

Evaluation of a Method to Improve the Mass Identification Power of Multiturn Time of Flight Mass Spectrometers

Frank Gunzer

Information Engineering and Technology Faculty, German University in Cairo, Cairo, Egypt

Abstract. Time of flight mass spectrometry is a well known technique to analyze gaseous substances, for example in environmental monitoring, and belongs to the standard techniques in instrumental analysis. The advantages are a theoretically unlimited mass detection range and a very fast response time. The main disadvantage is that in order to achieve a high mass resolution, the flight path along which different analyte ions fly with different speed has to be quite long. Multiturn time of flight mass spectrometers solve that problem by making the analyte ions fly on a closed loop instead of a long path. This principle allows realizing any flight path length, but the direct relation between flight time and analyte mass is lost once faster ions overtake slower ions, so that a certain flight time can belong to ions of different mass. Here a method to resolve that ambiguity is evaluated with help of finite element methods simulations. The results show that this method can indeed resolve the ambiguity, but only for a certain mass range and with a great reduction of the mass resolving power compared to what is normally achievable with multiturn techniques.

Keywords: multiturn time of flight mass spectrometry, ion trajectory, mass resolution, environmental monitoring techniques

1. Introduction

One of the most important techniques in order to analyze and identify unknown substances is mass spectrometry. This method allows determining the mass to charge ratio of analyte ions, and since in most applications the analyte's charge after ionization is one, the mass can be detected directly. One specialization is time of flight mass spectrometry [1-3], where the analyte is ionized and the ions are accelerated with help of one or a series of electric fields. The ions then fly along a flight path of a certain length with different velocities. The acceleration field provides the same kinetic energy to all ions, so that the flight velocity is a function of the analyte mass. In order to separate the masses well from each other, long flight paths of a few meters length are necessary which makes time of flight mass spectrometers large instruments. On the other hand, the flight time of the ions is in the microsecond range and thus the response speed very fast.

One major goal of time of flight mass spectrometer improvements is the reduction of the instrument size, which means especially reducing the flight path without compromising the mass resolution. One such principle which has already been proposed over 40 years ago is the multiturn time of flight mass spectrometer [4]. Instead of flying along a long path, the ions fly on a closed path many times. Thus the device dimensions can be made smaller, and any flight path length can be achieved by making the ions fly a certain number of loops. There exists, however, a limit regarding the flight path length that can be achieved. Normally, the flight time is a direct measure for the mass. When on a closed loop the fast ions start to overtake the slow ions, this relation is lost, since a certain flight time from that moment on can belong to different masses. Thus, multiturn time of flight mass spectrometers have been used to analyze only single masses, e.g. using mass filters in particle accelerators and then analyzing a single species; a very high mass resolution of over 30000 has been reported [5].

In order to overcome the problem of losing the flight-time-mass-relationship, a method was proposed 2012 in a patent [6]. Once the ions have left the closed loop path, an electric field oriented perpendicular to

the flight path is switched on, giving the ions a vertical velocity component. Again, the vertical velocity depends on the mass of the ions. If this vertical field strength is constant, all the ions would hit the detector in the same spot. Thus, a changing voltage, e.g. a voltage ramp, is used, so that the ions experience a stronger deflection the later they arrive at this field due to their separation in the closed loop path. If a spatial detector is used, then the graphical representation of the vertical deflection depending on the flight time after leaving the closed loop path shows parallel lines, where each line belongs to a certain number of loops spent in the closed path. In this paper this principle is investigated with help of finite element method simulations in order to find out how well it works in theory but also under realistic conditions with non-ideal electric fields and when applied on ions having a certain initial spatial distribution.

