

Dear Reviewers!

Thanks a lot for your notes, comments and questions. We hope that they improve our understanding of the problems associated with processes in the laser single particle mass spectrometer. Please, find our answers/comments on your notes below:

**Anonymous Referee #3**

**Received and published: 22 September 2019**

Chen et al. described a modified SPAMS to increase particle hit rate using a pulse delayed extraction technology. Indeed, the increase in hit rate is an improvement of instrumental performance. The attempt is exciting and novel. However, there are still concerns about the manuscript. Therefore, I recommend a major revision of the manuscript.

1. The delaying of ions, with an extra of 100 ns, can lead to secondary ion-ion and ion-neutral reactions. The artifact could cause inevitably shift of mass spectra, and the results could not be compared directed with current literature. Therefore, I would like to see some comparisons in both lab and field results between this new model and the commercialized instruments. Related discussion is also necessary.

The objective of this work is to demonstrate an increase in hit rate when applying Delayed Extraction (DE). In our opinion, this is demonstrated very convincingly, and a physical explanation of the observed effect is given in the work. This effect depends only on the particle charge and the presence of a static electrical field. Particle charge is an absolutely common property for both laboratory and natural particles. The ion formation processes during laser desorption/ionization of a particle is not considered in detail in this paper, and therefore, comparison with other devices by the type of spectra obtained is hardly appropriate here. By the way, we presented such a comparison of mass spectra of PSL particles in the supplement. As we noted in the first answer, there is a noticeable effect of DE on the shape of the spectrum, which is due to the features of the operation of time-of-flight mass spectrometers, and, possibly, reactions in a cloud of desorbed molecules. The mechanisms of ion formation as part of a complex of processes during laser exposure to a particle are of great interest, and are the subject of our further research. But in this publication we did not go deep into these issues, since they are not directly related to the observed effect, and their detailed exposition requires a much larger volume.

There are two other considerations:

1) we have the initial ion velocity spread after laser desorption / ionization of a particle. Due to the delay, we transform the velocity spread into the coordinate ion spread (time-lag focusing), which is correlated with the velocity spread. If ions significantly undergo ion-molecular reactions within a 100 ns delay, the resulting coordinate spread after the delay will be not correlated with the velocity spread any more. And we would not receive a gain in resolution. But we get it.

2) the particle composition after the laser shot is electrically neutral. That is, recombination reactions between positive and negative ions can occur. The rate constant of this process is in any case no less than that of the reactions between ions and neutrals. Then, if such reactions had a significant effect, then we would see a decrease in the signal in the case of DE due to recombination/neutralization of a part of the ions. We do not see it, but rather, on the contrary, we observe a slight increase in the signal; hence, by our mind, the reactions of the formed ions do not particularly change in the case of DE.

2. Increase of hit rate is undoubtedly an improvement of instrumental performance. However, single particle methodology is a partially sampling, meaning that the representation of full particle population is a major concern. The limited increase of hitrate and the unknown artifact, the balance should be considered cautiously. Again, the reviewer would like to see a discussion on this issue.

Indeed, particles observed by single-particle MS are a partial statistical sampling from an aerosol array. This sampling is carried out in several steps during analysis in the MS. These are the transmission of the aerodynamic system, the hit rate in the ion source, the work of which is devoted to the increase, and the processes of formation and registration of ions. In our opinion, an increase in hit rate brings the sampling closer to the total aerosol array in terms of the number and size distribution of the detected particles

Увеличение частоты ударов, несомненно, является улучшением инструментальных характеристик. Тем не менее, методология отдельных частиц является частичной выборкой, что означает, что представление всей популяции частиц является серьезной проблемой. Ограниченнное увеличение битрейта и неизвестного артефакта, баланс следует рассматривать осторожнно. Опять же, рецензент хотел бы увидеть обсуждение этого вопроса.

3. A serious proof-reading is necessary.

OK, we'll do it once again, and we'll correct the manuscript

4. In Introduction, the reviewer recommends introducing a brief history of SPMS development.

We added the reference [Pratt, K.A., Prather, K.A., 2012. Mass spectrometry of atmospheric aerosols. Recent developments and applications. Part II: On-line mass spectrometry techniques. Mass Spectrom. Rev. 31, 17-48] in the introduction section.

5. The organization of the Method part should be improved. Please pay more attention to how your delaying system is designed.

6. Figure 2, it is not necessary to show the Y-axis in a logarithmic way, a linear one is enough.

In our opinion, a plot with Y range of 3 orders of magnitude is hardly shown in a linear way.

7. Section 3.3, I would like to see some mass spectra of field (envirionment) particles.

We presented some mass spectra in the supplementary material for comparison. . We plan to make a detailed comparison in future work in relation with the study of ionization mechanisms.

8. Conclusion needs to be re-written. Please focus on what you did, the result, the benefit, and scientific implications.

We'll try to revise the conclusion.

9. Miner revisions 1. Line 16, the full spell of DC is not provided.

OK, we updated the sentence

2. "Delay extraction" is not proper because delay is used as a noun or a verb; "Delayed extraction" could be more appropriate.

Thanks, we corrected the sentence

3. Line 32, some high cited literature (Pratt and Prather, 2012) is not cited.

The reference added in the Introduction section

4. The space between paragraphs was not apparent; please add space into them.

The formatting is updated

Ref. Pratt, K.A., Prather, K.A., 2012. Mass spectrometry of atmospheric aerosols – A “Recent developments and applications. Part II: On-line mass spectrometry techniques. Mass Spectrom. Rev. 31, 17-48.

Please also note the supplement to this comment: <https://www.atmos-meas-tech-discuss.net/amt-2019-163/amt-2019-163-RC2supplement.pdf>