Mass selective blanking in a compact multiple reflection time-of-flight mass spectrometer

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Received 15 October 1998; accepted 1 March 1999

Abstract

In a time-of-flight mass spectrometer with a reflectron (RTOF), an additional small ion mirror, named Hardmirror, is used to increase the mass resolution and to efficiently blank out selected mass lines. Since the mass resolution of a RTOF spectrometer mainly depends on the effective ion driftpath, an increase in mass resolution is achieved by enlarging the driftpath, either by expanding the distance between the ion source and the reflectron or by using multiple reflections. The overall dimension of the instrument was severely constrained so that an elongation of the driftpath was not an option. Using multiple reflections, facilitated by the Hardmirror, we found a way to double the flight path without doubling the distance between the source and the reflectron. In addition with this design we were able to blank out selected mass lines by reducing its intensities by a factor of more than 1000. Blanking out mass lines is performed with an electrical pulse temporarily added to the potential of the Hardmirror’s backplane electrode. The effect of this blank pulse is to geometrically defocus ions so they do not reach the detector. (Int J Mass Spectrom 188 (1999) 189 –197) © 1999 Elsevier Science B.V.

Keywords: Mass spectrometer; Time-of-flight; Reflectron; Multiple reflections; Mass suppression

1. Introduction

For a space application in molecular mass spectrometry we needed a small, light weight mass spectrometer with high mass resolution, high sensitivity, and simple operation. High mass resolution is necessary to separate elements or molecules with slight mass differences like the mass doublet CO and N₂. The weight and the size of instruments used in space applications mounted on spacecrafts have to be as light and as small as possible, respectively. Therefore, our choice was a time-of-flight system with an ion reflector (reflectron). Having only electrostatic ion-optical elements, such a system allows a compact and light weight design. The reflectron has two useful features allowing for good mass resolution. The first feature is to reflect the ions which doubles the driftpath and the second is to compensate for the time-of-flight differences arising from the ion’s initial energy distribution by sending the faster ions on an appropriate detour inside the reflectron. The faster ions penetrate the reflectron deeper than the slower ions resulting in a longer flight path. In this way it is possible to almost compensate for the different time of flight of ions having different initial energy. The mass resolution of a reflectron time-of-flight mass spectrometer (RTOF) is given by the total time-of-

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flight of the ions over the time spread of an ion peak at the detector resulting from the initial ion bunching in the ion source [1] [see Eq. (1)].

In the recent past there have been a few reports on high-resolution reflectron time-of-flight mass spectrometers. Using a grid reflectron and a sophisticated orthogonal extraction source a mass resolution of 35 000 was achieved with a 3.5 m overall length instrument [2]. Using a grid free reflectron and a 4 m overall length instrument mass resolutions between 10 000 and 20 000 were obtained [3]. By using laser-ion sources, high mass resolution were achieved with a reflectron TOF mass spectrometer [4]. Most of these high resolution mass spectrometers have a long overall size and they often use sophisticated ion sources, e.g. a pulsed laser beam followed by a special optic device to use on small ion bunches [5,6]. Since the overall length of our instrument was limited to about 1 m and expanding the driftpath by making the overall size longer was not possible, we had to find a different way for increasing the mass resolution of our TOF instrument with a gridless reflectron. Also, the level of complexity of the ion source is limited because the instrument has to work automatically for years in space. The question was: How can we do this when the overall length and the diameter of the system are already fixed? The solution was to have multiple reflections. In the literature there are several reports about mass spectrometers with ion trajectories performing multiple reflections on their way from the ion source to the detector [6–9]. Beussman et al. [6] and Cornish and Cotter [7] describe tandem time-of-flight mass spectrometer in which the ions follow a Z-shaped trajectory, using two identical reflectors. Mass resolutions between 1000 and 3000 have been reported for very compact instruments. Su [8] uses two sets of electrostatic fields established by two sets of grids to carry out multiple reflections. They achieved a mass resolution of about 3500 for a very concise instrument (<0.3 m instrument length). However, the ions have to pass grids several times, which limits the ion optical transmission considerably, especially when performing many reflections. Wollnik and Przewloka [9] has developed a time-of-flight system where ions can be reflected up to 7 and more times but the mass resolution stayed below 1000.

