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(54) **GENERATION OF AN EXACT THREE-DIMENSIONAL QUADRUPOLE ELECTRIC FIELD.**

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US-A- 2 939 952
US-A- 3 527 939
US-A- 3 648 046

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Description

This invention relates to a method of generating a three-dimensional rotationally symmetric quadrupole electric field or an electric field of higher multipole moments inside an electrode structure forming the boundary of the field by application of a resultant electric potential Φ_{qo} to the electrode structure.

Up to now, three-dimensional rotationally symmetric quadrupole fields were generated by an array of metallic electrodes with hyperbolic isopotential surfaces (US-A 2 939 952 and US-A 3 527 939). As an example in Fig. 1 the standard structure is shown, which consists of a ring electrode (1) of radius r and two end caps (2) of distance $2z_0$. r_0 and z_0 are characteristic dimensions, which are related to the spacings of the hyperbolic surfaces from the center of the structure. The application of the three-dimensional rotationally symmetric quadrupole field to trap ions and charged particles and to study the properties of the trapped species and to generate mass spectra is well reported in the literature (Quadrupole Mass Spectrometry- and Its Applications, P.H. Dawson, Ed., Elsevier, Amsterdam, 1976, and D. Price and J.F.J. Todd, Int. Mass Spectrom. Ion Processes, 60 (1984) 3).

For the generation of mass spectra chiefly four methods are described:

- Mass analyser method, disclosed in US-A 2 939 952,
- The mass-selective storage method disclosed in US-A 3 527 939,
- The mass-selective instability method disclosed in US-A 4 540 884,
- Detection of image currents disclosed in US-A 2 939 952, published in E. Fischer, Z. Phys., 156 (1959) 26, employing Fourier Transformation.

The generation of a three-dimensional electric quadrupole field by hyperbolically shaped metallic electrodes generates several severe problems:

- The manufacturing of electrodes is complicated and costly.
- Due to the finite size of the electrodes, field imperfections are generated.
- Since gaps exist between ring and cup electrodes the resulting quadrupolar field is easily influenced by charges accumulated on the surface of the electrodes.
- The detection of the image current signal generated by the ions is disturbed by other electric fields.
- The image current generated by the charged particles depends on their position in the trap, resulting in a noise signal.

Finally, there is one further important disadvantage in generating a three-dimensional electric quadrupole field using hyperbolically curved electrodes:
It is impossible to generate additional electric fields within the same interior region of the electrodes without any interference with the first electric field.

However, employing metallic electrodes of hyperbolic surface is not the only possibility of generating three-dimensional quadrupole fields, although up to now only electrode surfaces following the equipotential surfaces at the boundary of the electric field are commonly used because of prejudice.

Accordingly, it is an object of the invention to provide a method and the corresponding structures for generating a three-dimensional quadrupole electric field or an electric field of higher multipole moments which is much more exact, using no hyperbolically curved metallic electrodes and thus presenting the possibility of superimposing additional homogeneous electric fields without interference with the first electric field.

This object is achieved according to the invention by continuously varying the resultant electric potential Φ_{qo} across the electrode structure.

Since the electric potential applied to the electrode structure is not chosen to be constant, but varies continuously across the electrode structure, those surfaces of the electrode structure forming the boundary of the electric field do not have to be parallel to the equipotential surfaces of the electric field at its boundary. In other words, those parts of the electrode structure forming the boundary of the electric field do not necessarily have to be curved, but are only required to form contours corresponding to the boundary conditions of an implied resultant electric potential generating the quadrupole electric field or an electric field of higher multipole moments.

In one embodiment of the invention the resultant electric potential is continuously varied with position on the surface of the electrode structure adjacent to the electric field. In another embodiment the resultant electric potential is composed of a plurality of single electric potentials being applied each to separate electrodes forming the electrode structure. In both cases as a result there will be an electric potential continuously varied across the electrode structure and generating a quadrupole field.

As a special case of a continuously varied resultant electric potential there can be chosen a linearly varied resultant potential. Even for this special choice there exists an infinite plurality of possible boundary conditions for the resultant electric potential generating the three-dimensional rotationally symmetric quadrupole electric field or an electric field of higher multipole moments. Amongst these boundary conditions there is again a special solution, namely the case of a double-cone shaped boundary in which an applied linearly varied electric potential generates a quadrupole field. Such a double-cone shaped structure can be manufactured very easily and with high precision.

By the choice of an adapt second potential applied to the electrode structure, a second electric field inside the electrode structure which is homogeneous in symmetry axis direction can be generated and superimposed to the quadrupole field without interaction. The possibility of creating such a homogeneous electric field not interfering with the quadrupole electric field is one of the major advantages of the method according to the invention.

The main application of this method will be the field of mass-spectrometry, especially the mass selected analysis of stored ions. In one variant of the method according to the invention the ions to be analyzed are generated outside the electrode structure. They could be e.g. components of an ion beam directed into the electrode structure. Another possibility is the creation of ions out of neutral particles inside the boundary of the quadrupole field. In this case the ionization may be performed by electron impact, ion-impact or resonant photon absorption. Accordingly for the generation of the ions an electron beam, a primary ion beam or a laser beam can be employed. It can be of advantage, if the ionizing beams are pulsed. In this case it is possible to perform the mass-spectrometric analysis of the stored ions in a time-dependent mode by running a plurality of measuring cycles. In certain applications, it might be, on the other hand, desirable to use a c.w. ionizing beam, for example, if a scattering experiment with a primary ion beam shall be performed or, if charge exchange processes are to be studied.

In a variant of the method according to the invention, the above mentioned second, homogeneous electric field inside the boundary of the quadrupole electric field or the electric field of higher multipole moments is used for a mass-to-charge specific excitation of the fundamental frequencies of the ions to be analyzed. This will cause a resonant movement of the excited charged particles in the direction of the symmetry axis. As a result of this resonant movement image current signals are induced in the electrode structure which can be differentially detected and processed into a frequency-analyzer. Employing Fourier Transformation techniques for the frequency analysis can be especially advantageous.

In another variant of the method according to the invention the excitation of the ions under investigation by the second homogeneous field is used for ejecting the ions out of the boundaries of the first electric field and detecting them with a charge-sensitive detector. This can be, for example, desirable, if the number of ions under investigation inside the electrode structure is so small, that the image current induced by the ion movements has an amplitude below the noise signal level. In this case the detection of single ions by an adapt detector, like e.g. a secondary electron multiplier, a channeltron or multi-channel-plates, might be the only alternative to the image current method.

In an embodiment of the invention an electrode structure is operated according to the methods described above. This electrode structure defines on the one hand the boundary of the electric quadrupole field or the electric field of higher multi-pole moments, on the other hand the behaviour of the electric potential being applied to the electrode structure and generating the electric field.

In one embodiment those parts of the electrode structure facing the electric field and defining the boundary of the field consist of electrically resistive material. This can be accomplished either by coating a non-conductive substrate material with resistive material at those parts adjacent to the electric field, or one can use resistance wires for the construction of the electrode structure.

In both cases the operation of the electrode structure is similar to that of a continuous potentiometer and the construction consists substantially of a single part.

In embodiments of the invention the resistance wire can be helically wound or constructed to form a double umbrella frame-work.

In a further embodiment of the invention the electrode structure is built of metallic material. In this case the electrode structure is constructed of a plurality of metallic sheets to which a plurality of single electric potentials is applied constituting a resultant electric potential which in turn generates the quadrupole electric field or an electric field of higher multipole moments. The spatial boundary of the rotationally symmetric quadrupole field can be defined by circular holes with successively varying radii whereby the metallic sheets are disposed with faces parallel in equal or unequal distances.

In an embodiment the metallic sheets are linked together by a resistance network. In this case it is not necessary to generate an adapt potential for each sheet but the negative and the positive output of a single voltage source is applied to the ends of the electrode structure and the resistances of the network are chosen such that the potentials and the single sheets form a resultant continuously varying potential.

In an embodiment the metallic sheets are equally spaced and the resistors are of the same resistance. This facilitates the manufacturing of the electrode structure.

In a further embodiment the metallic sheets with equal areas are equally spaced. Applying RF-voltage to this electrode structure one can even omit the resistance network.

For the passing of the particles under investigation and, if necessary, the ionization means, like e.g. an electron beam, the electrode structures according to the invention comprise apertures. Especially when beams are employed, it is of advantage to dispose the apertures at opposite points of the boundary surface with respect to the symmetry center of the electrode structure. In the case of an "airy" construction, like the helically wound resistance wire or the metallic sheets, the apertures are already built in by the construction principle.

In an embodiment of the invention with a double-cone shaped electrode structure two ring plane electrodes distant $\pm 1\ z_o$ from the plane defined by the annular contact line of the two cones are provided for detecting the image currents of ions moving in symmetry axis direction inside the field boundary.

The invention will now be described and explained in greater detail by way of the embodiments shown in the drawing, it being understood that the features described in the specification and shown in the drawing may be used in other embodiments of the invention either individually or in any desired combination.

