

Atmos. Chem. Phys. Discuss., referee comment RC1
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Comment on acp-2022-498

Anonymous Referee #1

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-RC1>, 2022

"An intercomparison study of four different techniques for measuring the chemical composition of nanoparticles," by Caudillo et al., compares measurements made by 4 different methods that have, to a varying degree, sensitivity that allow them to measure sub-100 nm diameter particle chemical composition. Such intercomparisons are rare, as many involve specialized instruments that are not often available for side-by-side intercomparisons. It is, however, important to point out the unique sensitivities that are inevitable with any measurement technique. Therefore, this manuscript represents a potentially important contribution to measurement science and therefore might eventually be suitable for publication in ACP. I have several concerns that I would like to authors to address before I consider this manuscript suitable.

Major comments.

- I think it's important for the authors to define early on what it means for an instrument to "measure the composition of <100 nm particles." Clearly the method must be able to sample particles in this size range, but most instruments are capable of this including the Aerodyne AMS. The FIGAERO CIMS, filter-based methods, EESI-TOF, DAI, and many other methods can measure nanoparticle composition but only if the sampled population consists only of nanoparticles, since none of these methods have a means of size-separating sampled particles. Even instruments that are not designed to efficiently sample nanoparticles are able to do so provided that the sampling time and mass concentration of sampled nanoparticles are large enough. Can the authors be more descriptive of what makes these instruments the focus of this study? Are you looking specifically at instruments that measure the composition of sub-100 nm particles with a certain time resolution and concentration range?
- Following my first point, it seems important that any intercomparison study of instruments that measure nanoparticles should very clearly characterize sample size, specifically is the mass distribution of sampled particles, as well as sampling times. Unfortunately, in this manuscript very little attention is paid to this. The closest thing I

could find is a mention of sample size and mass is “intensity” plots (units of counts/sec) in Figure S1. In that figure, there is no information on the mass distribution of particles sampled by the TD-DMA or filters, and how this mass distribution compares to those for the other two methods. It appears that most of the FIGAERO and EESI signals are coming from the latter part of the 4-hour period, so those samples may be biased by that sampling condition whereas the filter and TD-DMA mass-average over the entire period of the particle formation event. Please provide more analysis of this important issue.

- Line 104: Since this is a paper about nanoparticle characterization, why wouldn't a perfect instrument also be capable of measuring particles of sufficient mass concentration and with time scales that represent ambient conditions? It's not sufficient, in my view, to let the vague phrase “in newly formed particles” (Line 102) quantify these conditions. Also, where does size-resolved properties come into play? If this is primarily a study of instruments that are only suitable in lab, then yes this is an appropriate definition of a perfect instrument. But none of these instruments were tested in this way.
- Section 2.1.2: It's important to state here that the TD-DMA is can run in size-resolved mode but was not run this way in order to maximize sample size. Sample size is key to these intercomparisons so it's important for the reader to understand situations in which the instrument operation was altered for these studies. Specifically, it appears that 4 hours were needed for TD-DMA and 15 min collection for FIGAERO. This is an important distinction and the reader needs to know why this compromise was made in order to properly assess differences in these methods.
- Lines 204 and 227: How long were filter samples collected? This is important for comparison to other methods.
- Line 223: I don't understand ... I thought 15 min collections??? Do you mean thermogram data were averaged? Also in the next section you say that you averaged TD-DMA to 1 sec, so it's a bit confusing to say that the raw data were processed to 1 min but the PMF was done on 1 sec data.
- Line 231: I believe there is actually a body of work that explored thermal degradation in FIGAERO (D'Ambro et al., 2019; Lopez-Hilfiker et al., 2015; Stark et al., 2017; Wang and Hildebrandt Ruiz, 2018). Please discuss and reference relevant studies.

D'Ambro, E. L., Schobesberger, S., Gaston, C. J., Lopez-Hilfiker, F. D., Lee, B. H., Liu, J., Zelenyuk, A., Bell, D., Cappa, C. D., Helgestad, T., Li, Z., Guenther, A., Wang, J., Wise, M., Caylor, R., Surratt, J. D., Riedel, T., Hyttinen, N., Salo, V.-T., Hasan, G., Kurtén, T., Shilling, J. E., and Thornton, J. A.: Chamber-based insights into the factors controlling epoxydiol (IEPOX) secondary organic aerosol (SOA) yield, composition, and volatility, *Atmos. Chem. Phys.*, 19, 11253–11265, <https://doi.org/10.5194/acp-19-11253-2019>, 2019.

Lopez-Hilfiker, F. D., Mohr, C., Ehn, M., Rubach, F., Kleist, E., Wildt, J., Mentel, Th. F., Carrasquillo, A. J., Daumit, K. E., Hunter, J. F., Kroll, J. H., Worsnop, D. R., and Thornton, J. A.: Phase partitioning and volatility of secondary organic aerosol components formed from α -pinene ozonolysis and OH oxidation: the importance of accretion products and other low volatility compounds, *Atmos. Chem. Phys.*, 15, 7765–7776, <https://doi.org/10.5194/acp-15-7765-2015>, 2015.

