OPTOELECTRONICS AND ADVANCED MATERIALS – RAPID COMMUNICATIONS Vol. 2, No. 9, September 2008, p. 537 - 542

Effect of intermediate free region inclusion to resolution of the double field mass spectrometer

Ş. ŞENTÜRK[*], O.ÖZSOY[a]
Department of Physics, Dumlupınar University, Kütahya, 43100 Turkey
[a]*Department of Industrial Electronics, Kayseri Vocational Collage, Erciyes University, Kayseri, 38039 Turkey*

Inclusion of the intermediate field-free region to the ionization-acceleration zone of the double field system was considered. The region improves the mass resolution and the mass resolution further increases with the enlargement of this region. However, the reduction of the electric field increases with the enlargement that needs to be taken into account since this reduction can appear as a signal to noise ratio difficulty due to particle energy decreasing.

(Received July 18, 2008; accepted August 1, 2008)

Keywords: Mass resolution, Second order compensation method, Field-free region of the ionization-acceleration, Double field time of flight mass spectrometer.

1. Introduction

Time of flight (ToF) mass spectrometer is based on a simple mass separation principle. But, it has been known since Thomson carried out his experiments on ionized particles. Willey and McLaren observed that ions of a particular mass to charge ratio would reach the detector with a spread in arrival times due to the effects of uncertainty in the time of ion formation, location in the extraction field and initial kinetic energy, resulting in reduced reduction. They also devised an instrument, incorporating a pulsed two grids ion source, to compensate for temporal, spatial and initial kinetic energy distributions [1]. Afterwards, the double field time of flight mass spectrometer, developed by Wiley and McLaren, has improved the mass resolution over the conventional single field ToF mass spectrometer [2,3]. W.A.de Heer and P. Milani included an intermediate field free-region to the ionization–acceleration zone of the double field system and reported the improved mass resolution with the effective ionization scheme [4]. The improved resolution and the ionization scheme are significant for the cluster physics since the system allows one to study masses over a large range without fragmentation, and also contributes to the better signal to noise ratio due to collection of more ions in the ionization region [4-7]. Besides these, as known, ToF process has some unusual advantages; from view of other mass analyzers which are as follows: unlimited mass range in theory, low cost, ideally pulsed or spatially confined, spectra can be obtained for extremely small amounts, complete mass spectrum for each ionization event and no need for scanning the ion beam etc. [1]. Chandezon *et al.* combined the Wiley-McLaren's geometry with the W.A.de Heer and P. Milani's approach and reported higher transmission and better resolution [5]. The higher transmission was explained due to the non-inclusion of the field free-region to the ionization-acceleration zone for the double field system. The double-field system with the non field-free region in the acceleration-ionization was also subject of the various studies [8-12].

In this report, we propose a study for the effect of the field-free region to the mass resolution of the double field system within the second order approach. For the spectrometer arrangement, double field system with the field-free intermediate region included in the ionization-acceleration zone is taken into account together with the Wiley and McLaren's geometry explained in section 2 along with the mathematical treatment. Then, second-order compensation method is presented. The results and discussions are given in section 4. Conclusion is drawn in the last section.

2. Theoretical approach for the spectrometer

2.1 Description of the spectrometer

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

In this system, the ionization–acceleration zone consists of three regions: the R-1, R-2 and R-3, of which the R-2 is the field-free intermediate region. In region 1, particles are ionized and they are pushed through region 2 by static electric field $\overline{E}_1$. The region 2 is the field free region, hence no force from the electric field is acting on the particles. The electric field $\overline{E}_2$ accelerates the particles further. In the free flight zone (R-4), the accelerated particles drift freely and experience no electric field along where the ion packets of different masses are separated. The mass separated particles then arrive at the grounded microchannel plates (MCP) detector.

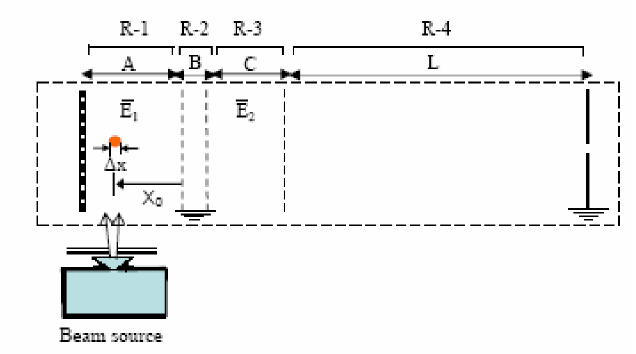


Fig.1. Block diagram of the time of flight (ToF) spectrometer with the cluster source perpendicular to the axis.