2. Experimental

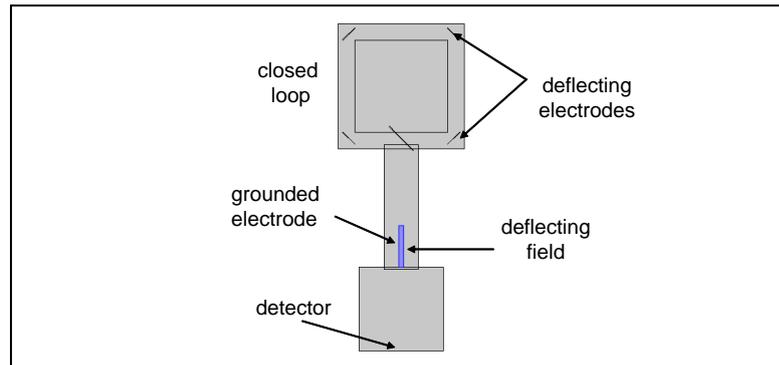


Figure 1: Set up showing the closed path loop and the deflection region

The simulations have been carried out with help of the finite elements method solver COMSOL (www.comsol.com). The set up is without any relevant modification the same as the one described in the patent and includes a closed loop path and the deflection field part (figure 1). Since it is not the goal to develop the perfect closed path set up for ions, this part has been simulated by using walls together with perfectly elastic collisions. Applying four such walls each oriented at an angle of 45 degrees with respect to the flight path leads thus to a perfectly rectangular flight path. The flight path difference between two walls is 25 cm so that the total flight path length is 100 cm, as described in the patent. The total flight path once leaving the closed loop has a length of 50 cm, where the ions first travel 20 cm before entering the perpendicular deflection field of length 10 cm, and then travel another 20 cm in order to reach the detector. Via a fifth wall, the ions are extracted in a perpendicular fashion from the closed loop path and led into the deflection area. During the normal flight in the closed loop, this wall is excluded from the simulation, and included at the time of ion extraction in order to simulate an extraction mechanism that can be switched on and off. The deflection field is created as given in the patent by two electrodes with a distance of 1 cm between them. A voltage ramp with a slope of 100V per 50 μ s is applied to one electrode, the other electrode is grounded. The voltage ramp starts at the same time when the ions are extracted from the closed loop path.

Initially, the electric field an ideal field between the electrodes only, but a realistic field that extends into the surrounding of the electrodes and thus influences the flight path especially after deflection between the electrodes has also been simulated. Similarly, the initial ion release point is a circle with a radius of 0.01 cm. In order to simulate an initial ion distribution that is more realistic, and also in order to simulate ion trajectories deviating from the ideal trajectories, also a larger circle has been simulated with 0.05 cm radius. The ions have been represented by single particles, each one carrying one positive elementary charge and the corresponding ion mass. The ion trajectories have been calculated by Newton Mechanic principles, the mesh size for the simulation had a density of ca. one knot per 100 μ m, the time stepping was 5 ns.

3. Results and Discussion

3.1. Basic Evaluation of the Principle

Under the conditions described in the experimental section, the patent shows that when using a flight time in the loop of 200 μ s the total flight time ranges between 210 and 260 μ s for ions with a mass between

500 and 2000 dalton. The deflection ranges from 2 to 16 mm. Figure 2 shows the result of the simulation for the same conditions.

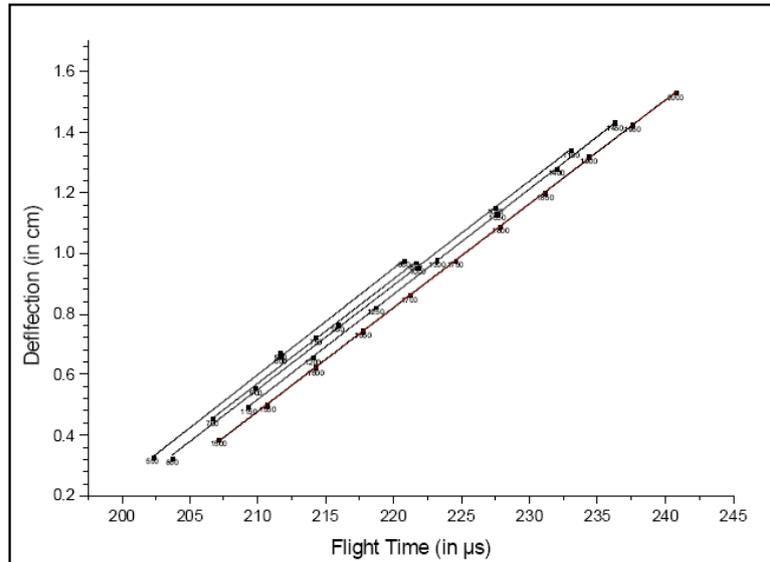


Fig. 2: Distribution of flight times and deflections for ions with masses between 500 and 2000 dalton under the conditions given in [6]. Each line represents a certain number of loops in the closed path.

As can be seen, the deflection distribution shows six lines, each representing a certain number of loops inside the closed path. The deflection separation is in the range of 100s of μm . This is large enough to be separated with help of modern CCD chips which allow for pixel sizes in the lower 10s of μm . Thus, with help of a two dimensional detector, flight time and deflection can be unambiguously linked to a certain ion mass. In order to improve the resolution, the deflection voltage can be increased, or the distance flying after the deflection field can be increased. Correspondingly, simulations changing this distance and the deflection voltage have been carried out.

