The nano-scanning electrical mobility spectrometer (nSEMS) and its application to size distribution measurements of 1.5-25 nm particles by Weimeng Kong, Stavros Amanatidis, Huajun Mai, Changhyuk Kim, Benjamin C. Schulze, Yuanlong Huang, Gregory S. Lewis, Susanne V. Hering, John H. Seinfeld, and Richard C. Flagan

This study describes in considerable detail a powerful instrument that has already produced valuable experimental data on new particle formation in the carefully controlled CLOUD experiment (Wang et al. 2020). The instrument is able to generate with fine sensitivity and resolution a size distribution in the 1.5-25 nm range in 60 s, which is apparently faster than previously achieved. Additionally, the article provides extensive information on design criteria, which should be most valuable in future studies aimed at making comparable measurements with improved performance. The experimental and interpretive challenges overcome are great in many fundamental dimensions, including sampling, charging, transmission, size resolution, sensitivity of detection, speed of measurement, etc. Handling all these problems in a single instrument has required a difficult strategic thinking on components choices, and this is also carefully discussed with extensive knowledge of related literature. Globally considered this is an outstanding contribution to the field of atmospheric measurement, which should by all means be published. The choice of journal is also excellent, as the article provides an ideal venue for discussion of the many challenges involved in these measurements, as well as on the many possible alternative experimental tools that were not chosen.
In my discussion I will focus on these other alternatives. I realize that the authors have contributed their own practical solution to their global measurement problem, including a fair amount of justification for their strategic choices. They have accordingly no duty to engage in the more extensive discussion I propose. Nevertheless, given their wide experience, their response would be exceedingly useful to the many colleagues familiar with the various components of this instrument, but not necessarily with their optimal integration into a functioning system.

1. The two-stage condensation detector is justified as follows: *Some single-stage CPCs have been operated at sufficiently high supersaturation to activate particles as small as 1 nm diameters, but in the experiment for which this instrument has been developed, where measurements must be made in a high-radiation environment, this can lead to nucleation within the CPC. Therefore, we took a more conservative approach that has proven robust and effective for sub-10nm particle detection, namely a two-stage CPC, in which the first stage employs a low vapor pressure working fluid, typically diethylene glycol (DEG) that can activate small particles with minimal risk of homogeneous nucleation (Iida et al., 2009).*
Assuming that the nucleation region cannot be shielded, the effect of radiation would be to create small ions in air, similar to those produced in the X-ray chamber, but not removable by the DMA. One must then select a vapor able to discriminate between small ions produced by radiation and 1.5 nm particles. But why would this be precluded in common CPC vapors? In theory (say in Thomson's classical model for nucleation on charged particles) all vapors have critical activation curves that depend on size, which theoretically enables the exclusion of small air ions. Furthermore, Tauber et al. (ChemPhysChem 2018, 19, 3144– 3149) have recently found significant differences between the critical supersaturation for various atomic ions in butanol vapors. Similarly, Attoui and colleagues (doi: https://doi.org/10.1016/j.jaerosci.2021.105772) report that Kanomax's fast CPC can detect 2 nm particles. My point is that there may be single CPC solutions to the detection problem that, in addition to being simpler, would be faster. If these

solutions are presently unknown or insufficiently reliable, please state so, as this would provide a healthy stimulus for developing them.

2. DMA selection. The selection of the DMA used is justified because "*radial opposed migration ion and aerosol classifier (ROMIAC), can classify nanometer-sized particles with minimal degradation of its resolution or diffusional losses.* Another advantage of ROMIAC noted is that it achieves resolving powers comparable to those of conventional DMAs, though at substantially reduced flow rates. Nevertheless, given that a key advance in the new instrument is to reduce measurement time, it would seem that a larger gas flow rate would be preferable. For instance, the Half-Mini DMA has a residence time typically below 1 ms in the analyzer.[1] Another important issue we have recently noted is that high resolution is directly relevant to measurement speed because the residence time in the analyzer is almost identical for all ions of a given mobility, and therefore appears as a pure delay easily corrected in a fast measurement.[2] In that study we argue that a full mobility scan can be completed within a few seconds by combining a detector with a response faster that 20 ms with the half-mini DMA. Although such a fast CPC exists, that claim remains to be experimentally substantiated.

