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Hyperboloid mass spectrometers for space exploration

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Abstract

In this article we discuss some results that we have been able to achieve in the development of hyperboloid mass analyzers for "VEGA" and "Mars-96" space programs, for the "Mir" orbital station, and also for a mobile GCMS complex. We present several different electrode systems that increase the functional capabilities of hyperboloid mass spectrometers. We also discuss the key principles of hyperboloid mass analyzer optimal design and some of the interesting technical solutions that enabled us to develop light and reliable analyzers with high thermal and mechanical stability. We describe some of the conceptual analyzers that we have developed: an analyzer based on an axially symmetric ion trap; an ion trap with elliptical electrodes; an ion trap with a cone-shaped endcap electrode (three-dimensional monopole); an axially symmetric ion trap energy analyzer; a light multiple mass filter with hyperboloid electrodes. The results of our experimental studies are also included. (Int J Mass Spectrom 189 (1999) 9–17) © 1999 Elsevier Science B.V.

Keywords: Mass analyzer; Ion trap; Quadrupole mass filter; Monopole mass filter; Energy analyzer (energy filter)

1. Introduction

Currently, dynamic mass spectrometry is represented mostly by hyperboloid mass spectrometers (HMS). The remarkable properties of these instruments are based on a rf electric field with a quadratic distribution of potential. The invention of the quadrupole mass filter by Paul [1] has led to the development of new instruments, a variety of which are widely used for different scientific and technical purposes. In this publication we describe hyperboloid mass spectrometers, that have been developed in our laboratory for space research.

Since 1970 our laboratory has been developing HMS for space exploration. We participated in such prominent space research programs as the "VEGA" program (Venus and Halley's Comet exploration program) and the "Mars-96" program. We have developed a mass spectrometer for analysis of the external atmosphere of the "Mir" orbital station. We have also developed mobile instruments for GCMS. In this article we will try to introduce the reader to our experience of design and development of HMS electrode systems that could meet the specific needs of mobile equipment and mass spectrometers based on such electrode systems.

The unique conditions of space flights, such as launching and landing, place additional constraints on such devices. The "earth-based" counterparts of space-oriented instruments have fewer restrictions and usually lower specification. In addition to sensitivity, resolution, dynamic range, mass range, etc., the space instruments must have small weight and overall

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dimensions, high impact resistance, and vibration stability.

In the space programs we usually had to develop several versions of each instrument at first. Then, each version was carefully investigated and only one was chosen. For example, for the "Venus-Halley's Comet" program we developed an analyzer with conventional axially symmetric ion trap and an analyzer with a three-dimensional axially symmetric trap, one endcap electrode which had a hyperbolic profile, and another one that had a cone-shaped profile. During the development of the mass spectrometer for analysis of the external atmosphere of the Mir orbital station, we have investigated the possibility of energy analysis of the charged particles using an ion trap with elliptical electrodes. In collaboration with the Vernadsky Institute of Geo and Analytical Chemistry, RAS, and Space Research Institute, RAS, we developed a quadrupole mass filter with light-walled electrodes and an analyzer manufactured from separate sections. Each of those sections was a quadrupole unit with hyperbolic thin-walled electrodes.

All these electrode systems were manufactured using original, adjustment free technology, developed in our laboratory for manufacturing light-walled electrodes with intricate profile.

2. Geometry of hyperboloid electrode systems

In the general case, the shape of potential that is formed by hyperboloid electrode systems can be described by [2]

$$\varphi(x, y, z) = \frac{\varphi_x}{1 + p_0 + n_0}\left\{1 + p_0 + k_0 n_0 + \frac{1 - k_0}{d_a^2}\left[x^2 - (1 + p_0)z^2 + p_0 y^2\right]\right\}$$

where x_a, y_a, d_a are the closest distances between the centre of the electrode system and electrodes along the corresponding axes; $n_0 = x_a^2/d_a^2$; $p_0 = x_a^2/y_a^2$; $k_0 = \varphi_z/\varphi_x$; $\varphi_x = \varphi(x_a, 0, 0) = \varphi(0, y_a, 0)$; $\varphi_z = \varphi(0, 0, d_a)$; φ_x and φ_z are the potentials applied to electrodes.