Figure 3 shows the result of these simulations. The voltage ramp is steeper with a slope of $200\text{V}/50\mu\text{s}$, in effect doubling the deflection voltage. Furthermore, the distance between deflection field and detector has been changed to 40 cm (lower graph). An increase of the detector distance improves the separation from each group of masses, as can be seen in the larger distance between the lines. But now the relation between flight time and deflection is not a linear one anymore, for certain high masses the deviations from linearity become quite strong. The reason is that for that deflection voltage the ions do not fly through the whole distance of the deflection electrodes anymore, but reach the ground electrode before reaching the end. The linear relationship between deflection and flight time is a complex function of the deflection voltage. The higher the deflection voltage, the closer the ions come to the ground electrode at the end of the deflection field. If they leave the deflection field before reaching the ground electrode, the voltage difference they experience depends then on the mass, since heavier ions spend more time in the deflection field, and in that longer time the voltage change caused by the ramp is stronger. Since the total difference depends on the value of the voltage ramp at the time of leaving the deflection field, but also on the position in the field, only if the ions leave the deflection region without experiencing a voltage change exclusively caused by the ramp and thus excluding the position in the field, then the relation between deflection and arrival time at the detector will be a linear one. This puts an upper limit on the mass range that can be detected; masses that are so high that they move so slowly through the deflection region and reach the ground electrode will not be part of the linear function that represents the relation between deflection and total flight time for the other masses. However, by simulations as presented here this maximum mass can be determined.

3.2. Influence of the Initial Ion Cloud Diameter

Another critical factor is the size of the ion cloud. The simulations presented so far have been calculated with an ion cloud radius of $100\mu\text{m}$ which is a realistic size when using focussed laser beams as ionization source. If the radius of the cloud is increased to $500\mu\text{m}$ (again with a distance of 40 cm between deflection

field and detector, deflection ramp voltage $200\text{V}/50\mu\text{s}$), which might in reality be a result of Coulomb repulsion of the ions, or imperfections of the electric fields that force the ions on the closed loop path, the variations in total flight time are relatively small; but the variations in displacement are larger due to the change of the electric field and the different positions the ions have in the field (i.e. the different voltage differences the ions of the cloud then experience). The variation is at least of the size of the ion cloud radius, but according to the simulation even slightly larger due to the deflection field. Figure 4 shows these variations. The problem is that already at such a small increase of the ion cloud's size, the data points would not necessarily be unique for a certain mass, there might be overlap. In the graph this is shown with help of two linear fits between the original data points, and with help of the spread of data points the larger ion cloud size would create. Controlling this size is thus a very critical factor, so that in reality ions clouds of smaller than $200\ \mu\text{m}$ radius have to be ensured along the whole travel path of the ions. This is quite challenging regarding the quality of electric fields (constant voltage, geometric set up) to guide the ions along their path.

A similar problem might arise from realistic deflection fields. In the simulations described here, this field was confined to a rectangular shape between two linear electrodes. In a realistic set up, the field lines would extend beyond the electrodes in a more elliptic form. These deviations from a parallel field would have corresponding effects on the acceleration of the ions and this displacement achieved on the detector. However, the simulations with the complete electric field yielded for the flight time a relative constant shift of $(-2.2 \pm 0.1)\%$ and for the displacement a shift of $(1.2 \pm 1.3)\%$. The reason is that the field strength quickly drops outside the area enclosed by the deflection electrodes, e.g. the horizontal field strength responsible for the displacement drops to 10% of its value in-between the electrodes already at a distance of 1 cm from the end of the deflection electrode area, which is short compared to the length of the flight path in this area of 10 cm.

4. Conclusion

One of the most important questions has not been answered so far: the mass resolving power. From the flight times in fig. 2 the time difference between two masses can be deducted, which is of the order of 110 ns at mass 1050. The flight time variation for the ion beam with 0.05 cm radius is of the order of 30 ns at that mass. The time difference between two masses gets smaller with increasing mass, and from the data in figure 2 it can be concluded that at a mass of ca. 3800 two mass peaks could not be separated anymore given a flight time variation of 30 ns per mass. This number is calculated for the ideal case ignoring any broadening mechanisms. Basically, this would allow to build a mass spectrometer with a minimum flight tube size of 40 cm plus the size for the closed path loop (which can be made much smaller than shown here, since only the total path length in the loop is important, which can be achieved for any loop size by adjusting the number of loops spend in it). Thus the resolving power of commercial time-of-flight mass spectrometers with a flight tube of 1 m length could be reached with a set up which is only 50% of that size. However, a multiturn mass spectrometer normally allows for much higher resolving powers so that the method investigated here in principal allows to overcome the greatest problem of this type of mass spectrometer. It still allows for size reductions, albeit at a great cost of resolving power and, which was not described in the patent, only for a certain mass range before the linear mass-displacement relationship is lost and thus the mass identification becomes ambiguous. Furthermore, this is valid only for relatively small ions clouds with a controlled radius of smaller than $200\ \mu\text{m}$.

