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 #1

Received and published: 3 July 2019

This paper quantifies the improvement in SPMS hit rate resulting from particle beam deflection inside the electric field. It proposes that using delayed extraction helps to solve this problem and the results look convincing. I recommend the publication of this paper in AMT after the following major and minor comments are addressed.

Major comments: I would be really interested in seeing a comparison is mass spectra collected in DC and DE mode. In the DC mode, the ions produced by the laser are accelerated into the ToF immediately, but under the DE mode, they hang around the extraction region for an extra 100 ns, during which ion-ion and ion-neutral reactions can take place. It is possible that that would produce somewhat different fragmentation patterns. I would appreciate if the authors gave some discussion of those possible effects.

> Actually, we don't observe a significant difference between mass spectral peaks in DE mode and DC mode, except their intensity and resolution. In our article we address other issues. i.e. the hit rate and the intensity of peaks in mass spectra. We have prepared the mass spectra acquired in DC and DE modes for comparison, for those who are interested in this matter, and we will put them in the supplementary material.
> Actually, the plasma cloud after laser ionization is composed of ions, electrons and neutrals, and it is generally neutral. The plasma expands and disintegrates over time, and, at the same time, ion-neutral reactions and recombination processes between ions and electrons take place. If the effect of a strong electric field on the expansion of ions and electrons beyond 100 ns was significant, the signal in the case of DE would be weaker. On the contrary, we observe some increase in positive and negative ions signal in case of DE in comparison to the DC extraction mode. It can be assumed that the interaction of ions and neutrals makes a larger contribution than the recombination of ions with electrons. Presumably negative ions are formed by the capture of electrons by neutrals, while positive ions can be transformed into some cluster ions via interaction with neutrals.
> Thus, we can assume that the 100 ns delay can increase the interaction of charged particles with neutrals. It can also be assumed that the degree of ionization in the cloud is low. Below are three figures illustrating the comparison of

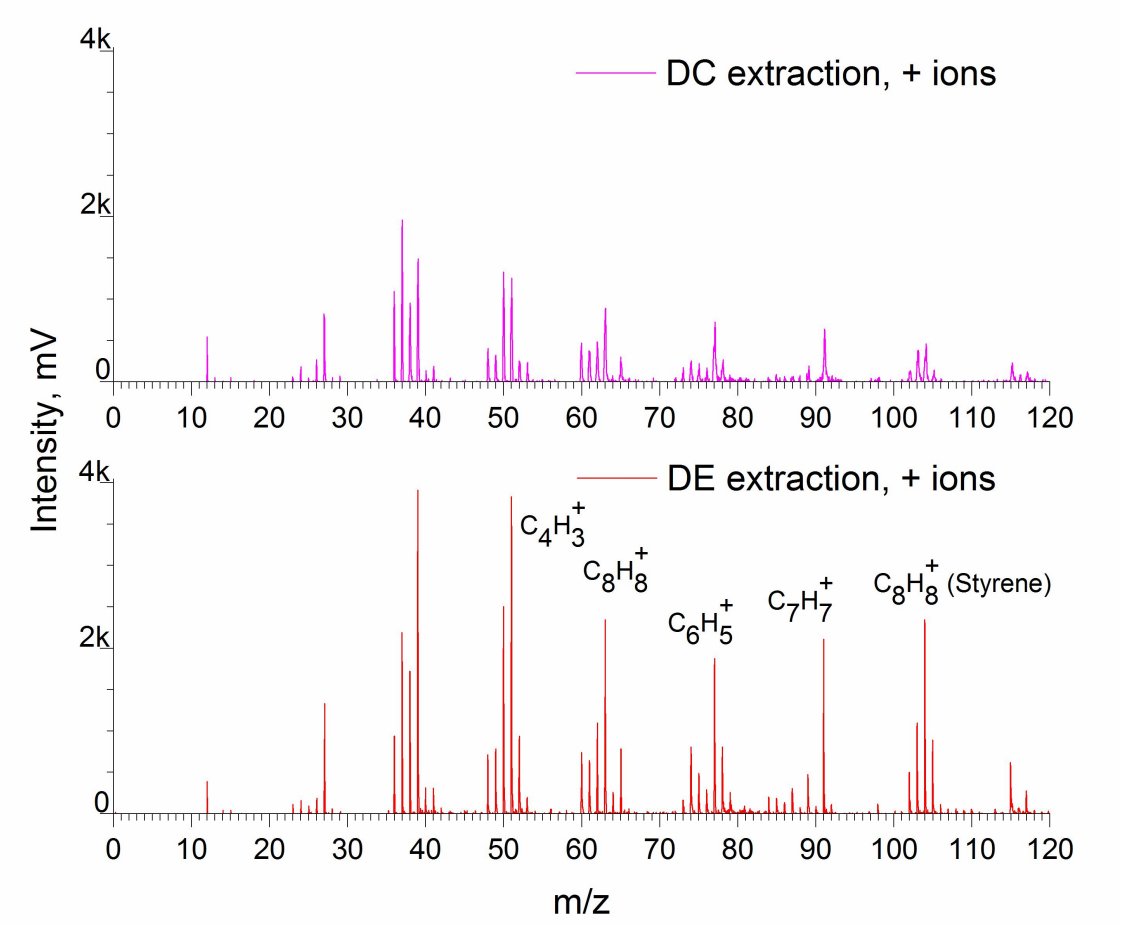


**Fig. 1. Comparison of positive ions mass spectra obtained from PSL particles using SPAMS instrument with DC and DE extraction modes, in the mass range 0<m/z<120.**

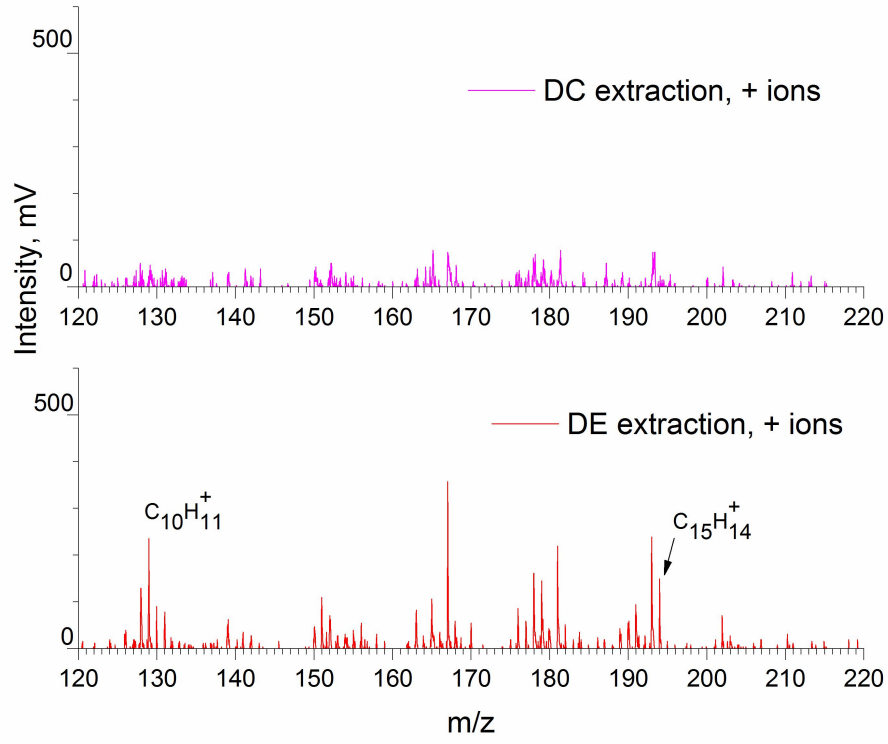


**Fig. 2. Comparison of positive ions mass spectra obtained from PSL particles using SPAMS instrument with DC and DE extraction modes, in the mass range 120<m/z<220.**

