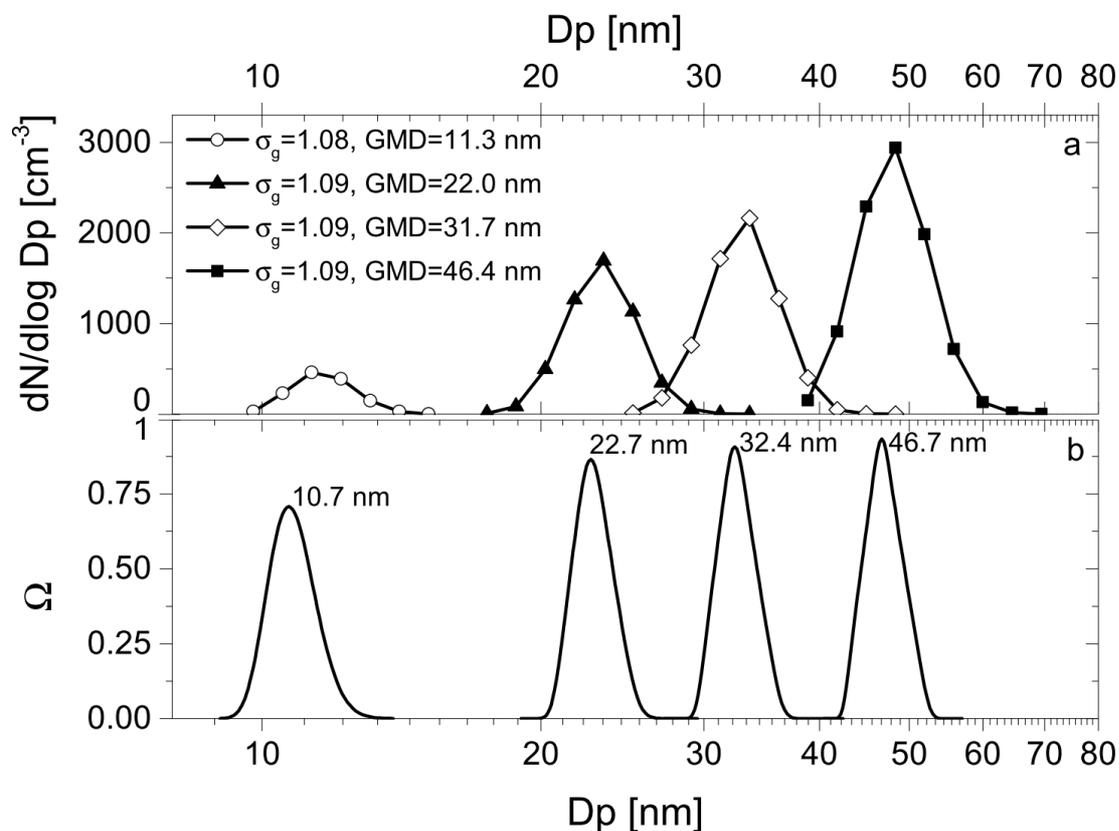


Fig. 3. Comparison of the performance of the rDMA coupled to an SMPS system (a) with theoretical transfer functions (b). A sheath flow of 4 SLM and voltages of 116 V, 504 V, 1003 V and 2000 V resulted in geometric mean diameters measured by an SMPS system of 11.3 nm, 22.0 nm, 31.7 nm and 46.4 nm, respectively. The theoretical transfer functions peak at 10.7 nm, 22.7 nm, 32.4 nm and 46.7 nm, respectively.

The following paragraph was added to page 3866, line 1:

Additionally, the theoretical transfer functions including particle diffusion (Stolzenburg and McMurry (2008), Zhang and Flagan (1996)) for the sequential setup of the rDMA and the cylindrical DMA as described above are shown. The maxima of the calculated transfer functions lie within a maximum deviation of 0.7 nm of the geometric mean diameter calculated from the size distributions of the tandem DMA measurements. Differences between the measured distributions (Fig. 3 a) and the theoretical transfer functions (Fig. 3 b) are thought to be due to additional broadening in the real flow path through the rDMA and the SMPS's cylindrical DMA.

