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Three-dimensional trap with excitation of ion oscillations at the stability boundary of the Mathieu diagram

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Received February 15, 2023
Revised April 19, 2023
Accepted April 20, 2023

Vibrations of charged particles in compositions of three-dimensional high-frequency quadrupole and static homogeneous electric fields in the stable region and in the vicinity of the stability boundary of the Mathieu diagram are investigated. Using a pseudopotential model of a rapidly oscillating field, it is shown that the motion of charged particles during linear scanning of a secular frequency is described by the Airy differential equation. Based on the properties of solutions of the Airy equation, a method of ion mass separation with resonant excitation of oscillations at the stability boundary of the Mathieu diagram has been developed. To implement the method, the ion-optical system of the three-dimensional trap is supplemented with corrective electrodes. Computer modeling has determined the optimal potentials of the correcting electrodes, at which the errors of the distributions of quadrupole and homogeneous fields do not exceed 10^{-4} and $2 \cdot 10^{-3}$. Keywords: superposition of quadrupole and homogeneous fields, Airy differential equation, mode of resonant excitation of oscillations, three-dimensional ion trap with correcting electrodes.

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DOI: 10.61011/TP.2023.06.56531.25-23

Introduction

The selective properties of high-frequency (HF) quadrupole electric fields are widely used in mass spectrometry to separate ions by specific charge [1]. But strictly speaking, the possibilities of the rapidly oscillating fields for increasing the resolution and sensitivity of quadrupole ion mass analyzers are practically exhausted. To improve the analytical parameters of mass spectrometers of this class, the methods were developed for selecting ions in quadrupole HF fields by superposition of excitation homogeneous fields [2] to them. In this case, the movement of ions is described by the inhomogeneous Mathieu differential equation. One of the independent solutions of the equation is the excitation function, which is not related to the initial parameters (coordinates and velocities) of the particles. In this case, it becomes possible to significantly improve the analytical parameters of quadrupole mass-spectrometers by optimizing the excitation function.

The methods considered in [2] assume excitation of ion oscillations by a harmonic homogeneous field in the depth of the first zone of the stability diagram. However, due to the low rise rate and the irregularity of the excitation function, the analytical capabilities of the method turned out to be limited.

The method development is the excitation of ion oscillations at one of the stability limits of the Mathieu diagrams, where the excitation function increases without limit. The method is implemented in the superposition of quadrupole and homogeneous fields with slow scanning of the Mathieu parameter a from the depth of the stability zone from $a = 0$ to the boundary value $a = a_{\text{bound}}$. When crossing the stability boundaries of the Mathieu diagram, the ion oscillations acquire a regular, rapidly growing nature, which contributes to the achievement of high resolution of quadrupole mass-analyzers.

The aim of the study is to analyze the motion of charged particles in a combination of static homogeneous and quadrupole radio-frequency fields under mass-selective resonant excitation of ion oscillations at the boundary of the Mathieu diagram.

1. Motion of charged particles in quadrupole HF fields with oscillations excitation at the stability boundary

The mode of resonant excitation of oscillation can be created in a three-dimensional ion trap by superposition of uniform excitation field to a quadrupole field. For this case the potential distribution in the working area of the analyzer is described by the function

$$\varphi(r, z, t) = \frac{[U(t) + V\cos\omega t][z^2 - \frac{r^2}{2} + \frac{r_0^2}{2}]}{z_{01}^2 + \frac{r_{01}^2}{2}} + \frac{U_{\text{exc}}(t)}{2z_{01}} Z, \tag{1}$$

where z_{01} and r_{01} — minimum distances from the center of the ion-optical system (IOS) of hyperbolic end and ring electrodes; V, ω and $U(t)$ — amplitude, frequency and the constant component of the supply voltages slowly changing during the mass sweep; $U_{\text{exc}}(t)$ — excitation voltage. Under the action of voltage $U_{\text{exc}}(t)$ the excitation field uniform along the axis Z is formed between the end electrodes.