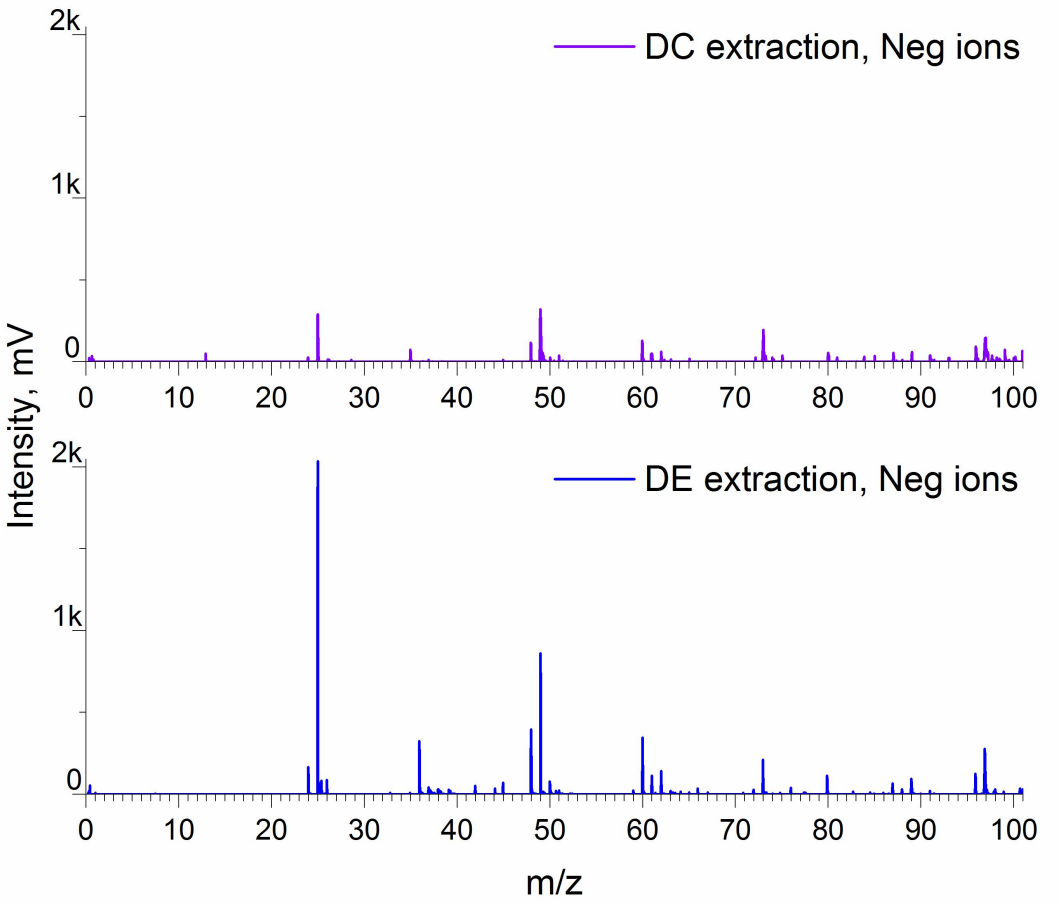


**Fig. 3. Comparison of negative ions mass spectra obtained from PSL particles using SPAMS instrument with DC and DE extraction modes, in the mass range 0<m/z<120.**

Numerous English usage errors, especially with respect to article placement, inconsistent pluralization and subject-verb agreement. These usually don't inhibit understanding, but please have someone proofread it. I did not list them all.

Thanks for the note about the language. We have corrected a number of errors by proof-reading.

Minor comments: p.2 lines 57-58: while high cost is a problem, I am not sure I agree that neutralizers are very inconvenient, especially compared to other aerosol instrumentation used routinely.

Actually, the commercial X-ray neutralizer has two disadvantages, one is the price, it is more than 20,000 dollars if you want to buy a new one. The other is the X-ray lamp life time, which is only 8000 hours typically, and you need to change it frequently

p.2 lines 59-60: I would also dispute that "most" instruments use Nd:YAG as the ionization source. There are quite a few prominent examples of the SPMS technology that use the excimer. In fact, there is a citation to Zelenyuk et al., (2006) paper in the same paragraph, which is describes an excimer-based instrument. It seems like your solution is primarily useful for instruments in which the distance between the sizing and ionization regions is large (i.e. ATOFMS or SPLAT), but not PALMS (sizing and ionization in the same physical instrument region). Differences in instrument design should be clarified here.

About Nd:YAG – we agree, and we'll change the sentence in the article (many instruments instead of Most instruments)

p. 3, line 69: you used "impact rate" instead of "hit rate" here, please be consistent.

Corrected to “hit rate”

Section 3.1 reads as though it belongs in the "Instruments and methods", since no actual data is presented yet.

We agree, the section 3.1 is transformed to 2.1. “Key factors affecting the efficiency” in the Instruments and Methods section.

Figure 4: why is there so much scatter in the DC measurements?

The scatter can be related to the stochastic change in the surface charge of the particles. By the way, we have found a mistake in the Figure 4. Actually, it shows the hit rate per 1 second. In the manuscript, we described the whole time scale for this Figure as 30 minutes but actually it is 30 seconds. Because the hit rate was counted in every second, the particle detection rate is less than 10/second, so the result shows scattering according to the $\sqrt{N}$ Poisson low. So we have change the minute into second in the Figure 4.

p.6: for completeness, it would help to show the same glass slide experiment in the DE mode. The divergence in the case of DC potential is dramatic. If the extraction pulse is applied instead, is the width of the beam at the slide significantly closer to the "voltages off" condition?

Unfortunately, it is hard to reproduce the experiment with the glass slide, as the instrument which was used for it is under construction now. But we don’t suppose it will show any critical results, as the extraction pulse width is short (5 μS), and the path of the particle moving with the velocity 100 m/s will be 0.5 mm. Hence, the effect of deflection will be ~ two orders of magnitude lower than in case of the DE. Hence, the spot size on the glass slide is supposed to be the same as that obtained without the electrical field (Fig.5), and we’ll not get any extra information.

Note please, that in case of DE operation, this HV pulse does not affect on the trajectory of the particular sized particle, as it is applied after it is ionized. On the other hand, the HV pulse is unlikely to affect other particles, since the average particle counting frequency is less than 100 Hz. Actually, the 266nm laser has a max repetition of 100 Hz, that is why the maximal counting frequency is 100 Hz.

p. 7-8, lines 223-225: I am not sure I follow what experiment the authors have in mind by pre-selecting particles based on charge. I suggest this be fleshed out a bit more or removed.

We have added some more details about a possible realization to pre-select particles by their mass/charge ratio in front of the ion source. It is just an idea which would need a significant additional work for it realization

**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

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.

We have reported the detail of the time-delay system on the article "Improvement in the Mass Resolution of Single Particle Mass Spectrometry Using Delayed Ion Extraction". (https://link.springer.com/article/10.1007/s13361-018-2037-4)

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 (envrionment) 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 aerosolsâ˘ A˘TRecent 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

# Increase of the particle hit rate in laser single particle mass spectrometer by pulse delayed extraction technology

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**Abstract.** Single particle mass spectrometer (SPMS)~~is the instrument providing a plenty of~~can provide a wealth of valuable information on chemical and physical parameters of individual particles in real time. One of the main performance criteria of the instrument is ~~the~~ efficiency of particles detection (hit rate). Most of SPMS instruments use constant electrical field (DC) extraction, ~~when~~where the stationary high voltage is applied to the extraction electrodes. As the aerosol particles initially carry a certain charge, those with high amount to charge~~y~~ can be deflected by this electric field and lost, thus decreasing the hit rate. ~~It was~~ We realized ~~in this work,~~ that the delay extraction technique can eliminate the stochastic dispersion of the particles beam caused by their deflection in the stationary electric field. As the result, the hit rate of the instrument can be significantly improved. Also, as the effect of the deflection in the electric field is mass dependent, it can cause ~~the~~ distortion of the measured size distribution of the particles. Hence, the delay extraction technique can bring the ~~measured~~ recorded distribution closer to the actual~~real~~ one. ~~Thus,~~ We found that the delay extraction technique provides ~~not only~~ mass resolution improvement as well as~~, but also~~ increases the hit rate. The gain in the hit rate depends on the type of the particles. It can be two orders of magnitude for model particles, and up to 2-4 times for real particles. In the present work we report experiments and results showing the effect of the delay extraction on the ~~particles~~ beam divergence caused by particles charge, the hit rate improvement and the effect of the delay extraction on the measured particles size distribution.