7: 3867, 1: *If the PEEK piston seals against the wall of the desorption region, then what creates the flow that is needed to pull constituent gases through the transfer capillary? Is the mechanism diffusion (that is, a perfect seal)? If that is the case then line 10 should be corrected since it's stated here that the region upstream of the capillary is at atmospheric pressure. Is it possible that there is a small gas leak surrounding the piston that allows gases to enter with the desorbed compounds? If it is the latter, then compounds that partition to and from the walls of the desorption region are likely major contributors to the background spectrum.*

The necessary flow from the desorption chamber towards the MS is due to the pressure difference in both parts (the MS is at about 10^{-6} mbar). The pressure in the desorption chamber is initially at ambient pressure and will drop once the chamber is sealed. Still, the pressure in the chamber remains well above the pressure in the MS during the entire analysis period, ensuring a maintained flow.

Once the PEEK piston is in the desorption position the chamber is assumed to be sealed, which is evident in a pressure drop observed with the MS, even though the flow towards the MS is very small (in the order of a few mL per minute).

The corresponding passage on page 3867, line 10 has been revised to:

The capillary fulfills the tasks of transferring the sample directly to the ionization region in the TOF-MS as well as ensuring the necessary pressure drop from the desorption region to the MS operating at a pressure of less than 1×10^{-6} mbar.

8: *Sections 2.3-2.4: It would be very useful for the reader to understand the exact procedure for analysis of a sample, and how long each step takes. On pg 3870, line 1, it seems that the desorption region is heated to 150C between collection and analysis. It would seem to me that this would require a long waiting period between collection and analysis. 3868, 4: It is important to point out that monoterpenes are precursors to the formation of oxidized organic compounds, which contribute to the growth of particles. This sentence makes it seem as if the monoterpenes themselves are constituents of particles, and I do not believe there is evidence of this in the literature.*

An additional figure has been added to the revised manuscript (Fig. 6) to clarify the exact desorption procedure. As can be seen in Figure 6, heating of the desorption region from 100 °C to 160 °C takes about 3 min and does already desorb a considerable amount of collected material from the filament/chamber walls. The signal from the desorbed material is already decreasing while the filament is still heating up.

