
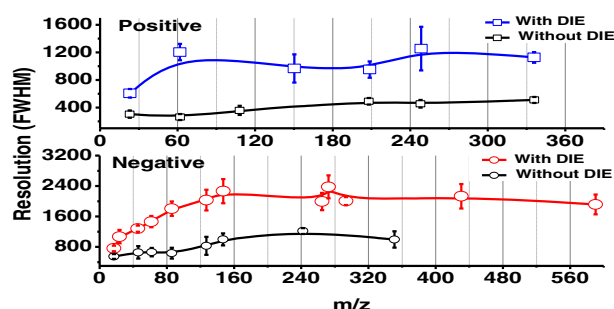


APPLICATION NOTE

Improvement in the Mass Resolution of Single Particle Mass Spectrometry Using Delayed Ion Extraction

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Abstract. A specific delayed ion extraction (DIE) technique, which combines a standard rectangular extraction pulse with an exponential pulse, was introduced for a single particle mass spectrometry (SPMS) instrument, and it can focus ions in a wide mass range and results in a mass resolution improvement for the mass range of the studied ions. The experimental results indicate that the average mass resolution for positive ions is about 1000 when the mass-to-charge ratio

(m/z) is greater than 70, and for negative ions, when the m/z is greater than 70, the average resolution can reach 2000. The highest mass resolutions achieved so far are 1260 for positive ions and 2400 for negative ions for SPMS, which are very beneficial for mass peak interpretation and chemical compound identification. The primary applications for atmospheric particle measurements show that the high mass resolution of SPMS with the DIE technique is very beneficial for the analysis of carbon and metallic element containing particles, and $^{39}\text{K}^+$ with C_3H_3^+ and $^{41}\text{K}^+$ and C_3H_5^+ in organic particles were successfully differentiated using SPMS. The results indicate that SPMS with DIE technique can significantly ease mass peak interpretation and improve the mass assignment ability during analysis. Furthermore, existing SPMS instruments can be improved by a facile retrofitting process to implement the DIE technique.

Keywords: Single particle mass spectrometry, Delayed ion extraction, Mass resolution improvement, Bipolar time-of-flight mass analyzer, Environmental particle analysis

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Introduction

Single particle mass spectrometry (SPMS), which can simultaneously determine the aerodynamic size and chemical compounds of individual aerosol particles in real time [1, 2] has been extensively used in many research fields [3, 4]. Laser

desorption/ionization (LDI) is usually used for ion formation in SPMS, and this high-energy ionization type can ionize most chemical compounds in aerosol particles including insoluble black carbon, metal, dust, and primary and secondary organic aerosols [1]. The ions produced by LDI have large initial ion velocities, which greatly increases the difficulty in achieving high-resolution mass spectra for mass analyzers. For matrix-assisted laser desorption ionization (MALDI), Juhasz et al. [5] assumed that the ion velocity generated by LDI is related to the laser wavelength, analyte, matrix, and ion polarity. A study of polypeptide molecules with MALDI by Beavis et al. [6] has shown that the average initial velocity is 750 m/s, and 300–1000 m/s for masses in the range of 1000–10,000 amu. For

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smaller ions of around 220 amu, the velocities are distributed in the range of 500–2000 m/s. The ions produced by direct LDI normally have masses less than 1000, but they have a greater initial speed. As determined by Hansen et al. [7], the velocity distributions of polymer ions with LDI is in the range of 200–6000 m/s. Compared with the normal laser surface ionization, such as LDI and MALDI, the laser ionization of SPMS has two obvious characteristics. One is that the ionization objects are flying particles, and the particles for ionization have initial velocities in the range of 50–300 m/s depending on the particle size [8, 9]. Another characteristic is that the ionization process is similar to an omnidirectional explosion, resulting in a wide initial kinetic energy distribution for the products. Vera et al. [10] showed that the velocities of ions from the ionization of polystyrene latex spheres (PSLs) is in the range of 0–2000 m/s. Thus, two factors affect the mass resolution of the SPMS: spatial dispersion and energy dispersion. For a single particle, the spatial dispersion for generated ions equals to the particle size, which is really small. However, the initial energy dispersion caused by laser ionization cannot fully be compensated by the reflective time-of-flight mass analyzer, especially for the ions with the same velocity but in the opposite direction [11], resulting in poor mass resolution for SPMS. Presently, the normal mass resolution for SPMS is about 500 [12].

