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Designing reflectron time-of-flight mass spectrometers with and without grids: a direct comparison

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Abstract

A direct comparison of a reflectron time-of-flight mass spectrometer equipped with a two stage gridded reflector to one with a gridless was carried out by ion trajectory simulations using a set of starting conditions which represent the different sources of signal broadening in a reflectron. The mass resolution was calculated from the flight time distribution and determined for a broad range of reflector voltages. The results show that the gridded reflector can be adjusted to give higher resolution for all starting conditions and in particular is less affected by ion beam divergence. However, when in addition the transmission is taken into account the gridless reflector is superior as long as the divergence of the ion beam can be kept small. The diameter of the ion beam has a much weaker effect on the instrument's performance. The ratio of the two reflector voltages resulting in best performance is a constant for both instruments, but while the absolute values have to be adjusted to the ion beam parameters in the case of the gridded reflector, they only weakly depend on diameter and divergence of the ion beam in the case of the gridless reflector. (Int J Mass Spectrom 206 (2001) 181–190) © 2001 Elsevier Science B.V.

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1. Introduction

The increasing popularity of time-of-flight (TOF) instruments in the field of mass spectrometry is due to a number of factors such as the availability of fast electronics, the success of ionization techniques employing pulsed lasers, particularly matrix assisted laser desorption/ionization (MALDI), and some basic features of the TOF mass spectrometry (TOF-MS), such as high transmission, robustness, and its ability to record the whole mass spectrum quasi simultaneously. Nevertheless, it were the instrumental measures to increase the resolution of time-of-flight mass analyzers, the Wiley-McLaren ion source [1] and the invention of the reflectron by Alikanov and Mamyrin and co-workers [2] that brought it back on the stage of mass spectrometry after a rather weak start. The Wiley-McLaren ion source shifts the point of minimum size of an ion bunch in the flight direction further away from the ion source, so that it is reached at longer flight times, thus increasing the mass resolution. The point along the drift path where this happens is termed space focus. The reflectron images the spatial distribution of the ion bunch at this space focus onto a point at a larger distance from the ion source by means of an ion

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reflector containing a retarding and a reaccelerating electric field. This results in increased ion flight times and thus, in better separation of ions of different mass up to resolution values of several 10^4 [3].

The original idea of the reflectron was based on homogeneous fields in the reflector as only such can be handled mathematically in an analytical way. Under standard operating conditions of a reflectron the values of the retarding and the reflecting field are chosen such that the flight time broadening at the detector due to different kinetic energies of the ions are eliminated to second order of the Taylor expansion.

In reality homogeneous fields can be approximated by the use of very fine grids which confine the inhomogenities to the vicinity of the grid meshes. One of the problems related to the use of such grids is their limited transmission which usually is about 90% or less. As each grid in a reflector has to be passed twice by the ions this leads to a loss of about one third of them during their passage through this device. This was one of the reasons for the creation of the gridless reflector [4], which offers increased transmission at the price of inhomogeneous fields [5]. Thus, analytical calculations regarding the performance of a reflectron equipped with a gridless reflector are impossible and ion trajectory calculations have to be carried out in order to optimize it. The operation of a gridless reflector in the form described by its inventors is further complicated by the addition of a weak third electric field in front of the other two reflector fields which is claimed to be necessary in order to achieve good resolution for ion beams with finite diameter and divergence.

The inhomogeneous fields of the gridless reflector can act as an ion lens which is able to reduce the transversal diameter of the ion bunches and to compensate for a possible divergence of the ion beam which otherwise could reduce the percentage of ions that reach the detector surface. This is a double edged effect: On the one hand it increases the instrument's transmission, but on the other hand, the focusing of ions with almost equal velocity but different flight paths (drift lengths) necessarily leads to a broadened flight time distribution and therefore, reduces the mass resolution. It depends on the individual requirements of a certain mass spectrometric analysis if the transmission or the resolution should be optimized or if a middle course should be steered. In general, as long as the masses of interest are well resolved in a specific spectrum it is the number of counts in a digitizer's channel representing the centroid of an ion signal that determines its quality. This quantity on the other hand depends linearly on the transmission of the instrument and on its resolution (at least as long as the signal peak shapes are close to a Gaussian distribution as for this the peak height is proportional to the inverse peak width for a given peak area). Summing up it is helpful to define a new quantity which we would like to term "mass spectrometric brilliance" following its optical counterpart [6]. In optics the brilliance of a radiation source is determined by the ratio of its spectral intensity at a certain wavelength and its bandwidth. In mass spectrometry the spectral intensity can be compared to the number of ions counted in a certain channel of the mass spectrum per time unit and the bandwidth can be replaced by the inverse resolution. Therefore, we can define the mass spectrometric brilliance as the product of ion transmission and resolution at a certain mass.

