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(51) INT CL:
H01J 49/42 (2006.01) ***H01J 49/04*** (2006.01)
H01J 49/40 (2006.01)

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(58) Field of Search:
INT CL **H01J**
Other: **ONLINE: EPODOC, WPI, TXTE.**

(54) Title of the Invention: **Electrostatic trap mass spectrometer**
Abstract Title: **Electrostatic trap mass spectrometer**

(57) A means of significantly improving the acquisition speed and space charge capacity of electrostatic traps is provided by using substantially two dimensional X-Y fields of planar symmetry and substantial extension of the electrostatic trap in a third z direction. The electrostatic trap mass spectrometer comprises an ion source 42, a pulsed ion convertor 43, ion injection means 44, an electrostatic trap 45 with two parallel electrostatic mirrors 46 spaced apart by a field free region 47 and means 48 for bounding ions in a z direction. Electrodes 49 for image detection are also provided. The trap is substantially a two dimensional trap of planar symmetry within the X-Y plane which is arranged by substantial elongation of mirrors 46 in the direction z.

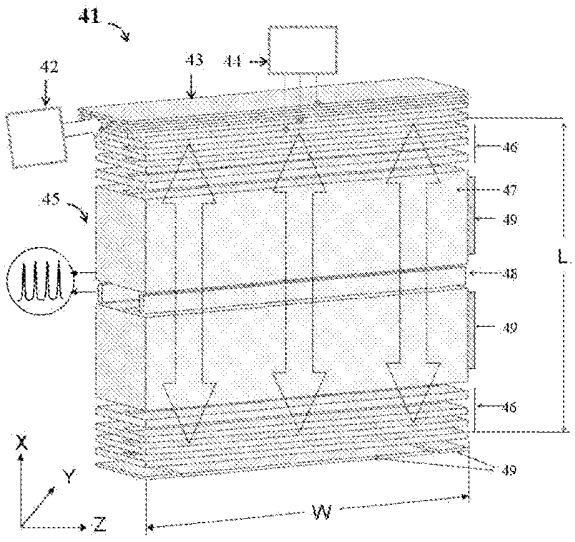


Fig.4

GB 2476964 A

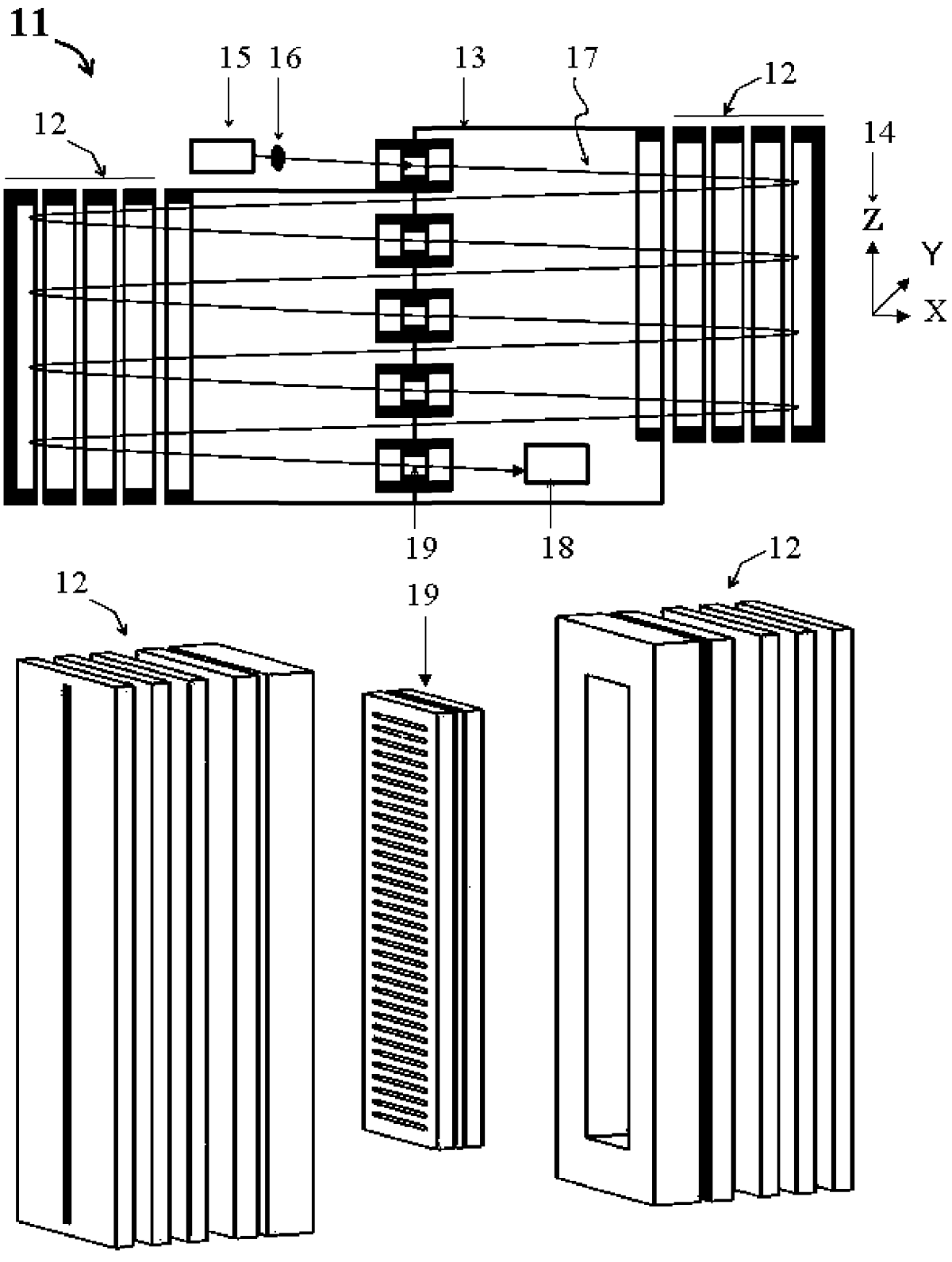


Fig.1. Prior Art

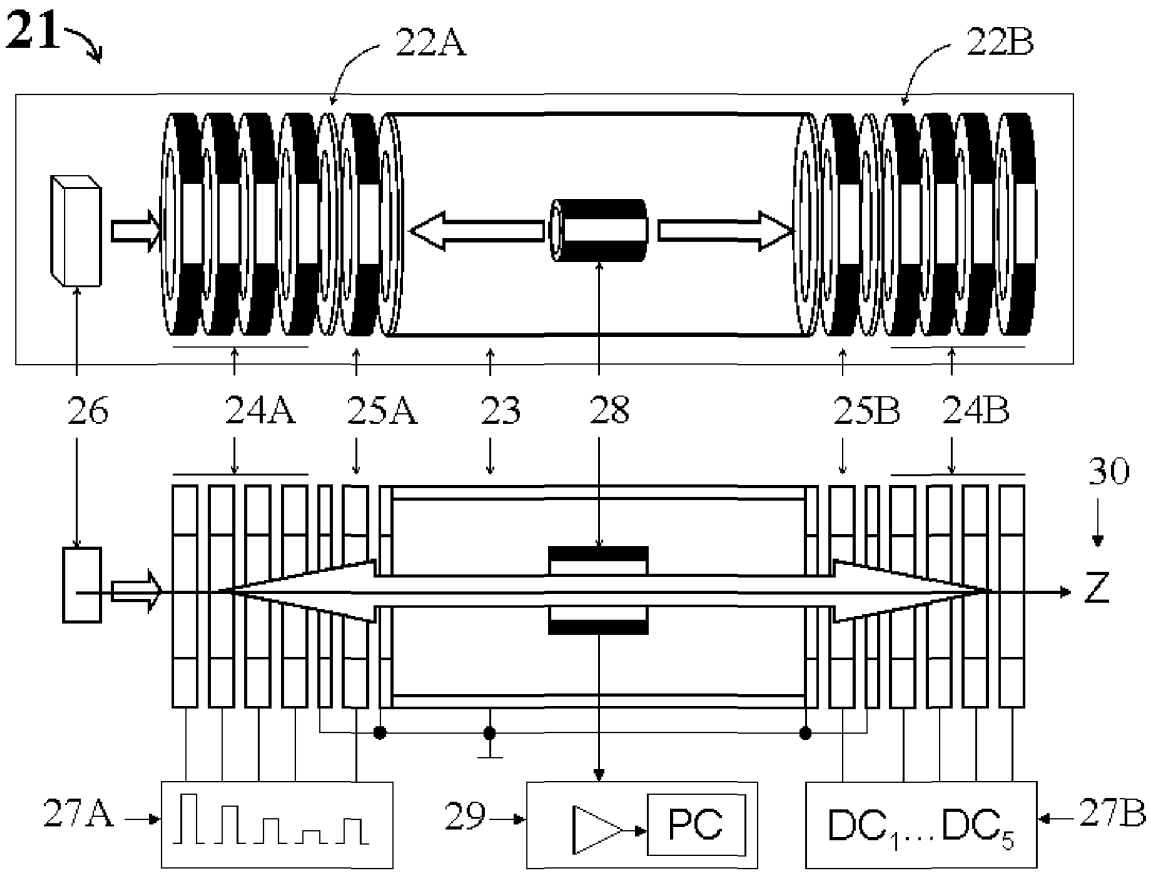


Fig.2. Prior Art

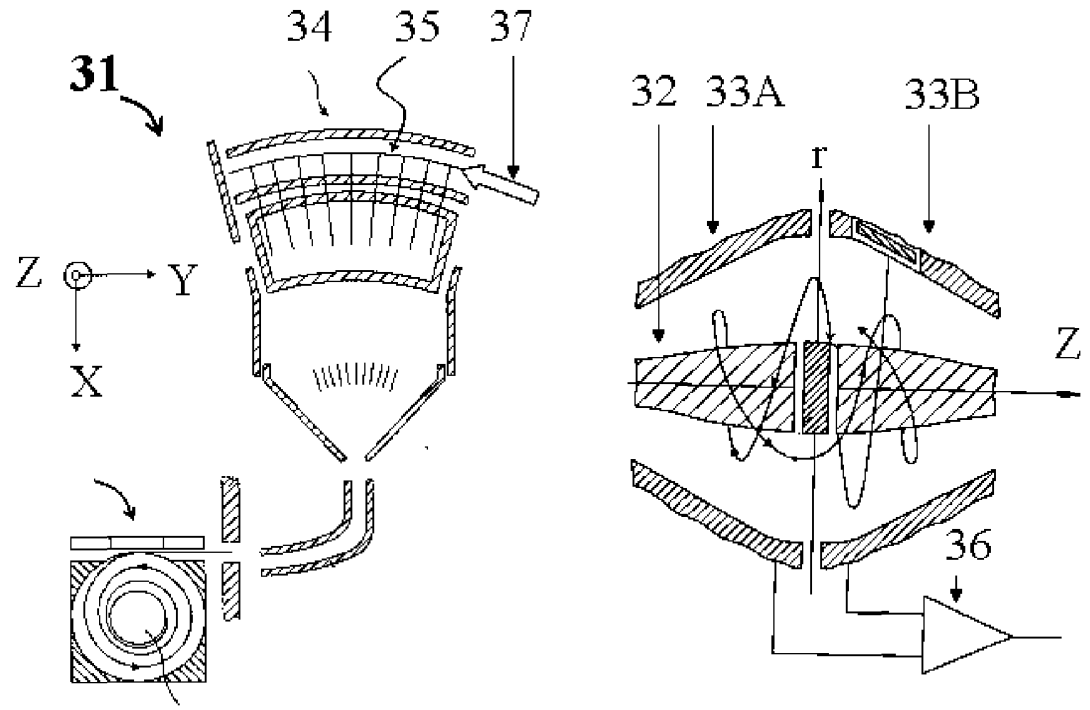


Fig.3. Prior Art

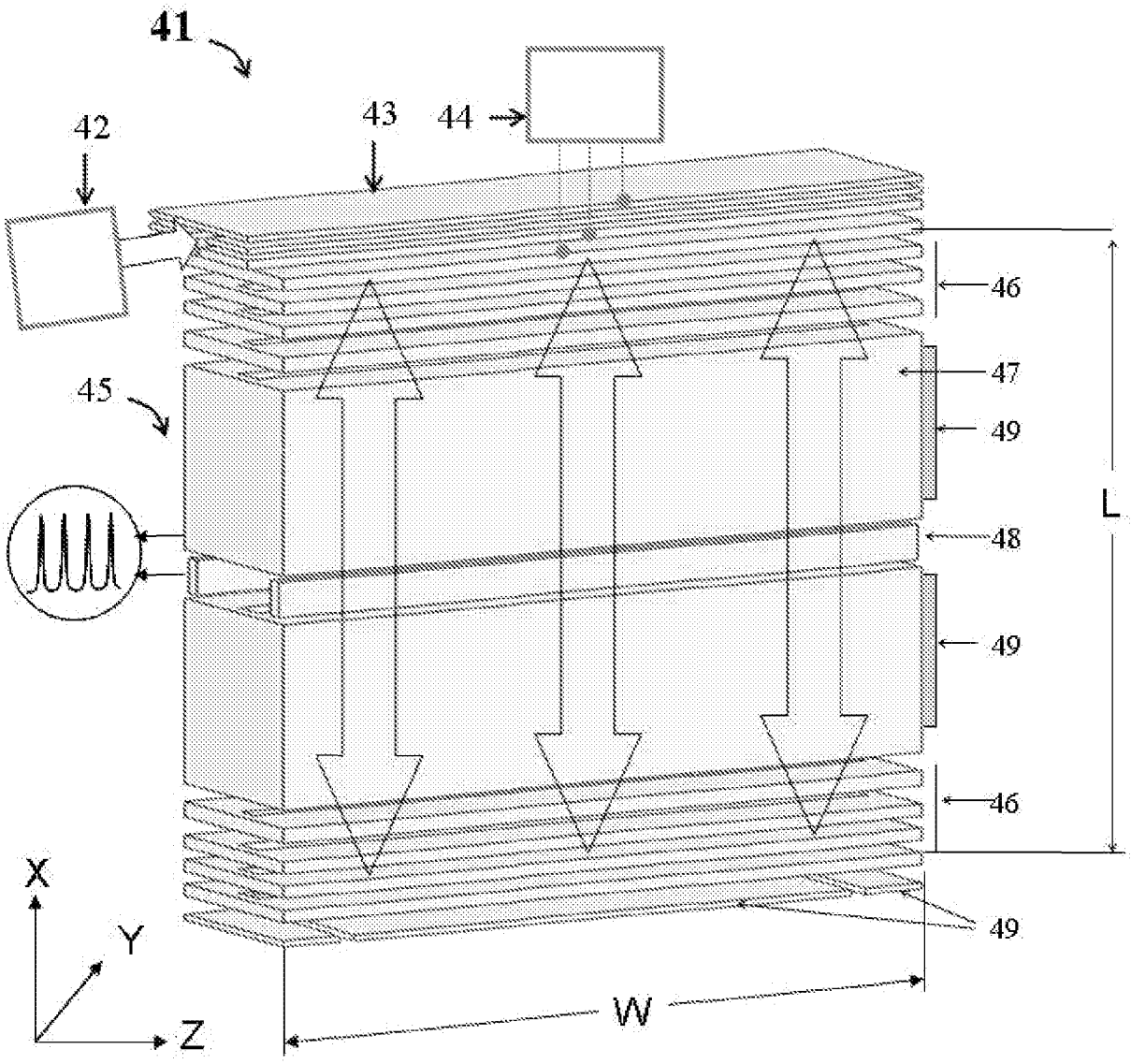


Fig.4

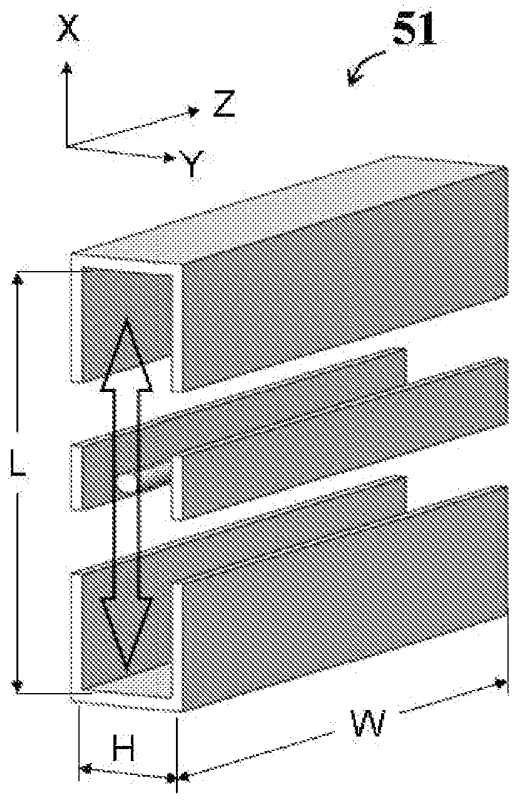


Fig.5-A

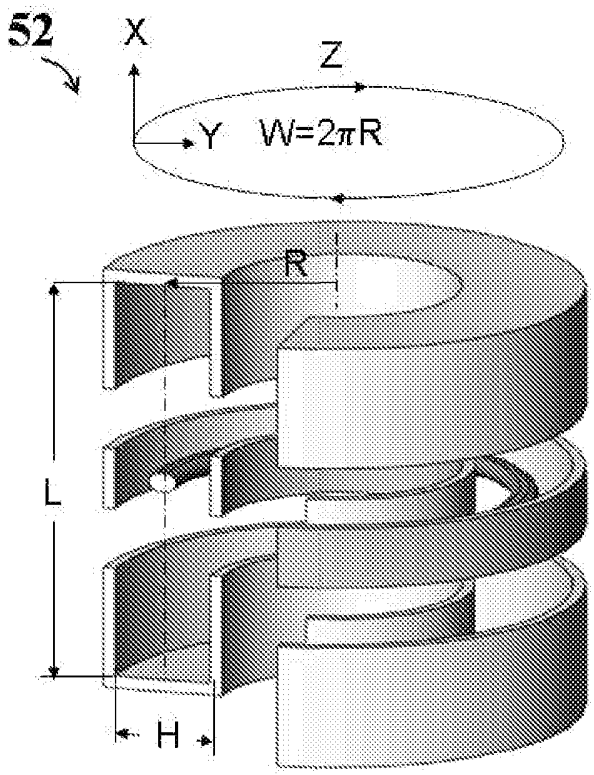


Fig.5-B

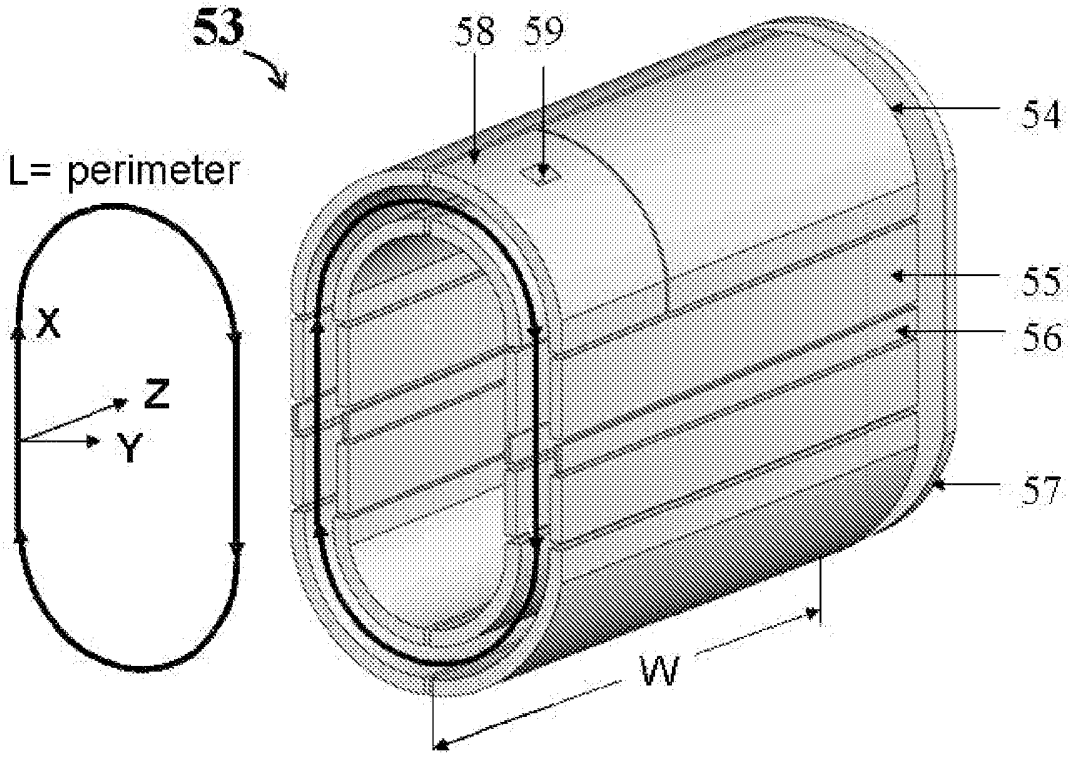


Fig.5-C

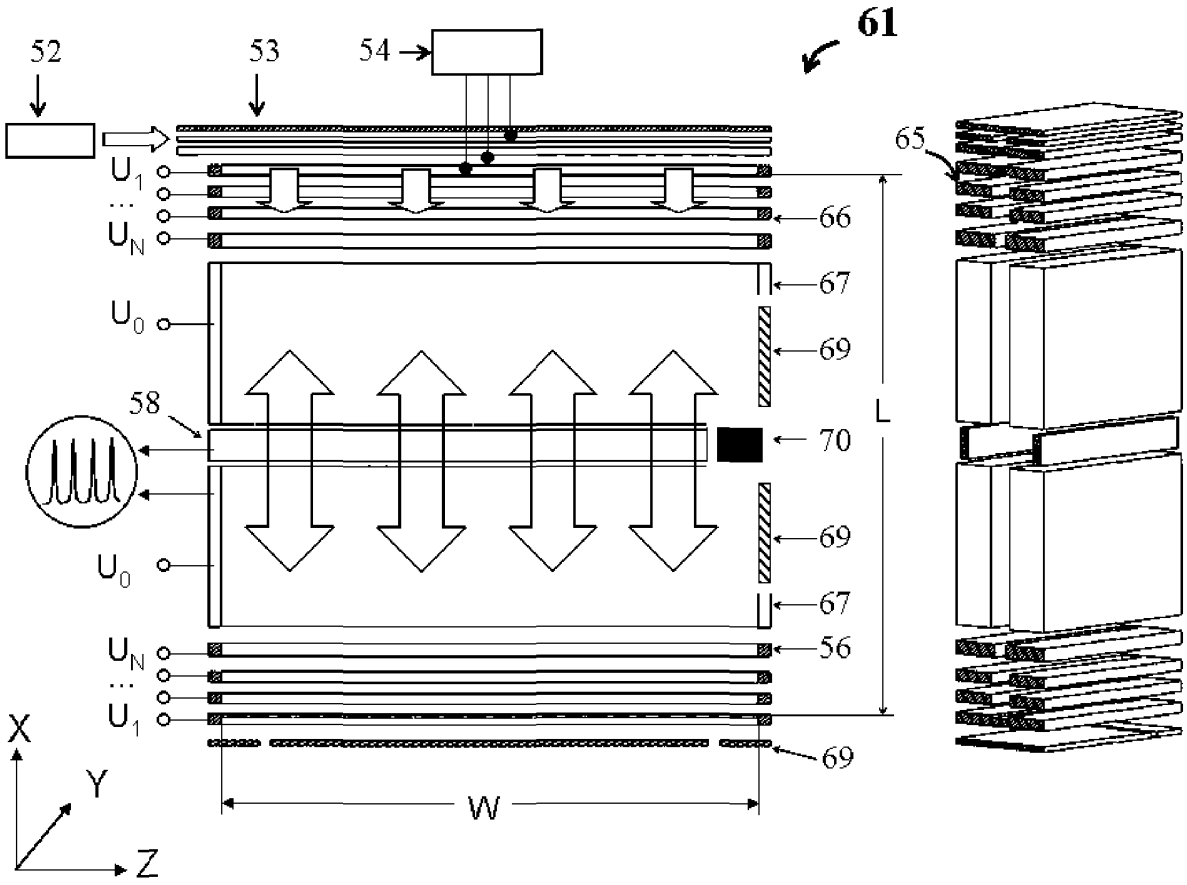
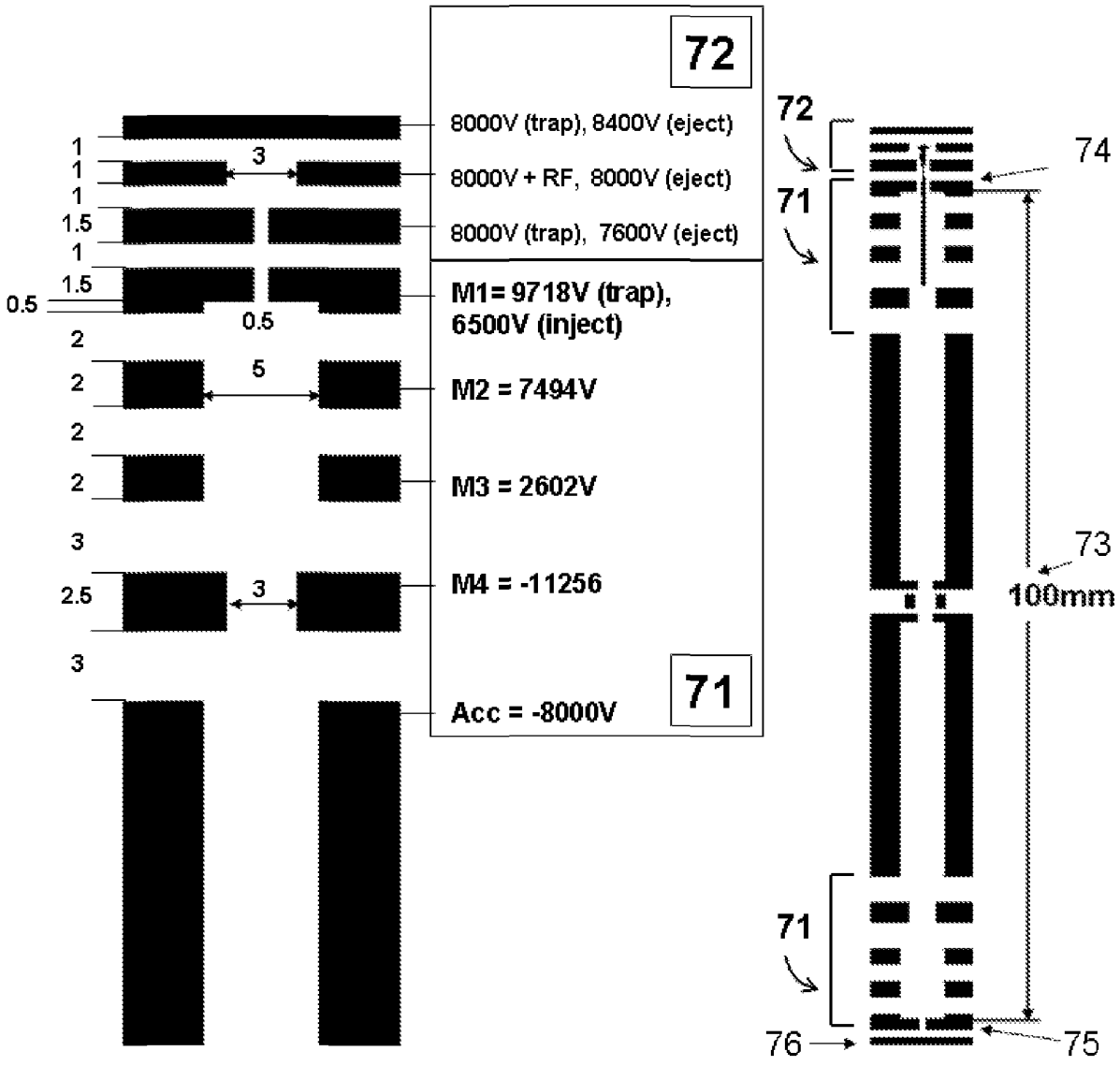


Fig.6


72
8000V (trap), 8400V (eject)
8000V + RF, 8000V (eject)