In the drawing

- fig. 1 shows a metallic structure with hyperbolic isopotential surfaces for generation of a three-dimensional rotationally symmetric electric quadrupole field by application of the potentials $\pm \Phi_{qo}$ to the ring (1) and end cap electrodes (2);
- fig. 2 shows plane curves in symmetry axis coordinates cross section as a function of r and z with the applied potential varying linearly along these curves;
- fig. 3 shows rhombic plane curves with linearly varied potential;
- fig. 4 shows equipotential lines for the potential generated according to fig. 3 in the rz plane (fig. 4a) and in the xy plane (fig. 4b);
- fig. 5 shows equipotential lines of a homogeneous electric field superimposed to the quadrupolar or higher multi-pole electric field in the structure shown in fig. 3;
- fig. 6 shows a cone shaped surface of region in which exact three-dimensional quadrupole fields and additional homogeneous electric fields are generated;
- fig. 7 shows an embodiment of the electrode structure comprising densely placed equidistant metallic sheets with circular holes to form the inner surface of the cone;
- fig. 8 shows an embodiment of the electrode structure comprising a helically wound resistance wire;
- fig. 9 shows an embodiment of the electrode structure comprising an umbrella framework of resistance wires;
- fig. 10 shows a block diagram of an advantageous realization of the invention;
- fig. 11 shows the shape of excitation pulse for ion excitation in the electrode structure; and
- fig. 12 show pulse sequences employed for generation of mass a and b spectra.

The invention provides a method and the corresponding structures of generating an exact three-dimensional quadrupole field or an electric field of higher multipole moments and a method and corresponding structures for superimposing further homogeneous electric fields in symmetry-axis direction on the first field. The application of the device to store charged particles and to generate mass spectra by simultaneous or consecutive detection of the image currents induced by the charged particles in the electrode structure or by charge detection is also presented.

Principles of Mass Analysis of Charged Particles Trapped in Electric Quadrupole Fields

If positive and negative voltages

$$\pm \Phi_{qo} = \pm (U - V \cos\omega t) \quad (1)$$

are imposed separately on a ring plane electrode and two end-plane electrodes of a cone shaped structure, described in detail later on, three-dimensional rotationally symmetric quadrupole fields are generated within the interior region of the electrode structure. This field will be called trapping field. With ionizing radiation or an electron beam of sufficient energy passing the trap structure, neutral molecules inside the trap are ionized and a number of ions of different mass-to-charge ratio m/q is generated with certain initial conditions of motion.

The trajectories of the charged particles in the fields can be expressed by the canonical form of the linear Mathieu equation

$$\frac{d^2 r}{d^2 \xi} + (a_r - 2q_r \cos 2\xi) r = 0$$

$$\frac{d^2 r}{d^2 \xi} - (a_z - 2q_z \cos 2\xi) z = 0 \qquad (2)$$

with parameters

$$a_r = \frac{8qU}{mr_o^2 \omega^2} \qquad a_z = \frac{16qU}{mr_o^2 \omega^2}$$

$$q_r = \frac{4qV}{mr_o \omega^2} \qquad q_z = \frac{8qV}{mr^2_o \omega^2} \qquad \xi = \frac{\omega t}{z} \qquad (3)$$

The solution of the Mathieu equation leads to stable or unstable trajectories of the charged particles, depending only on the selection of the parameters (3). For a given set of parameters, U, V, r_o, the charged particles of a certain m/q range have stable trajectories, the other charged particles have unstable trajectories. The charged particles of the same mass-to-charge ratio have the same motion regularities which can be considered as the sum of an infinite series of sinusoidal oscillations with frequencies

$$\omega_o = \frac{\beta_{r,z}}{2} \omega$$

$$\omega_1 = \left(1 - \frac{\beta_{r,z}}{2}\right)\omega \qquad (4)$$

$$\omega_2 = \left(1 + \frac{\beta_{r,z}}{2}\right)\omega \qquad \ldots.$$

The characteristic parameters $\beta_{r,z}$ satisfy $0 \leqq \beta$ 1 and have a known relationship with parameters $a_{r,z}$ and $q_{r,z}$. Therefore a relationship between the β values and the m/q ratios can be obtained

$$\beta_{r,z}\ (a_{r,z},\ q^{r}{}_{.z}) = \beta_{r,z}\left(\frac{m}{q}\right) \qquad (5)$$

The component frequencies of ion motion are unique and specific for particular m/q ratios. According to the selected range of stable ions, in practical operation a_r and a_z can be set to zero.

If some form of voltages $\pm \Phi_{zo}$ (t) is imposed additionally on the two end plates of the cone-shaped electrode structure, a second electric field is superimposed in axial (z) direction on the first field. This second field will be called excitation field. It acts on the stored charged particles as expressed by the even linear Mathieu equation

$$\frac{d^2 r}{d\xi^2} + (a_r - 2q_r \cos 2\xi) r = 0$$

$$\frac{d^2 z}{d\xi^2} - (a_z - 2q_z \cos 2\xi) z = F(\xi) \qquad (6)$$

The force F (ξ) depends only on time and not on position of the charged particles.

According to the theory of differential equations the solution of eq. (6) consists of one independent part with initial conditions and of a second part given in eq. (2). When the excitation frequency matches the characteristic frequency of a charged particle with certain m/q or a subharmonic thereof, resonance occurs and the trapped particle moves with a frequency equal to the characteristic frequency. The amplitude of motion will grow linearly with time. The motion of the trapped particles is now coherent in z direction. If the characteristic frequencies of charged particles differ from the excitation frequency no resonance occurs.

In summary, the said quadrupole fields have two functions: to trap charged particles with a certain range of m/q ratios and to cause oscillations with frequencies characteristic for the different m/q ratios of the charged particles. With the aid of excitation fields the characteristic frequencies of the trapped charged particles can be excited, so that the motion is coherent in the z direction. Usually the above mentioned frequencies are in the RF-range.

Generation of Potential Distribution

A Short Description of Theoretical Foundation

In the absence of space charge electrostatic potentials Φ obey the Laplace equation

$$\nabla^2 \Phi = 0 \quad (7)$$

with boundary conditions

$$\Phi \,|_s \quad (8)$$

With given boundary conditions (e.g. the contours of a curved surface and the corresponding potential values on the surface) unique electrostatic fields can be defined within the interior region of the boundaries. However, if once a definite electrostatic field has been defined according to eq. (7) a wide variety of corresponding boundary conditions according to (8) is still possible. If the potential values on each point of a curved surface correspond to the values of the definite electrostatic field at this point, the Laplace equation (7) and the boundary conditions (8) are also satisfied. If we apply this idea to three-dimensional quadrupole fields, we can select the ideal boundary conditions and the ideal electrode configurations for practical applications.

In cylinder coordinates r and z the potential constituting an exact three-dimensional rotationally symmetric quadrupole field is expressed as

$$\Phi_q = \Phi_{qo} \frac{r^2 - 2z^2}{r_o^2} \quad (9)$$

It can be shown that the field resulting from the potential (9) can be generated within interior regions closed by curved surface which is formed by revolution of a plane curve by potentials varied along this plane curve. The equation of the plane curve in plane polar coordinates ρ, Θ, in symmetry-axis coordinate cross section, is

$$\frac{d\rho}{d\theta} = \frac{\rho[\frac{3}{2}\sin 2\theta \,(\frac{4\rho^2}{b^2}\{1 + 3\sin^2\theta\} - 1)^{1/2} \mp (1 - 3\sin^2\theta)]}{\frac{3}{2}\sin 2\theta \mp (3\sin^2\theta - 1)(\frac{4\rho^2}{b^2}\{1 + 3\sin^2\theta\} - 1)^{1/2}} \quad (10)$$

where

$$b = \frac{d\Phi s}{ds} \quad (11)$$

For example, with b = 0 and Φ_s = constant, one obtains from eq. (10) that electrodes with hyperbolic isopotential surfaces, expressed as

$$r^2 - 2z^2 = \text{constant} \quad (12)$$

yield the correct potential (cf. fig. 1).

The second, most important selection is b = constant,

$$b = \frac{d\Phi_s}{ds} = \text{constant} \qquad \Phi_s = bs \quad (13)$$

The potential values vary linearly along the plane curves.

In fig. 2 some of the corresponding plane curves in symmetry-axis coordinates cross section are shown with conditions

$$\left[\frac{\phi_o}{r_o}\right] < b \le \frac{2\sqrt{2}}{\sqrt{3}} \left[\frac{\phi_o}{r_o}\right] \quad (14)$$

The outermost curve is for b = 0.3 V/cm, the next for b = 0.8 V/cm, the third is for b = 1.2 V/cm and the innermost curve is for b = 1.633 V/cm.

As a special case there exist simple rhombic closed-plane curves on which the potential varies linearly. This is shown in fig.3.

Let the expression of one rhombic line AB be

$$z = -\frac{z_o \cdot r}{r_o} + z_o \qquad 0 \leqq r \leqq r_o \quad (15)$$

With the aid of eq. (9) one obtains

$$\Phi_{q,s} = \Phi_{qo} \left(\frac{2r}{r_o} - 1 \right) \qquad (16)$$

Obviously, the potential values on line AB vary with r. Therefore exact three-dimensional quadrupole fields can be generated within an interior region with boundaries revolved in symmetry axis by plane rhombic curves:

$$\begin{aligned} r^2 - 2(z - z_o)^2 &= 0 \qquad z \geq 0 \\ r^2 - 2(z + z_o)^2 &= 0 \qquad z < 0 \end{aligned} \qquad (17)$$

The corresponding contours of the equipotential lines are shown in fig. 4a for the zr plane and in fig. 4b for the xy plane.