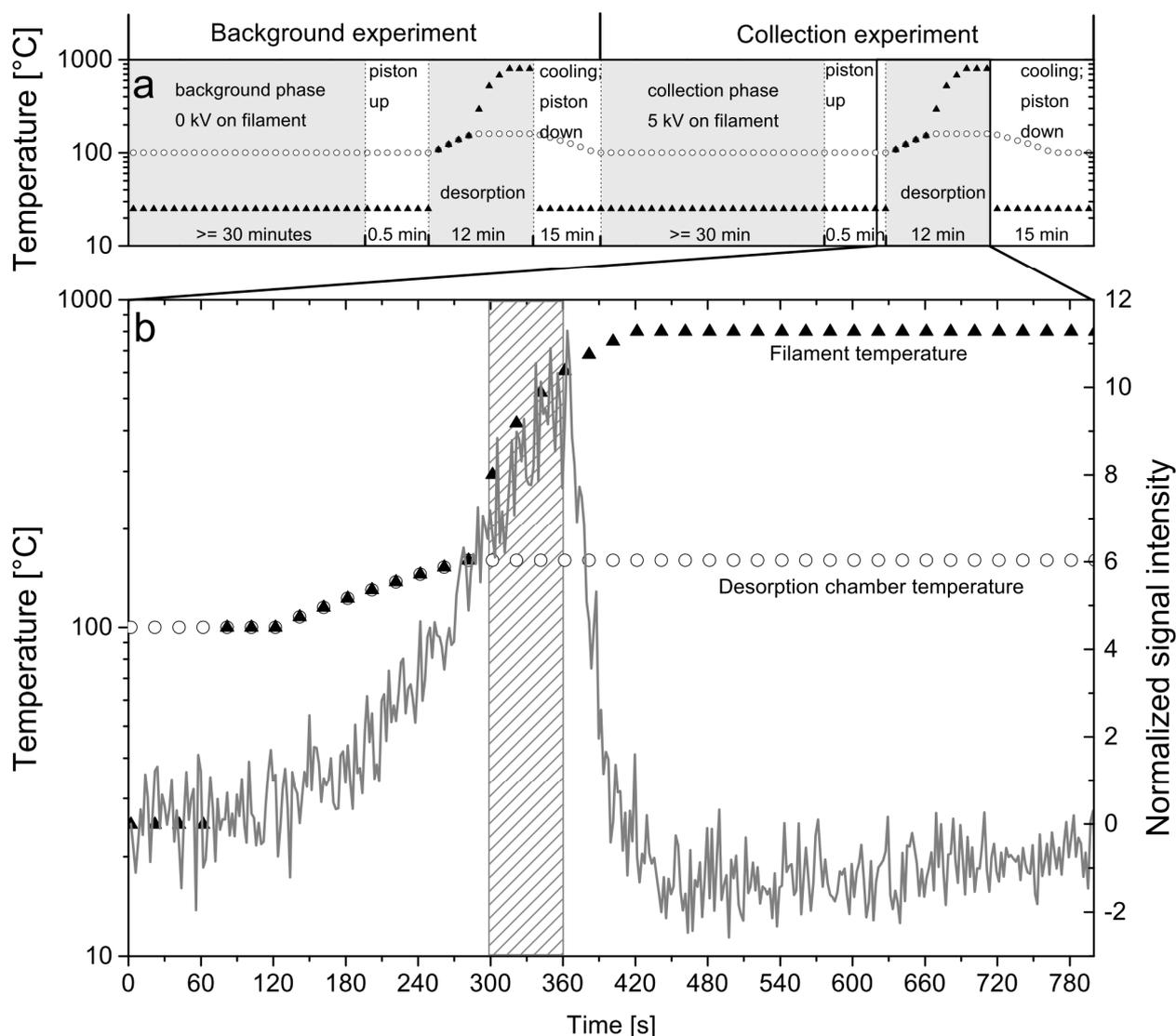


Fig. 6. (a) Sketch of the procedure for the background and collection experiments, with temperature courses of the desorption chamber (white circles) and the NiCr filament (black triangles). (b) Time evolution of the averaged signal from major organic peaks (m/z 43, 53, 65, 67, 77 and 91) during the desorption of oxidized alpha-pinene particles. The PEEK piston was in desorption position at second 60. Temperatures of the desorption chamber and the filament are also shown. The hatched area denotes the one minute averaging period used for the mass spectrum shown in Figure 7 b.

Page 3870, line 1 was changed to:

Once the piston reached its final position, the desorption chamber was heated from 100° C to 160° C.

Page 3868, line 4 was changed to:

Being a monoterpene, camphene ($C_{10}H_{16}$) represents one of the major compound groups with oxidation products contributing to the growth of secondary particles.

9: 3868, 29: *adding a charcoal denuder to the flow between the flow tube and CACHUP will likely modify the composition of particles by decreasing the saturation ratio of ambient gas phase organic compounds. It would seem to me that to use of a "background spectrum acquisition" would allow the subtraction of the contribution of ambient organic vapors. Please explain why the denuder was deemed necessary (rather than subtracting the contribution of these gas-phase organics using a background spectrum acquisition).*

We agree with the referee that the charcoal denuder will alter the configuration of the flow reactor, and thus, the composition of the particles. In particular, the evaporation of volatile species will be enhanced. Additionally, the charcoal denuder effectively reduces the reaction time of alpha-pinene and ozone. This is both consistent with our observation that the particle size slightly decreases when using the denuder compared to the same flow tube configuration without the denuder. However, application of the denuder significantly decreased the MS signal attributed to gas phase species both during sample and background spectrum acquisition. Therefore, subtraction of the background spectrum from the sample spectrum yields less noise and a clearer signal of the desorbed sample. The denuder will not be required in ambient measurements when the organic gas phase contribution to both the sample and the background spectrum will very likely be much smaller.

10: 3870, 20: *In this sentence you compare the mass spectrum obtained using CACHUP to published spectra. What techniques were used to obtain those spectra, and what basis do you have to expect them to be similar?*

In both studies the particle spectra were measured by means of a high resolution time of flight aerosol mass spectrometer (HR-TOF-AMS). Similar to our TOF-MS, the HR-TOF-AMS is also equipped with electron ionization, resulting in comparable fragmentation patterns of the sampled particle compounds. We do not expect our measured spectra to be exactly the same as the ones measured by Chhabra et al. (2010) and Shilling et al. (2009), in particular due to the different particle sizes analyzed. However, the basic molecular fragments from electron ionization are still considered to be comparable.

The corresponding paragraph was extended:

The presented mass spectra are consistent with published studies on laboratory generated particles from ozonolysis of alpha-pinene (e.g. Chhabra et al., 2010; Shilling et al., 2009). In both studies high resolution time of flight aerosol mass spectrometers (HR-TOF-AMS) with electron ionization were used. As CHACHUP is also equipped with electron ionization the general fragmentation patterns are expected to be comparable.