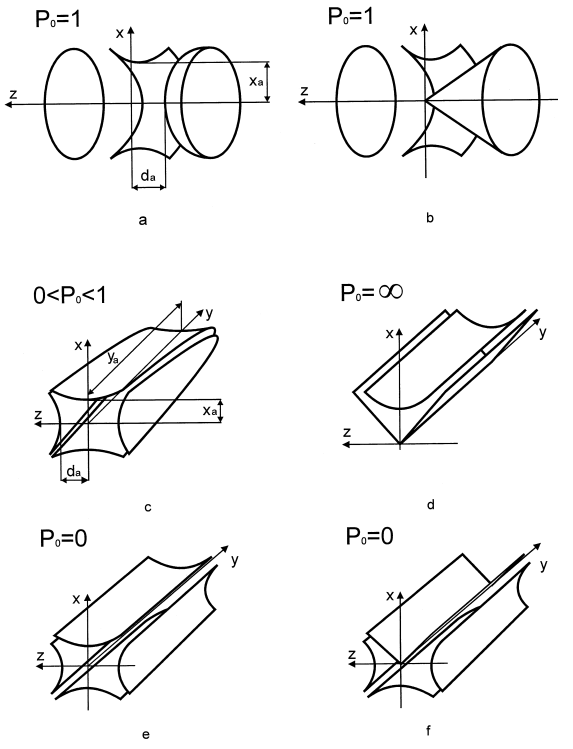

Fig. 1. Geometry of electrode systems for hyperboloid mass analyzers.

The electrode surface with potential φ_x can be described by

$$n_0 d_a^2 = x^2 - (1 + p_0)z^2 + p_0 y^2 \quad (1)$$

For an electrode with potential φ_z we have

$$-(1 + p_0)\, d_a^2 = x^2 - (1 + p_0)z^2 + p_0 y^2 \quad (2)$$

By selecting the appropriate values of n_0 and p_0 we could describe all the diversity of hyperboloid electrode systems forming both three-dimensional and one-dimensional electric fields with a quadratic potential distribution.

In the case of $p_0 = 1$, Eqs. (1) and (2) describe the electrode system of axially symmetric ion trap; when $p_0 = 0$, they describe the electrode system of the quadrupole mass filter and when $p_0 \to \infty$, they describe the electrode system of the monopole mass filter (Fig. 1).

For the three-dimensional ion trap the values of x_a,

y_a, d_a are close to each other, i.e. the n_0 and p_0 values are close to 1. The value of k_0 is often equal to zero but in order to increase the electric field density it can be taken equal to -1.

As mentioned above, when $p_0 = 1$, the hyperboloid electrode system has axial symmetry [Fig. 1(a)]. It consists of three electrodes: two endcaps and a ring, which represent parted hyperboloids and one-sheet hyperboloid of revolution, respectively. The value of geometric quotient n_0 is often taken between 0.5 and 2. Such electrode systems are traditionally used to develop ion trap analyzers.

Hyperboloid electrode systems with $0 < p_0 < 1$ [Fig. 1(c)] that form three-dimensional electric fields are being increasingly used. The ring electrode and the endcap electrodes of this system are elliptical in cross section. The ellipticity of electrodes allows for two-dimensional sorting* of the charged particles. In addition, we have the opportunity to modify the configuration of general stability zones.

For mass filters with elongated electrode systems p_0 is close to zero, and only a part of the hyperboloid electrodes is used. In the case when $p_0 \neq 0$ we have mass analyzers with a longitudinal field [2]. There are two analyzers of such type: an analyzer with quadratic potential distribution along the direct axis y (quadratic reflectron) and an analyzer with linear potential distribution (linear reflectron). The practical use of the mass reflectron is that an elongated electrode system greatly decreases the influence of a rf component of the field on ion oscillation along the axis of movement. An ion trajectory projection on this axis is mostly determined by the dc component of the field [3]. For the mass filter operating in the conventional mode of longitudinal sorting this remarkable property of a "vanishing rf component" increases sorting time and permissible longitudinal velocity spread, because ions are decelerated and then reflected in the longitudinal direction. Thus the required electrode system length can be decreased. For ions in a quadratic reflectron we have time of flight π times greater than that of the conventional mass filter under the same conditions [2].

