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# Mass spectrometer based on conversion of spectra

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## Abstract

This article presents the results of numerical investigations of mass analyzer parameters. The principle of mass spectrometer operation is based on the shock mechanism of the ion beam conversion of spectra. Mathematical simulation of the ion motion is carried out in the fields of a mass spectrometer consisting of an ion source converter and an energy analyzer with a two-dimensional electrostatic field and a plane of symmetry. A mass spectrometer of this kind is shown to have the following parameters: 1–1600 u—operational mass range,  $\sim 1600$  mm—relative mass resolving power,  $\sim 300$  mm—the maximum dimension of the mass analyzer. We have established the basic requirements to be met by the electric pulse generator that will provide the operation of the mass spectrometer under study. (Int J Mass Spectrom 202 (2000) 139–145) © 2000 Elsevier Science B.V.

*Keywords:* Dynamik mass analyzer; Ion source converter; Electric pulse generator; Mass resolution; Energy resolution

## 1. Introduction

Recently [1] we have demonstrated the possibility of creating a mass spectrometer based on a new theory of mass separation. The essence of the theory is as follows. A particle with mass  $m$  moving with kinetic energy  $E_0$  obtains additional energy  $\Delta E$  if, within a short period of time  $\Delta t$ , it is acted upon by force  $F$  in the direction of motion. The final particle kinetic energy is

$$\begin{aligned} E &= E_0 + \Delta E \\ &= E_0 + (F \cdot \Delta t) \sqrt{2E_0/m} + (F \cdot \Delta t)^2/2m \end{aligned} \quad (1)$$

where

$$(F \cdot \Delta t) = \int_0^{\Delta t} F(t) \cdot dt$$

is the value of particle impulse change. Thus a monoenergetic beam of ions with different masses can be converted into an energy dispersed beam.

This phenomenon can become the basis for a mass spectrometer of a new type. The spectra are converted in the ion source converter when the accelerated ions are passed through the space between the electrodes of a condenser. The electric potential difference is applied to the electrodes as a consequence of voltage pulses. The final spatial separation of ions is carried out in an electrostatic energy analyzer coupled with the source converter. This enables one to relate the particle energy spectrum uniquely to the mass spectrum.

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The proposed mass spectrometer has the radiofrequency (RF) mass spectrometers based on linear acceleration of ions of selected masses [2] as its closest analogue, as far as the principle of operation is concerned. For example, according to work [3], the RF mass spectrometer includes an ion source, a mass filter for selectively increasing the kinetic energy of the ions of the predetermined mass, and a detector to determine the quantity of selected ions. An alternating current voltage is applied to the mass filter. The selected ions that receive the maximum energy level are referred to as synchronous ions. Other ions with either larger or smaller molecular mass obtain additional energy considerably lower than that of the synchronous ions. The frequency of electrical voltage of the mass filter is changed to identify the ions of various mass as synchronous. The relative mass resolving power of the RF mass spectrometers generally does not exceed 150.

The proposed mass spectrometer differs in principle from the RF mass spectrometers. (1) The additional kinetic energy of ions does not depend on the frequency of the alternating current voltage of the ion source converter, which results in the same frequency for ions of various masses. All the ions receive additional energy according to Eq. (1). (2) In the proposed mass spectrometer the additional energy obtained by the ions considerably exceeds the initial energy of ions, contrary to the RF mass spectrometers, where the additional energy of synchronous ions is much smaller. (3) The major advantages of the proposed mass spectrometer are a considerably higher mass resolving power and higher sensitivity.

To determine the prospective characteristics of the mass spectrometer consisting of an ion source converter of central symmetry and an axially symmetric energy analyzer its operation was simulated mathematically in work [1]. The mass resolving power and the sensitivity of the spectrometer were shown to be limited by the energy spread of the ions due to the shock impulse transition in various parts of the nonhomogeneous electric field of the spherical condenser in the source converter. In this study we present our latest data on a mass spectrometer of a

new type, taking into account the results obtained previously [1].

