

Author Response to Anonymous Referee #1 of “Electrodynamic balance–mass spectrometry of single particles as a new platform for atmospheric chemistry research” by A.W. Birdsall et al.

We thank the referee for their thoughtful comments, which have helped improve the manuscript. Our replies are below (referee comment in **bold**, response in normal face, new manuscript content in *italics*, removed manuscript content in ~~strike-through~~).

The authors might consider including a sentence or two on the use of optical traps since these are also used with great success to study atmospherically relevant particles.

We agree that optical traps are a highly valuable platform for single particle studies. The introduction's treatment of levitated droplet experiments does acknowledge that optical, electrodynamic, and acoustic traps have all been used to study levitated particles. To clarify and emphasize the important contributions of both EDBs and optical traps, we will amend the Introduction as follows (p. 1, line 27):

"Researchers have studied particles deposited onto a substrate, or alternately, particles levitated by means of a "trapping" force originating from an electric field, radiation pressure of a laser beam, or acoustic waves. Levitated droplet experiments are appealing because they mimic aerosol particles in the ambient environment in certain key ways: the presence of a surrounding bath gas, an enhanced surface-to-bulk ratio, the absence of physical contact with a substrate, and the ability to study supersaturated particles. ~~Multiple laboratories have analyzed levitated droplets using optical techniques, which can be used to track evaporation and condensation via highly precise particle sizing, as well as some changes in chemical composition (reviewed in Krieger et al., 2012).~~ *Using electrodynamic or optical forces, multiple laboratories have analyzed levitated droplets using optical techniques such as Raman spectroscopy and Mie resonance spectroscopy (earlier work reviewed in Krieger et al., 2012). A number of different properties have been studied in this way, including vapor pressures (Cai et al., 2015; Cotterell et al., 2014; Huisman et al., 2013; Krieger et al., 2017), hygroscopic growth (Cai et al., 2015; Cotterell et al., 2014; Rovelli et al., 2016), optical properties (Mason et al., 2015), liquid-liquid phase separation (Stewart et al., 2015), diffusivities and diffusion coefficients (Bastelberger et al., 2017; Lienhard et al., 2014), and oxidative aging (Dennis-Smith et al., 2014).*"

The topic of droplet size and the ion signal intensity produced from it should be discussed more coherently in the manuscript.

We thank the referee for a number of suggestions to clarify the manuscript on the topic of droplet size and ion signal intensity. We address the individual points below.

The authors mention 10-30 micrometers in the introduction, but it is not clear whether this is limited by the balance or mass spectrometer.

The EDB can operate with smaller diameters; the operating diameter was chosen for a number of other factors (particle injection, ease of transfer to ionization region, magnitude of MS signal). We will clarify discussion of size range in the Introduction with the following change (p. 2, line 28):

"Here we describe a newly-developed system that couples an electrodynamic balance (EDB), which levitates aerosol particles ~~with diameters on the order of 10–30 micrometers~~ for an arbitrarily long amount of time, with mass spectral analysis of the entire particle. *We operate with particles of diameter approximately 10–30 μm for reliable acquisition of quantifiable mass spectra, though the EDB can levitate particles of smaller diameter.*"

[...] droplet size and/or analyte mass sampled is not given in the discussion or captions of Figures 2 and 3.

We will clarify in the Figure 2 and 3 captions and surrounding body text that the figures are from a 20 μm diameter particle:

§ 2.5 (p. 6, line 20): "Fig. 2 presents a sample time trace of selected ion signals arising from ejection and ionization of a 20 μm diameter PEG-200 particle."

§ 3.1 (p. 8, line 4): "A sample mass spectrum of a PEG-200 particle (Fig. 3) shows that the signal from ~~the droplet~~ *droplets with diameters on the order of 20 μm* can be easily detected."

Fig. 2 caption (p. 16, line 3): "Here the time series corresponding to a mass spectrum of Fig. 3, of a single PEG-200 droplet *with diameter 20 μm* , is shown."

Fig. 3 caption (p. 17, line 2): "Sample mass spectrum of a droplet consisting of polyethylene glycol, average molar mass 200 g mol^{-1} (PEG-200), *droplet diameter 20 μm* ."

Nor is it discussed in any detail Section 3.4, which otherwise gives an excellent discussion of particle-to-particle signal variability.

