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Description

This invention relates to a quadrupole mass filter as used with mass spectrometers.

One type of mass spectrometer that is extensively used for qualitative and quantitative analysis of chemicals employs one or more quadrupole mass filters. In such spectrometers, quadrupole mass filters incorporating four conductive metal rods are supported on mounts made of an insulating material. The rods are energized by combined direct current (d.c.) and alternating current (a.c.) voltage to achieve selective mass focusing. An example of such a mass filter is described in US-A-4032782 which discloses a method of maintaining filter stability by thermal matching of the rods and the mounts.

In US-A-3321623, a multipole mass filter is described in which the conductive rods are connected to a radio frequency (a.c.) supply such that the radio frequency voltage between the two of one pair of conductive rods is unbalanced. This system provides for some improvement in the resolving power of a mass filter.

To obtain accurate readings and interpretations of analyses performed by mass spectroscopy, it is highly desirable that the mass peak waveforms obtained by the scans are smooth and not characterized by spurious splits or depressions which affect the spectral quality of the data. In prior art systems, it has been observed that such spurious splits and depressions of the mass peaks occur frequently, thus deleteriously affecting the interpretation of the resulting data.

According to this invention there is provided a quadrupole mass filter, for use in a mass spectrometer, comprising first and second pairs of conductive rods; a source of direct current voltage and a source of radio frequency voltage for each pair of rods; wherein said conductive rods provide a time varying electric field to focus ions of narrow band of masses; characterised by tuned circuit means for adjusting the magnitude of the radio frequency voltage supplied to one of said pairs of conductive rods relative to that supplied to the other one of said pairs of rods, so that a radio frequency voltage unbalance is produced between said pairs of rods.

We have discovered that by unbalancing the radio frequency voltages applied to the pairs of quadrupole rods spurious splits and depressions are substantially reduced, the mass peaks being smooth and devoid of spurious signals and deformations.

Further, the filter of an embodiment of the invention has good ion transmission and hence sensitivity especially for high mass ions.

The invention will now be described by way of example with reference to the drawing which is a schematic circuit and block diagram of a filter according to an embodiment of this invention.

With reference to the drawing, a quadrupole mass filter incorporates two pairs of conductive rods 10a, 10c and 10b, 10d disposed in a configuration that provides a hyperbolic field through which ions of the materials under investigation travel. The rods 10, which may be made of molybdenum, are connected to an electrical circuit that provides d.c. voltage and r.f. or alternating current (a.c.) voltage. The circuit network includes a tuned circuit that controls the magnitudes of the r.f. and d.c. voltages which are applied to the filter rods. The tuned or r.f. resonant circuit is a low loss, high Q circuit, and the phase relation of the r.f. voltage supplied to the two pairs of rods 10a,c and 10b,d is substantially 180°. The rods act to provide a time varying electrostatic field to focus a narrow band of masses.

In operation, a mass control voltage is derived from a control device, such as a computer or sweep generator and applied through an input resistor 12 to a summing point 14. The control voltage is used as a reference that sets the mass to which the mass spectrometer will respond. A feedback voltage V_{fb} is obtained from a measuring device 38, which is coupled to the rods 10 and to the tuned circuit, as will be described hereinafter. If a non-zero voltage appears at the summing point 14, this voltage is amplified by an error voltage amplifier 16 and the amplified voltage is fed to the control input of an r.f. generator 18. The r.f. generator 18 supplies an r.f. signal, having a frequency in the range of 1.0-2.0 MHz for example, to the tuned circuit, which comprises an inductive network consisting of inductances 20 and 22 and a capacitive network comprising capacitive elements 34 and 36. A center coil 24, which preferably has one or two turns, is coupled to the output of the generator 18 and is disposed at the center between the two inductances 20 and 22 to supply r.f. power to the tuned circuit.