## 2. Mass spectrometer and methods of investigation

An ion source converter with a homogeneous electric field plane condenser was chosen at the exit to exclude a considerable energy spread of ions during the energy conversion process. In this work the mass spectrometer is assumed to consist of an ion source converter with plane condenser and energy analyzer with a two dimensional electrostatic field and with a plane of symmetry [4]. From the data in [4] the potential of this field in volts is

$$\Phi = \Phi_0 \cdot \varphi(x, z) \quad (2)$$

where

$$\varphi(x, z) = \frac{\sinh^2 2\pi \cdot x - \sin^2 2\pi \cdot z}{(\cosh 2\pi \cdot x + \cos 2\pi \cdot z)^2}$$

is a dimensionless function of the field geometry;  $\Phi_0$  is the maximal field potential in volts. Here  $x = X/l$ ,  $y = Y/l$ , and  $z = Z/l$  are the dimensionless coordinates;  $X$ ,  $Y$ ,  $Z$  are rectangular coordinates in meters; and  $l$  is the linear scale in meters. The potential along axis  $x$  is  $f(x) = \tanh^2 \pi \cdot x$ . The field (2) has ideal focusing properties in the  $xy$  plane for the ion beams entering the field at angles  $70^\circ \leq \Theta \leq 85^\circ$  to the axis  $y$ . In the  $zy$  plane the beams are focused only in the angle range  $\beta < \pm 2^\circ$  to the axis  $x$ . The great linear energetic dispersion of the field ensures an energy resolution better than  $dE/E = 0.0005$ . The choice of the characteristic values of the electrostatic system as scales for the physical parameters of the system enables one to use the mathematical model in reduced variables, which simplifies the analysis of the ion motion dynamics. The following equations of the ion motion in the field are derived by use of the Lagrangian:

$$\ddot{x} = \frac{4\pi \cdot \sinh 2\pi \cdot x (\cos 2\pi \cdot z \cdot \cosh 2\pi \cdot x + 1 + \sin^2 2\pi \cdot z)}{(\cosh 2\pi \cdot x + \cos 2\pi \cdot z)^3}$$

$$\ddot{z} = \frac{4\pi \cdot \sin 2\pi \cdot z (\cos 2\pi \cdot z \cdot \cosh 2\pi \cdot x + 1 - \sinh^2 2\pi \cdot x)}{(\cosh 2\pi \cdot x + \cos 2\pi \cdot z)^3}$$

$$\ddot{y} = 0$$

Here  $\ddot{x}$ ,  $\ddot{y}$ ,  $\ddot{z}$  are second order derivatives with respect to time  $\tau$ . The time magnitude in these equations is  $\tau = t/a$ , where  $t$  is real time in seconds and

$$a = 1.01856 \cdot 10^{-4} \cdot l \cdot \sqrt{\frac{M}{\Phi_0}} \quad (3)$$

$M = m/m_0$  is the mass of ions in atomic units,  $m$  is the mass of ions in kg, and  $m_0$  is the proton mass in kg. For a definition of  $a$  we have used an invariance of the Lagrangian as related to the multiplication by an arbitrary multiplier.

The initial conditions of motion at time  $\tau = 0$  are:  $x_{\tau=0} = X_0/l$ ,  $y_{\tau=0} = Y_0/l$ ,  $z_{\tau=0} = Z_0/l$ ,  $\dot{x}_{\tau=0} = (a/l)dX_0/dt$ ,  $\dot{y}_{\tau=0} = (a/l)dY_0/dt$ ,  $\dot{z}_{\tau=0} = (a/l)dZ_0/dt$ . The initial ion kinetic energy  $E_0 = mv_0^2/2$ , the final kinetic energy,  $E$ , and amplitude of voltage pulses  $V(t)$  in dimensionless forms are, respectively:

$$W_0 = \frac{E_0}{q\Phi_0} \quad (q \text{ is the ion charge in coulombs}) \quad (4)$$

$$W = \frac{E_0}{q\Phi_0} + \frac{\Delta E}{q\Phi_0} = W_0 + W_c \quad (5)$$

$$\gamma = \frac{V(t)}{\Phi_0} \quad (6)$$

For Eq. (1) to be fulfilled, the voltage duration  $\Delta t$  must be shorter than the time of flight  $t_f$  in space  $L$  between the electrodes of the condenser according to the relationship

$$\Delta t < t_f = 0.7197 \cdot 10^{-4} \cdot L \cdot \frac{\sqrt{M}}{\sqrt{U_0 + 0.5\sqrt{V}}} \quad (7)$$

where  $L$  is expressed in meters and  $U_0$  is the accelerating potential of the ion source. As shown in our