When $p_0 = 0$ there is no longitudinal field along the y axis, and we have the quadrupole mass filter, Fig. 1(e). For the quadrupole mass filter we usually take $n_0 = 1$ and $k_0 = -1$.

If we assume $p_0 \rightarrow \infty$, Eq. (1) describes the monopole mass filter of von Zahn [4], and Eqs. (1) and (2) describe the electrode system of the monopole mass filter [Fig. 1(d)].

The substitution of one endcap electrode by a cone-shaped one, Fig. 1(b), leads to absolutely new results. We call such mass analyzers "three-dimensional monopole mass spectrometers" because of the shape of their stability diagram. The triangular stability zone turns into a "stability band" located near a stability boundary. Thereby the one-dimensional sorting (see prior footnote) of ions could be implemented.

In comparison to the monopole mass filter, the analysis sensitivity can be greatly increased by using an electrode system, which consists of three hyperboloid electrodes and an angled electrode, Fig. 1(f). Having all the advantages of one-dimensional sorting, such instruments provide greater sensitivity than the sensitivity of the monopole mass spectrometer, and sensitivity just a little worse than the quadrupole mass filter.

Historically, the geometry of HMS electrode systems has been a reasonable compromise between high field accuracy and production costs. This is the reason why cylindrical rods for the quadrupole mass filter were introduced.

There have been many attempts to simplify an electrode system of the ion trap. We also have done such work in our laboratory. Since we have developed a robust technology for manufacturing identical light-wall electrodes with an intricate shape, we saw the

* Within the axially symmetric ion trap ions are sorted along three coordinate axes z, x, and y. In this case three borders of the stability diagram are used, and we have three-dimensional sorting (although, two borders for the x and y coordinates coincide: $r^2 = x^2 + y^2$). In the case of an ion trap with elliptical electrodes two borders can be used, for instance, along the z and x axes (when the working point along the y coordinate is located inside the stability diagram). Thus, the ion sorting within such analyzers is two dimensional. The mass filter also utilizes the two-dimensional sorting. One-dimensional sorting is implemented by using stability diagram borders along one coordinate (for instance, during the operation in a narrow upper zone of the stability diagram). A device with one-dimensional sorting is also Zahn's monopole mass filter.

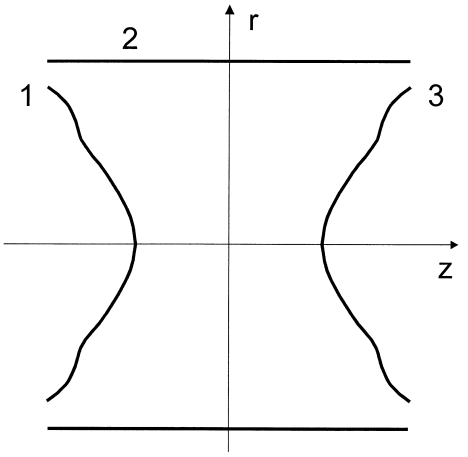

Fig. 2. Ion trap with a cylindrical ring electrode (2) and the endcap electrodes [(1) and (3)] of a special shape.

problem in getting through the difficulty of alignment of the endcap electrodes against the plane of symmetry of the ring electrode. We have found the solution for this problem in "eliminating of the plane of symmetry" of the ring electrode. A barrel electrode has been used as a ring electrode, and the field optimization was carried out by selection of the appropriate profile of the endcap electrodes, Fig. 2. This minimizes the field distortions of the odd orders, which dramatically reduce sensitivity and distort mass peak shape.

