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

Anonymous Referee #2

Received and published: 19 July 2017

> *Dear Anonymous Reviewer #2,*
>
> *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.*

Referee Comments for Osman, M. et al., "Real time analysis of insoluble particles in glacial ice using single particle mass spectrometry"

General Comments

The authors implement a PALMS to successfully employ nebulizer+instrument techniques previously used by single particle soot photometers to make measurements of particle classification, size and concentration in ice core samples from Greenland. Though limited by a low particle transmission that is currently inherent to the PALMS instrument, the methodology still manages to result in new, interesting measurements that to my knowledge have not been realized before, making this a very worthy manuscript for publication after addressing some relatively minor concerns.

The results also provide substantial motivation to continue to push the transmission efficiency capabilities of the PALMS instrument, the results of which would make the methods used here a much more viable path towards measurement of particle concentrations and size distributions in ice cores. The presentation of the goals, setup, methodology and results are generally very clearly stated, with very few exceptions (notes below). Further, the manuscript seems to have been carefully prepared, as I struggled to find any typos, spelling errors or poor grammar. Below, I suggest some minor corrections to be addressed, including explanation of their monitoring of potential background contamination levels and system stability. Also, I suspect there may be an error in their calculation of nebulization efficiency (though it results in only a small change in the quoted number). Finally, I recommend more carefully explaining the differences in interpreting PALMS vs SP2 measurements of black carbon / soot.

Specific Comments

C1) Page 3, line 18: Also see Katich et al., 2017 (doi:10.1080/02786826.2017.1280597), which provides a lengthy closely-related discussion on aerosolizing particulate from snow and ice.

> *We thank you for pointing us to this recent study + discussion therein, which had been previously unknown to the authors; the reference for Katich et al., 2017 has now been included (Pg. 3 Line 19).*

C2) Page 7, line 5,6: Did the authors intersperse regular measurements of 'blanks' (i.e. ultra-pure water) to quantify the average background level of particulate seen by PALMS when using a 'clean' nebulization system? There is mention of looking for background from the stainless steel band saw (not what I'm concerned about here) and of sonicating the parts between samples. But I wonder if there is a quantification of average background levels due to any residual particulate in the nebulizer lines? How does this compare to signal levels? Negligible?

We did not systematically implement measurements of blanks between samples as the reviewer describes here. Our methodology was to flush the flow line continuously with an inert N_2 gas-flow (for ~15 min) between samples to remove residual particulates prior to the next measurement. To answer this point we now state the following in Sect. 2.3 (Pg. 7 Lines 8-9):

"Between runs, the nebulizer and sampling beaker were cleaned and sonicated for 15 minutes using ultrapure (Milli-Q; 18.2 MΩ) water, and the flow-line flushed continuously with the inert carrier gas."

We do acknowledge the utility of the reviewer's suggestion to regularly implement blanks between measurements and have also included the following in 3.2.4 (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), ii) incorporating regularized tests for drifts in SPMS extraction efficiency and employing "blank" tests between sample measurements in order to improve delineation to changes in background particulate levels, iii) achieving a greater number of particle measurements (either through improvements in particle extraction/PALMS transmission or longer sample integration times), and 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)."

C3) Page 8, line 19: Please clarify the phrase "rate of liquid nebulization"… same as rate at which liquid is fed to the nebulizer i.e. liquid uptake rate? Does this occur at a user controlled pump rate, or is it self-aspirating? If you have control over the pump rate, this could be another way to tweak the rate of particulate delivered to the PALMS inlet.

The "rate of liquid nebulization" is the average volumetric loss rate of the liquid sample during nebulization of the sample. This rate is indirectly user-controlled by setting the "wet" gas flow rate to the nebulizer (i.e., F_wet). However, while increasing the wet flow rate to the nebulizer could increase the rate of particulate delivered to the PALMS inlet, it was determined that water saturation (i.e., quenching) of the particles became problematic at much higher rates than that quoted in the manuscript (2 lpm). The following text has been added to Sect. 2.3.2 (Pg. 8, lines 23-24) to clarify:

"…V_{neb} is the rate of liquid nebulization (i.e., a prescribed volumetric loss rate of the sample, determined here using a scale; $4.4 \cdot 10^{-6} \pm 1.6 \cdot 10^{-6}$ mL sec^{-1})"

C4) Page 9, line 23: Agreed, the nebulization efficiency can drift over time, even substantially, depending on the solution being nebulized. Was this monitored by occasionally measuring transmission of the 8.8e6 particles/cc solution in between samples? If so, perhaps show a summary of nebulization stability in supplemental material?