Figure 8 of the article shows that the resolution of the ROMIAC is excellent even for the sophisticated nucleation studies pursued. However, the figure also shows that the width of the spectrum of all monomobile particles used spans several seconds in the 60 s temporal spectrum. A DMA of higher resolution would not only resolve perfectly the 3.4 and 2.9 particles (partially overlapping in Figure 8). Even more usefully, much narrower peaks would enable much faster scans without loss of resolution.

One could be led to conclude from the nucleation event illustrated in Figure 11 that a temporal resolution of 1 minute is adequate. This may be true for events lasting several minutes, but perhaps not in situations where the reservoir of vapor available for particle growth is more limited. Given that the improved time resolution of the instrument of Kong et al. enabled the capture of nucleation events that would have been missed with slower prior equipment, one may surmise that currently undetectable events will be capturable by future devices having more temporal resolution.

There is another potential advantage of higher resolution in nucleation studies, as well as in other situations with a natural mechanism to produce narrow size distributions. If the signal is concentrated into a narrow range of sizes, being able to resolve them would increase the signal. In Figure 8 of Kong et al. one sees that the peak corresponding to 3.4 nm particles spans a size range from 2.9 to about 3.9 nm. The atmospheric nucleation spectrum shown in Figure 11 includes mobility peaks of comparable width, suggesting that perhaps the real size distribution along the growth curve is considerably narrower and taller than can be captured with the available resolving power. In other words, higher resolution would enable detecting lower intensity as well as shorter nucleation events. It would also provide a more precise measurement of the growth rate.

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[1] J. Fernandez de la Mora, Expanded flow rate range of high-resolution nanoDMAs via improved sample flow injection at the aerosol inlet slit, J. Aerosol Sci. 113, 265-275, 2017

[2] J. Fernandez de la Mora, L.J. Perez-Lorenzo, G. Arranz, M. Amo-Gonzalez, H. Burtscher, Fast high-resolution nanoDMA measurements with a 25 ms response time electrometer, Aerosol Science and Tech., 51(6), 724 – 734, 2017

3. Soft X-ray ionizer. This element does not receive as detailed a description as other components of the system. The choice of a bipolar source is defended based on the freedom it offers to examine positive and negative polarities. This is indeed a most useful feature, especially for particles of such small sizes, whose charging probability has not been yet well studied. Soft X-rays have an evident regulatory advantage over radioactive sources. However, all ionization sources relying on energetic particles pose a danger of converting organic volatiles into involatile species, causing artificial nucleation events in sufficiently polluted atmospheres. The details of how this tendency is moderated by Kong et al. would be of interest to the reader. In this realm, it is worth noting that the advent of electrospray ionization did change this situation long ago in the case of unipolar sources. One relevant feature of electrospray ionization at atmospheric pressure is that, in contrast to electrical discharges, ions are created under strictly thermal conditions. Vapors are certainly introduced through the evaporation of a solvent. However, in high conductivity electrosprays, solvent flow rates may be as small as 10^{-7} g/s. For this reason, electrosprays of pure volatile solvents containing volatile salts such as ammonium acetate have had an increased use in chemical analysis as a clean and efficient ionization source for vapors. [3] More recently, bipolar electrospray sources combining a positive and a negative emitter [4] have provided a clean substitute for bipolar sources based on ionizing radiation. There is some literature on the ionization probability of unipolar ES sources with vapors, and some untested calculations of how this probability would depend on particle size.[3] We are not aware of studies on the size dependence of the charging probability of nanoparticles in bipolar ES sources, but a similar ambiguity exists for bipolar sources of ionizing radiation. Hopefully these two gaps will be filled soon.

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