

Interactive comment on “On-line determination of the chemical composition of single activated cloud condensation nuclei – a first investigation of single urban CCN and CCN obtained from sea water samples” by Carmen Dameto de España et al.

Anonymous Referee #2

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The authors’ comments to the individual points raised by the reviewer are given below in italics and in blue

Dameto de España et al present results of coupling a CCN-VACES to a LAAPTOF in gain information about the chemical composition of individual CCN. I believe this is a worthwhile endeavor to pursue (single-particle mass spectrometry of previously activated particles); however, I agree with the comments of Reviewer 1 about the authors’ claims about their data, especially in considering their experimental design, data checks, and data interpretation with respect to their stated goal and asserted conclusions.

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See our comments to the points raised by reviewer 1

Further experimental and data analysis work are necessary to improve the quality of the work and support the claims made. The analysis of the chemical composition of activated urban CCN and SSA are worthwhile endeavours and likely deserve separate papers themselves focused on the details of the science results obtained, as a detailed investigation of the science is lacking here, with only a cursory examination of the mass spectra is provided. My detailed comments are provided below.

*The current MS is a technical paper to demonstrate the feasibility of our main aim, i.e. that the separation of activated CCN and their chemical analysis can be done, and not a paper on measurement campaigns. The challenge is: **a)** to separate CCN (i.e. particles that can be activated to grow to large droplets under conditions of specific supersaturations) from the non-CCN aerosol, and: **b)** to analyse the chemical composition of the individual CCN. Real world CCN are a subfraction of the atmospheric aerosol and – except for their activation behaviour – not distinguished by unique characteristics that can be easily measured. In the urban aerosol of Vienna we see that the measured activation ratio of the aerosol is much lower than the activation ratio expected from the size distribution (Burkart et al, 2012, Dameto de Espana et al., 2017), so size is not the main characteristic.*

In reviewing the references, I have two major concerns. There are 4 references included that are non-peer-reviewed conference abstracts (including an EGU abstract, for example). In the main text, these citations seem to suggest more confidence in the references than is warranted. For example, Lines 167-168 states “A first pilot study on the ability of the LAAPTOF to detect and analyse aqueous droplets was performed by Dameto de España et al. (2018b).” This is a reference to the 2018 Aerosol Technology Conference in Bilbao, Spain; I checked the conference website and could not even find an abstract to refer to, only the presentation title. In addition, the reference list includes four references without journals or DOIs provided, so they could not be traced. Shen et al 2018b should be updated from the AMTD to AMT version.

The references to the earlier conferences were added to show that parts of the study were already presented at conferences, so we think that these references should be included. We will, however, clarify already in the text that these are conference presentations and not full-scale peer reviewed papers. - done

The reference Shen et al. will of course be updated - done

As Reviewer 1 also discusses, the authors assert that the LAAPTOF measured aqueous droplets (as a main conclusion of their paper), but no information about particle size is provided in the data presented, and this is needed to confirm their hypothesis. To test this assertion, it would be best measure the particle size following the CCN instrument and within the LAAPTOF for comparison.

Because of the set-up of the LAAPTOF (a closed instrument that cannot be taken apart) this measurement is not possible

What is the size distribution of activated droplets?

*The size distribution of droplets produced by the original VACES has been investigated previously e. g. by Saarikoski S., Carbone S, Cubison MJ, Hillamo R, Keronen P., Sioutas C., Worsnop D.R, Jimenez J.L.” Evaluation of the performance of a particle concentrator for on-line instrumentation”. *Atmospheric Measurement Techniques* 7, 2121-2135, 2014; and Geller, M.D., Biswas, S., Fine, P.M. and Sioutas, C. “A Compact Aerosol Concentrator for Use in Conjunction with Low Flow-Rate Continuous Aerosol Instrumentation.” *Journal of Aerosol Science*, 36, 1006-1022, 2005. The size distribution of the droplets in these studies had it maximum between 4 and 5 μm . This info will be added to the revised MS. - done*

The main point for our MS, however, is that the droplets are larger than the cut size of the virtual impactor of the VACES (1.5 μm) and, when they arrive at the point of ablation, larger than 300 nm (the size limit set in our experiment for the triggering of the ablation laser). This info was already contained in the original MS, and has been further stressed in the revised MS

What is the size distribution measured by the LAAPTOF? Without knowledge of the particle size, it is not possible to determine whether the particles analyzed were indeed aqueous droplets when measured. Since the impactor removed particles greater than 1.5 μm , then any particle detected by the LAAPTOF at less than 1.5 μm had lost water. Even particles measured by the LAAPTOF at greater than 1.5 μm may have also partially evaporated if they had started out as much larger droplets.

