Reviewer 2

The nanoscaning electrical mobility spectrometer is a very useful instrument because of its response time and sensitivity for small particles.

Few questions or methods are not discussed in the text or are not clear. I listed few of them below. That will help the readers to have the responses. It will help to precise that the particles used to calibrate the instrument are electrically (positive) charged. Sizing sub 2 nm with a charger dma cpc is another problem to my opinion. Indeed the chemistry of the particles is changed by the attached ion on the particle. And the chemistry is important for the activation of sub 2 nm particles, see Kangasluoma et al (2013) in Aerosol Sci Technol.;

We appreciate the reviewer's pointing out this very insightful paper. Kangasluoma et al. (2013) observed that composition more strongly affects detection efficiency than does charge state for CPC detection of mobility classified molecular ions smaller than about 1.5 nm. Furthermore, in comparing DMA/CPC signals to high resolution mass spectrometric analysis of the classified inorganic particles, they found that a substantial fraction of particles at 1.5 nm did not match the composition of the generated particles, making the concentrations of those very small particles uncertain. This key reference supports our inference, and suggests reasons that the size distribution below about 1.5 nm is difficult to quantify with the present instrument. We will cite this paper in the revised manuscript.

Regarding the charge state of the aerosol, and its impact on the CPC performance: we note that the focus of this work is on the nanoSEMS system. The CPC testing reported in this manuscript only addresses use of the CPC as a detector for a mobility analysis system. As such, the aerosol used in testing the CPC has all been performed with mobility classified, and, therefore, charged particles. The CPC counting efficiency data presented in Fig. 6 are for positively charged particles.

Jiang et al. 2011 in the same journal have used by the way the concept of SMPS to detect neutral particles in the sub 2 nm range. You should cite their work.

Jiang et al. (2011a) should indeed be cited for the first development of the DEG-SMPS that extended the sizing range of an SMPS based on the TSI nano-DMA to sizes approaching 1 nm, as well as for the first application of the instrument in concert with mass spectrometric methods that show that the two methods yield consistent size distributions in the size regime where they overlap (Jiang et al., 2011b). We will cite these important works.

Regarding enumerated comments:

We note that the primary focus of this paper is the scanning-mode ROMIAC, which has enabled creation of the nSEMS. The integrated nSEMS system also requires a charge conditioner (charger), and a detector (a condensation particle counter, CPC). Other charge conditioners, even others based upon soft x-ray sources, could be substituted for the present design without changing the essential characteristics of the instrument. Similarly, other detectors than the two-stage condensation particle counter (CPC) that we developed

and used as the detector within the nSEMS could be subsituted in the nSEMS, altering its performance in detail, but not its essential character.

Due to delays caused by the COVID-19 pandemic, full characterization of the soft x-ray charge conditioner employed in this study could not be completed in time for this study. The necessary experiments will soon resume; the design of the charge conditioner and its performance (particle losses and output charge distribution) will be the subject of a separate paper. The only place where the charge conditioner affects results presented in this paper is example of its application presented in Fig. 11. The assumptions made regarding the performance of the charge conditioner are discussed in the responses to queries given below, and will be made clear in the revised manuscript.

With that caveate, this paper focuses on the integrated measurement system, and provides the detail needed to analyze the data that it generates. We provide greater detail on the core component of the nSEMS, i.e., the classifier (ROMIAC), than we do on the soft x-ray charge conditioner or the two-stage CPC. However, as discussed below in response to specific questions, the performance of the two-stage CPC is taken into account in the calibration studies through which we determined the transfer function of the *integrated instrument* beginning downstream from the charge conditioner. We feel that the information provided is sufficient to understand, or quantitatively interpret the data from the *nanoSEMS system*.

Work is continuing that will provide the level of detail requested in some of the reviewer's enumerated comments, and will be presented in future papers. Given that data obtained with the nSEMS have already formed the basis of published papers, we would like to avoid the additional delays that the additional work on the subcomponents will require.

1°/ Why this 'precise' diameter of 1.5 nm? Is it a limit of the detector or the classifier or the charger. Tetraethylammonium bromide produces 1.11 nm (mobility diameter) has been used by Attoui (2018 Journal of aerosol science).

In the original work on the mobility classifier (the ROMIAC) used in the nSEMS, Mui et al. (AST, 2017) calibrated the ROMIAC in voltage stepping mode using tetra-alkylammonium halides, including tetraethylammonium bromide. The ROMIAC can extend the sizing range to 1.1 nm size. While it would be great to report size distributions closer to 1 nm, in ambient or atmospheric simulation chamber measurements, counts are recorded for sub-1.5 nm particles, even when none are present. In measurements of inorganic calibration particles, Kangasluoma et al. (2013) observed many impurity counts in this size range that were attributed to impurities. Hence, we limit the reported sizing range to that in which we have confidence that we are measuring particles from our sample rather than impurities or gas ions. This will be clarified in the revised manuscript, and the Kangasluoma paper will be cited.