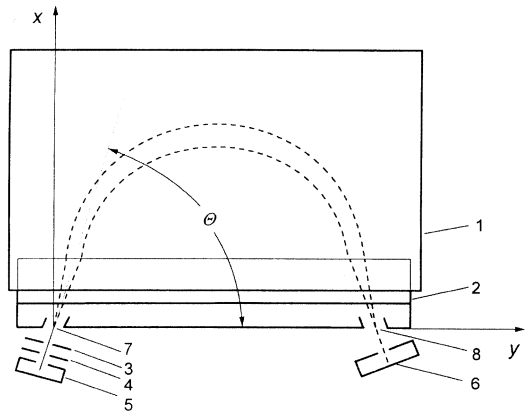


Fig. 1. Schematic of mass spectrometer electrodes (side view). 1 and 2 are electrodes of the energy analyzer; 3 and 4 are the condenser-converter electrodes; 5 is an ion source; 6 is an ion detector; and 7 and 8 are the entrance and exit slits, respectively.

numerical investigations, the optimal relationship is  $\Delta t = 0.7 \cdot t_f$ .

To determine the potential of the mass spectrometer characteristics in question, a mathematical simulation of the ion motion in the ion source converter and in the energy analyzer was carried out. Fig. 1 (the side view of the mass spectrometer) and Fig. 2 (the end view) show the arrangement of mass spectrometer electrodes: 1 and 2 are the field forming electrodes of the energy analyzer; 3 and 4 are the electrodes of the condenser converter; 5 is the ion source; 6 is the ion detector; 7 is the entrance slit; and 8 is the exit slit of the energy analyzer. In this study we did not consider the ion production mechanism. Ions are emitted from the source at angle range  $\Theta_1 \ll \Theta_2$ . Electrodes 2 and 3 are grounded, the pulsing voltage  $+V(t)$  is applied to electrode 4, and electrode 1 is under potential  $\Phi_0$ . The ions are accelerated by potential  $U_0$  in the ion source; then they are acted upon by the voltage pulse  $V(t)$  in the condenser-converter space between electrodes 3 and 4.

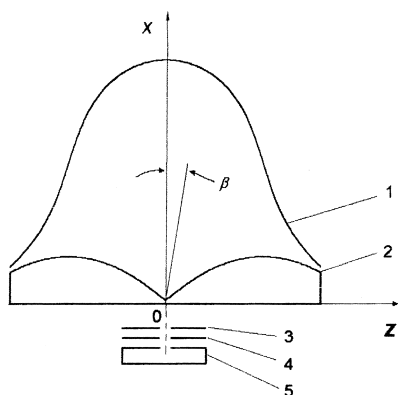


Fig. 2. Schematic representation of mass spectrometer electrodes (end view). 1 and 2 are electrodes of the energy analyzer; 3 and 4 are the condenser-converter electrodes; 5 is an ion source.

Equations of the ion motion in the ion source converter and energy analyzer are solved numerically. Electrodes 1 and 2 correspond to the equipotentials of the analyzer field with values 0 and 0.97, respectively. The value of the linear scale is  $l = 100$  mm. The distance between slits 7 and 8 is equal to  $l$ . The value of the maximal potential is  $\Phi = 2500$  V. Numerical investigations are carried out with variation of all values affecting the ion motion:  $x_0, y_0, z_0, 4 < L < 8$  mm; the sizes of all slits are  $0.2 \times 4$  mm,  $200 \text{ V} \leq U_0 \leq 500 \text{ V}$ ,  $76^\circ \leq \Theta \leq 81^\circ$ ,  $-3^\circ \leq \beta \leq +3^\circ$ , and the pulse frequency is within the range  $10^5 \leq \nu \leq 10^6 \text{ s}^{-1}$ .

### 3. Discussion

(1) It was shown that the energy spread of ions in the conversion process in the source converter was negligibly small. The changes of the value  $\Delta E$  and, respectively, those of the value  $y$  can be derived from function  $y(\tau_0)$ . Here  $y$  is the coordinate of intersection point of the ion trajectory with the electrode surface 2, and  $\tau_0$  is the initial phase or time when the ions reach the condenser gap of the source converter. Value  $\tau_0$  is expressed in units of the repetition period of voltage pulses. To illustrate, Fig. 3 shows results of calculations of  $y(\tau_0)$  for the ions with mass 300 u under the conditions  $\gamma = 1.099$ ,  $\nu = 1 \cdot 10^6 \text{ s}^{-1}$ ;  $\Delta t = 1.5 \cdot$