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 nm) = $8.8x10^6$ 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,

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

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 % ($\Delta\varepsilon_{neb}/\Delta t$ = $0.18 \cdot 10^{-5}$ s^{-1}, $0.08 \cdot 10^{-5}$ s^{-1}, and $-0.30 \cdot 10^{-5}$ s^{-1}, respectively).

Importantly, results of the three tests indicated that 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 ε_{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* $\varepsilon(D_p$ *= 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 response).

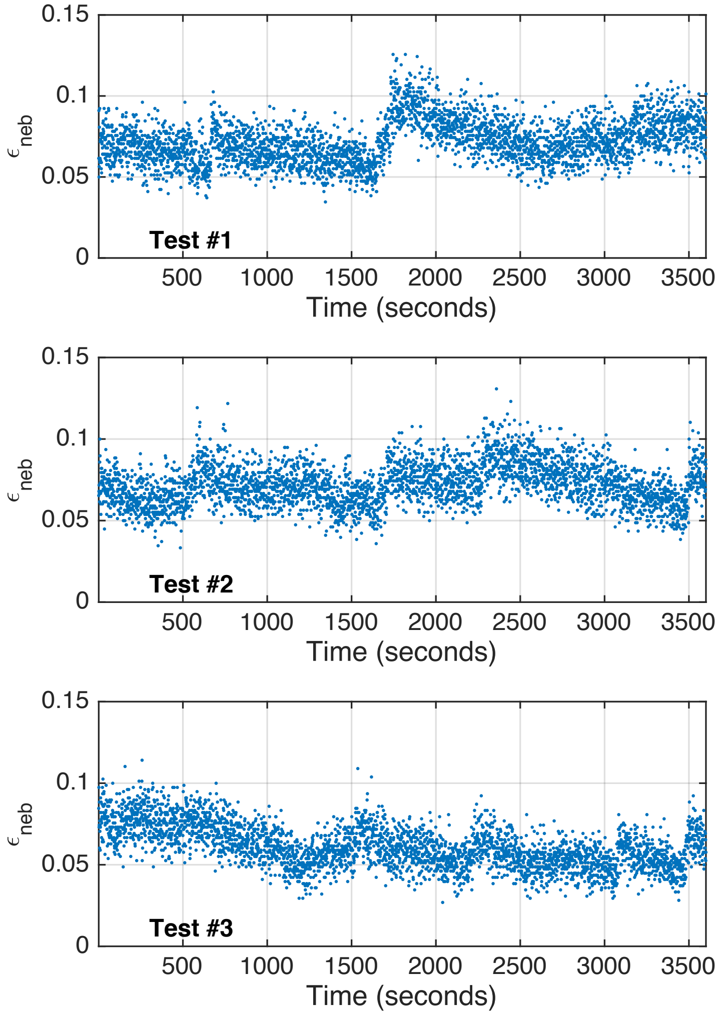

Fig. R1. Results of three separate nebulization drift tests.

C5) Page 11, line 6: The statement, "Scaling the efficiency curve by the ratio of excess-flow to the PALMS inlet flow", I believe should read "Scaling the efficiency curve by the ratio of TOTAL-flow to the PALMS inlet flow." Further, I don't think I agree with the calculation of the nebulization efficiency, where it is achieved simply by making the correction due to particle loss from low PALMS sample flow. I would argue the following: If a nebulizer's efficiency is defined as the ratio of 'the rate of particles emerging in aerosol from the nebulizer' (call it Raerosol = Naerosol/sec) to 'the rate of particles introduced to the nebulizer' (call it Rintroduced, which is known from your known PSL concentration and liquid uptake rate), then to know Naerosol, you have to work backwards from the number of particles that PALMS sees.

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For convenience, we have copy and pasted the aforementioned attached .pdf below:

__Page 11, line 6__: The statement, "Scaling the efficiency curve by the ratio of excess-flow to the PALMS inlet flow", I believe should read "Scaling the efficiency curve by the ratio of __TOTAL__-flow to the PALMS inlet flow."