Stark, H., Yatavelli, R. L. N., Thompson, S. L., Kang, H., Krechmer, J. E., Kimmel, J. R., Palm, B. B., Hu, W., Hayes, P. L., Day, D. A., Campuzano-Jost, P., Canagaratna, M. R., Jayne, J. T., Worsnop, D. R., and Jimenez, J. L.: Impact of Thermal Decomposition on Thermal Desorption Instruments: Advantage of Thermogram Analysis for Quantifying Volatility Distributions of Organic Species, *Environ. Sci. Technol.*, 51, 8491–8500, <https://doi.org/10.1021/acs.est.7b00160>, 2017.

Wang, D. S. and Hildebrandt Ruiz, L.: Chlorine-initiated oxidation of n-alkanes under high-NO_x conditions: insights into secondary organic aerosol composition and volatility using a FIGAERO-CIMS, *Atmos. Chem. Phys.*, 18, 15535–15553, <https://doi.org/10.5194/acp-18-15535-2018>, 2018.

- Line 265: This is well-known and should have been discussed previously when the methods were introduced (with references). Here are some that I know about:

Lopez-Hilfiker, F. D., Iyer, S., Mohr, C., Lee, B. H., D'Ambro, E. L., Kurtén, T., and Thornton, J. A.: Constraining the sensitivity of iodide adduct chemical ionization mass spectrometry to multifunctional organic molecules using the collision limit and thermodynamic stability of iodide ion adducts, *Atmos. Meas. Tech.*, 9, 1505–1512, <https://doi.org/10.5194/amt-9-1505-2016>, 2016.

Modeling the Detection of Organic and Inorganic Compounds Using Iodide-Based Chemical Ionization, Siddharth Iyer, Felipe Lopez-Hilfiker, Ben H. Lee, Joel A. Thornton, and Theo Kurtén, *The Journal of Physical Chemistry A* 2016 120 (4), 576-587, DOI: 10.1021/acs.jpca.5b09837

- Section 3.2 and Figure 5: Why isn't the background subtracted for the TD-DMA data. Also it is very difficult to compare spectra when the temperature range is so different. Can the TD-DMA data be plotted over the same temperature range? In general, I felt that very little in the way of analysis is provided in this section.
- Section 3.3. First of all, the title is not very descriptive. I would suggest something like "Discussion of advantages and disadvantages of methods for measuring sub-100 nm SOA." Overall, I have a lot of concerns about this section. Every point made in this section could have been stated even before this study began, having been established elsewhere. Firstly, the discussion in the first paragraph really appears to emphasize that this was not a very well-characterized intercomparison study (actually finally here I see that the filters were collected for 8 hours ... that should appear earlier in the paper as I have already suggested). The first paragraph is just stating the sampling conditions. The second paragraph discusses the implications of sampling longer. The third and fourth paragraphs just say more things about the sampling for the TD-DMA and HRMS analysis. Most of the information up to this point should be in the methods section. The point made in line 429 and following regarding FIGAERO has been made by several others (see references above) although this may be a new finding for the TD-DMA. Line 436 discusses extraction of filter samples, another well-studied problem. The paragraph of the importance of ionization has been already well-studied. Summarizing, in reading this, it appears that all the main conclusions of this study have already been made elsewhere. So other than be reminded of them, is there any reason why a someone should read this manuscript? Please don't misinterpret this question because I think this is a very rich study with a lot of data. I just don't feel that if Section 3.3 contains the main take-aways from this study, then I feel that this study does not have a lot of things to teach us about these methods.

Minor corrections:

- It is very difficult to see the shaded regions of Figure S1e and f.
- Line 55: "nanoparticles" has a lot of possible definitions. For the abstract, I would prefer to see a mobility or physical diameter range mentioned.
- Lines 66 and 111, 295: A more accurate work instead of "calculating" is "estimating" or "modeling"
- Line 121: imprecise -- constituents (not particles) are transferred to the gas phase

- Line 128: Do the authors mean SOA in sub-100 nm particles here?
- Line 167: "signal" is an imprecise term. Suggest "a more accurate determination of particle constituents" or some-such
- Lines 169 and 184: It is important to note that HOMs, as defined here, are different because of the I⁻ chemistry or NO₃⁻ chemistry. In the text it makes the reader believe that these are the same compounds.
- Line 188: imprecise language -- particles obviously need to be collected. Replace with "batch collection" perhaps.
- Line 194: Imprecise definition of electrospray. Solvent evaporation leads to Coulomb fissioning and/or direct ion desorption.
- Line 197: provide reference ... is it still Lopez-Hilfiger?
- Lines 219 and 225: were processed and were averaged
- Line 228: what postprocessing? Why is there a line break here?
- Line 275: correct term is soft ionization techniques
- Line 354: Not a good idea to start a new paragraph with "On the other hand". Suggest: "For the purpose of comparison,"
- Line 395: imprecise: "when applying the methods presented here to the measurement of laboratory-generated sub-100 nm diameter SOA."