

Interactive comment on “A chemical analyzer for charged ultrafine particles” by S. G. Gonser and A. Held

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The following is a review of “A chemical analyzer for charged ultrafine particles” by Gonser and Held. As the authors point out, the ability to determine the molecular species that comprise newly formed atmospheric aerosol is a key step towards understanding and predicting impacts of new particle formation (NPF) on climate and human health. Few techniques exist for performing such measurements, which is a testament to the difficulties associated with collecting sufficient quantities of nanometer-sized aerosol and the ability to efficiently analyze sample sizes of a nanogram and smaller. It is therefore imperative that new techniques are developed that can provide unique perspectives on the composition of ultrafine aerosol.

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In this manuscript, the authors present an instrument called the “Chemical Analyzer for Charged Ultrafine Particles,” or CACHUP. CACHUP, an acronym that makes me crave French fries, is presented and its performance demonstrated using the direct application of known masses of camphene to the filament, and by analyzing 25 nm diameter particles generated by the ozonolysis of α -pinene. Overall the authors do a good job of describing the technique and its performance. However, prior to publication I feel that some points in this manuscript should be clarified and some inaccuracies addressed. My main concerns will be presented below, prefaced with the page and line number.

3861, 5: Nucleated particles can grow by condensation and by coagulation with particles of similar size. Coagulation is especially important when considering the “growth” of the nucleation mode of a size distribution as it seems the authors are describing here.

3862, 9: Both here and in the concluding remarks (3872, 5), the authors state that a unique feature of CACHUP has something to do with being “commercially available.” In this sentence (pg 3862), it seems that the message is that this instrument is commercially available. Please correct or provide more details about what is meant by this statement. Was the intention here to state that this inlet can be used with a commercially-available ion source and mass spectrometer? Even most custom instruments use commercially-available mass spectrometers.

3864,20: The extrinsic charging efficiency is the same as the overall charging efficiency if the only flow that enters the charger is the sample flow, and the only flow that exits the charger is the flow containing the charged particles. Please clarify if this is the case for the charger used here. In Fig. 2, I am surprised by the low charging efficiency of this charger. For the unipolar chargers used in the TDCIMS and NAMS, and described in detail in McMurry et al. (2009), charging efficiency was 100% for particles larger than 30 nm.

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3864, 29 (and 3872, 26): I am not aware of a pre-separator that can operate at atmospheric pressure with a cut-off at 30 nm. Can the authors provide an example of a technique that could be used for this?

3865, top paragraph: In your discussion of multiple charging, it would be good to reference the 2009 McMurry et al. characterization of their charger (mentioned above), and in particular Fig 2 which quantifies the charge distribution using that technique.

3865, 25 and Fig 3: Are the distributions shown in Fig 3 transfer functions for the RDMA's? This would require the use of a TDMA inversion routine (e.g., TDMAFit by Stolzenburg or TDMAinv by Gysel (2009)).

3867, 1: If the PEEK piston seals against the wall of the desorption region, then what creates the flow that is needed to pull constituent gases through the transfer capillary? Is the mechanism diffusion (that is, a perfect seal)? If that is the case then line 10 should be corrected since it's stated here that the region upstream of the capillary is at atmospheric pressure. Is it possible that there is a small gas leak surrounding the piston that allows gases to enter with the desorbed compounds? If it is the latter, then compounds that partition to and from the walls of the desorption region are likely major contributors to the background spectrum.

Sections 2.3-2.4: It would be very useful for the reader to understand the exact procedure for analysis of a sample, and how long each step takes. On pg 3870, line 1, it seems that the desorption region is heated to 150C between collection and analysis. It would seem to me that this would require a long waiting period between collection and analysis. 3868, 4: It is important to point out that monoterpenes are precursors to the formation of oxidized organic compounds, which contribute to the growth of particles. This sentence makes it seem as if the monoterpenes themselves are constituents of particles, and I do not believe there is evidence of this in the literature.

3868, 29: adding a charcoal denuder to the flow between the flow tube and CACHUP will likely modify the composition of particles by decreasing the saturation ratio of am-

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bient gas phase organic compounds. It would seem to me that to use of a "background spectrum acquisition" would allow the subtraction of the contribution of ambient organic vapors. Please explain why the denuder was deemed necessary (rather than subtracting the contribution of these gas-phase organics using a background spectrum acquisition).

3870, 20: In this sentence you compare the mass spectrum obtained using CACHUP to published spectra. What techniques were used to obtain those spectra, and what basis do you have to expect them to be similar?

3870, 29: The statement that the analysis of 25 nm α -pinene SOA particles that are collected for periods ranging from 0.5 to 2 hours results in the same observed spectra is in contrast to the main conclusion from Winkler et al. (2012). How do you account for this difference?

3871, 4: It is not clear to me that you addressed the issue of multiply-charged particles in the α -pinene SOA experiments.

3871, 7: It is also important to note that high concentrations of gas phase precursors will create a fundamentally different type of particle compared to ambient levels. This is because higher saturation ratios of organics will drive higher volatility species into aerosols.

3873, 15: It should be pointed out that a major source of the background could also be the desorption region itself. Even though that chamber is heated to 150C, the filament reaches temperatures of up to 800C so there will always be compounds (like ammonium sulfate) that will partition to walls under these conditions and desorb from the walls due to radiative heating from the filament during analysis.

References cited:

Gysel, M., G. B. McFiggans, et al. (2009). "Inversion of tandem differential mobility analyser (TDMA) measurements." *Journal of Aerosol Science* 40(2): 134-151.

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McMurry, P. H., A. Ghimire, et al. (2009). "Sampling Nanoparticles for Chemical Analysis by Low Resolution Electrical Mobility Classification." *Environmental Science & Technology* 43(13): 4653-4658.

Winkler, P. M., J. Ortega, et al. (2012). "Identification of the biogenic compounds responsible for size-dependent nanoparticle growth." *Geophysical Research Letters* 39.

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