The solution we found is similar to the tandem-type mass spectrometer with the main difference that we use one of the ion mirrors more than one time (see Fig. 1). Opposite of the reflectron, with an inner diameter of 80 mm, we placed a much smaller ion mirror, called Hardmirror, with an inner diameter of 40 mm on the system’s ion optical axis between the ion source and the detector. In this configuration the ions fly from the ion source to the reflectron, from there to the Hardmirror and then back again to the reflectron and after a final reflection to the detector. The hole flight path of such ion trajectories is almost doubled, which leads to a doubling of the ion's time of flight and finally to an enhanced mass resolution. It is theoretically possible to double the mass resolution, which is hardly possible for a real system, because the time spread is also increasing when enlarging the flight path. The two ion mirrors can compensate for time-of-flight differences up to second-order but higher-order focusing is not possible with two stage ion mirrors resulting in an increased time spread.

In addition, we have to handle a high dynamic range, where single ion detection on the one side and detection of millions of ions per ion bunch on the other side have to be accommodated. Thus, it is important to protect the detector from high ion intensities because detection of very intensive mass lines will cause a gain reduction with time and finally the microchannel plates (MCP) will go blind. Therefore, a system was needed reducing the ion-optical transmission for selected parts of the mass spectrum.

A common way to eliminate ions from the spectrum is to deflect them with deflection plates or with an ion deflecting gate as is used by Beussman et al. [6] and Cornish and Cotter [7]. Our limited space and particularly the limited number of power supplies did not allow an implementation of deflection plates nor of a gate. We found that the Hardmirror is also able to suppress high ion intensities by geometrically defocusing the ions. We were successful in blanking out selected mass lines by suppressing their intensities by a factor of more than 1000. The amount of suppression can be varied in a wide range from 0 to 1000
depending on the amplitude of the blank out pulse. In normal operation mode the Hardmirror’s potentials together with the reflectron are optimized to reach maximum time and space focusing at the detector. Blanking out of mass lines is due to geometrical defocusing in the Hardmirror by temporarily adding an electrical pulse to the backplane electrode of the mirror. This means that all the ions in the Hardmirror are geometrically defocused and absorbed in the structure of the RTOF system when the pulse is on. Although the blanked out ions are deflected in the system we could not measure any increase in background.

In this article we present the design of the Hardmirror, its performance in the RTOF system and the geometrical boundaries we had to respect. Finally, we show results concerning the mass resolution, the transmission properties and the suppression of blanked out ions.

2. Description of the system

The reflectron time-of-flight system is schematically shown in Fig. 1. The system has an overall length of 1 m, with an effective flight path of about 4 m. The separation between the ion source and the detector is 75 mm. The Hardmirror is located in the center between ion source and detector. The reflectron and the Hardmirror are placed on the system’s ion optical axis. A field free region with a length of about 0.8 m lies between this two components, where the so-called field free drift path is located.

Two different ion sources are used: a storage ion source and an orthogonal extraction ion source. The storage ion source is an improved two stage electron impact storage ion source as it was invented by Wiley and McLaren [1]. This source uses the electron beam storage capability to accumulate the ions, which are continuously produced in the ionization area. The ions are periodically extracted by a pulse of 2 μs duration with an amplitude of 350 V and slopes faster than 5 ns.