The charged particles motion in the potential field (1) is described by differential equations [3]:

$$\frac{d^2z}{dt^2} + \frac{\omega^2}{4}[a_z(t) - 2q_z \cos\omega t]z = f_{\text{exc}}(t), \tag{2}$$

$$\frac{d^2r}{dt^2} - \frac{\omega^2}{4}[a_r(t) - 2q_r \cos\omega t]r = 0, \tag{3}$$

where

$$a_z(t) = 2a_r(t) = 8eU(t)/(z_{01}^2 + r_{01}^2/2)\omega^2 m,$$

$$q_z(t) = 2q_r(t) = 4eV(t)/(z_{01}^2 + r_{01}^2/2)\omega^2 m$$

— Mathieu parameters; e and m — charge and mass of ions; $f_{\text{exc}}(t) = eU_{\text{exc}}(t)/2z_{01}m$ — particles acceleration under the action of a uniform field.

In the absence of excitation (2) and (3) are the Mathieu equations [4]. Stable and unstable solutions $z(t)$ and $r(t)$ of the equations are separated by boundaries$am(q_z)$ and $b_{m+1}(q_z)$, where $m = 0, 1, 2, \ldots$. When crossing the boundaries from the stable region to the unstable one, the solutions of the differential equations increase without limit. The method of axial output of ions from a three-dimensional trap is based on this property of solutions of the Mathieu equations [5]. The method is implemented at $a_z = 0$ by scanning the parameter $q_z(t)$ through the boundary $b_1(q_z)$. The problem of axial output is the dependence of the ion output time from the analyzer on the initial coordinates z_0 and the particle velocities v_{0z}. In this case, even in the presence of a buffer gas the resolution turns out to be low.

The resolution of quadrupole analyzers with sequential output of ions through the stability boundaries can be increased by imposing the excitation field uniform along the axis Z on the quadrupole field. In this case, the general solution $z(t)$ of the differential equation (2) is the sum of free $z_1(t)$ and forced $z_2(t)$ components. A particular solution $z_2(t)$ of the inhomogeneous equation (2) is determined by the action $f_{\text{exc}}(t)$ of the homogeneous excitation field and can be considered as a function of excitation. Since $z_2(t)$ does not depend on random values of the initial parameters of the particles z_0 and v_{0z}, the method resolution will be determined by the relation at the moment of excitation t_{exc} (ion output from the analyzer) of values of functions $z_1(t_{\text{exc}})$ and $z_2(t_{\text{exc}})$. The condition $z_2(t_{\text{exc}}) \gg z_1(t_{\text{exc}})$ of the resolution increasing of quadrupole mass-analyzers with resonant output of ions can be implemented by selection of methods of mass sweep and mode optimization.

The analysis of the oscillations of charged particles in the superposition of rapidly oscillating quadrupole and uniform excitation fields showed the efficiency of the resonant inference output method when scanning the parameters $a_z(t)$ and $q_z(t)$ from the first stability region upto crossing the boundary $a_{0z}(q_z)$ of Mathieu diagram. In this case, the mode of monopolar oscillations $z_2(t) > 0$ of charged particles is realized, which improves the analytical parameters of the method and simplifies its implementation.

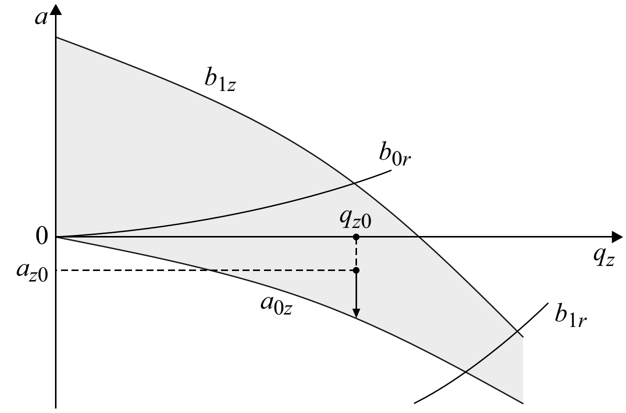

Figure 1. Scheme for scanning the parameter $a_z(t)$ to the stability boundary $a_{0z}(q_z)$.

During the resonant output of ions, the oscillations are excited at secular frequency, which depends on the stability parameter $\Omega_s = \beta\omega/2$. At the boundary $a_{0z}(q_z)$ the stability parameter is $\beta_z = 0$ and the secular frequency is $\Omega_s = 0$. Therefore, to excite oscillations at the boundary $a_{0z}(q_z)$, one should use a static uniform field formed under the action of a dipole voltage $U_{\text{exc}}(t) = U_{0\text{exc}}$. In this case, $f_{\text{exc}}(t) = f_0 = eU_{\text{exc}}/2z_{01}m$.