In the Wiley and McLaren's geometry, there is no field-free region in the ionization-acceleration zone [2]. Hence one obtains Wiley-McLaren's geometry from Fig.1 by removing region *B*. The geometry then has R-1 and R-3 as an ionization-acceleration zone that is followed by drift zone R-4 and ends with the MCP detector. The explanation given above also holds for this system, except the field-free region (R-2).

2.2. Mathematical treatment for time-of-flight calculation

The total flight time of a particle with the mass of particle *m* and electronic charge *q*, starting from the initial distance x of the first grid with an initial velocity υ along the spectrometer axis, is the sum of the partial flight times of the each region. For simplifying the calculations; the reduced parameter approach was used to formulate the flight time. 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, c=C/L is reduced length of the region 3 and E= $(V_a/V)(L/A)$ is the reduced value of the electric field in region 1, where V_a is the accelerating potential. These notations follow de Heer *et al.* and Chandezon *et al.* studies [4,5]. Hence, the lengths are normalized to *L* and the voltages to *V*. The total flight time obtained 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 double field system with the field-free region included in the ionization-acceleration zone, the function reads as follows:

$$f(X,S)=$$

$$\left[\frac{2(\sqrt{S^2+EX}-S)}{E}\right]+\left[\frac{2b}{\sqrt{S^2+EX+1}}\right]+$$

$$\left[2c\left(\sqrt{S^2+EX+1}-\sqrt{S^2+EX}\right)\right]$$

$$+\left[\frac{1}{\sqrt{S^2+EX+1}}\right] \tag{2}$$

From Eq.(2), one obtains the function for the double field system having the non-field free region by taking *b*=0 that reads the following one:

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

$$\left[2c\left(\sqrt{S^2+EX+1}-\sqrt{S^2+EX}\right)\right]+\left[\frac{1}{\sqrt{S^2+EX+1}}\right] \tag{3}$$

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 the following;

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

$$\left[2c\left(\sqrt{EX+1}-\sqrt{EX}\right)\right]+\left[\frac{1}{\sqrt{EX+1}}\right]. \tag{4}$$

and the Eq.(3) reads as follows:

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

The Eqs.(2-3) define the time of flight mass spectrometer in general while the Eqs.(4-5) describe the spatial mode operation of the spectrometer that allows to minimizes the velocity component effect of the mass resolution, thus, this is common in use. Note that the function is affected by the *E*, *b* and *c* reduced parameters. Having optimized the values of these parameters for the proper behavior of the function, it remains to fix the values for the *A*, *L* and applied voltages. The values determine the properties of the spectrometer.

3. The second-order compensation method and mass resolution

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

$$\frac{\partial T}{\partial x}=0. \qquad (6)$$

From the Eq.(6), $T(x,v)$ function possesses either a maximum, a minimum or a point of inflection at $x=x_0$. In order to approach the ideal case, de Heer and Milani's method controls the $T(x,v)$ function having a maximum and a minimum, and the mean distance X_0 is measured from the last grid of the region 1 to the ionization volume, being somewhere between the local points.

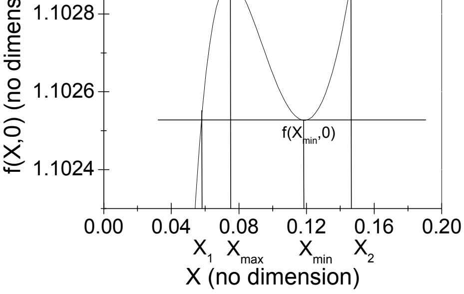


Fig. 2. Plot of f (X,0) function with respect to the initial ions position X.

