Atmospheric
Measurement
Techniques

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Discussions

Interactive comment on "Electrodynamic balance measurements of thermodynamic, kinetic, and optical aerosol properties inaccessible to bulk methods" *by* S. S. Steimer et al.

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The authors would like to thank Referee #2 for the careful review and valuable comments and queries. We address the reviewer's comments in our response given below. We will incorporate corresponding changes and clarifications in a revised version of the manuscript.

Referee #2: I didn't see the vapor pressure or Henry's Law constant of shikimic acid stated in the paper. It should be clear that it has sufficiently low volatility such that

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evaporation of the organic component is not a large concern here. It would also be good to bring in some discussion of the very nice new method for retrieving organic component volatility and hygroscopicity from aerosol optical tweezers experiments recently described by Cai et al. (2014, 2015).

Authors' response: We did not study the vapor pressure of shikimic acid. As we wrote in the introduction our main reasons for choosing shikimic acid as a proxy for oxygenated reactive organic compounds of aerosol were first, that its single double bond makes it very suitable for several analytical techniques for studying ozonolysis [Steimer et al., 2014]. Second, shikimic acid aqueous solutions do not easily crystallize and form semi-solid or even glassy particles at low humidity and/or low temperatures. The ozonolysis study requires thermodynamic as well as diffusivity data which are the main focus of this paper. As the referee points out, it is important that volatility of the aerosol particle in our setup is sufficiently low. (See also the corresponding remark in our answer to referee #1.) While we used our setup previously to determine vapor pressures of organic compounds [Huisman et al., 2013, Soonsin et al., 2010] we did not determine the vapor pressure of shikimic acid. However, estimations methods [Compernolle et al., 2011] predict a vapor pressure of 10^{-8} Pa at 290 K, which is low enough to neglect evaporation during our experiments. Also, in our STXM experiments [Steimer et al., 2014] we did not observe any evaporation of a micron size particle in vacuum for several hours.

Referee #2: I felt it wasn't clearly stated that at low RH ('dry') the organic acid/water particle does effloresce, at least I assume that is what is going on. Was a phase change observed, and is this was explains the observed hysteresis? This aspect was not clear in the paper.

Authors' response: We apologize for expressing only indirectly that aqueous shikimic

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acid never effloresced in our experiments. The hysteresis seen in panel (a) of Fig. 3. are due to kinetic limitations of water uptake not due to phase transitions. We will add a paragraph to the revised paper at page 693 where we discuss Fig. 3(a): **Addition to the text for the revised manuscript (italics):** Below a relative humidity of about 0.3 the data show hysteresis loops, indicating delayed water uptake upon humidification and delayed water release upon drying (Zobrist et al., 2011). *However, these are not caused by deliquescence and efflorescence (i.e. the crystallization of shikimic acid) but by kinetic limitations. Crystalline particles in the size range of our particles show deviations from spherical shape which are easily detected in our setup when measuring the 2-dimensional angular optical scattering pattern [Krieger and Meier, 2011] or in fluctuations in the resonance spectra shown in Fig. 2(c) [Zardini and Krieger, 2009]. We detected no sign of crystallization in our experiments even at the driest conditions.*

Referee #2: Where was RH measured in the system? You could validate the RH probe's measurements this from hygroscopic growth measurement of known salt droplets – use changes in droplet size and refractive index to retrieve water activity and thus RH - have you?

Authors' response: See also our comment to referee #1. We discuss this at the end of the first paragraph of section 2: 'Relative humidity (RH) is measured by a capacitive RH probe with an integrated temperature sensor (U.P.S.I., France, model G-TUS.13R) mounted in the upper end cap of the EDB in close proximity to the levitated particle ($<$ 10 mm distance). The sensor was calibrated with deliquescence relative humidities of common salts and the saturation vapor pressure over ice at several temperatures. Capacitive RH probes are known to show some hysteresis and we conservatively estimate the accuracy to be no worse than 3 %.' An example of the calibration at 290 K is shown in Fig.1. We confirmed the calibration using the known growth mass growth

curve of aqueous NaCl.

Referee #2: Sect. 3.2: The assumption that K is a constant. What magnitude of uncertainty does this introduce?

Authors' response: According to Ray et al. (1991) this introduces an maximum error of 1%. Please note that this error is non cumulative.