Three options for scanning the parameters $a_z(t)$ and $q_z(t)$ to the boundary $a_{0z}(q_z)$ are possible: 1 — cby hanging $a_z(t)$ at $q_z(t) = \text{const}$, 2 — by changing $q_z(t)$ at $a_z(t) = \text{const}$, 3 — by changing $a_z(t)$ and $q_z(t)$. In all cases, at the coordinate r the parameters a_r and q_r are in a stable region and do not have a significant effect on the particles mass separation process. Consider the case of mass sweep by scanning according to the linear law of the constant component of the supply voltage $U(t)$ at constant parameters V and ω [3]:

$$U(t) = \nu_U t, \tag{4}$$

where $\upsilon_U = U_m/T$ and T — speed and duration of mass sweep. In this case, the parameter $a_z(t)$ also changes according to the linear law

$$a_z(t) = \frac{8e\nu_U}{(z_{01}^2 + \frac{z_{01}^2}{2})\omega^2 m} t. \tag{5}$$

The scheme of oscillations excitation when scanning the parameter $a_z(t)$ to the boundary $a_{0z}(q_z)$ is shown in Fig. 1.

At $q < 0.5$, $a_{0z}(q_z) \approx q_z^2/2$ is valid, and taking into account (4) for the excitation time dependence describing the mass sweep law we obtain

$$t_{\mathrm{exc}} \approx \frac{eV^2}{(z_0^2 + r_0^2/2)\omega^2 v_U} \frac{1}{m}. \tag{6}$$

Due to the parameter $a_z(t)$ changes during the sweep process, the differential equations (2) and (3) are non-stationary. Taking into account the inertial nature of the mass sweep at $T \gg 2\pi/\omega$, the solution of the equation of ions motion along the axis Z can be represented by the sum of free $z_1(t)$ and forced $z_2(t)$ components [3]. Function $z_1(t)$ depends on random parameters of particles z_0 and v_{0z}, and excitation function $z_2(t)$ for given $f_{\mathrm{exc}}(t)$ is deterministic.

To solve the differential equation (2) and find the functions IFx29x E and $z_2(t)$, we use the model of a rapidly oscillating quadrupole field in the form of a static pseudopotential field [6]:

$$\varphi_p(z,t) = \frac{U(t) - U_p}{z_0^2 + \frac{r_0^2}{2}} z^2 - \frac{U_{\mathrm{exc}}}{2z_0} z = 0, \tag{7}$$

where $U_p = eV^2/(z_{01}^2 + r_{01}^2/2)\omega m$ — pseudopotential of the quadrupole HF field along the axis Z. Using (7), we transform (2) to the differential equation of the harmonic oscillator

$$\frac{d^2z}{dt^2} + \Omega_s^2(t)z = f_0, \tag{8}$$

where

$$\Omega_s(t) \cong \sqrt{2e[U_{\mathrm{exc}} - U(t)]/(z_0^2 + r_0^2/2)m}$$

— secular frequency of oscillations. Equation (8) is non-stationary due to time variation of natural frequency $\Omega_s(t) = \beta(t)\omega/2$, where β — stability parameter.

In the first stability zone for $q < 0.5$, the approximation [7] is valid:

$$\beta \approx \sqrt{a_z(t) - a_{0z}(q_z)}. \tag{9}$$

The approximation accuracy (9) increases as parameter $a_z(t)$ approaches the stability bpumdary $a_{0z} \approx q^2/2$. Then, taking into account (5) for the natural oscillation frequency, we obtain

$$\Omega_c(t) \simeq \Omega_0\sqrt{1 - t/t_{\mathrm{exc}}}, \tag{10}$$

where $\Omega_0 \approx q\omega/2\sqrt{2}$ — the initial value of the secular frequency.