8000V (trap), 7600V (eject)
M1= 9718V (trap), 6500V (inject)
M2 = 7494V
M3 = 2602V
M4 = -11256
Acc = -8000V
71
1
1
1
1.5
1
1.5
0.5
0.5
2
2
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3
2.5
3
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5
3
72
71
74
73
100mm
71
76
75

Fig. 7

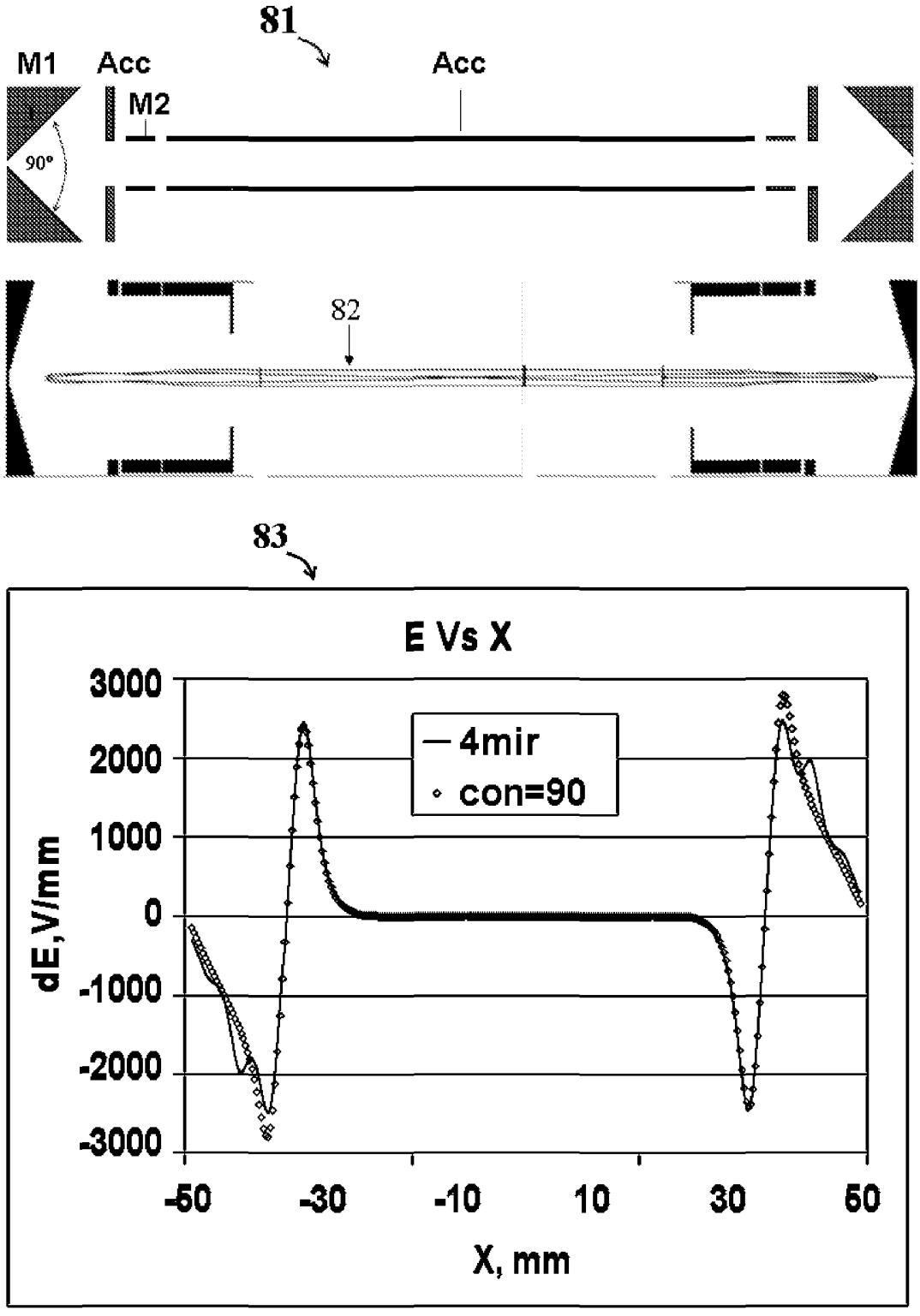
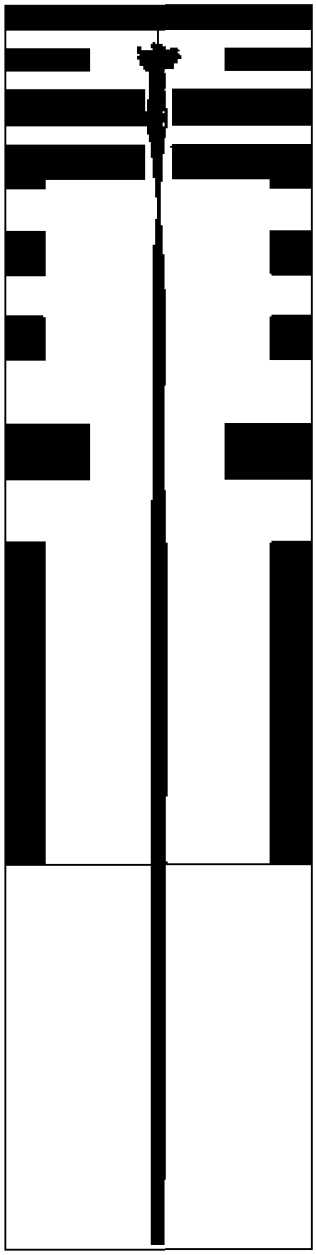

81
M1
Acc
M2
Acc
90°
82
83
E Vs X
3000
2000
1000
0
-1000
-2000
-3000
dE,V/mm
4mir
con=90
-50
-30
-10
10
30
50
X, mm

Fig.8



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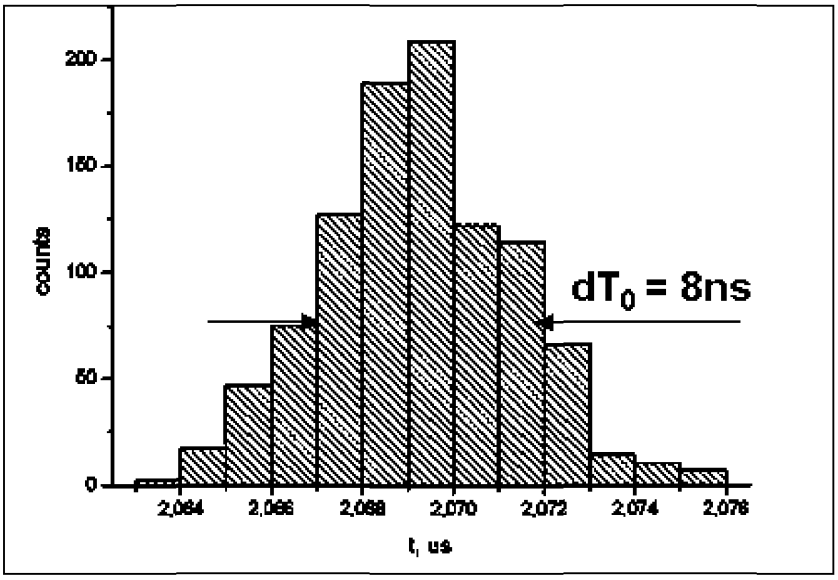

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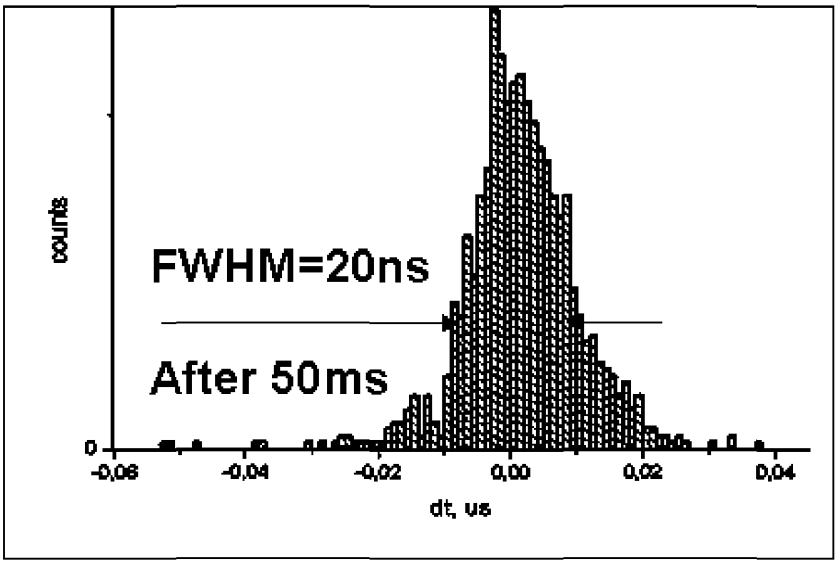


Fig.9C

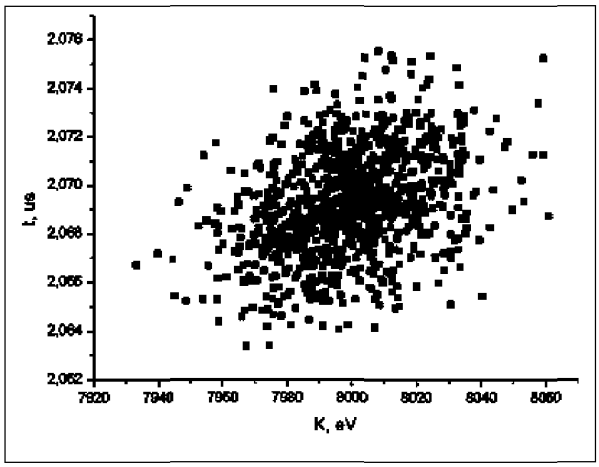
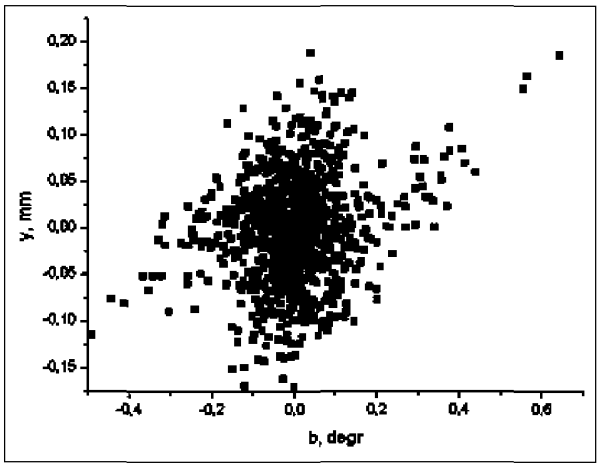


Fig.9-D



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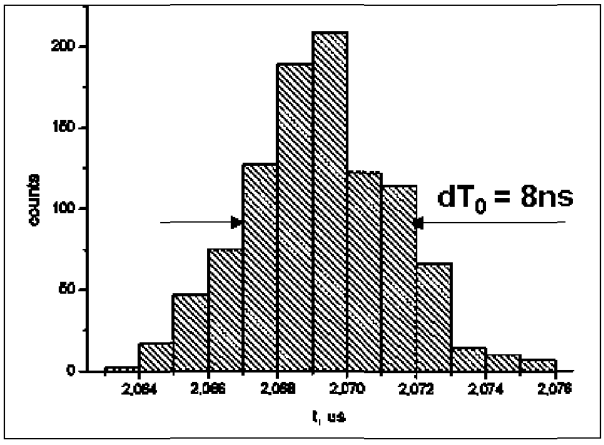
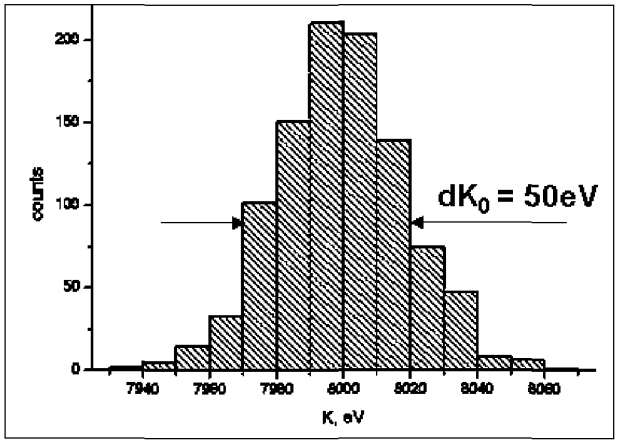


Fig.9-F



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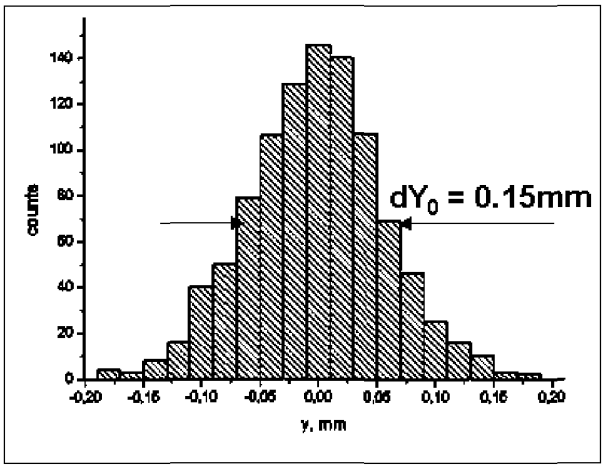

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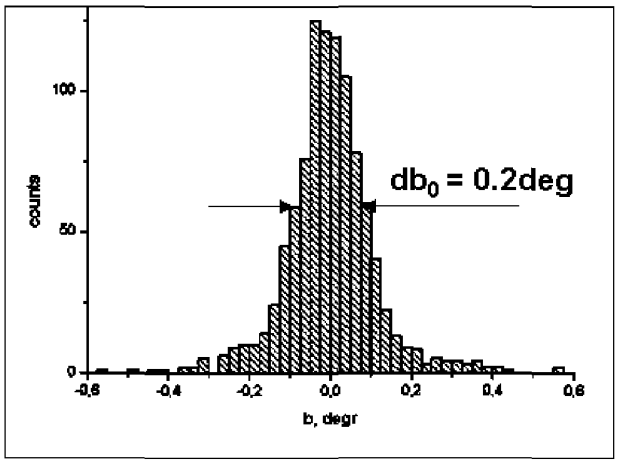

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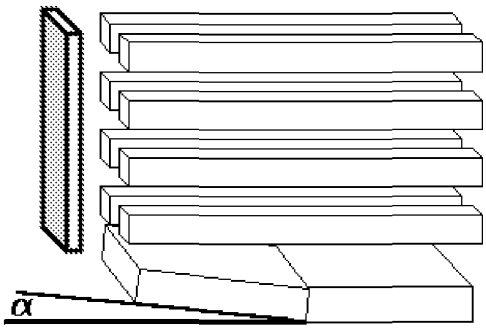

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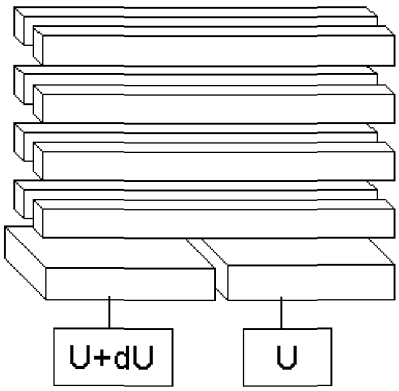

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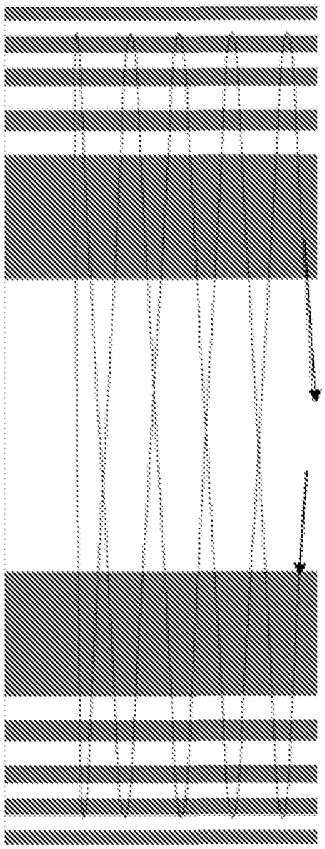

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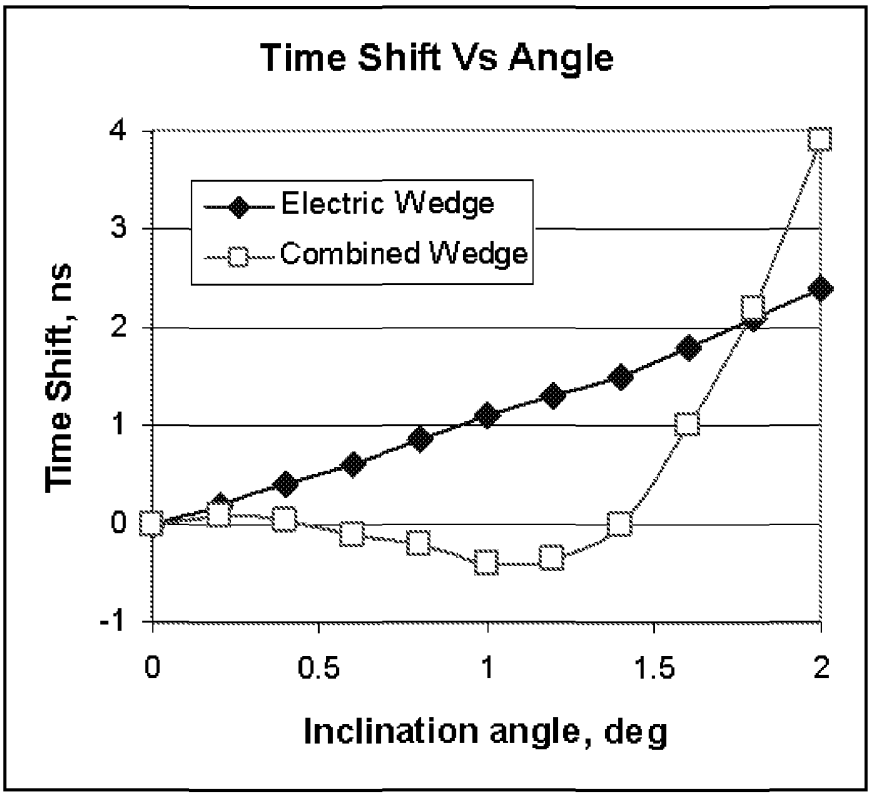

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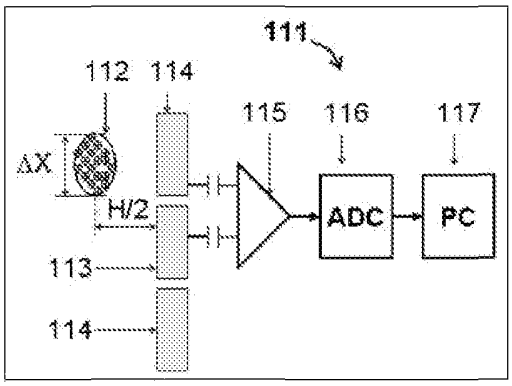

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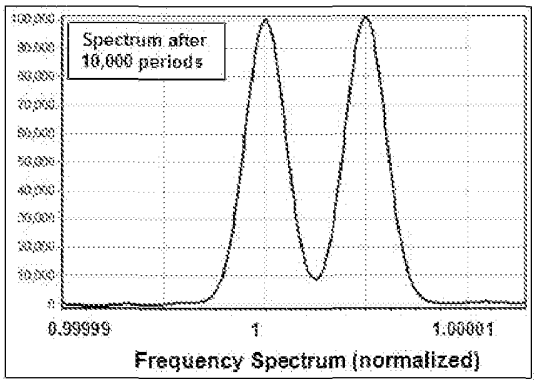
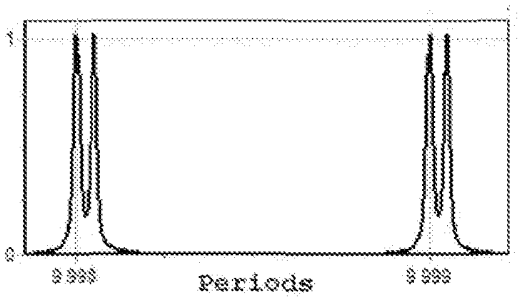