3. Design and manufacturing principles for electrode systems of HMS

The development of a HMS with high analytical performance relies, first of all, upon the "principle of independence of ion oscillations." This principle requires the field with quadratic potential distribution along the axes to be formed within the ion trap. Ion oscillations are independent (uncoupled) in this ideal field only. The natural solution of this problem is to use electrodes with a hyperboloid profile. But there is a big problem with this approach—the dimensions of the electrodes must be limited. This means that each analyzer must have a boundary region (BR), which distorts the ideal potential distribution within the ion trap. The problem of the BR selection can be divided in two parts: selection of electrode boundaries along the respective coordinate axes and selection of BR geometry (BRG). Apparently, a successful selection of BRG can greatly decrease analyzer dimensions. Thus, electrode system symmetry of the quadrupole mass filter unambiguously determines its BRG: the maximum dimensions of each electrode along different coordinate axes must be the same. But for the ion trap the problem of BRG selection is rather difficult. We have developed "the compensated charge principle," which makes possible the selection of the BRG for the electrode system of a HMS in the general case. According to this principle, the BRG should be selected in the following way: surface charge density integrals taken through the surface of ideal electrodes within their boundary must be equal to each other.

The following equation illustrates the compensated charge principle for the ion trap:

$$(z_{\mathrm{rl}}/d_a)\lfloor n_0 + (z_{\mathrm{rl}}/d_a)^2 \rfloor = 2(z_{\mathrm{ecl}}/d_a)\lfloor (z_{\mathrm{ecl}}/d_a)^2 - 1 \rfloor \quad (3)$$

where z_{rl} is the size limit of the ring electrode along the axis of symmetry z; and z_{ecl} is the size limit of the endcap electrode along the same axis.

We have conducted extensive computer simulations of the field within a three-dimensional ion trap with BR. As we have discovered, following the compensated charge principle leads to minimal departure of the field distribution from the ideal (quadratic).

In most cases the electrode system of the ion trap must have slits for injection or ejection of the charged particles. Unlike the boundary region, these slits are located in the working volume of the analyzer, and therefore substantially distort the field. In order to reduce the influence of the slits, we must follow the basic rule: the slits must not perturb symmetry of the field. Each slit in one electrode must have "a compensating" slit in the other electrode. The geometry of the compensating slits can be defined according to the principle of "the compensated charges." An ionizing electron beam can be injected, for example, through a ring slit in the ring electrode of the axially symmetric ion trap, and the endcap electrodes must have "com-

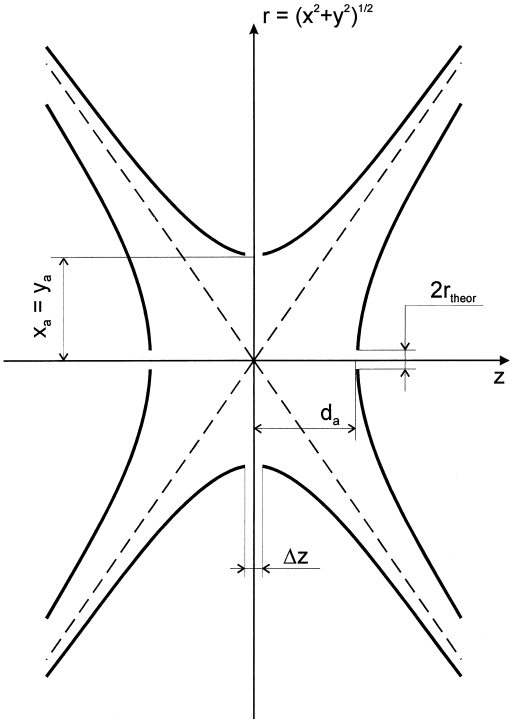

Fig. 3. Geometry of an axially symmetric ion trap with a ring slit of Δz thickness in the ring electrode and the respective compensating holes (with a diameter of $2r_{\text{theor}}$) in the endcap electrodes.

pensating holes" (when the ring slit lies in the plane of symmetry of electrode system). If the slit is positioned off the plane of symmetry, the endcap electrodes must have a "compensating" ring slit. In the case of electron beam injection along the symmetry axis z, the slits in the endcaps must be identical, and the ring electrode must have a compensating ring slit in the plane of symmetry.

