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Ionization scheme of the time of flight mass spectrometer

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In the time of flight mass spectrometer arrangement, ionization scheme is significant for the resolution perspective besides the other parameters. The scheme also contributes to improvement of the signal to noise ratio, particularly for low signal level. The ionization scheme along with the mass resolution was considered for the time of flight mass spectrometer with the three-field within the second order compensation. The double field is also provided. From the resolution obtained, triple and double field systems possess almost similar resolution with large ionisation region. When the triple system having better resolution with the small ionisation region is taken into account, the ionization scheme becomes significant for the field selection of the time of flight mass spectrometer.

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1. Introduction

Time of flight (ToF) mass spectrometry can be described as the detecting of the ions on basis of the m/q ratios. It is essential to highlight that ions formed by a short ionization event are accelerated by means of an electrostatic regions to a common energy and fly throughout a drift path to the detector. Thus the light ions arrive earlier than the heavies one and a mass spectrum is detected. The ToF measuring for each one leads to determination of its mass. Finally, this process is repeated with repetition rate, which depends on the time-of-flight of the highest mass to be recorded.

The double field time of flight mass spectrometer, developed by Wiley and McLaren, has improved mass resolution over the conventional single field ToF mass spectrometer [1,2]. The ionization scheme of this system with the mass resolution was further improved by W.A.de Heer and P. Milani [3]. The geometry of the spectrometer utilized in the study is similar to the Wiley-McLaren one, but it includes an intermediate field free-region in the ionization–acceleration zone and with this system a mass resolution higher than 1000 was reported for 10 cm long ionization region. Chandezon *et al.* [4] combined the Wiley-McLaren geometry with the W.A.de Heer and P. Milani method and reported higher transmission and better resolution. The double field system was also subject of the various studies [5-9].

The effective ionization scheme introduced by W.A.de Heer and P. Milani allows one to collect more ions, hence providing better signal to noise ratio [10,11] and with this method particles with masses over a large range can be investigated without fragmentation [3,4]. The fragmentation causes difficulty for the experimentalist. To the best of our knowledge, ionization scheme of the three-field system for the ToF mass spectrometer has not been reported. In this report, the effective ionization scheme of the three-field was studied together with mass resolution. For providing comparison, the spectrometer with the double field is also considered. First, the spectrometer arrangement is explained and mathematical treatment is driven. Then, second-order compensation method and ionization scheme are presented. The results, discussions and then conclusion are given.

2. Theoretical approach for the spectrometer

2.1. Description of the spectrometer

The block diagram of the ToF spectrometer used is given in Fig.1. The spectrometer has two distinct parts, namely, ionization-acceleration zone and free flight zone. The cluster source in this arrangement is placed perpendicular to the spectrometer axis.

For the three-field system, the ionization–acceleration zone consist three regions called the R-1, R-2 and R-3, respectively (see Fig.1a). In region 1, particles are ionized and they are pushed through region 2 by static electric field $\overline{E}_1$. The electric field $\overline{E}_2$ accelerates the ionized particles further. The final acceleration takes place in the region 3 for the particles. The region 4 (R-4) is the free flight zone. The accelerated particles drift freely in this region and experience no electric field along where the ion packets of different masses are separated. The mass separated particles then arrive to the grounded microchannel plates (MCP) detector. The same explanation is also hold for the double field system (Fig. 1b), but the final acceleration occurs in the region 2 (R-2).

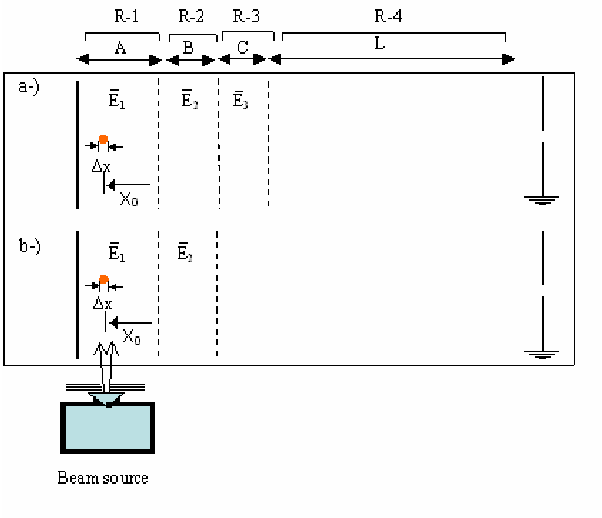

Fig. 1. Block diagram of the ToF spectrometer with the cluster source perpendicular to the axis. (a) The spectrometer with the three-field system. (b) The double field time of flight mass spectrometer.

