The theoretical possibilities of increasing the resolution and sensitivity of a time-of-flight mass spectrometer with orthogonal ion injection are considered. The effects are achieved by using inhomogeneous electrostatic fields of special configurations both in the accelerating and focusing parts of the device – a cylindrical immersion objective and a transaxial mirror, respectively. It is shown that the use of an inhomogeneous cylindrical field of a special configuration as an ion accelerator opens up the possibility of a multiple reduction in the energy spread of ions in injected ion packets, associated with the so-called "turnaround time" and, therefore, a significant (two or more times) increase in the limiting resolution of the mass spectrometer. The use of a transaxial electrostatic mirror as a time-of-flight mass analyzer makes it possible to significantly increase the sensitivity of the mass-spectrometer due to the implementation of triple space-time-of-flight focusing of ion packets. Key features include reduced ion energy spread, increased maximum resolution, and improved sensitivity due to triple focusing in space and time of flight. This research lays the foundation for expanding the capabilities of time-of-flight mass spectrometry, providing a more efficient and powerful tool for a wide range of scientific and industrial applications. The effects are achieved by using inhomogeneous electrostatic fields of a special configuration in both the accelerating and focusing parts of the device – a cylindrical immersion lens and a transaxial mirror, respectively. Numerical calculations of the system – a four-electrode cylindrical immersion lens in combination with a three-electrode transaxial mirror – are presented, which confirm the conclusions of the theory

Keywords: time-of-flight mass spectrometer, cylindrical immersion lens, transaxial electronic mirror, pulse generator, rotation time

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IMPROVING THE RESOLUTION AND SENSITIVITY OF AN ORTHOGONAL TIME-OF-FLIGHT MASS SPECTROMETER WITH ORTHOGONAL ION INJECTION

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1. Introduction

Mass spectrometry stands as a cornerstone in analytical chemistry, biochemistry, and various scientific disciplines, offering unparalleled capabilities in the identification and characterization of molecules. In the contemporary landscape, the imperative for scientific research in this field is underscored by the pressing demand for advancements in analytical technologies. The need for precision in identifying complex molecular structures has never been more crucial, given the intricate nature of materials encountered in various scientific and industrial applications.

In the realm of analytical sciences, the constant evolution of challenges demands a parallel evolution in methodologies. The intricacies of modern scientific questions necessitate a nuanced approach that can provide both high resolution and sensitivity in mass spectrometry analyses. The existing gaps in achieving this delicate balance hinder the full potential of mass spectrometry in addressing complex analytical scenarios prevalent in fields such as proteomics, metabolomics, materials science, pharmaceutical research, environmental monitoring, and forensic analysis.

The relevance of scientific research in mass spectrometry is evident in its potential impact on practical applications. The outcomes of such research hold the promise of revolutionizing the way we approach molecular characterization in diverse industries. A breakthrough in achieving a harmonious balance between resolution and sensitivity would

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not only advance fundamental scientific understanding but would also translate into tangible benefits across a spectrum of fields, from developing new drugs to ensuring the environmental sustainability of industrial processes.

In this ever-changing scientific landscape, the pursuit of higher resolution and sensitivity in mass spectrometry is not just a theoretical endeavor; it is a practical necessity. The advancements in this field have far-reaching implications, promising to enhance our ability to unravel the complexities of molecular structures and pushing the boundaries of what is achievable in analytical sciences. As we navigate the challenges of the 21st century, the relevance of mass spectrometry research becomes increasingly apparent, offering a key to unlocking new dimensions in scientific exploration and industrial innovation.

Therefore, studies that are devoted to refining the capabilities of mass spectrometry instruments, particularly in achieving a balance between resolution and sensitivity, are of utmost scientific relevance. The pursuit of higher resolution and sensitivity in mass spectrometry is not merely an academic exercise; it is a practical necessity with far-reaching implications. These studies represent a crucial step toward addressing the analytical challenges of our time, offering a key to unlocking new dimensions in scientific exploration and industrial innovation.

2. Literature review and problem statement

The literature on orthogonal time-of-flight mass spectrometers (TOF) with high resolution and sensitivity reflects a rich history of technological advances and innovative techniques. Researchers have continuously studied various aspects of ion optics, electrostatic fields, and reflector designs to expand the capabilities of TOF mass spectrometry.

The paper [1] mass spectrometer with high resolution and sensitivity presents promising results, demonstrating a significant reduction in the energy spread of ion packets due to the use of inhomogeneous electrostatic fields, which showed that the strategic use of inhomogeneous electrostatic fields at the stages of ion acceleration and mass analysis effectively solves the problems associated with "circulation time". But there are unresolved issues related to relatively low sensitivity for two main reasons. One of them is that both the orthogonal ion accelerator (pulser), which forms an ion beam, and the electrostatic mirror, which acts as a time-of-flight mass analyzer, use homogeneous electrostatic fields formed between flat finely structured grids. Homogeneous fields cannot provide spatial focusing of ions, which leads to their loss in the ion package, and the presence of fine-grained grids significantly aggravates the situation.

The paper [1] focuses on introducing an orthogonal source of electronic shock, showcasing its potential for achieving high mass resolution. The research contributes significantly to the optimization of ion sources, a critical aspect in enhancing the capabilities of TOF mass spectrometers. However, the work predominantly addresses ion source optimization, leaving unexplored aspects related to ion packet focusing and the spatial distribution of ions. The absence of exploration in these areas might be attributed to the inherent complexity of incorporating inhomogeneous electrostatic fields in multiple stages of ion acceleration and mass analysis. In [2], researchers delve into reflectors with orthogonal ion acceleration based on flat mirrors without a grid. This work expands our understanding of ion trajectory control and acceleration mechanisms, offering insights into the design features of orthogonal acceleration systems. However, the research primarily addresses reflector design, overlooking the challenges associated with ion packet losses due to the absence of spatial focusing. The omission might be rooted in the methodological difficulty of implementing non-homogeneous electrostatic fields in these components, especially considering practical limitations in fabrication and stability.

In the work [3], the authors present a flat mass spectrometer design with several reflectors, emphasizing practical and efficient layouts. This contribution primarily addresses the improvement of resolution through the introduction of a reflector and the utilization of orthogonal ion injection (o-TOF) methods. However, a notable gap exists in the exploration of ion packet losses and sensitivity issues associated with different acceleration methods. The absence of investigation into the impact of diverse acceleration approaches on sensitivity could be attributed to methodological challenges. The intricate dynamics of non-uniform electrostatic fields and the associated ion packet control might pose significant hurdles, limiting a comprehensive analysis within the scope of this research.