The other ion source is a commercial orthogonal extraction ion source [10]. Here, a continuous flow of ions, focused by a separate entrance optic, enters the extraction region of the ion source orthogonally and is then extracted into the RTOF system (for more details see deHeer and Milani [11]). The extraction frequency for both sources is 10 kHz. Due to the source’s acceleration potentials, the ion’s kinetic energy is 3.325 keV, and an energy spread of ±5% is assumed. Both sources have an electrostatic lens located after the acceleration stage to create a parallel or a slightly converging ion beam. The reflectron we use is a grid free two stage ion mirror with an electrostatic lens at the entrance [12,13]. The inner diameter of the reflectron is 80 mm and its total length with the lens is 265 mm. The electrical field in the mirror is established by 10 electrodes built by 19 guard rings made of stainless steel, which allows the electric field gradient to divide into two stages to ensure a second-order time focusing condition. The slope of the electrostatic potential for both stages is linear but the first slope is steeper than the second one.
As proposed by Mamyrin et al. [14] the first stage reaches an electrical potential of 67% of the ion’s energy and the second stage 105%. This means that the first stage has a linear potential increase from 0 up to 2400 V and the second one from 2400 up to 3600 V. All the potentials used in this article are related to the ground level of the system. The total geometrical length of the first stage is 56 mm and of the second one is 80 mm.

The reflectron lens has a length of 72 mm and a potential range from 0 to $-5$ kV. As we show later, this lens is used to switch from single reflection to triple reflection by simply adjusting the lens potential. Single reflection mode means that the ions are directly reflected from the ion source to the detector by the reflectron without passing through the Hardmirror. Triple reflection corresponds to the three reflections that the ions experience when the Hardmirror is in use; two reflections in the reflectron and one in the Hardmirror (see Fig. 1). In Sec. 3 we give detailed explanations about the design and the function of the Hardmirror. The detector consists of two microchannel plates in a chevron configuration. The anode has a special design to adapt its impedance correctly to the signal line [15,16]. The detector’s signals are capacitively decoupled to allow a floating operation of the system. The acquisition and processing of the electrical detector signals are done by a time-to-digital convertor (TDC) (2 GHz Fast Multiscaler, Model 7886, Fast ComTec) or alternatively by the analog-to-digital convertor (ADC) of a digital storage oscilloscope (LeCroy 9384 TM). Both data acquisition units are triggered by the extraction pulse. The TDC is mainly used with the orthogonal extraction ion source, because the ion intensity is substantially weaker than the intensity delivered from the storage ion source [13], typically yielding 1 ion per shot.

3. The Hardmirror

As we have already mentioned, the Hardmirror’s two main purposes are to blank out, respectively, suppress selected mass lines and to increase the mass resolution by maintaining the system’s overall size of the RTOF spectrometer. The mass resolution $R$ is given by

$$ R = \frac{T}{2\Delta t} $$

with $T$ the time of flight of a mass, and $\Delta t$ is the full width at half maximum (FWHM) of its peak in the time spectrum. From a theoretical point of view it is possible to double the mass resolution if we double the time of flight by doubling the ion’s flight path and by maintaining the time spread $\Delta t$ of an ion packet. In a real system we have to take into account that doubling of the flight path leads to an increased time spread, because the time focusing characteristics of two stage ion mirrors compensate flight time differences of ions arising from the initial energy distribution only to the first- and second-order. Higher-order terms of the flight time dispersion and geometrical aberrations like paraxial trajectories or inhomogeneous electric fields, which are not compensated by a two stage ion mirror, are responsible for an increased time spread. But the time spread will not be doubled if we double the time of flight because the contributions of this higher-order terms to the time spread are quite small compared to first- and second-order effects.

In order to have the blanking out of individual mass lines without perturbing neighboring lines, the blank out device has to be located close to a time focus along the ion trajectories. Moreover, the flight time through the Hardmirror has to be small, so that the temporal spread of the ion packets is considerably lower than the time difference between two adjacent mass lines. The short flight time inside the Hardmirror basically results in a reversal of the trajectories on a plane rather than in an extended volume like in the reflectron. Therefore we call this device Hardmirror. In order to maintain the total time of flight spread of an ion packet in the system, the Hardmirror was also built as a two stage reflectron, however with very short time focal lengths. Although the time spread is growing when doubling the time of flight we were able to increase the mass resolution of our laboratory system with Hardmirror by a factor of more than 1.7. This is a
satisfactory result if we bear in mind that we only added the Hardmirror to the already existing system and no changes of the outer dimensions were made.

The location of the Hardmirror in the RTOF system and its dimensions were the result of an intensive evaluation. Because of the Hardmirror’s position between the ion source and the detector, which was the most desirable place for ion-optical reasons, there is only limited physical space with maximal possible dimensions of 50 mm in outer diameter and 70 mm in length by keeping a gap of 10 mm to the source.