Fig.11-C



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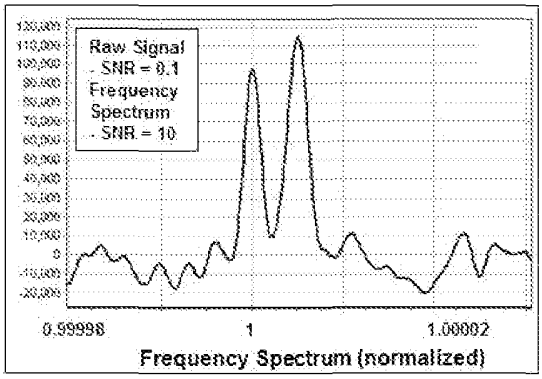

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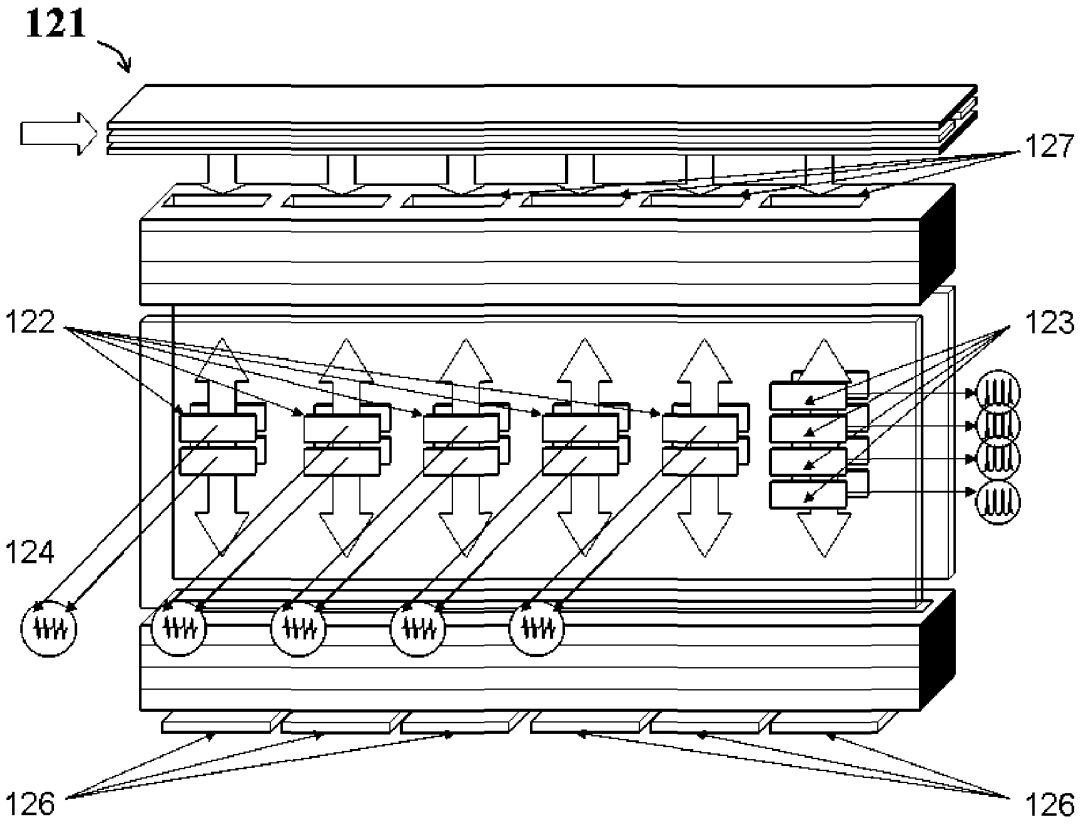

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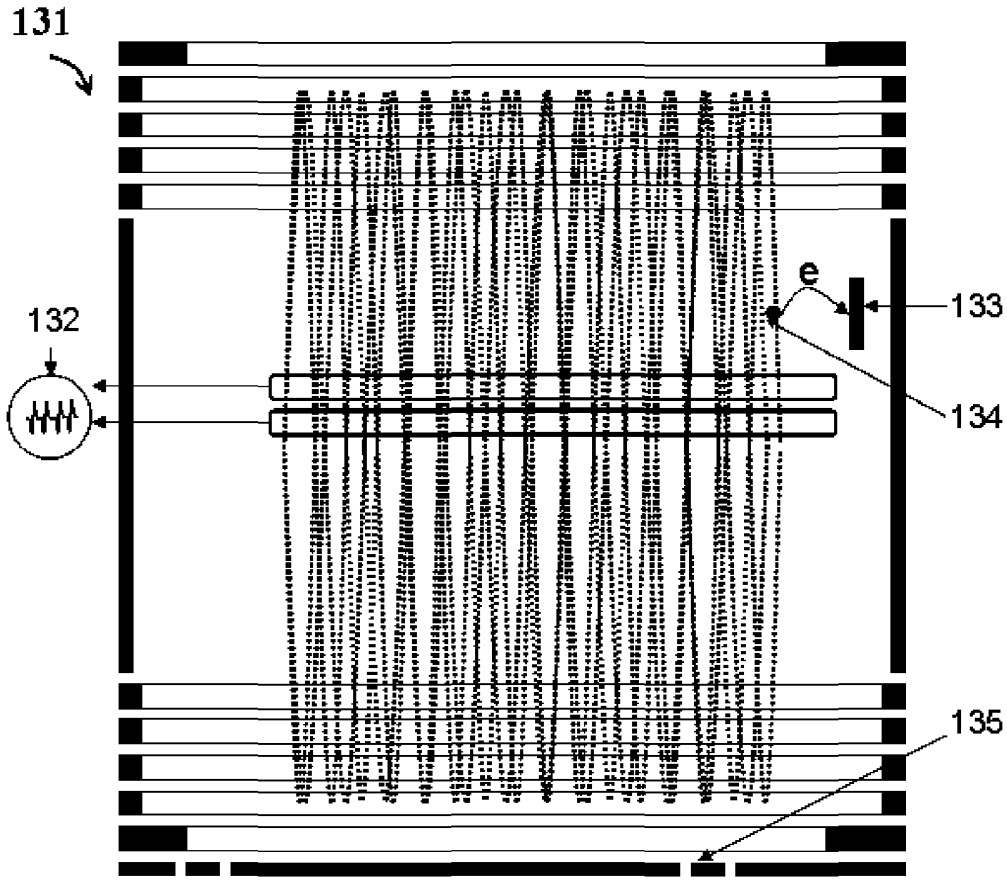

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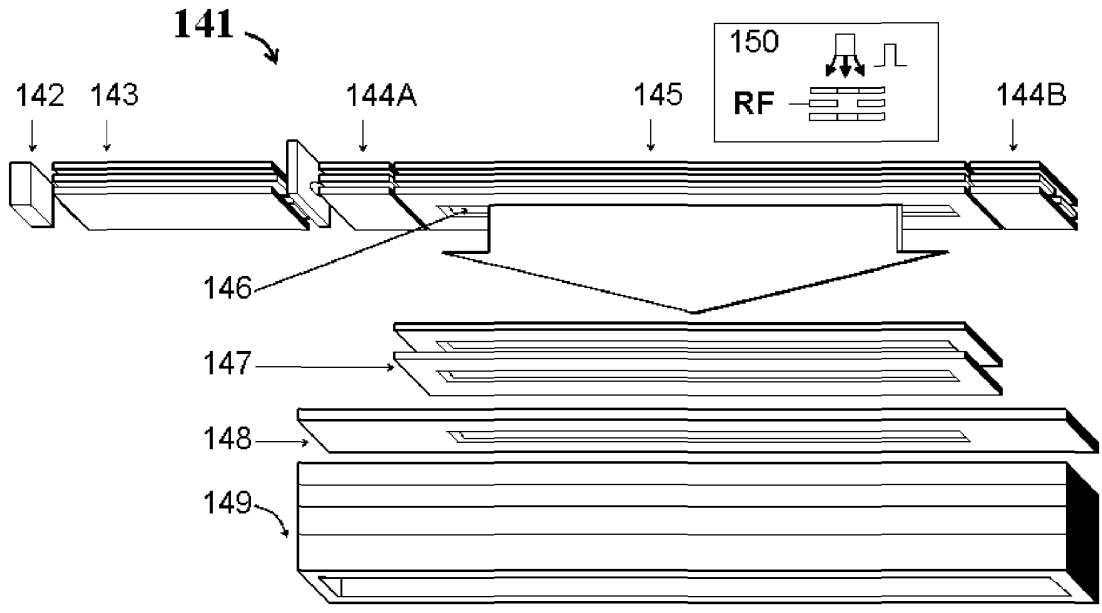

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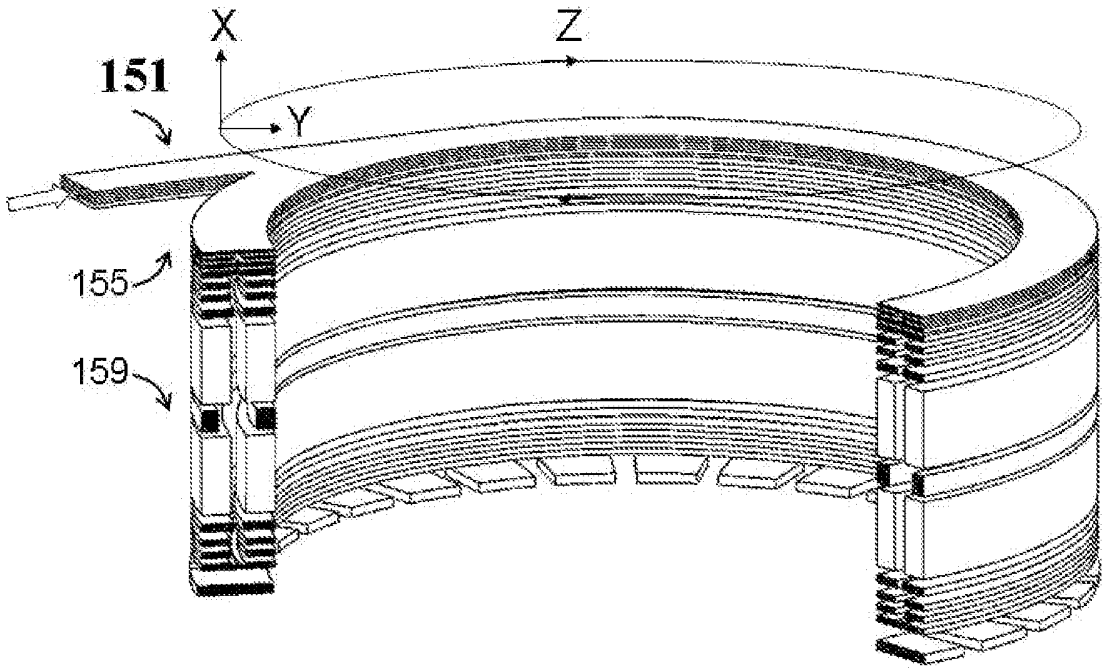

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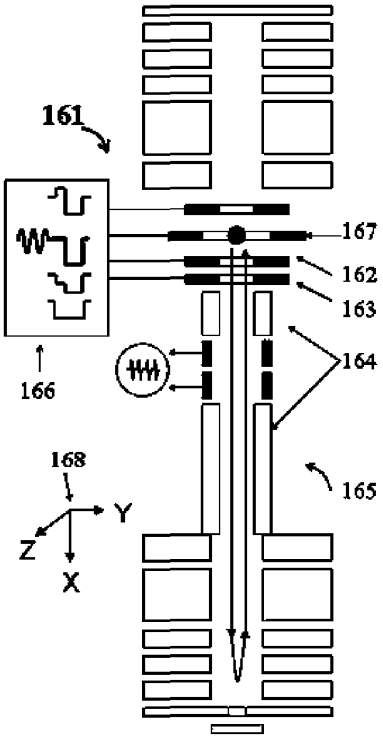

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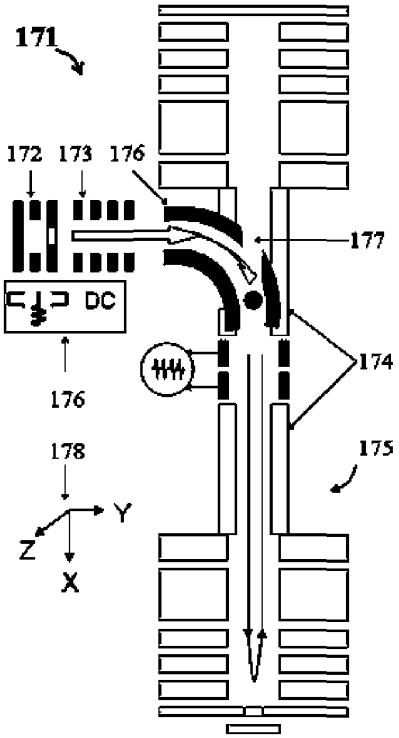

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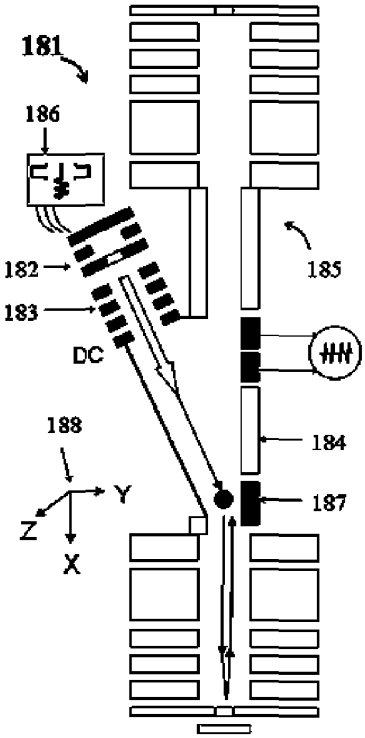

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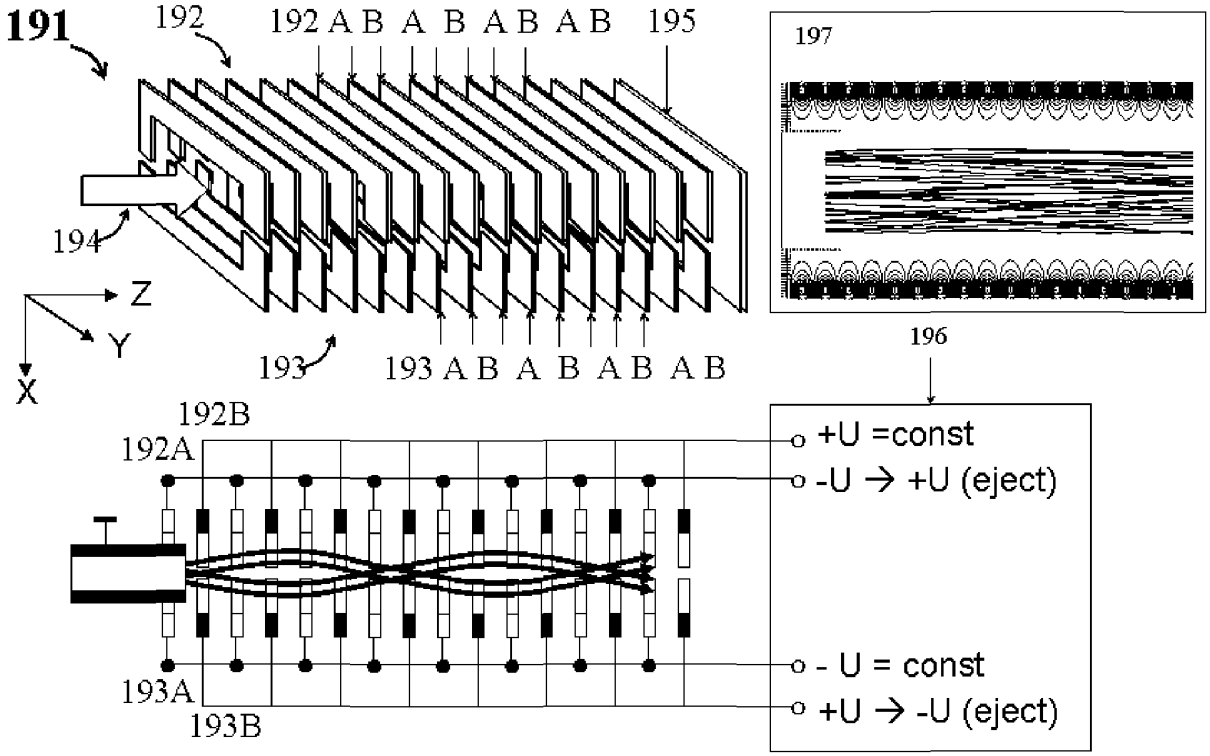
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192
192 A B A B A B A B
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197
194
Z
Y
X
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193 A B A B A B A B
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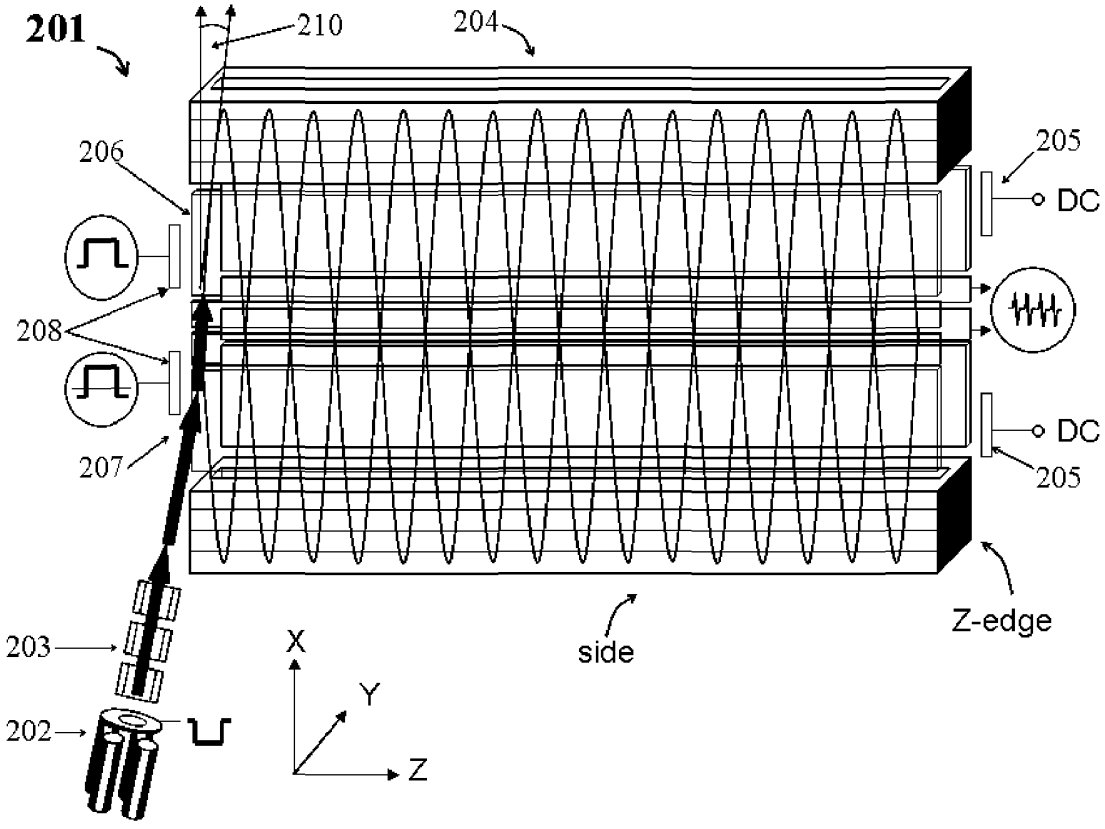
192B
192A
+U =const
-U → +U (eject)
- U = const
+U → -U (eject)
193A
193B

Fig.19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DC
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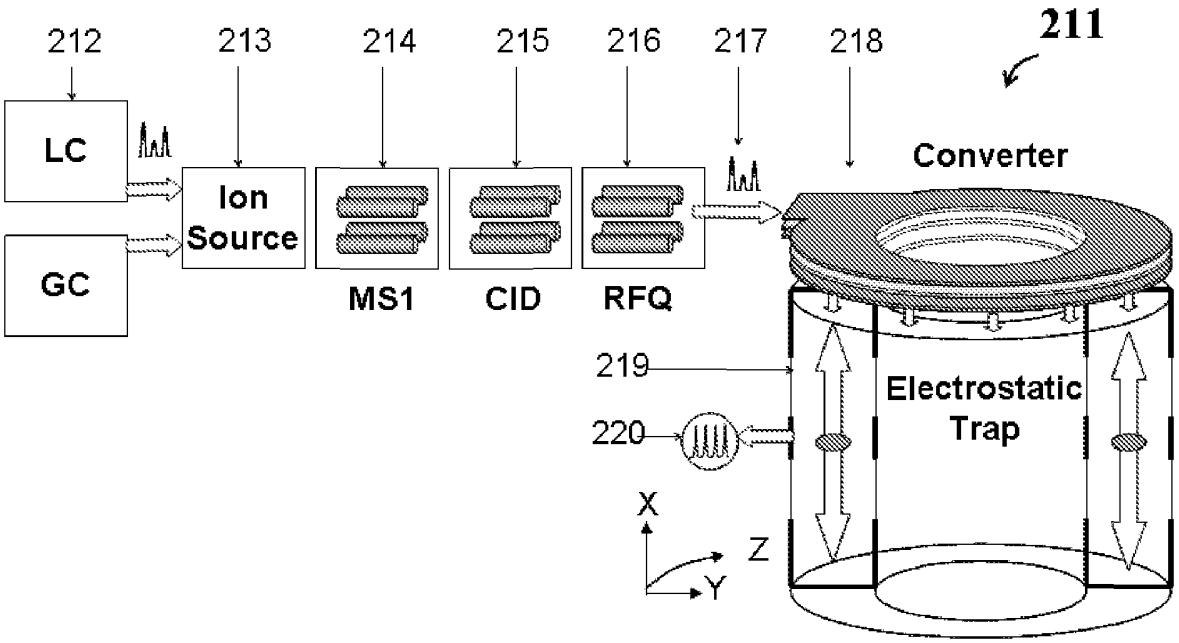
203
202
X
Y
Z
side
Z-edge

Fig.20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213
214
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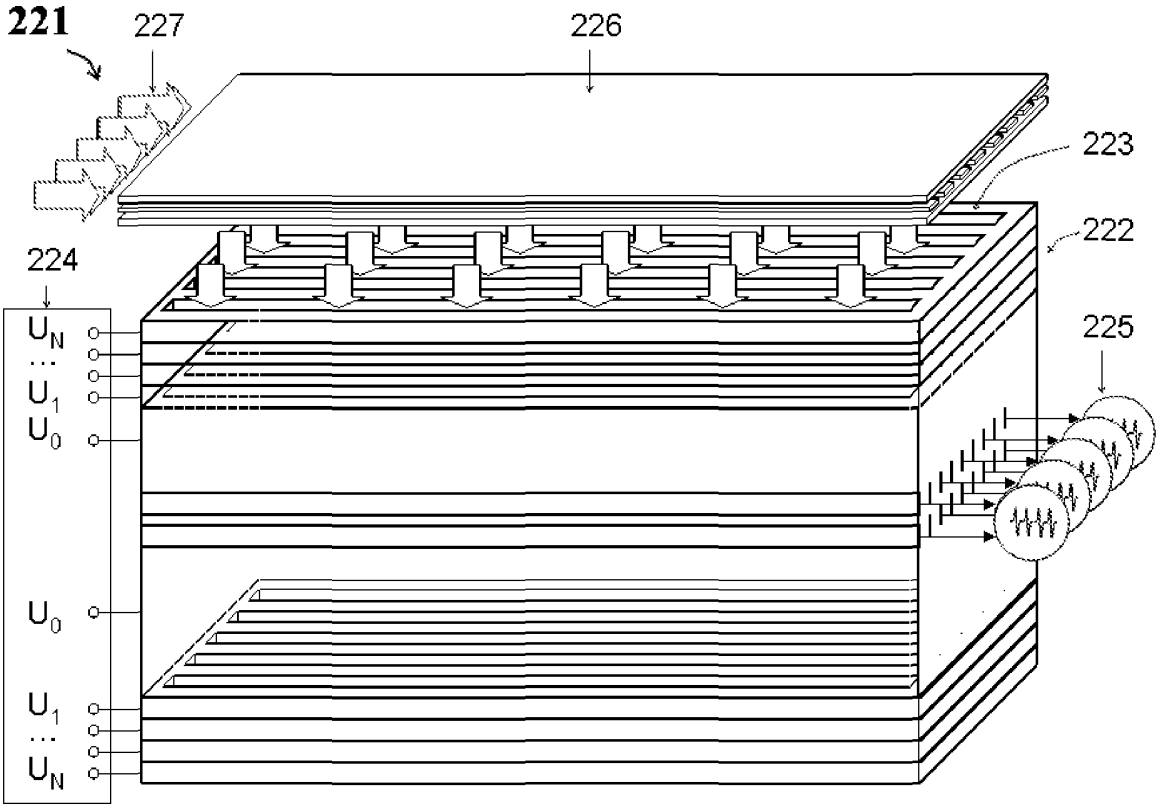
218
211
LC
GC
Ion Source
MS1
CID
RFQ
Converter
219
220
Electrostatic Trap
X
Z
Y