Substituting (10) in (8), we obtain

$$\frac{d^2z}{dt^2} + \Omega_0^2\left(1 - \frac{t}{t_{\mathrm{exc}}}\right)z = f_0. \tag{11}$$

By introducing dimensionless time $\eta = (t/t_{\mathrm{exc}} - 1)\varphi_0^{2/3}$ and coordinates $W = z/z_m$, where $\varphi_0 = \Omega_0 t_{\mathrm{exc}}$, $z_m = e\pi U_{\mathrm{exc}}\sqrt[3]{t_{\mathrm{exc}}^2/\Omega_0^4}/2z_0 m$, equation (11) is transformed into Airy differential equation [8]:

$$\frac{d^2W}{d\eta^2} - Wy = \frac{1}{\pi}. \tag{12}$$

A pair of independent solutions to equation (12) is expressed in terms of the Airy functions $Ai(\eta)$ and $Bi(\eta)$:

$$W_1(\eta) = C_1[Ai(\eta) + Bi(\eta)] + C_2[Ai(\eta) - Bi(\eta)],$$

$$W_2(\eta) = \frac{2}{3}Bi(\eta) + \int_0^\eta [Ai(\xi)Bi(\eta) - Ai(\eta)Bi(\xi)]d\xi, \tag{13}$$

where C_1, C_2 is determined by the initial conditions.

After the approximate calculation of the integral in (13) and inverse change of variables, the solution of the differential equation (8) takes the form: in the stability region $0 < t < t_1$:

$$z_1(t) = \frac{1}{\sqrt[4]{1 - t/t_0}}\left[z_0 \cos\varphi(t) + \frac{v_{0z}}{\Omega_0} \sin\varphi(t)\right],$$

$$z_2(t) = \frac{z_m}{\pi\varphi_0^{2/3}}\left[\frac{1}{1 - t/t_0} = \frac{1}{\sqrt[4]{1 - t/t_0}} \cos\varphi(t)\right], \tag{14}$$

in the excitation region $t_1 < t \leq 2t_{\mathrm{exc}} - t_1$:

$$z_1(t) \simeq z_1(t_1) + z_1'(t_1)(t - t_1),$$

$$z_2(t) \simeq z_2(t_1)\left[c_1 + c_2\frac{t - t_1}{t_1} + \frac{3}{2}c_1c_2\left(\frac{t - t_1}{t_1}\right)^2\right], \tag{15}$$

where $\varphi(t) = \frac{2}{3}\varphi_0\left[1 - \sqrt{(1 - t/t_{\mathrm{exc}})^3}\right]$, $t_1 = (1 - 1/\varphi_0^{2/3})t_{\mathrm{exc}}$, $c_1 \approx 0.355$, $c_2 \approx 0.259$.

The use of pseudopotential model (7) of the rapidly oscillating quadrupole field in compiling the differential equation (8), which does not take into account the HF components of the oscillations of charged particles. determines the approximation of expressions (14), (15). The level of error is estimated by the value

$$z_{\mathrm{HF}}(t) = \frac{q_z}{2}[z_1(t) + z_2(t)]\sin\omega t. \tag{16}$$

The high-frequency component (16) in free and forced oscillations of ions can be the reason for the ambiguity with the period $2\pi/\omega$ of the mass peaks of the analyzer, which is minimized with the parameter q decreasing.

Results of the numerical solution of the differential equation (2) — motion of ions in three-dimensional quadrupole trap with parameters $z_{01} = r_{01} = 60$ mm, $V = 3000$ V, $f = 0.4$ MHz, $v_U = 3 \cdot 10^5$ V/s, $U_{\mathrm{exc}} = -5$ V — are shown in Figures 2 and 3. The results of numerical simulation and calculations by formulas (14), (15) coincide up to the HF component of oscillations $z_{\mathrm{HF}}(t)$.

As can be seen from Fig. 2, the superposition of the uniform excitation field on a rapidly oscillating quadrupole field makes it possible to implement the condition $z_2(t_{\mathrm{exc}}) \gg z_1(t_{\mathrm{exc}})$ of achieving the high resolution of the ion resonant output method. The ratio $z_2(t_{\mathrm{exc}}) \gg z_1(t_{\mathrm{exc}})$ can be maximized by optimizing the mode parameters. The trajectories of motion of ions with masses $M = 200$ and 100 Da are shown in Fig. 3. The excitation time in accordance with (6) is in inverse proportion to the mass of the ions.