In Fig. 2., a plot of the function produced with the parameters of A=13 cm, B=0 cm, C= 1.5 cm, L= 1.5 m, V_a=2.221 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. The region [X_1,X_2] defined by the local points is usable ionization region, see Fig.2. In this region, the resolution reads the following:

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

where the f_{mean} is as follow

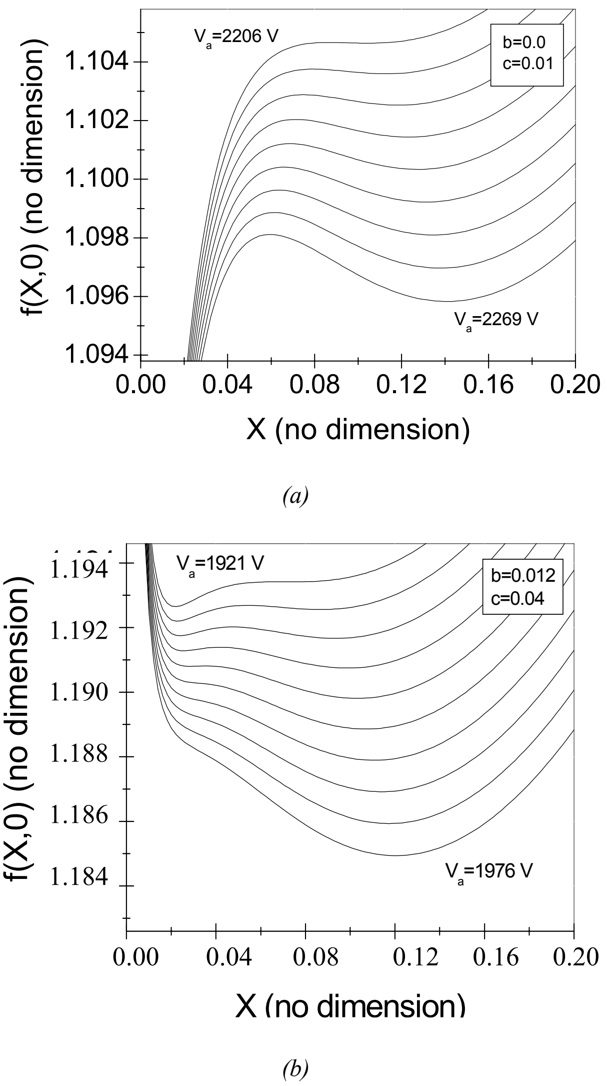
$$f_{mean}=\frac{f(X_{\min})+f(X_{\max})}{2}. \qquad (8)$$

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

4. Results and discussion

Within de Heer and Milani's approach, evolution of the function was obtained through varying the voltage of V_a and the evolution was followed in the range of 0 cm ≤ *B* ≤ 1.8 cm with a step of 0.15cm considering the various values of *C* that is 1.5 cm ≤ *C* ≤ 6 cm with a 1.5 cm step. In this way, intermediate field-free region of the ionization-acceleration zone and length of the *C*-region were varied, see Fig.1, for the regions. Regarding the values of *B*, *B*=0 is corresponding to the double field system with the non-intermediate region defined by Eq.(3), while rest of the values of *b* define the double field system with the intermediate field region given by Eq.(2). The other parameters: *A*=13cm, *L*= 1.5m and *V*=5kV are considered that meet the requirements of the method.

The plot of the function for *B*=0 cm, *C*=1.5cm and *B*=1.8 cm *C*=6 cm is presented in the Fig.3, in that the *c* and *b* values are the reduced parameters. For the previous values, the function has the inflection point at voltages around 2.206 kV and the inflection point is close to 1.921 kV for further case, 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 further increase of voltage, the local points shift away from each other, resulting in the enlargement of the ionization region Δx.



(a)

(b)

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

For each graph produced through the *b* region variation together with the region *c* values, the mass resolution was estimated via Eqs. (7) and (8). The obtained mass resolutions for these variations are given in Fig. 4. As seen from the figure, the inclusion of the intermediate region improves the mass resolution compared to the non-inclusion case presented with *b*=0 on the graph. The mass resolution increases further with the enlargement of the intermediate region. For the contribution of the region *c*, the enlargement of this region also improves the mass resolution given on the graph for the various values.

