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Interactive Comment

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

E. Asmi et al.

Received and published: 1 December 2008

First of all, we would like to thank the reviewers for their excellent and relevant comments and suggestions, which truly helped us to improve the manuscript. We have now changed the manuscript according to their suggestions. Our responses to the specific comments are given below.

For: Anonymous Referee #1

"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?"

Reply: This is true. We will correct it in the abstract that negative ion mobilities were measured with higher accuracy (compared to the reference set-up). This was the common case. The discrepancy was partly due to the fact that the positive ion mobilities were measured more accurately in case of "standards", while in case of "other calibration methods" it was the other way around. Different sections discuss different methods (5.1 and 5.2). Also, negative standard mobilities were not as well defined as the positive standards.

"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."

Reply: We will improve this. We also add the mobility detection accuracy and precision based on linear fittings for the whole data and their error estimates.

"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)."

Reply: Yes, we do this.

"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."

Reply: We think "charged" is a more appropriate term because this it not bipolar neutralization process. The idea is to charge the particles to known charging distribution (depending on the charging current and the initial charge distribution of particles) which is not the equilibrium distribution.

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"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 dependent of relative humidity, precision on the flowrate measurements? Precision on the voltage?)."

Reply: This is a complicated task and we will explain this more detailed in the manuscript. The high resolution DMAs were calibrated with the positive standards (THAB). Flow rate was then never actually measured because calibration with the standards was considered more accurate method. The mobility scale was tested several times per day and after the DMA had stabilised to a constant temperature (short time in the morning before the measurements) the scale remained unaltered throughout the day. RH might have a small effect on the ion mobilities according to Ude and Fernandez, 2005. However, as our ion ratios (e.g. monomer/dimer ratio) were same as determined by Ude and Fernandez, 2005, this was not an issue in the measurements.

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

Reply: This was maybe poorly explained in the manuscript and we will add some explanations. Standards are monomobile but without the additional DMA selection, we get all ions, i.e. polymers (dimer, trimer,...), in the same spectrum. Although the monomer is usually the strongest peak, the other ions add unnecessary mess. As they are easy to cut out, we did that. The DMA selection itself does not affect the mobility of the standards and does not make them polydisperse.

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"Page 17264 Line 7; I suggest using "chosen" instead of "selected" which is confusing" Reply: We will change this.

"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?"

Reply: The same answer as for 3.2: to get rid off the extra polymers. (N)AIS measures the ions with 21 electrometers continuously, the four voltages are kept constant throughout the cycle and thus the voltage is not scanned as in a "normal" DMA.

"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 clusterclean? How were blank levels? What was the relative humidity inside the system?"

Reply: Additional dilution was added because it is not possible to use aerosol flow rates of over 60 lpm in the high resolution DMAs. RH decreased with the dryer dilution air but this shouldn't have an effect on the ion size because ions were not hygroscopic and also, as mentioned before, in case of standards the determined ion ratios were similar as determined by Ude and Fernandez, 2005. Black levels were basically zero with some additional noise from the electrometers. The dilution air was then cluster clean, or at least the cluster signal could not be separated from the electrometer noise signal.

"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."

Reply: The division between chapters is made to distinguish between different calibration set-ups. We will make the chapter names more separate and clear.

"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 explic-

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itly 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."

Reply: Ultrafine CPC has a lower cut-off size of 3 nm, we will add this to the text and also will improve the clarity of the text. CPC was not used under 4 nm size. Results were corrected with the CPC detection efficiency and the diffusion losses, as mentioned in the end of the chapter. Electrometer losses were tested with different flow rates and sizes and they were negligible above 2 nm size. The electrometer losses were shortly mentioned later in the results section when it was used to measure smaller particles. The (N)AIS/CPC concentration ratio was only higher in the very smallest sizes and this was not an issue in 4 nm size range.

"5. Results 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?"

Reply: Yes, we will change that.

"Can you quantify the lower accuracy of the THAB negative mobility measurement? Accuracy is different from precision, please use the appropriate term."

Reply: Yes, you are right. We will check the use of correct terms. One possible explanation for the lower accuracy is given in the manuscript in the following text. It is explained that the characterization of the negative "standard" peaks was only based on the DMA voltage selection and the stability of the ions was thus uncertain. 8, S9552-S9564, 2008

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"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?"