In ion-optical simulations with [17] we tested several types of mirrors having the required dimensions. Anticipating a high loss of intensity when using a mirror with grids, we decided from the beginning to design a grid free unit. We started with a grid free ion mirror with three cylindrical electrodes having a diameter of 40 mm in analogy to the design of Berger [18]. This seemed to be a good solution because the Berger mirror has a second-order focus condition and the system is grid free. The problem we had with this design was that the total length required for the three cylindrical electrodes was much too long to fit in the space available for the Hardmirror. But simulations with such an ion mirror gave us an idea about the necessary potential distribution to solve our problem, so we had to find another geometry providing the same field distribution. In the next step we closed the mirror on the backside by substituting the third cylindrical electrode by a solid plane, the backplane electrode, with a specially formed surface and we shortened the first electrode in such a way that the mirror’s length is now fitted to the space in the RTOF system (see Fig. 2). The backplane’s sophisticated shape is due to a profound analysis of the electrical field in the area where the ions reverse their direction. The backplane has exactly the same shape and the same potential as the equipotential surface of the electrical field near the ion’s reversal point. The advantage of such a formed backplane is to keep the blank out amplitude at a low voltage level, that is indispensable for a sharp blank process. In the next step we made the other two electrodes equal long; each has a length of 20 mm and a diameter of 40 mm.

Considering the entrance electrode as a lens, we now had a two stage ion mirror with an electrostatic lens in front.

The ion beam passes the outside of the Hardmirror twice very closely (see Fig. 1), so that an electrical field reaching out from the Hardmirror will have an adverse effect on the ion trajectories. We realized that a fourth electrode following the lens is indispensable. The purpose of this electrode is to prevent the lens field from penetrating the field free drift path. This is done by adding one more cylindrical electrode with a length of 15 mm and by enclosing all the other potentials with this fourth electrode which operates as a shield (see Fig. 2). Now the potential of the field reaching out of the Hardmirror near the ion path is less than 0.1% of the ion’s kinetic energy, and the influence can therefore be neglected.

Fig. 2. Cutaway drawing of the Hardmirror. The Hardmirror has a length of 68 mm and an aperture of 40 mm. The electrical field is established by four electrodes; three cylindrical ones (drift, lens, deceleration/acceleration) and a backplane electrode with a special formed surface to keep the blank pulse’s amplitude low. The entrance electrode together with the box enclosing the other potentials work like a field shelter to restrict the scattering field of the Hardmirror.
In the final design, the Hardmirror has a total length of 68 mm and an outside diameter of 48 mm, between the electrodes there is always a 1 mm gap. The electrodes have adjustable potentials in a range from 2 to 5 kV except the Hardmirror lens having a negative potential from 0 to $-3$ kV with respect to the system ground. For normal operation the backplane has a potential of 3.6 kV, the following electrode, the deceleration/acceleration potential, has an electrical voltage of 3.1 kV and the lens has $-0.6$ kV.

For triple reflection the reflectron must have accurate potential values. For the reflectron lens an electrical voltage of at least $-3.5$ kV is required, higher values up to $-4.5$ kV are possible. Below $-2.5$ kV there exists only the single reflection mode, this means that the Hardmirror is no longer used because the ions are directly reflected from the source to the detector. It was neither possible to perform triple reflection with a low lens voltage nor possible to perform single reflection with a high lens voltage. The point is that the ion path has two different forms depending on the potential of the reflectron lens. For single reflection the shape of the ion path is similar to the letter V, but for triple reflection the path looks like two letters U, which are slightly tilted to each other (see Fig. 1). The ion path shape is changing from V to double U by increasing the lens’s potential from $-2$ to $-3$ kV. The higher the electrical voltage of the lens, the more the ion beam is bent.