In the manuscript [4] introduces monopole as an orthogonal accelerator in TOF analyzers, showcasing alternative avenues for ion acceleration. While the research provides valuable insights into diverse acceleration methods, it does not delve deeply into the challenges associated with implementing these alternatives. Objective reasons, such as the complexity of incorporating non-homogeneous fields in practical designs, might contribute to this limitation. The difficulties in achieving both high resolution and maintaining ion packet integrity with diverse acceleration methods pose a methodological challenge that warrants further attention in future research. Monopole has also been investigated as an orthogonal accelerator in TOF analyzers, presenting alternative approaches to ion acceleration. Such a variety of acceleration methods opens up opportunities for increasing sensitivity and resolution in mass spectrometry [5]. The conditions for preserving the parallelism of ion beams in the vertical plane after passing through the system can be determined if two linearly independent particular solutions of equation are known. In this case, it is necessary to take into account that equation has a singular point defined by the equality [6]. For a cathode lens, this assumption is not valid since the charged particles leave the cathode at an angle of 0 to 90 degrees, and all the particles emitted by the cathode further participate in the formation of the crossover or the image of the cathode surface. In addition, in single and immersion lenses, the condition of the smallness of the spread of charged particle energies with respect to the values of the axial potential is satisfied throughout, while in the cathode lens, this condition is not satisfied in the cathode region. A more detailed explanation of these features of cathode lenses is given below. A number of works are devoted to the development of the theory of cathode lenses, taking into account the noted features in their initial conditions, for example, [7]. Also, in the equations of the trajectories of charged particles, decomposition into a number of small parameters for the analysis of the aberration characteristics of cathode lenses is carried out by analogy with the theory of electronic mirrors, which was developed a little earlier. Due to the fact that small parameters are associated with

initial conditions, it was necessary to clarify the differences between the conditions of motion of charged particles in the area of their extraction in cathode lenses and in the area of reflection of charged particles in electronic mirrors.

Despite significant progress made in the development of orthogonal time-of-flight mass spectrometers (TOF) with high resolution and sensitivity, a number of problems and areas of improvement remain. One of the main problems is the need to further optimize the designs of ion optics and reflectors in order to achieve even higher mass resolution. Although recent studies have shown notable improvements, there remains untapped potential for improving these technologies.

The problem of chromatic temporal aberrations is a significant obstacle to achieving optimal sensitivity in TOF mass spectrometry. Moreover, the translation of technological advances into practical applications in various fields, as recent research in the field of criminology and geospatial analysis has shown, calls for standardized methodologies and protocols. Ensuring the efficient use of these high resolution and sensitivity mass spectrometers in various fields is crucial to maximize their effectiveness.

3. The aim and objectives of the study

The aim of this work is to identifying the possibility of increasing the resolution and sensitivity of a time-of-flight mass spectrometer with orthogonal ion injection by using a pulse generator with a cylindrical immersion lens and a transaxial mirror as a time-of-flight mass analyzer.

To achieve this aim, the following objectives are accomplished:

– calculate three-electrode transaxial mirrors with mathematical modeling and calculations for a three-electrode transaxial mirror using plates as electrodes;

– describe the trajectories of ion packets in a field-free space using the appropriate equation of motion to describe the trajectory of an ion packet in the absence of an electric field.

4. Materials and methods

The primary focus of the research is an orthogonal time-of-flight mass spectrometer (TOF-MS) and the enhancement of its resolution and sensitivity. Specifically, the research investigates the application of orthogonal ion injection to achieve improvements in these key performance metrics. Orthogonal ion injection refers to introducing ions into the mass spectrometer in a direction perpendicular to the primary ion path, which can have implications for the instrument's analytical capabilities.

The main hypothesis of the research is likely centered around the idea that implementing orthogonal ion injection in an orthogonal time-of-flight mass spectrometer can lead to increased resolution and sensitivity. The researchers may propose that this modification to the ionization and injection process will result in improved mass spectral data quality, allowing for better identification and quantification of analyses.

Certain assumptions may be made in the research to simplify the scope of the research or to facilitate the experimental setup. Possible assumptions include the assumption of idealized conditions for ionization and injection processes, the assumption of specific environmental factors that may affect device performance, or the assumption of a specific sample matrix that may affect ionization efficiency.

To make the research feasible and manageable, certain simplifications have been adopted. For example, the research focuses on a certain range of analytes and a certain set of experimental conditions. The mass spectrometer model has also been simplified to emphasize the effect of orthogonal ion injection, ignoring certain complexities that are present in real devices.

This study uses the method of numerical calculations of two ion-optical systems:

1) a four-electrode immersion lens with an inhomogeneous electrostatic field, the inclusion of which in the acceleration region of the ion source allows:

– firstly, to create a primary time focus with a multi-fold reduced width of the ion packet at the boundary of the ion source field and, therefore, lays the foundation for increasing the maximum resolution by two or more times of the time-of-flight mass spectrometer compared to existing devices of a similar type under equal conditions (dimensions);

– secondly, to form a parallel ion beam in two mutually perpendicular directions, transverse to the direction of ion movement, which is necessary to reduce ion losses in the field-free drift space, i.e. to increase the sensitivity of the device as a whole;

2) a three-electrode transaxial mirror, which provides spatial focusing of a parallel ion beam in two mutually perpendicular directions to a point simultaneously with time-of-flight focusing on ion energy, thereby providing an increase in the resolution and sensitivity of the device.

This article presents formulas for calculating the distribution of potentials, spatial and time-of-flight characteristics of the systems under consideration and describes in detail (maybe in too much detail) the methodology for calculating electrostatic systems with a feature such as mirror and emission systems. The calculation results are presented in the form of graphs and tables.

Fig. 1 shows a diagram of one of the possible variants of an orthogonal accelerator with an inhomogeneous electrostatic field of two-dimensional symmetry. It differs from the schemes of conventional orthogonal accelerators with a uniform field in that the ion acceleration region (from the grounded grid to electrode 4 inclusive) contains gridless electrodes 2, 3 and 4, made in the form of a pair of parallel plates separated by straight gaps, and located at the same distance from the median plane of the system. The combination of these gridless electrodes with a preceding flat-shaped grid electrode with a pulling potential U_{pull} forms an inhomogeneous electrostatic field of two-dimensional symmetry – a four-electrode cylindrical immersion objective.

Let's introduce the Cartesian coordinate system x, y, z, aligning its z axis with the optical axis of the immersion objective, and the planes xz and yz with its middle plane and the plane perpendicular to it, respectively. Then the equations of paraxial trajectories of ions in a cylindrical immersion objective can be written as:

$$\sqrt{\Phi}x' = \text{const}, \tag{1}$$

$$2\Phi y'' + \Phi' y' + \Phi'' y = 0, \tag{2}$$

which completely coincides with the equations of trajectories in the paraxial approximation for two-dimensional electron lenses [5].

