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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 is the instrument providing a plenty 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 DC extraction, when the stationary high voltage is applied to the extraction electrodes. As the aerosol particles initially carry a certain charge, they can be deflected by this electric field thus decreasing the hit rate. It was 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 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 can bring the measured distribution closer to the real one. Thus, the delay extraction technique provides not only mass resolution improvement, 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 have reviewed the principle, structure and applications of SPMS in detail (Murphy, 2007; Nash et al.,

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2006; Noble and Prather, 2000). SPMS usually use an aerodynamic lens to form and to transfer aerosol beam from the atmosphere into the vacuum system and to focus particle beams. Usually the two-beam laser caliper is used to measure the particle speed and size before the "sized" particle pass through a high-energy pulsed laser beam. When the particles are ionized by the laser radiation, a bunch of positive and negative ions is formed. Produced ions are accelerated by strong electrical field in the time-of-flight mass spectrometer (TOF MS) and finally detected and registered by data acquisition system based on fast ADC. Compared to the traditional off-line particle methods, the SPMS can exclude the stage for preliminary collection and preparation of the particles, and provides high real time 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 in the order of a few milliseconds. However, it is generally necessary to accumulate single particle data over a period of time to obtain statistically significant data information. The application of the SPMS to atmospheric aerosol analysis and investigation of chemical processes with atmospheric aerosols require 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 a certain surface charge. Hence, in case of stationary electrical field in extraction region of SPMS, the particles can be deflected when they move through the ion source space. If the particle is shifted from the center of the laser beam, the ionization efficiency drops 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. 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. Most of instruments 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 considerable distance (about 10 cm) below 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

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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 rate being affected by the particle size. As a result, the dynamic laser trigger system was developed to realize the trigger compensation of particles with different particle sizes thereby achieving an improvement of the hit rate. However, this method is directed to solve the positional problem of the aerosol particle in the flight direction, and 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 small. 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).

In our previous works we have used the double exponential pulse delay extraction technique to improve the resolution of SPMS (Chudinov et al., 2019; Li et al., 2018).This solution provides 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 the half of the ion source with no DC electrical field. Therefore, the influence of the particle charge to its trajectory will be neglected in comparison to the usual ion source with stationary electrical field. In this paper we present our investigation of the effect of stationary and pulse extraction on the particle trajectory and on the hit rate of SPMS instrument.

2 Instruments 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 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, 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

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atomize the aqueous solution of the PSL and to produce controlled particles beam. The air flow with PSL particles was dried by a diffusion drying tube and then passed to SPAMS for analysis.

For particles distribution measurements the glass plate was installed under the ion source as it shown in the Fig.1. The distance between the centre of the ion source and the plate surface was 31.5 mm. After the glass plate was exposed under particles flows 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 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 to 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, 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 $2 \times 10^8\ Wcm^{-2}$.

When the delay extraction technique is not used, 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 mass of the particles, the amount of 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 decrease of the ionization efficiency and sharp drop in the hit rate.

When the delay extraction technique is used, the particles enter the extraction region kept at zero electrical field. Then the ionizing laser ionizes the particle, and 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 flight, thereby achieving a higher hit rate.

3.2 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 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

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effect of the electric field on the small particles is more obvious. 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 particle sizes is obviously increased in comparison to DC case (Fig.2 (b)). When the pulsed electric field strength exceeds 60 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 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, resulting in a decrease of the hit rate. In addition, when the electric field strength increases from 0 to 60 kV m^{-1}, the hit rate gradually increases from 5% to 100%. We suppose that the increase of hit rate with the electrical field strength in this range may be caused by increase of the resolving power of TOF MS. The lower the extraction electrical field strength, the bigger is the turnaround time in TOF MS, which in turn decrease the resolving power of the instrument. In case of big turnaround time, the peak width increases and the peak height decreases. So, such a small peaks can result in loss of ion current because of ADC threshold adjusted to reject low intensive peak accounted as a noise. The loss of ion current can in turn result in a miscount of some particles thus decreasing the hit rate. Also, at low extraction electrical field, an ion divergence can be enhanced, resulting in a loss of ion current during 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 improvement of the hit rate.