## 1 Introduction

Aerosol particles have a strong impact on the climate, environment and human health. These effects are closely related to physical and chemical properties of the particles. An in-depth understanding of the physical and chemical properties of individual particle is important for studying ~~of~~ various effects of aerosols. Single Particle Mass Spectrometer (SPMS) is an analytical tool that can provide the particle size and chemical composition of individual particles in real time. There are

many publications ~~whichthat~~have reviewed the principle, structure and applications of SPMS in detail (Murphy, 2007; Nash et al., 2006; Noble and Prather, 2000;Pratt and Prather, 2012)~~(Prather and Pratt, 2012)~~. SPMS usually use an aerodynamic lens to focus and form an aerosol beam and to transfer the ~~aerosol~~ beam from the atmosphere into the vacuum system ~~and to focus particle beams~~. As a common arrangement,~~Usually~~the two-beams of light laser caliper~~is used to~~ measures the particle speed and size rightbefore the "sized" particle passes~~through~~ into a high-power~~energy~~ pulsed laser beam. When the particles are evaporated and ionized by the laser radiation, ~~a bunch of~~ positive and negative ions are~~is~~ formed. ~~Produced~~ These ions are accelerated by the strong electric~~al~~ field in the time-of-flight mass spectrometer (TOF MS) and ~~finally~~ then detected and ~~registered~~ recorded by a data acquisition system based on a fast ADC. Compared to the traditional off-line particle methods, the SPMS ~~can exclude the stage used for the~~measurements can be conducted withoutpreliminary collection and preparation of the particles~~,and provides~~ providing~~high~~rapid real time analysis~~resolution~~. At present, SPMS is mainly used for characterization of physical and chemical properties of the particles, atmospheric chemical process analysis, atmospheric aerosol analysis and other environmental and material science applications(Bi et al., 2011; Kim et al., 2012; Li et al., 2014; Middlebrook et al., 2003; Roth et al., 2016). SPMS is fast, and ~~the~~ detection time for a single particle is typically o~~i~~n the order of a few milliseconds. However, it is ~~generally necessary~~common to accumulate single particle data over a period of time to obtain statistically significant ~~data~~ information about particle diversity. The application of the SPMS to atmospheric aerosol analysis and investigation of chemical processes with atmospheric aerosols requiresa high performance instrument. Hit rate is an important parameter of SPMS related to its performance. It is generally defined as the ratio of the number of spectra generated by laser ionization to the number of particles detected by the caliper lasers. There are many aspects that affect the hit rate of SPMS, including the particle size, physical and chemical properties (Dall'Osto et al., 2006; Zelenyuk et al., 2009) of the particle and the instrument design (Gemayel et al., 2016; Zhao et al., 2005).

It is well known ~~by~~(Dodd, 1953; Gunn and Woessner, 1956; Woessner and Gunn, 1956) that aerosol particles usually ~~have~~ carry a certain amount of surface charge. ~~Hence, in the case~~If such particles enter~~where~~~~of~~the~~a~~ the stationary electrical field ~~exists~~is ~~present~~in the extraction region of SPMS, ~~the particles~~they can be deflected ~~when~~ as they move through the ion source region~~space~~. ~~If~~ Once the particle trajectory~~hai~~s shifted from the center of the laser beam, the ionization efficiency can drop~~s~~ down significantly (Su et al., 2004). Hence the particle deflection in the ion source results in a decrease of the hit rate. In order to reduce the influence of the electrical field on the particle beam trajectory, an electrostatic neutralizer can be installed ~~on the way of the particles~~between the particle introduction and particle ionization regions. The electrostatic neutralizer generally uses a radioactive source based on 210Po, 241Am, 85Kr, or X-ray source (Demokritou et al., 2004; Kousaka et al., 1981; Nicosia et al., 2018; Pratt et al., 2009; Tsai et al., 2005). However, the management of radioactive sources is a difficult task, the equipment is relatively expensive, and it is very inconvenient to use it in the field measurements.

Another problem in SPMS is a particle beam divergence. There are many~~Most of~~ instruments that use Nd: YAG laser with $4^{th}$ harmonic generation (266 nm wavelength) as the ionization source. Since the Nd:YAG laser with lamp pumping requires more than 100 us delay between the lamp ignition and the laser pulse, it is necessary to place the laser ionization source at a

considerable distance (about 10 cm) ~~below~~ downstream of the second caliper laser. The particle beam is dispersed on the way from the caliper laser to the ionizing laser, and the increase of the beam width leads to a decrease in the hit rate. This problem can be solved using a laser with shorter delay time, such as excimer or nitrogen pulsed gas lasers (Alaime et al., 1983; Trimborn et al., 2002). The effect can be bigger especially for irregular non-spherical particles (Zelenyuk et al., 2006). Shortening the distance between the caliper laser and the ionizing laser can compensate ~~for~~ the influence of the particle shape to some extent (Cziczo et al., 2006; Thomson et al., 1997).

(Zelenyuk et al., 2009) also studied the shift of the trigger signals generated by particles with different sizes at the caliper laser, which resulted in the ~~impact~~ hit rate being affected by the particle size. As a result, the dynamic laser trigger system was developed to ~~realize~~implement the trigger compensation ~~of~~ forthe particles with different particle sizes thereby achieving an improvement of the hit rate. However, this method is directed to solve the positional ~~problem~~ spreadof the aerosol particles~~in the flight direction~~along the axis, ~~and~~ it does not contribute to the problem of lowering the hit rate caused by deflection of the aerosol in the direction perpendicular to the particle beam axis. This deflection is caused by static electrical field and depends on the ion source dimensions and on the electrical field strength. Unfortunately, the ion source cannot be built ~~very~~~~too small~~short enough to neglect particle deflection. But, it is possible to switch off the electrical field by using a delay extraction technique (DE)( Li et al., 2018; Chudinov et al., 2019) for ion sampling.~~.~~

In our previous works we have used the double exponential pulse delay extraction technique to improve the mass resolution of SPMS (Chudinov et al., 2019; Li et al., 2018).This solution provides mass resolution enhancement about 2-3 times over the broad mass range in comparison to the usual DC extraction. It is important, that in the delay extraction ion source particles pass to the middle~~half~~ of the ion source with no DC electrical field. Therefore, the influence of the particle charge ~~to~~on its trajectory will be neglected in comparison ~~to~~with the usual ion source with stationary electrical field. In this paper we present our investigation ~~of~~ on the effect of stationary and pulse extraction on the particle trajectory and on the hit rate of SPMS instrument.

## 2Instruments and methods

The SPMS used in this study is a commercial instrument from Hexin Analytical Instrument Ltd. (Guangzhou), which is normally called Single Particle Aerosol Mass Spectrometer (SPAMS). The detailed principle and design of the SPAMS has been described elsewhere in detail(Li et al., 2011). The commercial SPAMS was modified in two ways. First, the delay extraction technique is used instead of the original DC field extraction technology. The superposition of the rectangular and the exponentially shaped extraction pulses simultaneously improves the resolution over the wide mass range for positive and negative ions (Li et al., 2018) . After the improvement, the positive ions mass resolution > 1000 FWHM and the negative ions mass resolution > 2000 FWHM were achieved. Second improvement is the use of multi-channel superimposed signal acquisition technology. The native signal from MCP detector is equally split in two channels with different amplification ratio and acquired by two equal 8 bit ADC. Thus, the high dynamic range data acquisition system is capable of acquiring

signals ranging from 5 to 20000 ~~mv~~mV, and the dynamic range is nearly 40 times higher than that of the original SPAMS. This solution enables one, for instance, to detect high intensive alkali metal ions peaks together with a very weak ion signals from another elements or molecules at the same time(Shen et al., 2018).