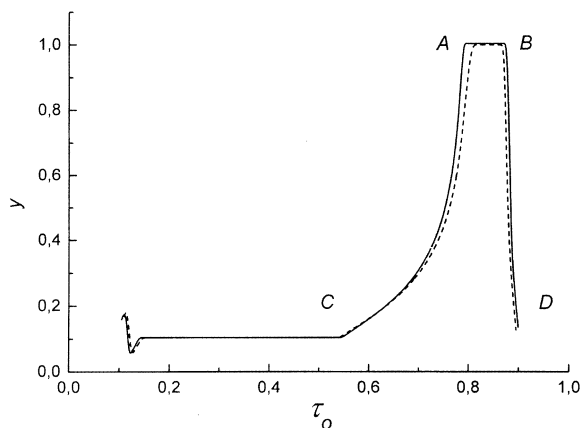


Fig. 3. Graph of the function  $y(\tau_0)$  for ions with  $M = 300$  u: solid line indicates rectangular pulses, dashed line indicates trapezoidal pulses.

$10^{-7}$  s,  $U_0 = 500$  V,  $\Theta = 78^\circ$ ,  $\beta = 0^\circ$ , and  $L = 6$  mm. The voltage pulses were rectangular. The part of the graph below  $y = 0.2$  represents the ions that reached the energy analyzer at  $\gamma = 0$ . The peak ABCD represents the ions accelerated at  $\gamma = 1.099$ . The height of the peak is proportional to the value of the additional energy ions obtained in the source converter

$$y(A) - y(C) \sim \Delta E \quad (8)$$

The difference of coordinates

$$\tau_0(A) - \tau_0(B) \sim \Delta t \quad (9)$$

determines the coefficient of the ion current utilization. It enables the estimation of the mass spectrometer transmission (as 0.1) and sensitivity. They can be considerably enhanced by increasing  $\Delta t$  and  $\nu$ . Thus in the optimal case function  $y(\tau_0)$  must have maximum values of  $\Delta\tau_0$  and  $\Delta E$ . Appropriate conditions are created by choosing  $y(\tau_0)$  depending on  $\nu$ ,  $\Delta t$ ,  $\gamma$ , and  $L$  in numerical investigations.

(2) The development of the electric pulse relaxation generator as an integral part of a new type of mass spectrometer described here is a technological challenge. The principles of operation were investigated by use of rectangular electric pulses. However, the development of the rectangular pulse generator with characteristics  $\nu \sim 1 \cdot 10^6 \text{ s}^{-1}$ ,  $\Delta t \sim 1 \cdot 10^{-7}$  s

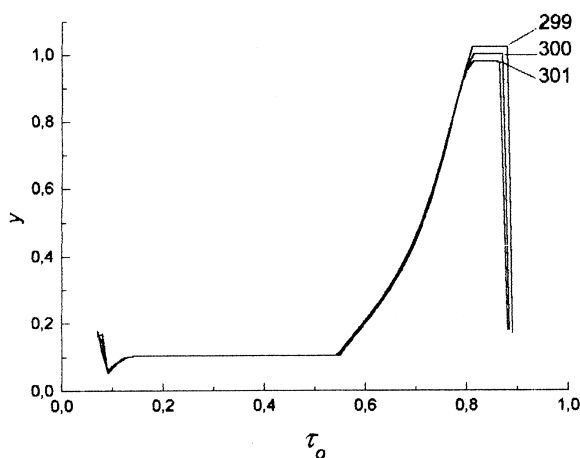


Fig. 4. Graph of the function  $y(\tau_0)$  for ions with masses 299 u, 300 u, and 301 u for triangular pulses.

and  $V(t) > 2000$  V appears to be a complex problem. For this reason we investigated the influence of the pulse shape on the mass spectrometer characteristics. Fig. 3 shows with the dashed line the function  $y(\tau_0)$  for the trapezoidal pulses with the pulse duration at the base identical to the rectangular pulses; however, the front duration is  $1 \cdot 10^{-8}$  s. This function does not differ practically from that for the rectangular pulses. The simulation of the mass spectrometer operation was carried out for triangular pulses where pulse duration at the base was equal to one of the rectangular pulses. The results obtained are in agreement with the predictions of the theory (1): the value of the additional energy  $\Delta E$  depends on the value of the impulse change of ions ( $F \cdot \Delta t$ ) and does not depend on the electric pulse shape. Fig. 4 shows the function  $y(\tau_0)$  for masses 299 u, 300 u, and 301 u obtained for triangular pulses. These functions were found to coincide with the functions in Fig. 3.