For particles used in the evaporation experiments the variability in measured diameters, using the spring-point technique, was found not to explain the variability in normalized signal as evaporation took place. In other words, the particle-to-particle variability was dominated by factors other than particles with $\sim 9 \mu\text{m}$ radius evaporating faster than particles with a $\sim 10 \mu\text{m}$ radius. This is what was meant in the manuscript by the statement, "The variability was not explained by the variability in measured starting particle diameter." (§ 3.4, p. 10, line 13)

We have since performed additional checks on the role of size variation in ion signal intensity and variability:

- We considered PEG-200 particles which were trapped and "immediately" ejected from the EDB (within 6 minutes of introduction), that were measured with the spring-point technique, and met the threshold of having sufficient signal (defined as at least 1000 counts at the m/z 283, PEG-6 channel). For these particles, there was no correlation between the particle diameter and raw signal. There is insufficient data to determine

whether within this size range there is any systematic difference in the amount of particle-to-particle signal variability.

- We have other data consisting of mass spectra for PEG-200 particles generated from solutions of varying weight fractions of PEG-200 in water. The weight fraction of PEG-200 in water can be taken as proportional to the starting trapped particle mass after fast water evaporation, since particle diameters were not measured with the spring-point technique. We compared particles generated from 10 wt% and 25 wt% PEG-200 mixtures, again restricting to particles immediately ejected from the EDB and over the signal threshold (1000 counts at m/z 283). The particle-to-particle raw signal variability was less for droplets from the 25 wt% mixture, but the normalized signal variability was similar for droplets from the two mixtures.

To clarify and summarize this analysis, we will update § 3.4 and Appendix A, including a new figure and caption:

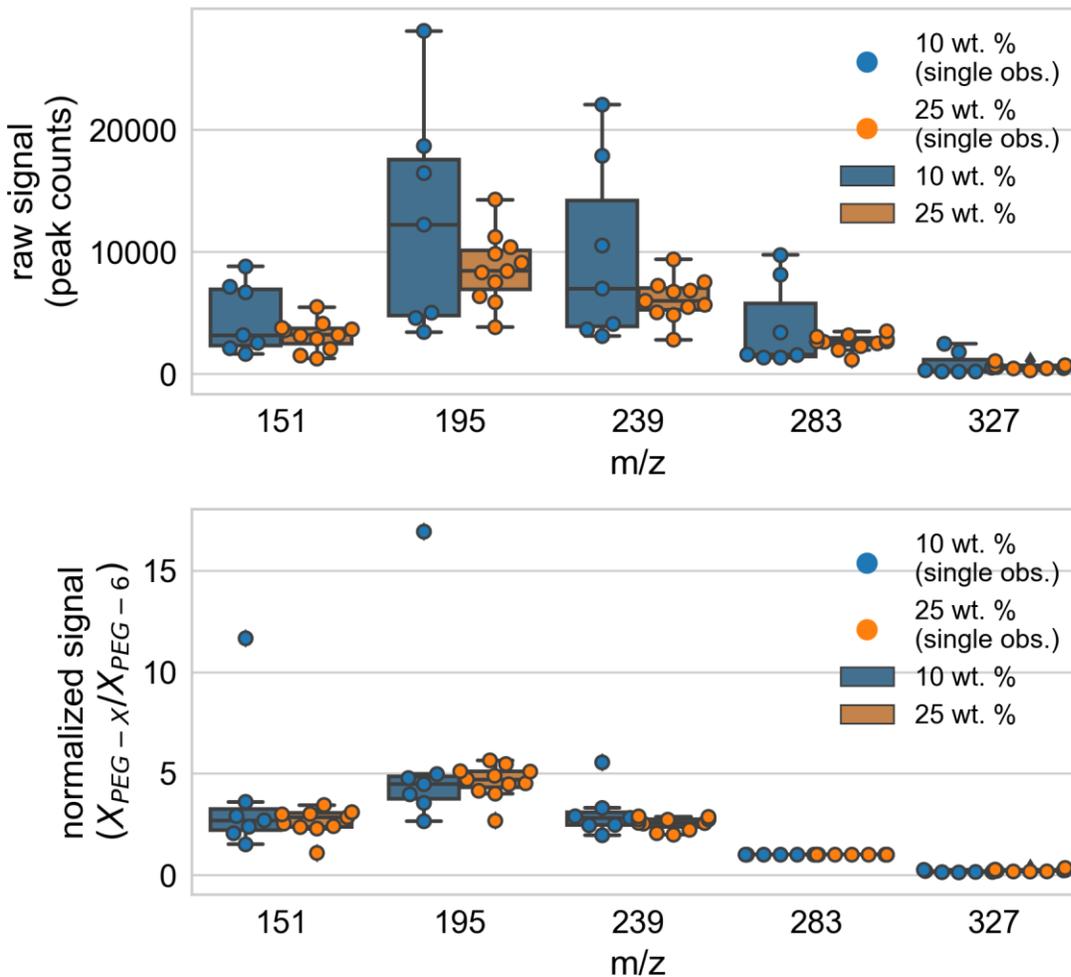
§ 3.4 (p. 10, line 13): "We investigated a number of possible factors contributing to the variability in signal. *Within the size range of particles analyzed during the evaporation experiments, variability in the particle diameter (approx. $\pm 10\%$), measured with the spring-point method, did not correlate to particle-to-particle variability in apparent evaporation rates, or to particle-to-particle variability in absolute signal. For two populations of PEG-200 particles with masses varying by a factor of approximately 2.5, higher variability in raw signal was observed for the smaller particles. In this data set the decreased particle-to-particle variability in normalized signal can also be readily observed (Fig. A1). From these analyses we conclude that though the particle-to-particle variability in raw signal may be affected by significant differences in particle mass, the variability in the normalized evaporation data was not explained by the variability in measured starting particle diameter.*"