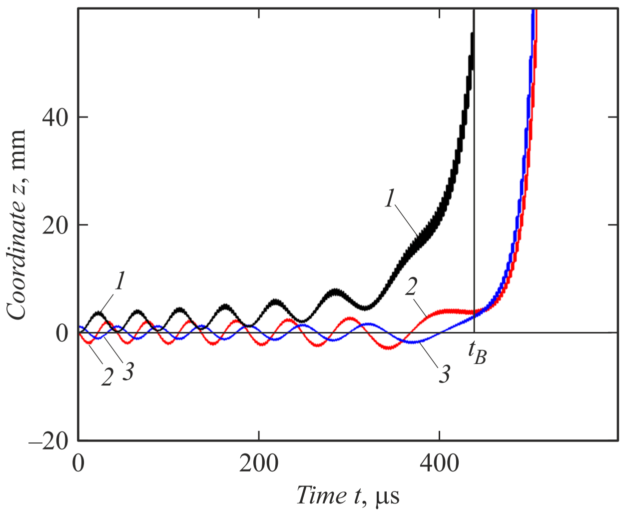

Figure 2. Trajectories of motion of ions with mass $M = 200\,\mathrm{Da}$ in three-dimensional ion trap: *1* — with an excitation uniform field; *2* — with initial energy IFx100x E eV; *3* — with initial coordinate $z_0 = 1\,\mathrm{mm}$.

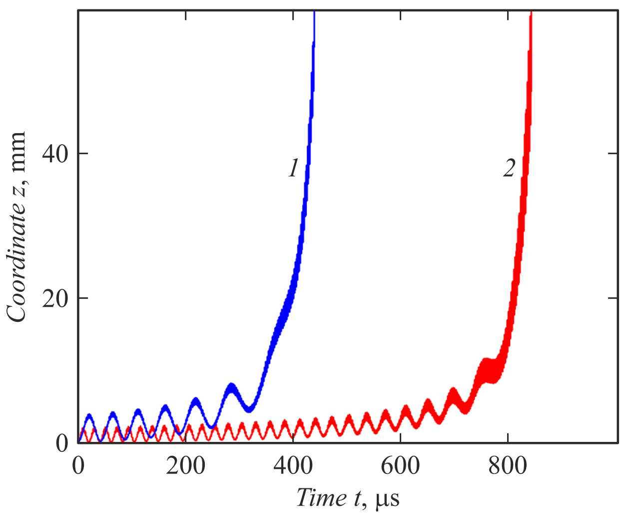

Figure 3. Trajectories of motion of ions with masses $M_1 = 200\,\mathrm{Da}$ (*1*) and $M_2 = 100\,\mathrm{Da}$ (*2*) and initial parameters $z_0 = 0$, $v_{0z} = 0$ in a three-dimensional quadrupole analyzer with resonant excitation of oscillations at the stability boundary $a_{0z}(q_z)$.

2. Ion trap with superposition of linear and uniform electric fields

The method of mass-selective separation of ions with oscillations excitation at the stability boundary $a_{0z}(q_z)$ can be implemented in IOS with two-dimensional or three-dimensional quadrupole rapidly oscillating fields upon superposition of uniform static excitation fields to them. To form fields with potential distribution (1), we use three-dimensional ion trap as IOS. The diagram of trap IOS is shown in Fig. 4. The feature of the ion trap in comparison with the known options of its use [1,5] is the power supply

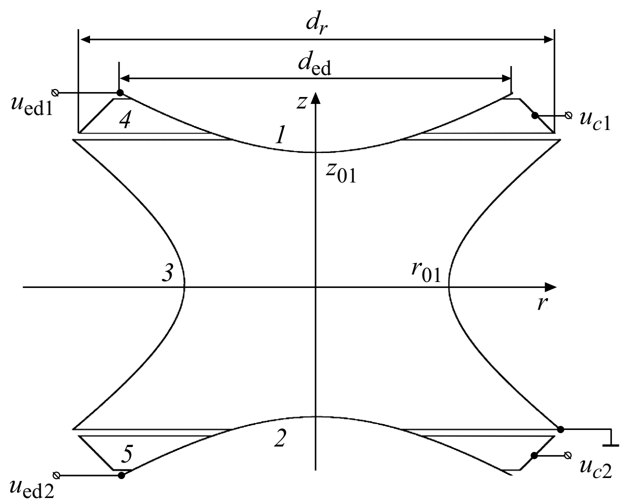

Figure 4. Diagram of IOS of three-dimensional ion trap with superposition of linear and uniform electric fields: *1, 2* — end; *3* — ring hyperbolic electrode; *4, 5* — correcting electrodes in the form of truncated cones.

system and the presence of correcting electrodes *4, 5*. The use of corrective electrodes allows, at limited sizes d_r and d_{ed}, to increase the accuracy of distributions of the quadratic along the axes Z and r and linear along the axis Z potentials.