In this work we present the results of ion trajectory calculations comparing the performance of a reflectron equipped with a gridded reflector to one with a gridless reflector under the aspects of mass resolution and transmission. In this case the gridless reflector does not make use of a third electric field which complicates the search for the optimum operating voltages significantly, but has the same design as the gridded one with the grids removed. The comparison is based on a set of starting conditions that reflect the individual sources of flight time errors [7]. Trajectory calculations of this kind can take into account the effect of the ions' spatial and momentum distribution in all three dimensions and are thus suited to give a realistic picture of the performance of a time-of-flight mass spectrometer.

2. Computational details

The ion trajectory simulations whose results are presented here, were carried out using the SIMION

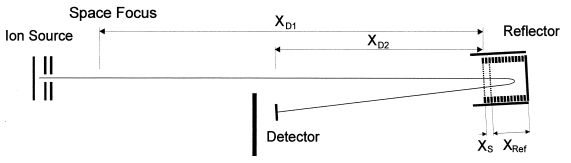

Fig. 1. Geometry of the reflectron used in simulations. The Wiley-McLaren ion source forms a second order space focus at a distance of 15 cm. From there the total drift length ($x_{D1} + x_{D2}$) is 100 cm. Length of the deceleration field x_S: 1.1 cm. Length of the reflector field x_{Ref}: 6.6 cm. Reflector angle: 3.1°. The detector surface is perpendicular to the reflector axis.

6.0 program [8] on a 330 MHz PC. The geometry of the mass spectrometer was chosen according to typical reflectron mass spectrometers as designed by us previously. Cylindrical symmetry was assumed for all three components of the reflectron, i.e. the ion source, the ion reflector and the detector. As all electrode surfaces are plane the geometry files were produced using a resolution of only two points per millimeter. The instrument dimensions used for the calculation are summed up in Fig. 1. When replacing the gridded reflector by the gridless one all parameters were left unchanged except the vertical position of the detector which needed a slight adjustment due to the different reflection characteristics of the gridless reflector.

For computation of the electric fields the default parameters of the SIMION program were used while the precision of the ion trajectory calculation had to be increased in order to get accurate flight times. User written programs as are supported by SIMION 6.0 were used for the stepwise change of the reflector voltages between individual flights, the calculation of the resolution after each flight, and the optimization of these voltages with respect to the resolution by use of a hill climbing algorithm with automatically refined grid steps. After recording the flight times of all ions the mass resolution was calculated from their standard deviation assuming a Gaussian distribution of flight times and using the 50% valley definition. These programs are available from the authors upon request.

The ion source voltages were kept constant for all calculations with the repeller at 911.3 V and a voltage of 568.8 V applied to the intermediate electrode. For the given ion source geometry this results in an ion beam with an average kinetic energy of 800 eV per ion and a second order space focus [9] at a distance of 15 cm from the ion source. The ion source electrodes were assumed to have centered holes with a diameter of 10 mm either covered with a perfect grid or left open. In the first case the divergence of the ion beam is determined by the initial momenta of the ions, whereas in the second case the field inhomogenities add a further contribution to the divergence whose value depends on the spatial distribution of the ions transverse to the direction of the accelerating field.

The calculations of the mass resolution as a function of the retarding and the reflecting field were performed in the voltage range from 460 to 560 V for the voltage applied to the deceleration electrode and 830–940 V for the reflector's back electrode using 1 V steps in each dimension.