In addition a homogeneous field can be generated in the same interior region by applying a second potential which varies linearly along the rhombic boundaries in a way different from the first, for example along the line AB, given in fig. 3

$$\Phi_{zs} = -\frac{\Phi_{z1} - \Phi_{z2}}{2\sqrt{2}\, z_o} r + \Phi_{z1} \qquad (18)$$

This generates the homogeneous field with equipotential lines as shown in fig. 5.

$$\Phi_z = \frac{\Phi_{z1} - \Phi_{z2}}{2z_o} z + \frac{\Phi_{z1} + \Phi_{z2}}{2} \qquad (19)$$

It can be shown that two or more definite electrostatic fields can be obtained within the same interior regions. Each of these fields can be generated by imposing the corresponding continuously varying potential values to the boundary surface. In this way exact three-dimensional quadrupole fields and additional exact excitation fields in symmetry-axis direction can be superposed without interference within the same interior region closed by the cone-shaped surface, shown in fig. 6. The potential constituting the resultant field is given in eq.(20)

$$\Phi(r,z) = \Phi_q + \Phi z = \frac{\Phi_{qo}}{r_o^2}(r^2 - 2z^2) + \frac{\Phi_{z1} - \Phi_{z2}}{2z_0} z + \frac{\Phi_{z1} + \Phi_2}{2} \qquad (20)$$

$+\Phi_{qo}$ and $-\Phi_{qo}$ are the applied potentials to generate a quadrupole field, Φ_{z1} and Φ_{z2} are the applied potentials to generate an additional electric field.

Realizations

The realization of the exact three-dimensional quadrupole field or an electric field of higher multipole moments according to the new method depends on the way of generation of continuously varied potentials on the corresponding boundaries. Such a continuously varied potential can be realized by a potentiometer-type structure employing electrodes made of electrically restistive material, with the voltage needed for generation of the required surface potential applied on the two ends of the electrode structure situated on the z-axis. Typical values of resistance between the two ends of the electrode are ranging from 1 to 100 kΩ.

In an embodiment of the invention the electrode structure consists of a nonconductive substrate material, e.g. ceramics. with an electrically resistive coating.

In a preferred embodiment the electrode structure consists of a polymeric halogenized polyolefin, especially of polytetraflouorine-ethylene (PTFE) like Teflon, having a high share of carbon ranging especially between 10 and 30% wt.

In a special embodiment the resistive material in the electrode structure comprises semiconductor material like Si, Ge or GaAs.

In another embodiment of the invention, a plurality of metallic sheets is employed as electrode structure, the sheets having circular holes with successively varying radii to form the inner surface of the rotationally symmetric field boundary and being densely placed parallel to each other and in equal or unequal distances.

These sheets are linked together by a resistance network dimensioned such that applying a voltage according to eq. (1) to the ends of the network results in a potential according to eq. (9). In the case corresponding to equal sheet distances, all resistors have equal resistance and the network can even be omitted if the areas of each metallic sheet are equal and radio frequency is supplied (cf. fig. 7).

Also other structures to generate the fields can be employed, especially in the case of cone-shaped boundaries. Among these are a structure with a helically-wound resistance wire, as shown in fig. 8, or a double-umbrella framework of resistance wires, shown in fig. 9.

The electrode structures according to the invention comprise apertures disposed at opposite points on the boundary surface with respect to the symmetry center of the cell. The particles to be studied inside the electric field and/or means for ionizing these particles can pass through those apertures. An embodiment of the electrode structure comprises sample beam inlets in the symmetry axis of the electrode structure coaxial with the ionizing electron beam or laser beam discussed later.

Now, as an example, the practical realization of a mass spectro-meter incorporating the electrode structure which consists of metallic sheets of equal surface areas arranged in equal distances, and connected by a network of equal resistors, will be discussed in detail, as applied to the simultaneous image current detection and frequency analysis of mass-selectively stored charged particles, positive or negative ions in this example. A block diagram is shown in fig. 10.

The three-dimensional quadrupole or higher multipole RF field is generated by the potential of the RF supply 10 connected to an electrode structure as shown in fig. 7. The additional homogeneous electric field is generated by the excitation waveform generator 11.

Ions are generated by a pulsed electron beam. The filament supply 12 operates the filament 13, the gate voltage supply pulses 14 the electron beam.

Instead of electron-impact any other ionization techniques can be applied. It is, for example, possible to use an ion beam for secondary ionization of particles inside the cell, especially if one wants to study scattering and charge transfer processes.

Also photoionization can be employed, preferably using a laser beam which can be c.w. or pulsed. Because of the high frequency-selectiveness of photoinization processes the masses of the particles under investigation inside the quadrupole field can be preselected by the choice of the proper excitation frequency leading to photoionization which can in turn be performed using a tuneable laser.

Alternatively, the ions to be studied inside the cell can be injected into the cell already in form of a pulsed or continuous ion beam.

To generate the image current corresponding to the ions of a certain m/q range with stable trajectories, stored in the trap, a pulse of excitation frequencies including all the characteristic frequencies of the ions under investigation is applied, well distributed as shown in fig. 11. The resonant ions absorb power and a coherent motion in z axis direction is generated.

In regard to the working mode and function the structure under consideration is equivalent to a capacitor consisting of a pair of parallel plates. After the excitation pulse, the image current signal induced by the coherent motion of the ions in z axis direction can be detected on the boundary of the structure as if it were a capacitor with parallel plates.

An especially important technique is to employ differential detection of the image current signal at two ring plane electrodes at $z = \pm 1/2\ z_o$ ($2\ z_o$ being the distance from apex to apex of the double cone structure) where the trapping voltage difference is always zero in order to substantially reduce trapping voltage interference with image current detection. Furthermore, a lock-in detector can be used to further reduce this interference in signal detection.

The image current signal is amplified with a high gain broad band amplifier 15. The resulting transient signal can be subjected to digital data processing after digitation with an analog-to-digital converter 16. The frequency spectrum of the characteristic frequencies of the stored ions can be obtained by any frequency analysis technique. Fourier transformation is especially well suited. The frequency analysis and the control is performed by a scan and acquisition computer 17. The timing sequences are referenced to the master clock 18.

Instead of detecting the image current, alternatively the stored ions after mass-to-charge selective ejection by excitation of the fundamental frequencies with the homogeneous electric field can be detected by a charge-sensitive detector like Secondary Electron Multiplier or channel plate. In this case the above mentioned ring electrodes are unnecessary and can even be omitted.

The spectrometer is operated in a pulsed mode, as shown in fig. 12.

In the case of fig. 12a the RF trapping voltage 20 is applied constantly during the experiment. First, all ions being possibly in the trap are quenched by a pulse 21 starting at a time t_1. At t_2 ions are generated with a pulse 22, e.g. an electron beam pulse of electrons having kinetic energy sufficient for ion formation. At t_3 ions are excited with pulse 23 and detected with detection pulse 24 starting at t_4. At the time t_5 a measuring cycle is completed.

In the pulse sequence of fig. 12b the quenching pulse 21 is not activated. Instead, the RF trapping voltage 20 is not constantly applied, but is started at time t_1 and disconnected at time t_5. Ions being in the cell after the time t_5 will, due to their finite kinetic energy, drift to the electrode structure and become neutralized or even pass the field boundary, if they, by chance, find the above mentioned apertures in the electrode structure. At the beginning of the next measuring cycle, with a great probability, there will be no more charged particles inside the field boundary.

The spectral resolution depends on the observation time of the transient signal generated by the coherently moving ions.

In the described electrode structures the trapping quadrupole or higher multipole field and the z axis excitation fields are both exact and without mutual interference, the trajectories of the ions are exactly described by the even linear Mathieu equation. This is a major advantage of the described electrode structure compared to any other trap techniques known. The excitation of the ions is independent of their position in the trap. The image current is proportional to the number of ions in the trap. The m/q ratios of the ions correspond to their characteristic frequencies.

Claims

1. Method of generating a three-dimensional rotationally symmetric quadrupole electric field or an electric field of higher multipole moments inside an electrode structure forming the boundary of said field by application of a resultant electric potential Φ_{qo} to said electrode structure characterized in that said resultant electric potential Φ_{qo} is continuously varied across said electrode structure.

2. Method as claimed in claim 1, characterized in that the resultant electric potential is continuously varied with position on the surface of said electrode structure adjacent said quadrupole or higher multipole field.

3. Method as claimed in claim 1, characterized in that a plurality of single electric potentials being applied each to separate electrodes forming said electrode structure constitute said resultant electric potential continuously varied across said electrode structure.

4. Method as claimed in claim 2 or 3, characterized in that said resultant electric potential is linearly varied along the curve of any center cross section plane of said electrode structure.

5. Method as claimed in any of the preceding claims, characterized by application of a second resultant electric potential to said electrode structure for generating a second, homogeneous electric field in symmetry axis direction superimposed to said three-dimensional rotationally symmetric quadrupole electrical field or the electric field of higher multipole moments without interaction.

6. Method as claimed in any of the preceding claims, characterized by application of the method to mass spectrometric analysis of stored ions.

7. Method as claimed in claim 5 and 6, characterized in that the ions to be analyzed are mass-selectively stored inside said boundary of said quadrupole or higher multipole electric field and that the mass-to-charge specific fundamental frequencies of the ions to be analyzed are excited by said second, homogeneous electric field.

8. Method as claimed in claim 7, characterized in that the image current signals in said electrode structure resulting from the movements of said ions due to resonant excitation by said second electric field are differentially detected.

9. Method as claimed in claim 8, characterized in that a mass spectrum of said ions is generated by application of frequency analysis to said image current signals.

