

Interactive comment on “Intercomparison of air ion spectrometers: a basis for data interpretation”

by S. Gagné et al.

Anonymous Referee #1

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General Comment: The authors compare an impressive number of (N)AIS. No other research group in the world would be able to carry out the experiments performed in this paper, which makes this study original and definitely deserve to be published in this journal.

First of all, the authors would like to thank the referees for their constructive comments. We believe that the changes generated by these comments make the manuscript easier to understand.

Specific Comments: Line 156: Assuming that the corona charger is not 100% efficient there should still remain electrically neutral particles; therefore, it seems inappropriate to state "particle-free" air. Also, it is not clear how the offset measurements are done. Is the classifying voltage applied during the offset measurements? Is the offset current affected by the presence of the classifying voltage?

We modified the section regarding the offset operation mode of the ion spectrometer. The unipolar charger is not 100% efficient in charging the particles and, therefore, the charger together with an electro-filter cannot provide the system with totally particle-free air. However, this is not a key factor for the offset measurements, as the ion spectrometer measures only the charged particles, and these particles are charged to the opposite polarity (or neutralized) compared to the polarity of particles classified and measured by the mobility spectrometer. So, these particles do not affect the offset measurements. For example in the negative DMA, most of the negatively charged particles will either recombine with the positively charged particles generated in the unipolar charger or will be filtered out in the electrical filter. We have changed the text to:

“[...] and the charged particles are partly removed with an electric filter. During this operation mode, the electric field in the DMA is the same as for the other modes. This procedure allows for the measurement of air free of positively or negatively charged particles (for the positive or negative DMAs, resp.) and thus the zero drift of the electrometers can be assessed as well as the RMS noise and noise due to parasitic currents.”

Line 174: It is not clear how the offset current measurement is done in the measurement protocol of the NAIS. Reader would think of two potential methods. One method is to create ion & particle-free air and apply classifying voltage and measure the offset current, which is the type of experiment performed in this paper. Another method is to apply zero classifying voltage and measure the offset current.

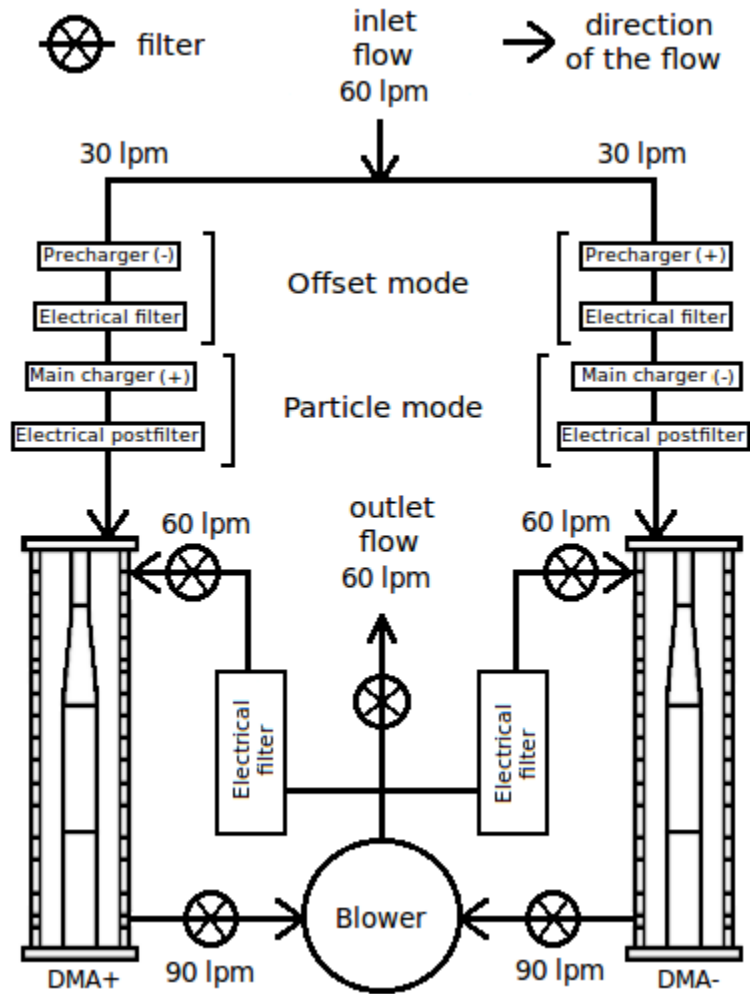
Here, the word “background” has been changed to “offset”. “Background” refers to the experiment presented here in Fig. 5 and “offset” refers to the offset operation mode of the ion spectrometers.