Eq. (3) can be successfully used to determine the geometry of compensating slits in electrodes of the axially symmetric ion trap (Fig. 3). We have calculated the field within the ion trap with a ring slit of varying width in the ring electrode, through which the ionizing electron beam can be injected. The extent to which the distribution deviates from a quadratic was estimated as the average deviation of the potential along the asymptote within the working volume from potential in the centre of electrode system. It was found that the presence of a compensating hole in the centre of the endcap electrodes substantially improves the field within the trap and field distortions are minimal if the radius of these holes was defined from Eq. (3). The results of simulation are shown in Table 1. Here values of relative width of a slit in the ring electrode $\Delta Z = \Delta z/d_a$ and their respective relative radii $R_{\text{theor}} = r_{\text{theor}}/d_a$ (Fig. 3) defined from Eq. (3) are presented. For estimation of accuracy ε of Eq. (3) optimal values of relative radius $R_{\text{model}} = r_{\text{model}}/d_a$ are also presented here. These values were defined from numerical calculations of the field within the ion trap for minimal departure of the potential distribution from a quadratic. From Table 1 we can see that the value of accuracy $\varepsilon = (R_{\text{theor}} - R_{\text{model}})/R_{\text{model}}$ does not exceed several percents. It means that Eq. (3) is quite reliable.

The second basic design principle is that such electrode systems should be vibration proof and impact resistant. In our case, it was very difficult to satisfy these requirements. At last, we have found an appropriate solution: we decided to make the thin-walled electrodes (with uniform wall thickness) and the walls were crimped around those places where ceramic insulators were connected with electrodes.

The electrode system of mass spectrometer "Malachit-V" was manufactured using technology developed for the Venus and Halley's Comet exploration program and sustained an impact load of up to 200 G and vibration of up to 40 G. Under these conditions, the distance between the electrodes did not change by

Table 1
An average deviation of the potential along the asymptote within the working volume from the potential in the centre of electrode system

ΔZ	0.010 53	0.021 05	0.026 32	0.042 11	0.057 89	0.073 69	0.084 21	0.094 74
R_{theor}	0.102 41	0.144 78	0.161 81	0.204 49	0.239 72	0.270 48	0.289 26	0.306 99
R_{model}	0.115 79	0.150	0.165 79	0.205 26	0.239 47	0.273 68	0.297 37	0.321 05
ε (%)	−13.067	−3.604	−2.461	−0.374	0.101	−1.185	−2.802	−4.581

more than 3 μm (when the analyzer overall dimensions were 85 $\times$ 85 mm).

The next important requirement is high thermal stability. There are basically two main effects of increasing the temperature of the electrodes: the electrode system base geometry changes (the distance between electrodes, for instance) and nonlinear field distortions appear. Whilst the former effect, can be dealt with (e.g. by calibration), the latter effect, which dramatically decreases the analytical performance of the device—cannot. The theoretical study of different methods of electrode mounting led us to the optimal principle—the so-called "free mount principle." According to this principle, each electrode is mounted to the adjacent electrodes only by means of ceramic insulators. This principle has been effectively used in our laboratory for ion trap electrodes and it is very effective for mass filters. So the analysis of mass spectra obtained with our quadrupole mass filter, which had thin-walled hyperboloid electrodes (1 mm thick and 300 mm long) has shown the following results: for a change in temperature of 200 °C the mass peak shifted by an amount that corresponded to a change of 38 μm in field radius, whilst the resolution and peak shape were unchanged.

Finally, one more vital development problem is the durability of the hyperboloid electrode systems for space exploration. This problem is especially important for the three-dimensional ion trap with injection of an ionizing electron beam. It is often impossible in mobile equipment to disassemble the analyzer for the cleaning of electrode working surfaces. We have developed a method for removing from electrodes the dielectric films that are caused by electron bombardment. We call this technique "self-purification." The working surfaces of electrodes are covered with a thin layer of indium. When the working parameters of the analyzer worsen, the electrode system is heated up for a short period of time to a temperature close to the melting point of indium ($\sim$150 °C) by a built-in heater. Such cleaning cycles can be carried out several times. With the technology we have developed, the durability of the ion traps has been increased up to 10 000 hours.