To form the field with quadratic potential distribution along the coordinates z and IFx46x E, a voltage $u_r(t) = U(t) + V\cos\omega t$. The uniform static field is formed under the action of exciting potentials on the end electrodes $U_{\mathrm{exc\_ed1}} = -U_{\mathrm{ex\_ed2}} = U_{\mathrm{exc}}$. In this case, $u_{\mathrm{ed1}} = u_r(t) + U_{\mathrm{exc}}$, and $u_{\mathrm{ed2}} = u_r(t) - U_{\mathrm{exc}}$.

In three-dimensional ion trap made of hyperbolic electrodes the distribution of the excitation field potential along the axis Z very differs from linear, and the accuracy of the quadratic distribution depends on the sizes d_{ed} and d_r of end and ring electrodes. To improve the accuracy of the potential distributions of the homogeneous and quadrupole fields at limited parameters d_{ed} and d_r, correcting electrodes *4, 5* in the form of truncated cones with potentials $u_{c1} = au_r(t) + bU_{\mathrm{exc}}$ and $u_{c2} = au_r(t) - bU_{\mathrm{exc}}$ (Fig. 4) are installed. With fixed parameters $z_{01} = r_{01}$, $d_{\mathrm{ed}} = 1.48z_{01}$, $d_r = 1.82z_{01}$ the optimal values of the coefficients $a_{\mathrm{opt}} = 0.55$ and $b_{\mathrm{opt}} = 30.8$ are determined. At optimal parameters a and b the relative errors $\delta = \Delta\varphi/\varphi$ of the potential distributions (Fig. 5) of the quadrupole and homogeneous fields did not exceed the values $|\delta_{sq}| < 10^{-4}$ and $|\delta_l| < 2\cdot 10^{-3}$, which correspond to the achievable resolution of the analyzer $R = M/\Delta M > 10^3$.

Conclusion

To study the oscillations of charged particles in compositions of nonstationary quadrupole and homogeneous static fields, the pseudopotential model of the rapidly oscillating

