

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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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. 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 endeavors 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.

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.

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. What is the size distribution of activated droplets? 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. 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.

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). 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. 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.

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.

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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.

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.

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.

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.

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. 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. How does the measured size distribution of these particles compare to those without

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“sufficiently clear” mass spectra?

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.

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.

Lines 276-277: The authors refer to m/z -46 & -62 (NO_2^- and NO_3^-) and m/z -80 and -97 (SO_3^- and HSO_4^-) 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.

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

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.

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.

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