Three different starting conditions were examined. (1) Twenty-one ions evenly distributed ±1 mm along the symmetry axis of the ion source in the first acceleration region. The average kinetic energy of the ions in the drift region is 800 eV with a standard deviation of 11.4 V. No initial momentum was given to the ions and thus, their kinetic energy distribution in the drift region is solely due to their different starting positions. It is this source of flight time error, which the reflectron was aimed to compensate. (2) Eight ions starting at the center point of the first acceleration field each with the typical kinetic energy at room temperature, i.e. 25 meV, but with different directions of their velocity vectors, starting with 0° in respect to the acceleration field vector and going up to 315° in increments of 45°. Such initial momenta cause the so-called turn-around errors in a time-of-flight measurement. In this case the ion source electrodes were covered with grids in order to achieve homogeneous acceleration fields. This is necessary to avoid an additional contribution to the ion beam divergence by lens effects. (3) Nine ions in a 2 mm × 2 mm area centered around the starting point of case (2). These starting conditions represent a somehow more realistic scenario as those in (1) as they resemble a typical ionization volume. With the center bores of the ion source electrodes covered with grids the acceleration fields are homogeneous and an ion beam without

divergence but with a nonvanishing diameter is produced. The average birth potential of the ions in this case is 800 V with a standard deviation of 17.1 V. (4) Same ion starting parameters as in case (3), but with the electrode bores left open. The field inhomogenities lead to an ion beam which is transversally focused about 14 cm from the ion source and then diverges with a full opening angle of 0.7°. Thus, these starting conditions allow one to study the influence of the ion beam divergence on the overall performance of the instrument.

In all cases the mass to charge ratio of the ions was chosen to be 100 Dalton per unit charge. Coulomb repulsion between the ions was not taken into account.

3. Results and discussion

Figs. 2 and 3 show the mass resolution calculated from the simulated ion trajectories in the reflectron as a function of the two reflector voltages in the case of starting conditions (1) (i.e. only spatial distribution along the symmetry axis of the ion source). Fig. 2 represents the results for the reflector with grids (=homogeneous fields) and Fig. 3 those for the gridless reflector. For the gridded reflectron the theoretical resolution exceeds 146 000 while it is reduced to 105 000 for the gridless. In both cases the maximum resolution is observed within a narrow band of the ratio $U_{\mathrm{Dec}}/U_{\mathrm{Ref}}$ which is 0.619 for the gridded reflector and reduced to 0.592 for the gridless. As for these starting conditions transversal focusing effects are not significant, this reduction of the optimum deceleration voltage can be explained by the longer time the ions can spend in the deceleration field of the gridless reflector. The sharp peaks, which are found along this band, are a result of the limited number of ions used for the simulation. The more ions were employed the more the valleys between these spikes were filled up. However, this was only checked for a small range of voltages in order to keep the runtime for the simulations reasonable.

Such high theoretical resolution results from flight time distributions with a width of the order of 0.1 ns.