2°/ The charger is the weak point of the study since there is no experimental work on the charging state of sub 3 nm with a bipolar charger. The authors are not giving lot of details about the charger they have used in terms of size of their chamber, concentration of ions nor residence time of the ions in the chamber.

As noted above, we will revise the paper to make it clear that this paper addresses the integration of the scanning-voltage ROMIAC with the two-stage CPC to create the nSEMS, and that the soft x-ray charge conditioner has not been fully characterized at this time.

The charging probability is a major weakness in all mobility-based measurements of ultrafine particles. The soft x-ray charge condition is a new design developed for this instrument, but which has been used on numerous other measurements. It was designed to minimize losses by avoiding the tortuous paths found in other soft x-ray chargers, and by emplying a short residence time (which also lowers the risk of new particle formation within the irradiated volume (Yun et al., 2009)). In initial characterization experiments, it yielded consistent results with conventional radio-isotope (^{210}Po and ^{85}Kr) charge conditioners in experiments in both chamber and calibration experiments, and applying the Wiedensohler (1988) empirical fit to the theoretically-derived, steady-state, bipolar charge distribution (Fuchs, 1963; Hoppel and Frick, 1986), as is commonly applied to DMA data analysis.

Figure 4 and the associated text will be modified to indicate that the space occupied by the charge conditioner was replaced with a straight tube of the length of the charge conditioner during the calibration experiments. The concentration of the classified particles entering the nSEMS was measured either with an aerosol electrometer, or a reference CPC. The response of the nSEMS, including the two-stage CPC is then measured.

3°/The important flowrate of 4.6 lpm is coming without any explanation about the charging state nor residence time.

4°/ Same thing about the losses versus the particles size in the charger, in the conditioner after the dma?

The input flow rate to the charge conditioner was selected based upon prior experience sampling from the CLOUD chamber for measurements using other instruments, combined with design simulations; the charge conditioner design was optimized for that flow rate. Losses in the charge conditioner do not affect the calibration data. They may have a modest effect the size distributions shown in Fig. 11 for the one application example that we report for the instrument; a caveate to this effect will be added to the discussion of those data.

5°/ Likewise about the mixing chamber of the mixing type cpc activator. There are no details on terms of size nor activation nor losses.

6°/ Likewise about the growth tube (if there is a growth tube) of the mixing type CPC. In page 7 line 47, the authors are talking about the growth tube used by Sgro and Fernandez de la Mora indeed. There are no details about the residence time the inner diameter nor length. Is the growth tube what they call 'condenser'? What is its length and inner diameter?

7°/ Same thing for the flow rate of '1, 5 lpm'. Why this particular value?

As noted above, the focus of this paper is on the nSEMS, which incorporates a two-stage CPC, but the unique component is the scanning-mode radial opposed migration aerosol classifier. The mixing type CPC is based upon the fast-mixing CPC design of Wang et al.

(2002), as modified by Shah and Cocker (2006), which affords a shorter response time than that of the particle size magnifier of Vanhanen et al. (2011). It was originally designed to supply activated particles to a TSI Model 3760 CPC butanol CPC operating at a flow rate of 1.5 L/min. That detection stage was replaced with a high flow (1 L/min) version of the Aerosol Dynamics Inc. water-based MAGIC CPC, operating at 1 L/min, improving the nSEMS time response due to the ADI detector's faster response. The 1.5 L/min flow was maintained; the excess flow was exhausted upstream of the MAGIC CPC.

Two aspects of the CPC performance are central to the interpretation of data from the nSEMS: (i) the counting efficiency as a function of size, and (ii) the time response of the detector system. The counting efficiency of the CPC was separately determined using the apparatus shown in Fig. 5, and is presented in Fig. 6. The integrated nSEMS transfer function was measured for a very slow scan (1400 s) for a number of sizes of mobility-classified particles, providing data that closely approximate the constant voltage transfer function.   It was also measured at the scan rate used in the experiments (60s).

By deconvoluting the two transfer function measurements, we extracted the time response of the integrated detector plus the ROMIAC and downstream plumbing. That time response was fitted to a model incorporating a single, well-mixed volume (a CSTR with an exponential decay in delay times) in series with a fixed delay (often described as a plug-flow reactor. The resulting response time function, which has an exponential decay time of 0.2 s, and a fixed delay of 0.7s, is shown in Figure S2. This characterization was employed in analysis of the data since the response time of the first (turbulent mixing) stage of the CPC was not separately measured. The time response of the second-stage detector CPC was sigificantly slower than the estimated exponential decay time of the mixing region of the first stage, 7.5 ms, which is slightly shorter than that measured by Shah and Cocker (2005) for an earlier version of the first stage (10 ms). The full residence time of the first stage is ~0.12 s, including the mixing region and the growth tube (which was labeled condenser in the original manuscript but will be changed to match the terminology that has become common in the literature).   Delays caused by mixing and by the finite volume within the CPC and elsewhere shift the peak in the transfer function. Figure 10 shows that, after accounting for those delays in data inversion for a 60 s scan, measurements agree well with that predicted in COMSOL simulations of the scanning ROMIAC.