Further, I don't think I agree with the calculation of the nebulization efficiency, where it is achieved simply by making the correction due to particle loss from low PALMS sample flow. I would argue the following: If a nebulizer's efficiency is defined as the ratio of 'the rate of particles emerging in aerosol from the nebulizer' (call it $R_{aerosol} = N_{aerosol}/sec$) to 'the rate of particles introduced to the nebulizer' (call it $R_{introduced}$, which is known from your known PSL concentration and liquid uptake rate), then to know $N_{aerosol}$, you have to work backwards from the number of particles that PALMS sees.

$$\varepsilon_{nebulization} = \frac{R_{aerosol}}{R_{introduced}} = \frac{N_{aerosol}/_{sec}}{R_{introduced}} = \frac{N_{aerosol}/_{sec}}{m_{psl} \cdot V_{neb}}$$

working backward from the number of particles need by PALMS…

$$\left(N_{aerosol}/_{sec}\right) = \underbrace{\left(\frac{N_{particles}\text{detected by PALMS}}{sec}\right)}_{(1)} \cdot \underbrace{\left(\frac{N_{particles}\text{introduced to PALMS}}{N_{particles}\text{detected by PALMS}}\right)}_{(2)} \cdot \underbrace{\left(\frac{F_{wet}+F_{dry}}{F_{inlet}}\right)}_{(3)} \underbrace{\left(\frac{F_{flow}}{F_{dry}}\right)}_{(4)}$$

where

(1) = f_{PALMS}

(2) = ε_{trans}

(3) = the correction introduced in the text

(4) = needed to correct for the fact that only 2/5 of the flow into PALMS has gone through the nebulizer (i.e. F_{dry} is just dilution air)

thus…

$$\varepsilon_{neb} = \varepsilon_{PSL} \cdot \frac{1}{\varepsilon_{trans}} \cdot \left(\frac{F_{wet}+F_{dry}}{F_{Dry}}\right) = \frac{\varepsilon_{PSL}}{\varepsilon_{trans}} \cdot \left(\frac{F_{flow}}{F_{Dry}}\right)$$

Plugging in some maximal numbers from figure 2, I get:

$$\varepsilon_{neb(max)} = \left(\frac{0.004}{0.15}\right) \cdot \left(\frac{5}{2}\right) \cong 6.7\%$$

it's not far off the quoted 4%, but as a matter of correctness, should be changed (assuming I've not erred).

*We thank the reviewer for sharing this concern, which was well articulated by the equations provided in his/her supplement. We agree with the reviewer's determination of the nebulization efficiency (void the incorporation of F_dry, which we believe should in fact be F_wet). However, we believe the reviewer's primary underlying concern (as it relates to miscalculation of the nebulization efficiency) was due primarily to a nomenclature error: we incorrectly stated "nebulization efficiency" as opposed to "extraction efficiency" in Sect 3.1. While 1) nebulization efficiency (i.e., Raerosol/Rintroduced, as defined by the reviewer) and 2) transmission efficiency can be viewed as two independent properties of the experimental set-up, both quantities are effectively encapsulated by 3) extraction efficiency (i.e., as per the reviewer e_psl = e_neb*e_trans*[F_wet/F_flow]); in this context, we believe our more-simplistic scaling correction remains valid.*

To avoid nomenclature confusion and to render our SPMS results more directly comparable to past studies (e.g., Schwarz et al., 2012, Ohata et al., 2013, Wendl et al., 2013, Katich et al., 2017), our simplistic scaling has been removed, and a revised discussion now including nebulization efficiency has been added to Sect. 3.1 (Pg. 11 Lines 18-24), including the addition of a similar derivation to that *of the reviewer's to Appendix 1 (Pg., 19-20, Lines, 22-27, 1-10):*

"A1. Calculating nebulization efficiency

Here, we derive the determination of nebulization efficiency (ε_{neb}; Sect. 3.1). We define ε_{neb} as the flow-weighted ratio of the rate of successfully nebulized particles per unit time relative to the (liquid) number concentration of particles introduced to the nebulizer, such that

$$\varepsilon_{neb} = \frac{f_{neb}(D_p)}{m_{PSL}(D_p) \cdot F_{neb}} \quad (A1)$$

where $m_{PSL}(D_p)$ and F_{neb} are as defined in eq. (1), and $f_{neb}(D_p)$ is the frequency of particles successfully nebulized (e.g., particles sec^{-1}) as a function of PSL diameter (D_p). In this case, $f_{neb}(D_p)$ is the quantity that must be solved for. We take

$$f_{neb}(D_p) = \frac{n_{PALMS}(D_p) \cdot F_{flow}}{\varepsilon_{trans}(D_p)} \cdot \left[\frac{F_{flow}}{F_{wet}}\right] \quad (A2)$$