Fig.21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U_N
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U_1
U_0
U_0
U_1
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U_N

Fig.22

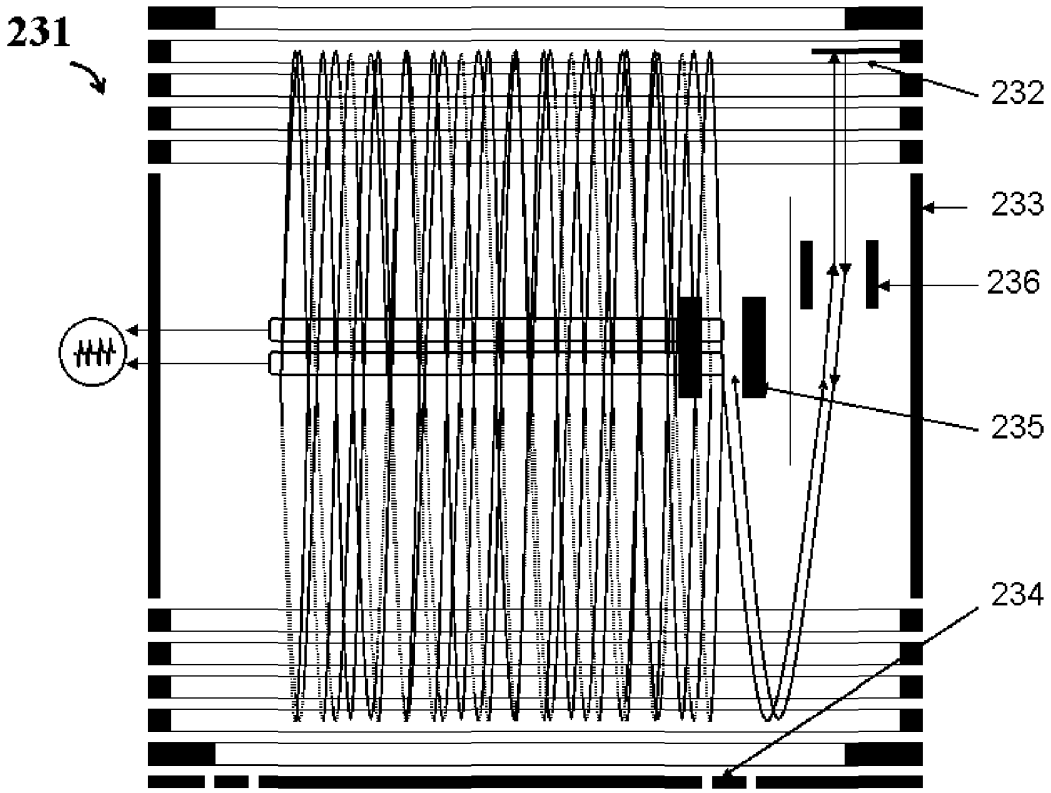

Fig.23

ELECTROSTATIC TRAP MASS SPECTROMETER

FIELD OF THE INVENTION

The invention relates generally to the field of electrostatic traps for trapping and analyzing charged particles and in particular electrostatic trap and time-of-flight mass spectrometers with image detection and Fourier analysis and method of use.

BACKGROUND OF THE INVENTION

Majority of modern electrostatic trap mass spectrometers (**E-Trap MS**) emerged from multi-pass time-of-flight mass spectrometers (**M-TOF MS**). The difference between the techniques is described below.

In M-TOF MS pulsed ion packets travel within electrostatic fields and follow a predetermined folded ion path from a pulsed source to a detector. Typical time-of-flight (**TOF**) detector is either a set of micro-channel plates (**MCP**) or secondary electron multiplier (**SEM**). Ion mass-to-charge ratio (**m/z**) is determined from ion flight time (**T**), since flight path is fixed for all ionic components and T is proportional to square root of ion m/z. To achieve high resolving power (also referred as 'resolution') electrostatic fields are designed to provide isochronous ion motion in respect to small initial energy, angular and spatial spreads of ion packets.

Most of E-Trap MS employ similar structure of electrostatic fields but arrange those fields such that ion packets are indefinitely trapped and follow the same path over and over again. In E-Trap MS the ion flight path is not fixed, since at any moment of time the number of motion cycles depends on ion m/z. Ion m/z is determined from frequency (**F**) of ion cyclic motion, since frequency F is reverse proportional to square root of ion m/z. Typical E-Trap MS detector is an image charge detector. Ions passing by an electrode induce an image charge of approximately 10nV per elementary charge. Such signal is amplified and recorded over a long period of time. In order to decipher periodic signals from multiple ionic components the resulting signal is analyzed with Fourier transformation, similarly to the well established Fourier Transform Ion Cyclotron Resonance (**FTMS**) mass spectrometers.

TOF MS

Time-of-flight mass spectrometry (**TOF MS**) is a powerful analytical technique. The range of TOF MS applications varies from life science to environmental control and elemental analysis. The application area determines the type of employed ion source. Amongst common ion sources are: Electrospray (ESI), Atmospheric Pressure Chemical Ionization (APCI), Atmospheric pressure Photo Ionization (APPI), Matrix Assisted Laser Desorption and Ionization (MALDI), Electron Impact (EI) and Inductively Coupled Plasma (ICP). It is of principal importance that modern ion sources are capable of delivering to TOF MS entrance up to 1E+9 ions/sec in case of ESI, APCI and APPI, up to 1E+10 ions/sec in case of EI and CI and up to 1E+11 ions/sec in case of ICP ion sources. This requirement is not met by existing TOF MS with dynamic range being limited to 1E+3/sec by counting data acquisition systems and to 1E+5/sec by analog data systems.

TOF MS is commonly used in combination with chromatography and as a second MS in tandem mass spectrometry primarily because TOF MS delivers >100 spectra/sec acquisition speed at full mass range. However, other analytical parameters are moderate compared to high end instruments like orbital traps or magnetic FTMS. Typical duty cycle of TOF MS is few percent if accounting ion losses at ion beam formation. Resolution of conventional TOF is limited to 20,000-30,000 for reasonable size packaging. Mass accuracy is worse than 1ppm being limited by ion statistics, by interference of isobaric peaks and by low isotopic abundance caused by poor peak shape at pedestal.

In the last decade there appeared multiple enhancements of the TOF MS technology aiming high resolution at the level of 100,000 and sub part-per-million (ppm) mass accuracy.

An important prior step towards high resolution TOF MS has been made with introduction of electrostatic ion mirrors. Mamyrin in US4072862 employed a double stage ion mirror to reach second order time-of-flight focusing with respect to ion energy spread. Frey et.al in US4731532 introduced grid free ion mirrors with a lens at the entrance to provide spatial ion focusing and to avoid meshes and associated ion losses. Further improvement of grid free ion mirrors has been made by Wollnik in R. Grix, R. Kutscher, G. Li U. Gruner, H. Wollnik. A Time-of-flight Mass Analyzer with High Resolving Power", Rapid Communication Mass Spectrometry, v.2 (1988) No5, 83-85. Such ion mirrors compensate energy

and spatial spreads to the second derivative and provide spatial ion focusing. From that point it became apparent that resolution of TOF MS is no longer limited by analyzer aberrations but rather by the time spread appearing in the pulsed converters, also referred as pulsed ion sources.

M-TOF MS

M-TOF MS employ multiple ion reflections between electrostatic ion mirrors to extend flight path while keeping reasonable size of the instrument. This allows diminishing effect of initial time spread onto resolution. A scheme with multiple reflections between parallel ion mirrors covered by grid has been described by Shing-Shen Su in "Multiple reflection Type Time-of-Flight Mass Spectrometer with Two Sets of Parallel Plate Eelectrostatic Fields", Int. J. Mass Spectrom., Ion Processes, v.88 (1989) 21-28. The instrument suffers ion losses at multiple passes through meshes. To avoid ion losses on grids Wollnik suggested using multiple individual coaxial gridless ion mirrors to form a folded **W-shaped ion path** (GB2080021 (1980); H. Wollnik, and M. Przewloka, "Time-of-Flight Mass Spectrometers with Multiply Reflected Ion Trajectories" International Journal of Mass Spectrometry and Ion Processes, v.96, (1990) 267-274.). The disadvantage is an angled passage through mirrors, which limits resolution to several of 10,000.

Nazarov in SU1725289 (1989) suggested using two planar and parallel gridless ion mirrors for M-TOF with W-shaped ion trajectories (**Planar M-TOF**). Since ions of all m/z follow the same zigzag trajectory the planar M-TOF retains full mass range. However, there are no means to prevent ion packets spreading in the drift direction which limits number of reflections to very few. To control ion drift in W-shaped M-TOF Verentchikov (WO2005001878) suggested using a set of periodic lenses, which are installed in a field free region between planar ion mirrors (**Fig.1**). A combination of planar M-TOF with a pulsing trap provides resolution of 50,000 and almost unity duty cycle in case of low intensive ion sources. However, space charge capacity of the analyzer is limited to 1000 ions/peak/pulse corresponding to 1E+6 ions per peak per second in case of single strong peak. When using intensive ion sources with ion flux up to 1E+9 ions/second the duty cycle (DC) becomes limited to DC=0.1% in most unfavorable case.

Another type of M-TOF - so called **Multi-turn TOF** employs electrostatic sectors to form spiral loop ion trajectories as described in T. Satoh, H. Tsuno, M. Iwanaga, Y. Kammei, "The Design and Characteristic Features of a New Time-of-Flight Mass Spectrometer with a Spiral Ion Trajectory", J. Am. Soc. Mass Spectrom., v.16 (2005) 1969-1975. Compared to planar M-TOF the spiral multi-turn TOF has notably higher ion optical aberrations and can tolerate smaller energy, angular and spatial spreads of ion packets. One would expect even lower duty cycle of multi-pass M-TOF MS compared to planar M-TOF MS.

E-Trap MS with TOF detector

E-Trap MS with TOF detector resemble features of both M-TOF and E-trap techniques and can be considered as a hybrid – E-Trap/TOF technique. Ions are pulsed injected into a trapping electrostatic field and experience periodic motion along the same ion path. Ion packets are pulsed ejected onto TOF detector after some delay corresponding to a large number of cycles. Since number of cycles depends on ion m/z the spectrum is complicated by overlapping signals of multiple ion species sampled after various numbers of cycles. To avoid overlaps the analyzed mass range is shrunk reverse proportional to number of cycles.

In GB2080021 (Figure 5) and US5017780 ion packets are reflected between coaxial gridless mirrors. Since ions repeat the same axial trajectory the scheme is called **I-path M-TOF**. Another type of hybrid M-TOF/E-trap is implemented within earlier described multi-turn M-TOF with electrostatic sectors. Looping of ion trajectories between electrostatic sectors is suggested by Ishihara in US6300625 and M. Ishihara, M. Toyoda, T. Matsuo, "Perfect Space and Time-of-flight Focusing Ion Optics in Multiturn Time-of-flight Mass Spectrometers", Int. J. Mass Spectrometry v.197 (2000) 179-189; D. Okumura, M. Toyoda, M. Ishihara, I. Katakuse, "A Compact Sector-Type Multi-Turn Time-of-Flight Mass Spectrometer MULTUM-2", Nuclear Instruments and Methods Phys. Research, A 519 (2004) 331-337. Ion packets are pulsed injected onto a looped trajectory and after a large number of loops the packets are ejected out onto a time-of-flight detector.

The main drawback of E-Trap with TOF detector is in limited mass range.

E-Trap MS with Frequency Detector

To overcome mass range limitations the I-path M-TOF has been converted into I-path electrostatic trap (**I-Path E-Trap**) in which ion packets are not ejected onto detector, but rather image

current detector is employed to sense frequency of ion oscillations as suggested in US6013913A by Hanson (1998); in US5880466 by Benner (1999), in US6744042 by Zajfman; Zaifman et.al. Phys. Rev. A, v.55/3, 1997, p R1577; Zaifman et.al, "Fourier Transform Time-of-flight Mass Spectrometry in an electrostatic Ion Trap", Analytical Chemistry, v.72, 2000, p.4041-4046. Such systems are referred as I-path E-traps or Fourier Transform (FT) I-path electrostatic traps. I-path E-traps are shown in **Fig.2**. An early proposal of I-path E-trap with image current detector has been made in US3226543, though primarily designed for mass analysis with additional mass selection by pulsing mirror caps.

Prior art I-path E-traps employ coaxial ion mirrors. Typical size between mirror caps is from 0.4 to 1m. Large size of the system inevitably causes low oscillation frequency (under 100kHz for 1000amu ions), large size of image detector (several cm), poor sensitivity of image current detector and slow acquisition speed. A combination of two leads to strong space charge effects, such as self bunching of ion packets and peaks coalescence.

In US5886346 Makarov suggested **Orbital Trap** - another type of E-trap with image charge detector (commercial name 'Orbitrap'). The Orbital Trap is a cylindrical and substantially three dimensional electrostatic trap with hyper-logarithmic field. The field structure is formed between a curved inner spindle electrode and a curved outer electrode. Pulsed injected ion packets rotate around the spindle electrode and oscillate in nearly ideal harmonic axial field. Image charge detector senses ion axial oscillations.

Compact structure of Orbitrap (typical id <4cm) helps to lower detection limit down to 5 elementary charges (A. Makarov, E. Denisov, "Dynamics of Ions of Intact Proteins in the Orbitrap Mass Analyzer", J. Am. Soc Mass Spectrom, v.20, 2009, No.8, pp 1486-1495). The combination of so-called C-trap (RF linear trap with curved axis and with radial ion ejection) with Orbitrap (shown in **Fig.3**) provides larger space charge capacity (**SCC**) per single ion injection SCC = 3E+6 ions/injection (A. Makarov, E. Denisov, O. Lange, "Performance Evaluation of a High-Field Orbitrap Mass Analyzer" J. Am. Soc Mass Spectrom, v.20, 2009, No.8, pp 1391-1396). However, orbital trap suffers slow signal acquisition. Signal acquisition with image detector takes 1 second for obtaining spectrum with 100,000 resolution at m/z=1000. Slow acquisition speed while being a disadvantage on its own also limits the duty cycle to 0.3% in most unfavorable cases. A combination of acquisition speed and duty cycle is further referred as throughput of mass analyzers.

Thus, in the attempt of reaching high resolution the prior art multi-reflecting time-of-flight mass spectrometers and electrostatic traps with image charge detector limit throughput of mass analyzers. For M-TOF typical duty cycle is under 0.1-0.3%. For E-traps the duty cycle is under 0.3-1% and data acquisition speed is limited to few spectra a second.

The goal of the present invention is to improve acquisition speed and duty cycle of high resolution electrostatic traps in order to match intensity of modern ion sources exceeding 1E+9 ions/sec and to bring acquisition speed to 50-100 spectra/sec required by tandem mass spectrometry while keeping resolution in the order of 50,000-100,000.

SUMMARY

I realized that parameters of electrostatic trap (E-trap) with ion frequency detection can be substantially enhanced if using substantially planar two-dimensional E-trap (**Fig.4**) instead of coaxial E-traps (**Fig.2**). For clarity, the invention employs two-dimensional fields of planar symmetry (**P-2D**) contrary to prior art employing two-dimensional fields of cylindrical symmetry (**C-2D**).

Use of P-2D fields and elongation of ion mirrors in one direction (Z in **Fig.4**) allows extending spatial volume of the analyzer, while keeping small distance between ion mirror caps (L in **Fig.4**). While high resolution is provided by isochronous properties of two-dimensional ion mirrors the duty cycle, space charge capacity and space charge throughput of the novel instrument are enhanced by:

- Larger volume occupied by ion packets within the two-dimensional E-trap;
- Larger volume occupied by ions within the elongated pulsed converter;
- Larger duty cycle of elongated pulsed converter;
- Shorter distance L between mirror caps which allows higher frequency of ion oscillations;
- Shorter distance between ion packets and detector (H/2) which allows using shorter ion packets.

The invention claims three geometries of substantially planar two-dimensional (P-2D) electrostatic fields which can be extended in one direction, namely:

- P-2D fields within parallel straight mirrors;
- Substantially P-2D fields within parallel mirrors being closed into cylinder and;

- Substantially P-2D fields within electrostatic sectors with a large curvature.

The invention also suggests method of acceleration of analysis in E-traps by using short ion packets and detecting frequency of multiple ion oscillations either with image charge detector with subsequent Wavelet analysis or with a TOF detector preferably supplemented by ion-to-electron converter. In the latter case the overlapping signals from multiple ionic components and from multiple reflection cycles are deciphered similar to Wavelet approach.

The E-trap of the invention overcomes multiple limitations of prior art electrostatic traps and TOF MS, such as limited space charge capacity of mass analyzer and of pulsed converter, limited dynamic range of detectors and low duty cycle of various pulsed converters. Estimated acquisition speed of 50-100 spectra/sec makes the novel E-trap well compatible with chromatographic separation and tandem mass spectrometry. Multiple enhancements appear while multiplexing of compact E-traps within the same analyzer. The invention also suggests resonant selection of particular ionic component and MS-MS analysis within the electrostatic trap.

According to the first aspect of the present invention there is provided an *electrostatic trap mass spectrometer* comprising:

- An electrostatic trap formed by two parallel ion mirrors spaced by a field free region, said mirrors are substantially two-dimensional with planar symmetry,
- At least one of said mirrors comprise a set of parallel electrodes with shape and potentials being arranged to provide isochronous multiple ion oscillations between said mirrors in the first X direction and stable ion confinement in the second Y direction;
- Bounding means in the third - drift Z direction
- An ion source for generating ions in a wide span of m/z values;
- A pulsed converter for accumulation and pulsed ejection of an ion ribbon elongated in the third Z direction;
- An injection means for injection of said ion ribbon into said electrostatic trap;
- A detector for sensing frequency of multiple ion oscillations within said trap.

According to one particular embodiment of the invention, said electrostatic ion trap further comprises at least one lens in said field free space for assisting ion confinement in Y direction.

According to the most preferred embodiment of the invention, the Z axis of said electrostatic trap *is curved* in order to wrap said electrostatic trap into cylinder. In another preferred embodiment, said drift Z axis is *straight*.

In order to accelerate frequency of ion oscillations an *acceleration voltage* of electrostatic trap is larger than one of the group: (i) 3kV; (ii) 5kV; (iii) 10kV; (iv) 20kV; (v) 30kV and *X length* of said electrostatic trap is smaller than one of the group: (i) 30cm, (ii) 20cm; (iii) 10cm, (iv) 5cm; (v) 3cm.

To make ion signals sharper in time the *ratio to X length* to Y height of mirror electrode windows is larger than one of the group: (i) 10; (ii) 15; (iii) 20; (iv) 25; (v) 30.

To enhance space charge capacity of planar electrostatic trap the ratio of *Z width to X* length of said electrostatic trap is larger than one of the group: (i) 1; (ii) 3; (iii) 3; (iv) 5; (v) 10. For the same reason in said trap wrapped into cylinder the ratio of curvature radius *R to X* length is larger than one of the group: (i) 1; (ii) 2; (iii) 3; (iv) 5; (v) 10.

To provide high resolving power of the analysis, said at least one ion mirror should have at least three *parallel electrodes* to provide all of the following ion optical properties of said electrostatic ion trap: (i) lateral ion focusing for indefinite ion confinement within the trap, (ii) at least second order time of flight focusing with respect to lateral spread and (iii) at least second order time of flight focusing with respect to ion energy. Even more preferably, at least one ion mirror comprises at least four *parallel electrodes* for providing third order time of flight focusing with respect to ion energy. Preferably, at least one ion mirror comprises at least one electrode with *attracting potential* which is at least twice larger than acceleration voltage by absolute value. In one embodiment, parallel plate electrodes of ion mirror are modified for reducing number of adjusted voltages and at least one ion mirror electrode comprises a grove and preferably triangular grove.

In order to trap ions indefinitely within said electrostatic trap, the preferred embodiment provides *bounding means* in Z direction. In various embodiments said bounding means comprise one of: (i) an electrode with retarding potential at Z edge of said field free region; (ii) uneven length of windows in mirror electrodes for distorting Z edge field of at least one ion mirror; (iii) at least one auxiliary electrode

and a slot in at least one outer mirror electrode for penetration of uneven auxiliary field into mirror; (iv) at least one mirror electrode bent near Z edges of said trap. Preferably, said *bounding means* comprise a combination of at least two above described repulsing means for mutual compensation of time-of-flight distortions.

To detect frequency of ion oscillations in said trap the invention employs either image current detector or time-of-flight detector. In one embodiment the detector comprises at least one electrode for sensing *image charge* and wherein signal from said detector is analyzed by Wavelet or Fourier transformation. Optionally said electrodes for sensing image charge comprise multiple *segments, connected to multiple preamplifiers* and multiple data acquisition channels. In another embodiment, ion detector comprises a *time-of-flight detector* sampling a portion of ions per one oscillation. Preferably, said time-of-flight detector further comprises an ion-to-*electron converting surface* and means for attracting secondary electrons onto the time-of-flight detector, wherein said converting surface occupies a fraction of ion path. Optionally, said time-of-flight detector is located within a *detection region* of said electrostatic trap and wherein said detection region is separated from main trap volume by adjustable electrostatic barrier in Z direction.

To accumulate ions from continuous ion sources prior to ion injection into electrostatic trap the preferred embodiment comprises an accumulating *pulsed converter.* In one embodiment, the converter comprises a vacuum portion of a linear radiofrequency (RF) ion trap with radial ion ejection. Preferably, said RF converter is aligned along the drift direction and, preferably, it comprises means for *ion repulsion* at Z edges. It is further preferable, that said ion vacuum RF ion trap converter is *rectilinear*, wherein one electrode of the rectilinear trap comprises a slit for ion radial ejection.

To provide cold cloud of ions within the pulsed RF converter the invention suggests multiple ways of ion cooling in gas collisions. In one embodiment, said vacuum ion trap converter comprises means for *pulsed gas* injection. In another and more preferred embodiment, said vacuum ion trap is in communication with a gaseous ion guide. Preferably, said vacuum ion trap is the extension of said gaseous ion guide and protrudes through stages of differential pumping.

In one particular embodiment, instead of RF ion trap said pulsed converter comprises a set of parallel electrodes with spatially *alternated electrostatic potentials* for periodic focusing and confinement of low divergent ion beam from said ion source.

To inject ions from the pulsed converter and into electrostatic ion trap the preferred embodiment comprises injection means. In one particular embodiment, said ion injection means comprise a *pulsed voltage supply* The supply temporarily lowers entrance potentials of said electrostatic trap at ion injection stage. Such injection assumes injection via a *slit* in one outer mirror electrode. In another particular embodiment, the injection is made via an *electrostatic sector* for transporting ion packets into said electrostatic trap. Yet in another particular embodiment, the injection is made via an injection window and ion trajectories are steered by at least one *pulse deflecting electrode.*

Preferably, the injection means comprise a circuit for *controlling ion filling time* from said ion source in order to keep the preset number of ions within a converter and within said electrostatic trap.

In addition to straight mass spectrometric analysis the preferred embodiment may be employed in various tandem mass spectrometric modes. In one embodiment, said electrostatic ion trap further comprises means for selective resonant *excitation* of ion oscillating motion. Said excitation is designated for mass selection, or subsequent fragmentation. Preferably, said ion trap further comprises a *surface for ion fragmentation* in the plane of ion turn in X direction which is preferably accompanied by a deflector for returning fragment ions into analytical portion of said electrostatic trap.

According to the second aspect, the present invention provides *a mass spectrometer* comprising *an array* of planar electrostatic traps described in the first aspect. Preferably, the array further comprises (i) *an array of pulsed converters* receiving a portion of ions from said ion source and (ii) means for multiplexing ion flow from said ion source into said multiple pulsed converters. The aspect of the invention capitalizes on compatibility of planar ion traps for multiplexing.