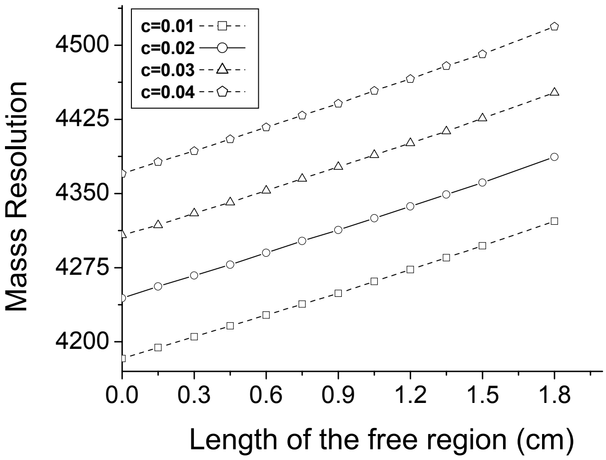


Fig. 4: The mass resolution with the variation of the free region length.

In Fig.5., the reduced electric field obtained from the graphs used for determining the mass resolution, was plotted, versus the length of the intermediate free region variation together with the C region values.

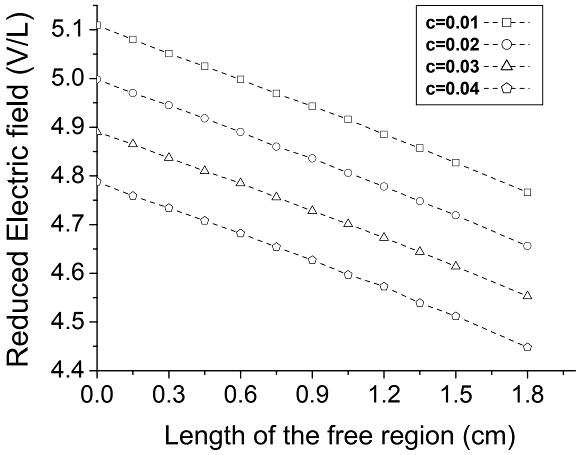
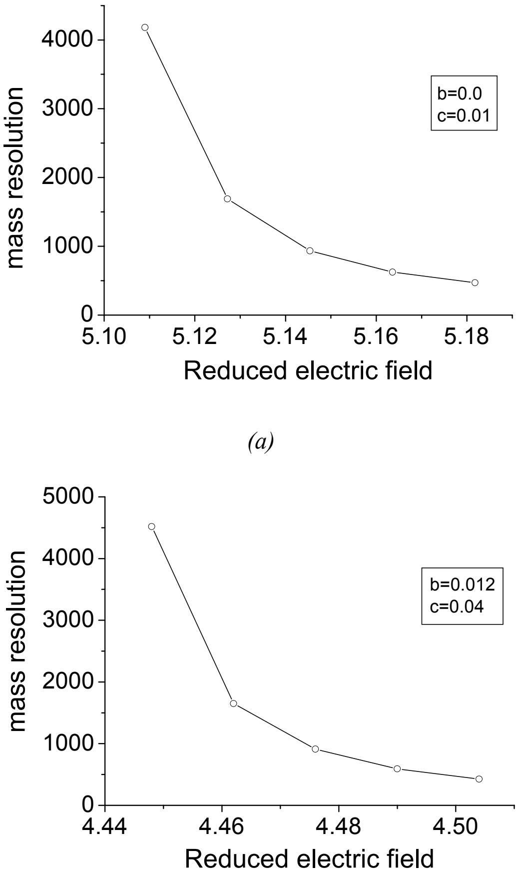


Fig. 5. The reduced electric field changes with the free region length variation.

From the figure, the reduced electric field decreases with the increase of the free region length. The enlargement of region *C* further decreases the reduced electric field. The decrease of the electric field implies that the particle receiving energy from the field drops. The particles then have less collision within the detector compared the energetic particles that in turn can cause a weak signal, hence arising the difficulty in signal to noise ratio.

For the limit values of *B* and *C* that is *B*= 0 cm, C= 1.5 cm and the *B*=1.8 cm, *C*=6.5 cm, the electric field was increased and the mass resolution was determined, (see Fig.3 for the exposed graphs). The obtained mass resolution with field variation is given in Fig.6 indicating that the increase of the electric field results in the mass resolution loss.