With this effect we have got two mass spectrometers in one, differing in the number of reflections: one time or three times. Given a fixed time window in the time spectrum for recording data, the single reflection mode has a wider mass range with a lower mass resolution while the triple reflection mode provides a high mass resolution but the mass range is only a quarter of the range from the single reflection mode. The mass range is defined as the range of mass lines recorded in a fixed time, which is restricted by the frequencies of the extraction pulser.

4. Blank out

In the three time reflection mode the Hardmirror can be used to blank out selected mass lines. Blanking out is a method to strongly suppress the intensity of selected mass lines during recording of a spectrum. The idea is to geometrically defocus ions of a selected mass while they pass the Hardmirror, without influencing the other ions.

Before the ions enter the Hardmirror they are already separated in packets of ions having the same $m/q$ ratio ($m =$ mass, $q =$ electrical charge). The potentials on the reflectron are set so that the mass packets are time focused shortly in front of the Hardmirror, their time spread at this location is very small and the packet separation causes a gap between the ion packets. If for a selected mass line the gaps to the previous and to the following packets are not too small ($>100$ ns) then this mass packet is, for a short time, alone in the Hardmirror. This short time is exactly the right moment to switch on the blanking out pulse which changes the electric field in the mirror in a way that the ions being inside the Hardmirror will be strongly defocused. With a backplane potential of about 4.1 kV the Hardmirror has time and geometrical focusing abilities, but with the pulse, having an adjustable amplitude of maximal 500 V, an extra potential is added to the backplane which has a large geometrical defocusing effect. After the ions have left the Hardmirror, the pulse is switched off and the previous potential distribution with the focusing abilities is established again. The time spread of the ion packets must be as small as possible to ensure that almost all ions from the selected mass line are effected in the same way. If the packet is too long not all ions are suppressed by the same factor, because of their different positions in the Hardmirror. To avoid large ion packets we adjusted the reflectron’s potentials so that its time focus lies only 60 mm in front of the Hardmirror. In this way the length of an ion packet inside the Hardmirror should be short enough to make sure that all ions of that packet are blanked out with the same pulser amplitude. With such a blanking out technique it is not possible to geometrically defocus the ions flying on the ion optical axis because of the Hardmirror’s cylindrical symmetry. This is one reason why not all ions of a mass line can be suppressed. Although the pulse was turned on, the few ions flying
in a small region around the optical axis still arrive at the detector.

The blank out pulse is performed by a high voltage bipolar pulser with rise and fall times smaller than 10 ns. The shortest on-time period is 100 ns. The suppression of the blanked out mass line depends on the amplitude of the pulse, which also has an influence on the width of the mass range. The higher the amplitude, the higher the suppression of the selected mass line and the wider the influenced mass range. To execute a blank out process the pulser must be switched on when the selected mass passes the Hardmirror, which is at about half of the total flight time of the selected mass line. The blank out effect can be checked online in the TOF spectra and so it is quite easy to find the perfect switch on time.

5. Results

With the Hardmirror we succeeded in increasing the mass resolution by a factor of 1.7. In Fig. 3 a high resolution spectrum is shown with a FWHM mass resolution of more than 5000. This resolution was achieved by using the orthogonal extraction ion source. The best resolution we got with the storage ion source was about 3000 for triple reflection and 1800 for single reflection. The resolution using the storage ion source is limited by the ion’s turn-around time. In both cases the mass resolution met our requirements.

In comparison with the single reflection mode the ion transmission of the triple reflection mode is about 40%. If we take into account the ion’s special flight path in the triple reflection mode, the lower intensity due to a loss of ions is not a surprise. Although there was no loss of ions in our Hardmirror simulations we were not able in the laboratory to bring the full intensity to the detector. Results like this one can be used to give an estimation of the simulation’s accuracy which shows that we have got some differences between the simulation and the real system. The potentials of almost all electrodes must have accurate values to provide high resolution spectra, and the ranges of these values are often quite small. This means that if we consider the potential values as parameters only a few different parameter combinations can be used for a high mass resolution and it needs a lot of experience to find the very best combinations. Hopefully, by tuning these potentials we will be able to bring up the transmission to the levels in the simple reflection mode without losing the high mass resolution.