2.2. Mathematical treatment for the time-of-flight calculation

The total flight time of a particle with a mass *m* and a charge *q*, starting from the initial distance *x* of the first grid with an initial velocity *υ* along the spectrometer axis, will be the sum of partial flight times of each region. For formulating the flight time, the reduced parameter approach was used to simplify the calculations. The reduced parameters: X = x/L is the reduced initial position of the particle, S = $\upsilon(m/2qV)^{1/2}$ is the reduced initial velocity,

b = B/L is reduced length of the region 2 and E= $(V_a/V)(L/A)$ is the reduced value of the electric field in region 1. These notations follow de Heer et al. and Chandezon et al. studies [3,4]. We also use the reduced parameter c, α and β where c=C/L is the reduced length for the region 3, $\alpha=V_b/V$ and $\beta=(V-V_b)/V$. Hence the lengths are normalized to L and the voltages to V. The total flight time expressed by the reduced parameters reads

$$T(x,v) = L\sqrt{m/2qV}\, f(X,S)\,, \tag{1}$$

where f(X,S) is a dimensionless function. For the three-field system the function reads as follows:

$$f(X,S)=\left[\frac{2(\sqrt{S^2+EX}-S)}{E}\right]+$$
$$\left[\frac{2b}{\alpha}\left(\sqrt{S^2+EX+\alpha}-\sqrt{S^2+EX}\right)\right]$$
$$+\left[\frac{2c}{\beta}\left(\sqrt{S^2+EX+\alpha+\beta}-\sqrt{S^2+EX+\alpha}\right)\right]+$$
$$\left[\frac{1}{\sqrt{S^2+EX+\alpha+\beta}}\right]. \tag{2}$$

The function for the two-field system reads the following one:

$$f(X,S)=\left[\frac{2(\sqrt{S^2+EX}-S)}{E}\right]+$$
$$\left[2b\left(\sqrt{S^2+EX+1}-\sqrt{S^2+EX}\right)\right]+\left[\frac{1}{\sqrt{S^2+EX+1}}\right]. \tag{3}$$

For the beam source perpendicular to the spectrometer axis, the initial velocity component drops from the Eqs. (2) and (3). In this case the Eq.(2) reduces to following one;

$$f(X,0)=$$
$$\left[\frac{2\sqrt{EX}}{E}\right]+\left[\frac{2b}{\alpha}\left(\sqrt{EX+\alpha}-\sqrt{EX}\right)\right]+$$
$$\left[\frac{2c}{\beta}\left(\sqrt{EX+\alpha+\beta}-\sqrt{EX+\alpha}\right)\right]$$
$$+\left[\frac{1}{\sqrt{EX+\alpha+\beta}}\right]. \tag{4}$$

and the Eq.(3) reads as follows:

$$f(X,0)=\left[\frac{2\sqrt{EX}}{E}\right]+\left[2b\left(\sqrt{EX+1}-\sqrt{EX}\right)\right]+$$
$$\left[\frac{1}{\sqrt{EX+1}}\right]. \tag{5}$$

The Eqs.(2) and (3) define the flight time of the spectrometer in general while the Eqs.(3) and (4) describe the spatial mode operation of the spectrometer. The values in the equations determine the properties of the spectrometer.

3. Second-order compensation method and ionization scheme

Spatial resolution is to compensate dispersion of the initial positions of the ions generated in the ionization region. In an ideal case, condition for space resolution reads

$$\frac{\partial T}{\partial x}=0\,. \tag{6}$$

The condition indicates that $T(x,v)$ function possesses a maximum, a minimum or point of inflection at $x=x_0$. In order to approach this ideal case, de Heer and Milani method controls the $T(x,v)$ function that the function has a maximum and a minimum, and the mean distance X_0 measured from last grid of the region 1 to the ionization volume is between the local points.

In Figure 2, plot of the function produced with the parameters of A=13 cm, B=3 cm, C= 2 cm, L= 1.5 m, V_a=2.7885 kV and S=0 is illustrated, where V_a is the applied voltage for the first plate of the region 1 and S=0 is due to the perpendicular position of the beam source to the spectrometer axis.

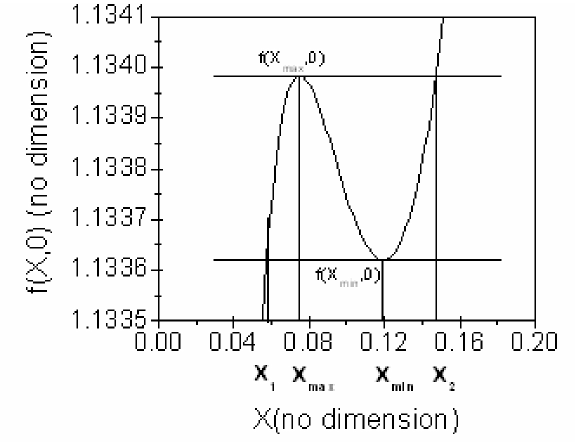

Fig. 2. Plot of f (X,0) function with respect to the initial ions position X.