According to the third aspect, the present invention provides a mass spectrometer comprising:

- An ion trap with isochronous periodic ion motion:
- A *time-of-flight detector* for sampling a small portion of injected ions per motion cycle.

Preferably, the TOF detector is supplemented by ion-to-electron converting surface within the ion path and means for sampling secondary electrons onto said time-of-flight detector located off the ion

path. The third aspect emphasizes that the novel feature – TOF detector sampling small portion of oscillating ions would benefit any type of ion trap of the group: (i) *electrostatic ion trap, (ii) magnetic ion trap; (iii) penning ion trap; (iv) radio frequency ion trap.*

According to the fourth aspect of the invention, there is provided a planar two-dimensional electrostatic ion mirror wherein at least one electrode has a triangular grove. Such mirror has fewer electrodes and is applicable for electrostatic traps and TOF MS and is particularly valuable for making spatially compact traps. The novel type of planar mirror electrode is separated into a separate aspect of the invention.

According to the fifth aspect of the invention, there is provided *an electrostatic trap mass spectrometer* comprising:

- A set of electrostatic sectors spaced by field free regions, each electrostatic sector being formed by two opposite coaxial electrodes having shape of sector of cylinder;
- Said electrostatic sectors being spatially arranged to close ion path into loop within X-Y plane
- An ion detector for sensing frequency of multiple ion oscillations within said trap;
- Wherein for the purpose of improving throughput and space charge capacity of said electrostatic trap, said electrostatic sectors are extended in the third – drift Z direction longer than distance between opposite sector electrodes.

Though electrostatic trap built of electrostatic sectors formally fit into definition of substantially planar electrostatic trap of the first aspect, the trap with electrostatic sectors is separated as an aspect of the invention since it has distinct topology and a number of generic features of purely planar traps are not applicable to sector solution.

According to the sixth aspect of the invention, there is provided an *electrostatic trap for charged particles* comprising:

- An electrostatic trap formed by two parallel ion mirrors spaced by a field free region, said mirrors are substantially two-dimensional with planar symmetry for isochronous multiple ion oscillations between said mirrors in the first X direction and stable ion confinement in the second Y direction;
- Bounding means in the third Z-direction;
- An injection means for injection of said charged particles into said electrostatic trap.

The aspect is separated since it claims a generic planar trap for charged particles rather than mass spectrometer built of planar electrostatic trap.

According to the seventh aspect of the invention, there is provided a preferred *method* of mass spectrometric analysis comprising the following steps:

- Generating ions in a wide span of m/z values within an ion source;
- Accumulating ions within a pulsed converter;
- Forming substantially two-dimensional X-Y electrostatic trapping field of planar symmetry, said field provides ion repulsion at X boundaries of the field and ion spatial focusing in Y direction;
- Forming an auxiliary repelling field at Z boundaries of said two-dimensional trapping field
- Pulse injecting said ions along X direction into said two-dimensional trapping electrostatic field;
- Sensing frequency of ion oscillations within said electrostatic trapping field;
- Converting frequency spectrum into mass spectrum.

Said electrostatic trapping field is preferably arranged to provide indefinite isochronous ion oscillations in the first X direction and also indefinite ion confinement in the second Y direction;

In one particular method the Z axis is *straight and in another* - said Z axis is closed into loop to wrap said substantially two-dimensional trapping field of planar symmetry into a *cylinder*. The cylindrical geometry is preferred since it automatically solves problem of bounding means in Z direction.

The method preferably employs ion accumulation within a fine *ribbon space*, said accumulation space is substantial extended and orientated along the Z direction and along extended direction of said electrostatic trap. Preferably, ion accumulation comprises radial ion confinement within *radio frequency* (RF) with the most preferred type of RF field - *multipolar* RF field in combination with *ion repulsion* at Z edges. The most preferred multipole RF trapping field is formed within *rectilinear* multipole ion trap at substantially vacuum conditions.

The invention provides multiple ways of reducing space phase of accumulated ion cloud within RF multipolar field. One method comprises a step of *pulsed gas* injection. In another method, said vacuum RF trapping field is arranged in communication with a RF field at substantially gaseous conditions and, preferably, the same said RF trapping field has substantially gaseous conditions upstream and substantially vacuum conditions at far end and in the vicinity of said electrostatic trap. Said communication between two regions is arranged either as *free ion exchange* between regions or a *slow ion propagation* through said vacuum RF trapping field during the time between ion injections into said electrostatic trap. In another method, ion accumulation within trapping RF field comprises *pulsed ion injection* into said RF trapping field, reflecting ions at the back Z end of said RF trapping field with subsequent pulsed locking of said RF trapping field at the entrance end

The method further comprises step of *automatic adjusting* of ion filling time in order to keep a preset target number of ions within the trapping vacuum RF field. The automatic adjustment is complemented by a step of *complete removal of* ion content of RF trapping field after ion injection into said electrostatic trap.

After ion accumulation said trapping RF field is preferably switched off to improve the subsequent step of ion injection into electrostatic trapping field. Then ion injection into said electrostatic trap is preferably made with *pulsed electric field* applied across said ion accumulation region. Preferably, strength of said pulsed electric field is adjusted to keep ratio of *ion energy spread* to acceleration energy equal to one of the group: (i) <10%; (ii) <5%; (iii) V3%; (iv) <1%.

For ion injection into electrostatic trap the method provides a variety of methods for ion injection into said electrostatic trapping field. In one particular method said ion injection is made with pulsed injection from RF trapping field *via a slit* in the outer mirror electrode. Then it is preferable keeping the RF trap in a close vicinity of the electrostatic trap to preserve m/z span of injected ions. In another method, said ion injection is made *via a pulsed deflecting* electrostatic field and via said field free space, said pulsed deflecting field is arranged either within curved electrostatic sector or by a deflection plate. In yet another method, said ion injection is made directly out of trapping radiofrequency field *protruding* through said field free space of electrostatic trap.

The invention allows MS-MS features within electrostatic trapping field. One method further comprises a step of *resonant excitation* of ion motion in any direction for one purpose of the group: (i) *removal* of non desired ion species from the electrostatic trap volume; (ii) *selection* of desired ion species with notched wide bandwidth waveform; (iii) *passing* of single ion species from one portion of said electrostatic trap to another portion. The method further comprises a step of ion *fragmentation* of selected ionic species by colliding them with a surface, said surface is located within said electrostatic trap volume at the plane of ion turning in X direction.

The invention provides considerations on a particular practical problem, wherein the ion optics scheme does not allow simultaneous grounding of both – ion accumulating RF trap and of field free region with detector. In one method, the pulsed converter is arranged at nearly grounded potential, wherein potential of field free space is arranged at nearly accelerating voltage and wherein said frequency detector is connected via capacitors. In another method, said pulsed converter is arranged at nearly acceleration potential, wherein field free space is arranged at nearly ground voltage and wherein said frequency detector is grounded. In yet another method, the RF trap is kept at ground potential at ion accumulation stage and DC potential of the RF trap is lifted for ion injection, which allows keeping field free space and frequency detector grounded.

For long ion accumulation the trapping field has to be at deep vacuum conditions to avoid ion on gas scattering. Partially the problem is solved by step of ion trap baking.

Various embodiments of the present invention together with a arrangement given illustrative purposes only will now be described, by way of example only, and with reference to the accompanying drawings in which:

Fig.1 presents a prior art planar multi-reflecting mass spectrometer with periodic lens for confining ions along a predetermined ion path

Fig.2 presents a prior art I-path electrostatic trap with image charge detection of ion oscillation frequency and two dimensional electrostatic field of cylindrical symmetry;

Fig.3 presents a prior art orbital trap with hyper-logarithmic two dimensional field of cylindrical symmetry in combination with radio-frequency curved ion pulsed converter called C-trap;

Fig.4 presents a block scheme of the preferred embodiment of the invention, also depicting major elements of the preferred embodiment and illustrated on the example of straight planar E-trap;

Fig.5-A presents topology of straight and planar two-dimensional electrostatic field of E-trap of present invention;

Fig.5-B presents topology of substantially two-dimensional electrostatic field of E-trap of present invention which is curved into cylinder for the purpose of ion trapping in Z-direction;

Fig.5-C presents topology and major components of substantially two-dimensional electrostatic field of E-trap of present invention, which is built of electrostatic sectors;

Fig.6 presents preferred embodiment of planar electrostatic trap of the present invention;

Fig.7 presents of sizes and voltages for one particular ion mirror with rectangular electrodes and for one particular for pulsed converter with rectilinear geometry of the invention.

Fig.8 presents an alternative type of ion mirror geometry and compares field distributions for ion mirrors of **Fig.7** and **Fig.8**;

Fig.9-A presents simulated trajectories of injected ion packets for E-trap presented in **Fig.7**;

Fig.9-B presents simulated turn around time for ion packets of **Fig.9A;**

Fig.9-C presents simulated time spread of ion packets after 50ms and assessing aberration limit of resolution above 1,000,000;

Fig.9-D shows simulated initial distribution in time-energy coordinates for ion packets of **Fig.9-A**

Fig.9-E shows simulated initial distribution in space-angle coordinates for ion packets of **Fig.9-A**

Fig.9-F shows simulated initial distribution in time for ion packets of **Fig.9-A;**

Fig.9-G shows simulated initial distribution in energy for ion packets of **Fig.9-A;**

Fig.9-H shows simulated initial spatial distribution for ion packets of **Fig.9-A;**

Fig.9-I shows simulated initial angular distribution for ion packets of **Fig.9-A;**

Fig.10-A presents embodiments of bounding means of the present invention provided to retain ions within E-trap in Z direction;

Fig.10-B presents another embodiment of bounding means of the present invention provided to retain ions within E-trap in Z direction;

Fig.10-C shows simulated ion trajectories at ion repulsion at Z boundaries with the use of combined Z-bounding means;

Fig.10-C shows simulated time distortions at ion repulsion at Z boundaries as a function of ion inclination angle when using either single electron wedge or combined means for Z-repulsion;

Fig.11-A presents a block diagram of image current detector for sensing frequency of ion oscillations within E-trap of present invention;

Fig.11-B shows simulated signal from single electrode image charge detector after 10,000 ion oscillations for ions with arbitrary m/z = 100,000 and 100,001.

Fig.11-C shows frequency spectrum obtained by wavelet analysis of signal in **Fig.11-B**;

Fig.11-D shows frequency spectrum obtained by wavelet analysis of signal similar to one in **Fig.11-B**, but with initial signal to white noise ratio SNR=0.1

Fig.12 presents embodiments with splitting of image charge detectors in Z and Y directions

Fig.13 illustrate a principle of using TOF detector with ion to electron converting surface for detection of ion oscillation frequencies

Fig.14 shows generalized schematic for ion converter of the invention

Fig.15 shows a schematic of a curved pulsed converter suited for cylindrical embodiment of electrostatic trap of present invention;

Fig.16 presents an embodiment of pulsed converter protruding through a field free space of electrostatic trap of present invention;

Fig.17 presents an embodiment of pulsed converter connected to electrostatic trap of present invention via an transporting electrostatic sector;

Fig.18 presents an embodiment of pulsed converter communicating with electrostatic trap of present invention via an opening in field free space and wherein ion injection is assisted by a pulsed deflector;

Fig.19 presents an embodiment of pulsed converter transferring medium energy ion beam within a set of periodic electrostatic lenses;

Fig.20 presents an embodiment of pulsed converter introducing ions via a Z-edge of field free region of electrostatic trap of present invention;

Fig.21 presents the most preferred embodiment of present invention wherein electrostatic trap is curved into cylinder for compact packaging and for avoiding Z-boundary distortions and wherein the electrostatic trap mass spectrometer is combined with a chromatograph and with first mass spectrometer for MS-MS; Such embodiment is intended for rapid and sensitive LC-MS-MS analysis;

Fig.22 demonstrates a principle of multiplexing of several electrostatic traps of present invention;

Fig.23 demonstrate principles of selecting of ionic species of interest with further subjection of those species to surface induced fragmentation and mass analysis of fragment ions within the same apparatus;

DETAILED DESCRIPTION

Referring to **Fig.1**, a prior art planar M-TOF **11** with periodic lens (WO2005001878) comprises two parallel gridless ion mirrors **12** separated by field free region **13**. Mirrors are substantially elongated along the drift axis Z **14** in order to form two-dimensional electrostatic field. Mirrors comprise at least 4 plate electrodes which are tuned such that to provide spatial ion beam focusing and confinement in Y direction and time-of-flight focusing with respect to ion energy and spatial coordinates. Details of mirror tuning are described in A.N. Verentchikov, M.I. Yavor, Y.I. Hasin, M.A. Gavrik, "Multi-reflecting TOF analyzer for high resolution MS and parallel MS-MS", Mass Spectrometry, v.2 (2005) 11-20 and Yavor M. et al, "Planar Multi-reflecting time-of-flight mass analyzer with a jig-saw path", Physics Procedia 1 (2008), 391-400. A pulsed converter **15** externally forms ion packets **16.** Ion packets are pulse injected into the analyzer at small angle to axis **X**. Ion packets are reflected between mirrors **12** while slowly drifting along the Z axis this way progressing along a zigzag trajectory **17** towards the time-of-flight detector **18**. Detector usually comprises either micro channel plates (MCP) or secondary electron multiplier (SEM). A set **19** of periodic lenses is inserted into a field free region **13** to retain ion packets along the zigzag trajectory **17**. Without such periodic lens ions would spread in Z direction and the number of ion reflections from ion source to detector would vary depending on inclination angle. Such spectrum would be hard to interpret. Since ions travel along the same path without overlapping, the TOF instrument **11** provides full mass range analysis. However, the spatial size of the ion packets has to be relatively small compared to conventional TOF analyzers.

A combination of planar MR-TOF with a pulsing trap allows reaching almost unity duty cycle in case of low intensive ion sources. However, in case of using intensive ion sources the duty cycle becomes severely limited by space charge capacity of the pulsing trap and of the analyzer. As described in ,B. Kozlov, Yu. Hasin, S. Kirillov, A. Monakhov, A. Trufanov, M. Yavor, A. Verentchikov, "Space Charge Effects in Multireflecting Time-of-flight Mass Spectrometer", Proc. of 54- th ASMS Conference on Mass Spectrometry, May, 2006, Seattle, WA, USA and in B.N. Kozlov, Yu,I. Khasin, S.N. Kirillov, A.S. Trufanov, M.A. Gavrik, A.N. Verenchikov, "Experimental Studies of space charge effects in multi-efleting time-of-flight analyzer" Nauchnoe Priborostroenie (Ru), v.16 (2006), No.3, pp. 49-58, the number of ions per pulse in the trap is limited under 3E+4 ions/shot/(full mass range). Space charge within the analyzer limits ion intensity under 1E+3 ions/shot/peak before affecting resolution and under 1E+4ions/shot/peak before affecting mass accuracy of analysis. The space charge limitation in trap-MR-TOF occurs because of small ion packets volumes. Within the trap the ion cloud area is about $10mm^2$. At intermediate focusing planes of the analyzer the ion packets get compressed under 100um length and ion packets volume becomes less than $1mm^3$. This allows estimating critical for TOF MS space charge density as 1E+3 ions/mm^3. At typical repetition rate of 1kHz the analyzer is capable of handling only 1E+6 ions/second/peak and 3E+7 ions/second/(full mass range), while presently existing intensive ion sources generate up to 1E+9 ions/sec. Thus, the duty cycle of MR-TOF is limited to 0.1% in the less favorable case of single intense peak and dynamic range is limited to 1E+5/sec.

Space charge effects in prior art MR-TOF have been treated theoretically. In the approximation of small space charge effect the maximal resolution of the MR-TOF instrument is estimated as ratio of the average field strength of the analyzer (approximately 10^4V/m) to field strength of space charge, which is approximately 0.01V/m at 1000 ions/mm^2. The number has been experimentally confirmed in MR-TOF analyzers (earlier referred papers by Kozlov et.al.).

Referring to **Fig.2**, a prior art E-trap **21** of US6744042 comprises two coaxial ion mirrors **22** – **22A** and **22B**, spaced by field free region **23**. Each mirror comprises 4 ring electrodes **24** with uniform repelling field and a single mirror lens **25** with repelling potential for spatial ion focusing. In simulations the system provides 10,000 resolution at 1% energy spread of ion packets. The coaxial E-trap **21** further comprises a pulsed ion source **26**, a set of pulsed power supplies **27A** and set of DC supplies **27B** connected mirror electrodes and an image current detector **28**. Spacing between mirror caps is 400mm and acceleration voltage is 4kV.

In operation, the ion source **26** generates ion packets at 4keV energy which are pulsed admitted into spacing between ion mirrors by temporarily lowering mirror voltages. After restoring mirror voltages the admitted ion packets oscillate between ion mirrors along the **Z** axis **30**, thus forming I-path ion trajectories. The beam is spatially focused to 2mm diameter and is extended along **Z** axis to approximately 30mm, i.e. ion packet volume can be estimated as $100mm^3$. Oscillating ion packets induce image current signal on cylindrical detector electrode. The signal is analyzed using Fourier transform analysis. Typical oscillation frequency is 300kHz for 40amu ions (corresponding to F=60kHz for 1000amu ions considered elsewhere in this application). Signal is acquired at 0.1-10 second time span.

The invention describes self bunching effects of space charge as the main factor governing time of flight properties of electrostatic trap. Estimation of signal based on typical detection threshold (at least 100 ions per packet) allows estimating typical number of ions per packet in US6744042 to be above 1E+6 ions, i.e. charge density in ion packets exceeds 1E+4 ions/mm^3, which is at least 10 times higher than in MR TOF of **Fig.1**.

Referring to **Fig.3**, a prior art orbital electrostatic trap **31** of US5886346 comprises two coaxial electrodes **32** and **33** forming a hyper logarithmic electrostatic field. Typical diameter of the orbital trap field is under 4cm. Ions (shown by white arrow **37**) are generated by external ion source (not shown), enter C-trap **34**, get stored within a C-trap **34** within a moderately elongated volume **35** and get pulsed injected into hyper-logarithmic field of the orbital trap **31**. Details of C-trap are presented in "Dynamic range of mass accuracy in LTQ Orbitrap hybrid mass spectrometer", JASMS 17 (2006) 977-982. Ramping of electric potential on the internal electrode **32** allows indefinite trapping of ions. Ion packets rotate around the central electrode **32**, while oscillating in axial parabolic field. The external electrode **33** is split into two **33A** and **33B** and a charge sensitive amplifier **36** detects differential signal induced by ion passage across the electrode gap. Fourier transform of image current signal provides spectrum of oscillation frequencies which then converted into mass spectrum.

An orbital electrostatic trap US (Makarov) with C-trap provides much larger space charge capacity per single ion injection – up 3E+6 ions per injection (JASMS 2009). Much higher space charge capacity of the Orbital trap appears because of:

a) Larger ion packets volume ~$100mm^3$ in the orbital trap and

b) Lower sensitivity of Orbitrap to phase shifts of ion oscillations compared to time-of-flight mass spectrometers which always deal with short ion packets.

However, orbital trap suffers slow signal acquisition - it takes 1 second for obtaining spectrum with resolution ~100,000. Slow acquisition speed appears a disadvantage on its own for specific applications, like MS-MS analysis of proteome samples. Besides, the slow acquisition also limits the overall handled ion flux to 3E+6 ions/second/(full mass range) at 100,000 resolution. Thus, in the less favorable case the duty cycle of the orbital trap is limited to 0.3%. Dynamic range is limited to 2E+4/sec.

Thus, in the attempt of reaching high resolution the prior art M-TOF MS and E-traps do limit space charge capacity and throughput of mass analyzers. In most unfavorable cases duty cycle of high resolving power MS is under 0.1-0.3%. The present invention overcomes multiple limitations of prior art..

PREFERRED APPARATUS AND METHOD OF INVENTION

The present invention significantly improves acquisition speed and space charge capacity of electrostatic traps with frequency detector. Primarily space charge capacity is improved by using substantially two-dimensional X-Y fields of planar symmetry and by substantial extension of electrostatic trap in the third direction Z.

Referring to **Fig.4**, and at the level of schematic drawing, the preferred embodiment **41** of electrostatic trap (E-trap) mass spectrometer comprises: an ion source **42**, a pulsed ion converter **43**, ion injection means **44**, an E-Trap **45** with two parallel electrostatic mirrors **46** spaced by field free region **47,** means **48** for bounding ions in the drift **Z** direction and electrodes **49** for image current detection. Said E-trap is substantially two dimensional trap of planar symmetry within **X-Y** plane which is arranged by substantial elongation of mirrors **46** in the drift direction **Z.**

The preferred method of mass spectrometric analysis for the purpose of enhancing analysis throughput comprises the following steps: (a) forming substantially two-dimensional trapping

electrostatic field of planar symmetry (P-2D) in X-Y plane, wherein said field allows repetitive and isochronous ion motion along the first, time-of-flight direction X and wherein said field provides indefinite ion confinement in the second – Y direction; (b) providing weak electrostatic fields at Z edges of the P-2D field in order to bound ion motion in Z direction; (c) generating ions in the external ion source; (d) accumulating ions within a pulsed converter; (e) pulse injecting ion packets from said pulsed converter into said electrostatic field such that ions experience periodic isochronous motion along said axis X; (f) sensing frequency of ion oscillations along X axis by image current detector and (g) converting frequencies of ion oscillations into mass spectrum.

Preferably, said P-2D electrostatic field and said pulsed converter are substantially extended along the third direction Z. Preferably, Z/W ratio of the novel E- trap is larger than 1, 3, 10 or 30.

The novel planar E-trap differs from prior art M-TOF by the following:

- While M-TOF employs periodic lens to confine ions in Z direction and enforces all ion packets to follow the same trajectory, the novel planar E-trap allows ion occupying the entire width of the trap, which increases volume occupied by ions and solves the problem of limited space charge capacity;
- While M-TOF by principle of detection requires very compact packets in X direction, while E-trap allows much longer packets which again increases space charge capacity of E-trap;
- While M-TOF employs time-of-flight principle, i.e. measurement of flight time for determined flight path, the novel E-trap employs principle of electrostatic traps, i.e. ions are allowed to oscillate within the trap and detector measures frequency of ion oscillations
- Besides, extension of novel E-trap in Z direction is accompanied by elongation of pulsed converter which increases space charge capacity of the converter.

The novel planar E-trap differs from prior art coaxial E-traps and Orbital coaxial traps by the following:

- There is distinct difference in the electric field topology. While prior art E-traps employ axially symmetric cylindrical fields the novel planar E-trap employs substantially two dimensional fields of planar symmetry.
- While topology of prior art fields does not allow field extension in one dimension (I-path coaxial E-trap of prior art confines ion packets along the axis and orbital trap is well defined in all three directions), the field of the novel E-trap can be extended in one dimension to increase space charge capacity of the trap.
- Because of extending field in one direction, the novel planar E-trap allows significant shortening of cap-to-cap distance which accelerates ion oscillation frequencies and accelerates analysis.
- Contrary to prior art, the novel E-trap allows reducing distance between ion packets and detector, which also accelerates the analysis without affecting space charge capacity of the trap;
- Besides, the novel planar E-trap employs pulsed converter extended in Z direction which increases space charge capacity of the converter.

Coaxial electrostatic trap with I-path is chosen as the prototype of the invention.

TOPOLOGIES OF P-2D FIELD

Referring to **Fig.5**, the annotation of Cartesian axes is kept throughout the entire application as:

- X – direction along ion isochronous trajectories, trap X dimension is called length L;
- Y – direction in which ion packets are kept narrow, trap Y dimension is called height H;
- Z – direction of ion packets extension, trap Z dimension is called width W;

Referring to **Fig.5**, the isochronous and substantially planar two-dimensional field (P-2D) of the invention is achievable in at least 3 cases:

- P-2D field **51**, formed by straight, parallel and planar ion mirrors spaced by field free region (**Fig.5-A**);
- Substantially P-2D field **52** between parallel mirrors which retain X-Y field structure of **51** but are curved along the curved Z axis or wrapped into cylinder of large radius compared to X length of the trap (**Fig.5-B**);
- Substantially P-2D field of **53** between curved electrostatic sectors which is stretched in Z direction much longer than distance between opposite sector electrodes (**Fig.5-C**).

Referring to **Fig.5-C**, the embodiment **53** of E-trap formed with electrostatic sectors is less preferred and will not be discussed further within the application. For this reason I provide short description here. The embodiment of sector E-trap **53** comprises: electrostatic sectors **54** separated by field free space **55**, image charge detector **56** and boundary means **57**. Preferably, one sector has an electrically isolated segment **58** with a window **59** for ion pulsed admission into the trap. Preferably Z width of E-trap **53** is larger than X-perimeter.