The capacitive network of the tuned circuit includes the capacitive elements 30 and 32 which represent the capacitances of the wiring, mass filter and cables of the system. The capacitances 34 and 36, which are tied to test points TP1 and TP2, are selected so that the circuit is resonant at the desired frequency of operation, and so that the r.f. voltages measured at the test points TP1 and TP2 have a predetermined unbalance. The capacitances 34 and 36 may be fixed capacitors of selected value or variable capacitors. In either case, the values of the capacitances are such that they meet the requirements of resonance and r.f. unbalance.

Each inductance 20 and 22 is coupled at one end respectively to capacitive elements 26 and 28, which are tied to a reference potential such as ground. The other end of each inductance 20 and 22 is coupled to test points TP1 and TP2 respectively, which are connected to capacitors 34 and 36 respectively. The junction of the inductance 20 and capacitive element 34 is connected to opposing rods 10a and 10c, whereas the junction of the inductance 22 and capacitive element 36 is connected to opposing rods 10b and 10d. The inductances and capacitive elements form an LC resonant circuit which provides high r.f. voltage operation, up to3,000 peak volts for example.

Since the precise values of some of the capacitive elements of the tuned circuit are not known, the need for adjustments of the capacitive values of the tuned circuit to effectuate the r.f. unbalance is determined by an r.f. voltage measuring device such as an oscilloscope. The measuring device is coupled to the test points TP1 and TP2, and to the pairs of rods 10. The capacitors 34 and 36 are adjusted to obtain the desired unbalance. The adjustments may be made manually, or automatically in response to the measurement seen at the measuring device. Alternatively the inductors 20 and 22 may be formed with an unequal or different number of turns on opposite sides of the center tap to produce the desired r.f. voltage unbalance, or may be variable inductances that may be adjusted.

The output feedback V_{fb} of negative polarity from the measuring device 38 represents the difference in r.f. voltage between the rod pair 10a, 10c and the rod pair 10b, 10d. This feedback voltage is fed through a feedback resistor 40 to the summing point 14 to be combined with the mass control voltage of positive polarity. As described heretofore, the non-zero sum of the two voltages provides an error signal that is processed by the feedback loop including the tuned circuit and measuring device 38 to compensate for the error and drive the summed voltage at junction 14 towards zero.

The feedback voltage V_{fb} provided by the detector or measuring device 38 is also used to produce the positive and negative d.c. voltages which are applied to the rods 10 in order to produce the mass filtering action of the quadrupole. The feedback voltage is fed through a resolution controls circuit 40 which controls the slope and intercept of the d.c. signal, and thus allows for proper adjustment of mass resolution. The d.c. voltage is applied through parallel channels, one of which incorporates a phase inverting amplifier 44, to a d.c. rod polarity reversible switch S1. The switch S1, which is operated manually, or under computer control if so desired, reverses the d.c. voltage polarity to enable detection of positive or negative ions by the quadrupole filter. In actual operation, it is desirable to switch rapidly between positive ion analysis and negative ion analysis, and in such cases computer control is employed.

The positive and negative d.c. signals are passed respectively through voltage amplifiers 46 and 48, and applied to the junctions between the inductances 22 and 20 and the bypass capacitors 28 and 26, for application through the tuned circuit to the rod pairs 10.

Although the use of the switch S1 at the input of the voltage amplifiers 46 and 48 is a preferable implementation because it does not require switching of high voltage, bipolar d.c. rod voltage amplifiers are required to enable supplying either positive or negative output signals from each amplifier. In an alternative approach, a switch S2 is used at the output of the voltage amplifiers 46 and 48, and each amplifier needs only to supply a single polarity d.c. signal, one positive and the other negative.

With the implementation disclosed herein, the d.c. rod voltages are delivered to the quadrupole rods through the inductive coil structure. In such case, the center tap of coil 24 is isolated from the system ground and the r.f. circuit is completed by use of grounded bypass capacitors 26 and 28 which serve to complete the r.f. circuit while preventing excessive r.f. voltage from reaching the d.c. rod voltage amplifiers 46 and 48.