such that the scalar quantity $\left[\frac{F_{flow}}{F_{wet}}\right]$ acts as a correction for the flow balance of particles actually passing through the nebulizer (Figure 1) and $\varepsilon_{trans}(D_p)$ corrects for the size-dependent particle transmission of PALMS. Note that $n_{PALMS}(D_p)$ and F_{flow} are as previously defined in eq. (1). Plugging eq. (A2) into (A1), and via relation to eq. (1),

$$\varepsilon_{neb} = \frac{\varepsilon(D_p)}{\varepsilon_{trans}(D_p)} \cdot \left[\frac{F_{flow}}{F_{wet}}\right] \quad (A3)$$

as defined in eq. (6)."

C6) Page 16, line 6: Regarding the 0.8 g/cm3 density used for soot… What density are you referring to? Void free rBC? All recent literature that I know of uses either 2.0 g/cm3 (a bit of an old number) or 1.8 g/cm3, so maybe this is a typo, or maybe you have actually used the wrong number, or maybe you are referring to a density that isn't clarified. Please comment…

Assuming general compositional similarity between BC and soot, we used an effective soot density value of 0.8 g/cm^3 following the experimental work of Moteki and Kondo (2010) and Kiselev et al. (2010), and as implemented by Schwarz et al. (2012). We have therefore retained 0.8 g/cm^3, though have clarified that this is indeed an effective density value (Pg. 16, line 18-19).

C7) Figure 4: It is important to note somewhere that the soot size distributions here are not directly comparable to typical rBC size distributions shown in literature that are measured via incandescence, i.e. SP2 measurements. My understanding is that PALMS will only measure the size of the entire soot-containing particle (via a scattered-light signal), which includes any 'coating' that is combined with the BC particle, and is not a measurement of the 'core' refractory BC mass. On the other hand, SP2 measurements will separate the rBC core mass (or volume-equivalent-diameter, VED) from the coating associated with an individual rBC particle. This rBC core VED distribution is what is typically shown in literature. So one could not compare the soot distributions shown here to, say, Schwarz et al. 2013 ("Black Carbon Aerosol Size in Snow"). A slightly expanded discussion on the interpretation of SP2 vs PALMS measurements of soot/rBC is recommended.

We thank the reviewer for this valuable suggestion, and the following discussion was included at the end of Sect. 3.2.4 (Pg. 17-18 Lines 13-24):

"There are notable inherent differences between SPMS- and SP2-derived soot size distribution determinations, however. Namely, whereas SP2 can differentiate the volume-equivalent diameter of refractory soot-components in compositionally-heterogeneous particles (Schwarz et al., 2012), our SPMS approach presumes a particle to be comprised wholly of soot if its mass-spectrum is classified as such. Thus, depending upon the morphology, internal mixing state, and ionization potential of the analyzed soot particles, SPMS may be subject to positive size distribution biases (Fig. 4)."

Technical Corrections

Page 3, line 15: ‘Schwartz’ should be Schwarz.

Typo has now been corrected (Pg. 3, line 15).

References*:*

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.

Katich, J. M., Perring, A. E., and Schwarz, J. P.: Optimized detection of particulates from liquid samples in the aerosol phase: Focus on black carbon, Aerosol Science and Technology, 51:5, 543-553, doi: 10.1080/02786826.2017.1280597, 2017.

Kiselev, A., Wennrich, C., Stratmann, F., Wex, H., Henning, S., Mentel, T. F., Kiendler‐Scharr, A., Schneider, J., Walter, S., and Lieberwirth, I.: Morphological characterization of soot aerosol particles during LACIS Experiment in November (LExNo), J. Geophys. Res., 115, D11204, doi:10.1029/2009JD012635, 2010.

Ohata, S., Moteki, N., Schwarz, J., Fahey, D., and Kondo, Y.: Evaluation of a Method to Measure Black Carbon Particles Suspended in Rainwater and Snow Samples, Aerosol Sci. Technol., 47, 1073–1082, doi:10.1080/02786826.2013.824067, 2013.

Schwarz, J. P., Doherty, S. J., Li, F., Ruggiero, S. T., Tanner, C. E., Perring, A. E., Gao, R. S., and Fahey, D. W.: Assessing Single Particle Soot Photometer and Integrating Sphere/Integrating Sandwich Spectrophotometer measurement techniques for quantifying black carbon concentration in snow, Atmos. Meas. Tech., 5, 2581-2592, doi:10.5194/amt-5-2581-2012, 2012.

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