Authors' response to referee comment RC2
on manuscript
"Development of an Automatic Linear Calibration Method for High Resolution Single Particle Mass Spectrometry: Improved Chemical Species Identification for Atmospheric Aerosols"

We thank Referee #2 for the comments and suggestions. We have addressed every comment and made significant changes to improve the paper. Again, the referee's comments are greatly appreciated.

Referee Comments in black bold.

Authors' Response in blue.

Changes in manuscript in Red italic.

Major comments

This study reports the development of an automatic linear calibration method for analyzing mass spectral data acquired with single particle mass spectrometers with mass resolution of ∼ 2000. The paper also shows the successful application of this method to analyzing lab generated sea spray particles and some ambient aerosols. This work is important given the broad application of single particle mass spectrometry in atmospheric studies and aerosol research and improvement of the chemical resolution of this technique is important. The scope of the work fits well within AMT and the manuscript is generally well written. I recommend acceptance for publication after following comments are addressed.

Response:

We are grateful for the comments given by the referee and hope our new automatic linear calibration method can be applied into more versions of aerosol mass spectrometry for atmospheric studies. Also we have addressed all the comments in the following paragraphs.

Specific comments:

1. Line 119,change to "dried by"

We have made correction to that.

Changes in manuscript:

Line 135-136:

"The ambient particles were dried by a diffusional dryer before being sampled by the HR-SPAMS."

2. Fig. S2, the caption for this figure needs to be rewritten to better present the information content.

We have rewritten the caption of the Fig.S2 to better present the information content.

Changes in supplementary material:

"Fig.S2 partial enlarged detail in the sing particle mass spectra for the

explanation of the m/z bin value"
Changes in manuscript:
Line 141-144:
"Noticeably, due to the technical limitation of data acquisition, the whole HR-SPAMS spectrum is not continuous but divided by a large number of m/z bins, which are described in Fig.S2(a partial enlarged detail in the single particle mass spectra) and can be viewed as the probability density histogram of the m/z."

3. Line 171, what does a.u. stand for? How were the thresholds selected?
a.u. stands for the arbitrary unit, which is used widely in the averaged aerosol mass spectra for ion intensity. The absolute ion intensity threshold adopted in the YAADA (Yet Another ATOFMS DATA Analyzer, www.yaada.org) for SPAMS is 5 a.u., so the thresholds we used (15 a.u. for ambient aerosol and 8 a.u. for sea spray aerosol) can be considered reasonable just in case of the interfering signals in the aerosol mass spectra.

4. The description on Step 3 given in the paragraph on pages 6 and 7 is a bit hard to follow. How exactly is the calibration conducted? Are the measured m/z bins determined from the "traditional method" mentioned in Step 0? What exactly is the "traditional method" involved? How many bins are selected for each m/z?
(1)The detailed statement of the Step 3 is that: First, we will get the measured m/z bins determined from the "traditional method", just as described in the Step 0. And these bins were not sufficiently accurate. Then, we picked up some reference ions to make a linear regression between the two set of variables (measured vs. theoretic reference ion m/z bin values). The obtained calibration parameters (a slope and an intersect) from linear regression were used to calibrate every bin value for this mass spectrum. However, the m/z bin values are fixed numbers (they are not continuous). So we had to assign the calibrated m/z value to its closest m/z bin value. Finally, the correct aerosol mass spectra can be acquired. We had made some revisions to make it easier to read in the Step3;

(2)The measured m/z bin values were determined from the "traditional method" mentioned in the Step 0;

(3)The "traditional method" was more like a coarsely-calibrated method, which usually selected a few particles with distinct ion patterns. Fig3 and Table S1&S2 had reported there were around five of larger bin numbers offset for the ionized species. What's more important is that every particle mass spectra were different from each other and needed its own calibration parameters. So the "traditional method" is not enough for the SPAMS data processing.

(4)One specific bin was selected for each m/z as shown in the Fig.S2
Changes in manuscript:
Line 193-195:

"The measured m/z bin values of the reference ions mentioned in the Step0 were calibrated based on their theoretic (or true) m/z bin values."

Line 197-199:

"Then we used these parameters to make the calibration for every bin value in this mass spectra. Finally, the m/z of the whole spectrum had been corrected."

5. Give units for "measurement m/z" and "theoretical m/z" on the axis labels in all the Figures presented in this paper.

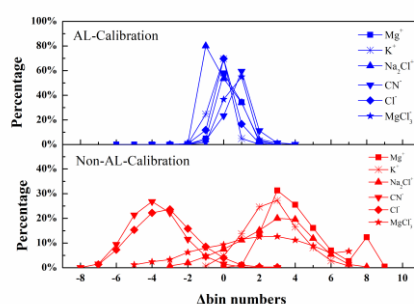
The unit is Dalton. We have updated all m/z axis labels in in the revised paper.

6. Figure 3, the symbols are hard to differentiate, consider to revise. The spectra a and b look identical, are they really represent sea spray aerosol and ambient aerosol respectively?

Thanks for pointing this out. It was a mistake and has been corrected now. We have also separated the figure into 2 panels to make them easier to differentiate.

Changes in manuscript:

Line 548-553:

"a.

b.

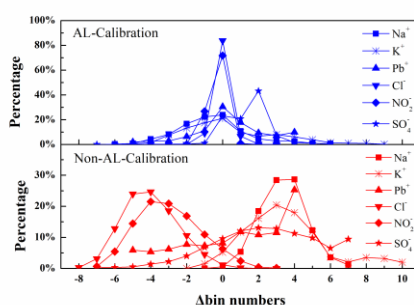



Figure 3. Probability distributions of the marker peak locations before and after Automatic

Linear Calibration (AL-Cal) for (a) sea spray aerosol and (b) ambient aerosol "

7. Figure 4, what is "error limits"? How was is calculated?

The "error limit" is the delta bin number which is concluded from the Table S1&S2 and Fig.3,

representing the accepted error range (around 3 bin numbers) after the calibration for a m/z bin value.

Changes in manuscript:

Line 252-254:

"Figure 4 reports the average positive and negative mass spectra for the laboratory generated sea spray aerosols and the error limits mean the concluded accepted error range."

7. Line 250, change to "Ca2+"

Actually the ion fragment generated from the SPAMS can only carry one charge, so the Ca^+ is reasonable.

9. Line 266, define "LR-SPAMS"?

We have give a definition for that.

Changes in manuscript:

Line 295-297:

"In contrast, it is impossible for a low resolution (LR)-SPAMS to provide such detailed time variation measurement of these peaks."