

Comment on acp-2022-498

Anonymous Referee #3

Referee comment on "An intercomparison study of four different techniques for measuring the chemical composition of nanoparticles" by Lucía Caudillo et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2022-498-RC2>, 2022

Caudillo et al. performed an intercomparison of four widely used techniques for analyzing sub-100 nm particle chemical compositions based on the dataset from the same CLOUD experiment. The manuscript is full of technical details and the discussions on the advantages and disadvantages of TD-DMA, FIGAERO, EESI-TOF, and UHPLC-HESI-HRMS are comprehensive. I think it will be more acceptable to enclose some discussion on what's new about science from the experiment that the intercomparison can bring to us before the manuscript is suitable for publication in ACP. I only have the following four major concerns:

- About time resolution: since the four techniques have very significantly different time resolutions, it should be very careful to compare the chemical compositions obtained, especially for a typical nucleation experiment, where the particle size (mass) distributions and gas-phase chemistry are always changing. I could argue that the different observations from the four techniques may be simply because they are looking at different samples. Of course, there is no perfect instrument, so how to align the timelines of the four techniques to make more direct intercomparisons should be discussed.
- About aerosol size: I think more details should be provided about how TD-DMA collects all sub-100 nm particles since DMA is designed to do size selection. Also, from Fig. S1, it looks like about 4 hours later, the particle size distribution has two modes. How does the sampling work during this period?
- About PMF analysis and scientific findings: what are the samples analyzed by PMF? Are they from the same experiment (Fig. S1) or are they compiled from different experiments (-50 C, -30 C, -10 C)? Are the PMFs different in different experiments? What new science can be learned from them? This is a very technical manuscript with few discussions about the science that we can learn from the intercomparison. It is better to make some conclusive scientific statements at the end of Section 3.2.1, just like the paragraph in Line 317.
- About positive and negative modes: the ionization efficiency depends on the ion polarity and the molecular property. For example, (-)ESI can be more sensitive to those molecules tending to denote protons, thus the mass spectrum cannot represent the complete information of chemical composition. It will be beneficial to add some

discussion about the effects of the ionization efficiency and the polarity on the completeness of aerosol chemical composition detection when comparing the fractions of compounds with different carbon numbers and volatilities.