All activated CCN (i.e. droplets) exiting the virtual impactor of the VACES are >1.5 μm at that point. The LAAPTOF is intentionally set to 300 nm lower size limit to analyse also droplets that had already evaporated to some extent.

Also key to the assertion of the measurement of aqueous droplets is the work of Zelenyuk et al (2006, Analytical Chemistry, “Evaporation of water from particles in an

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aerodynamic lens inlet: An experimental study”), which was completed using a single particle mass spectrometer, and is not cited by the authors.

The reference will be added. Zelenyuk et al. 2006 however, dealt with particles that had been grown under sub-saturated conditions (maximum relative humidity: 85%), where droplets attain a stable size. In our experiments we deal with CCN activated at supersaturated conditions, where the droplets no longer are in equilibrium and do not have stable (wet) sizes

I agree with Reviewer 1 that the introduction needs revision. The general components of the introduction would be best referenced using reviews to more comprehensively cover the literature and avoid inaccurate statements. The authors should also focus on previous work that can be most directly compared to this study. For example, on lines 61-62, the authors discuss SSA smaller than 200 nm (even though this study only examined SSA > 300 nm) with two example papers, one of which didn't even measure SSA (Pratt et al 2009).

See our comments to the points raised by Reviewer #1 – the introduction will be revised. The difference between SSA and our sea water CCN will be clarified already in the introduction – we do not analyse real world SSA. - done

Another inaccurate statement is on lines 71-72 where it is stated that “single particle laser ablation...been widely used to analyse bulk chemical composition”. The statement on Line 90 “All these studies performed with the various types of single particle mass spectrometer analysed dry particles.” is also inaccurate, as driers are not always used upstream of single particle mass spectrometers; the authors should better review the literature and then amend this statement, as driers are often NOT used.

The introduction will be revised and any inaccurate statements will be corrected. - done

It is also inaccurately stated that Neubauer et al (1997) analyzed “aqueous solutions”, when in fact they analyzed aqueous aerosol. Also, lines 98-104 do not present a thorough review of single-particle mass spectrometry measurements of particles <0.2 μm in diameter, as many other studies have examined this size range; however, this study doesn't examine this size range either so reviewing these papers doesn't seem necessary. It is important to instead include more discussion of previous single-particle mass spectrometry measurements of cloud droplet residuals, as this is most relevant to this work, and is key for establishing the uniqueness of this work.

*The main difference is that we analyse the composition of particles that can be activated as CCN, while cloud droplet residues are particles that have potentially undergone chemical reactions and/ or coalescence with other droplets during their “life” as cloud droplets **We decided not to discuss studies on cloud droplet residues in detail, but stress the difference between CCN and cloud droplet residues and cloud processing.***

Line 157: The authors state that particles from 70 nm – 2.5 μm are transmitted with 100% efficiency and cite the instrument user manual, but I am not aware of any published study proving this. Further, the authors themselves note that spectra were only obtained for particles > 0.3 μm , and they do not provide data showing the transmission efficiency of their instrument as setup for this study. I am not aware of any aerodynamic lens inlet available that transmits this full particle size range at 100% efficiency.

Here we have to rely on the user manual. We intentionally set the lower size detection limit at 0.3 μm to exclude smaller particles.

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The authors refer to Liu et al (1995a, 1995b) for their aerodynamic lens, but Liu et al (1995b), which shows experimental data, does not show 100% transmission over this size range either.

Again, we have to rely on the user manual

Lines 162-164: The goal of this work is to measure aqueous droplets >1.5 μm in diameter, but the authors only do a PSL size calibration from 350-1500 nm, meaning that, if they did measure larger particles (diameter not reported), they would be extrapolating their size calibration and significantly increasing uncertainty. To claim that the droplets did not lose water, the particle size is critical to report, and as such, the authors should increase their size calibration to the full 2.5 μm , which they state is their upper size range.

We do not claim that the droplets do not lose water between the exit of the CCN-VACES and the ablation stage – we claim that droplets enter the LAAPTOF and can be analysed. We do not make any statement as to size (except that they are > 0.3 μm when the ablation laser is triggered). The whole MS will be checked and this point will be clarified where needed. - done

Figures 1 & 3: These figures show the LAAPTOF diagram and carbon black mass calibration spectra, but since this paper does not focus on the development of the LAAPTOF itself, these figures are not needed. As listed in Section 2.2, there are already several papers published on the LAAPTOF.

