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Atmospheric
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Discussions

Interactive comment on "Results of the first air ion spectrometer calibration and intercomparison workshop" *by* E. Asmi et al.

Anonymous Referee #1

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General comments

This article is important and necessary as it provides an evaluation of the (N)AIS performances, an instrument which is increasingly used and difficult to calibrate for small entities such as cluster ions. I recommend publication after a few changes are made, and some specific questions answered. Overall, the article would benefit of synthetic and clear quantified conclusions at each stage. As a result of such an intercomparison, I would expect an evaluation of the sizing accuracy (+ or -X nm or X%) and its variability among the different AIS (+or- Y nm or %) first as an average and then for given size ranges and for given concentration ranges. The same is expected regarding the ability of the (N)AIS to retrieve the total concentrations for a given size range and concentration range.

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Specific comments

Abstract

The authors should homogenize the paper (and the abstract)regarding the (N)AIS accuracy in mobility detection for negative and posotive polarities: in the abstract the accuracy is mentioned to be best for the positive ions, while in the conclusion it is claimed to be best for the negative polarity. In the heart of the paper, section 5.1 seem to indicate positive while section 5.2 mentions negative. Can the observed differences in the conclusions of the different parts of the paper explained?

The abstract should be more quantitative and the authors should precise differences or similarities with explicit numbers. For ex.: "Differences between the (N)AISs were small" is a subjective statement.

1. Introduction

I would suggest a change in the structure, by starting the introduction with the broad concerns and closing down to the AIS measurements (exchanging the paragraph page 17259 lines 20 to page 17260 line 14 with the first two paragraphs of the introduction).

2. Ion spectrometers 2.1. Air Ion spectrometer page 17262, line 13: "they are further charged using an unipolar corona charger..";, I suggest using "further balanced" or "neutralized" instead.

3. Instruments for calibration of the ion spectrometers 3.1 High resolution DMAs DMAs are later used for calibrating the mobility detection accuracy of the (N)AISs. Hence, the main features which should be described here are not only their mobility resolution but also their precision (how were they themselves calibrated against mobility standards associated to mass spectrometers, how stable are these calibrations? Are they dependant of relative humidity, precision on the flowrate measurements? Precision on the voltage?).

3.2. Mobility standards In general, I do not understand why the mobility standards were

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not directly used for calibrating the (N)AISs, without using selecting DMA at least for positive mobilities. If they are singly charged, monomobile, while using an additional selecting device? It seem to me that the advantage of using well-known sized standard is lost by using the same set up than the one used for silver polydispered aerosols. Page 17264 Line 7; I suggest using "chosen" instead of "selected" which is confusing

4. Methods Same remark as in 3.2.: why not measuring the electrospray directly with the (N)AIS. (N)AIS spectra were hence integrated, or averaged over the whole DMA scanning time? How long did a DMA scanning time was?

Page 17265; "the sample flow was diluted with an additional clean pressurized air.." what was the effect of dilution? Was it enhanced in order to evaluate possible artefacts linked to the additional of extra air (recombination, drying)? Was the dilution air cluster-clean? How were blank levels?

What was the relative humidity inside the system?

4.4 Hauke-DMA silver calibration It is not very clear to me why this paragraph is distinct from the previous one, which has a similar title.

Page 17266, line 26: "the electrometer and the CPC showed similar concentrations and thus after a short time only the CPC was used" The CPC size cut should be explicitly mentioned. I understand that since the aerosol arriving at the CPC and electrometer are only the charged fraction since it is first selected by the DMA, it is normal that the CPC and electrometer measure the same for aerosol which size is higher than the CPC size cut (maybe this could be mentioned for clarity). However, how can this be true also for particles smaller than the CPC size cut? Could it be that there are losses in the electrometer as well as in the CPC? Could this be the cause of the higher ratio of (N)AIS to CPC for a higher mobility? If the CPC size cut question is excluded, please explain why.

5. Results

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5.1 Response to peak mobilities As this is also the goal of next paragraph, I suggest the title of this paragraph is changed to something more specific. "response to standard ions peak mobilities" would be more appropriate?

Can you quantify the lower accuracy of the THAB negative mobility measurement? Accuracy is different from precision, please use the appropriate term. Are peaks wider spread or the modes more deviating from the expected value for negative ions? Can you quantify the "more deviation" term? How different is it from the positive polarity? Effect of RH for the TMAI monomere which seem to less fragmentate?

5.2. Detection of mobility and concentration of ions The title is not precise enough nor different form previous paragraph. "Calibration of mobility and concentration using silver particles"would be more appropriate? Here the conclusion are that (N)AIS are also undersizing the selected silver particles, especially for positive ions. Can you quantify the variability in the sizing accuracy among the different AIS (value of the std dev on average, and for given size ranges) ? Page 17269, line 21: "It is difficult to characterise the stability of the ion distribution and thus in the cluster ion range the monomobile standards should be considered as the most reliable calibration method". Why would the standard ions be more stable than the silver particles? Or is it the DMA selection which is not stable for cluster sizes?

5.3. Detection of total particle concentration

I understand that the NAISs underestimate the particle concentrations at low sizes, while the (N)AISs are overestimating the ion concentrations at low sizes. This should be stated clearly and lead to conclusions regarding the hypothesis on the charging state of particles of this size at equilibrium.

5.5 Calibrations with reduced calibration aerosol concentration

Page 17273, line 10: "At low concentrations, the measurement time per spectrum should be increased.." Could the authors test an increase of the (N)AIS resolution time

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from 1 to 2 min in order to check for this hypothesis?

5.6 Intercomparisons

The authors explain that the reason for discrepancies between AIS and NAIS for ions larger than 2 nm is a higher background noise in the NAIS leading to higher concentrations. However, from Fig 12 and 13, it seems that the NAIS measurements are closest to the BSMA size distributions, which are presented earlier as a reference for ion concentration. Does this mean that the NAIS measurements are the most reliable despite the highest background noise? Why are the BSMA not used in interpreting the results?

6. Conclusions

Page 17275, lines 4-6: I am not sure that I understand right the explanation of the authors why the AIS is less accurate in retrieving ion mobility for charged silver particles than for standard ions. Can they be more explicit? Page 17275, line 20: "However, the (N) AIS seems to be more reliable at moderate and high ion and aerosol concentration". Can you quantify how reliable the measurements are for given concentration ranges. Page 17275, line 25: "..negative mobilities were detected with better accuracy".Opposite to what is written in the abstract.

Overall I would suggest re-writing the conclusion with a better organisation of the different findinds. In the present form I find it very confusing.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 17257, 2008.