Thus the new type of mass spectrometer can function with a relaxation generator of electric pulses of an arbitrary shape. This considerably simplifies its technical design.

(3) In the mass spectrometer we propose the mass dispersion rises with increasing  $\Delta E$ . For this reason we chose the contribution of initial kinetic energy  $W_0$  in the total energy [Eq. (5)] less than the additional energy  $W_c$ . With the chosen coordinate  $y$  at the exit

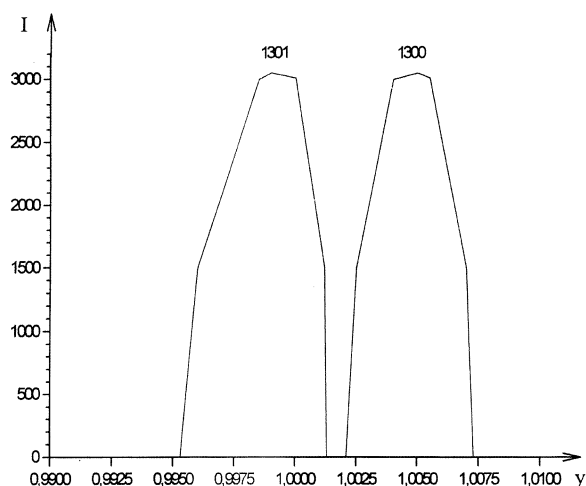


Fig. 5. Relative magnitude of peaks of masses 1300 u and 1301 u.

slit 8, the value of the total energy must be  $W = 1.099$ . The optimal value of the initial energy was found to be  $W_0 \leq 0.2$ .

Relationship (1) enables us to find the following dependence of the mass resolving power  $R_m$  on the energy resolving power  $R_E$  of the analyzer, which is a part of the mass spectrometer

$$R_m = \frac{1}{1 + \alpha} R_E \quad (10)$$

where

$$\alpha = \frac{2mE_0 + (F \cdot \Delta t) \sqrt{2mE_0}}{(F \cdot \Delta t)^2 + (F \cdot \Delta t) \sqrt{2mE_0}} < 1$$

Thus the value of the energy resolving power is the limit value for the mass resolving power. In our case we have  $R_E = 2000$ .

Fig. 5 shows the results obtained for magnitudes of the ion peaks with masses 1300 u and 1301 u when ions of  $M = 1300$  u reach the exit slit 8. The calculations were carried out assuming that  $\gamma = 1.485$ ,  $U_0 = 200$  V, and  $76^\circ \leq \Theta \leq 80^\circ$ . The shape of the peaks depends on the number of the calculated points. From the above data the value of mass resolving power can be found to be  $\sim 1600$ .

(4) The mass spectrum scanning can be carried out by two methods in the mass range 1–1600 u: by

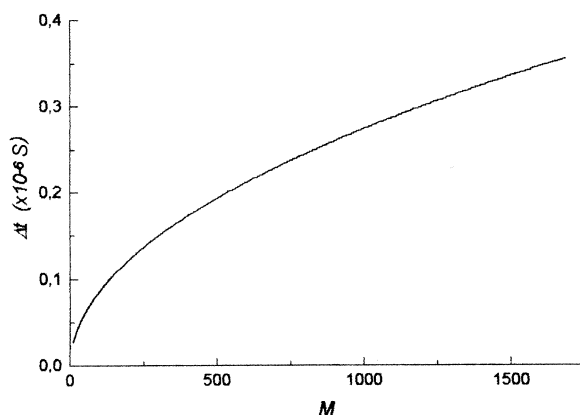


Fig. 6. The dependence of the mass spectrum scanning parameter  $\Delta t$  on mass,  $M$ .

changing the value of the duration  $\Delta t$  of the voltage pulse and by changing the value of the voltage pulse amplitude  $\gamma$ . Fig. 6 shows the dependence  $\Delta t$  on  $M$  calculated under conditions  $\gamma = 1.099$ ,  $U_0 = 500$  V,  $\nu = 1 \cdot 10^6$  s $^{-1}$ ,  $\Theta = 78^\circ$ ,  $\beta = 0$ , and  $L = 6$  mm for rectangular pulses. This curve is approximated by the polynomial

$$\Delta t = -0.3217 \cdot 10^{-10} + 0.8670 \cdot 10^{-8} \cdot M^{1/2} \\ - 0.7096 \cdot 10^{-12} \cdot M \\ + 0.1238 \cdot 10^{-13} \cdot M^{3/2}$$