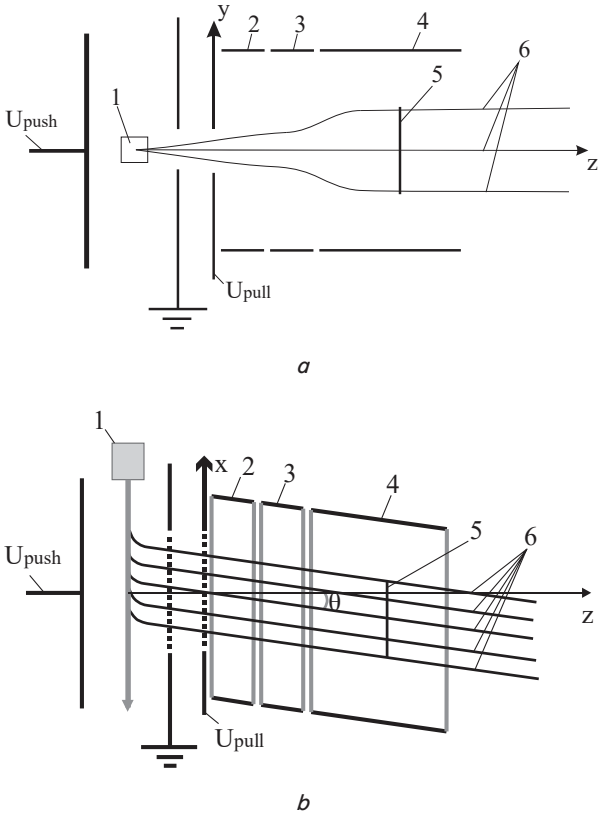


Fig. 1. Scheme of an orthogonal ion accelerator: *a* — front view; *b* — side view; 1 — ion source; 2–4 — immersion lens electrodes; 5 — the position of the primary time focus; 6 are ion trajectories; θ — the angle between the direction of the ion beam and the axis *z*

Here and below, $\Phi=\Phi(z)$ is an axial distribution of the electrostatic potential, and the primes denote differentiation with respect to the variable *z*.

It follows from equation (1) that in the middle plane *xz* the initially parallel ion beam retains its parallelism after passing through the system.

The conditions for preserving the parallelism of ion beams in the vertical plane *yz* after passing through the system can be determined if two linearly independent particular solutions of equation (2) are known. In this case, it is necessary to take into account that equation (2) has a singular point $z=z_u$ defined by the equality $\Phi(z_u)=0$. In emission systems, particles are emitted at this point. Therefore, in accordance with [6], these particular solutions must be chosen as follows: one solution $p=p(z)$ is an analytic function, and the other solution $g=g(z)$ can be represented as:

$$g=\sqrt{\Phi q}, \tag{3}$$

where $q=q(z)$ is an analytic function satisfying the equation:

$$2\Phi q''+3\Phi' q'+2\Phi'' q=0, \tag{4}$$

following from (2) and (3).

Functions *p* and *q* must satisfy the following initial conditions given at the singular point:

$$p_u=q_u=1, \tag{5}$$

$$p'_u=-\frac{\Phi''_u}{\Phi''_u}, \tag{6}$$

$$q'_u=\frac{2}{3}p'_u. \tag{7}$$

Then the inclination of the paraxial trajectories to the optical axis can be represented in terms of these particular solutions of equation (2) in the form:

$$y'=y_u p'+\frac{2\sqrt{\Phi}}{\Phi'_u}\overline{y}'_u g', \tag{8}$$

where y_u and $\overline{y}'_u$ is the distance of the ion from the axis *z* and its inclination to this axis at the point of emission $z=z_u$. Here and below, the index "*u*" marks the values of the quantities at the point $z=z_u$.

As can be seen from (8), the condition of parallelism $(y'=0)$ in the image space originating from the point source $(y_u=0)$ of the ion beam (the collimator mode of operation of the immersion objective) is determined by the equality:

$$g'=0. \tag{9}$$

According to [6], the position of the primary time focus $z=z_T$ (the plane of time-of-flight energy focusing of ions) created by the immersion objective is determined by the formula:

$$z_T=z_u+\frac{2\Phi_0}{\Phi'_u}\left\{1+\frac{1}{2}\int_{z_u}^{z}\left[\sqrt{\frac{\Phi_0}{\Phi}}\left(\frac{\Phi'-\Phi'_u}{\Phi}\right)+\frac{\Phi'_u}{\Phi_0}\right]\mathrm{d}z\right\}. \tag{10}$$

The limiting resolution of the time-of-flight mass reflectron can be calculated by the formula [7]:

$$R=\frac{L}{\Delta z_\upsilon}, \tag{11}$$

where *L* is the effective drift distance of the mirror; Δz_υ is the width of the ion packet at the primary time focus, determined only by the turnaround time of the ion:

$$\Delta t_\upsilon=2k\sqrt{\varepsilon}\,/\,E_{push}, \tag{12}$$

where ε is the initial energy of the ion of charge *q* and mass *m*, $k=\sqrt{2q/m}$, and E_{puch} is the strength of the uniform electrostatic field created in the area of accumulation of ions of the orthogonal accelerator.

Taking into account (12), the width of the ion packet at the primary time focus of the ion accelerator with a uniform field can be calculated by the formula:

$$\Delta z_\upsilon=u_{acc}\Delta t_\upsilon, \tag{13}$$

where Δt_υ this is the time of flight of the ion packet in the primary time focus, and u_{acc} is calculated as follows:

$$u_{acc}=k\sqrt{U_{acc}}, \tag{14}$$

is the ion velocity at the boundary of the accelerator field, where U_{acc} is the accelerating potential of the uniform field.

In a cylindrical immersion objective, the turnaround time of the ion retains its value if the condition [8]:

$$E_{push} = \Phi'_u, \quad (15)$$

is fulfilled, where Φ'_u is the strength of the non-uniform electrostatic field of the immersion objective at the boundary of the homogeneous electrostatic field with the strength E_{puch}. Then the width of the ion packet in the primary time focus of the ion accelerator with a non-uniform field can be calculated by the formula:

$$\Delta\bar{z}_\upsilon = \bar{\upsilon}_{acc}\Delta t_\upsilon, \quad (16)$$

where:

$$\bar{\upsilon}_{acc} = k\sqrt{\bar{U}_{acc}}, \quad (17)$$

is the ion velocity at the boundary of the field of the immersion objective, and $\bar{U}_{acc}$ is the accelerating potential of the inhomogeneous field.

Taking into account (13)–(17) let's obtain:

$$\frac{\Delta z_\upsilon}{\Delta\bar{z}_\upsilon} = \sqrt{\frac{U_{acc}}{\bar{U}_{acc}}}. \quad (18)$$

This means that in order to reduce the width of the ion packet in the primary time focus of the ion accelerator, it is necessary to decrease $\bar{U}_{acc}$ in comparison with U_{acc}. However, this possibility requires the fulfillment of condition (15), which imposes certain requirements on the design of the immersion objective.

Taking into account that:

$$E_{push} = U_{push} / d_{push}, \quad (19)$$

$$\Phi'_u = \alpha\bar{U}_{acc} / d_{acc}, \quad (20)$$

where U_{push} is the potential of the pushing electrode, d_{push} is the distance from the pushing electrode to the ground grid, d_{acc} is the distance between the plates of gridless electrodes of the immersion objective, α is a dimensionless coefficient, let's obtain:

$$\bar{U}_{acc} = \frac{d_{acc}U_{push}}{\alpha d_{push}}, \quad (21)$$

which account for (21), relation (19) takes the form:

$$\frac{\Delta z_\upsilon}{\Delta\bar{z}_\upsilon} = \sqrt{\frac{\alpha d_{push}U_{acc}}{d_{acc}U_{push}}}. \quad (22)$$

According to [9], U_{push}=1000 V, $U_{acc}\approx 5U_{push}$, d_{push}=4 mm. The results of calculation of the dependence of the ratio of the widths $\Delta z_\upsilon / \Delta\bar{z}_\upsilon$ in the ion packet on d_{acc} in the primary time focus, taking into account these data and α=2.5, are presented in Table 1.

