Interactive comment on "A method for sizing submicrometer particles in air collected on formvar films and imaged by scanning electron microscopy" by E. Hamacher-Barth et al.

Anonymous Referee #1
Received and published: 13 August 2013

This study presents a method to measure the size of submicrometer atmospheric particles collected on the copper grids with formvar film using SEM. Using secondary electrons emitted from the particles when interact with electron beam at low voltage, the authors established a method to quantify the size distribution of atmospheric particles collected on the TEM grids by an electrostatic precipitator. The authors use polystyrene latex spheres for calibration and use measurements of size distribution by TDMPS for comparison with two particle samples collected during ASCOS. Furthermore, the authors stated that the determined size and morphology of particles can be related to transformation processes. Overall, this is a well-written paper, easy to follow and read. The subject of this paper is to provide a useful technique to obtain statistical information for off-line particle measurements by electron microscopy with a reasonable instrumental time. It is important and appropriated for publication in this special issue. However, I have a main concern about the novelty of this method. The automated analysis of submicron particles by computer controlled SEM has been established in the last decade which the authors might have also noticed (for example, Poelt et al., 2002, Scanning vol. 24, 92-100). What are the improvements as compared to the currently available methods? The authors should elaborate and demonstrate the significant improvements of this method. Thus, I would suggest for publication as a technical note after revision.

Major comments:

1, as stated above, I suggest the authors demonstrate clearly the advantages or improvements of this method. A literature discussion of previous methods or studies on automated methods based on SEM is also needed

The method we present here is not an automated method based on SEM. Therefore it did not seem appropriate to include a literature discussion of automated SEM imaging.

The following statement was added to the manuscript (chap. 1, Introduction) for clarification:

"Microscopic methods, however, are tedious and time consuming and big progress has been made to develop automated scanning methods in the submicron size range (Poelt et al., 2002; Ocker, B., 1995). But these automated methods require a highly plain substrate and sufficiently good contrast between the aerosol particles and their background (Poelt et al., 2002). We therefore scanned the aerosol samples manually to ensure that aerosol particles are imaged over all size ranges without any disturbances by stigmatism or defocus."

2, As for some particles, such as organic dominated particles, these won't yield many secondary electrons, especially using low accelerating voltages and beam currents similar to these used in this study. This may cause significant underestimation of the size and number of particles for particles less than 50 nm.

By using Polystyrene (PS) spheres we showed that in organic material a sufficiently high number of secondary electrons is generated and produces a signal that results in an image which represents the particles at an appropriate size. PS spheres with diameters of 20, 40 and 60 nm and larger were imaged and a standard deviation for sizing of the spheres was in a range from 18% for the 20 nm PS spheres down to 7.3% for the 60 nm spheres (see table 1 of the manuscript). It has to be noticed that for the 20 nm and 40 nm PS spheres the manufactuerer used another technique rather than electron microscopy (dynamic light scattering) to determine the size particles.

Furthermore the good agreement of the SEM sizing with the TDMPS measurements especially at

diameters below 50 nm (see fig. 9 and 10) demonstrates that size and number of particles were determined with sufficient accuracy.

Also, for these small particles, it is truly hard to get stigmatism right when imaging the particles that may contribute the error in circularity and elongation determination.

We corrected frequently for stigmatism before images of particles were taken. A statement was added to chap. 2.2 Grid screening protocol: *"Focus and stigmatism were controlled and corrected frequently before the particles were imaged."*

Why do you measure the size distribution on particles smaller than 100 nm using SEM when you have in-situ, real time, measurements by TDMPS?

The purpose of our method is the characterization of individual particles in terms of size and morphology. This is only possible with SEM, where individual particles can be imaged. TDMPS measures size resolved particle number concentrations without any information on size and morphology of individual particles.

The morphology of the particles below 50 nm may not change from 20 to 50 nm. It will be more informative to provide size resolved morphological parameters for the sample A and B (Table 2) similar to Table 1.

Bigg and Leck (2001) observed aerosol particles down to 10 nm diameter with TEM. These aereosol particles showed very distinct and different morphologies. We thus had to assume that the aerosol particles collected under the ASCOS expedition show a similar variety in morphology.

Bigg, E.K. and Leck, C.: Properties of the aerosol over the central Arctic Ocean, J. Geophys. Res. 106:D23, 32101-32109, 2001.

3, In the conclusion, lines 20-24, Page 5424, and related discussions in the text, the authors stated that "the latter has shown to be very useful in providing information on possible aerosol transformation processes: : :". I agreed in part of this statement, the size distribution and morphology of particle can provide some information for the aging processes. But, more careful evaluations should be discussed to draw further conclusions, such as lines 20-27, page 5421.

The focus of the article is the description of the method and to demonstrate its potential (see page chap.1, Introduction, the last two paragraphs). In a subsequent article which is in preparation we will focus on the impact of seasonal and meteorological conditions on aging/transformation processes of the aerosol particles.

In this study, the authors may need to discussion on the effects of sampling (coalescences and impaction of particles on the TEM grids) and the nature of particles (liquid, solid, or viscous) on the size distribution and morphology observed by SEM (discussion in page 5421, lines 14-20).