Delayed ion extraction (DIE) is an effective method to improve the mass resolution of time-of-flight mass spectrometry (TOFMS). With DIE, the ions produced by the ionization source will not be accelerated instantly, and they will fly for hundreds of nanoseconds before the pulsed extraction is used. The mass resolution can be improved because of the correlation between the velocity and position of the ions. With a proper delay time, the slower ions will receive enough extra potential energy to catch the faster ions, thus minimizing the ion packet width. DIE was originally introduced as time-lag focusing by Wiley and McLaren for an electron ionization time-of-flight mass spectrometer in the 1950s [13]. Subsequently, this method was successfully employed for LDI-TOFMS. The most successful application of DIE is its combination with MALDI-TOF, which enhances the mass resolution and has been widely accepted. However, the optimum time delay is mass dependent, which leads to low-quality mass spectra for masses far from that of the optimum ion [11]. Promising early approaches include the use of different dynamic acceleration fields, such as post-source pulse focusing [14] and dynamic field focusing [15]. During SPMS development, the DIE method was also mentioned to improve the mass resolution [10]. Nevertheless, there have been few papers specifically describing the advantages of DIE in practical applications, and they do not describe whether the delay leads to an enhanced mass resolution over a wide mass range for SPMS.

Here, a specific DIE method was successfully introduced in our laboratory-developed single particle aerosol mass spectrometry (SPAMS). A delayed bipolar pulsed extraction potential replaced the original DC potential to accelerate the delayed ions. It highly enhanced the mass resolution in both positive and negative ion modes over the whole mass range.

Instrumentation

The SPMS used in this study is a laboratory-developed instrument, a single particle aerosol mass spectrometer. The principle and performance of the SPAMS instrument has been described by Li et al. [16]. Normally, the mass range for the SPAMS is about 1–500 amu, the particle size is in the range of 200–2000 nm, and the resolution is about 500. A mixed methanol solution of $\text{Pb}(\text{NO}_3)_2$ and NaI was used for aerosol generation (TSI 9302) to produce particles containing large metal chelate compounds, which can form high-mass ions on laser ionization. The generated particles were dried through a drying tube and subsequently, directly injected into the SPAMS for analysis.

In this experiment, to obtain the best mass resolution for the whole mass range for SPAMS, a special extraction pulse combining a standard rectangular pulse with an exponential pulse was developed. Franzen proved the advantage of the exponential pulse extraction compared to normal square pulse extraction by mathematical study and experiment [15]. The effect of the bipolar exponential pulse was originally estimated using Simion 7.0 software. Then, the actual exponential pulse were tested by the SPAMS instrument at variable delay times to obtain the best resolution. The delay extraction pulse waveforms are shown in Figure 1. The typical delay time is about 100–200 ns, and the bipolar extraction pulse has a typical width of 5 μs with amplitude increase exponentially from 680 V to the maximum, 1350 V. In the experiment, the DIE voltages are generally 680 V for DC pulse and 250 V for exponential pulse.

Figure 2 shows the original bipolar ion source structures without and with DIE. In the original bipolar ion source, the ions produced by laser ionization were instantly transmitted to the field-free region of the TOF mass analyzer by extraction and acceleration. The acceleration zone consists of several parallel electrodes of equal distance. An extraction potential was applied to the first electrode, and an acceleration potential was applied to the last electrode. The field in the acceleration zone was kept stable by the voltage divider resistors between the electrodes. After modification, the extraction electrode was isolated from the accelerated electrodes. A 21 M Ω resistor was used to connect the first accelerated electrode to the ground.