10. Method as claimed in claim 7, characterized in that said ions are ejected out of the boundaries of said quadrupole field and detected with a charge-sensitive detector.

11. Use of an electrode structure in a method as claimed in any of the preceding claims, characterized in that those parts of said electrode structure facing said quadrupole or higher multipole electric field and

thus defining the boundary thereof consist of electrically resistive material.

12. Use of an electrode structure as claimed in claim 11, characterized in that said electrode structure comprises a nonconductive substrate material coated with resistive material at the parts facing said quadrupole or higher multipole field.

13. Use of an electrode structure as claimed in claim 11, characterized in that said electrode structure consists of one or more resistance wires defining said boundary of said quadrupole or higher multipole field.

14. Use of an electrode structure in a method as claimed in any of the claims 1 to 6, characterized in that said electrode structure consists of a plurality of metallic sheets having each a circular hole defining the boundary of said quadrupole or higher multipole field whereby the radius of said hole varies successively from sheet to sheet, the sheets being densely placed with faces parallel in equal or unequal distances.

Patentansprüche

1. Verfahren zum Erzeugen eines dreidimensionalen rotationssymmetrischen elektrischen Quadrupolfeldes oder eines elektrischen Feldes von höheren Multipolmomenten innerhalb einer Elektrodenstruktur, die die Grenze des Feldes durch Anlegen eines resultierenden elektrischen Potentials Φ_{qo} an die Elektrodenstruktur bildet, dadurch gekennzeichnet, daß das resultierende elektrische Potential Φ_{qo} kontinuierlich über die Elektrodenstruktur variiert wird.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß das resultierende elektrische Potential kontinuierlich mit der Position an der Oberfläche der Elektrodenstruktur angrenzend an das Quadrupolfeld oder höhere Multipolfeld variiert wird.

3. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß eine Mehrzahl von einzelnen elektrischen Potentialen, die jeweils an separate Elektroden angelegt werden, die die Elektrodenstruktur bilden, das resultierende elektrische Potential bildet, das kontinuierlich über die Elektrodenstruktur variiert wird.

4. Verfahren nach Anspruch 2 oder 3, dadurch gekennzeichnet, daß das resultierende elektrische Potential linear entlang der Kurve einer beliebigen zentralen Querschnittsebene der Elektrodenstruktur variiert wird.

5. Verfahren nach einem der vorhergehenden Ansprüche, gekennzeichnet durch Anlegen eines zweiten resultierenden elektrischen Potentials an die Elektrodenstruktur zur Erzeugung eines zweiten homogenen elektrischen Feldes in Richtung der Symmetrie-Achse, das dem dreidimensionalen rotationssymmetrischen elektrischen Quadrupolfeld oder dem elektrischen Feld von höheren Multipolmomenten ohne gegenseitige Beeinflussung überlagert ist.

6. Verfahren nach einem der vorhergehenden Ansprüche, gekennzeichnet durch die Anwendung des Verfahrens zur massenspektrometrischen Analyse von gespeicherten Ionen.

7. Verfahren nach Anspruch 5 und 6, dadurch gekennzeichnet, daß die zu analysierenden Ionen massenselektiv innerhalb der Grenze des elektrischen Quadrupol- oder höheren Multipolfeldes gespeichert werden, und daß die Masse-zu-Ladungspezifischen fundamentalen Frequenzen der zu analysierenden Ionen durch das zweite homogene elektrische Feld angeregt werden.

8. Verfahren nach Anspruch 7, dadurch gekennzeichnet, daß die Bildstromsignale in der Elektrodenstruktur, die aus den Bewegungen der Ionen aufgrund von Resonanzanregung durch das zweite elektrische Feld resultieren, differentiell detektiert werden.

9. Verfahren nach Anspruch 8, dadurch gekennzeichnet, daß ein Massenspektrum der Ionen durch Anwendung einer Frequenzanalyse auf die Bildstromsignale erzeugt wird.

10. Verfahren nach Anspruch 7, dadurch gekennzeichnet, daß die Ionen aus den Grenzen des Quadrupolfeldes hinausgeworfen und mit einem ladungssensitiven Detektor detektiert werden.

11. Verwendung einer Elektrodenstruktur in einem Verfahren nach einem der vorhergehenden Ansprüche,

dadurch gekennzeichnet, daß diejenigen Teile der Elektrodenstruktur, die dem elektrischen Quadrupol- oder höheren Multipolfeld gegenüberliegen und somit dessen Grenzen definieren, aus elektrisch resistivem Material bestehen.

12. Verwendung einer Elektrodenstruktur nach Anspruch 11, dadurch gekennzeichnet, daß die Elektrodenstruktur ein nicht leitendes Substratmaterial aufweist, das an den dem Quadrupol- oder höheren Multipolfeld gegenüberliegenden Teilen mit resistivem Material überzogen ist.

13. Verwendung einer Elektrodenstruktur nach Anspruch 11, dadurch gekennzeichnet, daß die Elektrodenstruktur aus einem oder mehr Widerstandsdrähten besteht, die die Grenze des Quadrupol- oder höheren Multipolfeldes definieren.

14. Verwendung einer Elektrodenstruktur bei einem Verfahren nach einem der Ansprüche 1 bis 6, dadurch gekennzeichnet, daß die Elektrodenstruktur aus einer Mehrzahl von metallischen Platten besteht, die jeweils ein kreisförmiges Loch aufweisen, das die Grenze des Quadrupol- oder höheren Multipolfeldes definiert, wobei der Radius des Loches sukzessiv von Platte zu Platte variiert, und wobei die Platten dicht aneinander und die Flächen parallel in gleichmäßigen oder ungleichmäßigen Abständen angeordnet sind.

Revendications

1. Procédé pour produire un champ électrique quadripolaire tridimensionnel de rotation symétrique ou un champ électrique de moments multipolaire plus élevés dans une structure d'électrodes formant la limite dudit champ par application d'un potentiel électrique résultant Φ_{qo} à ladite structure d'électrodes, caractérisé en ce que ledit potentiel électrique résultant Φ_{qo} est continuellement varié en travers de ladite structure d'électrodes.

2. Procédé selon la revendication 1, caractérisé en ce que le potentiel électrique résultant est continuellement varié par rapport à une position sur la surface de ladite structure d'électrodes adjacent dit champ quadripolaire ou multipolaire plus élevé.

3. Procédé selon la revendication 1, caractérisé en ce qu'une pluralité de potentiels électrique unique étant appliqué chacun à des électrodes séparés formant ladite structure d'électrodes constituent ledit potentiel électrique résultant qui est continuellement varié en travers ladite structure d'électrodes.

4. Procédé selon la revendication 2 ou 3, caractérisé en ce que ledit potentiel électrique résultant est linéairement varié le long de la courbe de n'importe quelle surface d'une coupe en travers centrale de ladite structure d'électrodes.

5. Procédé selon l'une quelconque des revendications précédentes, caractérisé par application d'un second potentiel électrique résultant à ladite structure d'électrodes pour la génération d'un second champ électrique homogène dans la direction d'un axe symétrique superposé audit champ électrique quadripolaire tridimensionnel de rotation symétrique ou le champ électrique de moments multipolaire plus élevé sans interaction.

6. Procédé selon l'une quelconque des revendications précédentes, caractérisé par application du procédé à une analyse spectrométrique de la masse des ions emmagasinés.

7. Procédé selon les revendications 5 et 6, caractérisé en ce que les ions à analyser sont emmagasinés selon la masse dans ladite limite dudit champ électrique quadripolaire ou multipolaire plus élevé et en ce que les fréquences fondamentales spécifiques de la masse par rapport à la charge des ions à analyser sont excités par ledit second champ électrique homogène.

8. Procédé selon la revendication 7, caractérisé en ce que les signaux de courant d'image dans ladite structure d'électrodes résultant des mouvements desdits ions causés par une excitation résonante par ledit second champ électrique sont détectés de manière différentielle.

9. Procédé selon la revendication 8, caractérisé en ce qu'un spectre de masse desdits ions est engendré par application d'analyse de fréquence auxdits signaux de courant d'image.

10. Procédé selon la revendication 7, caractérisé en ce que dits ions sont éjectés hors des limites dudit champ quadripolaire et détectés avec un détecteur sensible aux charges.

11. Utilisation d'une structure d'électrodes selon un procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que ces parties de ladite structure d'électrodes qui sont face audit champ électrique quadripolaire ou multipolaire plus élevé et donc définissant la limite de celui-ci se composent de matériel électrique résistant.

12. Utilisation d'une structure d'électrodes selon la revendication 11, caractérisé en ce que ladite structure d'électrodes comprend un matériel de substrat non-conducteur enduit de matériel résistant aux parties qui sont face audit champ quadripolaire ou multipolaire plus élevé.

13. Utilisation d'une structure d'électrodes selon la revendication 11, caractérisé en ce que ladite structure d'électrodes se compose d'un ou de plusieurs fils métallique de résistance définissant ladite limite dudit champ quadripolaire ou multipolaire plus élevé.

14. Utilisation d'une structure d'électrodes selon un procédé selon l'une quelconque des revendications 1 à 6, caractérisé en ce que ladite structure d'électrodes se compose d'une pluralité de plaques métalliques ayant chacune un trou circulaire définissant la limite dudit champ quadripolaire ou multipolaire plus élevé par lequel le rayon dudit trou varie consécutivement de plaque en plaque, les plaques étant placées de manière dense avec faces parallèles en distances égales ou inégales.