Appendix A:

p. 13, line 29: "Appendix A: Characterization of mass spectrometer fragmentation, ~~and~~ sensitivity, and signal variability"

p. 13, line 30: "The appendix includes data on PEG mass spectral relative sensitivities (Table A1) and fragmentation patterns (Table A2). *The role of normalization and particle size on particle-to-particle mass spectrum signal variability was analyzed (Fig. A1). Mass spectra for a set of PEG-200 particles were considered: those for particles "immediately" ejected from the EDB after trapping (defined as within 6 minutes of introduction), and with spectra over the signal threshold (defined as at least 1000 counts in the m/z 283, PEG-6 channel). The particles were generated from two different solutions of PEG-200 in water: 10% and 25% by weight. After fast water evaporation, the weight fraction can be taken as proportional to the starting trapped particle mass. (A full set of spring-point diameter measurements are unavailable.) The particle-to-particle raw signal variability (Fig. A1, top) was less for droplets from the 25 wt. % mixture, but the normalized signal variability (Fig. A1, bottom) was similar for droplets from the two mixtures. In both cases, the variability in the normalized signal is smaller than the variability in the raw signal.*"

[...]



“Figure A1: Analysis of the role of normalization and particle size on particle-to-particle mass spectrum signal variability, comparing particles generated from solutions of 10 and 25 wt. % PEG-200. Top: particle-to-particle raw signal variability. Bottom: particle-to-particle normalized signal variability. Box-and-whisker plots are shown for each tracked m/z (corresponding to PEG-3 through PEG-7), with outliers defined as observations more than 1.5 times the interquartile range beyond the low and high quartiles. Individual observations are overlaid as points (distributed horizontally for clarity).”

One gets the sense that the absolute signal variability is much greater than the 20-30% normalized signal variation reported by the authors.

Yes, reducing the particle-to-particle variability in absolute signal is the reason we used a normalized signal, and we state this in the manuscript (§ 2.5, p. 6, line 22: "To account for particle-to-particle variability in MS signal, peaks were normalized to the PEG-6 parent ion signal at 283 m/z."). The figure we are adding to Appendix A will help give examples of the absolute and normalized signal variability (see above). We are continuing work to see if we

can reduce the amount of absolute signal variability, but we anticipate future experiments with this setup will continue to require an internal standard for quantification.

Furthermore, it seems that the PEG droplet size studied in this experiment represents a practical lower limit, since working with a smaller size would probably have led to an unacceptably high fraction of particle spectra being filtered out from further analysis.

It is true that with the setup described in the manuscript, it would become difficult to obtain sufficient signal in the mass spectra of smaller particles to quantify evaporation as we do here. However, we do not see this as a permanent limitation. We are working on improving the EDB-to-ionization transfer and the ionization source design so that smaller particles can be reliably quantified. We will expand on this point in the appropriate point in the Conclusion (§ 4, p. 12, line 15):

"Implementing an alternate ionization scheme could remove the limitation of only detecting molecules that are sufficiently volatile to vaporize quickly upon impact on the 220 °C platform. *Modification of the ionization scheme may also be necessary to obtain sufficient signal when working with smaller particles or analyte compounds present in smaller quantities.*"

Section 2.2. Spring point measurements were made with 18 um diameter PMMA spheres. Is it possible that the existence of doublets and/or larger aggregates of PMMA spheres could have influenced the results?

We will add the following to § 2.2 to explain why agglomerates did not influence the spring-point calibration (p. 4, line 25):

"The spring point of each sphere was measured for a number of different AC amplitude–frequency combinations, with a total of 22 spring point measurements over 4 different PMMA spheres. *We ruled out the possibility of doublets or larger aggregates by observation of the droplet behavior by eye. Agglomerates show distinct scattering intensity fluctuations because of Brownian rotational motion in the EDB, which are easily detected by observing the image of the particle. Additionally, if the spring point had been measured using an aggregate with mass twice that of a single sphere or greater, the value would have been clearly anomalous and discarded.*"

Section 3.2.1. "Particle" in line 13 of this page (fourth line of the section) should be plural.

Corrected.

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