In order to further confirm that the particles are deflected by the action of the electric field, we conducted further experiments. Taking the 720 nm PSL microsphere as an example, we compared the hit rate of a 720 nm PSL beads under constant DC electric field only, 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 case the electrostatic neutralizer was used. This difference can be caused by a residual charge remaining on the particles even after the X-ray neutralizer. 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 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

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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 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 hit 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 the gathering glass plate surface. The resulting particle displacement is proportional to the particle charge, so, from the trace in Fig.6 (A) we 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 reported in the literature results are in 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 $m\ z^{-1}$, 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 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 for 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

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operation were switched alternately after 10 minutes. Four sets of both DC and DE extraction data were acquired for 80 minutes. The hit rate was calculated as the ratio of the ionized particles number to the number of sized particles. The hit rate data were extracted for the groups of particles selected 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 were registered, of which 4569 were ionized, while in the DE mode, 12030 particles were registered, 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 dispersion of particle deflection by their size in case of DC extraction. The integral hit rate for the experiment with 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 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 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 auxiliary external devices such as electrostatic neutralizers, maximize the hit rate of aerosol particles, and decrease the distortion of the measured size distribution of particles. Experiments have shown that for PSL microspheres, the smaller the particle size, the greater the gain in the hit rate. There is no dependence of the hit rate from the particle size for particles with diameter more than 500 nm when delay extraction was used. For the real application it means that this method minimizes losses in the hit rate, which in turn effects 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 parameters. It

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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 deflecting plates before the ion source.

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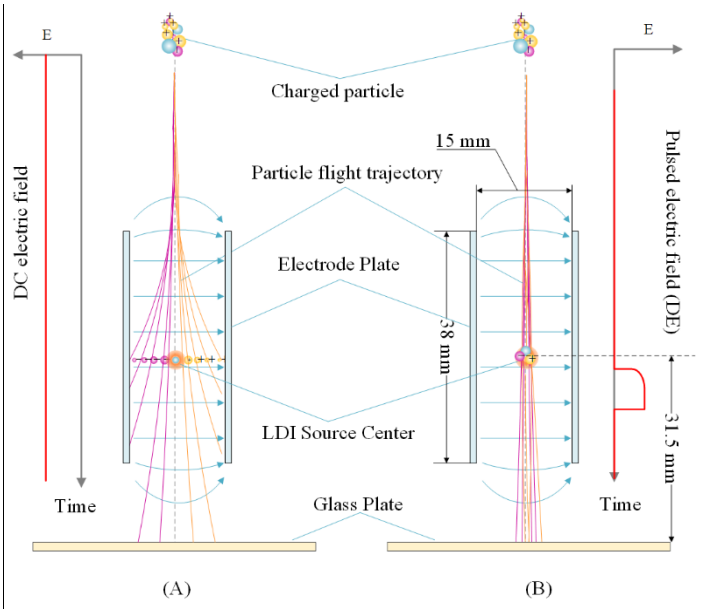

320 **Figure 1: Experimental setup. The glass plate position and extraction region dimensions are shown for two cases: (a) stationary electrical field extraction; (b) delay extraction.**