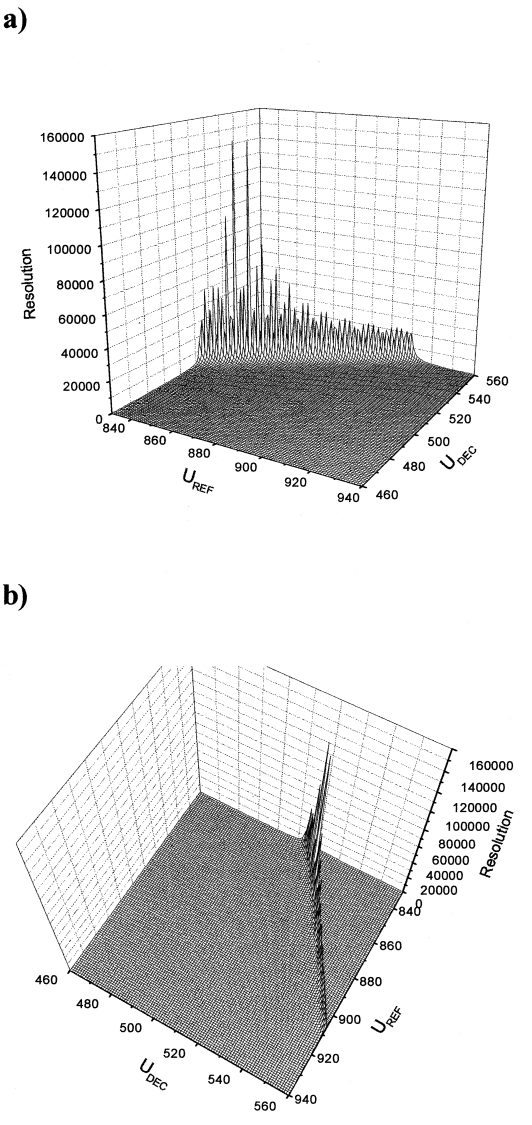

Fig. 2. Mass resolution plotted as a function of the reflector voltages for the reflectron equipped with a gridded reflector under starting conditions (1) (see the text), i.e. only spatial distribution of the ions along the ion source axis.

It is clear that such values cannot be reached in reality where a couple of additional effects, such as the finite bandwidth of the detector and the electronics, limit the minimal peak width to around 1 ns. Against this background the maximum achievable resolution of the gridded and the gridless reflector have to be regarded as equal.

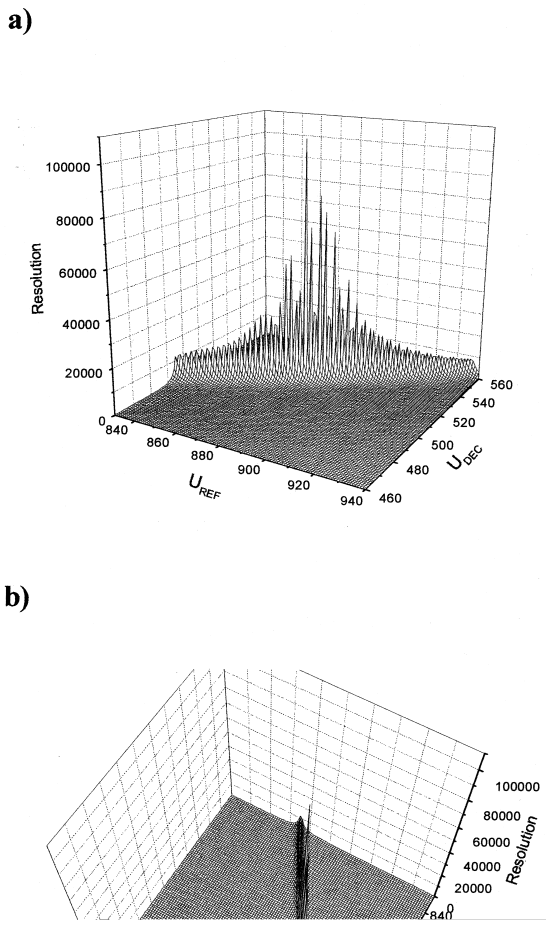

Fig. 3. Mass resolution plotted as a function of the reflector voltages for the reflectron equipped with a gridless reflector under starting conditions (1) (see the text), i.e. only spatial distribution of the ions along the ion source axis.

Fig. 4. Mass resolution plotted as a function of the reflector voltages for the reflectron equipped with a gridded reflector under starting conditions (2) (see the text), i.e. same starting point and initial kinetic energy (0.025 eV) but different directions of the velocity vector.