Fig. 7 shows the dependence  $\gamma$  on  $M$  calculated for

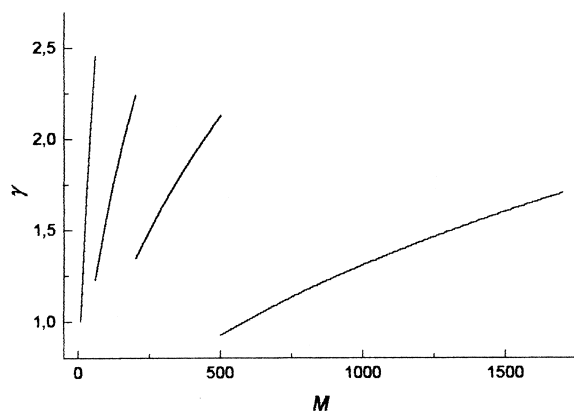


Fig. 7. The dependence of the mass spectrum scanning parameter  $\gamma$  on mass,  $M$ .

conditions  $\nu = 1 \cdot 10^6$  s $^{-1}$ ,  $U_0 = 500$  B,  $\Theta = 78^\circ$ ,  $\beta = 0$ ,  $L = 6$  mm,  $\Delta t = 3 \cdot 10^{-8}$  s (for  $10 < M < 60$  u),  $\Delta t = 6 \cdot 10^{-8}$  s (for  $60 < M < 200$  u),  $\Delta t = 1 \cdot 10^{-7}$  s (for  $200 < M < 500$  u),  $\Delta t = 2.3 \cdot 10^{-7}$  s (for  $500 < M < 1700$  u) (the pulses are rectangular). These curves are approximated by the polynomials:

$$\gamma = 0.0108 + 0.3115 \cdot M^{1/2} + 0.982 \cdot 10^{-3} M \\ - 0.5498 \cdot 10^{-4} M^{3/2}, \quad 10 < M < 60 \text{ u}$$

$$\gamma = 1.207 - 0.2032 M^{1/2} + 0.03513 \cdot M \\ - 0.1101 \cdot 10^{-2} M^{3/2}, \quad 60 < M < 200 \text{ u}$$

$$\gamma = 0.191 + 0.06135 \cdot M^{1/2} + 0.1957 \cdot 10^{-2} M \\ - 0.3702 \cdot 10^{-6} M^{3/2}, \quad 200 < M < 500 \text{ u}$$

$$\gamma = -0.2181 \cdot 10^{-2} + 0.0417 M^{1/2} - 0.1058 \cdot 10^{-4} \\ + 0.1227 \cdot 10^{-6} \cdot M^{3/2}, \quad 500 < M < 1600 \text{ u}$$

In our opinion the first method of spectrum scanning is preferable because of the relatively small amplitude values of  $\gamma$ .

#### 4. Conclusion

In [1] we demonstrated the possibilities of a mass spectrometer based on the new theory of mass separation. We considered a mass spectrometer consisting of the ion source converter of central symmetry and an axially symmetric energy analyzer. It was shown that the mass resolution and sensitivity of the spectrometer are limited by nonhomogeneity of the electric field in the spherical condenser space of the ion source converter.

In this study we have presented the results of our investigations of a mass spectrometer consisting of the ion source converter with a plane condenser and an energy analyzer with a two-dimensional electrostatic field and plane of symmetry. From the above we conclude that systems of this kind have many advantages over axially symmetric systems in design, technical characteristics, and cost of manufacture.

As a result of mathematical simulation of the spectrometer's operation we have determined its characteristics: (1) The frequency of the voltage pulses repetition is within the range  $1 \cdot 10^5$ – $1 \cdot 10^6$  s<sup>-1</sup>. (2) The amplitude of the rectangular pulses is within the range 500 V–2500 V. (3) The amplitude of the triangular pulses is within the range 1000 V–5000 V. (4) The duration of pulses is within the range  $3 \cdot 10^{-8}$ – $5 \cdot 10^{-7}$  s. (5) The operational mass range is 1–1600 u. (6) The relative mass resolving power is ~1600. (7) The maximal size of the mass analyzer is ~300 mm.

It should be mentioned that this progressive model of the mass spectrometer can also be used as an electron spectrometer. Therefore it would be very

useful to investigate solid body surfaces because they could be used to measure mass spectra, energy spectra of ions, and energy spectra of secondary electrons emitted at a surface.

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