We have observed that with an unbalance of the r.f. voltages that are applied to the rods, the shapes of the mass peaks become smooth and afford a significant improvement in mass spectroscopy operation, particularly in quantitative analysis of high mass chemicals. There is a clear seperation between adjacent mass peaks without the spurious signals that are experienced in prior art systems and affect the accuracy of the spectroscopic readout. To obtain the desired unbalance, one or both of the capacitive elements are adjusted so that they are different in value. Similarly, the inductive elements may be adjusted to a different value, or adjustments both of inductance and capacitance may be made to achieve the required imbalance of r.f. voltages. In a preferred implementation, the r.f. voltage at one pair of rods, say 10a, 10c is approximately 1.4 times that at other pair of the rods 10b, 10d.

Claims

1. A quadrupole mass filter, for use in a mass spectrometer, comprising first and second pairs of conductive rods (10a, 10c, 10b, 10d); a source of direct current voltage (38, 42, 44, 46, 48) and a source of radio frequency voltage (18) for each pair of rods wherein said conductive rods provide a time varying electric field to

focus ions of a narrow band of masses; characterised by tuned circuit means (20, 22, 26, 28, 34, 36) for adjusting the magnitude of the radio frequency voltage supplied to one of said pairs of conductive rods (10a, 10c or 10b, 10d) relative to that supplied to the other one of said pairs of rods (10b, 10d or 10a, 10c) so that a radio frequency voltage unbalance is produced between said pairs of rods.

2. A filter as claimed in Claim 1, characterised in that said tuned circuit means comprises at least first and second capacitances (34, 36) coupled respectively to said first and second pairs of rods (10a, l0c; 10b, 10d), said capacitances providing a controlled amount of unbalance in the radio frequency voltage applied to the rods.

3. A filter as claimed in Claim 1 or Claim 2, characterised in that said tuned circuit means comprises at least first and second inductances (20, 22) coupled respectively to said first and second pairs of rods (10a, l0c; 10b, 10d), said inductances providing a controlled amount of unbalance in the radio frequency voltage applied to the rods.

4. A filter as claimed in Claim 3, characterised by a center coil (24) coupled to the output of said source of radio frequency voltage (18), and electrically coupled between said inductances (20, 22).

5. A filter as claimed in Claim 3 or Claim 4, characterised by bypass capacitors (26, 28) connected to said inductances (20, 22).

6. A filter as claimed in any preceding claim, characterised by a radio frequency voltage measuring device (38) for sensing the difference in voltages between said first and second pairs of rods (10a, 10c; 10b, 10d).

7. A filter as claimed in Claim 6, characterised by means for providing a mass control voltage for setting a reference to which said filter responds.

8. A filter as claimed in Claim 7, characterised by means (40) coupled to said voltage measuring device (38) for providing a feedback voltage to a summing point (14) at which said mass control voltage and said feedback voltage are summed to form a combined voltage.

9. A filter as claimed in Claim 8, characterised by an error voltage amplifier (16) coupled between said summing point (14) and said voltage source (18) for amplifying said combined voltage.

10. A filter as claimed in any one of Claims 6 to 9, characterised by switching means (S1) coupled to said measuring device (38) for providing a d.c. voltage to said pairs of rods (10a, 10c; 10b, 10d).

11. A filter as claimed in Claim 10, characterised by voltage amplifiers (46, 48) coupled between said switching means (S1) and said tuned circuit means (20, 22; 26, 28; 34, 36).

12. A filter as claimed in Claim 10 or Claim 11, characterised by means (S2) for reversing the polarity of the said direct current voltage applied to the rods.

