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Development of a Gated Electrostatic Ion Trap for Recirculating Ions Through a Charge Detection Tube

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Development of a Gated Electrostatic Ion Trap for Recirculating Ions Through a Charge Detection Tube

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The determination of the mass of large (>1 megadalton) electrospray ions requires a mass spectrometer that operates at high resolution in order to resolve the large number of adjacent m/z states. An alternative analytical approach is to measure simultaneously the charge and velocity of individual ions. We have described the development of a technique to measure the charge on individual electrospray ions using a Faraday tube connected to a charge sensitive amplifier. The low noise charge-measuring detector responds to the image charge of individual ions as they pass through a metal tube. It operates at a noise level of 50 electrons rms and readily measures ions carrying more than 250 charges. Ions carrying more than 100 charges are detected with this system, however, the measurement of the mass of ions carrying less than 250 charges is compromised by electronic noise associated with the amplifier. Improved precision for mass measurements could be gained from signal averaging as obtained from repetitious measurements of ion charge. Here we describe the recent development of a gated electrostatic ion trapping technique for determining the mass of megadalton and larger electrospray ions.

The gated electrostatic trap consists of ion mirrors mounted at each end of a detector tube that captures the image charge signal of passing ions. The mirrors force ions to cycle back and forth many times through the detector tube, thus allowing repeated measurements of ion charge and velocity to be made. Voltages applied to the electrodes define potential valleys for reflecting ions into the detector tube. Ions are introduced into the trap by gating one of the mirrors to 0 volts, thus allowing ions to pass through the mirror and into the detector tube. The image charge signal of an entering ion enables the entrance mirror, thus closing the gate to the trap. The ion then passes back and forth through the detector tube many times until it acquires an unstable trajectory and collides with the detector tube. Trapping times as long as 10 ms have been observed for ions in this trap which provided as many as 450 remeasurements of ion charge and velocity. A more complete description of this instrumental technique was published recently.

Figure 1 shows the signal produced as an ion passes through the Faraday tube. At the top of the figure, an arrow describes the path of an ion as it approaches and then travels through the detector tube. The lower trace shows the image charge signal as a function of ion position with respect to the detector tube. The image signal incipiently appears as the ion approaches the tube, reaches a maximum when the ion is inside the tube and then vanishes after the ion exits the tube. The rise time of the image charge signal influences how well ion velocity is measured. Shielding provided by end caps, positioned adjacent to the ends of the detector tube, forces the image charge signal to appear abruptly, thus producing an image charge signal with a fast rise time. Providing that the detector tube is several times longer than its diameter, the image charge of the ion is captured efficiently. The upper trace shows the amplified and differentiated image charge signal used to measure charge and velocity. Pulse height is proportional to charge and the time...
between a positive pulse and the following negative pulse is the time an ion resides in the tube. Ion mass is calculated from these measurements and ion energy. Ion energy is established in the electrospray source by voltages applied to the various ion lenses.

A cross section of the detector and ion trap is shown in Fig. 2. The detector tube is mounted between two sets of parallel metal plates. The plates are drilled with holes that align with the bore of the detector tube. Ions are introduced into the trap by gating the entrance set of electrodes to 0 volts while maintaining the opposing set at voltages appropriate for reflecting ions into the detector tube. After an ion enters the tube and is detected, the entrance set of plates is electrically enabled before the ion turns around in the mirror and returns through the detector tube. Enabling the entrance mirror, closes the gate to the trap, and causes the ion to remain trapped between the mirrors. While voltages are applied to both mirrors, ions can not enter the trap. The zigzag line in the detector tube approximates the path of a trapped ion and shows that an ion typically follows a path nearly parallel to the bore of the tube.