Thus, while we do not present full characterization of the mixing particle activation stage or separate measurements of the transient response of the two-stage CPC, the data needed to interpret and invert the data were measured and are reported.

8°/ A hot wire is used for the calibration of the instrument but there are no information nor reference of this method. Is it the same method used by Peineke et al 2009 (Journal of aerosol science)? If yes why the authors are using a charger in the figure 5. Peineke and Schmidt Ott 2007 (Journal of Aerosol Science) claim that the particles are self-charged in negative and in positive mode.

The device that we used is similar to that of Peineke et al. (2006). We will cite that paper.

9°/ Why the charger (neutralizer) is not used any more in the figure 5 for the same hot wire generator?

As reported by Peineke et al. (2006), many of the particles generated by the hot-wire source are positively charged when formed. Passing the very small particles through a bipolar charge conditioner reduces the number of charged particles. A comment to this effect can be added to the paper.

10°/ The PSM as a sizer has been introduced by Gamero and Fermandez de la Mora (paragraph 3.2 in Gamero 2000 Journal of aerosol science). Not by Sgro and Fernandez de la Mora (2004) as said the authors. **Citation***: https://doi.org/10.5194/amt-2021-62-RC2*

We thank the reviewer for pointing out this error. The proper paper will be cited.

References:

Fuchs, N A. 1963. "On the Stationary Charge Distribution on Aerosol Particles in a Bipolar Ionic Atmosphere." *Geofisica Pura E Applicata* 56 (1): 185–93. doi:10.1007/BF01993343.Hoppel and Frick (1986)

Jiang, Jingkun, Jun Zhao, Modi Chen, Fred L Eisele, Jacob Scheckman, Brent J Williams, Chongai Kuang, and Peter H McMurry. 2011. "First Measurements of Neutral Atmospheric Cluster and 1–2 Nm Particle Number Size Distributions During Nucleation Events" 45 (4): 2–5.

Jiang, Jingkun, Modi Chen, Chongai Kuang, Michel Attoui, and Peter H McMurry. 2011. "Electrical Mobility Spectrometer Using a Diethylene Glycol Condensation Particle Counter for Measurement of Aerosol Size Distributions Down to 1 Nm." Aerosol Science and Technology 45 (4): 510–21. doi:10.1080/02786826.2010.547538.

Kangasluoma, J, H Junninen, K Lehtipalo, J Mikkila, J Vanhanen, M Attoui, M Sipila, D Worsnop, M Kulmala, and T Petaja. 2013. "Remarks on Ion Generation for CPC Detection Efficiency Studies in Sub-3-Nm Size Range." *Aerosol Science and Technology* 47 (5): 556–63. doi:10.1080/02786826.2013.773393.

Peineke, C, M B Attoui, and A Schmidt-Ott. 2006. "Using a Glowing Wire Generator for Production of Charged, Uniformly Sized Nanoparticles at High Concentrations." *Journal of Aerosol Science* 37 (12): 1651–61. doi:10.1016/j.jaerosci.2006.06.006.

Shah, SD, and DR Cocker. 2005. "A Fast Scanning Mobility Particle Spectrometer for Monitoring Transient Particle Size Distributions." *Aerosol Science and Technology* 39 (6): 519–26. doi:10.1080/027868291004652.Vanhanen (2011)

Wang, J, VF McNeill, DR Collins, and RC Flagan. 2002. "Fast Mixing Condensation Nucleus Counter: Application to Rapid Scanning Differential Mobility Analyzer Measurements." *Aerosol Science and Technology* 36 (6): 678–89. doi:10.1080/02786820290038366.

Wang, J, VF McNeill, DR Collins, and RC Flagan. 2002. "Fast Mixing Condensation Nucleus Counter: Application to Rapid Scanning Differential Mobility Analyzer

Measurements." *Aerosol Science and Technology* 36 (6): 678–89. doi:10.1080/02786820290038366.

Yun, Ki Myoung, Sin Young Lee, Ferry Iskandar, Kikuo Okuyama, and Naoko Tajima. 2009. "Effect of X-Ray Energy and Ionization Time on the Charging Performance and Nanoparticle Formation of a Soft X-Ray Photoionization Charger." *Advanced Powder Technology* 20 (6): 529–36. doi:10.1016/j.apt.2009.07.002.