11: 3870, 29: *The statement that the analysis of 25 nm alpha-pinene SOA particles that are collected for periods ranging from 0.5 to 2 hours results in the same observed spectra is in contrast to the main conclusion from Winkler et al. (2012). How do you account for this difference?*

In the work of Winkler et al. (2012) flow tube generated particles from ozonolysis of alpha-pinene were measured with the TDCIMS, using a HR-TOF-MS and a quadrupole mass spectrometer. Both mass spectrometers were equipped with chemical ionization and the sample was analyzed in the positive and negative ion mode. Winkler et al. (2012) found that some of the oxidized compounds in the collected particle sample were volatile. For a comparison of samples collected for different time periods this has to be taken into account since the collection time will have a strong influence on the composition of the sampled compounds due to evaporation of volatile compounds. In particular, this was observed for compounds measured in positive ion mode.

Since we used an activated charcoal denuder downstream of the flow tube, we expect evaporation of the most volatile compounds from the particles prior to collection. Thus, the composition of the particles generated in our flow tube experiments is likely dominated by less volatile compounds. This was also evident from measuring the particle size distribution after the flow tube with and without the denuder. With the denuder, the particle size distribution showed a shift towards smaller particles. Moreover, for the mass spectra presented in the manuscript we did not perform a quantitative analysis of the area for every observed peak individually. Therefore, we did not infer the

dependence of the collection time on the composition of individual compounds in our aerosol sample. Thus, the comparison of the different mass spectra is mostly qualitative.

12: 3871, 4: *It is not clear to me that you addressed the issue of multiply-charged particles in the α -pinene SOA experiments.*

The influence of multiply charged particles was minimized in the flow tube experiments by using a radioactive neutralizer.

To illustrate the negligible influence of doubly charged particles consider the following:

A doubly charged particle with the same electrical mobility as a singly charged 25 nm particle has an approximate diameter of 36 nm. The fraction of singly charged 25 nm particles for a radioactive neutralizer is about 10.5 %, while the fraction of doubly charged 36 nm particles is about 0.2 %. The mass of a 25 nm particle is about 33 % of the mass of a 36 nm particle. Accounting for the charged fractions and the mass differences, the doubly charged 36 nm particles will contribute about 6 % to the collected particle sample.

The corresponding sentence was changed to:

Overall, the collection experiments show good performance of our instrument in flow tube experiments. The collection times can be extended to multi-hour periods and the use of a radioactive neutralizer is reasonable despite its poor charging efficiency, minimizing the contribution of multiply charged particles in the sample.

13: 3871, 7: *It is also important to note that high concentrations of gas phase precursors will create a fundamentally different type of particle compared to ambient levels. This is because higher saturation ratios of organics will drive higher volatility species into aerosols.*

We agree with the referee that much higher than ambient precursor concentrations will make the chemical composition of lab-generated particles different from ambient aerosol. However, the aim of this manuscript is to characterize and evaluate the operation of CACHUP, and in particular its capability to analyze sub-30 nm particles. For an investigation of particles comparable to ambient aerosol, the experimental conditions have to be modified.

This is now clarified in the revised manuscript (page 3871, line 6):

Crucial for such experiments is the ability to produce particle formation events with growth rates similar to the ones observed in the atmosphere. If the growth rates are too high particles of a distinct diameter will not be present for a time period sufficient for collecting the necessary aerosol mass. Therefore, the concentration of gas phase precursors has to be chosen close to ambient concentrations yielding particles with a chemical composition comparable to atmospheric particles.

14: 3873, 15: *It should be pointed out that a major source of the background could also be the desorption region itself. Even though that chamber is heated to 150C, the filament reaches temperatures of up to 800C so there will always be compounds (like ammonium sulfate) that will partition to walls under these conditions and desorb from the walls due to radiative heating from the filament during analysis.*

The desorption region cannot be ruled out as one potential source for the background signal.

The following sentences have been added to page 3870, line 11:

A second reason for performing blank measurements is the condensation of evaporated particle compounds from the filament onto the desorption chamber walls. Even when the desorption region

is heated to 200 °C, condensation of low volatile species cannot be ruled out when the filament is heated up to 800 °C.

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