In order to satisfy all the requirements mentioned, we have developed an adjustment free method of manufacturing electrodes, based on electroforming. Electrolytic copper was used as the main material for this purpose. Depending on the construction of electrode system, destructive and nondestructive matrix forms are used. We have received the best results for electrode systems with precision of 1–2 μm by using metal forms. The thickness of the electrode wall can be easily varied from 0.2 mm to several millimeters. The electroforming technique allows us to form the electrodes easily with apertures for electron injection. In order to make the electrode system resistant to hostile environments, we covered the working surface of electrodes with an appropriate protective coating (Au, Cr, Ni, In, Ga, Re, etc.). A protective coating passivates the surface of electrodes and decreases the exoelectron emission caused by charged particle bombardment by 10–100 times.

4. Mass analyzers of HMS in practical use

These hyperboloid electrode systems and our original method of their manufacturing have been used in a series of mass spectrometers designed for mobile systems and for space exploration.

The three-dimensional ion trap for the Venus-Halley's Comet program was based on an axially symmetric electrode system with $x_a = y_a = z_a =$ 19 mm and overall dimensions 85 $\times$ 85 mm. The electrode edges were made parallel to the symmetry axis in order to reduce the overall dimensions. Ceramic insulators were embedded into the edges and provided precise electrode alignment and isolation for the ring and endcap electrodes. The ionizing electron sheet beam was injected through a slit of 0.3 mm thickness in the ring electrode. The endcaps had a gauze with a transparency of 40% and a diameter of 19 mm for ion ejection. The departure of electrode profile and alignment from the theoretical values did not exceed 4 μm. The electrodes were made from copper 0.8 mm in thickness and had a total weight of 250 g. They were coated with 3 μm of gold for protection. They withstood vibration up to 40 G for 15 min and resisted up to 140 impacts of 200 G.

Use of such electrode systems in conventional

Fig. 4. Three-dimensional ion traps developed in our research laboratory. The upper row (from the left): the axially symmetric ion trap; the axially symmetric ion trap with a cone-shaped endcap electrode (three-dimensional monopole); the ion trap with elliptical electrodes. At the bottom: a hyperbolic electrode and a cone-shaped endcap electrode.

earth-based devices allowed us to achieve a resolution of 3×10^3; minimum detective pressure of 1×10^{-14} Torr, and dynamic range up to 10^6. The electrode configuration and experimental results are shown in Fig. 4 and 5, respectively.

We found that the use of axially symmetric hyperboloid electrode systems for energy analysis of charged particles is very effective. Such energy analyzers have optical efficiency of up to 20%–40% with energy resolution of 100. Combining energy analysis with mass analysis in one instrument is very promising. Switching between mass analysis mode and energy analysis mode can be done by simply changing the shape of driving voltage. For operation in mass analysis mode dc and rf components of driving voltage are applied to the electrodes. In the energy analysis mode only a dc potential is being applied. One of the possible implementations of energy analyzers, based on an axially symmetric electrode system and developed in our laboratory is shown in Fig. 6. In this analyzer we used axially symmetric electrode system of the ion trap with $x_a = y_a = z_a = 19$ mm and overall dimensions 85 × 85 mm. The ring electrode of this system has a ring slit and the output endcap electrode has a gauze in the centre, which is necessary for mass analysis. Furthermore, the input and the output endcaps have additional coaxial ring slits for injection and ejection of the charged particles

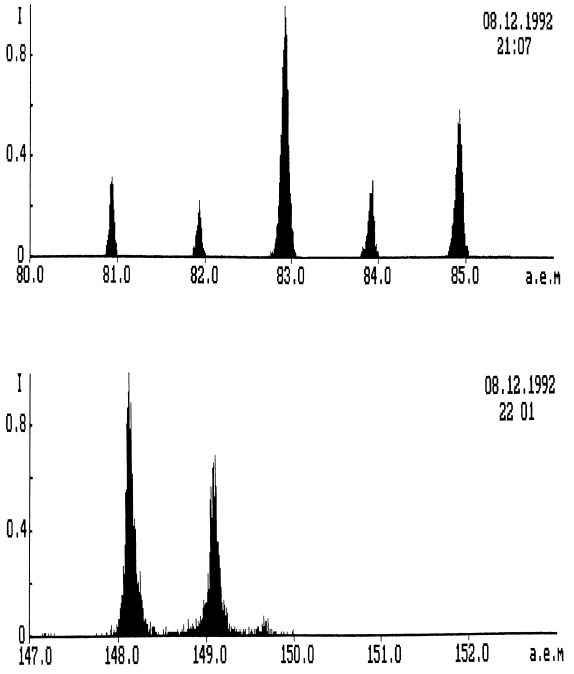

Fig. 5. Mass spectra obtained with the axially symmetric ion trap.