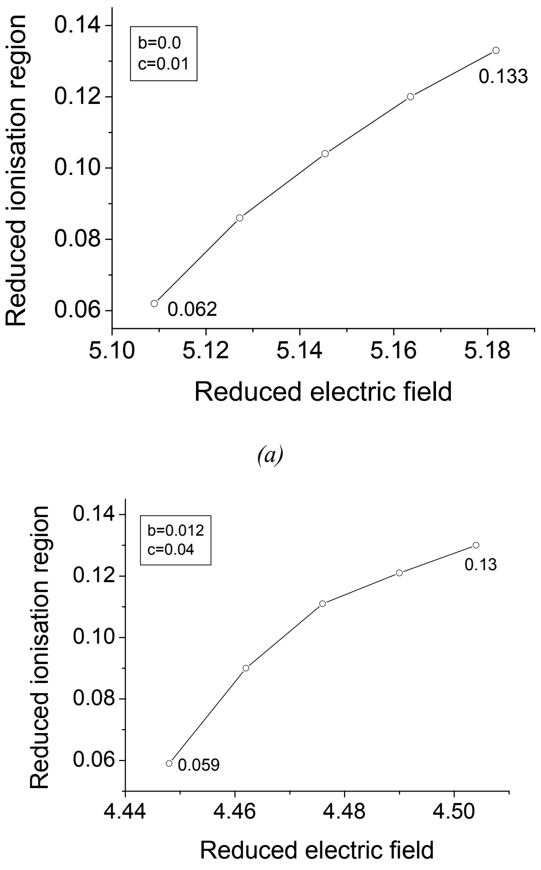
(a)

(b)

Fig. 6.: The mass resolution variations with the electric field (a) B=0 cm and C=1.5 cm, (b) B=1.8 cm and C=6.5 cm.

Hence, care is needed for using the enlarged field-free intermediate region within the ionization-acceleration zone. Otherwise, one can face the weak signal problem. The electric field can be increased to recover the signal to noise ratio problem, but the mass resolution decrease occurs.

The region was determined for the limit values of the B and C given in Fig. 7 since the implemented method provides the information on the ionization region defined in Fig.2. The ionization value enlarges with the electric field increases. The determined values for the B= 0 cm and C=6.5 cm are higher than the B=1.8 cm and C=6.5 cm ones. When the behaviour is combined with mass resolution variation and the electric field given in Fig.6, the mass resolution decreases along with the ionization region enlargement as expected.



(a)

(b)

Fig. 7. The ionization region variation with the reduced electric filed. (a) B=0 cm and C=1.5 cm, (b) B=1.8 cm and C=6.5 cm.

5. Conclusion

From the results presented, the mass resolution increase goes along with the inclusion of the intermediate field-free region to the ionization-acceleration zone and the enlargement of this region. However, the electric field decreases with the enlargement of this region that can turn out as a signal to noise ratio problem. One can increase the electric field, but the mass resolution loss takes place. Hence the use of the enlarged intermediate free region within ionization-acceleration zone unambiguously requires attention.

References

[1] A.R. Bottrill, Ph. D. Thesis, University of Warwick, 2000.

[2] W. C. Wiley, I. H. McLaren: Rev. Sci. Instrum. **26**, 1150 (1955).

[3] H. S. Katzenstein, S. S. Friedland, Rev. Sci. Instrum. **26**, 324 (1955).

[4] W. A. de Heer, P. Milani: Rev. Sci. Instrum. **62**, 670 (1991).
[5] F. Chandezon, B. Huber, C. Ristori: Rev. Sci. Instrum. **65**, 3344 (1994).
[6] Ş. Şentürk, J. P. Connerade, D. D. Burges, N. J. Mason, J. Phys B: Atom Mol. Opt. Phys. **33**, 2763 (2000).
[7] V. Kasperovich, G. Tikhonov, K. Wong, P. Brockhaus, V. V. Kresin, Phys. Rev A **60**, 3071 (1999).
[8] D. P. Seccombe, T. J. Reddish, Rev. Sci. Instrum. **72**, 1330 (2001).
[9] C. W. S. Conover, Y. Y. Twu, Y. A. Yang L. A. Bloomfield: Rev. Sci. Instrum. **60**, 1069 (1989).
[10] H. D. Eland: Meas.Sci.Technol. **4**,1522 (1993).
[11] Ş. Şentürk, K. Harigaya and O. Özsoy: Czech. J. Phys. **55**, 1275 (2005)
[12] Ş. Şentürk, Czech. J. Phys. **56**, 211 (2006).

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[*] Corresponding author: ssenturk@dumlupinar.edu.tr
osozsoy@gmail.com