Revendications

1. Filtre de masse quadripolaire, à utiliser dans un spectromètre de masse, comportant des première et seconde paires de tiges conductrices (10a, 10c, 10b, 10d) ; une source de tension continue (38, 42, 44, 46, 48) et une source de tension radiofréquence (18) pour chaque paire de tiges, lesdites tiges conductrices produisant un champ électrique variant avec le temps pour concentrer des ions d'une bande étroite de masses ; caractérisé par un moyen (20, 22, 26, 28, 34, 36) à circuit accordé destiné à ajuster l'amplitude de la tension radiofréquence appliquée à l'une desdites paires de tiges conductrices (10a, 10c ou 10b, 10d) par rapport à celle appliquée à l'autre desdites paires de tiges (10b, 10d ou 10a, 10c) afin qu'un déséquilibre de tension radiofréquence soit produit entre lesdites paires de tiges.

2. Filtre selon la revendication 1, caractérisé en ce que ledit moyen à circuit accordé comporte au moins des première et seconde capacités (34, 36) couplées, respectivement, auxdites première et seconde paires de tiges (10a, 10c ; 10b, 10d), ladite capacité établissant une valeur maîtrisée de déséquilibre dans la tension radiofréquence appliquée aux tiges.

3. Filtre selon la revendication 1 ou la revendication 2, caractérisé en ce que ledit moyen à circuit accordé comporte au moins des première et seconde inductances (20, 22) couplées, respectivement, auxdites première et seconde paires de tiges (10a, 10c ; 10b, 10d),

lesdites inductances établissant une valeur maîtrisée de déséquilibre dans la tension radiofréquence appliquée aux tiges.

4. Filtre selon la revendication 3, caractérisé par une bobine centrale (24) couplée à la sortie de ladite source de tension radiofréquence (18), et couplée électriquement entre lesdites inductances (20, 22).

5. Filtre selon la revendication 3 ou la revendication 4, caractérisé par des condensateurs (26, 28) de découplage connectés auxdites inductances (20, 22).

6. Filtre selon l'une quelconque des revendications précédentes, caractérisé par un dispositif (38) de mesure de tension radiofréquence destiné à capter la différence des tensions radiofréquence entre lesdites première et seconde paires de tiges (10a, 10c ; 10b, 10d).

7. Filtre selon la revendication 6, caractérisé par un moyen destiné à produire une tension de commande de masse pour établir une référence à laquelle ledit filtre réagit.

8. Filtre selon la revendication 7, caractérisé par un moyen (40) couplé audit dispositif (38) de mesure de tension pour produire une tension de réaction à un point de sommation (14) auquel ladite tension de commande de masse et ladite tension de réaction sont additionnées pour former une tension combinée.

9. Filtre selon la revendication 8, caractérisé par un amplificateur (16) de tension d'erreur couplé entre ledit point de sommation (14) et ladite source (18) de tension radiofréquence afin d'amplifier ladite tension combinée.

10. Filtre selon l'une quelconque des revendications 6 à 9, caractérisé par un moyen (S1) de commutation couplé audit dispositif (38) de mesure pour appliquer ladite tension continue auxdites paires de tiges (10a, 10c ; 10b, 10d).

11. Filtre selon la revendication 10, caractérisé par des amplificateurs (46, 48) de tension couplés entre ledit moyen de commutation (S1) et ledit moyen à circuit accordé (20, 22 ; 26, 28 ; 34, 36).

12. Filtre selon la revendication 10 ou la revendication 11, caractérisé par un moyen (S2) destiné à inverser la polarité de ladite tension continue appliquée aux tiges.

Ansprüche

1. Quadrupol-Massenfilter zur Verwendung in einem Massenspektrometer, mit einem ersten und einem zweiten Paar leitfähiger Stangen (10a, 10c, 10b, 10d), einer Gleichspannungsquelle (38, 42, 44, 46, 48) und einer hochfrequenten Spannungsquelle (18) für jedes Stangenpaar, wobei die leitfähigen Stangen ein zeitlich veränderliches elektrisches Feld bereitstellen, durch das Ionen eines schmalen Bandes von Massen fokussiert werden, **gekennzeichnet** durch abgestimmte Schaltungseinrichtungen (20, 22, 26, 28, 34, 36) zum Einstellen der Größe der einem der Paare leitfähiger Stangen (10a, 10c oder 10b, 10d) zugeführten hochfrequenten Spannung gegenüber der dem anderen der Stangenpaare (10b, 10d oder l0a, 10c) zugeführten hochfrequenten Spannung, so daß zwischen den Stangenpaaren ein Ungleichgewicht der hochfrequenten Spannung erzeugt wird.