Referee #2: Sect. 3.4.2: Is the value for the diffusivity of water in the pure solute required? If so how did you obtain or deal with this? This aspect was confusing to me.

Authors' response: No, it is just one of the parameters to be obtained by fitting all data points. Its temperature dependence is parametrized as shown in eq. (11).

Referee #2: Sect 3.4.2: This section on the retrieval of water diffusivity just seemed to end in a rather unsatisfactory way. This is a shame as 'direct' measurements of water diffusivity in particles are rare and valuable. There was virtually no discussion of the actual properties obtained from your analysis, and almost no discussion of the data plotted in Fig. 9. While this is a technical paper focused on the method, some discussion of what the obtained data means and if it is reasonable would certainly help here. Are there any other experimental measurements of water diffusivity in this or related systems to compare to? Or estimates of diffusivity, perhaps from viscosity data and Koop's framework [Koop et al., 2011]?

Figure 9: Adding a second y-axis that estimates equilibration timescale for a given particle size for that value of water diffusivity would be a valuable addition to this figure. Again, the measured water diffusivity values are put into almost no context. What is

there significance? This figure is barely discussed in the text.

Authors' response: We did not attempt to compare the diffusion data with those of other compounds, because that would require a careful discussion beyond the scope of this manuscript focusing on the technical aspects of our technique. However, we agree with the reviewer that this may cause some frustration for the reader. Since water diffusivity has been measured by us for sucrose [Zobrist et al., 2011] we add to Fig.9 the diffusivity for two of the temperatures (293.5 K and 250.5 K), see Fig. 2.

A brief discussion will be added to the last paragraph before the conclusion section of the revised manuscript. **Addition to the text for the revised manuscript:** Fig. 9 also show water diffusivity in aqueous sucrose for the highest and lowest temperature measured here. While the logarithm of diffusivity of water increases with water activity almost linearly in shikimic acid, sucrose shows less increase under dry conditions. In general the diffusivity is smaller in sucrose, but at all temperatures the diffusivity agrees within one order of magnitude for dry conditions (up to a water activity of about 0.25) and deviates at most by two orders (at water activity of about 0.5). Further investigations are needed to determine whether water diffusivity in aqueous organic compounds behaves similarly with temperature and water activity for different compounds and to which degree a model compounds like shikimic acid may serve as a proxy for secondary organic aerosol.

Referee #2: There seemed to be little discussion of how accurately this technique could measure the desired properties, and a comparison to the abilities of other techniques. See for example the paper by Mason et al. (2012). Please add more discussion of the accuracy/uncertainties in the measured properties using your methods, and how these compare to other methods.

Authors' response: We did not attempted to make a comprehensive comparison, nor review the abilities of other techniques. For that it would have been necessary to study one or several systems which had been measured with other techniques before. However, we will add the reference suggested by the referee to the ones mentioned in the introduction.

Referee #2: Page 695, line17: typo, 'being'; Page 697, line 7: typo, 'were'; Page 702, line 6: missing word, 'This mainly'

Authors' response: will be corrected in the revised manuscript.

Full figure captions:

Fig. 1: Calibration of RH sensor using the deliquescence relative humidity of common salt particles in the EDB, and flushing the chamber with dry nitrogen gas (from a liquid nitrogen reservoir) to obtain a data point under dry conditions.

Fig. 2: D_{H_2O} as a function of a_w for the investigated temperatures indicated by different colors. Different symbols represent different particles. The lines represent fits to equation Eq. (9). Solid lines were fitted with an α calculated according to Eq. (9), dotted lines with $\alpha = 1$. For comparison the faint, short dashed lines show the parametrization of D_{H_2O} for sucrose of Zobrist et al. (2011) for 250.5 K and 293.5 K.

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Ray, A. K., Soury, A., Davis, E. J., and Allen, T. M., Appl. Optics 30, 3974–3983 (1991).

Soonsin, V., Zardini, A. A., Marcolli, C., Zuend, A., and Krieger, U. K., Atmos. Chem. Phys. 10, 11753–11767 (2010).

Steimer, S. S., Lampimäki, M., Goz, E., Grzinic, G., and Ammann, M., Atmos. Chem. Phys. 14, 10761–10772 (2014).