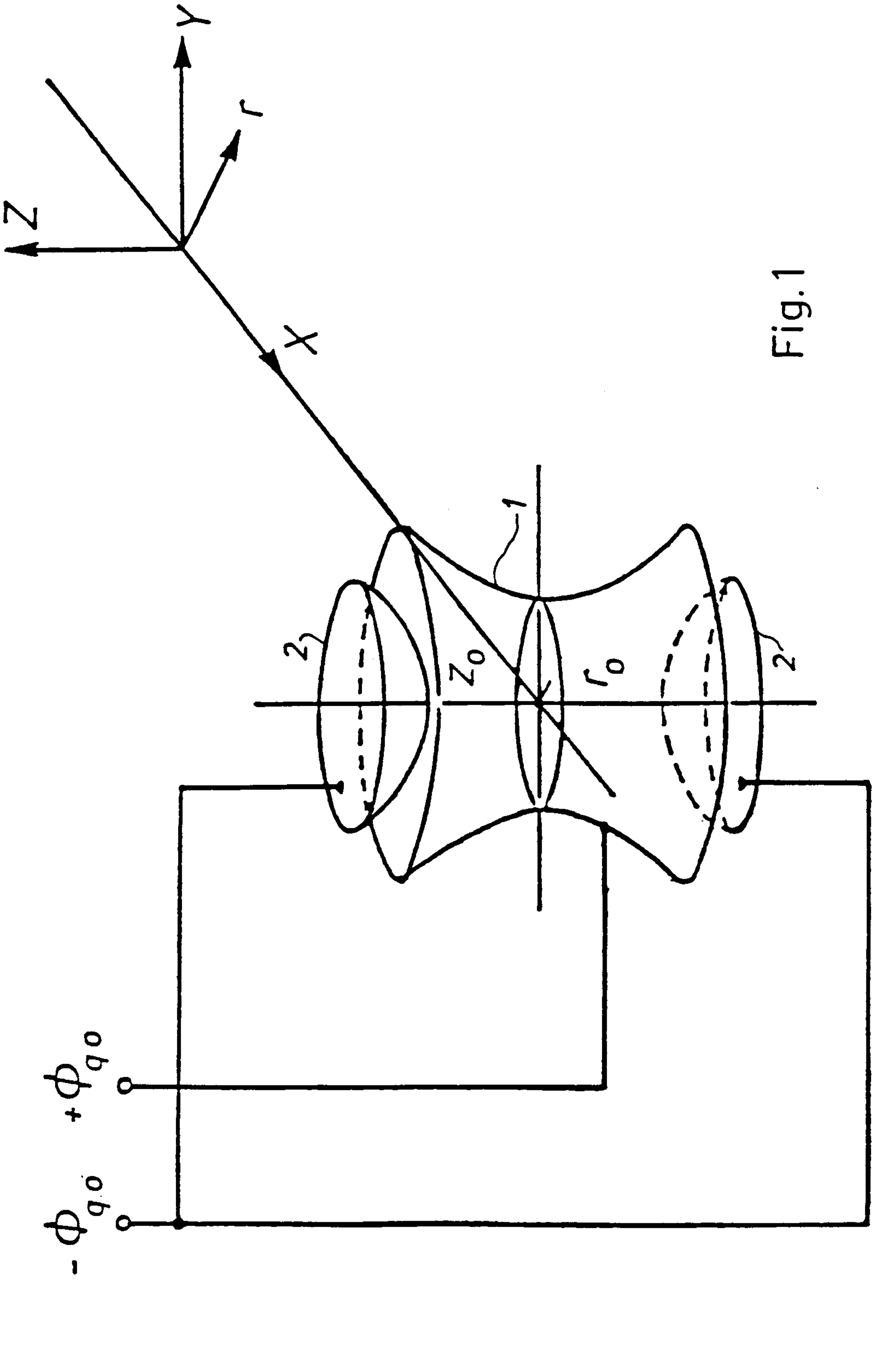

Fig.1

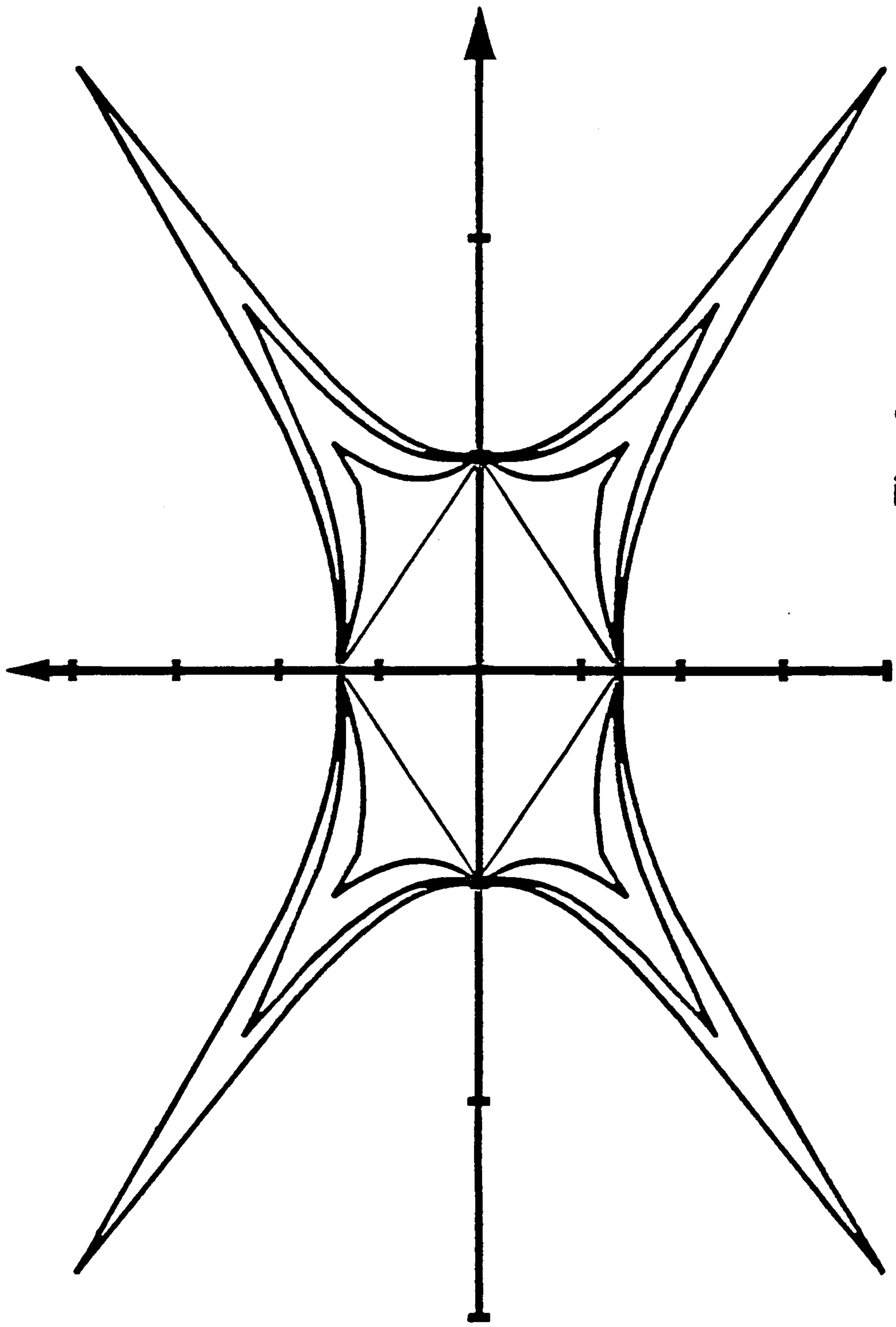

Fig. 2

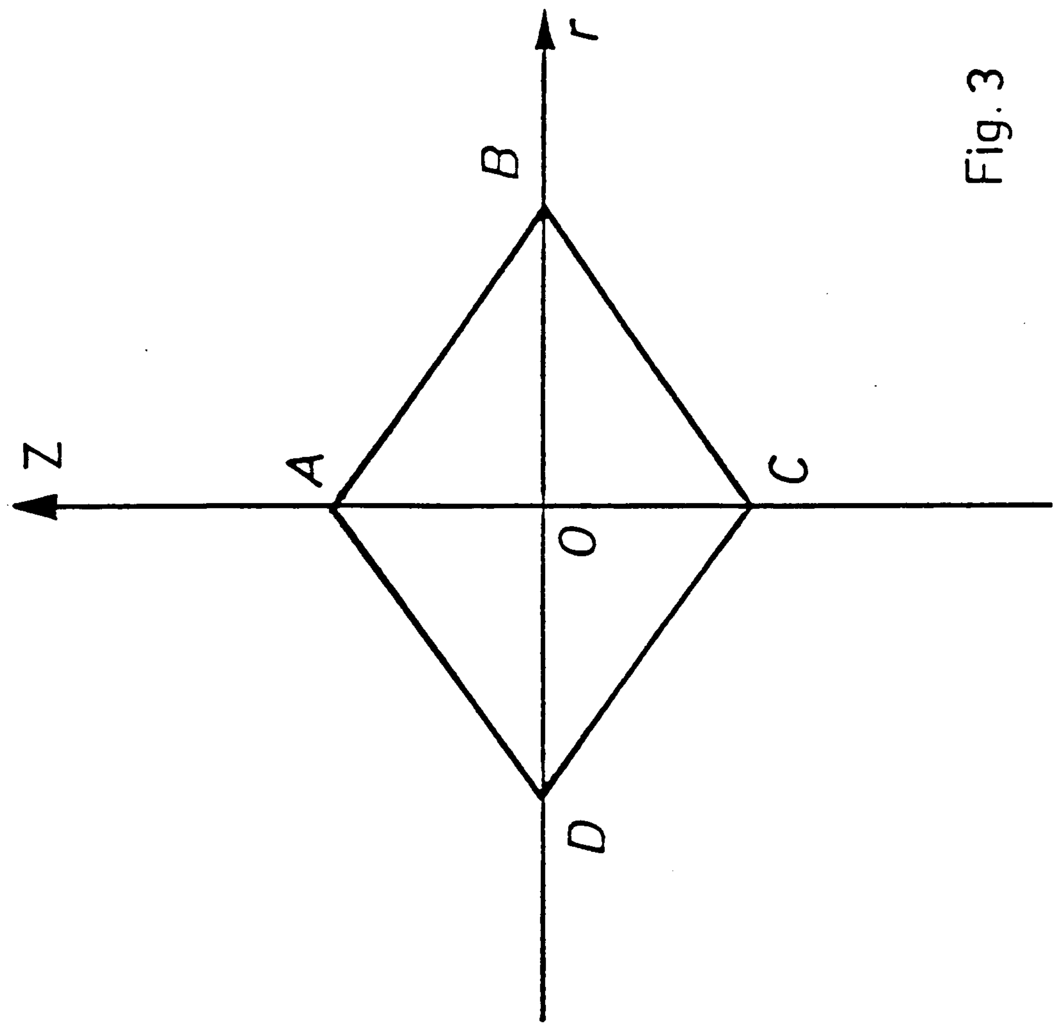

Fig. 3

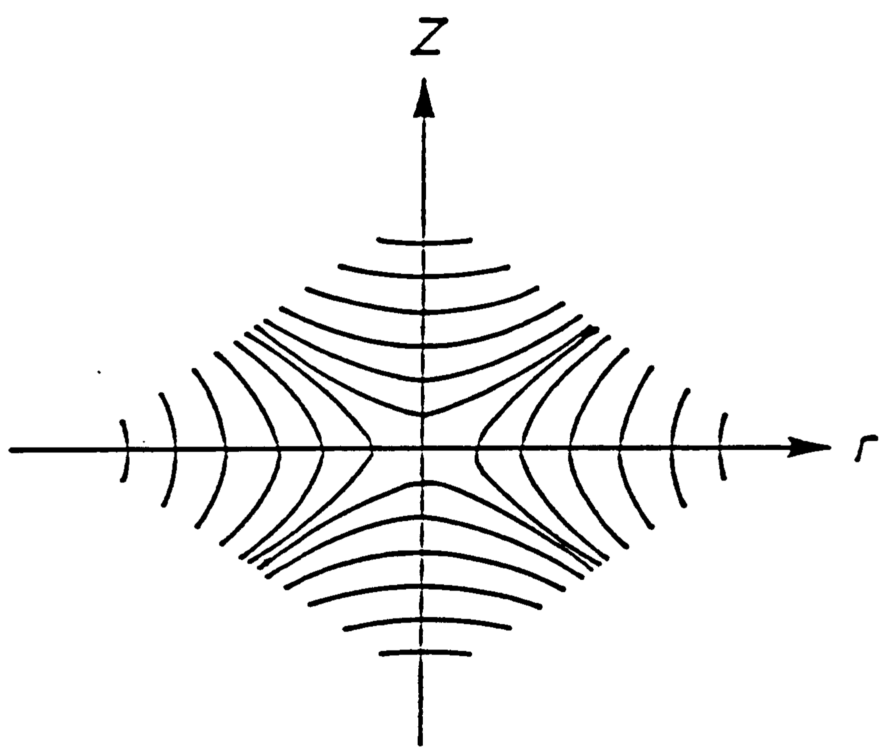