2. Filter nach Anspruch 1, dadurch gekennzeichnet, daß die abgestimmten Schaltungseinrichtungen wenigstens eine erste und eine zweite Kapazität (34, 36) enthalten, die an das erste bzw. zweite Stangenpaar (10a, 10c; 10b, 10d) angeschlossen sind, wobei die Kapazitäten eine gesteuerte Größe des Ungleichgewichts der an die Stangen angelegten hochfrequenten Spannungen erzeugen.

3. Filter nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß die abgestimmten Schaltungseinrichtungen wenigstens eine erste und eine zweite Induktivität (20, 22) enthalten, die an das erste bzw. zweite Stangenpaar (10a, 10c; 10b, 10d) angeschlossen sind, wobei die Kapazitäten eine gesteuerte Größe des Ungleichgewichts der an die Stangen angelegten hochfrequenten Spannungen erzeugen.

4. Filter nach Anspruch 3, gekennzeichnet durch eine mittlere Spule (24), die an den Ausgang der hochfrequenten Spannungsquelle (18) angeschlossen und elektrisch zwischen die Induktivitäten (20, 22) geschaltet ist.

5. Filter nach Anspruch 3 oder 4, gekennzeichnet durch an die Induktivitäten (20, 22) angeschlossene Bypass-Kondensatoren (26, 28).

6. Filter nach einem der vorstehenden Ansprüche, gekennzeichnet durch eine Meßeinrichtung (38) zum Messen einer hochfrequenten Spannung, zum Erfassen der Differenz der am ersten und zweiten Stangenpaar (10a, 10c;

10b, 10d) anliegenden hochfrequenten Spannungen.

7. Filter nach Anspruch 6, gekennzeichnet durch Einrichtungen zum Bereitstellen einer Massensteuerspannung, zum Einstellen eines Bezugswertes, auf den der Filter anspricht.