In operation, each sector is composed of a pair of coaxial electrodes. Potentials on electrodes are adjusted to constantly steer ion packets along the sector curvature. Sectors are arranged spatially to provide a closed loop ion orbit in X-Y plane while maintaining isochronous ion oscillations along the curved X axis. Multi-turn TOF with electrostatic sectors of prior art are known to provide first order chromatic focusing and relatively large time-to-spatial aberrations. The embodiment **53** differs from prior art multi-turn TOF by substantial extension of the electrostatic field in Z direction, using bounding means **57** rather than focusing means (i.e. Matsuda focusing plates with the field penetrating to symmetry plane) in Z-direction and by using detection principle of electrostatic trap, rather than TOF detection. Those novel features improve space charge capacity and solve mass range problem of prior art multi-turn TOF.

PLANAR E-TRAP

Referring to **Fig.6**, the preferred embodiment of planar E-Trap **61** of the invention comprises an ion source **62**, a pulsed ion converter **63**, ion injection means **64**, a planar electrostatic ion trap **65** with two planar and parallel electrostatic mirrors **66** substantially elongated in the drift direction Z and spaced by field free region **67,** electrodes **68** for image current detection and means **69** for bounding ions in the drift direction. Optionally, image current detection means are complimented by time-of-flight detector **70**.

It is of principle importance that planar electrostatic ion trap **55** is substantially elongated in the drift direction Z in order to increase space charge capacity of the trap and to improve analyzer acceptance of ion packets.

It is also of principle importance to provide high quality of spatial and time-of-flight focusing of planar electrostatic trap with respect to ion spatial and energy spreads. Planar ion mirrors contain at least 4 mirror electrodes. In prior art M-TOF such mirrors are known to provide indefinite confinement of within the X-Y plane, third order time-of-flight focusing with respect to ion energy, second order time-of-flight focusing with respect to spatial spreads and second order time-of-flight focusing with respect to cross terms including spatial, angular and energy spreads.

The drawing depicts multiple details of the planar E-trap, namely rectilinear RF pulsed converter, preferred structure of mirror electrodes, particular embodiment of bounding means. Those fine details are discussed below in separate sections.

In operation, ions of wide mass range are generated in the external ion source **62**. Ions get into pulsed converter **63** and in the preferred mode are accumulated in the converter **63** extended along Z axis. Periodically ion packets (shown by arrows) are pulsed injected out of converter **63** into the planar E-trap **65** with the aid of injection means **64**. Ion packets are injected along **Y** axis and start oscillating between ion mirrors **66**. Because of moderate ion energy spread in Z direction individual ions slowly drift in **Z** direction. Ion oscillation trajectories are shown by double sided arrows. Periodically once per hundreds of X-reflections individual ions reach the Z-edge of the electrostatic trap they get soft reflected by bounding means **69** and this way revert their slow drift in Z direction.

At every reflection ions pass by detection electrodes **68** and induce image current signal. The ion packet length is preferably kept comparable to intra electrode spacing in Y direction. Periodic image current signal is recorded during multiple ionic oscillations, get analyzed with Fourier transformation or wavelet transformation to extract information on oscillation frequencies. Such frequencies get converted into ions m/z values, since frequencies are reverse proportional to square root of ion m/z. Resolution of Fourier analysis is roughly equal to number of acquired oscillation cycles. However, in the preferred mode of electrostatic trap operation I expect a much faster spectra acquisition. This is achieved by keeping the ion packets short and comparable to Y dimension of electrostatic trap, i.e. ~ 1/20 of X size of the trap. Signals will be much sharper and the required acquisition time is expected to drop proportional to ion packet relative length. In analogy to TOF MS technology the resolving power is limited as R=Ta/2dT, where Ta is analysis time and dT is ion packet time duration.

Preferred the E-trap 61 has the following parameters:

In order to accelerate frequency of ion oscillations and to enhance space charge capacity of the E-trap an *acceleration voltage* of electrostatic trap is larger than one of the group: (i) 3kV; (ii) 5kV; (iii) 10kV; (iv) 20kV; (v) 30kV and *X length* of said electrostatic trap is smaller than one of the group: (i) 30cm, (ii) 20cm; (iii) 10cm, (iv) 5cm; (v) 3cm.

To make ion signals sharper in time the *ratio to X length* to Y height of mirror electrode windows is larger than one of the group: (i) 10; (ii) 15; (iii) 20; (iv) 25; (v) 30.

To enhance space charge capacity of planar electrostatic trap the ratio of *Z width to X* length of said electrostatic trap is larger than one of the group: (i) 1; (ii) 3; (iii) 3; (iv) 5; (v) 10. For the same reason in said trap wrapped into cylinder the ratio of curvature radius *R to X* length is larger than one of the group: (i) 1; (ii) 2; (iii) 3; (iv) 5; (v) 10.

For acceleration of the analysis it is further preferred to keep height Y of the trap at least 10 times smaller than length X. This allows forming relatively short ion packets in X direction which improves speed of data acquisition and space charge throughput of electrostatic traps.

The preferred gas pressure in the electrostatic planar trap **71** is sustained under 10^{-9}Torr and most preferably is under 10^{-10}Torr to avoid ion on gas scattering.

For clarity of description multiple details of electrostatic trap of the invention are described below in separate sections. Those sections cover:

- Space charge capacity and space charge throughput of the novel electrostatic trap;
- Optimal parameters of ion mirrors
- Aberration limit of resolution;
- Embodiments of bounding means;
- Embodiments of the pulsed converter and injection means;
- Embodiments of image current detector;
- Embodiments of time-of-flight detector;
- Embodiments of injection means;
- Strategies of automatic adjustment of the trap filling and analysis time;
- Methods of mass selection within E-trap;
- Multiplexing of electrostatic traps and combination of E-trap with chromatographic devices and tandems for MS-MS.

SPACE CHARGE CAPACITY OF E-TRAP

Increased space charge capacity and space charge throughput of the novel electrostatic trap is the primary goal of the invention. Extending electrostatic ion trap width Z enhances space charge capacity of the electrostatic trap and of the pulsed converter.

For estimation of space charge capacity and speed of analysis I will assume the following exemplar parameters of E-trap: Length X = 100mm, X size of detector =3mm, height Y of intra-electrode gap =5mm, Width Z=1000mm, acceleration voltage =8kV. Based on later presented estimations I assume ion packet height Y =1mm and length X = 5mm.

For those numbers the volume occupied by ion packets can be estimated as V= 5,000mm^2. In other words, the ion packet volume is 5,000 times greater than in prior art M-TOF MS. Besides, electrostatic trap of present invention provides 10 times greater field strength compared to M-TOF and based on M-TOF experience the critical charge density of E-trap can be assessed as n_Q =1E+4ions/mm^3. Those two advantages are expected to allow 50,000 times more ions per injection compared to M-TOF. Space charge capacity of novel electrostatic trap is estimated as 5E+7 ions per injection:

SSC= $V*n_Q$ = 5E+3(mm^3)*1E+4(ions/mm^3) = 5E+7 (ions/injection)

Also in later sections of the application the acquisition time is estimated as 20ms, i.e. acquisition speed is 50 spectra/sec. The space charge throughput of novel electrostatic trap can be estimated above 2E+9 ions/sec per single mass component, which matches ion flux from the modern intensive ion sources.

The above estimations are made assuming relatively short (5mm) ion packets. If not using advantage of short ion packets and analyzing just frequency of the signal the packets height could be made comparable with the single reflection path, say 50mm. Then space charge capacity becomes 10 times higher and equal to 5E+8 ions per injection, while acquisition speed drops 10 times. Space charge throughput (capacity per acquisition time) remains the same, while speed of the analysis drops. Thus, it is advantageous using short ion packets.

The particular embodiment **63** of the pulsed ion converter (a later described rectilinear RF converter with radial ion ejection) approaches the space charge capacity of the electrostatic mass analyzer. Preferably, the inscribed diameter of the rectilinear RF converter is between 2 and 6mm and X dimension of the converter is 1000mm. Typical diameter of ion thread is 0.5mm and the occupied volume is 250mm^3. Space charge disturbance appear only when potential of the ion thread exceeds kT/e = 0.025V. One can calculate that such threshold corresponds to 1E+7 ions per injection. Accounting 50Hz repetition rate of ion ejection the space charge throughput of the pulsed converter is 5E+8 ions/sec, which also matches ion flux from the modern intensive ion sources.

PLANAR ION MIRRORS

Referring to **Fig.7**, in order to estimate the utility of the invention, there is shown one particular example of electrode sections of planar electrostatic trap **71** of the invention together with the planar linear radiofrequency trap – ion converter **72**. Ion converter is described in more detail in later section.

Ion mirrors with high quality of spatial and time-of-flight focusing are known within multi-reflecting time-of-flight technology (M-TOF). Ion mirrors of the present invention resemble ion mirrors of prior art planar M-TOF. However, the present invention has a number of modification of ion mirror design, primarily driven by (a) a necessity of relatively wide spaces between electrodes to avoid electrical discharges at large acceleration voltage and small mirror size and (b) considerations on ion pulsed injection into electrostatic trap.

The drawing depicts sizes and voltages in particular example **71** of ion mirrors in E-trap for a chosen acceleration voltage is U_{acc}= -8kV. In one particular embodiment the voltages may be offset to allow grounding of the field free space. The distance **73** between mirror caps is L=100mm, each ion mirror comprises 4 plates with square windows of 5mm and 3mm high (for M4 electrode). To assist ion injection via mirror cap, the outer plates **74** of ion mirrors are provided with slits for ion injection; the potential on the outer plate **74** is pulsed. To avoid electrical discharge between mirror plates the ion mirror **71** is designed to have 3mm intra electrode gap for M4 electrode with highest voltage. Such gap is sufficient to stand at least 15kV voltage difference.

For the purpose of even distribution of ion packets along the Z dimension and for the purpose of compensating minor mechanical misalignment of ion mirrors the invention suggests a use of electrostatic controllable wedges. Referring to **Fig.7,** slit in the bottom electrode **75** allows penetration of fringing field created by at least one auxiliary electrode. In one particular embodiment, the auxiliary electrode **76** is tilted compared to mirror cap to provide linear Z-dependent fringing field. Depending on the voltage difference between the bottom mirror cap and the auxiliary electrode the field would create a linearly Z dependent distortion of the field within electrostatic trap in order to compensate small imprecision of parallelism of two mirror caps. In another particular embodiment, a linear set of auxiliary electrodes is stretched along the Z direction. Optionally, voltages of auxiliary electrodes are slowly varied in time to provide ion mixing within the volume of electrostatic trap. Other utility of electrostatic wedge electrodes is described below in multiple sections.

Few practical considerations should be taken into account at mirror construction.

Mechanical accuracy and mirror parallelism should be under 10^{-4} of cap to cap distance L, which translates into accuracy better than 10 microns at L=100mm.

Accounting small thickness of mirror electrodes (2-2.5mm) it is preferred employing rigid materials, such as metal coated ceramics. For precision and ruggedness, the entire ion mirror block may be constructed as a pair of ceramic plates with isolating groves and metal coating of electrode surfaces. A portion of groves should be coated to prevent charging by stray ions.

Referring to **Fig.8**, an alternative mirror shape is employed to reduce number of static and in particular number of pulsed potentials. The shape of cap electrode is composed of straight and angled segments. Such electrode shape could be made, for example, with electric discharge machining. In addition to acceleration potential of field free (Acc) space the mirror employs two other potentials M1 and M2. Proportional geometry of the trap **81** is expanded vertically to show shape of ion trajectories 82. The axial distribution **83** of electric field strength E in the trap **81** is similar to one in previously described ion mirror **71** made of plates with rectangular window.

RESOLVING POWER OF E-TRAP

Referring to **Fig.9**, aberration limit of resolving power (also referred elsewhere as resolution) is defined is simulated together with parameters of injected ion packets for electrostatic trap presented in **Fig.8**. Ion cloud prior accumulated within the RF converter 72 is assumed to have thermal energy. Trajectories of injected ions are shown in **Fig.9-A**. Apparently the beam is focused tightly. The turn around time is estimated as 8-10ns as shown in **Fig.9-B**. The estimated time width of ion packets after 50ms of oscillations is only 20ns, i.e. the idealized electrostatic trap of the invention has aberration limit of resolution above 1,000,000. Details on ion packet initial distribution in time-energy coordinates are shown in **Fig.9-C**. Initial distributions in angle-axial displacement coordinates are shown in **Fig.9-D**. Initial distributions for individual coordinates are shown in **Fig.9-E to Fig.9-I**.

Thus, simulations suggest that RF pulsed converter and simple injection means are capable of forming compact ion packets within the E-trap and for such ion packet parameters the aberration limit of the novel E-trap exceeds one million. This make us believing that practically achieved resolution is rather limited by (a) chosen time duration of ion packets, (b) time spread introduced by image charge detector and (c) time distortions introduced by Z-bounding means.

Let us estimate some of those distorting factors and asses parameters of the particular electrostatic trap **71**. At 8keV acceleration the velocity of 1kDa ions is 40km/s. Then frequency of ion passage by detector is F=400kHz and flight time per single pass T_1=2.5us. Accounting that ion packets are 20-25-fold shorter, i.e. 4~5mm long, the packet time width for 1kDa ions is about 0.1us. Then to acquire spectra with 100,000 mass resolution (corresponding to 200,000 time of flight resolution) it would take 20ms, i.e. approximately 50 times faster than in orbital traps. This is a very substantial gain in speed of data acquisition. Earlier I showed that faster acquisition also converts into very substantial gain in space charge capacity of the electrostatic trap.

BOUNDING MEANS

Bounding means vary depending on the E-trap topology.

Referring back to **Fig.5B**, the most preferred embodiment of bounding means for cylindrical electrostatic trap comprises wrapping itself of the analyzer into cylinder. Simulations suggest that distortion of isochronous ionic motion and of spatial ion confinement occur only at radius R of the analyzer bend equal or larger than ion trap length L. Note, that other practical analyzer shapes are possible, such as stadium shape, wherein straight segmented are bounded by half cylindrical elements. The preferred size of cylindrical electrostatic trap of the invention is H=100mm and R=160mm, which is equivalent to 1000mm perimeter. The cylindrical trap provides similar analytical volume at more compact packaging than the planar trap of **Fig.5-A**.

Referring back to **Fig.5-C**, the preferred embodiment of bounding means for trapping electrostatic sectors comprises either deflector at Z edges of field free region or Matsuda plate known in the prior art. Both solutions provide repulsion of ions at Z boundaries.

Z bounding means for planar electrostatic traps comprise multiple embodiments, though skillful in the art may find other types of bounding means.

Referring to **Fig.10-A**, one embodiment of bounding means comprises weak bend of ion mirrors relative to Z axis which would cause ion reflection at Z-edges as shown in **Fig.10-C**. One option is to mechanically bend mirror electrodes, for example, by using uneven ceramic spacers between metal electrode plates.

Referring to **Fig.10-B** an alternative electronic bend can be achieved by splitting mirror cap electrode and applying additional retarding potential to edge sections. Another embodiment for electronic edge bending is provided with aid of fringing fields penetrating through the slit of mirror cap.

Again referring to **Fig.10-A**, yet another embodiment of the bounding means comprises an additional electrode installed at the edge of field free region. The solution causes slower ion motion in the Z edge area and thus positive time shift. Since other means of **Fig.10-A** and **Fig.10-B** introduced negative time shift a combination of those means would allow partial mutual compensation of time shifts as shown in **Fig.10-D** presenting simulation results for time shifts per edge reflection. Note that by properly choosing average ion energy in Z direction and combining two bounding means one can reach a zero average time shift for ion packets. Still, because of ion energy spread in Z direction there would occur time expansion of ion packets, but not shifting in oscillation frequency!

Referring to **Fig.10-D** time spreading of the ion packets in the Z-edge area could be estimated. For particular presented example at angle within 1.5 degree time spreading of 1000 amu ions per single Z-reflection remains under 0.5ns. Now assuming α=1 degree average angle (energy in Z direction =3eV/charge) and accounting large analyzer width W=1000mm such edge deflections occur once in every 500 oscillations, i.e. once in every 1ms. Time spread at Z-reflections is less than 5E-7 of flight time. Thus, at moderate inclination angles of ~ 1degree the Z-edge deflections would not affect resolution of E-trap up to R = 1,000,000.

E-TRAP WITH IMAGE CURRENT DETECTOR

Referring to **Fig.11-A**, detection means **111** comprise at least one detection electrode **113** and a differential signal amplifier **115** picking the signal between said detector electrode and surrounding electrodes **114**. Flying by ion packet **112** induce image current signal. The signal is differentially amplified, recorded with analog to digital converter **116** and is analyzed either by Fourier transform method or applying a wavelet analysis within a computer **117**. To sustain regular periodic signal, it is preferable keeping detection electrodes in the middle of field free region. For the same purpose it is preferable to arrange ion injection such that intermediate time focusing plane coincide with the middle of field free region.

To accelerate spectra acquisition it is preferable using relatively short ΔX ion packets in X direction. The gain in analysis speed could be estimated as ratio of analyzer length L to the ΔX length of ion packets, with accounting of signal spread by image current detector. Applying numbers for particular embodiment in **Fig.6** the packet length is ΔX=3mm, detector spread is 3-4mm (both add as squares), then the observed signal corresponds to 5mm effective length. For L= 100mm, the acceleration factor equals to 20.

Referring to **Fig.11-B**, the result is illustrated by model simulations. Transient signal is modeled as an image signal between detectors **113**. For each ionic component the signal is spread by 1/20 of flight period assuming Gaussian spatial distribution within ion packets. **Fig.11-B** shows a segment of signal shape for two ionic components with arbitrary masses 1 and 1.00001. Because of very similar masses and frequencies the raw signal of ionic components becomes separated only after 10,000 oscillations. Referring to **Fig.11-C**, using wavelet analysis of 10,000 oscillations the frequency spectrum is recovered. Ionic components are resolved with 200,000 time-of-flight resolution and 100,000 mass resolution. Thus, Wavelet analysis provides mass separation 20 times faster than Fourier analysis of the same signal. Referring to **Fig.11-D**, the analysis enhances signal-to-noise ratio (SNR) proportional to the square root of analyzed periods. In the particular analyzed case the initial spectrum had white noise with RSD 10 times stronger than signal amplitude, i.e. SNR=0.1. After analysis the frequency spectrum has SNR=10, i.e. 100 times better than raw signal. The enhancement equals to square root of 10,000 (i.e. number integrated oscillations). Thus, there is a price paid for speed – 20 fold acceleration of analysis would reduce SNR by 5 fold within individual spectrum. Note, that the detected signal would have non compromised mass accuracy, since ion statistics would not be affecting mass accuracy.

Accounting specifics of ion detection it becomes apparent that signal acquisition should preferably incorporate strategies with variable acquisition time. Longer acquisitions are preferable if ion signal coming of the ion source is weak. Strategies with adjustment or automatic adjustment of ion signal strength and spectral acquisition time are discussed below in the section dedicated to ion injection.

Referring to **Fig.12**, in one particular embodiment, the detection electrodes are split into number of segments either in Z direction **122** and/or X direction **123**. Each segment is then sensed by separate preamplifiers **124** or **125** and optionally connected to separate acquisition channels. Splitting **122** in Z direction allows reducing detector capacity per channel and this way enhances bandwidth of data system. Indeed, capacity between adjacent 100cm wide electrodes is in the order of 100pF, which is 5 times more than capacity in magnetic FTMS instrument. Splitting electrodes drops capacity of individual segments in proportion to Z width of segments. The splitting also allows detecting homogeneity of ion filling of electrostatic trap in Z direction if acquiring data with multiple data channels. In case of large imperfections in analyzer geometry there may appear Z-localization of trapped ions or frequency shifts correlated with Z position. Then a set of auxiliary electrodes **126** could be used for redistributing ions in the Z direction and for compensating frequency shifts.

As will be described below, multiple Z-sections of electrostatic trap may be filled with ions of narrow mass range. Ions are localized in Z-sections of electrostatic trap which is arranged by spatial

modulation in electrode shape **127**. This would allow using narrow bandwidth preamplifiers for multiple detector segments in order to enhance signal to noise ratio.

Splitting **122** of detection electrodes in X direction is likely to accelerate frequency analysis, to improve signal to noise ratio and to remove higher harmonics in frequency spectra by deciphering phase shifts between adjacent detectors. The drawback of such solutions is in raising cost of the instrument by adding extra amplifiers and ADC and in slowing down post-acquisition analysis.

One important practical consideration is the noise induced by power supplies. Typical frequency of pulsed power supplies is in 20-40 kHz range, which appears out of frequency range for ionic signals in the preferred embodiment. This also means that detectors could be floated and capacitive coupled to differential signal amplifier. Still it is safer to keep detectors at ground voltage and surrounded by ground electrodes. In one particular embodiment, the grounded mirror plate is used as a detector. In another particular embodiment, the field free region of the analyzer is ground and ions are injected either from a floated pulsed converter or ions are pulsed accelerated to full energy prior or at the time of ion packet injection into the electrostatic trap.

One embodiment of image charge detector comprises a lens at ground potential in the middle of the field free space. Such lens electrodes would be surrounding image charge detector electrode, which allows keeping image charge detector at nearly ground potential.

Another embodiment of image charge detector comprises capacitive coupling of amplifier to floated image charge detector electrodes.

Yet another embodiment employs a hollow electrode attached to a pulsed power supply. Such electrode is installed between ion pulsed converter and E-trap. Ions are ejected from pulsed converter at nearly grounded potential, get into the hollow electrode – an elevator. During ion passage through the elevator the potential of elevator is brought to acceleration value. Energetic ions get injected into E-trap which can be operated with the grounded field free region. This in turn allows keeping image charge detectors at nearly grounded potential.

E-TRAP WITH TIME-OF-FLIGHT DETECTOR

Referring to **Fig.13**, in addition to image current detector **132** ions are also detected by a more sensitive time-of-flight detector **133**, such as micro-channel plate (MCP) or secondary electron multiplier (SEM). The principle concept of such detection lies in detection of only a small fraction of injected ions per one oscillation cycle. Preferably to detect a small portion of ions per oscillation the detector is placed at far Z-edge of the electrostatic trap. Preferably, in order to make the detector compact and free of dead zones an ion-to-electron converting surface **134** is placed into the ion path and SEM detector is placed outside of the ion path. Optionally, a probability of hitting converter is controlled electronically. Ions hitting ion to electron converter emit secondary electrons. A weak electrostatic or magnetic field is employed to collect secondary electrons onto the SEM. Preferably, ion packets are formed short (say under 10ns) to further accelerate the analysis.

In one particular embodiment, ions are allowed to reach detector whenever they travel into the Z-area of detector.

In another particular embodiment, ions are bound within a free oscillation area and then after ions are well mixed along Z direction, they are allowed to travel into detection area, for example by changing potentials on auxiliary electrode **135**. Such bounding and release are preferably arranged with the aid of electronic wedge electrodes as described in the section dedicated to bounding means.

Yet in another particular embodiment, the converter occupies only small fraction of ion path area and a chosen fraction of ions are sampled at every ionic oscillation.

Yet in another embodiment, ions are directed towards a detector from a small E-trap volume by a short sampling electric pulse, in order to reduce overlapping of different ionic components on the detector and to simplify spectral frequency deciphering. Such sampling pulse could be Z-deflecting pulse providing ion packets a kick to overcome weak Z barrier. Alternatively the sampling pulse could be Y deflecting pulse to divert ion packets from axial trajectory onto i-e converter.

In all of those embodiments, the detector receives ions during multiple ion reflections. There is formed a signal which is similar to image current signal – peaks of various mass components overlap at some particular moments, but not all the time. This allows deciphering oscillation frequencies of every component. Contrary to image current detector, the TOF detector is preferably deals with much sharper peaks. Besides, TOF detector is more sensitive, since it is capable of detecting single ions. Compared to

TOF, the invention allows extension of detector dynamic range by orders of magnitude since ion signal is spread onto multiple cycles.

The novel detection method is applicable to much wider class of TOF and E-trap mass spectrometers. The principle could be employed in already existing multi-pass and multi-turn analyzers, though they do not employ planar electrostatic fields. The invention does not require making E-trap compact. The novel detection principle could be also employed in magnetic FTMS instruments.

ION INJECTION INTO E-TRAP

The application contains multiple embodiments for pulsed converter and injection means.