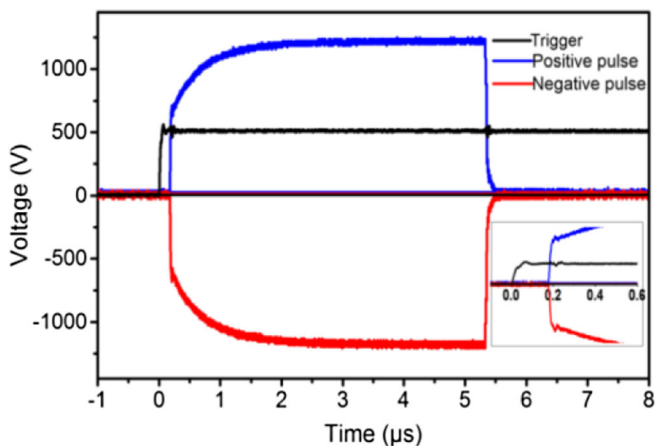


Figure 1. The bipolar delayed ion extraction pulse waveform

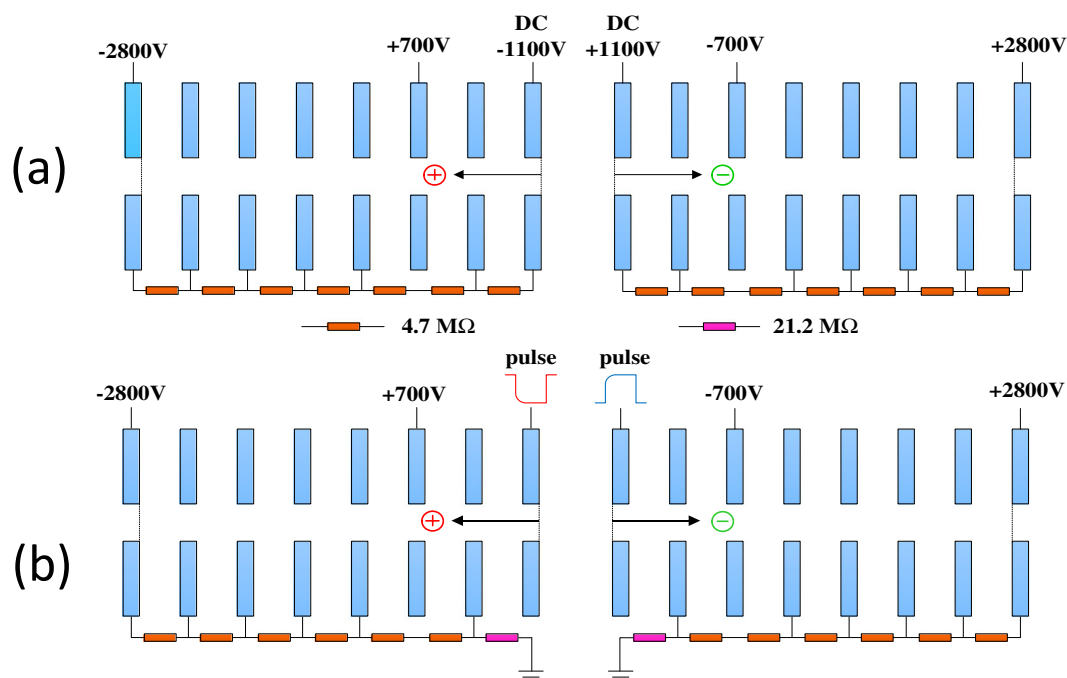


Figure 2. Bipolar ion source structures without (a) and with (b) DIE

Then, the pulse potential can be applied to the extraction electrode. The resistors and voltages applied to the various acceleration plates in Figure 2b were all modeled using the Simion 7.0 software.