Fig. 4a

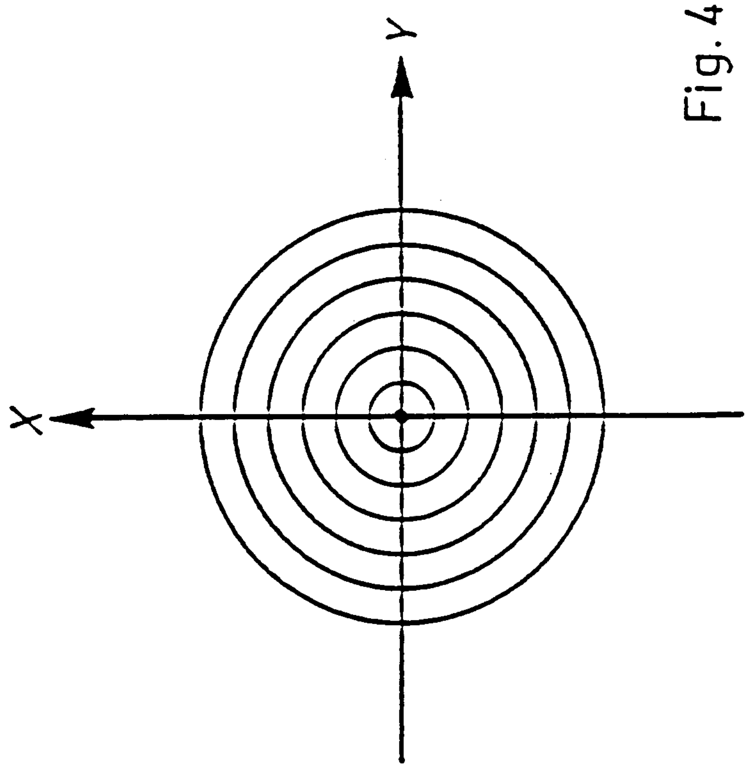

Fig. 4 b

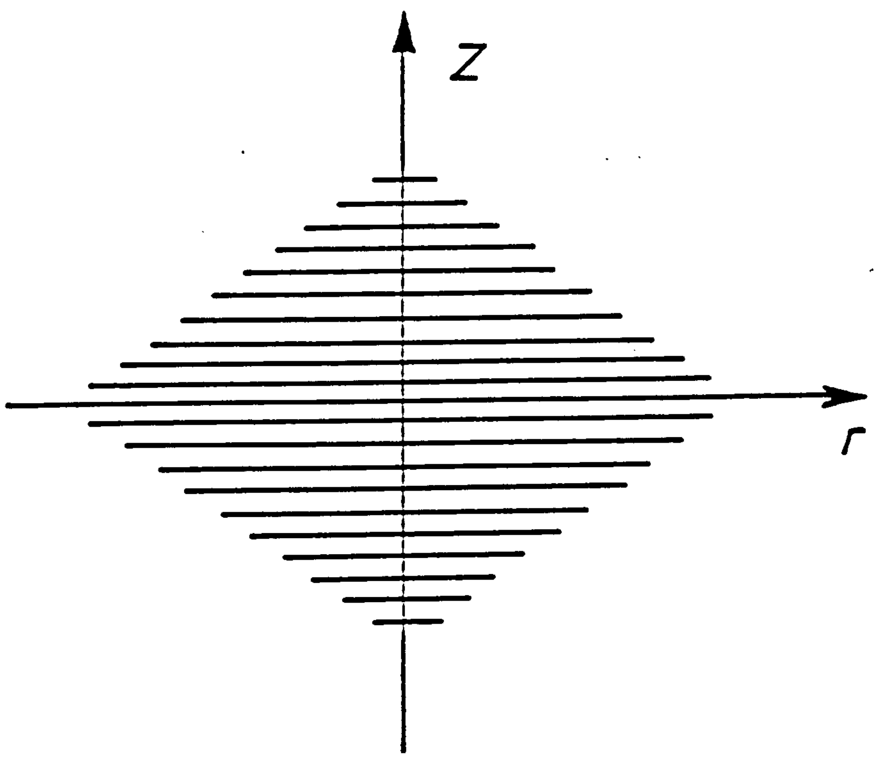

Fig. 5

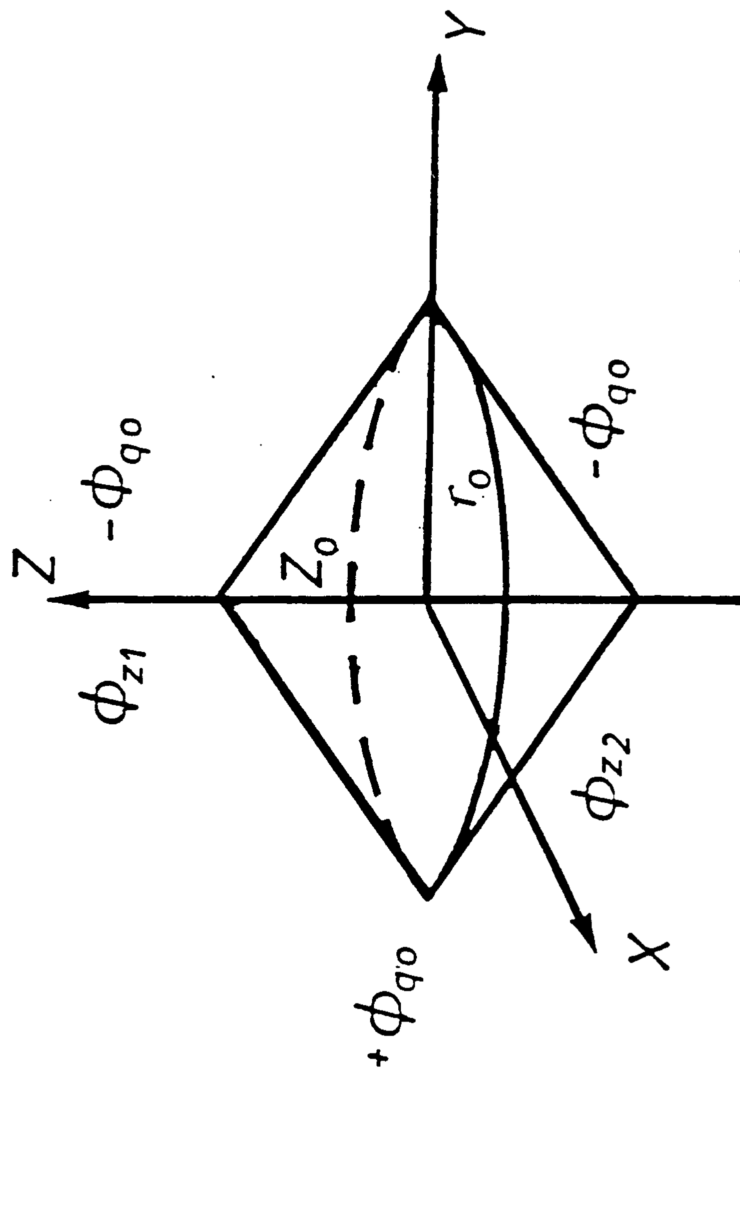

Fig. 6