The test particles used in the experiment were standard polystyrene latex microspheres (PSL) with particle sizes of 320 nm, 510, 720, 960, and 1400 nm purchased from Duke Scientific. The commercial aerosol generator TSI 9302 was used to atomize the aqueous solution of the PSL and to produce a controlled ~~particles~~ beam of particles. The air flow with PSL particles was dried by a diffusion drying tube and then passed to the SPAMS for analysis.

For an independent particle~~s~~size distribution measurements the glass plate was installed under the ion source as ~~it~~ shown in the Fig.1. The distance between the ~~center~~centre of the ion source and the plate surface was 31.5 mm. After the glass plate was exposed under the particles flow~~s~~, the photo of the particles collected on the glass plate surface was acquired by Olympus CX31RTSF microscope. The density profile of the collected particles was extracted by the free ***Image J*** software.

## ~~3~~2.1 Key factors affecting the efficiency

Figure 1 shows a schematic representation of the SPAMS ion source. The Nd: YAG laser beam is focused ~~o~~in the center of the ion source where particles are ionized by laser radiation. The 266 nm laser operates in $TEM_{00}$ mode with Gaussian distribution. The $e^{-1}$width of the focused gaussian laser beam ~~cross-over~~ is about 300 μm. Factors that actually affect the ionization efficiency are the total laser pulse energy and the location of the particle in the focused laser spot. ~~The 266 nm laser operates in $TEM_{00}$ mode with Gaussian distribution.~~ As the particles size is more than 300 times smaller~~less~~ than that of the focused laser beam width each particle is ionized by a virtually uniform laser power density., ~~therefore the~~But, when the beam of the particles is wider than the diameter of the laser beam in the ionization region the particles in the beam can be exposed to~~can be exposed under~~ very different laser energy fluences resulting in a great difference in ionization efficiency. Therefore, when the particles travel near~~are at~~ the edge of the laser spot, it becomes~~is~~ impossible to generate enough ions to be detect such particles~~ed~~.

In our experiments, the pulse energy of the laser was set to 0.6 mJ and the pulse duration is 7.2 ns, which corresponds to the laser power density in the focal point of about $2\times10^{8}$ $Wcm^{-2}$.

When the delay extraction technique is not used, the two DC high voltage potentials are constantly applied to the extraction electrodes of the original bi-polar SPAMS ion source. When the charged particles enter the space of the ion source, they start to be deflected under the action of the DC electrical field. The amount of deflection is related to the speed and the mass of the particles, the amount of the surface charge and the electric field strength. Thus, during the flight through the ion source, the particles gradually deviate from the laser centre point, resulting in the decrease of the ionization efficiency and ~~the~~a significant drop in the hit rate.

When the delay extraction technique is used, the particles enter the extraction region while the electrical field is kept at zero. Then the laser ionizes the particle, and the HV extraction pulse is applied with 100 ns delay after the laser pulse. So, there is no electric field between the ion source plates before the particles are ionized by the laser. Thus, the charged aerosol particles are not deflected by the electric field force during their flight, thereby achieving a higher hit rate.

## 3 Results and discussions

### ~~3.1 Key factors affecting the efficiency~~

~~Figure 1 shows a schematic representation of the SPAMS ion source. The Nd: YAG laser beam is focused toon the center of the ion source where particles are ionized by laser radiation. The $e^{-1}$ of the focused laser beam cross-over is about 300 μm. Factors that actually affect the ionization efficiency are the total laser pulse energy and the location of the particle in the focused laser spot. The 266 nm laser operates in $TEM_{00}$ mode with Gaussian distribution. As the particles size is more than 300 times less than that of the focused laser beam width, therefore the particle can be exposed under very different laser energy fluence resulting in a great difference in ionization efficiency. Therefore, when the particles are at the edge of the laser spot, it is impossible to generate enough ions to be detected.~~

~~In our experiments, the pulse energy of the laser was set to 0.6 mJ, which corresponds to the laser power density in the focal point of about $2\times10^{8}$ $Wcm^{-2}$.~~

~~When the delay extraction technique is not used, the two DC high voltage potentials are constantly applied to the extraction electrodes of the original bi-polar SPAMS ion source. When the charged particles enter the space of the ion source, they start to be deflected under the action of the DC electrical field. The amount of deflection is related to the speed and the mass of the particles, the amount of the surface charge and the electric field strength. Thus, during the flight through the ion source, the particles gradually deviate from the laser centre point, resulting in the decrease of the ionization efficiency and sharpthe significant drop in the hit rate.~~

~~When the delay extraction technique is used, the particles enter the extraction region while the electrical field is kept at zero electrical field. Then the ionizing laser ionizes the particle, and the HV extraction pulse is applied with 100 ns delay after the laser pulse. So, there is no electric field between the ion source plates before the particles are ionized by the laser. Thus, the charged aerosol particles are not deflected by the electric field force during their flight, thereby achieving a higher hit rate.~~

### 3.~~2~~ 1 The experiment with PSL particles.

The influence of the electric field on the hit rate was studied by using PSL beads of five different particle sizes. In the Fig.2 the dependencies of the hit rate from the electrical field strength for DC and DE mode are shown. It can be seen that under the same DC electric field strength (Fig.2 (A)), the hit rate of the particles from 320 nm to 1400 nm increases, indicating that the effect of the electric field on the small particles is more ~~obvious~~pronounced. As the DC electric field strength increases, the hit rate of the particles of each size gradually decreases, indicating that the particles are deflected by the electric field force.

Under the DE mode, the hit rate for ~~all~~the particles ofall sizes is obviously increased in comparison ~~to~~with the DC case (Fig.2 (b)). When the pulsed electric field strength exceeds 60 ~~KV~~ kV $m^{-1}$, the hit rate of the particles above 520 nm is close to 100%, indicating that the flight path without electric field is essential for the increase of the hit rate of the particles. The hit rate of the 320 nm PSL particles is 40%, which is much lower than 100% of other particles. This is mainly due to the

focusing effect of the aerodynamic lens. The divergence of the particle beam itself is higher than that for the particles above 500 nm, which result~~sing~~ in the~~a~~ decrease of the hit rate. In addition, when the electric field strength increases from 0 to 60 ~~KV~~ kV $m^{-1}$, the hit rate gradually increases from 5% to 100%. We ~~suppose~~ speculatethat the increase of the hit rate with the electrical field strength in this range may be caused by the increase of the resolving power of TOF MS. The lower is the extraction electrical field strength, the bigger is the turnaround time in TOF MS, which in turn decreases the resolving power of the instrument. In the case of a big turnaround time, the peak width increases and the peak height decreases. ~~So, such a small peaks~~ This, in turn, can result in a loss of measured ion current because of ADC threshold adjusted to reject the low intensity~~ve~~ peaks accounted as a noise. The loss of the recorded ion current can in turn result in a miscount of some particles thus decreasing the hit rate. Also, at the low extraction electric~~al~~ field, an ion divergence can be enhanced, resulting in a loss of ion current during the ion flight to the detector.

In the Fig.3 dependencies of the hit rate increment achieved for DE mode compared to DC mode case are shown. It can be seen that for different particle sizes, the hit rate gain increases sharply with the increase of the electric field strength, especially for small particle size. For 320 nm particles, the hit rate can be increased by more than 100 times at an electric field strength over 180 kV $m^{-1}$. This result shows that the DE technique can effectively eliminate the influence of the electric field intensity on the flight path of the particles, avoid the use of additional peripheral devices such as electrostatic neutralizers, and result in an improvement of the hit rate.

It is worth noting that the mass spectra obtained with DE have a higher resolution, but it is approximately the same set of peaks as those obtained with the injection of ions in a constant field (CF). Peaks in the mass spectrum obtained with DE are narrower and, on average, have larger amplitude. The influence of ~100 ns delay is not reflected in the composition of peaks in acquired mass spectra. Mass spectra of PSL particles acquired in DE and DC modes are presented in the supplementary material for comparison. The mechanisms of ion formation as the 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 i~~In this work we did not ~~go deep~~focus on~~into~~ these issues, since they are not directly related to the observed increase of the hit rate.