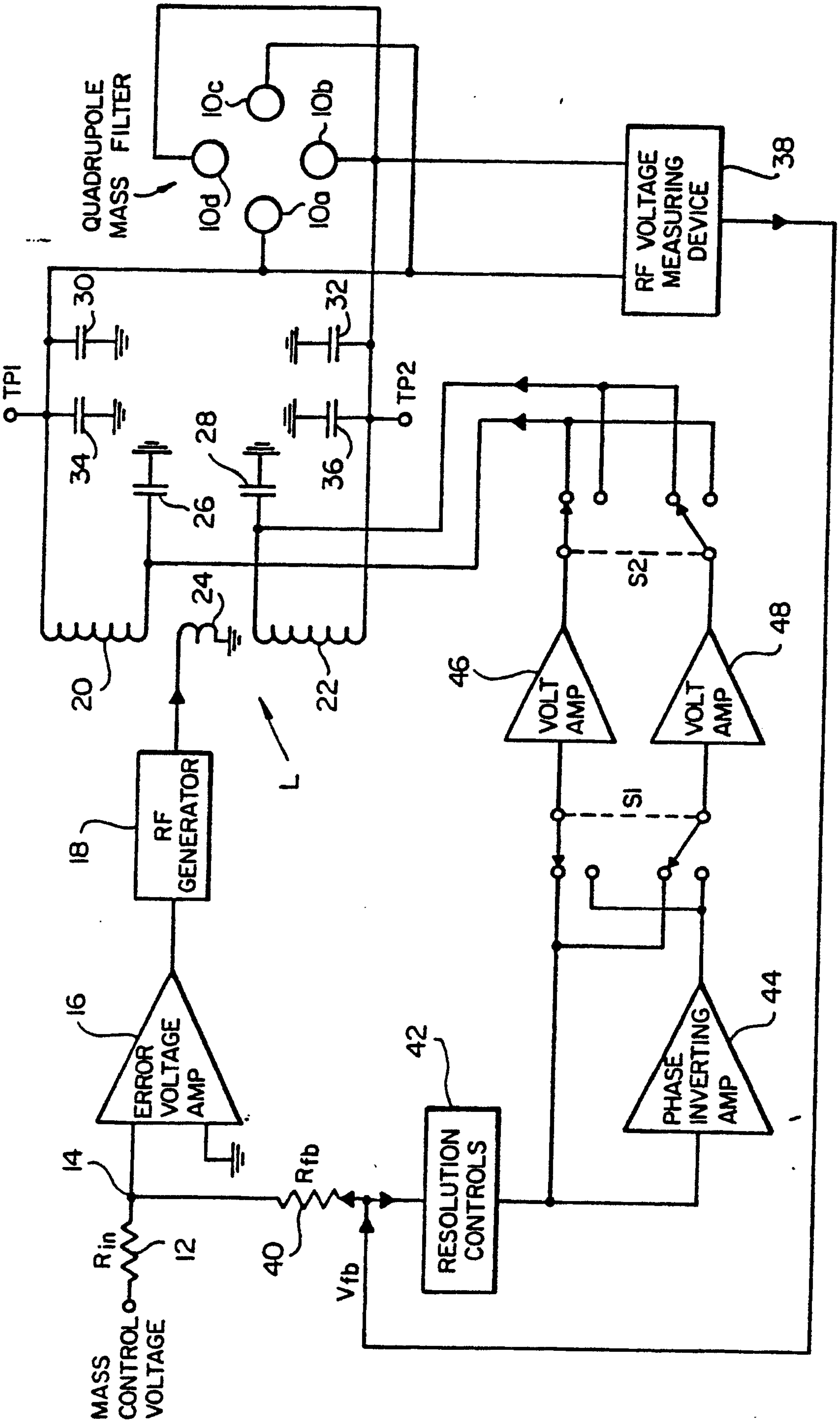
8. Filter nach Anspruch 7, gekennzeichnet durch an die Spannungsmeßeinrichtungen (38) angeschlossene Einrichtungen (40) zum Zuführen einer Rückkopplungsspannung an einen Summierpunkt (14), an dem die Massensteuerspannung und die Rückkopplungsspannung zur Bildung einer kombinierten Spannung summiert werden.

9. Filter nach Anspruch 8, gekennzeichnet durch einen Fehlerspannungsverstärker (l6), der zwischen den Summierpunkt (14) und die hochfrequente Spannungsquelle (18) geschaltet ist, zum Verstärken der kombinierten Spannung.

10. Filter nach einem der Ansprüche 6 bis 9, gekennzeichnet durch eine an die Meßeinrichtung (38) angeschlossene Schalteinrichtung (S1) zum Anlegen der Gleichspannung an die Stangenpaare (10a, 10c; 10b, 10d).

11. Filter nach Anspruch 10, gekennzeichnet durch zwischen die Schalteinrichtung (S1) und die abgestimmten Schaltungseinrichtungen (20, 22; 26, 28; 34, 36) geschaltete Spannungsverstärker (46, 48).

12. Filter nach Anspruch 10 oder 11, gekennzeichnet durch Einrichtungen (S2) zum Umkehren der Polarität der an die Stangen angelegten Gleichspannung.


QUADRUPOLE MASS FILTER
10a
10b
10c
10d
RF VOLTAGE MEASURING DEVICE
38
30
32
34
36
TP1
TP2
26
28
24
20
22
L
RF GENERATOR
18
ERROR VOLTAGE AMP
16
14
R_{in}
12
MASS CONTROL VOLTAGE
R_{fb}
40
V_{fb}
RESOLUTION CONTROLS
42
PHASE INVERTING AMP
44
VOLT AMP
46
VOLT AMP
48
S1
S2