Reply: Good questions. There are only small changes in the width of the peaks, i.e. deviation or precision, in negative polarity compared with the positive. The main difference is in the accuracy, i.e. the deviation from the expected value. This deviation will be later shown in Figs. 4 and 5. We will make the sentences more precise.

"Effect of RH for the TMAI monomere which seem to less fragmentate?"

Reply: RH should not be a problem for well defined positive standards (check previous answers). We would more suspect this deviation of the TMAI monomer peak value was due to the (N)AIS lower precision at such a small ion size.

"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?"

Reply: It is difficult to find out a more descriptive title for the chapter. We did not calibrate the mobility nor the concentration but the (N)AISs and also other than silver particles were used in calibrations.

"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) ?"

Reply: For mobilities, we calculated the median value of standard deviation versus mean measured value for each calibration set-up result and added these numbers to the text. For concentrations, we simply calculated the median of average ratios and standard deviation.

"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

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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?"

Reply: As you said, the standards are one mobility only and considered very stable, whereas the DMA selected particles have a small distribution of mobilities. Thus, they are more vulnerable to dynamical prosesses and then evolution of the distribution. Especially cluster ions can be very unstable and distribution might change rapidly. Typically calibration standard molecules are considered standards for the reason that they are known to be very stable.

"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."

Reply: In case on NAIS and particles the "low sizes" are around 4 nm as in case on (N)AIS and ions they are around 1 nm. The reasons for the over/underestimations are explained separately as they depend on different things and are not related.

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

Reply: Unfortunately, we don't have any (N)AISs available at the moment. This issue will be tested better in future calibrations.

"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

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the most reliable despite the highest background noise? Why are the BSMA not used in interpreting the results?"

Reply: Very good point! BSMA can be considered more reliable but with such low concentrations, also BSMA has a high noise in sizes above the cluster sizes (as it also measures with electrometer and electrometers have always noise). Thus, it is actually difficult to say which one is closer to the BSMA. With the limited time available in calibrations, we did not have time to test the effect of noise more carefully and thus we are only presenting some possible hypothesis for the sources of errors in the text.

"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?"

Reply: We will make this more explicit. What we are suggesting are different factors that might affect the detection of mobility in (N)AIS. In case of monomobile standards, we know that the discrepancies between standard mobility and measured mobility are due to (N)AIS. However, in case of silver particles, already the mobility of ions going into the (N)AIS might not be exactly known and thus it is difficult to say how big fraction of the discrepancy is due to (N)AIS (reacting differently for polydisperse aerosol) and how big from the calibration method (mobility determination of the calibration aerosol).

"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."

Reply: Because calibrations were really time consuming, we could not test all the different concentrations but most of the measurements were done with quite high concentrations (relative to normal atmospheric concentrations). We added a linear fit (slope of one) and error estimate for that to have some kind of estimate of the mobility detection accuracy of the (N)AISs.

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"Page 17275, line 25: "..negative mobilities were detected with better accuracy". Opposite to what is written in the abstract."

Reply: True, this one is correct.

"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."

Reply: Yes, we will.

"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."

Reply: We want to thank you for your very helpful comments. We will improve especially the structure and the clarity of the conclusions section. It is very difficult to give exact numbers for sizing accuracy because 1) There were small differences in sizing accuracy between (N)AISs. 2) Calibration aerosol concentrations varied between calibrations and were generally high. They are also not comparable to atmospheric concentrations as the calibration aerosols were monomobile, or close to monomobile. We did not have time to test with different concentrations, and it was even not possible in some cases. 3) The reasons for the partly non-linear response in mobility detection accuracy shown by (N)AISs are not clear. Also, there were some discrepancies between calibration methods. The same applies to concentration accuracy, which was not a linear response at all. 4) In reality, the (N)AIS measures distributions of ions

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and not a one value (here represented as geometric mean). The shape of the transfer function should also be taken into account somehow. That is why we decided to report our results as they were and discuss about the possible reasons behind the observed values. However, as you wished to get exact number for the sizing accuracy, we decided to make a linear fit (in loglog scale as in figures) to the data with a slope of one. Then, this fit and standard deviation of the residuals was used as an error estimate for the mobility detection accuracy of the (N)AISs. The concentration accuracy was not a linear function of size and such a fit could not be made while we had no physical reason to assume any other form of response either.

For: Anonymous Referee #2

"This paper presents a calibration and inter-calibration of the majority of the (N)AIS instruments produced so far. This is a very important contribution and provides information that will be useful to everyone making field and laboratory measurements with the instruments. I also find the results very promising for the future use of the (N)AIS instruments. Especially since the authors have adopted several different calibration standards in order to cover the full mobility range in an adequate way. The paper fits well within the scoop of ACP and I recommend publication after minor revision."