Results and Discussion

Mass resolution and mass accuracy are two of the most important parameters in SPMS. The ionization laser for SPMS usually has a beam spot with a diameter in the range of 100–800 μm after focusing [17]. The particles measured by SPMS are usually with the aerodynamic diameter less than 3 μm , and particle ionization in different position of laser beam can cause flight time/mass assignment deviations, which leads to the spectral interpretation challenging. This is particularly true for large ions with masses exceeding 200 amu, such as Pb^+ . Consequently, the voltage parameters must be optimized to reach a compromise between mass resolution and mass accuracy. Figure 3 shows the variations in the mass resolution and mass accuracy on the delay time for $^{208}\text{Pb}^+$. With increasing delay time from 40 to 200 ns, the mass resolution increased from 600 to 1200, and when the delay time exceeded 200 ns, the mass resolution began to decrease gradually. The results are consistent with those obtained using another instrument with DIE [18]. As the delay time changes, the time-of-flight for Pb^+ also changes, and the molecular weight for Pb^+ obtained using the original calibration values shows a linear variation with the delay time. It is obvious from the error bar in Figure 3 that the mass determination for Pb^+ is highly reproducible with mass deviations basically within ± 0.2 amu, which is much better than when using constant extraction method with mass deviations usually within ± 0.5 amu. The experimental results show

that the DIE technique can greatly improve the mass resolution and effectively reduce the mass drift of ions. Under the DIE conditions for SPMS, it is believed that the spatial dispersion of ions within the delay time should not exceed the diameter of the laser spots. For SPAMS, the initial ion velocity can be higher than 1000 m/s [10], which corresponds to about 1 eV for the m/z 208 (Pb^+) ions; thus, the spatial dispersion of the ion packet would have reached 400 μm within 200 ns delay time. This is very close to the diameter of the laser spot. Larger delay times will continue to increase the spatial dispersion of the ions, leading to a reduction in mass resolution. Figure 4 shows the mass resolution results for the SPAMS instrument with and without DIE for both positive and negative ions. It can be seen that, with increasing mass number, the mass resolution for both positive and negative ions increases gradually. For the positive

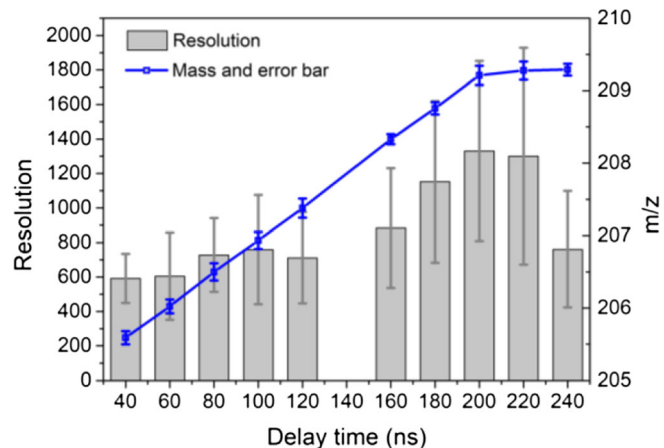


Figure 3. Dependence of the mass resolution and mass deviation on the delay time for $^{207}\text{Pb}^+$ measured by the SPAMS instrument

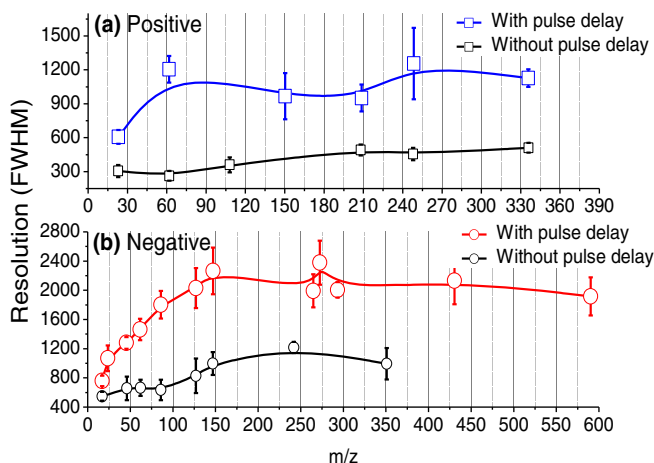


Figure 4. Mass resolution of the SPAMS instrument with and without the DIE for positive (a) and negative (b) ions