Table 1

The results of calculation of the ratio $\Delta z_\upsilon / \Delta\bar{z}_\upsilon$

α	U_{push}, V	d_{push}, mm	d_{acc}, mm	$\bar{U}_{acc}$, V	$\Delta z_\upsilon / \Delta\bar{z}_\upsilon$
2.5	1000	4	10	1000	2.24
2.5	1000	4	15	1500	1.83
2.5	1000	4	20	2000	1.58

As can be seen from these data, using an orthogonal ion accelerator with an immersion lens, it is possible to reduce the width of the ion packet at the primary focus and hence to increase the resolution of the time-of-flight mass spectrometer with orthogonal injection of ions by more than 2 times.

5. The results of the study of the transaxial electrostatic mirror

5. 1. Calculation of a three-electrode transaxial mirror

One of the possible configurations of a three-electrode transaxial mirror is shown in Fig. 2, where the electrodes consist of pairs of parallel plates separated by annular gaps with a common center of curvature.

The electron-optical characteristics of transaxial mirrors can be computed based on the theory of an electrostatic lens-mirror system with two planes of symmetry [10]. Let's introduce a rectangular coordinate system x_1, x_2, z, where the z-axis coincides with the optical axis of the mirror, and the x_1z and x_2z planes align with the symmetry planes of the field. The equations for paraxial trajectories in such a field with two planes of symmetry can be expressed as [10]:

$$\Phi x_i'' + \frac{1}{2}\Phi' x_i' + \left[\frac{1}{4}\Phi'' + (-1)^i Q_\varphi\right] x_i = 0. \quad (23)$$

where V_1–V_3 are potentials on the electrodes, z_1, z_2 are coordinates of the gaps, d is the distance between electrode plates, l is the length of the middle electrode, $\Phi=\Phi(z)$ is the potential distribution on the axis z, $Q_\phi=Q_\phi(z)$ is the quadrupole component of the electrostatic field, and the primes denote differentiation with respect to z.

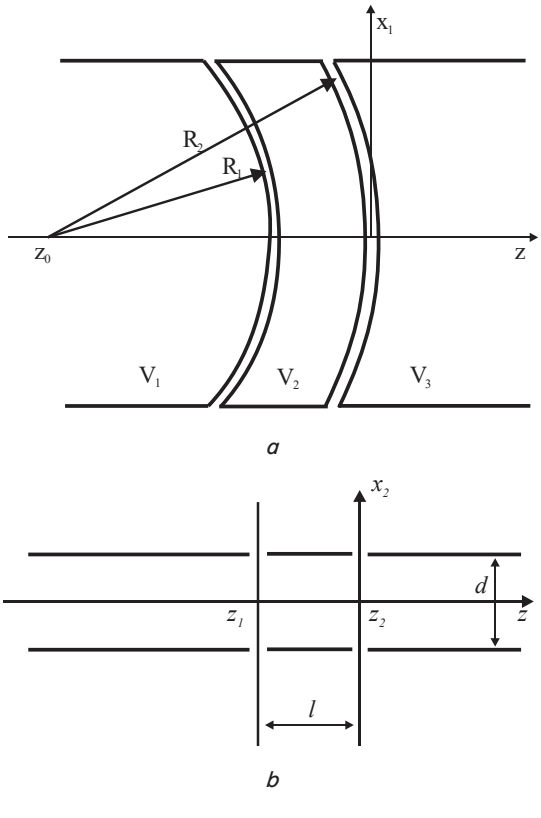


Fig. 2. Three-electrode transaxial mirror: *a* — plane x1z; *b* — plane x2z

It should be noted that when calculating electron mirrors, as in the case of emission systems, it is necessary to take into account the presence of a singular point in equations (23), which is determined by the equalities $\Phi(z_u)=0$, $\Phi'(z_u)\neq 0$. In accordance with the theory of electron mirrors [6], out of two linearly independent partial solutions of equations (23), one of which is an analytic function $p_i=p_i(z)$, and the other $g_i=g_i(z)$ can be represented as:

$$g_j=\sqrt{\Phi q_j}, \tag{24}$$

where $q_j=q_j(z)$ is an analytic function satisfying the equation:

$$\Phi q_j''+\frac{3}{2}\Phi' q_j'+\left[\frac{3}{4}\Phi''+(-1)^j Q_\varphi\right]q_j=0, \tag{25}$$

following from (23) and (24).

In this case, the initial conditions for the functions $p_j=p_j(z)$ and $q_j=q_j(z)$ are given at a singular point $z=z_u$:

$$p_{ju}=q_{ju}=1,\ p'_{ju}=q'_{ju}=-\frac{1}{2}\frac{\Phi''_u}{\Phi'_u}, \tag{26}$$

where and below, the index "u" denotes the values of the quantities for $\Phi(z_u)=0$.

These particular solutions determine the properties of spatial focusing and the cardinal elements of the mirror. To determine the cardinal elements, let's use the trajectories characteristic of a transaxial mirror. In the corresponding plane of symmetry x_jz (j=1, 2) the solution $p_j=p_j(z)$ describes trajectories whose forward and backward branches coincide, i.e. pass through the center of curvature of the mirror $z=z_{jC}$, and the solution $g_j=g_j(z)$ describes trajectories whose forward and backward branches are symmetrical with respect to the optical axis of the mirror, i.e. pass through the top of the mirror $z=z_{jV}$ [6]. When the object and its image are in a field-free space, the functions $p_j=p_j(z)$ and $g_j=g_j(z)$ are linear functions of z:

$$p_j=\left(z-z_{jC}\right)p'_j, \tag{27}$$

$$g_j=\left(z-z_{jV}\right)g'_j. \tag{28}$$

Taking these equalities into account, the cardinal elements of the transaxial mirror can be written as follows:

$$z_{jC}=z-p_j/p'_j, \tag{29}$$

$$z_{jV}=z-g_j/g'_j, \tag{30}$$

$$z_{jF}=\frac{1}{2}\left(z_{jV}+z_{jC}\right), \tag{31}$$

$$f_j=\frac{1}{2}\left(z_{jV}-z_{jC}\right), \tag{32}$$

where z_{jF} is the position of the focus of the mirror, and f_j is its focal length.

In the anamorphic mirror mode, the positions of the mirror foci for both planes of symmetry x_jz coincide:

$$z_{1F}=z_{2F}. \tag{33}$$

The properties of the time-of-flight focusing of a mirror are determined by the positions of the nodal planes of the time-of-flight focusing $z=z_T^{(k)}\left(k=1,2,3\right)$ and effective drift distance L, which are functions of only the axial distribution of the mirror [11]. The condition for time-of-flight focusing of ions in energy is determined by the equality [11]:

$$z+z_0=2z_T^{(k)}, \tag{34}$$

where k=1,2,3, which means that time-of-flight focusing in energy of the k-th order is achieved in the mirror if the object plane $z=z_0$ and the plane of the time-of-flight image z=const are located symmetrically with respect to the plane $z=z_T^{(k)}$. If the condition:

$$z_T^{(1)}=z_T^{(2)}=z_T^{(3)}, \tag{35}$$

is satisfied, in the mirror, time-of-flight focusing of ions in energy up to the third order inclusive is achieved.