Reply: We want to thank you for your positive feedback.

"General comments: Does the on-line software include corrections for losses of cluster ions, or have any off-line corrections been made?"

Reply: The online software takes into account the ion losses as it reports the numbers of ions with different mobilities. This was shortly explained in the description of the ion spectrometers. The program also gives the raw current signal measured with different electrometers, and of course, this does not take the losses into account. We used the raw-current values only when calculating the transfer functions of individual channels, otherwise we used the calculated (corrected) concentrations.

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"In this paper NAIS is spelled out as "neutral air ion spectrometer". To me this sounds awkward. Why not use "Neutral cluster & Air Ion Spectrometer" or "Neutral particle & Air Ion Spectrometer". I think that it is important to consider this carefully, since this paper will most probably be a very much used reference and can set the vocabulary standard."

Reply: This is a very good comment and actually "Neutral cluster & Air Ion Spectrometer" is the official name of the instrument. We will change the name.

"Some differences in detection efficiency and sizing of cluster ions between negative and positive ions are observed in the calibration. It would be interesting if the authors could discuss how this relates to the often observed differences in number and size of negative compared to positive cluster ions."

Reply: Yes, this is an interesting addition to the text. Typically in the atmosphere, positive ions are bigger and have higher concentrations. Now, as they were classified into too small sizes it looks like the difference between negative and positive ion sizes can be even larger than previously measured. Also overall, the cluster ions would be bigger in size. Additionally, as (N)AIS measured too high cluster ion concentrations which then leads to the conclusion that their numbers can be lower in the atmosphere then previously thought based on (N)AIS measurements.

"On page 17268 it is described that the geometric mean was used as a representative for the mobility in the (N)AISs. Combining this information with the transfer functions presented in figure 9 poses some question to me: could the un-symmetric shape of the transfer function influence the sizing and the differences between mono-mobility standards and DMA comparison? Would a modal value give a sizing in better agreement?"

Reply: Yes, the shape affects the sizing. We decided to use geometric mean instead of peak value because we thought the "tail" could not be excluded, and also because the stepwise behavior of the peak value. In the beginning of the analysis the mobilities were presented with peak values. The peak values are closer to the reference mobilities but

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this does not totally remove the sizing inaccuracy. We add a separate sentence to emphasise the effect of transfer function shape.

"Is the tail the reason for the deviation in sizing and if so, what is the reason for the tail and can it be avoided in future designs? I understand that these question may not be easy to answer, but I recommend the authors to consider them."

Reply: Yes, this is a very difficult question and we have used some time to think about this. Now, as we do not have any (N)AISs free for laboratory tests we can not resolve this issue, if even then. However, it is discussed in the paper that possibly some turbulence in the inlet of the (N)AISs could "throw" the ions towards the outer cylinder too soon, which would then lead to the tail. Definitely, this needs to be studied further because, as you said, it would be important to avoid the tail in future designs.

"Some details: P. 17261 line 26 What does "measured charge" refer to? Is it the charge polarity that can be studied in the respective columns?"

Reply: We will rephrase this. The sentence just means that electric filter removes charged particles.

"P. 17262 line 6-7 reads "conversed". Shouldn't it be "converted""

Reply: Converted might be more suitable here, we will change this.

"P. 17271 line 6-7 "The NAISs detected on average 's50% of the concentration of the reference CPC (Fig. 8)". To me, this implies that the detection efficiency is always less than 50%, sometimes negative. Please consider to rephrase."

Reply: Yes, you're right. We will rephrase.

"Figure 2-3 Colour code should be consistent: one colour for one instrument."

Reply: We will change it.

"Figures 4-7 How much of the variability is significant? Could a linear or polynomial fit

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be used in stead of the "mean" lines with all their variability?"

Reply: We wanted to present the results as realistic as possible. That is why we didn't use any fitting in figures. However, now we additionally fitted a linear line with a slope of one to the data to be able to give some kind of estimate on the mobility detection accuracy of the (N)AISs.

"Figure 7 Is the peak in over-detection for ions of mobility around 0.5 cm2/Vs significant?"

Reply: If this means that do these values differ significantly (95% confidence) from unity, then yes. That is also why we were not able to make a linear fit to the concentration plots.

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

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