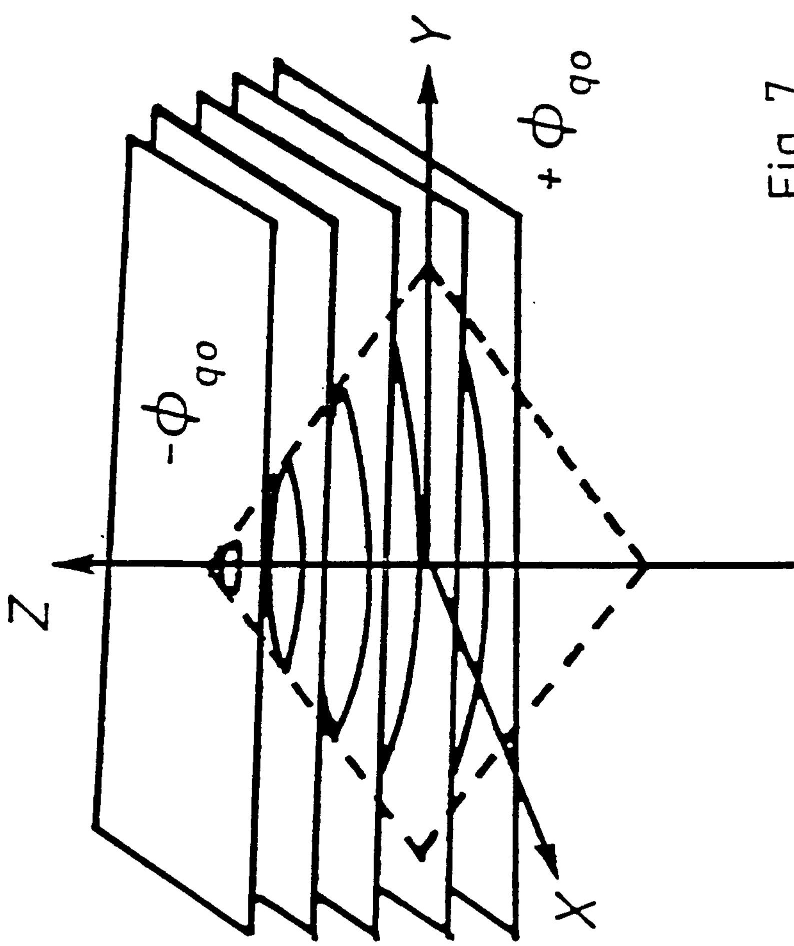

Fig. 7

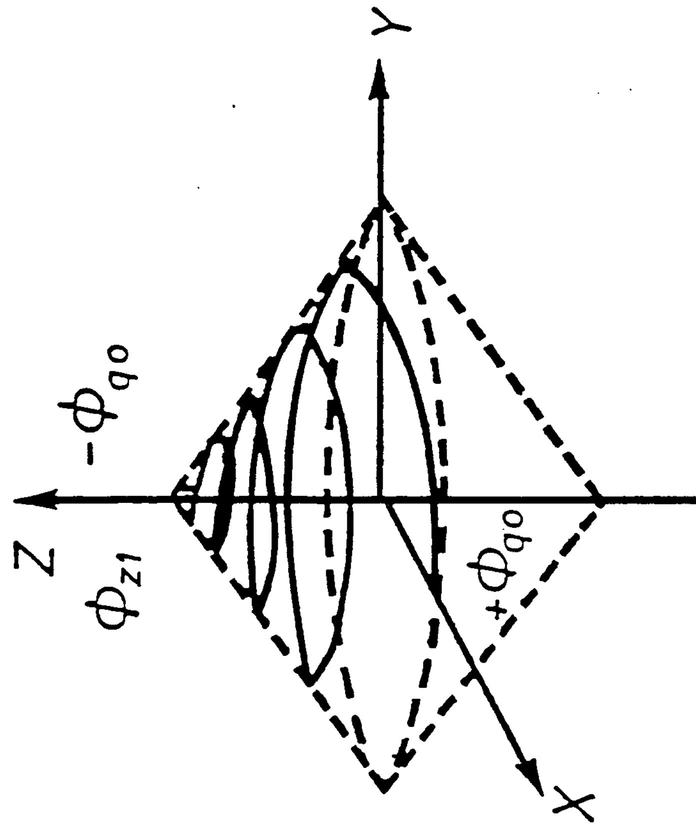

Fig. 8

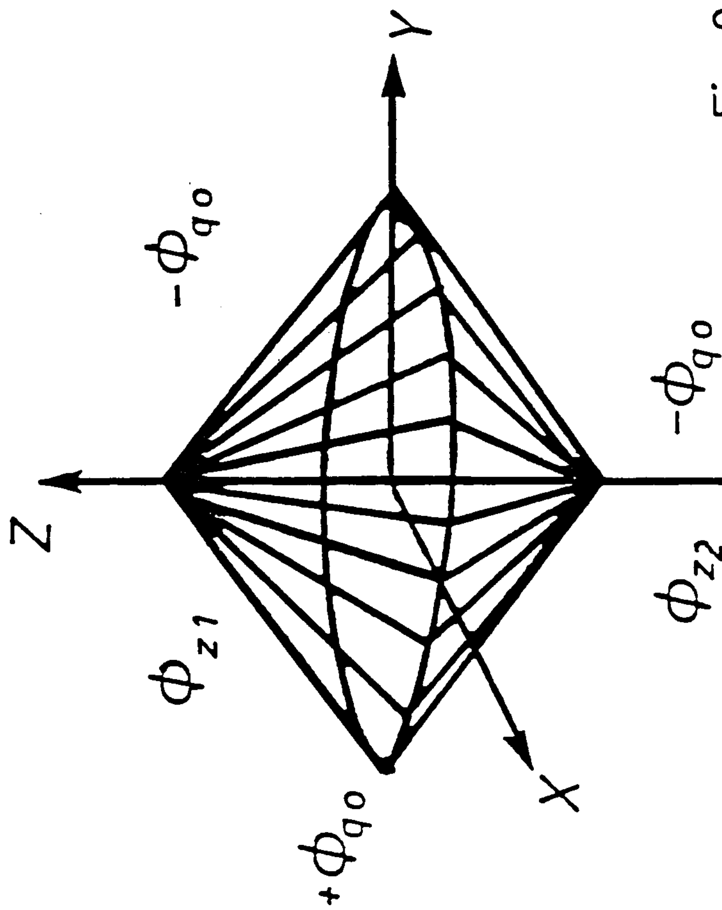

Fig. 9

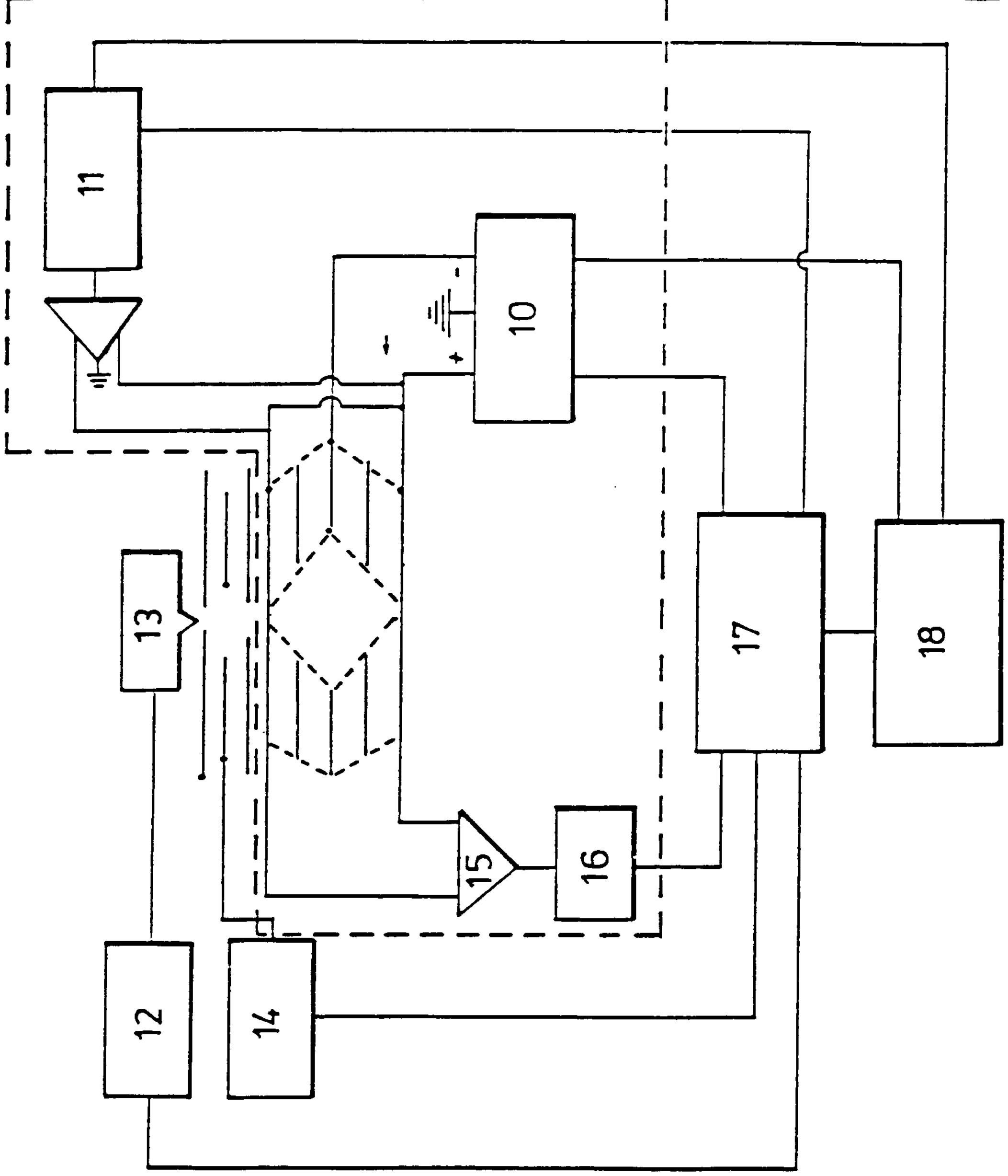

