Interactive comment on "Real time analysis of insoluble particles in glacial ice using single particle mass spectrometry" by Matthew Osman et al.

Anonymous Referee #1

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Review to "Real time analysis of insoluble particles in glacial ice using single particle mass spectrometry" by Osman et al., AMTD 2017

Dear Anonymous Reviewer #1,

We thank you for your valuable feedback. We have reviewed all your comments/suggestions, and have attempted to address each to the best of our ability below. Please refer to italicized and indented portions for responses.

The manuscript by Osman and coworkers describes the application of a laser ablation single particle mass spectrometer on the analysis of particles in ice core samples. The authors describe the extraction of particles from the samples, the efficiency of particle transfer into the mass spectrometer and also attempt to perform a quantitative measurement of mass concentrations. The manuscript is well written and fits into the scope of AMT. Methods and results are clearly explained and presented. However, I have one major issue that is described below:

Major comments

While I do not have any concerns about the chemical analysis, which has been done by SPMS numerous times for atmospheric particles, I have serious problems with the mass concentration measurement:

C1) - The size dependent extraction efficiency curve was measured using PSL particles, a method that is called "external calibration" (referenced to Wendl et al., which is not an SPMS but an SP2 paper).

Since the SP2 remains the most common single particle, online methodology currently employed in ice core analyses, the experimental framework presented in Wendl et al. (2014) is viewed here to be a plausible surrogate for comparisons to our new SPMS-based single particle approach. Text has now been included in Sect. 2.3.4, making it explicit that the Wendl et al. (2014) "external calibration" approach is based on SP2 methods (Pg. 9 Lines 21-24):

"As defined by Wendl et al. (2014), an "external" calibration approach, as commonly employed in SP2-based measurements of refractory black carbon in glacial snow and ice, assumes that ε for a given monodisperse PSL standard scales with an unknown, morphologically/compositionally-heterogeneous and polydisperse, ice core sample."

Additionally, to provide a more direct comparison between SP2 and SPMS techniques, we have now incorporated a new section (3.1.1; Pg. 11-12 Lines 25-27, 1-23) entitled "Comparison of SPMS to SP2-based single particle methods in snow and ice".

C2) - The measured efficiencies are very low (highest values for 657 nm PSL particles are around 0.40%). This results in a very large correction factor needed to derive the mass concentration in the sample.

While we acknowledge this potential fallback, we point out that the relatively low extraction efficiency is largely a result of differences inherent to SP2 vs. PALMS transmission and measurement

capabilities, which have now been better contrasted/clarified in Section 3.1.1 (Pg. 12 Lines 12-22):

"More recent studies have achieved high nebulization efficiencies (~50%) up to ~2 μm using the CETAC Marin-5 pneumatic nebulizer (Teledyne CETAC Technologies, Ohaha, NE, USA; Mori et al., 2016; Katich et al., 2017). In this context, however, it is noted that achieving too high of an extraction efficiency could be disadvantageous for SPMS, should the number of particles reaching the SPMS inlet exceed that instrument's max transmission rate (~10 particles sec-1 for PALMS; Cziczo et al., 2006) where the limit is data writing and laser repetition rate. This does not affect SP2, which can more rapidly measure the incandescence of carbonaceous material passing through a continuous laser (i.e., 2-3 orders of magnitude higher), though with the cost of i) not delivering information on internal mixing state or ii) aerodynamic size (as opposed to black-carbon volume equivalent diameter). More efficient nebulization at relevant SPMS sizes, coupled to more rapid excimer lasers and data writing, would increase the data acquisition rate."

C3) - The efficiency is assumed to be independent of shape and composition. This is certainly an oversimplification.

We agree with the reviewer that this is indeed an important assumption underlying our methodology. We have now included text in 2.3.2 (Pg. 9 Lines 23-24) acknowledging the assumption more explicitly:

"... assumes that ε for a given monodisperse PSL standard scales with an unknown, morphologically and compositionally-heterogeneous and polydisperse, ice core sample."

We have additionally included the following text at the end of Sect. 3.2.4 encouraging future studies to explore these assumptions in greater detail (Pg. 17-18 Lines 25-29, 1-7):

"While our results show potential exists for using SPMS to determine insoluble mass concentrations of particles in snow and ice, they also identify areas where more work is needed before SPMS can be used as a quantitative tool. These include: i) executing multiple extraction efficiency (eq. 1) calculations as a function of particle class (in addition to size), (...)"

C4) - Drifts in nebulizer efficiency have not been considered.