Time-of-flight focusing in energy up to the third order, inclusive, simultaneously with stigmatic spatial focusing of ions into the detector window aligned with the mirror focus, is achieved when the condition:

$$z_T=z_T^{(1)}=z_T^{(2)}=z_T^{(3)}=z_{1F}=z_{2F}, \tag{36}$$

is satisfied. In this case, the effective drift distance can be calculated by the formula:

$$L=z_u^*-z_T, \tag{37}$$

where:

$$z_u^*=z_u+\frac{1}{2}\int_{z_u}^{z}\sqrt{\frac{\Phi_0}{\Phi}}\frac{\left(z_u-z\right)}{\Phi}\Phi' \mathrm{d}z, \tag{38}$$

is the position of the effective reflection plane of the mirror.

The study of an orthogonal time-of-flight mass spectrometer, emphasizing high resolution and sensitivity, has yielded significant results. The study successfully demonstrated a noticeable increase in resolution and sensitivity, which is explained by the synergistic effect of two key factors: the calculation of three-electrode transaxial mirrors consisting of parallel plates, and numerical analysis of a four-electrode cylindrical immersion lens and a three-electrode transaxial mirror. These elements significantly affect the spatial and temporal focusing of the mass spectrometric system, laying the foundation for improved performance.

5. 2. Description of the course of the ion packet trajectories

For the considered mirror, when the gaps between the electrodes are infinitely small, the axial potential distribution can be represented as [12]:

$$\Phi\left(z\right)=\frac{1}{2}\left(V_1+V_3\right)+\sum_{i=1}^{2}\left(V_{i+1}-V_i\right)U_i, \tag{39}$$

where:

$$U_i=\frac{1}{\pi}\mathrm{arctg}\exp\mathrm{sh}\left[\frac{\pi\left(z-z_i\right)}{d}-\frac{0.2923d}{z-z_0}\right], \tag{40}$$

where U_i is the potential on the i-th electrode d is the distance between the electrode plates, z_i is the coordinate of the i-th gap, and z_0 is the coordinate of the curvature center of the interelectrode gaps. In this case:

$$Q_{\varphi} = \frac{1}{4}\Phi'' + \frac{1}{2(z-z_0)}\Phi'. \quad (41)$$

When passing to the Cartesian coordinate system ($x_1 \to x$, $x_2 \to y$), the equations of paraxial trajectories (23) take the same form as those for transaxial electron lenses [13]:

$$2\Phi x'' + \Phi' x' - \frac{1}{(z-z_0)}\Phi' x = 0, \quad (42)$$

$$2\Phi y'' + \Phi' y' + \left[\frac{1}{(z-z_0)}\Phi'\right] y = 0. \quad (43)$$

The calculation results for a three-electrode transaxial mirror are presented in Table 2 and Fig. 3. Table 2 shows the relationship between the geometric and electrical parameters of the mirror, which provide conditions for time-of-flight focusing of ions in energy up to the third order, inclusive, simultaneously with spatial focusing in the focal plane of the mirror $z=z_F$. The origin of coordinates is aligned with the gap between the second and third electrodes.

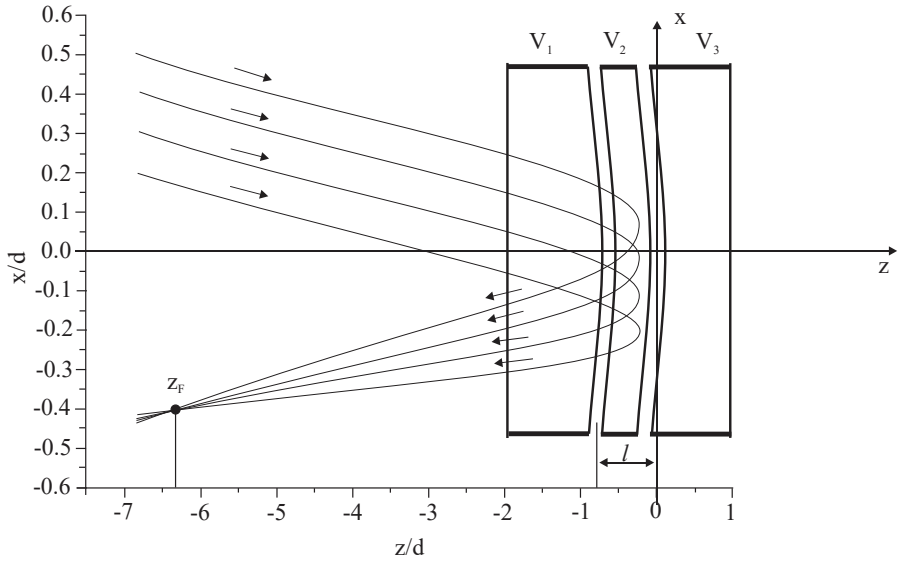
Fig. 3 shows the course of trajectories in a three-electrode transaxial mirror.

Table 2

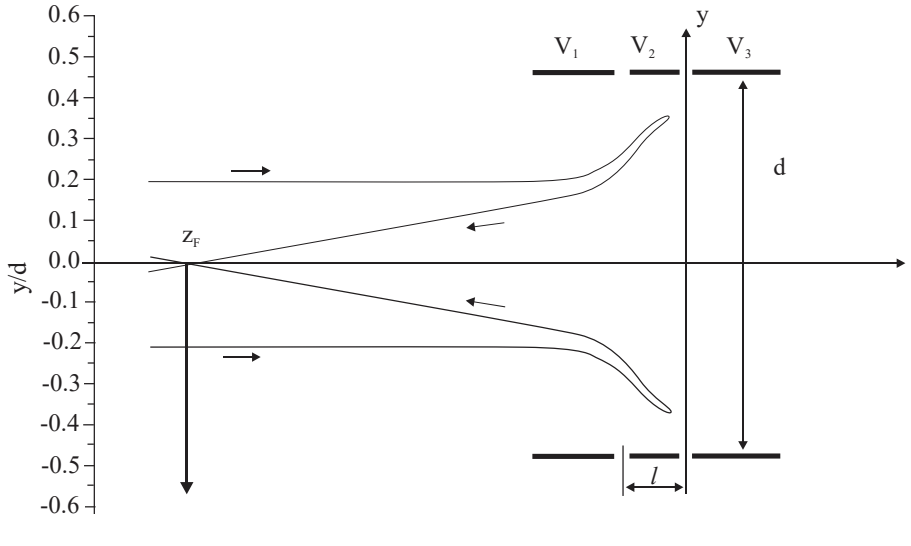
Parameters of a three-electrode transaxial mirror