We added more information to the description of the offset operation mode in section 2.1 in order to answer this question. The offset mode indeed requires that the classifying voltage is applied to the mobility analyzer while the sample should be mostly ion-free. Alternative methods to apply zero classifying voltage is not applicable because it does not enable to take into account all possible parasitic currents.

Line 216-220: I believe that a schematic for the experimental setup is needed. It is hard to understand how these 5-flow system works.

We have added a schematic figure of a NAIS (Fig. 1). It should improve the understanding of the flows and the understanding of the different modes, including the offset mode.

Line 236: Was filtered air free of ions as well? If any ions remain in the filtered air they should affect the background measurements.



The authors realize the need for a figure describing the experimental setups, and it has been included to the manuscript (Fig. 2). The dilution air was indeed filtered, and we assume that commercially available filters provide particle-free air, regardless of them being neutral or charged.

As discussed above, we think that the experimental setups are now, after adding two figures, substantially better described.

Line 244: The phrase “ion-spectrometer DMA transfer function” is a confusing term. It is better to mention ion spectrometer transfer function. I believe that the author is not trying to evaluate the transfer function of a system consisting of DMA and ion spectrometer in series since the author assumes that the DMA generates monodisperse particles. If I were to be the author of this paper I would not to use the word DMA unless I am referring to the DMA as the monodisperse aerosol generator.

The authors fully agree with the referee. The phrase in this section was confusing and the mention to the ion spectrometer's own DMA was removed: “ion spectrometer transfer function”. However, as the ion spectrometers do have differential mobility analyzers of their own, the abbreviation DMA can still be used to describe the DMA parts of the ion spectrometers, the DMPS, or the DMAs used as monodisperse particle generators.

Line 326-331: Authors should state at the beginning of the paragraph that the Ion-DMPS was used as a reference for the measured charged fraction. The difference between charge ratio and charged fraction are not clearly explained.

We added the following text into the manuscript:

[...] This instrument was used as a reference instrument to compare the charged fraction, the fraction of particles that are charged in the particle distribution. The Ion-DMPS is designed to measure the charge ratio: the ratio of the ambient, “naturally” charged particle concentration to the neutralized (electrical bipolar steady-state) ion concentration. This quantity is equivalent to the ratio of the ambient charged fraction to the neutralized charged fraction. The NAIS measures the charged fraction: the ratio of the ion concentration to the total particle concentration. The neutralized charged fraction in the bipolar steady-state is known (Wiedensohler, 1988) so the charged fraction at ambient can be calculated from the Ion-DMPS charge ratio and compared to the charged fraction derived with the NAISs.[...]

Line 349-354: Although the turbulence causes ions to land onto wrong mobility channel the ion deposition rate should be conserved. Equivalently, although the width of the transfer function is broader and extra signal is present at the tail, the area under the transfer function should be conserved. For this reason the suggested reasoning for the increased total concentration sounds inconsistent. In addition, it might be a bit careless to use the word “background” in this paragraph because authors mention in line 174 that offset (or background) is already subtracted from the signals of a sample aerosol.

The authors would like to bring to the referee's attention that the concentration peaks presented in Fig. 1 (now Fig. 3) are normalized, i.e. the area under the curve is one. The deposition rate can still be conserved, this figure only points out that the peak is broader.

To avoid confusion, we changed “a small background” into “small concentrations”.

Line 382-385 & Line 388-389: It is hard to understand these reasoning. If the reference detector is measuring concentration at the DMA exit under the same flow settings regardless of the DMA type why the difference observed in Figure 2 (middle row & center column and middle row & right column) are affected by concentration and losses? One source of this confusion is the insufficient description of the experimental setup.

The concentrations of the reference instruments, the electrometers and the CPC, were all corrected

for losses based on the tube length and diameter, and the flow in the tube. The flow settings were different for both setups: the Hauke-DMA had an aerosol flow 4 lpm whereas the HDMA had an aerosol flow around 10 lpm (it should now be clearer from Fig. 2). Due to different flow rates and concentrations in the two calibration setups, the losses were different, and so were the corrections. Another possible source for this discrepancy might be the difference in the mixing of flows in both setups.