In order to further confirm that the particles are deflected by the action of the electric field, we conducted several further experiments. Taking the 720 nm PSL microsphere as an example, we compared the hit rate of a 720 nm PSL beads under the constant DC electric field only, under the DC electric field with electrostatic neutralizer and delay extraction combined with or without neutralizer. The Fig.4 shows the hit rate value for the measurement period of ~30 minutes. It can be seen that the particle hit rate after the use of the electrostatic neutralizer has increased from the average level of 20% to the level exceeding 85%, indicating that the surface charge of the particles has a great influence on the hit rate. However, the average hit rate of the particles obtained by the DE technique is close to 96%, which is slightly higher than that of the hit rate measured in the case when the electrostatic neutralizer was used. This difference can be caused by a residual charge remaining on the particles even after the usage of X-ray neutralizer (Model TSI 3088). The higher hit rate achieved by delay extraction is caused by the absence of electric field influence on the particles motion.

Further~~,~~ two experiments were performed to measure particle beam divergence under the influence of electrical field formed between two electrodes of extraction region of SPMS. The particles ~~was~~ were collected on the surface of the glass plate, as it is shown in the Fig.1. In the first experiment (Fig.5 A,B) no voltage was applied to the electrodes, and the resulting spot just represents 720 nm particles beam profile as the result of aerodynamic dynamic lens action. The profile was fitted by Gauss envelope, and the average beam width extracted from the Gaussian curve is a little more than 0.1 mm. The second experiment (Fig.6 A, B) was performed when DC potentials (+/-1000 V) were applied to the extraction region electrodes according to the usual working conditions in case of DC extraction mode. The trace of the same 720 nm PSL beads on the glass plate is shown in Fig.6 (A).

The particle divergence is significantly increased in this case. Using Image J program, the trace profile was extracted, and then the Gaussian fitting was uploaded on the data. The space distribution of the particles can be easily transformed into the particle charge distribution as we deal with the calibrated PSL beads. The ion beam displacement at the exit of the extraction region (Fig.6 (A,B)) was analyzed by (Liu et al., 1995), and it can be described by simple equation:

$$\Delta x_1 = \frac{1}{2}at^2 = \frac{1}{2}\frac{q}{m}\frac{V_H}{m_p d}\left(\frac{L_1}{U_p}\right)^2 \quad (1)$$

Here $q$ and $m_p$ are particle charge and mass, $d$ and $V_H$ are the distance and voltage difference between two flat extraction electrodes, $L_1$ is the electrodes height, $U_p$ is the particle longitudinal velocity, $a$ is the acceleration of the particle caused by the extraction electrical field and t is the particle dwell time in the extraction region. The equation was derived by simplified assumption that the particle moving between the plates is accelerated by the constant horizontal electrostatic force. Then the particle with the horizontal speed moves until it hits the gathering glass plate. The resulting particle displacement in the position of the gathering glass plate is:

$$\Delta x = \Delta x_1 + \Delta x_2 = \frac{1}{2}\frac{qV_H}{m_p d}\frac{L_1(L_1+2L_2)}{U_p^2} \quad (2)$$

Here $L_2$ is the distance from the lower edge of the extraction electrode ~~and~~to the gathering glass plate surface. The resulting particle displacement is proportional to the particle charge, so, from the trace in Fig.6 (A) we can extract the particle charge distribution shown in Fig.6 (B). The average particle charge extracted from the Gaussian envelope is 60 elementary charges. There are multiple publications where this electrification charge was measured for different types of particles(Dodd, 1953). The results reported in the literature ~~results~~ are in a good agreement with our estimation made for 720 nm PSL beads.

Using known particle mass, velocity, extraction voltage and electrodes dimensions, we have extracted the particle displacement per unit charge in the middle point where ionizing laser is shooting to. For the parameters of our instrument this displacement is 12.5 *μm~~m~~* $z^{-1}$, where z is the number of elementary charges on the particle. Hence, the particle with the average 20 elementary charges will be deflected ~250 μm from the ionizing laser spot ~~center~~centre. Taking into account the Gaussian profile of the focused laser beam of 300 μm, the hit efficiency will be greatly affected by such displacement.

### 3.3 Comparison of environmental testing

The comparison of the detection efficiency for the instrument with DC extraction and with DE used for the actual atmospheric particulate matter detection is shown in Fig.7 (A,B).Aerosol particles from laboratory room air were analyzed by SPMS used in this work. In order to ensure that aerosol composition is stable during the experiment, the DC and DE modes of operation were switched alternately after 10 minutes. Four sets of both DC and DE extraction data were acquired ~~for~~in80 minutes. The hit rate was calculated as the ratio of the ionized particles number to the number ofsized particles. The hit rate data were extracted for the groups of particlesselected by size; bin value was 20 nm while the whole range was 200-1000 nm.The data of four sets by 10 minutes each, both for DC and DE extraction modes, were summed. In the DC mode, in 40 minutes, a total of 12174 particles w~~ere~~as~~registered~~recorded, of which 4569 were ionized, while in the DE mode, 12030 particles were ~~registered~~recorded, and 8228 were ionized for the same time.

It is seen from Fig.7A, that the centre of the distribution obtained with DC extraction (Blue~~,~~ circles) is shifted to the higher particles size. This behaviour corresponds to our results obtained for the model PSL particles. Fig.7B shows the hit rate gain for the DE technique to the DC extraction, obtained from the data plotted in Fig.7A. It should be noted, that usage of delay extraction eliminates the distortion of particle distribution, which results from the dispersion of particle deflection by their size in case of DC extraction. The integral hit rate for the experiment with the real particles is ~ 25% higher in case of delay extraction (Fig.7A), while the gain in hit rate achieved for small particles is ~ 4 times bigger than that measured for DC extraction (Fig.7B).

The hit rate for the real atmospheric aerosol is lower than that for the standard PSL beads mainly due to the shape of the particles. In the actual atmosphere, the shape of the particles is much more complicated than the PSL sphere. For example, the aged carbon particles tend to be spherical, and the hit rate is relatively high, while the fresh black carbon particles exhibit a chain structure, so the divergence during their flight is probably bigger, resulting in lower hit rates(Ghan et al., 2012). In general, using the delay extraction technique, the hit rate of environmental particles with size < 500 nm can be significantly improved, and the obtained particle size distribution becomes closer to the real one.

## 4 Conclusion

Aerosols often carry surface charges. When charged particles fly through the SPMS ion source, they can be deflected by the action of constant electric field, resulting in a substantial drop in the hit rate. When delay extraction is used in SPMS, the instrument efficiency is improved because the particles are not deflected by the action of the stationary electric field. The absence of the DC electrical field in this method allows one to avoid the use of the auxiliary external devices such as electrostatic neutralizers, maximize the hit rate of the aerosol particles, and decrease the distortion of the measured size distribution of particles. Experiments have shown that for PSL microspheres, the smaller is the particle size, the greater is the gain in the hit rate. There is no dependence of the hit rate ~~from~~on the measured particle size for particles with diameter more

than 500 nm when ~~delay extraction~~DE~~was~~is used. For the real application it means that this method minimizes losses in the hit rate, which in turn ~~e~~affects ~~on~~ the measured size distribution of the particles.

The experiments with environmental aerosol have also shown that SPAMS with delay extraction technology can improve the average detection efficiency of the actual atmospheric aerosol by more than 25%, and improve the hit rate for small (<500 nm) particles more than four times. It should be noted that the charge of the particles is connected with ~~particle~~their parameters. It means that a pre-selection of particles based on their charge can be used to extract extra information from the data acquired by SPMS. It could be done, for example, by using two pairs of deflecting plates before the ion source. By choosing the deflection voltage, only particles with a specific mass/charge ratio will pass this double deflector and can be ionized in the ion source.