Ion injection into electrostatic trap of the invention has to satisfy several conditions:

- Pulsed converter should accumulate ions between injections to enhance duty cycle of ion utilization from continuous ion sources;
- Space charge capacity of the converter should be at least 1E+7 ions and ideally above 1E+8 ions to match space charge capacity of electrostatic trap analyzer;
- Preferably, ion storage volume of the converter has to be large and ideally in the order of $100mm^3$ to avoid space charge saturation at long ion storage up to 20msec;
- Preferably, injected ion packets have to be extended along drift Z direction and ideally the packet length match analyzer length, expected to be inn the order of 1000mm
- Preferably, the converter should be placed in close vicinity of the analyzer to avoid limitations on mass span of the injected ions due to time of flight effects;
- Preferably, gas pressure in the converter is under 1E-7 Torr and ideally under 1E-8 Torr to avoid elevated gas pressure in the analyzer;
- Preferably, energy spread of injected ions should stay under 3-5% of acceleration energy, and ideally under 1%, which would correspond to approximately 100eV/charge.
- Preferably, height of ion packets after injection should stay under 30mm and ideally under 3mm.

Injection means have to satisfy the following set of conditions:

- Match shapes of pulsed converter and electrostatic trap;
- Transfer ion packets with minimal time spread and angular spread;
- Provide short ion path ion to preserve mass span of ion packets;
- Provide isolation for differential pumping of pulsed converter and electrostatic trap;
- Provide minimal distortion onto potentials of electrostatic trap.

Referring to **Fig.14**, the embodiment of radio frequency (RF) pulsed converter **141** generalizes a group of embodiments and methods of ion injection. The converter **141** comprises a radio frequency (RF) ion trap **145** having entrance end **144A**, exit end **144B** and side slot **146** for radial ejection. Said converter is connected to a set of DC, RF and pulse supplies (not shown). Preferably, said pulsed converter is a rectilinear quadrupole as depicted in the figure, though the converter may comprise other types of RF ion traps like RF channel, RF surface, RF ring trap, etc. Preferably, RF signal is applied only to middle plates of the rectilinear converter **145** as shown in the icon **150**. Preferably, entrance and exit sections of the converter have electrodes with similar cross section, but those electrodes are electrically isolated to allow DC bias. Figure also depicts other components of electrostatic trap: a continuous or quasi-continuous ion source **142**, a gaseous and RF ion guide at intermediate gas pressure **143**, injection means **147** and a planar electrostatic trap **149** having a mirror cap electrode with injection slot **148**.

Referring to **Fig.15**, the pulsed converter **155** is curved into cylinder to match cylindrical shape of electrostatic trap **159**. Operation of the circular pulsed converter **153** is similar to below described operation of the straight pulsed converter **143**.

Referring back to **Fig.14**, in operation, ions are fed from ion source **142**, pass gaseous ion guide **143** and fill pulsed converter **145**. Said converter provides radial ion confinement by RF field. Further details of ion injection into electrostatic trap **149** are described below when detailing injection means **147**. Now let us concentrate on details of filling the converter.

In one particular method, ions are stored in the converter. For this ions are initially accumulated within the gaseous ion guide **143** and then are pulse injected from gaseous ion guide **143** into the converter **145** through the entrance end **144A**, pass through the converter **145** and get reflected at the exit end **144B** by either RF or DC barrier. After pulsed ion injection into the converter **145** the potential of the

entrance end **144A** is brought up to provide indefinite ion storage within the converter. The duration of the injection pulse is adjusted to avoid return of the lightest ionic component back into the gaseous ion guide **143**.

In another particular method, gaseous ion guide **143** and converter **145** constantly remain in communication and ions exchange freely between those devices for the time necessary for equilibrium between mass components within the converter **145**.

Yet, in another particular method, ions are continuously fed from gaseous ion guide **143** and pass through the converter **145** at small velocity (under 100m/s) and leave through the exit end **144B**. Accounting 1m length of the converter the ion propagation time is above 10ms, i.e. comparable to period between ejections into electrostatic trap (20ms for R=100,000). For this embodiment it is preferable using the same rectilinear electrodes and same RF power supply for both – gaseous ion guide and vacuum converter. In this case there will be no potential barrier between stages.

In those three methods, optionally, a portion of the converter is filled with gas pulse as shown in the icon **150** in order to reduce kinetic energy of ions, either for trapping or for slowing down their axial velocity. Such pulse is preferably generated with a pneumatic valve or by light pulse desorbing condensed vapors off the surface.

Again referring to **Fig.14**, one particular embodiment of injection means comprises an an accelerator **147**, an elongated slot **148** in the mirror cap electrode and a set of pulsed voltage supplies (not shown) connected to the converter **145**, to the accelerator **147** and to mirror electrodes.

In operation, once the converter **145** is filled with ions a voltage pulse is applied to at least one electrode of the converter to induce radial ion ejection through the side slot **146.** Optionally, but not necessarily the confining RF field is switched off prior to ion ejection. Ions accelerated in the accelerator **147** and get into electrostatic trap **149** via the slot in the mirror cap **148**. At injection time, potential of mirror cap **148** is brought lower to introduce ions into the electrostatic trap. Once the heaviest ions leave the region of mirror cap, the potential of mirror cap **148** is brought to normal reflecting value. In the particular example of electrostatic trap of **Fig.7**, the pulsed and reflecting mirror potentials are as shown in **Fig.7**.

Parameters of the converter and injection means are chosen to provide ion packets of 3 to 50mm long, low angular divergence (preferably under 1 degree), full energy (preferably 8,000 eV/charge) and with energy spread of ion packets under 100-300eV in time-of-flight direction **X**.

Repetition rate of injection means is defined by period sufficient to acquire spectra with desired level of resolution. As been described earlier, if injecting relatively short ion packets the oscillation period lasts for 20ms in order to reach R=100,000.

Referring to **Fig. 16 to 18**, there are described other embodiments of injections means which would suit RF pulsed converter of **Fig.13** and **Fig.14**.

Referring to **Fig.16**, one particular embodiment of injection means **161** comprises a rectilinear ion pulsed converter **162** and pulsed accelerator **163**, both protruding through the field free region **164** of the electrostatic trap **165** and a set **166** of power supplies which generates complex pattern of RF and pulsed voltages. Preferably RF signal applied only to middle electrode **167** of the converter 162. The Figure depicts the middle cut of the electrostatic trap in X-Y plane **168**. All components extend along the Z direction.

In operation, ions fill the converter **162**, while being confined by quadrupolar RF field. As been explained in description of **Fig.13**, there are at least three viable methods of operation of the converter: pulsed injection and trapping, free ion exchange between gaseous ion guide and converter and a pass through method.

Once the converter **162** is filled with ions the RF signal is switched off and a set of pulses is applied to the converter **162** and accelerator **163**. Ions are accelerated along the **X** axis and get into the field free region **164** of electrostatic trap **165**. Once ions are ejected the potentials on the converter **162** and accelerator **163** are brought to potential of the field free region **164**, such that ions penetrate through the converter and accelerator without distortions. The embodiment avoids pulsing of mirror voltages. However, it impedes the overall operation of the trap in several ways: the converter can not be filled before completing the acquisition cycle; there is expected interference of strong pulses and RF signals with the image current detector; complex RF and pulsed signals are likely to be noisy.

Referring to **Fig.17**, in another embodiment **171** injection means comprise a static accelerator **173** and a curved deflecting electrostatic sector **176**. The electrostatic sector **176** comprises two equidistant cylindrical electrodes fed by DC power supplies to create a uniform deflecting field. Said sector also has a side window **177**. A pulsed ion converter **172** is coupled to field free region **174** of electrostatic trap **175** via injection means **171**.

In operation, accumulated ions are pulsed ejected out of converter **172**, get accelerated within the static accelerator **176** and enter the sector **176**. The sector bends ion trajectories, such that they become aligned with the X axis **178** of the electrostatic trap **175**. Once all ion packets enter the electrostatic trap the sector field is switched off to allow multiple axial oscillations of ions between ion mirrors. Note that because of moderate requirements to initial time spread of ion packets the sector field can be made of any convenient angle, e.g. 90 degrees. Still isochronous and stigmatic sectors are preferred. Also note that electrostatic sector can serve as an aperture separating differentially pumped stages.

Referring to **Fig.18**, yet in another embodiment **181**, injection means comprise an electrostatic accelerator **183**, a window is the shroud **184** surrounding field free region of electrostatic trap **185**, a set of power supplies **186** and a deflector **187**. A pulsed converter **182** is oriented at small angle to the axis X **188**. In operation, ions are pulsed ejected from the converter **182** by applying pulsed voltages to electrodes of the converter and optionally switching off RF signal on middle electrode of the converter. Ion trajectory get steered by deflector **187** to become aligned with **X** axis and the symmetry axis of electrostatic trap **185**. Once ions are injected and start oscillating between ion mirrors the deflector **187** is switched off.

The solutions of **Fig.17** and **18** allow decoupling the converter from electrostatic trap and avoiding pulsed voltages on ion mirrors. However, those solutions pose limitations onto the injected mass to charge span due to time-of-flight effects within the deflecting devices.

Referring to **Fig.19**, yet in another particular embodiment, pulsed converter comprises electrostatic guide **191**. The guide is formed by two parallel rows of electrodes **192** and **193**. The spacing between rows **194** forms an ion channel along axis Z. Each row contains two alternated electrode groups **192A, 192B** and **193A, 193B.** The spacing between adjacent electrodes is preferably at least two times smaller than distance between the rows. The ion guide has an entrance side annotated by wide arrow **194**, which also indicate direction of entering ion beam. The ion guide has an exit side which is optionally equipped with reflector **195**. A switched power supply **196** feeds two equal and opposite polarity static potentials **U** and **–U**, to electrodes **152A, 152B** and **193A, 193B** in a spatially alternated manner. As one example, negative potential is applied to groups **192A** and **193A** and positive – to **192B** and **193B.** The potentials are switched as shown within the power supply block **196**.

In operation, a continuous, slow and low diverging ion beam is introduced via the entrance side of the ion guide. Preferably, potentials **U** on the guide relate to energy **E** of propagating ion beam **194** as **0.01U<E/q<0.3U**. Spatially alternated potentials create a series of weak electrostatic lens which retains ions within the channel. The retention of ions is proven in simulations. Ion trajectories are shown in the icon **197**. Once ions fill the gap the potentials on electrode groups **192A** and **193B** is switched to opposite polarity. This would create extraction field across the channel and eject ions between **193** electrodes.

In search for more convenient ion injection schemes one may consider sacrificing space charge capacity of the pulsed converter.

Referring to **Fig.20**, in one embodiment, injection means **201** comprise an RF ion trap **202** at intermediate gas pressure, transfer ion optics **203** and pulsed deflectors **208**. The injection means are located at Z edge of planar electrostatic trap **204** with bounding means **205.** Said electrostatic ion trap **205** further comprises a field free space **206** with a slot on Z edge **207**.

In operation, ions are generated within an external ion source (not shown) and are accumulated within the RF ion trap **202**. Periodically and synchronized with operation of electrostatic trap **204** the RF trap ejects ion packets 10-1000ns long. Ion packets get accelerated and transferred within the transfer ion optics **203** (which is preferably differentially pumped), get injected via a side (edge) slot **207** into the field free space **206** at small inclination angle to axis **X**. Optionally, ions get additional steering in pulsed deflection means **208** to reduce inclination angle **210** of ion trajectory. Once ions are injected into electrostatic trap they experience multiple reflections before hitting any of Z-edges of the electrostatic trap **204**. By that time the pulsed deflection means **208** are turned on to retain ions for a desired period of time. Because of naturally occurring spread in ions angular distribution eventually the ion packets get

spread all over Z-width of the electrostatic trap **204**, thus reducing space charge effects onto oscillation frequency.

AUTOMATIC ADJUSTMENT AND TANDEMS WITH E-TRAP

Most commonly mass spectrometers are coupled to chromatography for the purpose of separating components of analyzed mixtures in time. For multiple applications it is preferably employing tandem mass spectrometers, wherein for the purpose of compound identification a single ionic component is separated within the first stage mass spectrometer (MS1), get fragmented within fragmentation cell and masses of fragments are determined within the second mass spectrometer (MS2).

Referring to **Fig.21**, the most preferred embodiment **211** of the invention comprises sequentially connected chromatograph **212**, ion source **213**, a first mass spectrometer **214**, fragmentation cell **215**, gaseous radio frequency RF ion guide **216**, pulsed converter **218** and cylindrical electrostatic trap **219** with an image current detection **220**. Variation of ion flux into electrostatic trap is depicted by symbolic time diagram **217**.

The chromatograph **212** is either liquid (LC) or gas (GC) chromatograph. The ion source is selected based on application and may be of the list: Electrospray (ESI), Atmospheric Pressure Chemical Ionization (APCI), Atmospheric pressure Photo Ionization (APPI), Matrix Assisted Laser Desorption and Ionization (MALDI), Electron Impact (EI) and Inductively Coupled Plasma (ICP). The first mass spectrometer MS1 **214** is preferably quadrupole, though may be an ion trap or magnetic mass spectrometer. The fragmentation cell **215** is preferably collision activated dissociation cell, though may be an electron detachment or surface dissociation cell. The ion guide **216** may be a gas filled multipole with RF ion confinement. Optionally RF guide is rectilinear to match ion pulsed converter of electrostatic trap. The converter **218** is preferably a rectilinear RF device with radial ejection which is shown in **Fig.14** and **Fig.15**, though may be any converter shown in **Fig.16** –**Fig.20**. The electrostatic trap **219** is preferably cylindrical trap described in **Fig.15**, though may be a planar trap of **Fig.14** or circular sector trap depicted in **Fig.4C**. The electrostatic trap is employed as a second stage mass spectrometer MS2. Detection means are preferably a pair of differential detectors with single channel acquisition, though may comprise multiple detector segments split either in Z or X direction.

LC-MS-MS and GC-MS tandems imply multiple requirements on electrostatic trap, such as synchronization and adoption to variable signal intensity. Ion flux from ion source varies in time. Typical width of chromatographic peaks is 5-15 seconds in LC case and 1second in GC case. The invention provides acquisition speed up to 50 spectra a second which exceeds chromatographic requirements. The MS speed is mostly dictated by large ion flux 1E+9 ions/sec during strong chromatographic peaks. During weak chromatographic peaks the sensitivity of the instrument is limited by amplifier noise and by relatively short acquisition time. It is advantageous increasing trap filling time and data acquisition time during elution of weak chromatographic peaks, while accounting such adjustment is final determination of compound concentration. The information on ion flux from the source could be taken either from mass spectrometer signal itself or from ion current measurements on some electrode within the ion transfer optics. The duration of ion filling and signal acquisition could be increased up to 10 ten times before affecting GC separation and up to 50 times before affecting LC separation.

One preferred method of automatic adjustment of electrostatic trap operation is best suited for LC-MS and GC-MS analysis. The method comprises the following steps: admitting variable ion flux into the ion guide **216**; measuring momentarily ion current $\mathbf{I_F}$ from the ion guide into the converter; adjusting duration $\mathbf{T_F}$ of ion flow into the converter in order to fill the converter with the preset target number of charges $\mathbf{N_e=I_F*T_F/e}$; injecting ions from converter into the electrostatic trap **219**; adjusting data acquisition time within the electrostatic trap equal to $\mathbf{T_F}$ and attach the information on the fill time to spectra file; and then going towards the next time step. Mass spectrometry signal is then reconstructed with the account of recorded signal and fill time. Measurements of ion current into the converter could be assisted either with a small wire inserted into ion path or using electrodes of the transfer optics. Alternatively, ion current can be measured based on signal intensity from the previous spectra acquired at known fill time. Switching on and off ion flux into the converter can be assisted either by exit aperture of RFQ or by pulse deflecting ion optics.

For efficient operation of electrostatic trap it is further preferable filtering out ions of the unwanted mass range. As an example, in GC-MS the desired mass range is m/z> 50amu, in LC-MS for metabolomics applications m/z>100amu and in LC-MS for proteomics applications m/z>300. Mass

filtering is preferably done within RF ion guide by setting sufficiently high amplitude of RF signal (also defined by inscribed RFQ diameter and RF frequency).

Target number of charges N_e could be set with wide boundaries in order to quantize fill time. As an example fill time could be varied 2-fold per step. Additional criteria may be employed for setting the fill time T_F. For example, a minimal acquisition time could be set to maintain minimal resolution through chromatogram. A maximal acquisition time could be set to sustain sufficient chromatographic resolution. The user choice of the preset target number of charges N_e is expected to account the average signal intensity from the employed ion source, concentration of the sample and multiple parameters of the application.

Depending on the method of ion injection into the pulsed converter **218** the method of automatic adjustment may be modified in multiple ways. For example, ions may be accumulated within the RFQ ion guide in order to extend data acquisition time or to detect ultra trace compounds above the electronic noise of the image current data system.

For MS-MS analysis one can employ multiple strategies comprising:

- Data dependent analysis where parent mass and duration of individual MS-MS steps are selected after acquiring spectrum of parent masses;
- All mass MS-MS analysis at higher acquisition speed. As an example, complete MS-MS analysis of all parent ionic compounds could be carried within 1 second at 500 resolution of parent mass selection (suitable for including isotopic group of parent ions) and with resolution of fragment analysis equal to 10,000;
- Data dependent acquisition wherein parent ion masses and fill time is selected for high resolution analysis based on all mass MS-MS analysis at moderate resolution.

MULTIPLEXING OF E-TRAPS

Referring to **Fig.22** the electrostatic trap of the invention naturally fits multiplexing solutions. While individual trap is preferably formed by a layer of plates with aligned narrow slot in every plate the set of multiple electrostatic traps **221** is formed within similar layer of plates **222** with multiple narrow slots, wherein each aligned set of slots form an individual electrostatic trap **223**. Plates are attached to the same set of highly stabilized power supplies **224**, but have individual data acquisition channels **225**. The converter **226** is split onto multiple parallel and independent channels. The generic ion source has means for splitting ion stream into sub-streams depicted as white arrows **227**. The sub-streams are time fractions or proportional fractions of the main stream from ion source. Each fraction is directed into individual channel of the pulsed converter.

In one particular embodiment, **221** the sets of slots are arranged in parallel, in another particular embodiment (not shown) the set of slots are arranged radial. Obviously, there are multiple ways of slots alignment. Slots alignment scheme is partially bound to efficiency of arranging pulsed ion converters, to mechanical arrangement of detection electrodes and to convenient access to detection electrode. Partially, slots location depends on various practical constrains if using independent ion injection into individual set of slots which form a set of independent electrostatic traps.

In one particular method of the invention, multiple electrostatic traps are preferably operated in parallel for analysis of the same ion stream for the purpose of further enhancement of space charge capacity, resolution of the analysis and dynamic range of electrostatic trap. Gain in resolution is proportional to increasing of data acquisition time until the trap hit aberration limit. The gain in charge capacity and dynamic range is proportional to number of electrostatic ion traps if using equal ion loads into individual traps. An even stronger improvement of dynamic range may be obtained if varying a portion of ion loads between traps. Then electrostatic trap with maximal load would be employed for detection of weak compounds while electrostatic traps with the smaller load would be employed for unaffected detection of major ionic compounds. Then multiplexed electrostatic traps could be employed for coupling with even more intensive ion sources, such as electron impact ion source or inductively coupled plasma ionization source or glow discharge ion source.

In another particular method of the invention, multiple electrostatic traps are operated independent for analysis of multiple ion sub-streams. Such sub-streams are obtained either from different ions sources or could be time slices of the same ion stream. The most promising direction is analysis of time slices of main ion stream, formed in MS-MS analysis or past an ion mobility spectrometer. In this case time fractions of the main ion stream are diverted between multiple electrostatic traps in time dependent or data dependent fashion. Accumulation of diverted sub-streams within multiple channels of

pulsed converter **226** allows simultaneous injection into multiple channels of the multiplexed electrostatic trap **222**, as long as time diversion is tracked within the data acquisition system. Simultaneous ion injection into parallel electrostatic traps allows employing a single pulsed voltage for mirror cap electrode.

Yet in another particular method of the invention, the multiplexed analysis in a set of electrostatic traps is combined with a prior crude mass separation of ion streams into m/z fractions and forming sub-streams with narrow m/z range. This allows using narrow bandwidth amplifiers with significantly reduced noise level and this way improving detection limit, ultimately, to single ion. The dynamic range of such analysis is estimated as DR = 1E+9/second. Even further enhancement of dynamic range could be obtained if using automatic adjustment of the injected portion of sub-streams. While weak mass components could be recorded with a full ion load the strong mass components could recorded with a partial ion load.

Multiplexing of planar structures is perfectly compatible with ultra miniaturization while employing such technologies of trap making as micromachining, electro erosion, electroforming, laser cutting and multi-layer printed circuit boards technology.

One skillful in the art may find other practically attractive opportunities offered by multiplexing electrostatic traps at a moderate cost per extra trap, mostly related to extra detector and extra acquisition channel.

MASS SELECTION IN THE E-TRAP

Ion packets are indefinitely confined within the electrostatic ion trap and experience slow losses due to scattering on residual gas and due to coupling of ion motion to detection system. Still, it is expected that ions would experience at least thousands of oscillations with accurately sustained frequency. If desired, the number of oscillations within compact trap could be increased 10-100 fold just by using longer analysis time.

In one particular method of the invention, a weak periodic signal is applied to trap electrodes, such that the resonance between the signal and ion motion frequencies is utilized either for removal of particular ionic components, or for selection of individual ionic components with notched waveform, or for mass analysis with resonant ion ejection out of the ion oscillation volume onto a Time-of-flight detector or a fragmenting surface. Though within some particular oscillation cycles there is observed a spatial overlapping of different ionic components, the component of interest would be receiving distortion at every cycle, while the temporary overlapping component would be receiving only few distortions. If choosing distortion amplitude low and accumulate distortions through many cycles there will appear a sharp resonance in ion removal/selection

For ion removal it is preferable using electrodes in the field free region (like detection electrodes) and to apply a string of periodic Y deflecting short pulses which would exactly fit timing of ion packet passage for particular ionic component. For exciting axial (X direction) ion motion it is preferable to apply accelerating pulses either between electrodes in the field free region or to mirror caps. However, resonant ejection scheme in X direction does not practical.

Resonant excitation in Z direction is more preferable. The potential barriers at Z edges are weak (10-100eV) and it would take moderate excitation to eventually eject all ions of particular m/z range even if excitation pulses are applied within a fraction of Z width.

Referring to **Fig.23**, an example of MS-MS method claims an opportunity of MS-MS in electrostatic traps. Ion selection in electrostatic trap is accompanied by surface induced dissociation on the surface **232** of electrostatic trap **231**. An optimal location of such surface is at the plane of ion turn in the ion mirror. To avoid field distortion during majority of ion oscillation the surface **232** may be located at one Z-edge **233** of the electrostatic trap **231**. The surface is preferably located beyond the weak Z barrier, formed e.g. by electronic wedge **234**. Ion selection is achieved by synchronized string of pulses applied to electrodes **235**. Ions with mass of interest accumulate excitation in Z-direction and pass the Z barrier. Once primary ions hit the surface they form fragments which are accelerated back into the electrostatic trap. To avoid repetitive hitting of fragmentation surface a deflector **236** is employed. The method is particularly suitable in case of using multiple electrostatic traps wherein each trap deals with relatively narrow mass range of ions.

Although the present invention has been describing with reference to preferred embodiments, it will be apparent to those skilled in the art that various modifications in form and detail may be made without departing from the scope of the present invention as set forth in the accompanying claims.