Since only one sample (DS14-05) was measured for quantitative purposes, transmission of the 8.8e6 particles/cc solution was not tested between sample(s). We did, however, test whether systematic trends in nebulization drift could occur over the hour-long measurement period. This test was done by directing a particle-laden airflow (nebulized from the monodisperse, 746 nm PSL liquid standard: $m_{PSL}(D_p = 746 \text{ nm}) = 8.8\times10^6$ PSL particles cm^{-3}; Sect. 2.3.3), to an optical particle sizer (OPS; MesaLabs Bios DryCal 220), and performing continuous, one-second interval measurements over three separate ~1-hour long tests (i.e., the longest sample integration period in the manuscript). The nebulization efficiency (ε_{neb}) was calculated in this test as,

$$\varepsilon_{neb}\big(D_p = 746 \text{ nm}\big) = \frac{n_{OPS}(D_p=746\,nm)\cdot F_{flow}}{m_{PSL}(D_p=746\,nm)\cdot V_{neb}}$$

where n_{OPS} is the PSL number concentration measured by the OPS, and the flow rates F_{neb}, V_{neb} and, F_{wet} are as described in the main text. The long-term drifts in nebulization, calculated as the linear percent change over the hour-long measurement interval, were determined in the three tests to be 22%, 9.2%, and -33 % ($\Delta\varepsilon_{neb}/\Delta t = 0.18\cdot10^{-5}$ s^{-1}, $0.08\cdot10^{-5}$ s^{-1}, and $-0.30\cdot10^{-5}$ s^{-1}, respectively). Importantly, results of the three tests indicated that long-term drift direction was not systematic, as both negative and positive drift biases occurred over the one-hour nebulization periods (Fig. R1, shown below). It is thus reasonable to view the drift uncertainty as a simple spread about the hour-long mean of the three tests, in this case equating to $\varepsilon_{neb} = 0.068 \pm 0.013$ (1 s.d.), or ~18% relative uncertainty.

It is equally important to note that in our study, calculation of particle mass-concentration (eq. 4) does not explicitly incorporate estimates of ε_{neb}, but rather estimates of the extraction efficiency, ε (eq. 5), determined experimentally and independent of ε_{neb}. However, via eq. 6 (now included in the main text; see C5 below), ε is shown to be a function of ε_{neb} and transmission efficiency, ε_{trans}. Since past studies (e.g., Cziczo et al., 2006) have illustrated that PALMS transmission is relatively stable, we thus

take the uncertainty interval calculated for ε (~30% relative uncertainty at ε(Dp = 746 nm); eq. 5) to implicitly encapsulate uncertainties in nebulization efficiency.

The above information has been included as supplementary material, and the following sentence added to Sect. 3.2.4 (Pg. 16 Lines 23-26):

"Note that while no systematic trends in nebulization drift were found over either hour-long measurement period, short term fluctuations in nebulization could occur; for the present experiment, such fluctuations are assumed to be encapsulated as uncertainty about the extraction efficiency parameterization (eq. 5; see Supplementary Material for details)."

Overall, we agree with the reviewer that future mass-concentration applications using SPMS – especially those where multiple successive samples are measured for mass concentration – should implement regular standardized checks for performance drift between samples. Text has also been added to 3.2.4 making this latter suggestion explicit (Pg. 17-18 Lines 25-29, 1-7; refer to C2 above).
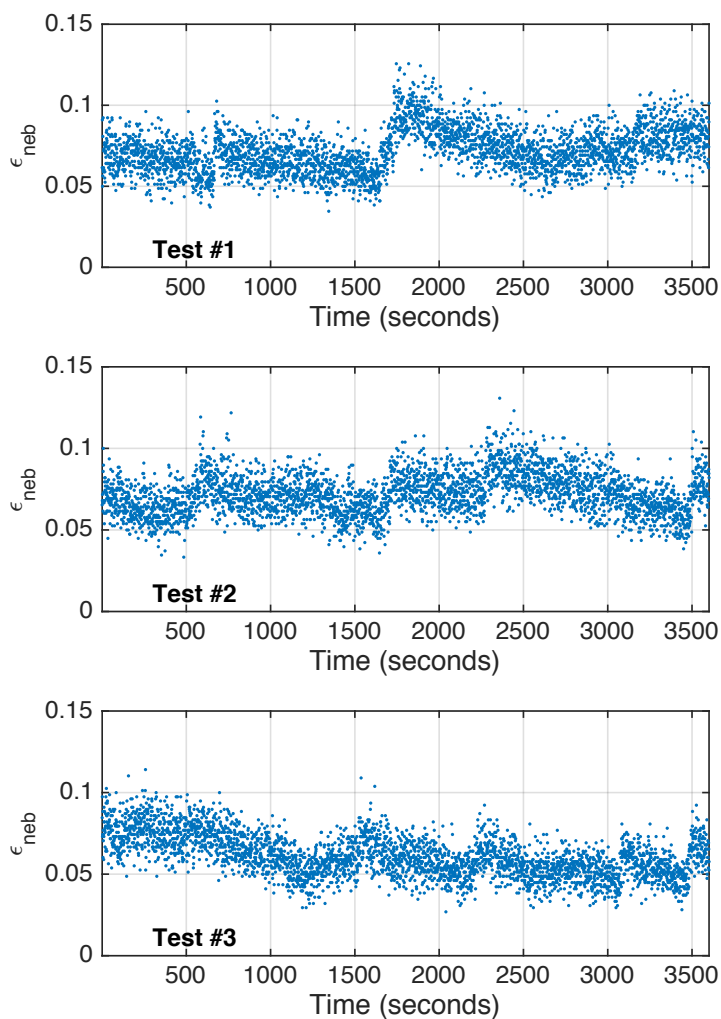

Fig. R1. Results of three separate nebulization drift tests.