As can be expected, choosing starting conditions with an initial momentum distribution of the ions [case (2)] results in a general reduction of the mass resolution accompanied by a broadening of the structure in the surface representing the resolution versus the reflector voltages (see Figs. 4 and 5). Several factors contribute to this behavior: a distribution of initial momenta leads to a growth of the ion bunch in its center of mass system, which the reflector can only compress to a certain degree. Although the turn-around error caused by the momentum component parallel to the acceleration field vector is only determined by the ion source conditions and not affected by the reflector, the distribution of ion kinetic energies

effect because of its transversal focusing, which leads to a crossover of the ion trajectories between reflector and detector for the voltages giving good resolution. Of course, the maximum resolution decreases with a

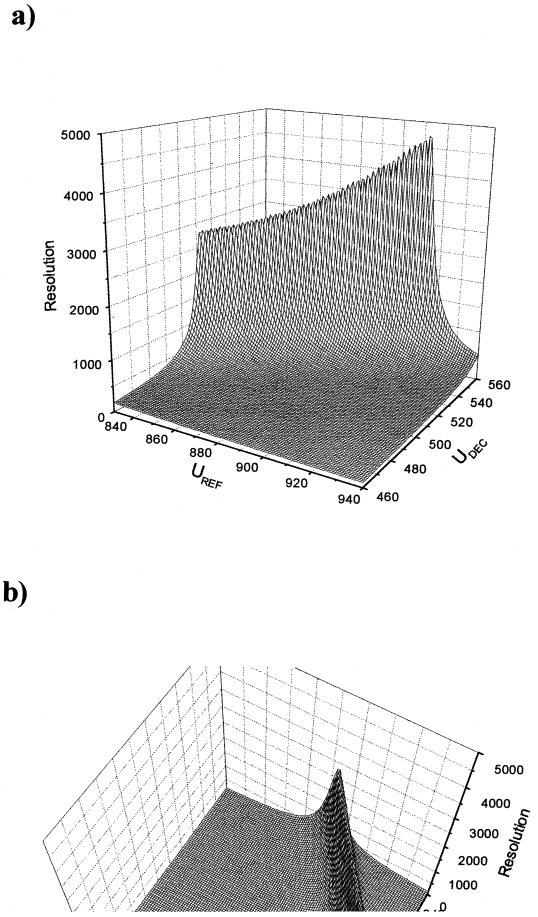

Fig. 8. Mass resolution plotted as a function of the reflector voltages for the reflectron equipped with a gridded reflector under starting conditions (4) (see the text), i.e. quadratic distribution of the ions in the first acceleration field of the ion source. The grids in the ion source electrodes are removed in this case resulting in a diverging ion beam.

Fig. 9. Mass resolution plotted as a function of the reflector voltages for the reflectron equipped with a gridless reflector under starting conditions (4) (see the text), i.e. quadratic distribution of the ions in the first acceleration field of the ion source. The grids in the ion source electrodes are removed in this case resulting in a diverging ion beam.

angle of 0.7°. Figs. 8 and 9 show the mass resolution of the reflectron with gridded reflector (Fig. 8) and the gridless (Fig. 9) as a function of the reflector voltages. The best values for the mass resolution are observed at the same ratio $U_{\mathrm{Dec}}/U_{\mathrm{Ref}}$ as for compensation of the kinetic energy distribution (Figs. 2 and 3). For the gridded reflector the maximum resolution can be found at high field strengths whereas the best values for the gridless can be found at about the same reflector voltages as with starting condition (3). For both types of reflectors the achievable resolution is significantly reduced compared to the nondivergent

beam. Whereas the gridded reflector still reaches a resolution of 4700, it is reduced for the gridless to only 1700. These simulations clearly show, that ion beam divergence is the most severe problem for the optimization of a reflectron in respect to mass resolution and should be reduced as far as possible. A transversal spread of the ion beam can be handled much better by the reflector, particularly the gridless one, as its divergence which necessarily leads to different types of trajectories.

As already pointed out the simulations presented here assume grids to be ideal. In reality a small electrostatic lens is formed through every mesh of a grid if it separates two regions of different electric field strength. The effect of such inhomogenities in the vicinity of grids on the performance of time-of-flight mass spectrometers was the subject of several investigations. Although some came to the conclusion that these effects are small or negligible [10,11] others indicate that they may considerably reduce the instrument's resolution and/or transmission [12,13]. A recent SIMION simulation which modeled the scattering of ions by grids in a reflectron shows that grids indeed have an important effect on sensitivity as well as on resolution [14]. We did not include realistic grids in the simulations at issue because their effects strongly depend on the type of grids used and the individual voltage settings in a particular instrument. In order to roughly guess the instruments transmission each grid is assumed to absorb 10% of the ions per passage. As in no case ions were lost to walls or electrodes this results in an overall transmission of 66% for the reflectron with grids in the reflector but without in the ion source and 53% in the case with additional grids in the ion source. The values for gridless reflectron are 100% if no grids cover the ion source electrodes and 81% if they are gridded.