in energy analysis mode (the ions originate from a point source *S* lying on the axis of symmetry). An experimental model of such an energy analyzer has

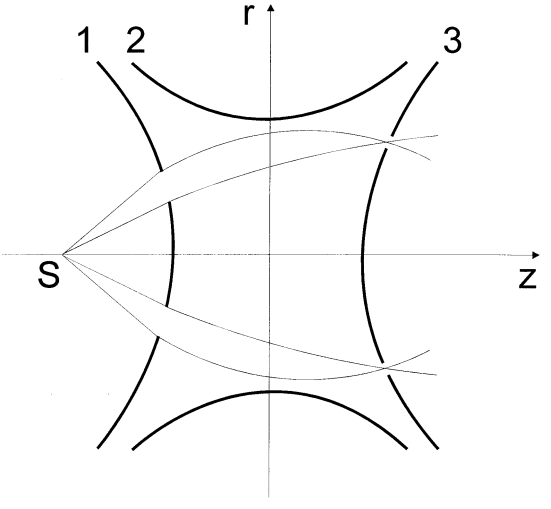

Fig. 6. Ion optic system of energy analyzer based on the axially symmetric hyperboloid ion trap. 1,3—the endcap electrodes; 2—the ring electrode.

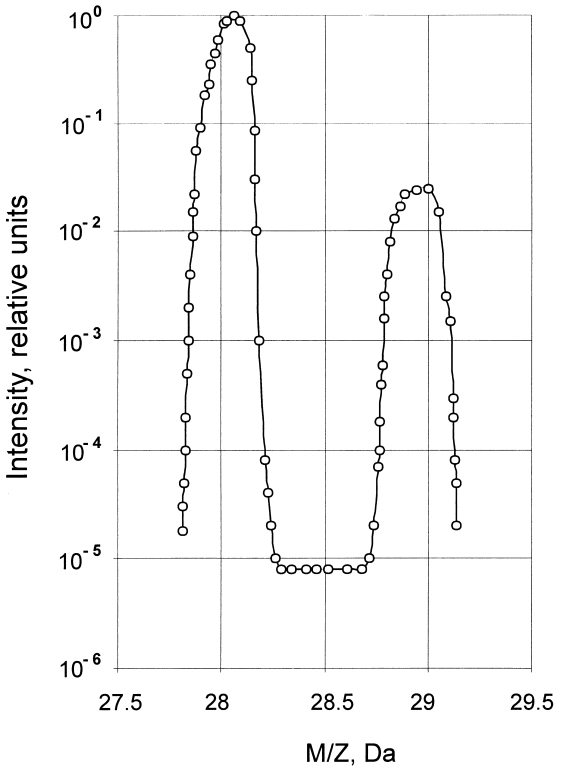

Fig. 7. Mass peak shape of *m/z* 28 Da obtained with three-dimensional ion trap with elliptical electrodes.

optical efficiency 4% with energy resolution of 100, which is acceptable if we remember that mass analysis can also be carried out.

A hyperboloid mass analyzer based on a hyperboloid electrode system with elliptical electrodes has the following dimensions: $x_a = 32$ mm, $y_a = 28.8$ mm, $d_a = 32$ mm; $p_0 = 0.81$, $n_0 = 1$. The electron beam was injected trough the radial slit in the ring electrode along the long axis, Fig. 4. The mass peak shape at *m/z* 28 obtained by a mass spectrometer equipped with such an electrode system is shown in Fig. 7. The mass peak has a good shape. The resolution, determined at 0.5 of the peak height is 140; at 0.1 it is 100; and at 10^{-6} it is 35. The obtained dynamic range is 10^6.