C5) During the PSL calibration experiments, the authors used an OPS to monitor particle concentration and size to measure the transmission efficiency in to the PALMS (which was found

to be between 1 and – 16%). Why has this (or another method to measure size and number) not been done during the ice core sample analysis? By such, the transmission efficiency into the PALMS would have been measured using the real sample particles. Non-spherical shapes of the insoluble particles can certainly influence the transmission efficiency. Furthermore, methods exist to measure particle concentration in liquids. A comparison of the derived particle concentrations from the SPMS with such a reference measurement would have helped in validating the results. At least a determination of the mass concentration by filtering the solution and weighing the filter would have been possible, although here larger particle may dominate the total mass concentration. Without any comparison to an independent measurement of the same sample, the quantification of the results seems not reliable and overstretches the capabilities of an SPMS.

We thank the reviewer for his/her suggestions, each of which is valid. We note that PALMS transmission capabilities are well-characterized, as validated by this and past studies (details found in Cziczo et al. (2006; 2013), thus the largest uncertainty likely arises from nebulization effects, as addressed above. More generally, as to the reviewer's primary concerns concerning mass concentration measurements, we iterate that this study's primary goal was not to "oversell" the use of SPMS for conducting mass concentration measurements of particles in snow and ice, but rather was in attempting to illustrate the feasibility of – including highlighting current fallbacks inherent in and the potential for future improvements to – the method. We hope that future studies may improve upon this baseline study by implementing comparisons to alternate well-founded techniques for measuring particle concentration in liquid (e.g., Coulter Counter techniques, UHSAS). These sentiments and suggestions have now been noted at the end of 3.2.4 (Pg. 17-18 Lines 26-29, 1-8):

"While our results show potential exists for using SPMS to determine insoluble mass concentrations of particles in snow and ice, they also identify areas where more work is needed before SPMS can be used as a quantitative tool. These include:
(...)
iv) comparing SPMS-derived particle concentrations with results from alternate, well-founded high-precision instrumentation (e.g., an Ultra-High Sensitivity Aerosol Spectrometer (UHSAS; Droplet Measurement Technologies Inc., Boulder, CO), or Coulter Counter instrumentation)."

Minor comments:

Page 11, lines 1-3: How was determined that all water was evaporated?

In general, PALMS will not provide spectra for particles that are water-saturated (i.e., "quenched"). However, for low-to-moderate degrees of water-saturation, PALMS can distinguish between wet and dry particles via water-cluster peaks (m/z = 18) that are prominent in the particle spectra (Murphy and Thompson, 1995). Determination of adequate water-evaporation could thus be experimentally determined by increasing the dry-to-wet flow ratio until evidence of water-saturation was eliminated in the particle spectra. The following text was added to Sect. 2.3 (Pg.'s 6-7 Lines 26, 1-2) clarifying this point:

"As PALMS generally does not provide spectra for water-saturated particles (Cziczo et al., 2006), the atomized particles were then adjoined with the dry flow, dropping the relative humidity and evaporating residual condensed water, resulting in dry residual particles entering the PALMS inlet."

Figures of mass spectra in appendix: What is the method to select which mass peaks are labeled. Apparently not always the largest peaks? Are peaks unknown/not identified, e.g. in Fig. A1, lowest panel, around m/z 90? Additionally, minor tick marks and/or grid lines help the reader to determine the m/z number of a peak in the mass spectrum.

In general, all major peaks corresponding to known ionic fragments are labeled. Specific details for this identification process can be found in prior studies, particularly references noted in Sect. 2.1 of the main text (e.g., Murphy and Thompson, 1997a,b; Cziczo et al., 2013). Many of the large peaks not labeled correspond to organic particles, or, in this study's case, particles that have undergone severe post-aqueous processing. There presently remains ambiguity in organic fragment identification, as is

the case for Fig. A1 for m/z ~ 90. The following text has been added (Pg. 20, Lines 15-17):

"All major peaks corresponding to known ionic fragments have been labeled (see Murphy and Thompson, 1997 a, b; and Cziczo et al., 2013)."

Grid lines and x-axis minor ticks have now been added to the (now Appendix 2's) mass-spectra plots.

References:

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Cziczo, D. J., Thomson, D. S., Thompson, T. L., DeMott, P. J., Murphy, D. M: Particle analysis by laser mass spectrometry (PALMS) studies of ice nuclei and other low number density particles, Int. J. Mass Spectrometry, 258, 21-29. 2006.

Murphy, D. M., and Thomson, D. S.: Chemical composition of single aerosol particles at Idaho Hill: Positive ion measurements, J. Geophys. Res., 102, 6353-6368, doi:10.1029/96JD00858, 1997a.

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Murphy, D. M., and Thomson D. S.: Laser Ionization Mass Spectroscopy of Single Aerosol Particles, Aerosol Science and Technology, 22(3), 237-249, doi:10.1080/02786829408959743, 1995.