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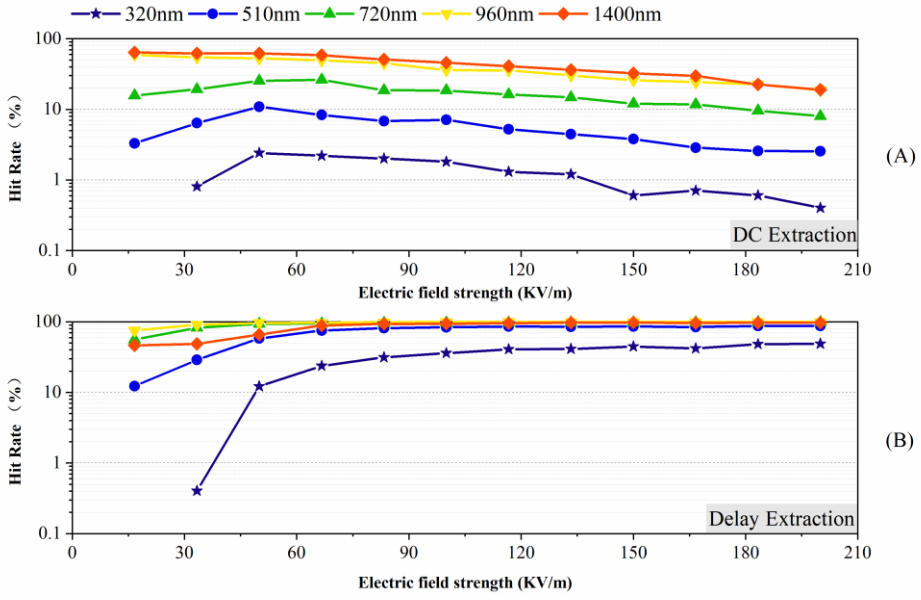

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Figure 2: Comparison of hit rate dependencies for different sizes of PSL particles in two cases: (A) constant electric field (DC extraction); (B) pulsed electric field (delay extraction, (DE)).

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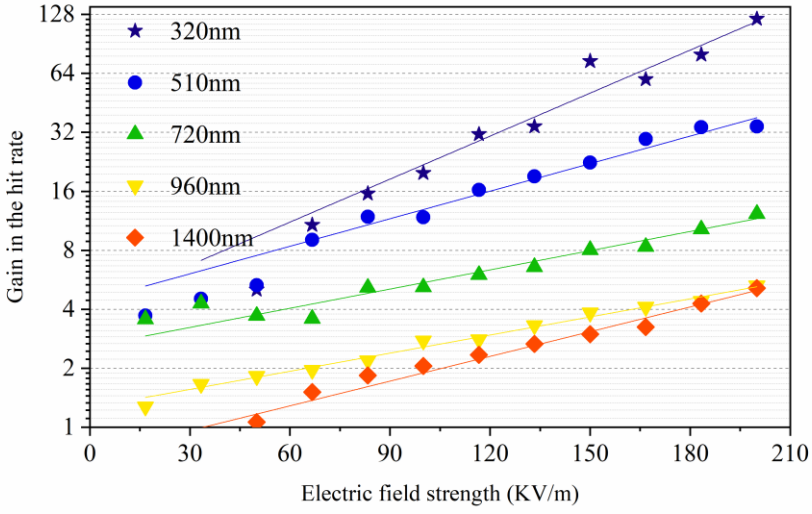

Figure 3: The gain in the hit rate achieved for different sizes of PSL particles plotted over the extraction electric field strength.

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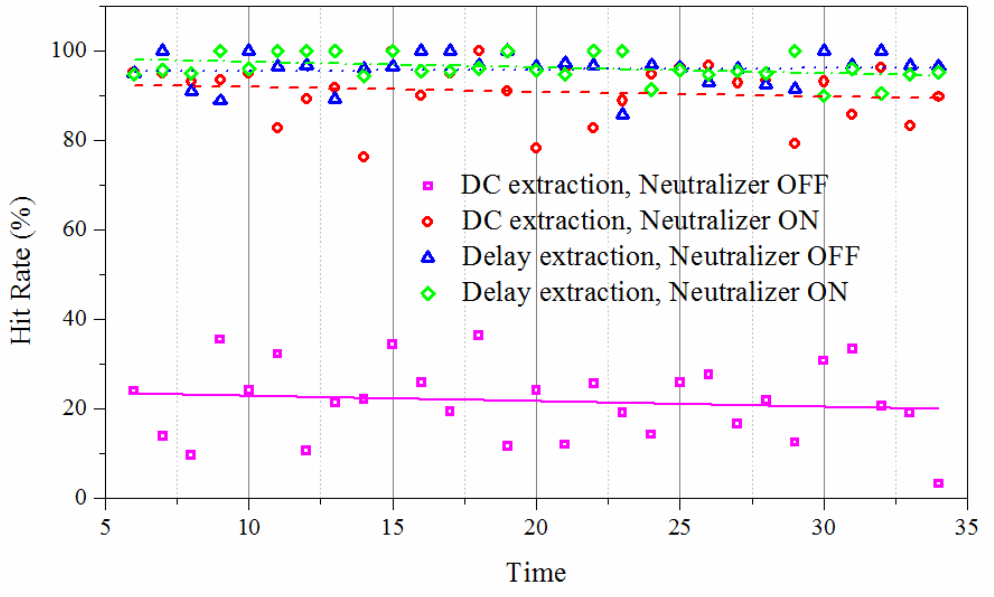