From fig.2; the region $[X_1,X_2]$ defined by the local points is an usable ionization region. In this region, the resolution reads the following:

$$\frac{m}{\delta m}=\frac{1}{2}\frac{T}{\delta T}=\frac{1}{2}\frac{f_{mean}}{f(X_{\max})-f(X_{\min})}, \tag{7}$$

where the f_{mean} is as follows;

$$f_{mean}=\frac{f(X_{\min})+f(X_{\max})}{2}. \tag{8}$$

Using the graphical values the resolution can be estimated with Eqs. (7) and (8).

4. Results and discussion

Within the *de Heer and Milani* approach, the evolution of the function obtained for the three-field defined by Eqs.(1, 4) within the voltage range of V_a from 2.7659 kV to 2.8223 kV and for the double fields from 2.7434 kV to 2.7997 kV defined by Eqs.(1,5) are given in Fig.3. Other parameters: A=13 cm, B=3 cm, C= 2 cm, L= 1.5 m for the three field system and A=13 cm, B=4.5 cm, L= 1.5 m for the two field system. The selected values for the parameters meet the requirement of the method.

From the Fig.3, it is shown that the function has the inflection point at voltages around 2.7659 kV for triple field system that is close the 2.7434 kV for double field, where the approach cannot be implemented since the functions do not possess local maxima and minima. The maxima and minima appear with increasing of the voltage. With the further increase of voltage, the local points shift away from each other resulting in enlargement of the ionization region Δx.

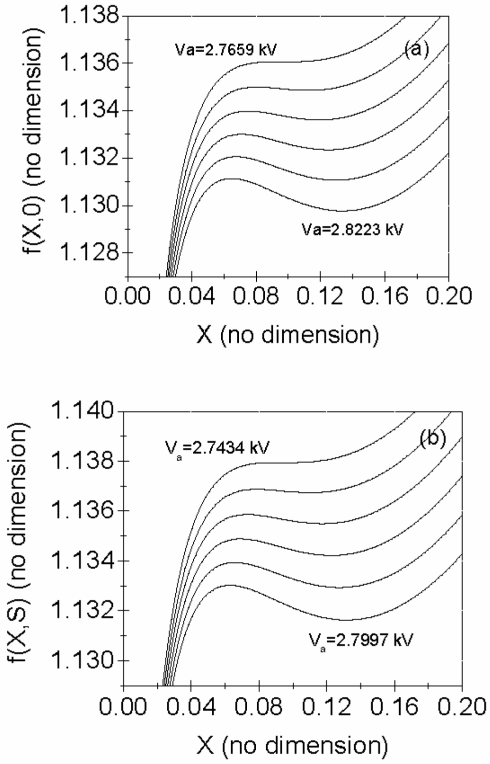

Fig. 3. Evolution of the f(X,0) function with varying the V_a where X is the initial ions position. (a) three-field system (b) double field system.

For each graph produced with varying of the voltage; the ionization region $[X_1,X_2]$ was determined, see Fig. 2 for the $[X_1,X_2]$ and the mass resolution was estimated via Eqs. (7,8). The ionization region values and mass resolutions are given in Table 1. From the Table 1, the increase voltage value of V_a leads to decrease of the resolution and enlargement of ionization region Δx for both systems. At voltages $V_a \leq 2.7828$ kV, the resolution is over the 2350 and the ionization region Δx is around less than 11.64 cm for the three fields. The region is larger than 13 cm and the corresponding resolution decreases from 1560 at higher voltage values (Table (a)). Regarding the double field system, the mass resolution and the ionization region values are similar to the three-field (Table 1(b)).

Table 1. The ionization regions and mass resolutions values in respect to V_a where m/δm represents the mass resolution and Δx is for the ionization region length. (a) three-field system (b) double field system.

a-)

V_a (kV)	m/δm	Δx(cm)
2.7716	1.06×10^4	7.00
2.7772	4.15×10^3	9.67
2.7828	2.35×10^3	11.64
2.7885	1.56×10^3	13.65
2.7941	1.13×10^3	15.28
2.7997	8.73×10^2	16.36

b-)

V_a (kV)	m/δm	Δx(cm)
2.7490	1.08×10^4	6.93
2.7547	4.21×10^3	9.60
2.7603	2.34×10^3	11.56
2.7659	1.54×10^3	13.38
2.7716	1.11×10^3	15.04
2.7772	8.60×10^2	16.27

The study reported by Seccombe *et al*. presents that the second order approach provides better resolution for the three-field system compared to the double field system for the interaction region sizes were of s= ±1 mm and ±2 mm [5]. The obtained results in this study indicate that the three-field system has almost similar mass resolution with the double field system within the second order compensation method when one possesses the larger ionization region. The similarity indicates that the resolution also depends on ionization region scheme. Hence, with the small ionization region the three field spectrometer provides better resolution than the double field spectrometer, but the resolution is almost similar for both three and double field spectrometer for the larger ionization region.

5. Conclusion

The present results point out that in the second order approach the ionization scheme leads to the similar mass resolution for double and triple fields of the time of flight mass spectrometer. The resolution of the three field systems is better with small ionization range. However, the resolution of the three fields and double fields are almost in similar for the larger ionization region.

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