V_2/V_1	$-V_3/V_1$	l/d	R_1/d	$-z_F/d$	L/d
0.0380	0.416	0.822	13.3	6.36	7.51

Fig. 4 shows one of the possible variants of the proposed time-of-flight mass spectrometer with orthogonal input of ions in two projections (*a* – in the *XZ* plane, *b* – in the *YZ* plane). In Fig. 4, 1 is an ion source; 2–4 are pulse generator electrodes without a grid; 5 is the main time focus; 6–8 are electrodes without a transaxial mirror grid; 9 is an ion detector.



a



b

Fig. 3. The course of trajectories in a three-electrode transaxial mirror: *a* – in the *XZ* plane; *b* – in the *YZ* plane

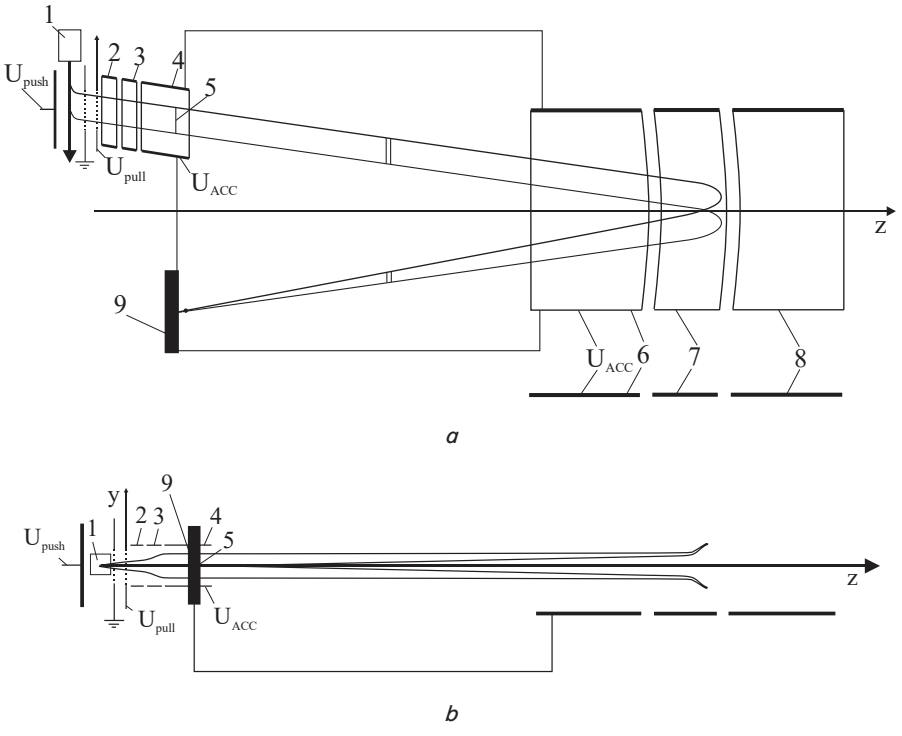


Fig. 4. Time-of-flight mass spectrometer with orthogonal ion injection in two projections: *a* — in the *XZ* plane; *b* — in the cross-sectional plane

This time-of-flight mass spectrometer operates as follows. A continuous ion beam formed in source 1 enters the accumulation region of the pulser, where, when a pulsed potential U_{push} is applied, an electrostatic field is created, which cuts out the ion packet from the continuous beam and accelerates it orthogonally to the original direction; the ion packet falling into the region of ion acceleration (pulser) with a non-uniform electrostatic field accelerates to energy qU_{acc}, flies in a field-free span space, is reflected by a mirror with an inhomogeneous field, flies in a field-free space and hits the detector [14–27].

6. Discussion of the results of the sensitivity study of the time-of-flight mass spectrometer

The results obtained from the study of the proposed modifications to the time-of-flight mass spectrometer with orthogonal ion injection provide valuable insights into the potential enhancements in resolution and sensitivity.

The properties of time-of-flight focusing in the transaxial mirror play a pivotal role in determining the efficiency of the mass spectrometer. Equation (27) establishes a critical condition for achieving time-of-flight focusing in energy, emphasizing the importance of symmetric positioning of the object and image planes. The fulfillment of conditions (28), (29) further enables not only time-of-flight focusing but also stigmatic spatial focusing of ions, providing a holistic enhancement to the instrument's performance.

The calculation results for a three-electrode transaxial mirror, as presented in Table 2 and Fig. 3, highlight the intricate interplay between geometric and electrical parameters. These parameters, including V_2/V_1, $-V_3/V_1$, l/d, R_1/d, $-zF/d$, and L/d, collectively contribute to achieving conditions for optimal time-of-flight focusing. Understanding these relationships is crucial for the design and optimization of the transaxial mirror to meet specific performance criteria.

The description of ion packet trajectories in the proposed time-of-flight mass spectrometer offers valuable insights into the instrument's operation. The unique design, incorporating a pulse generator with a cylindrical immersion lens and a transaxial mirror, allows for efficient ion acceleration, time-of-flight focusing, and spatial focusing. Fig. 4 provides a visual representation of the spectrometer's configuration, showcasing its key components, including the ion source, pulse generator electrodes, transaxial mirror, and ion detector.

The spectrometer operates by introducing a continuous ion beam into the pulser, where pulsed potentials create an electrostatic field for orthogonal ion acceleration. The subsequent reflection by the transaxial mirror and the ion's trajectory in a field-free space contribute to the overall performance leading to enhanced resolution and sensitivity.

Orthogonal time-of-flight mass spectrometer (o-tof ms) technology with high resolution and sensitivity has several distinctive features compared to ion cyclotron resonance mass spectrometry with Fourier transform orthogonal design provides improved resolution and sensitivity. The ions are accelerated in one direction and then measured in the orthogonal direction, providing advanced analytical capabilities. The technology is also based on measuring the time required for ions to travel a certain distance. This time-of-flight measurement allows for fast and accurate mass analysis, providing high resolution.

This technology is known for its high mass resolution, which allows it to distinguish ions with very close masses. This is crucial for the identification and characterization of complex mixtures of molecules. The system provides spatial and temporal focusing at the same time, contributing to the efficient and accurate analysis of ion trajectories. This simultaneous focusing improves the overall performance of the mass

spectrometer. The combination of a cylindrical immersion lens and a transaxial mirror with special configurations expands the unique capabilities of the technology. Numerical calculations and theoretical foundations support innovative design. The study demonstrates a significant decrease in the energy distribution of ion packets, which leads to an increase in resolution. This reduction is achieved through the use of inhomogeneous electrostatic fields.

It highlights the implications for mass spectrometry applications and suggests future exploration opportunities for further advancements. The overall there is the significant progress in enhancing time-of-flight mass spectrometry capabilities for diverse scientific and industrial uses.

The study successfully demonstrated a substantial increase in resolution and sensitivity by combining two key factors. Firstly, a reduction in the width of the ion packet in the primary time focus was achieved simultaneously with the formation of an ion beam parallel in two mutually perpendicular directions, facilitated by a cylindrical immersion objective. Secondly, high-quality time-of-flight focusing of ions in energy, coupled with stigmatic spatial focusing of an ion beam, was achieved by implementing the anamorphic mode in the transaxial mirror.

Numerical calculations were employed to determine the characteristics of a four-electrode cylindrical immersion objective and a three-electrode transaxial mirror, crucial factors influencing the spatial and time-of-flight focusing of the system. The theoretical substantiation of these factors has opened avenues for enhancing the performance of time-of-flight mass spectrometers.

