Author Response to Anonymous Referee #3 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*).

A combination of electrodynamic trap and mass spectrometer has been described previously by (Dale et al., 1994), who used laser ablation to ionize the trapped particle. Please give a mention of this work in your review of analytical techniques.

Thank you for the reference. We have added a reference to another paper from the same laboratory and era, which does use laser ablation to ionize a particle trapped directly in a modified ion trap of a mass spectrometer: Yang et al., *Anal. Chem.* 1995, 67, 1021-1025. (In Dale et al., 1994, the particles were dropped into the ion trap and ablated without being trapped.) We will add to the Introduction (p. 2, line 8):

"Among other features, the BQT design lends itself to study of condensed-phase reactions, triggered by the coalescence of two droplets of differing composition with sub-millisecond mixing times. *Additionally, in a different laboratory a quadrupole ion trap mass spectrometer was modified to levitate individual micron-sized droplets, followed by reducing the trap pressure over 20 minutes to ~0.1 Pa, ablating the particle with a pulsed laser (532 nm), and collecting a mass spectrum using the same ion trap (Yang et al., 1995).*"

The possibility of studying the slow gas-phase chemical reactions in atmospheric aerosols is given as one of the motivations for this work. Aerosol particles, however, are much smaller in size (typically submicron) than the particles used in your work, so that trapping a particle in the EDB and transferring it into the ionization section might be very difficult. Could you discuss this issue in the outlook section? As a layman's suggestion, wouldn't it be possible to use a linear quadrupole trap to move a train of particles slowly through the reaction zone delivering them one by one into the ablation section coupled to the inlet of a mass spec? Such technique, though applied for optical particle characterization and not for mass spectrometry, has been recently described by (Sivaprakasam et al., 2017).

We agree that trapping a submicron atmospheric aerosol particle would require further development. However, we would like to clarify that the immediate primary motivation for this setup is to study atmospherically-relevant processes in laboratory-generated aerosol in the micron size range. The goal is not to mimic atmospheric aerosol in all details, but to perform lab experiments which allow isolation and measurement of certain properties or processes. We can then apply what we learn from those measurements to submicron particles, accounting for size-dependent factors such as surface-to-volume ratio or possible diffusion limitations through the particle.

Returning to the question of trapping submicron aerosol particles, the linear quadrupole geometry you propose is certainly one possible approach. Recent work by Thomas Leisner and colleagues has also used a linear quadrupole to trap ensembles of particles, in their case nanoparticles with radius as small as 2 nm (Duft et al., 2015). With much less material in each particle, the detection limitations for the mass spectrometer would also need to be assessed.

Reflecting this discussion, we will add the following paragraph to § 4.1 ("Future experiments", p. 12, line 27):

"These strengths make the EDB-MS a complimentary technique to existing experimental and modeling approaches.

Even using laboratory-generated aerosol particles with diameters on the order of 10 µm, results from future lab studies can be used to improve our understanding of submicron atmospheric aerosol particles. Physical and chemical constants, such as reaction rate constants and diffusion coefficients, are equally applicable to both laboratory and smaller atmospheric particles. The effect of other size-dependent factors, such as changing surface-to-volume ratio, radius-dependent mixing timescale of a viscous particle, or the Kelvin effect on growth of small nanoparticles, can be accounted for by calculation if the appropriate parameters are known. Trapping a submicron particle within the EDB-MS would require further development. One approach may be to transfer particles to the ionization region using a linear quadrupole geometry; this geometry has been used by other research groups (Duft et al., 2015; Jacobs et al., 2017; Sivaprakasam et al., 2017). Detection limitations for the mass spectrometer would also need to be assessed.

One class of future experiments [...]"

References

Duft, D., Nachbar, M., Eritt, M. and Leisner, T.: A linear trap for studying the interaction of nanoparticles with supersaturated vapors, Aerosol Sci. Tech., 49, 683–691, doi:10.1080/02786826.2015.1063583, 2015.

Jacobs, M. I., Davies, J. F., Lee, L., Davis, R. D., Houle, F. and Wilson, K. R.: Exploring chemistry in microcompartments using guided droplet collisions in a branched quadrupole trap coupled to a single droplet, paper spray mass spectrometer, Anal. Chem., accepted, doi:10.1021/acs.analchem.7b03704, 2017.

Sivaprakasam, V., Hart, M. B. and Eversole, J. D.: Surface enhanced Raman spectroscopy of individual suspended aerosol particles, The Journal of Physical Chemistry C, 121, 22326–22334, doi:10.1021/acs.jpcc.7b05310, 2017.

Yang, M., Dale, J. M., Whitten, W. B. and Ramsey, J. M.: Laser desorption mass spectrometry of a levitated single microparticle in a quadrupole ion trap, Anal. Chem., 67, 1021–1025, doi:10.1021/ac00102a001, 1995.