Taking into account these transmission values and the maximum achievable resolution we can compare the overall performance of each instrument for the ion starting conditions (3) and (4), which resemble the two borderline cases which in realistic ion sources are always present simultaneously, by calculating its brilliance. The values are as follows: For the nondivergent beam with finite diameter: 3710 for the reflectron with gridded reflector in standard geometry and 7430 when its detector is turned perpendicular to the reflected ion beam. The reflectron with gridless reflector gives a brilliance of 7600.

For the divergent beam: 3100 for the reflectron with the gridded reflector and 1700 with a gridless. As pointed out previously values for cases that employ grids in the ion path have to be regarded as upper limits.

Summarizing these results shows that the performance of a reflectron equipped with a gridded reflector is less sensitive to the divergence of the ion beam as long as the grids do not severely scatter ions from the ideal path and the active detector surface is large enough to record a high percentage of the ions. On the other hand, the gridless reflector turns out to be superior if the ion beam is well collimated. Thus, the best configuration appears to be the combination of a gridless reflector with an ion source that produces a beam with very small divergence. This can be achieved by use of homogeneous acceleration fields but also more sophisticated ion source designs were suggested which offer favorable beam parameters even without the use of grids [15], thus further increasing the total transmission and avoiding other problems related to the use of grids in time-of-flight mass spectrometers. In the case of point-like ionization volumes it is advised to convert the diverging beam into one with small divergence but finite diameter by use of an ion lens as both, the gridded and the gridless reflector are less sensitive to this beam parameter.

4. Summary

The results of the computational comparison of the two identical reflectrons one equipped with a two stage gridded and the other with a two stage gridless reflector demonstrate that gridded gives the better resolution in the case of a divergent as well as in the case of a nondivergent ion beam (provided the detector surface is perpendicular to the reflected beam for the latter case). The calculations also make clear, that a small ion beam divergence is very important for

good performance of a reflectron. The ion beam diameter has a much smaller effect on the resolution. This is particularly true for gridless reflectors.

The picture changes somehow when in addition to the resolution the transmission is taken into account in order to characterize the overall performance of an instrument. When combining these two quantities to what we termed brilliance (=the product of transmission and mass resolution for a certain mass) the results of the gridless reflectron surpass those of the gridded one as long as the ion beam divergence is small. It has to be pointed out that this is not only true for sophisticated multistage reflectors but already for simple two stage reflectors as the one assumed for these simulations.

Another interesting observation valid for the gridded as well as the gridless reflector is the fact that the range of reflector voltage values which give good instrument performance is clearly defined along a narrow band when resolution is plotted as a function of the deceleration and the reflection voltage. This band is settled along a line of a certain value of the ratio $U_{\mathrm{Dec}}/U_{\mathrm{Ref}}$ which is independent of the chosen starting conditions except initial velocity distributions. Consequently, the reflector voltages can be optimized in a straightforward way by first setting the correct ratio $U_{\mathrm{Dec}}/U_{\mathrm{Ref}}$ and then maximizing the resolution by tuning U_{Ref} keeping this ratio constant. For the gridded reflector the absolute values for best performance differ depending on the ion beam's divergence and diameter. On the other hand, the gridless reflector performs best at about the same voltages independent of the ion beam parameters. Thus, it can be operated at certain standard conditions without to know the actual conditions of the ion beam. Keeping in mind that the reflectron time-of-flight mass spectrometer is still not to be found among the routinely used analytical instruments and that one of the reasons for this are problems with the automation of its operation, this point is of particular interest for the development of user friendly reflectrons. According to our results a very simple hill climbing algorithm is able to adjust the reflector voltages of a gridless reflectron.

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