ions without the DIE technique, the mass resolutions are all below 500, whereas with the DIE technique, the mass resolutions increase by a factor of two. The mass resolution for m/z 23 (Na^+) is 500, and, when the m/z exceeds 60 (C_5^+), the mass resolution increased to more than 1000, and the highest mass resolution is 1255 at m/z 150 (NaI^+). For negative ions without DIE, the mass resolutions are all less than 1000, and the lowest is 550 for m/z - 17 (OH^-). In contrast, with the DIE technique, the average mass resolution is above 2000 after the m/z exceeds - 127 (Γ^-), and the highest mass resolution is 2380 for m/z - 273. It is worth pointing out that the measured mass resolution is a common effect of various factors. For example, the flight time for the small ions is shorter, whereas the ion detector and other factors affect the small ions to a great extent, resulting in lower mass resolution.

The ion formation mechanism in SPMS was systematically studied by Reinard et al. [19]. The results suggested that ion formation by laser ionization had two stages, photoionization of laser desorbed neutrals giving cations and free electrons and collisions in the plume causing electron capture and competitive charge transfer, and the average positive ion yield were two to five times greater than the negative ion yield. Thus, reduced coulomb repulsions could be the major reason that the mass resolution of negative ions is higher than that of positive ions.

For the actual atmospheric particles analysis by SPMS, laser ionization can produce different ions with the same nominal mass because of the complex chemical compositions for particles. $^{39}\text{K}^+$ and C_3H_3^+ both have a nominal mass of 39, and a resolution at least 660 is required to differentiate them completely. The accurate distinction between $^{39}\text{K}^+$ and C_3H_3^+ is essential to determine whether the particle is a secondary organic aerosol or the particle originates from biomass burning [20]. The mass resolution with the DIE technique is sufficiently high to differentiate $^{39}\text{K}^+$ and C_3H_3^+ , and, furthermore, $^{41}\text{K}^+$ and C_3H_5^+ can also be entirely distinguished. Figure S1 shows the mass separation for $^{39}\text{K}^+$ with C_3H_3^+ and $^{41}\text{K}^+$ with C_3H_5^+ measured by the SPAMS instrument with the DIE technique.

The high mass resolution of SPAMS with DIE will greatly improve ability for the analysis of organic particles and expand its applications in the field of atmospheric chemistry. Figure S2 shows the positive mass spectra of atmospheric Pb-containing particles measured by SPAMS without and with the DIE, and figure S3 shows mass spectra of a typical atmospheric black carbon particle measured by SPAMS with DIE. The high-resolution mass spectra are very useful for the mass peak recognition and extraction, which reduces the difficulty in mass spectral interpretation. Not only for large mass ions but also for small mass ions of within 100 amu; in addition, the resolution with DIE is far higher than that without DIE, and the mass resolution for Na^+ , K^+ , and Cu^+ has increased by one or two times.

Conclusions

The ion extraction pulse, which combines a standard rectangular extraction pulse with an exponential pulse, has been shown to be an effective and simple technique for mass resolution enhancement for SPMS. It displays a considerable asymptotical mass resolution improvement to limiting value for both the positive and negative ions within the entire mass range studied. The highest mass resolutions achieved so far are 1260 for positive ions and 2400 for negative ions for SPMS. More effort will be spent to increase the mass resolution in future experiments. Additionally, the current implementation of the DIE method provides an easy way to improve existing SPMS instruments by retrofitting.

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