Significant progress has been made in the study of an orthogonal time-of-flight mass spectrometer with high resolution and sensitivity. The study successfully demonstrated a noticeable increase in resolution and sensitivity due to the use of two key factors.

Mainly due to the narrowing of the width of the ion packet in the main time focus and the simultaneous creation of a parallel ion beam in two mutually perpendicular directions through a cylindrical immersion lens, a significant decrease in the width of the ion packet was achieved during the study.

As well as the implementation of the anamorphic mode in the transaxial mirror contributed to the qualitative focusing of ions over the time of flight in combination with point spatial focusing of the ion beam. Numerical calculations played an important role in determining the characteristics of a four-electrode cylindrical immersion lens and a three-electrode transaxial mirror, which are key elements influencing the spatial and temporal focusing of the system.

The proposed time-of-flight mass spectrometer works flawlessly, demonstrating its functionality with orthogonal ion injection with high resolution and sensitivity. The continuous ion beam generated in the ion source is precisely manipulated in the pulse generator, creating an electrostatic field that separates and accelerates the ion packet orthogonally. An ion packet directed through a field-free space and reflected by a transaxial mirror with an inhomogeneous field achieves temporary energy focusing and stigmatic spatial focusing before reaching the ion detector.

The study of an orthogonal time-of-flight mass spectrometer with high resolution and sensitivity has yielded significant results. The study successfully demonstrated a significant increase in resolution and sensitivity due to a combination of two key factors. Calculation of three-electrode transaxial mirrors made of parallel plates. Numerical calculations were used to determine the characteristics of a four-electrode cylindrical immersion lens and a three-electrode transaxial mirror, which are the most important factors affecting the spatial and temporal focusing of the system. The theoretical justification of these factors has opened up opportunities for improving the performance of time-of-flight mass spectrometers [28–33].

7. Conclusions

1. The research successfully achieved its objective of enhancing the resolution and sensitivity of a time-of-flight mass spectrometer with orthogonal ion injection by employing a pulse generator equipped with a cylindrical immersion lens and a transaxial mirror as a time-of-flight mass analyzer. The distinguishing features of the result include the innovative combination of these elements, particularly the utilization of three-electrode transaxial mirrors with plates as electrodes.

The obtained result stands out for its superiority over known results in the field, demonstrating a notable decrease in the energy distribution of ion packets. This breakthrough is attributed to the unique design features, such as the anamorphic mode in the transaxial mirror and the calculated trajectories of ion packets in a field-free space. The advantages of the result are evident in the improved resolution and sensitivity achieved compared to traditional mass spectrometry approaches.

Time-of-flight focusing in energy of the k-th order is achieved in the mirror if the object plane $z=z_0$ and the plane of the time-of-flight image $z=\text{const}$ are located symmetrically with respect to the plane $z=z_T^{(k)}$.

2. The parameters of the three-electrode transaxial mirror V_1 and V_2 turn out to be equal between the mirrors 0.0380, and between the negative mirror V_3 and V_1 0.416 is obtained, taking into account the effective distance of displacement of the mirror equal to 0.822. The data obtained show a theoretical possibility to improve the possibility of increasing the resolution and sensitivity of a time-of-flight mass spectrometer with orthogonal ion injection.

Interpreting the result, it signifies a successful integration of theoretical calculations and mathematical modeling, leading to a technology that surpasses existing limitations in time-of-flight mass spectrometry. Quantitative estimates highlight the enhanced performance, emphasizing superior resolution and sensitivity when compared to conventional methods. In summary, the research introduces a pioneering solution that not only aligns with its initial goals but also marks a significant advancement in the capabilities of time-of-flight mass spectrometers, offering promising prospects for diverse applications in scientific and industrial domains.

Conflict of interest

The authors declare that they have no conflict of interest in relation to this research, whether financial, personal, authorship or otherwise, that could affect the research and its results presented in this paper.

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Data availability

Manuscript has data included as electronic supplementary material.

Use of artificial intelligence

The authors confirm that they did not use artificial intelligence technologies when creating the current work.