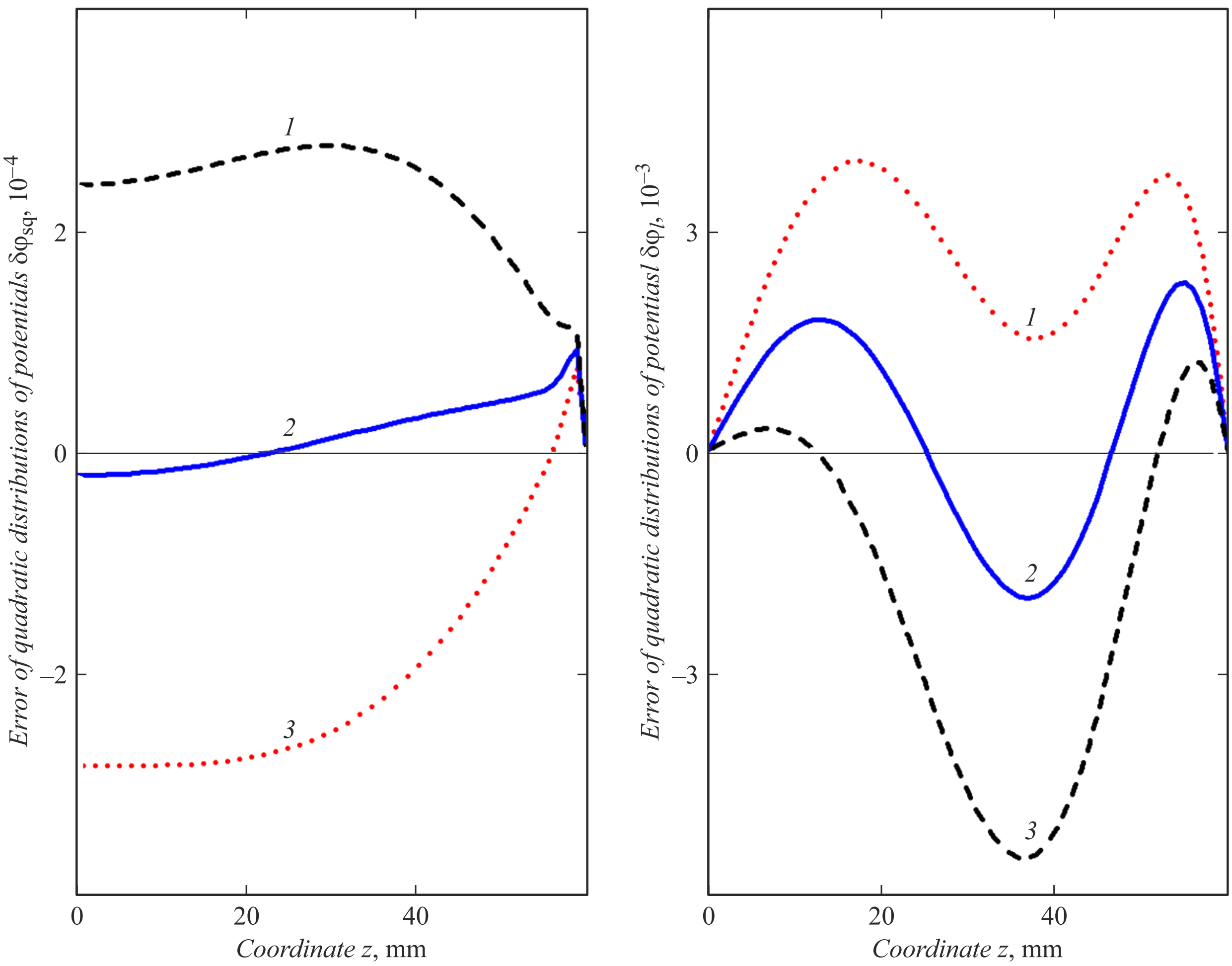

Figure 5. Dependences of relative errors: a — quadratic distribution of the potential *1, 2, 3* at $a = 0.50; 0.55; 0.60$ and b – linear potential distribution *1, 2, 3* at $b = 29.8; 30.8; 31.8$.

field is applicable. In the first stability region of the Mathieu diagram, at a constant q and linear change in the parameter $a(t)$ the motion of ions is described by Airy differential equations. The independent solutions $z_1(t)$ and $z_2(t)$ of the equations are oscillatory functions with slowly changing secular frequency and amplitude in the stable region and unlimited change in the vicinity of the boundary $a_0(q)$. Free component $z_1(t)$ — function with random parameters z_0 and v_{0z}, and deterministic excitation function $z_2(t)$ contains the monotonically increasing component in addition to the oscillating component and is a monopolar function. The properties of the solution $z(t) = z_1(t) + z_2(t)$ of the Airy equation form the basis of the method of ions separation by specific charge with resonant excitation of oscillations at the stability boundary IFx129x E under the influence of homogeneous static fields. The method efficiency is determined by the differences in the functions $z_1(t)$ and $z_2(t)$ in the stable and excitation regions. The analysis of the solutions of the Airy equation and the results of numerical simulation show that optimization of the mode parameters at the moment of oscillations excitation texc ensures the ratio $z_2(t_{\text{exc}}) \gg z_1(t_{\text{exc}})$ achievement, which provides a high resolution of the analyzer. The problem of the ambiguity of mass peaks due to the superimposition of HF component IFx98x on the secular oscillation is solved by minimizing the parameter q and choosing the optimal mass sweep method. The monopolarity of the excitation function $z_2(t) > 0$ simplifies IOS design and the ion registration system of the mass-analyzer.

To implement the method of resonant output of ions at the Mathieu stability boundary, IOSs with two- and three-dimensional quadratic potential distribution with elements of superposition of uniform excitation fields on them can be used. The simplest version of applying excitation potentials $\pm U_{\text{exc}}$ to opposite electrodes forms the field with large deviations from the uniform one. To increase the linearity of the potential distribution along the axis Z, the correcting electrodes in the form of truncated cones are installed along the boundaries of the hyperbolic electrodes of the three-dimensional trap. At optimal constant and high-frequency potentials on correcting electrodes, the errors of linear and quadratic potential distributions do not exceed the values $\delta\varphi_l < 2 \cdot 10^{-3}$ and $\delta\varphi_{sq} < 10^{-4}$, which corresponds to the achievable resolution $R > 10^3$.

Conflict of interest

The authors declare that they have no conflict of interest.

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Translated by I.Mazurov