Figure 3 shows the gated electrostatic trap aligned with an electrospray source supplied by Analytica of Branford. Large electrospray DNA ions are draw through a heated capillary in order to desolvate them, through a skimmer and into a hexapole ion guide before they enter the detector tube. In this system, the rods of the ion guide pass through a pump port thus dividing the ion guide into two sections with respect to the pressure along the longitudinal axis of the ion guide. In the set of experiments reported here, the first section of the ion guide is maintained at 80 mTorr, a pressure which effectively thermalizes the highly charged electrospray ions. The pressure in the second section of the ion guide is in the low $10^4$ Torr range. The ion guide is floated at 230 volts for the purpose of producing ions with appropriate transit times (10-15 µs) through the detector tube.

The upper trace in Fig. 4 shows a waveform generated by a trapped ion as it recirculated through the detector tube. The large negative transient at the beginning of the waveform corresponds to the time an ion entered the detector tube and triggered the closing of the electrostatic gate to the trap. The lower trace is an expanded view of the same trace. The time between a positive peak and an ensuing negative peak is the time for an ion to pass through the detector tube. The time between a negative peak and the next positive peak is the time it takes an ion to turn around in one of the ion mirrors. Each time an ion passes through the detector tube charge and time-of-flight are recorded. The waveform for trapped ions appears as a series of wavelets. Each wavelet in a trapped ion waveform provides a way to remeasure these parameters many times for each ion. Ion mass is calculated from every wavelet and an average mass for individually trapped ions is then calculated from all the wavelets in a waveform.

Figure 5 shows a mass spectrum of a mixture of plasmid DNA from pBR322 (2.88 MDa) and PhiX174 (3.6 MDa). This mixture was electrosprayed from a 0.4 mM Tris-HCl buffer containing 50% acetonitrile without prior sample desalting. This spectrum was obtained by recording trapped ion waveforms for approximately 2000 ions of each species, a process performed in about 8 min. The number of times individual ions recirculated through the detector tube varied widely. In this experiment, only the waveforms that contained at least 60 wavelets were processed to obtain the mass of individual ions. The mass resolution for the peaks in this mass spectrum is about 50.
Compared to a mass resolution of 5 for the one-pass method, the trapping technique improves the mass resolution by about a factor of 10, a significant enhancement. The mass resolving power of the instrument has not yet been measured accurately but preliminary measurements indicate that it is significantly higher than 50. A mass resolution of only 50 for the DNA in this sample derives primarily from the fact that the sample was not desalted before it was electrosprayed. The widths of the peaks in this mass spectrum are broad due to cationization of the DNA with sodium ions. We did not desalt the sample simply because we wanted to compare directly the resolution obtained with the gated electrostatic trap to gel electrophoresis samples which are typically not desalted. Desalting the sample has been shown to improve mass resolution because it decreases the heterogeneity of the DNA ions with respect to the number of sodium ions attached to a DNA ion. We are in the process of implementing desalting procedures for megadalton DNA ions so that we can determine the mass resolving power of this instrument.

In conclusion, the results presented here indicate that the gated electrostatic trapping technique provides significantly faster analyses and mass resolution comparable to gel electrophoresis for DNA ions in the megadalton size range when the sample is electrosprayed from a salt containing buffer.

Figure captions

Fig. 1. The electronic signal produced by a large electrospray ion passing through the Faraday detector tube.

Fig. 2. A schematic showing a cross sectional view of the detector positioned between two ion mirrors. The zigzag pattern drawn inside the detector tube approximates trajectories calculated with Simion 6.0.

Fig. 3. This figure shows how electrospray ions are guided into the gated electrostatic ion trap.

Fig. 4. A trapped ion waveform. The vertical axis is 1 V/div; the horizontal axis is 1 ms/div for the upper waveform and 20 μs/div for the lower waveform. This particular ion of pBR322 DNA carried 790 charges and was trapped for approximately 7.5 ms.

Fig. 5. A mass spectrum of plasmid DNA from pBR322 (2.88 Mda) and PhiX174 (3.6 Mda).


Figure 1
Figure 2
Figure 5

Mass, MDa

Counts/0.02 MDa bin

0 1 2 3 4 5 6 7 8 9 10

0 700 600 500 400 300 200 100