Figure 4: Hit rate count for four cases: DC extraction& no neutralizer, DC extraction& neutralizer ON, Delay extraction & no neutralizer, and Delay extraction & neutralizer ON.

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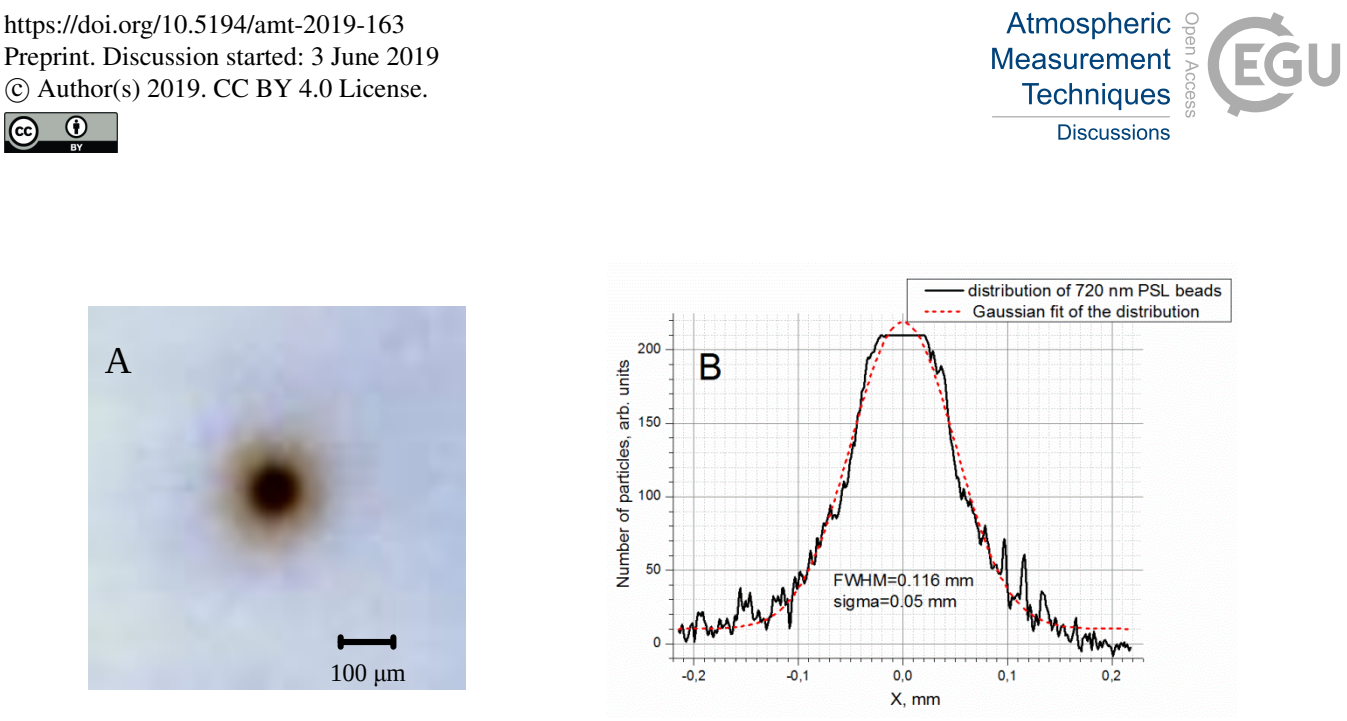

Figure 5: The distribution of 720 nm particles collected on the glass plate without electrical field. A – photo of the spot from particles collected on the glass plate. B – the density profile extracted from (A) by Image J software, and the Gaussian approximation of the profile.