"This may be explained by that, at small sizes, the transfer function of the Hauke DMA is wider and the concentration of silver particles available is smaller. Thus the losses (and corrections) are more important in the Hauke setup than in the HDMA setup."

Line 390-392: I believe that the background measurement of the AIS during the actual atmospheric aerosol sampling is performed by applying HV to the ESP installed at AIS inlet, not by sending ion & particle free air into the inlet as it was done in this experiment. Potential user of the AIS would like to know whether the expected background level measured in this study well represent the expected values during the actual atmospheric aerosol sampling.

As we explain better now, the offset measurements of the NAIS are made with air free of ions of the measured polarity. The ESP would only remove charged particles, and could be used to measure the background in ion mode. However, in our case, a zero voltage was applied to the DMA so that no particles (charged or neutral) sampled in the NAIS.

The point of such an experiment was to demonstrate that when measuring in a very clean environment (e.g. Antarctica), the background does not disappear despite subtracting the offset measurements of the NAIS.

Line 417-418: Since the background level is significant, as commented previously, it is important to state how the background measurement is performed and accounted in the inversion procedure of the (N)AIS. Kulmala et al (2007, Science) used NAIS in their field measurements and concluded in the abstract "A pool of numerous neutral clusters in the sub-3 nanometer size range is continuously present". Careful reader of this manuscript may wonder whether Helsinki group checked that the NAIS inversion procedure properly subtracted the background level due to corona ions from the values measured during field sampling before Helsinki group proved the presence of the thermodynamically stable neutral clusters in Kulmala et al (2007, Science).

This question is addressed to the authors of the paper Kulmala et al (2007, Science) regarding the results given in that paper. As a result of current study we can only state the following. Figure 3 shows that the NAISs detect <2 nm particles at the right mobility and that the background concentration is rather negligible compared to the peak concentration. Thus, we do not think that our results could explain the detection of all measured neutral clusters. However, we encourage the authors of the Kulmala et al. (2007) paper to answer to this question in their own name.

Kulmala, M., Riipinen, I., Sipilä, M., Manninen, H., Petäjä, T., Junninen H., Dal Maso, M., Mordas, G., Mirme, A., Vana, M., Hirsikko, A., Laakso, L., Harrison, R. M., Hanson, I., Leung, C., Lehtinen, K. E. J., and Kerminen, V.-M.: Toward Direct Measurement of Atmospheric Nucleation, Science, 318, 89–92, doi:10.1126/science.1144124, 2007.

Line 421-424: Careful reader may wonder whether the Fuchs surface area of the sampled atmospheric aerosol large enough to deplete a significant fraction of the corona ions within the residence time of the charging region or not.

As we explain in lines 421-424, the corona ions are attached onto the particles. Many corona ions are produced ($\sim 10^6 \text{ cm}^{-3}$) and it is very likely that they do not all attach to a particle. Also, the corona current as well as voltage, recorded automatically by the measuring program, do not show any deficit

of corona ions during high aerosol load. The corona current in chargers is adjusted automatically by a feedback circuit. The concentration was selected by device designers to maintain the product of ion concentration and residence time ($n \cdot t$) high enough to produce a quasi-stationary charge distribution on aerosol particles. We have modified one sentence in order to underline that not all the corona ions are depleted, although we cannot say what fraction.

*“When there are particles in the sample air, **part of** the corona ions charge the particles and do not contribute to the background anymore.”*

Figure 2 It is good to add somewhere in the caption that the test particle is silver for the results shown in this figure.

We added “All the points in this figures were obtained from calibration with silver particles.” at the end of the caption”.

It is difficult to understand how the measurements were performed to obtain the results in bottom row and left column of Figure 2. Were the charged particles once neutralized then charged again by NAIS or ANAIS? One source of this confusion is the lack of experimental schematic in this paper.

A figure of the experimental setup has been added. A neutralized particle population was sent to the (A)NAIS which was measuring in particle operation mode. In the particle operation mode, the particle are indeed charged again by the (A)NAIS's own corona chargers (see Fig. 2).