We have to write about the mass calibration we performed. As this is a small part of the MS, we prefer to keep this section, but we moved it to Section 2.2 where it belongs. done

Section 5.1: This section primarily discusses the mass calibration and spectra clustering setup. This information should be moved to the methods, as this is not new to this work, with several papers published already on these topics. Likewise, the columns in Tables 2 & 3 that correspond to the peaks chosen for calibration should not be in the results.

done – see response to previous comment. As we refer to these Tables in the section now moved to “methods”, we left the columns in the tables for reasons of economy in terms of space.

Lines 216-217: It is stated that “ca. 10% to 20% of the spectra obtained from the droplets were sufficiently clear for analysis”. What does this mean? I’m concerned that only 10-20% of the data obtained were analyzed, per Table 2, as this could bias the results.

We can only work with clear spectra, and can only work with what we have. The main message of the MS is that we can obtain spectra of single activated CCN. The clusters are shown to give a general overview of the CCN population which gave us spectra. We do not make a general statement on all CCN. This point was further clarified in the revised MS

Since water suppresses negative ion formation (Neubauer et al, 1997), does this mean that only 10-20% of the particles dried to the point that mass spectra could be obtained? What fraction of the particles had negative ions? In fact, this information this could potentially help support the claims of water still present on the particles

Unfortunately, the LAAPTOF software cannot provide the number of “positive only” spectra, so we do not have the info necessary to estimate the percentage of particles without negative spectra.

How does the measured size distribution of these particles compare to those without “sufficiently clear” mass spectra?

Unfortunately this cannot be done – we get the spectra from the LAAPTOF, but not the size distribution of the particles/droplets.

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Line 269: The authors claim here and elsewhere that m/z 18 is NH_4^+ and cite Brands et al (2011) and Hinz et al (2006). However, these instruments use higher wavelength lasers for desorption/ionization (Brands et al uses 266 nm and Hinz et al used 266 nm and 337 nm), at which m/z 18 does indeed correspond to NH_4^+ . However, these authors are using 193 nm, and as discussed by Murphy and Thomson (1997a, JGR), m/z 18 can correspond to both NH_4^+ and H_2O^+ (water) at this wavelength; this may even be helpful for the authors to examine further since they are studying aqueous aerosol.

Thank you for this helpful suggestion. After going back to the spectra, we found, however, that in most cases the ions usually associated with NH_4^+ (i.e. NO_3^- or SO_4^-) were present, so we deduce that in most cases m/z 18 indeed must have been NH_4^+

Lines 275: The authors claim here and elsewhere that m/z -16 and -17 (O^- and OH^-) correspond to water, but no reference is provided. Murphy and Thomson (1997b, JGR), who also used 193 nm LDI, found that O^- and OH^- were negatively correlated with relative humidity and were positively correlated with organic and silicon peaks instead.

The references for assigning O⁻ and OH⁻ to water are the studies by Johnston (2000), Neubauer et al. (1998) and Neubauer et al. (1997). Murphy and Thomson, however, used a dryer and consequently had dry particles. Under these conditions, water probably was more or less absent. Neubauer et al. (1998) however, showed ammonium sulfate spectra at different humidities (between <7 up to 80%) and found the O⁻ and OH⁻ peaks in all of these spectra. The height of the peaks, however, decreased with humidity. In the Neubauer et al. (1997) study, the authors state that the presence of water is indicated by the presence of strong O⁻ and OH⁻ peaks.

We will check for a possible correlation between O⁻ and OH⁻ and organic peaks as suggested – done. No such correlation was found.

Lines 276-277: The authors refer to m/z -46 & -62 (NO₂⁻ and NO₃⁻) and m/z -80 and 97 (SO₃⁻ and HSO₄⁻) as ammonium nitrate and ammonium sulfate here and elsewhere in the manuscript. However, it is not clear how the paired cation was determined, especially since not all particle types included ammonium.

The comment here refers to the central spectra obtained from fuzzy clustering. Fuzzy clustering suppresses weak signals, and as e.g. Na⁺ signals are rather weak, they are not visible in these spectra.

Figure 11: Why is this particle labeled “carbon and nitrate” when one of the most prominent peaks is sulfate?

This mistake will be fixed - done

Lines 441-444: The first two lines refer to a comparison of two samples, but seems to refer to Figure 20 twice, making this not understandable. It is then followed by perhaps a statement left in from coauthor editing(?) that states: “there is something wrong with this and the previous sentence—they both refer to San Sebastian but read as if they correspond to different samples”. This should be fixed.

This will be fixed - done

Lines 460-463: Information about particle clustering is not novel to this paper and

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therefore does not belong in the conclusions.

We agree – this info will be deleted – done