Fig.10

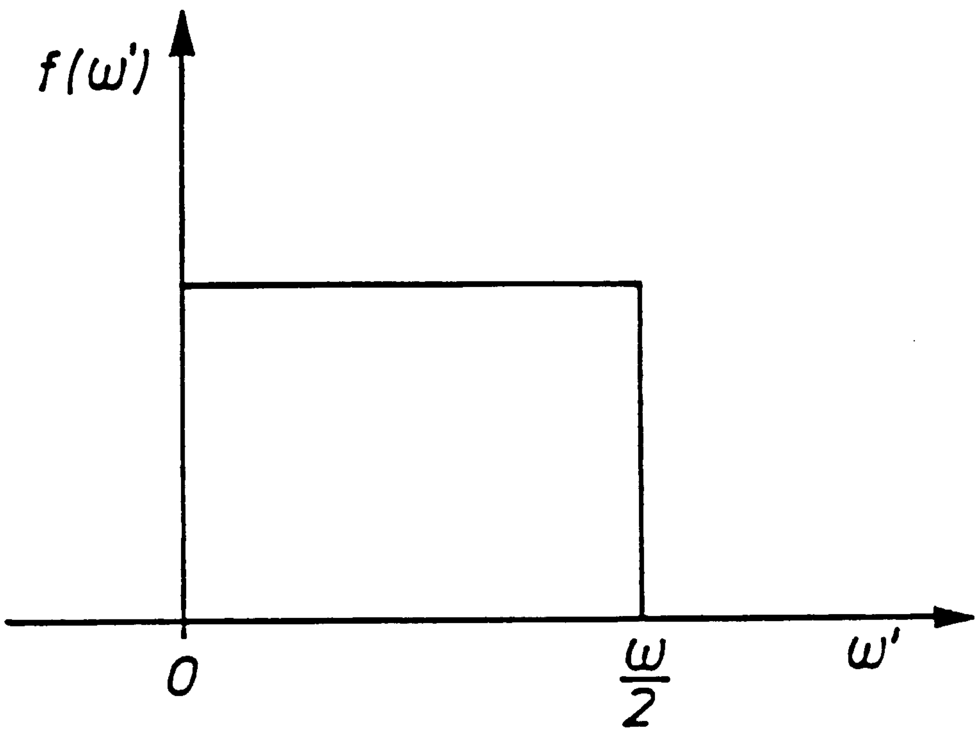

Fig. 11

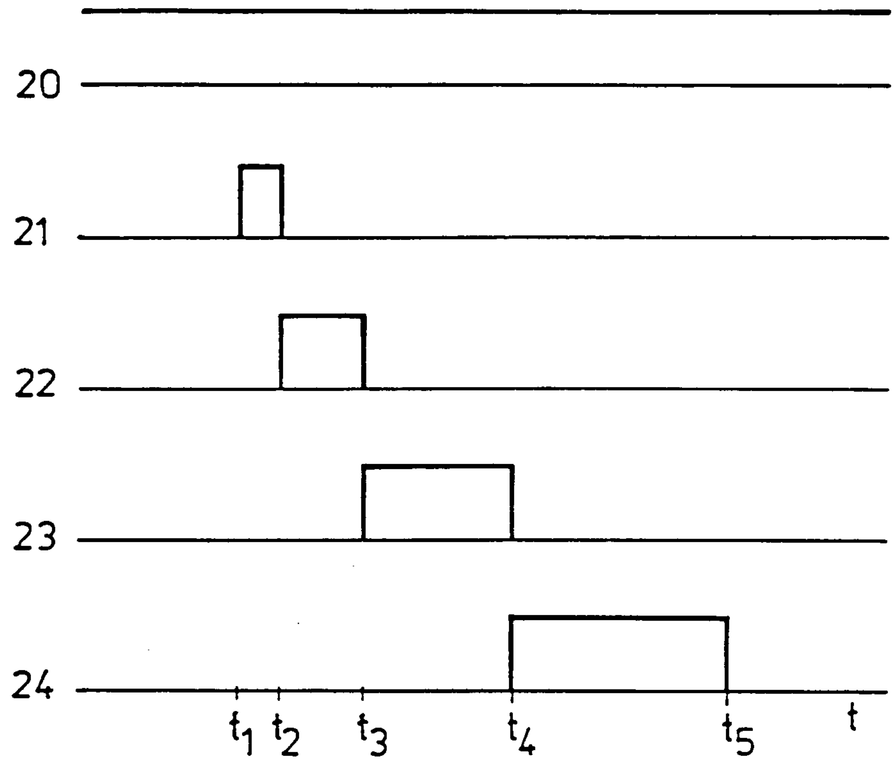

Fig. 12a

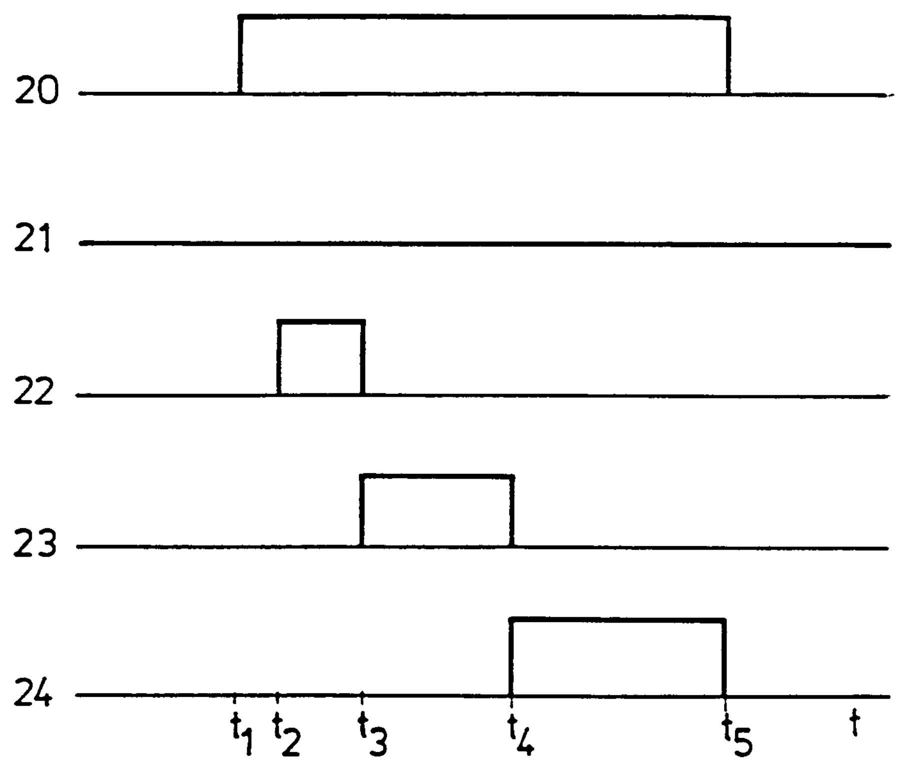

Fig. 12b