In Figs. 4 and 5 the results from the blanking out mode are shown using a gas mixture. The lower panel in Fig. 4 shows a normal triple reflection spectra with a mass range from mass 17 u up to mass 41 u, the upper panel shows the same window with the blank out pulser on with an amplitude of 400 V and with an on time of 1 µs. In Fig. 5 we show an analysis of the Hardmirror’s blank behaviour for this blank out process using several different pulse amplitudes. The blanked out mass line is centered at the mass 28 u (N₂), which we were able to suppress by a factor of almost 10³ using an amplitude of 400 V. For a 200 V amplitude the suppression is about 10². The blanked out mass range becomes larger when the amplitude is increased. For an amplitude of 400 V and a pulse period of 1 µs there is a mass suppressing effect from
the mass 24 u up to 32 u. The strength of suppression depends on how close a mass is situated with respect to the selected blank out mass line. For masses close to the mass 28 u the suppression is high and for the other masses the influence is becoming weaker and weaker the further away from the mass 28 u the lines are. If the amplitude is lower the total blanked out mass range is smaller, for example, a 100 V amplitude has a mass range which is influenced only from mass 25 u to 30 u. Of course the mass range is becoming larger if the width of the pulser is increased.

In Fig. 5 we present the relative intensities of different blank amplitudes normalized to the peak amplitude without blanking. A comparison between the intensities of the blank amplitudes which are normalized to the amplitude and normalized to the peak area is given in Fig. 6. No remarkable differences between these two analysis methods are found.

The suppression follows almost a semilog relation to the pulser amplitude, at least for amplitudes higher than 100 V. The reason why we have never tried to use a higher pulser amplitude than 400 V is that we are investigating a blank out process, which should have a high suppression with a lowest possible amplitude and for this an amplitude of 400 V was much enough.

For a given pulser amplitude the suppression can be increased if we try to shorten the distance between the pulsed backplane and the ion’s reversal point. This can be done by giving more kinetic energy to the ions or by redesigning the Hardmirror’s backplane. The effect of a shorter distance is that the electrical field from the pulse is higher the nearer to the backplane electrode the reversal point of the ions is located when pulsing, or in other words we can get the same blanking effect even with a lower pulser amplitude.

Fig. 4. The used gas is a mixture of Ar, C₂H₄, Kr, Ne, and Xe, each with a relative contribution of 17% and with a rest of N₂. This mixture provides a lot of mass lines in the range from 20 to 40 u, which is helpful to show the blanking out process. The blank pulse has a delay of 12 µs from the source’s extraction pulse that suppresses mostly the mass 26. The shaded area in the upper panel shows the affected mass range when the blank out pulse with an amplitude of 400 V and an on-time period of 1 µs is on. In the lower panel the regular spectra is shown which is recorded without using the Hardmirror pulser.

Fig. 5. The result from the blank out process shown in Fig. 4 are given. The suppression of the mass 26 is the highest one with a suppression of more than 10³ using a 400 V blank amplitude, followed by the mass 28 with a suppression of almost 10².

Fig. 6. Peak suppression vs. blank out amplitude for two analysis methods is plotted.
out effect with a lower pulse amplitude. According to this the normal potential value for the backplane electrode when the pulser is not working is in this case only 10–50 V higher than the ion’s kinetic energy.

Such a designed RTOF instrument is well suited for a space mission to analyze the atmosphere and ionosphere of the comet 46 P/Wirtanen [19,20]. The mass spectrometer is sufficiently compact with a high mass resolution. The blank out device can be used to suppress the water lines which are expected to be the most intensive components in the cometary gas. Of course the presented prototype of our instrument has not yet the required weight. It is too heavy with a reflectron and a Hardmirror made of stainless steel. The first goal was to have a good working mass spectrometer, which now will be redesigned and adapted to meet all the requirements necessary for a space instrument.

Acknowledgements

This work is supported by the Swiss National Science Foundation and the ESA PRODEX program. The authors wish to thank J. Fischer and A. Wenger for the excellent work making the mechanical design of the system. Furthermore, the authors are grateful to R. Liniger and H. Hofstetter for their contributions in the area of electronics and fabrication.

References