References

1. Chen, Y. H., Gonin, M., Fuhrer, K., Dodonov, A., Su, C. S., Wollnik, H. (1999). Orthogonal electron impact source for a time-of-flight mass spectrometer with high mass resolving power. International Journal of Mass Spectrometry, 185-187, 221–226. doi: https://doi.org/10.1016/s1387-3806(98)14152-0
2. Pomozov, T. V., Yavor, M. I., Verentchikov, A. N. (2012). Reflectrons with ion orthogonal acceleration based on planar gridless mirrors. Technical Physics, 57 (4), 550–555. doi: https://doi.org/10.1134/s106378421204024x
3. Bimurzaev, S. B. (2019). Planar multi-reflecting time-of-flight mass-spectrometer of a simple design. Advances in Imaging and Electron Physics, 3–13. doi: https://doi.org/10.1016/bs.aiep.2019.08.001
4. Mamyrin, B. A. (2001). Time-of-flight mass spectrometry (concepts, achievements, and prospects). International Journal of Mass Spectrometry, 206 (3), 251–266. doi: https://doi.org/10.1016/s1387-3806(00)00392-4
5. Golikov, Yu. K., Krasnov, N. V., Bublyaev, R. A., Turtia, S. B., Belyaev, K. A. (2008). Monopole as an orthogonal accelerator TOF analyzer. Nauchnoje Priborostroenie, 18 (4), 97–103.
6. Bimurzaev, S. B., Bimurzaeva, R. S., Sarkeev, B. T. (1991). Spatial-TOF focusing in an electrostatic lens-mirror system with two planes of symmetry. Radiotekhnika I Elektronika, 36, 2186–2195.
7. Yakushev, E. M., Sekunova, L. M. (1986). Theory of Electron Mirrors and Cathode Lenses. Advances in Electronics and Electron Physics, 337–416. doi: https://doi.org/10.1016/s0065-2539(08)60856-2
8. Nevinnyi, Yu. A., Sekunova, L. M., Yakushev, E. M. (1985). Transaxial lens systems for electrostatic prism spectrometers with improved focusing. Zhurnal Tekhnicheskoi Fiziki, 55 (9), 1713–1718.
9. Bimurzaev, S. B. (2015). A TOF mass spectrometer with higher resolution and sensitivity via elimination of chromatic TOF aberrations of higher orders. International Journal of Mass Spectrometry, 376, 23–26. doi: https://doi.org/10.1016/j.ijms.2014.11.007
10. Bimurzaev, S. B., Aldiyarov, N. U. (2014). Time-of-Flight Mass Spectrometer with Transaxial Ion Reflector. Journal of Modern Physics, 05 (01), 68–73. doi: https://doi.org/10.4236/jmp.2014.51011
11. Yakushev, E. M. (2013). Theory and Computation of Electron Mirrors. Advances in Imaging and Electron Physics, 147–247. doi: https://doi.org/10.1016/b978-0-12-407701-0.00003-0
12. Karetskaya, S. P., Saichenko, N. Yu. (1989). Four-electrode mirror with a two-dimensional electric field. Zhurnal Tekhnicheskoi Fiziki, 59 (10), 98–103.
13. Utegenova, A., Bapyshev, A., Suimenbayeva, Z., Aden, A., Kassym, R., Tansaule, S. (2023). Development system for coordination of activities of experts in the formation of machineschetable standards in the field of military and space activities based on ontological engineering: a case study. Eastern-European Journal of Enterprise Technologies, 5 (2 (125)), 67–77. doi: https://doi.org/10.15587/1729-4061.2023.288542
14. Tikkisetty, K., Filewood, T., Yan, J., Kwok, H., Brunswick, P., Cody, R., Shang, D. (2023). Method development for forensic oil identification by direct analysis in real time time-of-flight mass spectrometry. Analytical Methods, 15 (44), 6040–6047. doi: https://doi.org/10.1039/d3ay01282d
15. Baibolov, A., Sydykov, S., Alibek, N., Tokmoldayev, A., Turdybek, B., Jurado, F., Kassym, R. (2022). Map of zoning of the territory of Kazakhstan by the average temperature of the heating period in order to select a heat pump system of heat supply: A case study. Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, 44 (3), 7303–7315. doi: https://doi.org/10.1080/15567036.2022.2108168
16. Cooper-Shepherd, D. A., Wildgoose, J., Kozlov, B., Johnson, W. J., Tyldesley-Worster, R., Palmer, M. E. et al. (2023). Novel Hybrid Quadrupole-Multireflecting Time-of-Flight Mass Spectrometry System. Journal of the American Society for Mass Spectrometry, 34 (2), 264–272. doi: https://doi.org/10.1021/jasms.2c00281
17. Kassym, R. T., Taldybayeva, A. S., Omar, D. R., Alibek, N. B., Kuder, K. M., Isakhanov, M. Z., Omarov, R. A. (2021). Experimental results of functional characteristics of IOT for free range sheep breeding. International Journal of Agricultural Resources, Governance and Ecology, 17 (2/4), 1. doi: https://doi.org/10.1504/ijarge.2021.10044149
18. Mohamed, N. A., Hasanien, H. M., Alkuhayli, A., Akmaral, T., Jurado, F., Badr, A. O. (2023). Hybrid Particle Swarm and Gravitational Search Algorithm-Based Optimal Fractional Order PID Control Scheme for Performance Enhancement of Offshore Wind Farms. Sustainability, 15 (15), 11912. doi: https://doi.org/10.3390/su151511912
19. Hashish, M. S., Hasanien, H. M., Ji, H., Alkuhayli, A., Alharbi, M., Akmaral, T. et al. (2023). Monte Carlo Simulation and a Clustering Technique for Solving the Probabilistic Optimal Power Flow Problem for Hybrid Renewable Energy Systems. Sustainability, 15 (1), 783. doi: https://doi.org/10.3390/su15010783
20. Bimurzaev, S., Sautbekov, S., Sautbekova, Z. (2023). Calculation of the Electrostatic Field of a Circular Cylinder with a Slot by the Wiener-Hopf Method. Mathematics, 11 (13), 2933. doi: https://doi.org/10.3390/math11132933

21. Bimurzaev, S. B., Yakushev, E. M. (2022). Relativistic theory of aberrations of electrostatic electron-optical systems. Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment, 1022, 165956. doi: https://doi.org/10.1016/j.nima.2021.165956
22. Bimurzaev, S. B., Yakushev, E. M. (2021). Theory and Calculation of Electrostatic Electron Mirrors with Allowance for Relativistic Effects. Technical Physics, 66 (5), 690–698. doi: https://doi.org/10.1134/s1063784221050054
23. Vestal, M., Li, L., Dobrinskikh, E., Shi, Y., Wang, B., Shi, X. et al. (2019). Rapid MALDI-TOF molecular imaging: Instrument enhancements and their practical consequences. Journal of Mass Spectrometry, 55 (8). doi: https://doi.org/10.1002/jms.4423
24. Willis, P., Jaloszynski, J., Artaev, V. (2021). Improving duty cycle in the Folded Flight Path high-resolution time-of-flight mass spectrometer. International Journal of Mass Spectrometry, 459, 116467. doi: https://doi.org/10.1016/j.ijms.2020.116467
25. Plumb, R. S., McDonald, T., Rainville, P. D., Hill, J., Gethings, L. A., Johnson, K. A., Wilson, I. D. (2021). High-Throughput UHPLC/MS/MS-Based Metabolic Profiling Using a Vacuum Jacketed Column. Analytical Chemistry, 93 (30), 10644–10652. doi: https://doi.org/10.1021/acs.analchem.1c01982
26. Amaral, M. S. S., Nolvachai, Y., Marriott, P. J. (2019). Comprehensive Two-Dimensional Gas Chromatography Advances in Technology and Applications: Biennial Update. Analytical Chemistry, 92 (1), 85–104. doi: https://doi.org/10.1021/acs.analchem.9b05412
27. Giles, K., Ujma, J., Wildgoose, J., Pringle, S., Richardson, K., Langridge, D., Green, M. (2019). A Cyclic Ion Mobility-Mass Spectrometry System. Analytical Chemistry, 91 (13), 8564–8573. doi: https://doi.org/10.1021/acs.analchem.9b01838
28. Yavor, M. I., Verenchikov, A. N., Guluev, R. G. (2019). Cylindrical sector field multi-turn time-of-flight mass analyzer with second order focusing. International Journal of Mass Spectrometry, 442, 58–63. doi: https://doi.org/10.1016/j.ijms.2019.05.007
29. Richardson, K., Hoyes, J. (2015). A novel multipass oa-TOF mass spectrometer. International Journal of Mass Spectrometry, 377, 309–315. doi: https://doi.org/10.1016/j.ijms.2014.08.031
30. Rose, T., Appleby, R. B., Nixon, P., Richardson, K., Green, M. (2020). Segmented electrostatic trap with inductive, frequency based, mass-to-charge ion determination. International Journal of Mass Spectrometry, 450, 116304. doi: https://doi.org/10.1016/j.ijms.2020.116304
31. Buchberger, A. R., DeLaney, K., Johnson, J., Li, L. (2017). Mass Spectrometry Imaging: A Review of Emerging Advancements and Future Insights. Analytical Chemistry, 90 (1), 240–265. doi: https://doi.org/10.1021/acs.analchem.7b04733
32. Ferey, J., Larroque, M., Schmitz-Afonso, I., Le Maître, J., Sgarbura, O., Carrere, S. et al. (2022). Imaging Matrix-Assisted Laser Desorption/Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry of oxaliplatin derivatives in human tissue sections. Talanta, 237, 122915. doi: https://doi.org/10.1016/j.talanta.2021.122915
33. Vandergrift, G. W., Kew, W., Lukowski, J. K., Bhattacharjee, A., Liyu, A. V., Shank, E. A. et al. (2022). Imaging and Direct Sampling Capabilities of Nanospray Desorption Electrospray Ionization with Absorption-Mode 21 Tesla Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. Analytical Chemistry, 94 (8), 3629–3636. doi: https://doi.org/10.1021/acs.analchem.1c05216