We discussed the effect of impaction for HP in chap. 5.1, *"Halo particles"* , and impaction of GP in the same chapter in *"Gel particles*".

In addition, without further evidences, such as X-ray analysis (composition), how could you confirm that the microgel led to the size differences in sample A and B?

We concluded that the microgel and the halo particles cause the shifts of the accumulation mode compared to the TDMPS measurements because these types of particles appear only in the accumulation mode (see fig. 9 and 10). Furthermore the microgel particles are characterized by partly very poorly contrasting material (see chap. 6.1, *"Gel particles"*) and the satellites of the halo particles are often small and contrast very weakly (see chap. 6.1, *"Halo particles"*). This might give rise to an underestimation of the size of gel and halo particles and cause the observed shift of the accumulation mode peak to smaller particle diameters in the SEM derived size distributions compared to TDMPS measurements (see fig. 9 and 10). Single particles on the other hand are contrasting sharply and are easy to separate from the background (see chap. 6.1, *"Single particles"*). This results in a good agreement of the Aitken mode peak in size distributions from SEM and TDMPS as they are the only type of particles that appears in the Aitken mode.

Minor comments:

Page 5402, line 4, I suggest "The method allows the observation of submicrometer particles down to 20 nm in diameter collected on the substrates." Or similar statements that somehow show that you can detect very small particles.

The following statement was added: "*The method allows the observation of submicrometer particles down to 20 nm diameter*."

Page 5402, line 25, how about the particles serving as ice nuclei, which could be important to mixed phase clouds in polar regions. I suggest add few sentences on this implication.

We added the following statement: *"Furthermore aerosols serve as a source of ice nuclei and thereby contribute to the formation of mixed phase clouds (McFarquhar et al., 2013) which are frequently observed not only in the Arctic but also at lower latitudes (Shupe et al., 2008)."* to chap. 1, Introduction, lines 10-12.

Page 5405, line 2, should be "(SEM)"

This has been corrected.

Page 5405, lines 22-23, are the images token in automated mode? If yes, how do you make sure that when move to different grids, it is still on focus and with good contrast and brightness settings. These are crucial for particles smaller than 100 nm. In this section, I suggest the authors add few sentences how to obtain the representative particle population because it really depends how the particles were collected and distributed on the grids.

The statement *"Following the diagonals of the grid accounted for inhomogeneous particle distribution across the grid and aimed to image a representative particle distribution*" was added, see chapter 2.2.

Page 5406 lines 24-25, why use 40%?

We added the following statement to the manuscript: *"This threshold was chosen subjectively with respect to the often weakly contrasting particles; it was determined manually by comparing results from threshold values between 5% and 50%."*; see chapter 2.3.1.

Page 5413-5414, I feel that the main part of this section is redundant and can be shortened. The authors should keep this section short and relate it to the focus of this paper.

The chapter has been shortened.

Page 5413, line 22, "OOne" should be "One".

Thank you for pointing out this spelling mistake!

Page 5415, line 7, the Figs.13 and 14 appear here prior to Figs 9-12, it seems a little bit strange. I suggest the authors change the order of the figures or move this part of discussion in the later sections.

Sorry for the confusion, we corrected the numbering of the figure.

Page 5416, line 22, "undergoe" should be "undergo"?

Thank you!

Page 5417, lines 1-14, it is not very clear to me how the circularity and elongation were determined for halo particles. Did you only consider the core particle?

We determined the morphological parameters for the core particles of the halo particles; a corresponding sentence has been added in chap. 5.1, *"Halo particles"*: *"But the satellite particles are small and contrast very weakly. Thus they are difficult to capture with image processing and the determination of morphological parameters therefore was restricted to the core particles."*

Page 5432, as discussed above, it may be useful to calculate these parameters as a function of size, for example, in few groups, below 50, between 50 and 100, and above 100 nm?

A more detailed analysis of the morphological parameters as a function of size will be presented in a subsequent article which is in preparation.

Also indicate the particle numbers analyzed for each group.

The number of particles were added for each particle type in Table 2 (see below).

Table 2: Morphological parameters elongation and circularity with size ranges and number of particles for the observed particle types in Samples A and B.

Single particles (SP)				
	Number of particles	**Size range**	**Elongation**	**Circularity**
Sample A	310	30 – 300 nm	0.334 ± 0.08	0.845 ± 0.07
Sample B	307	30 – 300 nm	0.176 ± 0.090	0.670 ± 0.209
Halo particles (HP)				
	Number of particles	**Size range**	**Elongation**	**Circularity**
Sample A	19	116–227 nm	0.14 ± 0.067	0.830 ± 0.08
Sample B	23	51–233 nm	0.090 ± 0.05	0.845 ± 0.067
Gel particles (GP)				
	Number of particles	**Size range**	**Elongation**	**Circularity**
Sample A	36	70 – 322 nm	0.639 ± 0.077	0.728 ± 0.142
Sample B	32	70 – 532 nm	0.212 ± 0.089	0.165 ± 0.072

Pages 5445-5446, I suggest change the font size for the labels and x,y axsis, make it larger.

Thank for pointing this out, we changed the size for the labels.