quadrupole rod systems, this mass limit is sharply defined, less so with higher multipoles. The mass limit is a function of the frequency and the amplitude of the RF voltage. It is inversely proportional to the square of the frequency and proportional to the amplitude. For a specified frequency it is therefore the amplitude of the RF voltage which determines the lower mass limit. If light ions are also to be transmitted without losses, the RF voltage must have a small amplitude. The lower mass limit is given by the stability zone of the Mathieu differential equation for the motion of the ions in RF quadrupole fields. A pseudopotential cannot form for light ions because they are accelerated in just one half cycle of the RF voltage to such a degree that they are either propelled out of the storage field in a single half cycle or experience this propulsion by being excited in several half cycles.

[0013] The fact that quadrupole rod systems have an upper mass limit is less well known. The Mathieu differential equations state only that the restoring forces of the pseudopotential are smaller for heavy ions than for light ions: The restoring forces are proportional to the inverse of the mass of the ion. This means that light ions collect in the axis because the focusing pseudopotential is stronger for them, and heavier ions can only gather outside the axis, kept at a distance from the lighter ions by Coulomb repulsion.

[0014] With a quadrupole rod system that operates under high-vacuum conditions, the upper mass limit only makes itself felt during injection and when the rod system is overfilled. Even if the injection is only slightly oblique, the weak pseudopotential for heavy ions can no longer deflect them back to the axis; they hit the rods and are eliminated. If the system is overfilled, the space charge drives the heavy ions right up to the rods. If the quadrupole rod system is filled with a collision gas, there are two further components: the thermal diffusion brought about by gas collisions, which can drive heavy ions right up to the pole rods because of the weak pseudopotential opposing field, and the collision cascades in the case of ions injected with higher energy, whose lateral angles of deflection can randomly add up so that the ions crash into the pole rods. Both effects result in considerable losses of heavy ions. Furthermore, heavy ions are discriminated again during ejection from the ion guide because they are not in the axis.

[0015] The upper mass limit does not have a sharp cut off, but it does attenuate the intensity of heavy ions to such a degree that they can no longer be readily detected by a mass spectrometer. The rule of thumb for a quadrupole rod system is that when an ion mixture is injected, the ions whose mass is more than twenty times the lower mass limit are greatly attenuated by losses and can no longer be readily measured.

[0016] The existence of the upper mass limit is particularly inconvenient in the field of peptide analysis in proteomics. The aim here is to measure both individual amino acid ions, the so-called "immonium ions" in the range between 50 and 180 Daltons, and the mass range of the so-called digest peptides up to around 5,000 Daltons. But if the lower mass limit is set to around 50 Daltons, this results in an upper mass limit of around 1,000 Daltons, which is quite unacceptable for this type of analysis. This means that time-of-flight mass spectrometers with orthogonal ion injection, which are employed particularly because of the high mass range, cannot be used in connection with quadrupole ion guides of the present art.

[0017] One solution is to use hexapole or octopole rod systems. These have more favorable pseudopotential distributions for heavier ions with a steeper potential increase outside the axis in front of the pole rods, but the bottom of the potential well is flat close to the axis. The well defined pseudopotential minimum which exists in the axis of a quadrupole field does not exist here. The ions do not collect as accurately in the axis of these systems and therefore cannot be injected as favorably into subsequent systems. The collision focusing is weaker. The operation of time-of-flight mass spectrometers with orthogonal ion injection suffers from a poorer resolution because the required fine cross section of the ion beam can no longer be achieved.

[0018] With octopole rod systems, in particular, heavy loading with ions can lead to the heavier ions collecting way outside the axis, close to the rods because they are driven there by the space charge. This charge-dependent distribution of the ions in the interior is very unfavorable. It can even occur when there are no light ions at all in the ion mixture; the pure Coulomb repulsion between the heavy ions is sufficient. The ions collect on the surface of a cylinder; there is no collision focusing at all if a threshold ion density is exceeded.

SUMMARY

[0019] In accordance with the principles of the invention, a more inhomogeneous field distribution is generated in front of the pole rods of a multipole ion guide, preferably a quadrupole RF ion guide, by giving the pole rods a structured surface. In one embodiment, this can be achieved by using complex structures, termed "pole electrode systems" here, instead of the solid pole rods.

[0020] The surfaces of the pole electrode systems may consist of grids of structural elements; and neighboring structural elements can each be fed with different RF voltages so that a near field is created in front of each pole electrode system, said near field being formed from the strongly inhomogeneous electric RF dipole fields between the structural elements, and also a far field, which is produced by the RF voltages averaged over the surfaces of the structural elements. This grid can be made of very fine punctiform structural elements, in which case it forms a "point grid", or of one-dimensionally elongated linear structural elements, creating a "line grid".

[0021] The far field corresponds exactly to the field which is generated by the smooth pole rods of prior art. With four pole electrode systems this creates a corresponding quadrupole field.

[0022] The grids of the structural elements on the pole electrode systems can also particularly be "multipole grids", which means that neighboring structural elements of each pole electrode system belong to different structural element arrays; that the structural elements of a structural element array are electrically connected; and that the different structural element arrays are each separately fed with RF voltages. In particular, there can be precisely two such structural element arrays for every pole electrode system, resulting in a "bipolar grid".

[0023] A far field can exist only if the applied RF voltages do not fully balance each other out in the near field, but instead one of the applied RF voltages predominates and can