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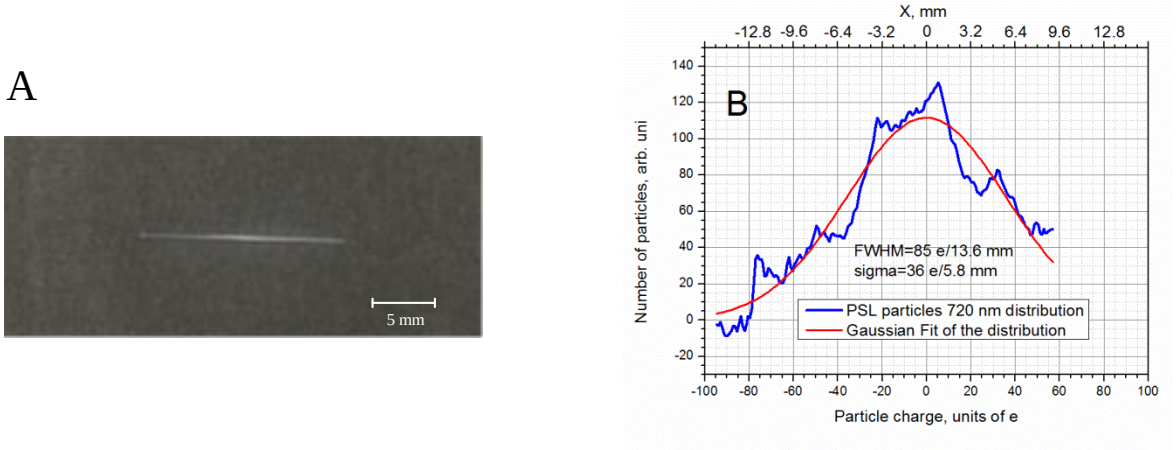

345 **Figure 6: The distribution of 720 nm particles moved through the electrical field formed with 2000 V potential difference between the electrodes in extraction region collected on the glass plate. (A) – photo of the trace from particles on the glass plate. (B) – the extracted particles charge distribution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

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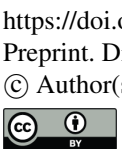

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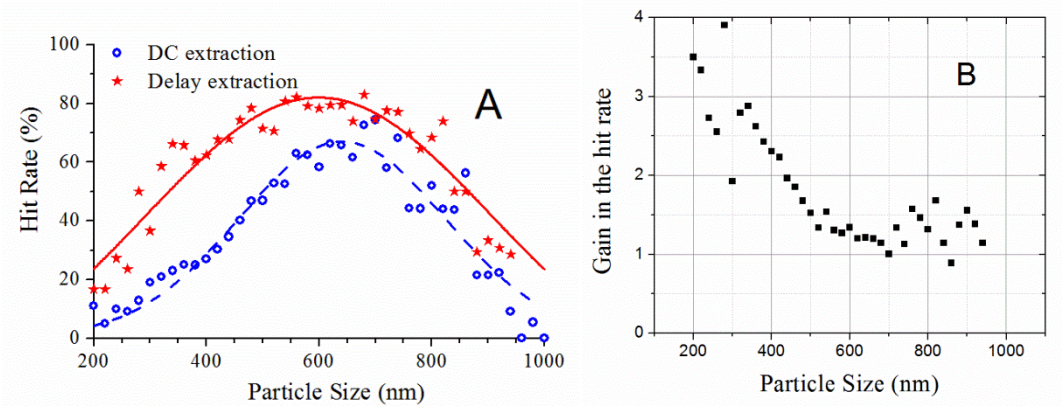

Figure 7: A – Particles size distribution of real aerosol particles. Blue, circles - DC extraction, Red, asterisks - delay extraction; B – the hit rate gain achieved by delay extraction (DE) plotted over the particles size.