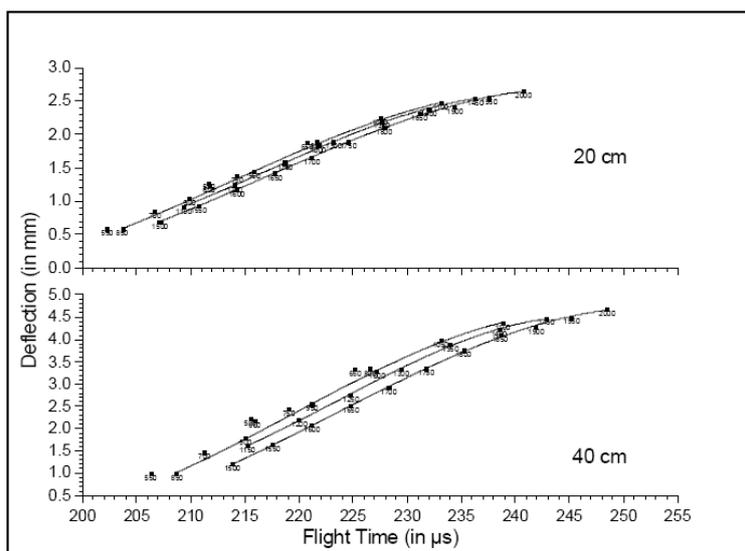


Figure 3: Distribution of flight times and deflections for ions with masses between 500 and 2000 with increased voltage (200V/50 μ s) and different distance between deflection and detection (20 cm / 40 cm).

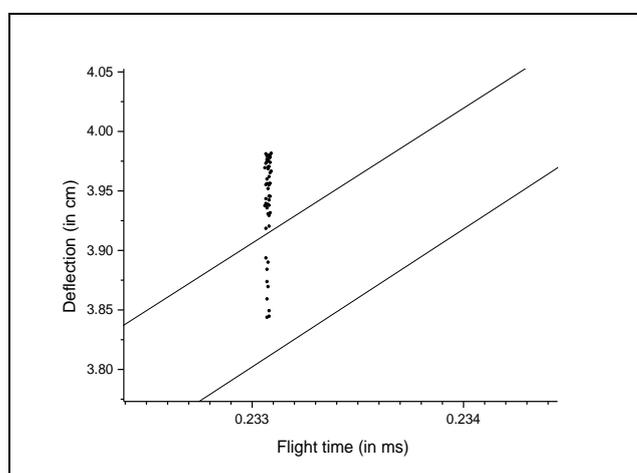


Figure 4: Variation of flight time for an ion cloud of 500 μ m radius. The lines show the linear fit for the mass points also shown in fig. 2 and fig. 3.

References

- [1] B.A. Mamyrin. Time-of-flight mass spectrometry (concepts, achievements, and prospects). *International Journal of Mass Spectrometry* 2001, **206**, 251-266.
- [2] S. Shrader. *Introductory Mass Spectrometry*. CRC Press, Taylor & Francis Group, Boca Raton, FL, USA.
- [3] J.H. Gross. *Mass Spectrometry*. Springer Verlag, Berlin Heidelberg, Germany.
- [4] W.P. Poschenrieder. Multiple-Focusing Time-of-Flight Mass Spectrometers Part II. TOFMS with Equal Energy Acceleration. *International Journal of Mass Spectrometry and Ion Physics* 1972, **9**, 357-373.
- [5] S. Shimma, H. Nagao, J. Aoki, K. Takahashi, S. Miki, M. Toyoda. Miniaturized High-Resolution Time-of-Flight Mass Spectrometer MULTUM-S II with an Infinite Flight Path. *Analytical Chemistry* 2010, **82**, 8456-8463.
- [6] T. Kinugawa, O. Furuhashi. Multi-Turn Time-Of-Flight Mass Spectrometer. Patent publication USA: US 2012/0112060 A1 (2012).