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## References

Alaime, C., Bertrand, J., Bonnet, L., El Masri, Y., Palffy, L., Pellegrin, P., and Prieels, R.: Stabilization of the light output delay of a pulsed nitrogen laser, Nuclear Instruments and Methods in Physics Research, 207, 423-427, http://doi.org/10.1016/0167-5087(83)90653-1, 1983.

Bi, X., Zhang, G., Li, L., Wang, X., Li, M., Sheng, G., Fu, J., and Zhou, Z.: Mixing state of biomass burning particles by single particle aerosol mass spectrometer in the urban area of PRD, China, Atmospheric Environment, 45, 3447-3453, http://doi.org/10.1016/j.atmosenv.2011.03.034, 2011.

Chudinov, A., Li, L., Zhou, Z., Huang, Z., Gao, W., Yu, J., Nikiforov, S., Pikhtelev, A., Bukharina, A., and Kozlovskiy, V.: Improvement of peaks identification and dynamic range for bi-polar Single Particle Mass Spectrometer, International Journal of Mass Spectrometry, 436, 7-17, http://doi.org/10.1016/j.ijms.2018.11.013, 2019.

Cziczo, D. J., Thomson, D. S., Thompson, T. L., DeMott, P. J., and Murphy, D. M.: Particle analysis by laser mass spectrometry (PALMS) studies of ice nuclei and other low number density particles, International Journal of Mass Spectrometry, 258, 21-29, http://doi.org//10.1016/j.ijms.2006.05.013, 2006.

Dall'Osto, M., Harrison, R. M., Beddows, D. C. S., Freney, E. J., Heal, M. R., and Donovan, R. J.: Single-particle detection efficiencies of aerosol time-of-flight mass spectrometry during the North Atlantic marine boundary layer experiment, Environmental Science and Technology, 40, 5029-5035, http://doi.org/10.1021/es050951i, 2006.

Demokritou, P., Lee, S. J., Ferguson, S. T., and Koutrakis, P.: A compact multistage (cascade) impactor for the characterization of atmospheric aerosols, Journal of Aerosol Science, 35, 281-299, http://doi.org/10.1016/j.jaerosci.2003.09.003, 2004.

Dodd, E. E.: The Statistics of Liquid Spray and Dust Electrification by the Hopper and Laby Method, Journal of Applied Physics, 24, 73-80, http://doi.org/10.1063/1.1721137, 1953.

Gemayel, R., Hellebust, S., Temime-Roussel, B., Hayeck, N., Van Elteren, J. T., Wortham, H., and Gligorovski, S.: The performance and the characterization of laser ablation aerosol particle time-of-flight mass spectrometry (LAAP-ToF-MS), Atmos. Meas. Tech., 9, 1947-1959, http://doi.org/10.5194/amt-9-1947-2016, 2016.

Ghan, S. J., Liu, X., Easter, R. C., Zaveri, R., Rasch, P. J., Yoon, J.-H., and Eaton, B.: Toward a Minimal Representation of Aerosols in Climate Models: Comparative Decomposition of Aerosol Direct, Semidirect, and Indirect Radiative Forcing, Journal of Climate, 25, 6461-6476, http://doi.org/10.1175/jcli-d-11-00650.1, 2012.

Gunn, R., and Woessner, R. H.: Measurements of the systematic electrification of aerosols, Journal of Colloid Science, 11, 254-259, http://doi.org/10.1016/0095-8522(56)90050-2, 1956.
Kim, M., Cahill, J. F., Su, Y., Prather, K. A., and Cohen, S. M.: Postsynthetic ligand exchange as a route to functionalization of 'inert' metal–organic frameworks, Chemical Science, 3, 126-130, http://doi.org/10.1039/C1SC00394A, 2012.
Kousaka, Y., Okuyama, K., and Endo, Y.: Calibration of differential mobility analyser by visual method, Journal of Aerosol Science, 12, 339-348, http://doi.org/10.1016/0021-8502(81)90023-9, 1981.
Li, L., Huang, Z., Dong, J., Li, M., Gao, W., Nian, H., Fu, Z., Zhang, G., Bi, X., Cheng, P., and Zhou, Z.: Real time bipolar time-of-flight mass spectrometer for analyzing single aerosol particles, International Journal of Mass Spectrometry, 303, 118-124, http://doi.org/10.1016/j.ijms.2011.01.017, 2011.
Li, L., Li, M., Huang, Z., Gao, W., Nian, H., Fu, Z., Gao, J., Chai, F., and Zhou, Z.: Ambient particle characterization by single particle aerosol mass spectrometry in an urban area of Beijing, Atmospheric Environment, 94, 323-331, http://doi.org/10.1016/j.atmosenv.2014.03.048, 2014.
Li, L., Liu, L., Xu, L., Li, M., Li, X., Gao, W., Huang, Z., and Cheng, P.: Improvement in the Mass Resolution of Single Particle Mass Spectrometry Using Delayed Ion Extraction, Journal of the American Society for Mass Spectrometry, 29, 2105-2109, http://doi.org/10.1007/s13361-018-2037-4, 2018.
Liu, P., Ziemann, P. J., Kittelson, D. B., and McMurry, P. H.: Generating Particle Beams of Controlled Dimensions and Divergence: II. Experimental Evaluation of Particle Motion in Aerodynamic Lenses and Nozzle Expansions, Aerosol Science and Technology, 22, 314-324, http://doi.org/10.1080/02786829408959749, 1995.
Middlebrook, A. M., Murphy, D. M., Lee, S.-H., Thomson, D. S., Prather, K. A., Wenzel, R. J., Liu, D.-Y., Phares, D. J., Rhoads, K. P., Wexler, A. S., Johnston, M. V., Jimenez, J. L., Jayne, J. T., Worsnop, D. R., Yourshaw, I., Seinfeld, J. H., and Flagan, R. C.: A comparison of particle mass spectrometers during the 1999 Atlanta Supersite Project, Journal of Geophysical Research: Atmospheres, 108, http://doi.org/10.1029/2001jd000660, 2003.
Murphy, D. M.: The design of single particle laser mass spectrometers, Mass Spectrom Rev, 26, 150-165, http://doi.org/10.1002/mas.20113, 2007.
Nash, D. G., Baer, T., and Johnston, M. V.: Aerosol mass spectrometry: An introductory review, International Journal of Mass Spectrometry, 258, 2-12, http://doi.org/10.1016/j.ijms.2006.09.017, 2006.
Nicosia, A., Manodori, L., Trentini, A., Ricciardelli, I., Bacco, D., Poluzzi, V., Di Matteo, L., and Belosi, F.: Field study of a soft X-ray aerosol neutralizer combined with electrostatic classifiers for nanoparticle size distribution measurements, Particuology, 37, 99-106, http://doi.org/10.1016/j.partic.2017.08.001, 2018.
Noble, C. A., and Prather, K. A.: Real-time single particle mass spectrometry: a historical review of a quarter century of the chemical analysis of aerosols, Mass spectrometry reviews, 19, 248-274, http://doi.org/10.1002/1098-2787(200007)19:4<248::aid-mas3>3.0.co;2-i, 2000.
Pratt, K. A., Mayer, J. E., Holecek, J. C., Moffet, R. C., Sanchez, R. O., Rebotier, T. P., Furutani, H., Gonin, M., Fuhrer, K., Su, Y., Guazzotti, S., and Prather, K. A.: Development and Characterization of an Aircraft Aerosol Time-of-Flight Mass Spectrometer, Analytical Chemistry, 81, 1792-1800, http://doi.org/10.1021/ac801942r, 2009.
Pratt, K. A. and Prather, K. A.: Mass spectrometry of atmospheric aerosols—Recent developments and applications. Part II: On-line mass spectrometry techniques, 31, 17-48, https://doi.org/10.1002/mas.20330, 2012.
Roth, A., Schneider, J., Klimach, T., Mertes, S., van Pinxteren, D., Herrmann, H., and Borrmann, S.: Aerosol properties, source identification, and cloud processing in orographic clouds measured by single particle mass spectrometry on a central European mountain site during HCCT-2010, Atmos. Chem. Phys., 16, 505-524, http://doi.org/10.5194/acp-16-505-2016, 2016.
Shen, W., Dai, X., Huang, Z. x., Hou, Z. h., Cai, W. g., Du, X. b., Zhou, Z., Li, M., and Li, L.: Improvement of the Dynamic Range of Data Acquisition System in Single Particle Mass Spectrometry, Journal of Chinese Mass Spectrometry Society, 39, 331-336, http://doi.org/10.7538/zpxb.2017.0119, 2018.
Su, Y., Sipin, M. F., Furutani, H., and Prather, K. A.: Development and Characterization of an Aerosol Time-of-Flight Mass Spectrometer with Increased Detection Efficiency, Analytical Chemistry, 76, 712-719, http://doi.org/10.1021/ac034797z, 2004.