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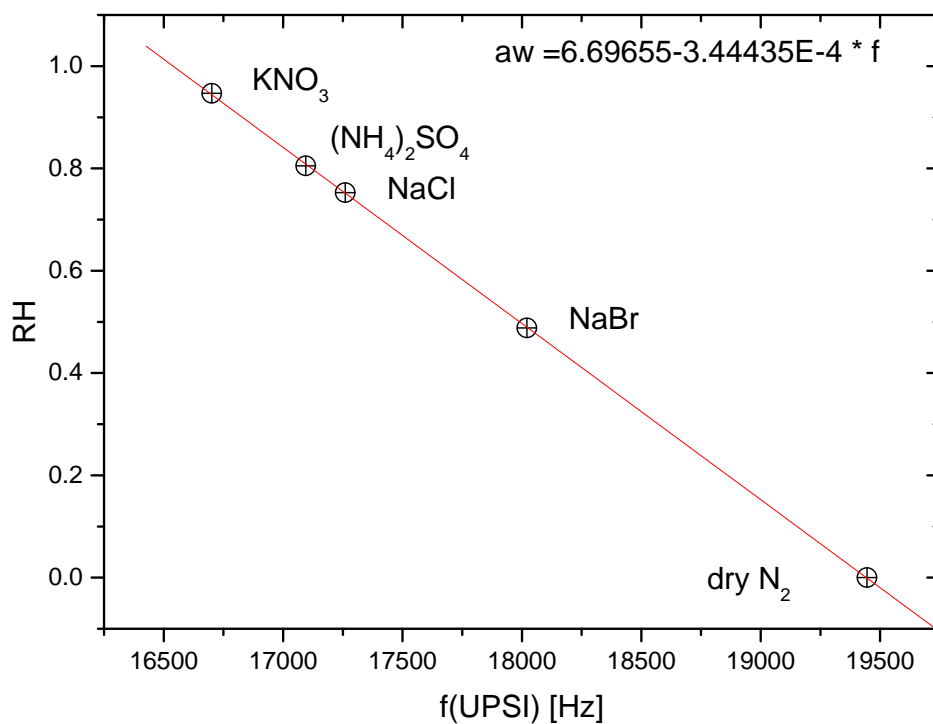Interactive comment on Atmos. Meas. Tech. Discuss., 8, 689, 2015.

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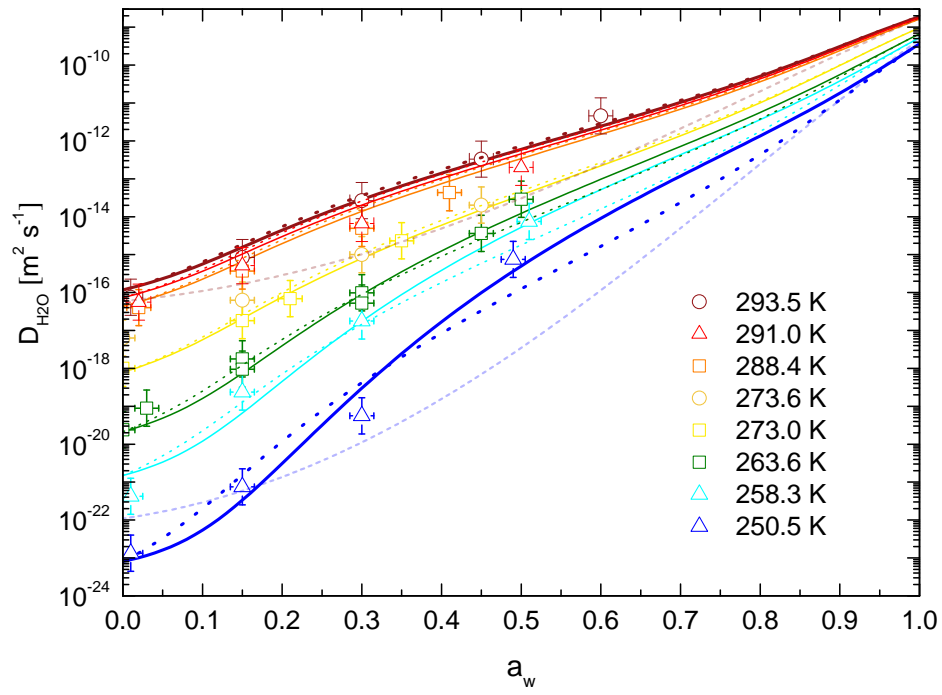**Fig. 1.** Calibration of RH sensor. For full caption see text.

Fig. 2. New Fig. 9. For full caption see text.

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