A mass spectrometer with a cone-shaped endcap electrode based on the axially symmetric hyperboloid electrode system has overall dimensions 85 × 85 mm

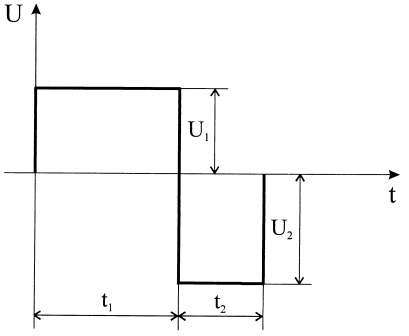

Fig. 8. A wave form of the driving rf signal for hyperboloid mass analyzers.

and $x_a = y_a = d_a = 19$ mm. The input endcap electrode is cone shaped. The cone generator surface is an asymptote of two hyperboloids of revolution—a ring and an output endcap electrodes. The output endcap electrode has a gauze with a transparency of 40%. The electrode mounting was provided by ceramic insulators located in the electrode edges. The ring electrode has a slit (0.3 mm thick) for the injection of the ionizing electron beam, Fig. 4. A resolution of 100 at 0.1 of the peak height with a good peak shape was obtained for the mass analyzer with a square wave rf signal (Fig. 8) with $(t_1 + t_2)/t_1 = 5$. A mass scanning was performed by varying a frequency of the signal [1], whilst $(t_1 + t_2)/t_1$ was kept constant. One of the main advantages of this device is that the resolution was constant within the mass range.

With the unique technology we have developed a light and robust hyperboloid electrode system for the quadrupole mass filters which can operate in extreme conditions. Such an electrode system was developed for the Mars-96 space program. In order to make this electrode system resistant to external forces we built it from separate sections. Each of these sections was a quadrupole unit. Electrode systems with electrodes from 66.6 to 600 mm long and the field radii 8.05, 8.2, and 10 mm were developed and investigated (Fig. 9).

The mass analyzer, which we have developed for Mars-96 space program, provides the dynamic range of 10^5, resolution up to 500 at 0.5 of mass peak height and a good peak shape. The field radius is 8.2 mm, the length of electrodes is 200 mm, and the weight is

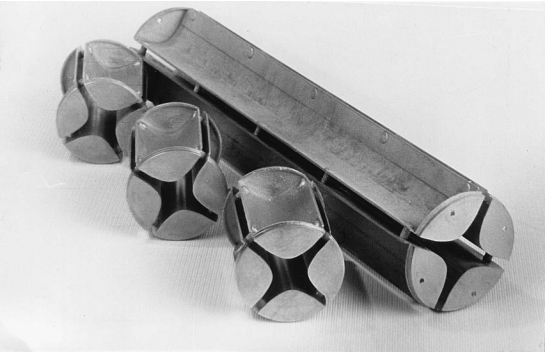

Fig. 9. Quadrupole electrode systems of different length and field radius for mass filters developed in our laboratory.

150 g. Mass scanning was performed by varying the frequency, whilst $(t_1 + t_2)/t_1 = 2$ was kept constant. We used a compact pulse generator with low power consumption. The pulse amplitudes were $U_1 = U_2 = 50$ V. The mass analyzer operates under temperatures of up to 200 °C with a constant resolution.

5. Conclusions

In this article we have shown that ellipticity of electrodes in a hyperboloid ion trap, the use of an electrode system with a cone-shaped endcap electrode, and improving the design of the mass filter electrode system improves the performance of mass analyzers.

We presented some general principles for development of light and robust electrode systems with high thermal and mechanical stability. These principles are based on optimization of the electrode boundary regions, which made it possible to optimize geometry of electrodes and geometry of slits for injection/ejection of the charged particles.

We have described design features of mass analyzers for space research developed in our laboratory.

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References

[1] W. Paul, H. Steinwedel, Z. Natur. 8a (1953) 448.
[2] E.P. Sheretov, Meas. Control Automation 11–12 (1980) 29–43.
[3] E.P. Sheretov, J. Techn. Phys. 49 (1979) 34–46.
[4] U. von Zahn, Rev. Sci. Instrum. 34 (1963) 1.