Thomson, D. S., Middlebrook, A. M., and Murphy, D. M.: Thresholds for Laser-Induced Ion Formation from Aerosols in a Vacuum Using Ultraviolet and Vacuum-Ultraviolet Laser Wavelengths, Aerosol Science and Technology, 26, 544-559, http://doi.org/10.1080/02786829708965452, 1997.

Trimborn, A., Hinz, K. P., and Spengler, B.: Online analysis of atmospheric particles with a transportable laser mass spectrometer during LACE 98, Journal of Geophysical Research: Atmospheres, 107, LAC 13-11-LAC 13-10, http://doi.org/10.1029/2001JD000590, 2002.

Tsai, C.-J., Lin, J.-S., Deshpande, C., and Liu, L.-C.: Electrostatic Charge Measurement and Charge Neutralization of Fine Aerosol Particles during the Generation Process, 2005.

Woessner, R. H., and Gunn, R.: Measurements related to the fundamental processes of aerosol electrification, Journal of Colloid Science, 11, 69-76, http://doi.org/10.1016/0095-8522(56)90021-6, 1956.

Zelenyuk, A., Cai, Y., and Imre, D.: From Agglomerates of Spheres to Irregularly Shaped Particles: Determination of Dynamic Shape Factors from Measurements of Mobility and Vacuum Aerodynamic Diameters, Aerosol Science and Technology, 40, 197-217, http://doi.org/10.1080/02786820500529406, 2006.

Zelenyuk, A., Yang, J., Imre, D., and Choi, E.: Achieving Size Independent Hit-Rate in Single Particle Mass Spectrometry, Aerosol Science and Technology, 43, 305-310, http://doi.org/10.1080/02786820802637915, 2009.

Zhao, Y., Bein, K. J., Wexler, A. S., Misra, C., Fine, P. M., and Sioutas, C.: Field evaluation of the versatile aerosol concentration enrichment system (VACES) particle concentrator coupled to the rapid single-particle mass spectrometer (RSMS-3), Journal of Geophysical Research: Atmospheres, 110, http://doi.org/10.1029/2004jd004644, 2005.

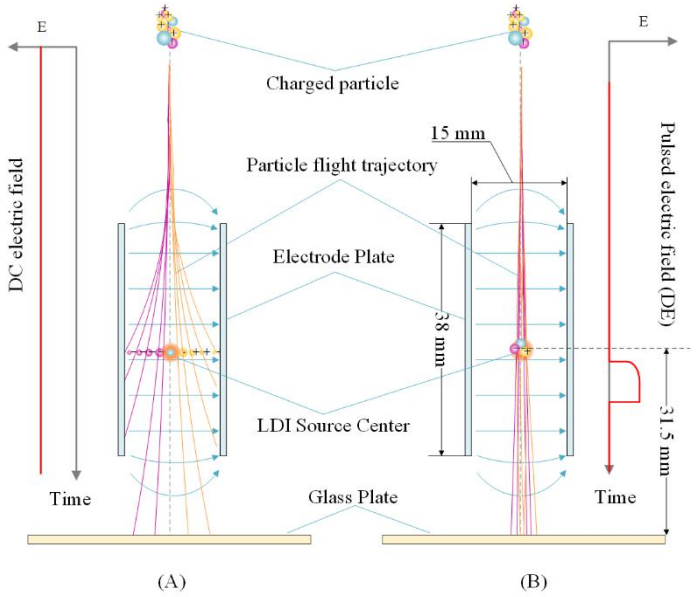



**Figure 1: Experimental setup. The glass plate position and extraction region dimensions are shown for two cases: (a) stationary electrical field extraction; (b) delay extraction.**

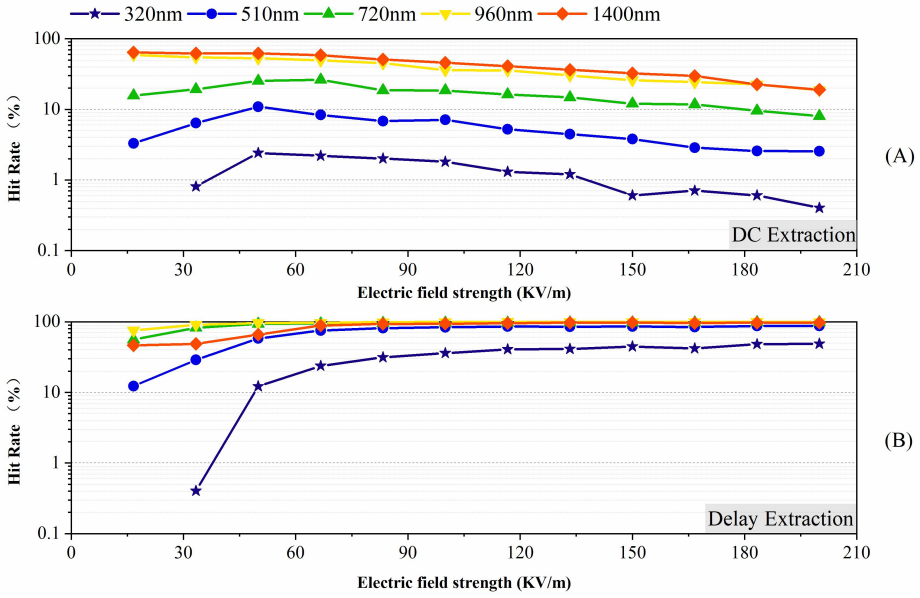



**Figure 2: Comparison of hit rate dependencies for different sizes of PSL particles in two cases: (A) constant electric field (DC extraction); (B) pulsed electric field (delay extraction, (DE)).**

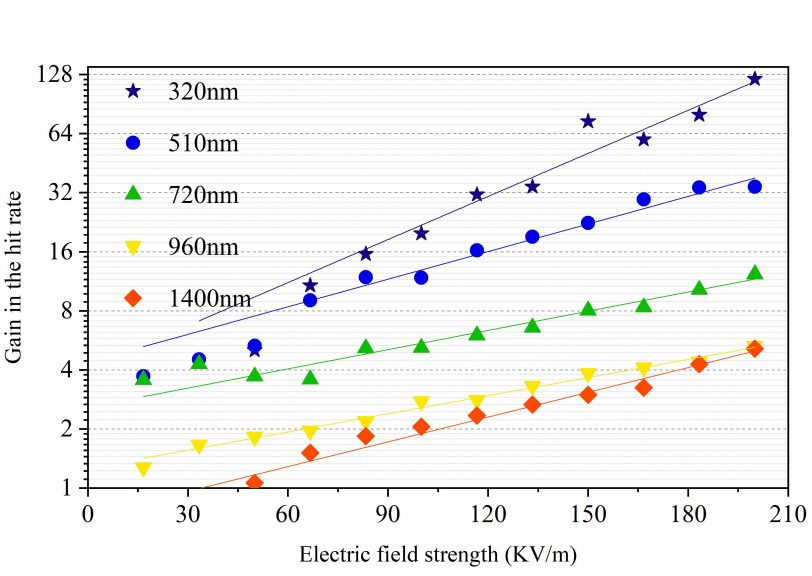



**Figure 3: The gain in the hit rate achieved for different sizes of PSL particles plotted over the extraction electric field strength.**