CLAIMS

What I claim is:

1. An *electrostatic trap mass spectrometer* comprising:
   a. An electrostatic trap formed by two parallel ion mirrors spaced by a field free region, said mirrors are substantially two-dimensional with planar symmetry,
   b. At least one of said mirrors comprise a set of parallel electrodes with shape and potentials being arranged to provide isochronous multiple ion oscillations between said mirrors in the first X direction and stable ion confinement in the second Y direction;
   c. Bounding means in the third - drift Z direction
   d. An ion source for generating ions in a wide span of m/z values;
   e. A pulsed converter for accumulation and pulsed ejection of an ion ribbon elongated in the third Z direction;
   f. An injection means for injection of said ion ribbon into said electrostatic trap;
   g. A detector for sensing frequency of multiple ion oscillations within said trap.
2. The electrostatic ion trap as in claim **1** further comprising at least one lens in said field free space for assisting ion confinement in Y direction.
3. The electrostatic ion trap as in claim **1**, wherein said drift Z axis is *straight.*
4. The electrostatic ion trap as in claim **1**, wherein said drift Z axis *is curved* in order to wrap said electrostatic trap into cylinder.
5. The electrostatic ion trap as in claim **1**, wherein *acceleration voltage* of electrostatic trap is larger than one of the group: (i) 3kV; (ii) 5kV; (iii) 10kV; (iv) 20kV; (v) 30kV.
6. The electrostatic ion trap as in claim **1**, wherein *X length* of said electrostatic trap is smaller than one of the group: (i) 30cm, (ii) 20cm; (iii) 10cm, (iv) 5cm; (v) 3cm.
7. The electrostatic ion trap as in claim **1**, wherein *ratio to X length* of said electrostatic trap to Y height of mirror electrode windows is larger than one of the group: (i) 10; (ii) 15; (iii) 20; (iv) 25; (v) 30.
8. The electrostatic ion trap as in claim **2**, wherein ratio of *Z width to X* length of said electrostatic trap is larger than one of the group: (i) 1; (ii) 3; (iii) 3; (iv) 5; (v) 10.
9. The electrostatic ion trap as in claim **3**, wherein ratio of curvature radius *R to X* length of said electrostatic trap is larger than one of the group: (i) 1; (ii) 2; (iii) 3; (iv) 5; (v) 10.
10. The electrostatic ion trap as in claim **1**, wherein said at least one ion mirror comprises at least one electrode with *attracting potential* which is at least twice larger than acceleration voltage.
11. The electrostatic ion trap as in claim **1**, wherein said at least one ion mirror has at least three *parallel electrodes* for providing all of the following ion optical properties of said electrostatic ion trap: (i) lateral ion focusing for indefinite ion confinement within the trap, (ii) at least second order time of flight focusing with respect to lateral spread and (iii) at least second order time of flight focusing with respect to ion energy;
12. The electrostatic ion trap as in claim **1**, wherein said at least one ion mirror comprises at least four *parallel electrodes* as shown in Fig.7 for providing third order time of flight focusing with respect to ion energy.
13. The electrostatic ion trap as in claim **1**, wherein said at least one ion mirror electrode comprises a triangular grove as shown in Fig.8.
14. The electrostatic ion trap as in claim **3**, wherein said *bounding means* in Z direction comprise one of: (i) an electrode with retarding potential at Z edge of said field free region; (ii) uneven length of windows in mirror electrodes for distorting Z edge field of at least one ion mirror; (iii) at least one auxiliary electrode and a slot in at least one outer mirror electrode for penetration of uneven auxiliary field into mirror; (iv) at least one mirror electrode bent near Z edges of said trap.
15. The electrostatic ion trap as in claim **14**, wherein said *bounding means* in Z direction comprise combination of at least two repulsing means for mutual compensation of time-of-flight distortions.
16. The electrostatic trap as in claim **1**, wherein said ion detector comprises at least one electrode for sensing *image charge* and wherein signal from said detector is analyzed by Wavelet or Fourier transformation.
17. The electrostatic ion trap as in claim **16**, wherein said electrodes for sensing image charge comprise multiple *segments*.

18. The electrostatic ion trap as in claim **17**, further comprising *multiple preamplifiers* and data acquisition channels per at least two of said individual segment of image charge electrodes.
19. The electrostatic trap as in claim **1**, wherein said ion detector comprises a *time-of-flight detector* sampling a portion of ions per one oscillation.
20. The electrostatic trap as in claim **19**, wherein said time-of-flight detector further comprises an ion-to-*electron converting surface* and means for attracting secondary electrons onto the time-of-flight detector, wherein said converting surface occupies a fraction of ion path.
21. The electrostatic trap as in claim **19**, wherein said time-of-flight detector is located within a *detection region* of said electrostatic trap and wherein said detection region is separated from main trap volume by adjustable electrostatic barrier in Z direction.
22. The electrostatic ion trap as in claim **1**, wherein said *pulsed converter* comprises a vacuum portion of a linear radiofrequency ion trap with radial ion ejection and wherein said converter is aligned along the drift direction.
23. The electrostatic ion trap as in claim **22**, wherein said ion vacuum ion trap converter comprises means for *ion repulsion* at Z edges.
24. The electrostatic ion trap as in claim **22**, wherein said ion vacuum ion trap converter is *rectilinear* and wherein one electrode of the trap comprises a slit for ion radial ejection.
25. The electrostatic ion trap as in claim **22**, wherein said vacuum ion trap converter comprises means for *pulsed gas* injection.
26. The electrostatic ion trap as in claim **22**, wherein said vacuum ion trap is in communication with a gaseous ion guide.
27. The electrostatic ion trap as in claim **26**, wherein said vacuum ion trap is the extension of said gaseous ion guide and protrudes through stages of differential pumping.
28. The electrostatic ion trap as in claim **1**, wherein said pulsed converter comprises a set of parallel electrodes with spatially *alternated electrostatic potentials* for periodic focusing and confinement of low divergent ion beam from said ion source.
29. The electrostatic ion trap as in claim **1**, wherein said ion injection means comprise a *pulsed voltage supply* for switching potentials of mass spectrometer between stages of ion injection and ion oscillation.
30. The electrostatic ion trap as in claim **1**, wherein said ion injection means comprise *a slit* in one outer mirror electrode.
31. The electrostatic ion trap as in claim **1**, wherein said ion injection means comprise an *electrostatic sector* for transporting ion packets into said electrostatic trap.
32. The electrostatic ion trap as in claim **1**, wherein said ion injection means comprise an injection window and at least one *pulse deflecting electrode* within said field free region.
33. The electrostatic ion trap as in claim **1**, wherein said ion injection means comprise a circuit for *controlling ion filling time* from said ion source.
34. The electrostatic ion trap as in claim **1**, further comprising means for selective resonant *excitation* of ion oscillations within said electrostatic trap.
35. The electrostatic ion trap as in claim **1**, further comprising a *surface for ion fragmentation* in the plane of ion turn in X direction.
36. The electrostatic ion trap as in claim **35**, further comprising a deflector for returning fragment ions into analytical portion of said electrostatic trap.
37. *A mass spectrometer* comprising *an array* of planar electrostatic traps of claim **1**.
38. The mass spectrometer as in claim **37** further comprising (i) *an array of pulsed converters* receiving a portion of ions from said ion source and (ii) means for multiplexing ion flow from said ion source into said multiple pulsed converters.
39. *A mass spectrometer* comprising:
    a. An ion trap with isochronous periodic ion motion:
    b. A *time-of-flight detector* for sampling a small portion of injected ions per motion cycle.
40. The mass spectrometer as in claim **39**, further comprising ion-to-electron converting surface within the ion path and means for sampling secondary electrons onto said time-of-flight detector located off the ion path.
41. The mass spectrometer as in claim **39**, wherein said ion trap is one of the group: (i) *electrostatic ion trap, (ii) magnetic ion trap; (iii) penning ion trap; (iv) radio frequency trap.*
42. *A planar two-dimensional electrostatic ion mirror* wherein at least one electrode has a triangular grove as shown in Fig 7.

43. *An electrostatic trap mass spectrometer* comprising:
    a. A set of electrostatic sectors spaced by field free regions, each electrostatic sector being formed by two opposite coaxial electrodes having shape of sector of cylinder;
    b. Said electrostatic sectors being spatially arranged to close ion path into loop within X-Y plane
    c. An ion detector for sensing frequency of multiple ion oscillations within said trap;
    d. Wherein for the purpose of improving throughput and space charge capacity of said electrostatic trap, said electrostatic sectors are extended in the third – drift Z direction longer than distance between opposite sector electrodes.
44. An *electrostatic trap for charged particles* comprising:
    a. An electrostatic trap formed by two parallel ion mirrors spaced by a field free region, said mirrors are substantially two-dimensional with planar symmetry for isochronous multiple ion oscillations between said mirrors in the first X direction and stable ion confinement in the second Y direction;
    b. Bounding means in the third – Z directions;
    c. An injection means for injection of said charged particles into said electrostatic trap.
45. *A method* of mass spectrometric analysis comprising the following steps:
    a. Generating ions in a wide span of m/z values within an ion source;
    b. Accumulating ions within a pulsed converter;
    c. Forming substantially two-dimensional X-Y electrostatic trapping field of planar symmetry, said field provides ion repulsion at X boundaries of the field and ion spatial focusing in Y direction;
    d. Forming an auxiliary repelling field *at Z* boundaries of said two-dimensional trapping field
    e. Pulse injecting said ions along X direction into said two-dimensional trapping electrostatic field;
    f. Sensing frequency of ion oscillations within said electrostatic trapping field;
    g. Converting frequency spectrum into mass spectrum.
46. The method as in claim **45,** wherein said electrostatic trapping field is arranged to provide indefinite isochronous ion oscillations in the first X direction and also indefinite ion confinement in the second Y direction;
47. The method as in claim **45**, wherein said Z axis is *straight*.
48. The method as in claim **45**, wherein said Z axis is closed to wrap said substantially two-dimensional trapping field of planar symmetry into a *cylinder*.
49. The method as in claim **45**, wherein *energy of injected ions per charge* is larger than one of the group: (i) 3kV; (ii) 5kV; (iii) 10kV; (iv) 20kV; (v) 30kV.
50. The method as in claim **45**,, wherein *X length* of said electrostatic trapping field is smaller than one of the group: (i) 30cm, (ii) 20cm; (iii) 10cm, (iv) 5cm; (v) 3cm.
51. The method as in claim **45**, wherein *ratio to X length* to Y height of said electrostatic trapping field is larger than one of the group: (i) 10; (ii) 15; (iii) 20; (iv) 25; (v) 30.
52. The method as in claim **47**, wherein ratio of *Z width to X* length of said electrostatic trapping field is larger than one of the group: (i) 1; (ii) 3; (iii) 3; (iv) 5; (v) 10.
53. The method as in claim **48**, wherein ratio of curvature radius *R to X* length of said electrostatic trap is larger than one of the group: (i) 1; (ii) 2; (iii) 3; (iv) 5; (v) 10
54. The method as in claim **45**, wherein *oscillation frequency* of 1000amu ions is larger than one of the group: (i) 100kHz; (ii) 200kHz; (iii) 300kHz; (iii) 500kHz; (iv) 1MHz.
55. The method as in claim **45**, wherein said substantially two dimensional electrostatic trapping field is formed within parallel ion *mirrors* spaced by field free region.
56. The method as in claim **52**, wherein potential in a portion of at least one ion mirror is *attracting* with absolute value exceeding ion energy per elementary charge.
57. The method as in claim **45**, wherein at least one of said ion mirrors has at least three parallel electrodes for providing all of the following *ion optical properties* of said electrostatic ion trap: (i) lateral ion focusing for indefinite ion confinement within the trap, (ii) at least second order time of flight focusing with respect to lateral spread and (iii) at least second order time of flight focusing with respect to ion energy;
58. The method as in claim **45**, wherein said at least one ion mirror comprises at least four parallel electrodes for providing *third order* time of flight focusing with respect to ion energy.
59. The method as in claim **45**, further comprising step of introducing *fringing field* penetrating into electrostatic field of said ion mirror, wherein said fringing field is variable along Z axis for at least one purpose of the group: (i) separating said electrostatic trap volume into portions; (ii) compensating mechanical misalignment of said mirror field; (iii) regulating ion distribution along axis Z, (iv) repelling ions at Z boundaries.

60. The method as in claim **45**, wherein said step of forming an auxiliary repelling field *at Z* boundaries of said two-dimensional electrostatic field comprises at least one of: (i) forming retarding potential at Z edge of said field free region; (ii) electronically distorting field of at least one ion mirror by fringing field penetrating through a slot in outer mirror electrode; (iii) distorting Z edge field of at least one ion mirror by making uneven length of windows in mirror electrodes; (iv) distorting Z edge field of at least one ion mirror by bending outer electrode of said ion mirror (v) combining any two repulsing means for mutual compensation of time-of-flight distortions.
61. The method as in claim **45**, wherein said injected ion *packets are made short* relative to X length of said trapping field.
62. The method as in claim **45**, wherein said step of sensing frequency of periodic motion comprises *image charge* detection.
63. The method as in claim **62**, further comprising a step of converting said signal into mass spectrum with *Fourier* transform analysis.
64. The method as in claim **62**, further comprising a step of converting said signal into mass spectrum with *wavelet* transform analysis.
65. The method as in claim **62**, wherein said image charge detection is made within *multiple sections* of said electrostatic trap field.
66. The method as in claim **65**, wherein said sensing image charge detection is accompanied by multi-channel data acquisition.
67. The method as in claim **66**, wherein said multi-channel detection is used for verifying *homogeneity* of ion density along Z direction within said electrostatic trap.
68. The method as in claim **45**, wherein said step of sensing frequency of periodic motion comprises a step of sampling a portion of oscillating ions onto a *Time-of-flight detector.*
69. The method as in claim **68**, further comprising a step of colliding a portion of oscillating ion packets with a ion-to-electron *conversion surface* and wherein secondary electrons are collected onto a Time-of-flight detector
70. The method as in claim **68**, wherein said time-of-flight detection is made within a *separate detection region* of said electrostatic trap and wherein said detection region is separated from main trap volume by an adjustable electrostatic barrier in Z direction.
71. The method as in claim **45**, wherein said step of ion accumulation within pulsed converter comprises ion accumulation within a fine *ribbon space*, said accumulation space is substantial extended and orientated along the Z direction and along extended direction of said electrostatic trap.
72. The method as in claim **71**, wherein ion path between said ion accumulation region and entrance into said field of electrostatic trap is made at least *3 times shorter* than X length of said electrostatic trap field.
73. The method as in claim **71**, wherein said step of ion accumulation comprises radial ion confinement of ion beam propagating along Z direction within a set of periodically focusing *electrostatic lenses*.
74. The method as in claim **71**, wherein said step of ion accumulation comprises radial ion confinement within *radio frequency* (RF) trapping field.
75. The method as in claim **74**, wherein said radio frequency (RF) trapping field is a *multipole* RF field.
76. The method as in claim **75**, wherein said step of radial ion accumulation within multipole RF trapping field comprises a step of *ion repulsion* at Z edges of said field.
77. The method as in claim **75**, wherein said multipole RF trapping field is formed within *rectilinear* multipole ion trap, and wherein one electrode of the trap comprises a slit for ion radial ejection
78. The method as in claim **75**, wherein said *multipole* ion trapping field is at substantially vacuum conditions.
79. The method as in claim **75**, wherein said step of radial ion confinement within RF trapping field comprises a step of *pulsed gas* injection.
80. The method as in claim **75**, wherein said vacuum RF trapping field is in communication with a RF field at substantially gaseous conditions.
81. The method as in claim **75**, wherein the same said RF trapping field has substantially gaseous conditions upstream and substantially vacuum conditions at far end and in the vicinity of said electrostatic trap.
82. The method as in claim **80**, wherein said RF field allows *free ion exchange* between regions at gaseous and vacuum conditions

83. The method as in claim **80**, wherein said accumulation step comprises *slow ion propagation* through said vacuum RF trapping field during the time between ion injections into said electrostatic trap.
84. The method as in claim **75**, said accumulation step within said trapping RF field comprises *pulsed ion injection* into said RF trapping field, reflecting ions at the back Z end of said RF trapping field with subsequent pulsed locking of said RF trapping field at the entrance end.
85. The method as in claim **75**, further comprising step of *automatically adjusting* of ion filling time in order to keep a preset target number of ions within the trapping vacuum RF field.
86. The method as in claim **75**, further comprising step of *complete removal of* ion content of RF trapping field after ion injection into said electrostatic trap.
87. The method as in claim **75**, wherein said step of ion injection into said electrostatic trap is made with *switching off* said trapping RF field.
88. The method as in claim **45**, wherein said step of ion injection into said electrostatic trap is made with *pulsed electric field* applied across said ion accumulation region.
89. The method as in claim **88**, wherein strength of said pulsed electric field is adjusted to keep ratio of *ion energy spread* to acceleration energy equal to one of the group: (i) <10%; (ii) <5%; (iii) V3%; (iv) <1%.
90. The method as in claim **45**, wherein said step of ion injection is made with pulsed injection *via a slit* in the outer mirror electrode.
91. The method as in claim **45**, wherein said step of ion injection is made *via a pulsed deflecting* electrostatic field and via said field free space, said pulsed deflecting field is arranged either within curved electrostatic sector or by a deflection plate.
92. The method as in claim **45**, wherein said step of ion injection is made directly out of trapping radiofrequency field *protruding* through said field free space of electrostatic trap.
93. The method as in claim **45**, further comprising step of *resonant excitation* of ion motion in any direction for one purpose of the group: (i) *removal* of non desired ion species from the electrostatic trap volume; (ii) *selection* of desired ion species with notched wide bandwidth waveform; (iii) *passing* of single ion species from one portion of said electrostatic trap to another portion.
94. The method as in claim **93**, further comprising step of ion *fragmentation* of selected ionic species by colliding them with a surface, said surface is located within said electrostatic trap volume at the plane of ion turning in X direction.
95. The method as in claim **45**, wherein said step of ion accumulation within pulsed converter is arranged at nearly ground potential.
96. The method as in claim **45**, wherein said step of sensing frequency of ion oscillations is made by detector at nearly ground potential.
97. The method as in claim **45**, wherein said step of ion accumulation within pulsed converter is arranged at nearly ground potential, wherein potential of said pulsed converter is elevated to accelerated potential prior to ion injection into said electrostatic trapping field and wherein field free space of said electrostatic trapping field is arranged at nearly ground voltage which allows keeping said frequency detector at nearly ground potential.
98. The method as in claim **45**, further comprising step of ion trap baking for reaching deep vacuum.
99. *A method* of mass spectrometry analysis comprising parallel analysis within an array of electrostatic traps of claim **45**, said array share the same vacuum chamber and same power supplies but have separate detection means.
100. The method as in claim **99**, further comprising step of ion accumulation within *multiple parallel* pulsed converters.
101. The method as in claim **100**, wherein ion flow from said ion source is multiplexed between said parallel pulsed converters.
102. *A method* of mass spectrometric analysis comprising the following steps:
    a. Forming an electrostatic trap from *electrostatic sectors* spaced by a field free regions, wherein electrostatic field allows isochronous periodic loop ion motion along the first curved X direction and stable ion confinement in the second, orthogonal Y direction;
    b. Sensing frequency of multiple ion oscillations within said trap by detector;
    c. Wherein for the purpose of improving throughput and space charge capacity of said electrostatic trap, said electrostatic trap is extended in the third – drift Z direction longer than distance between opposite sector electrodes.
103. *A method* of mass spectrometric analysis comprising steps of:

a. Forming trapping electrostatic field for indefinite trapping of ions;
b. Said trapping field has characteristic length L per single ion oscillation;
c. Injecting ion packets with a length much shorter compared to L;
d. Sensing image current signal by detectors which are much shorter compared to L and are located in the plane of intermediate and periodic time-of-flight focusing of injected ion packets;
e. Analyzing signal with *Wavelet* transformation for the purpose of acceleration of the analysis.

104. *A method* of mass spectrometric analysis comprising steps of:
a. Forming trapping electrostatic field for indefinite trapping of ions;
b. Said trapping field has characteristic length L per single ion oscillation;
c. Injecting ion packets with a length much shorter compared to L;
d. Colliding a small portion of oscillating ion packets with a ion-to-electron conversion surface located on the ion path and in the plane of intermediate time-of-flight focusing of ion packets
e. Collecting secondary electrons are onto a *Time-of-flight detector*
f. Reconstructing frequencies of ion oscillations for multiple ionic components.

105. The method as in claim **104**, wherein said ion ion-to electron conversion is located within a separate *detection region* of said trapping electrostatic field.

Application No: GB1000649.2 **Examiner:** Mrs Carol Wheeler

Claims searched: 1, 44 & 45 **Date of search:** 21 May 2010

Patents Act 1977: Search Report under Section 17

Documents considered to be relevant:

Category	Relevant to claims	Identity of document and passage or figure of particular relevance
A	-	WO 2008/047891 A3 (SHIMADZU CORPORATION) Abstract and Figures.
A	-	WO 2006/102430 A3 (LECO CORPORATION) Abstract and Figures.
A	-	WO 2007/044696 A1 (LECO CORPORATION) Abstract and Figures.
A	-	US 6888130 B1 (GONIN) Abstract and Figures.
A	-	WO 2008/063497 A3 (BROOKS AUTOMATION) Abstract and Figures.

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X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
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H01J

The following online and other databases have been used in the preparation of this search report

EPODOC, WPI.

International Classification:

Subclass	Subgroup	Valid From
H01J	0049/42	01/01/2006
H01J	0049/04	01/01/2006

Application No:	GB1000649.2	**Examiner:**	Mrs Carol Wheeler
Claims searched:	104	**Date of search:**	15 February 2011

Patents Act 1977
Further Search Report under Section 17

Documents considered to be relevant:

Category	Relevant to claims	Identity of document and passage or figure of particular relevance
Y	104	US 2005/0045817 A1 (YAMAGUCHI ET AL) Abstract and Figure 1.
Y	104	GB 2366909 A (BRUCKER DALTONIK GMBH) Abstract and Figures.
Y	104	GB 2436467 A (ITT MANUFACTURING ENTERPRISES, INC) Abstract and Figures.
Y	104	GB 2246468 A (FINNIGAN MAT GMBH) Abstract and Figure 1.
Y	104	US 2004/0217275 A1 (GONIN ET AL) Abstract and Figures.

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International Classification:

Subclass	Subgroup	Valid From
H01J	0049/42	01/01/2006

Subclass	Subgroup	Valid From
H01J	0049/04	01/01/2006
H01J	0049/40	01/01/2006

Application No:	GB1000649.2	**Examiner:**	Mrs Carol Wheeler
Claims searched:	103	**Date of search:**	15 February 2011

Patents Act 1977
Further Search Report under Section 17

Documents considered to be relevant:

Category	Relevant to claims	Identity of document and passage or figure of particular relevance
A	-	GB 2466551 A (BRUKER DALTONIK GMBH) Abstract and Figures.
A	-	US 2004/0102906 A1 (RODER) Abstract and Figures 10 & 11.
A	-	US 5436447 A (SHEW) Whole document.
A	-	WO 2004/019003 A3 (EFECKTA TECHNOLOGIES CORPORATION) Abstract and Figures 100 & 11.

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International Classification:

Subclass	Subgroup	Valid From
H01J	0049/42	01/01/2006
H01J	0049/04	01/01/2006
H01J	0049/40	01/01/2006

Application No:	GB1000649.2	**Examiner:**	Mrs Carol Wheeler
Claims searched:	43 & 102	**Date of search:**	15 February 2011

Patents Act 1977
Further Search Report under Section 17

Documents considered to be relevant:

Category	Relevant to claims	Identity of document and passage or figure of particular relevance
A	-	US 2009/0179150 A1 (KOVTOUN ET AL) Abstract and Figures 1, 4 & 5.
A	-	US 2007/0114383 A1 (UENO) Abstract and Figures 1 & 5.
A	-	WO 2007/104992 A3 (MICROMASS UK LIMITED) Abstract and Figures 1 & 2.
A	-	EP 2157600 A1 (SHIMADZU CORPORATION) Abstract and Figures 2 & 4.

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H01J	0049/04	01/01/2006
H01J	0049/40	01/01/2006

Application No:	GB1000649.2	**Examiner:**	Mrs Carol Wheeler
Claims searched:	42	**Date of search:**	15 February 2011

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Further Search Report under Section 17

Documents considered to be relevant:

Category	Relevant to claims	Identity of document and passage or figure of particular relevance
A	-	EP 0408288 A1 (KRATOS ANALYTICAL LIMITED) Abstract and Figure 3b.

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X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
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H01J	0049/40	01/01/2006

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Patents Act 1977
Further Search Report under Section 17

Documents considered to be relevant:

Category	Relevant to claims	Identity of document and passage or figure of particular relevance
X	39 at least	US 2005/0045817 A1 (YAMAGUCHI et al) Abstract, Figure 1 and accompanying description.
A	-	WO 2008/046594 A3 (THERMO FISHER SCIENTIFIC GMBH) Abstract and Figures.
A	-	GB 2403063 A (ANATOLI NICOLAI VERENTCHIKOV) Abstract and Figures.
A	-	GB 2455977 A (THERMO FISHER SCIENTIFIC GMBH) Abstract and Figures.
A	-	WO 2009/001909 A3 (SHIMADZU CORPORATION) Abstract and Figures.

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