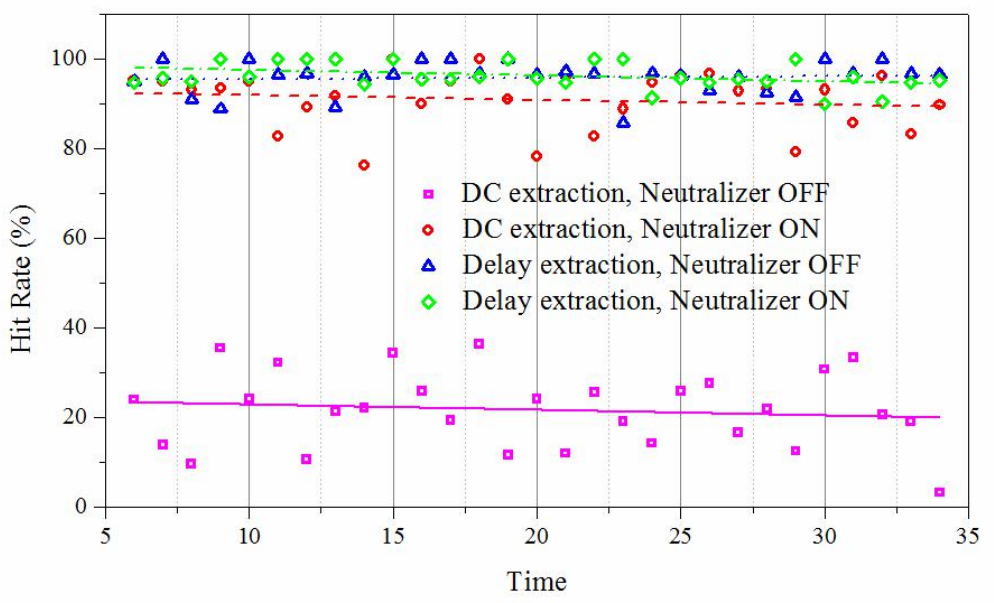
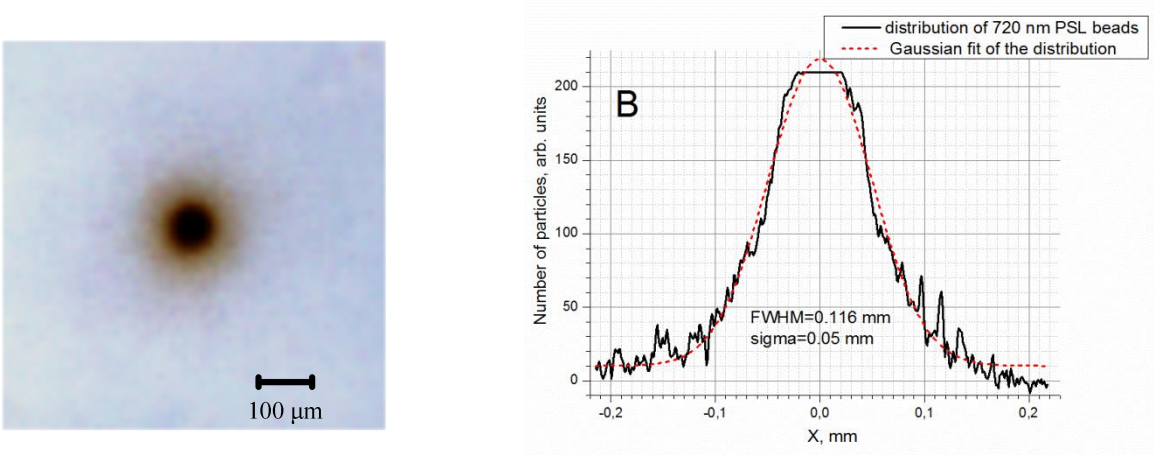



**Figure 4: Hit rate count for four cases: DC extraction& no neutralizer, DC extraction& neutralizer ON, Delay extraction & no neutralizer, and Delay extraction & neutralizer ON.**




385 **Figure 5: The distribution of 720 nm particles collected on the glass plate without electrical field. A – photo of the spot from particles collected on the glass plate. B – the density profile extracted from (A) by Image J software, and the Gaussian approximation of the profile.**

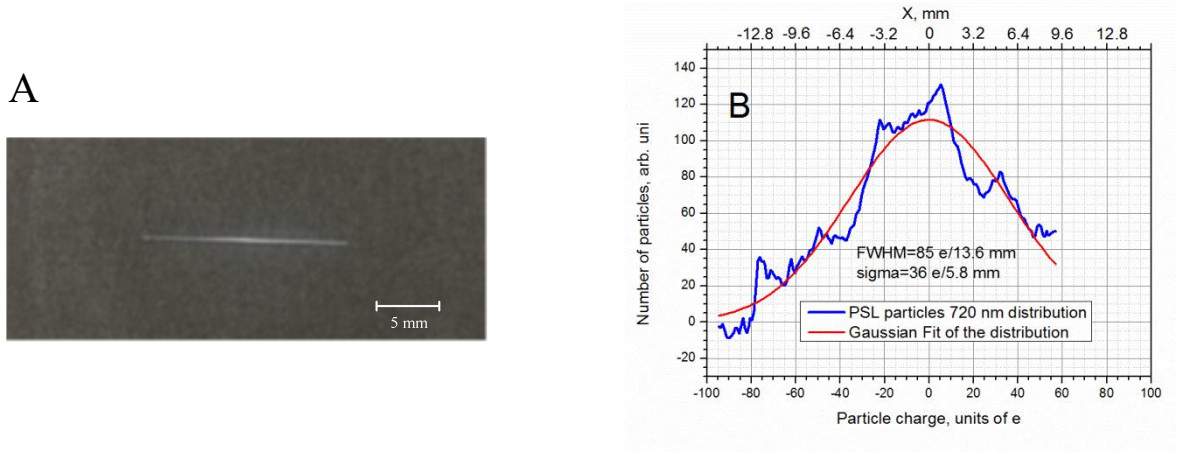



**Figure 6: The distribution of 720 nm particles moved through the electrical field formed with 2000 V potential difference between the electrodes in extraction region collected on the glass plate. (A) – photo of the trace from particles on the glass plate. (B) – the extracted particles charge distribution from the density profile (A) by Image J software, and the Gaussian approximation of the profile.**

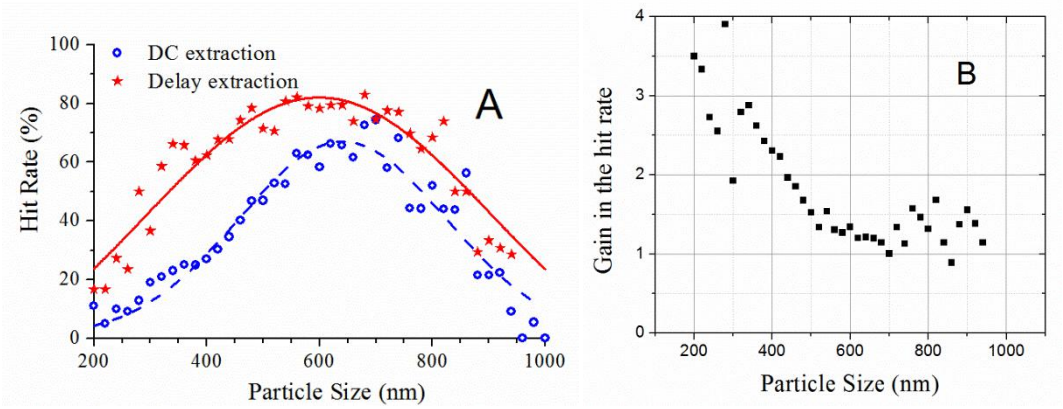



**Figure 7: A – Particles size distribution of real aerosol particles. Blue, circles - DC extraction, Red, asterisks - delay extraction; B – the hit rate gain achieved by delay extraction (DE) plotted over the particles size.**

400