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APPARATUS FOR ANALYSIS BY MASS SPECTROMETRY

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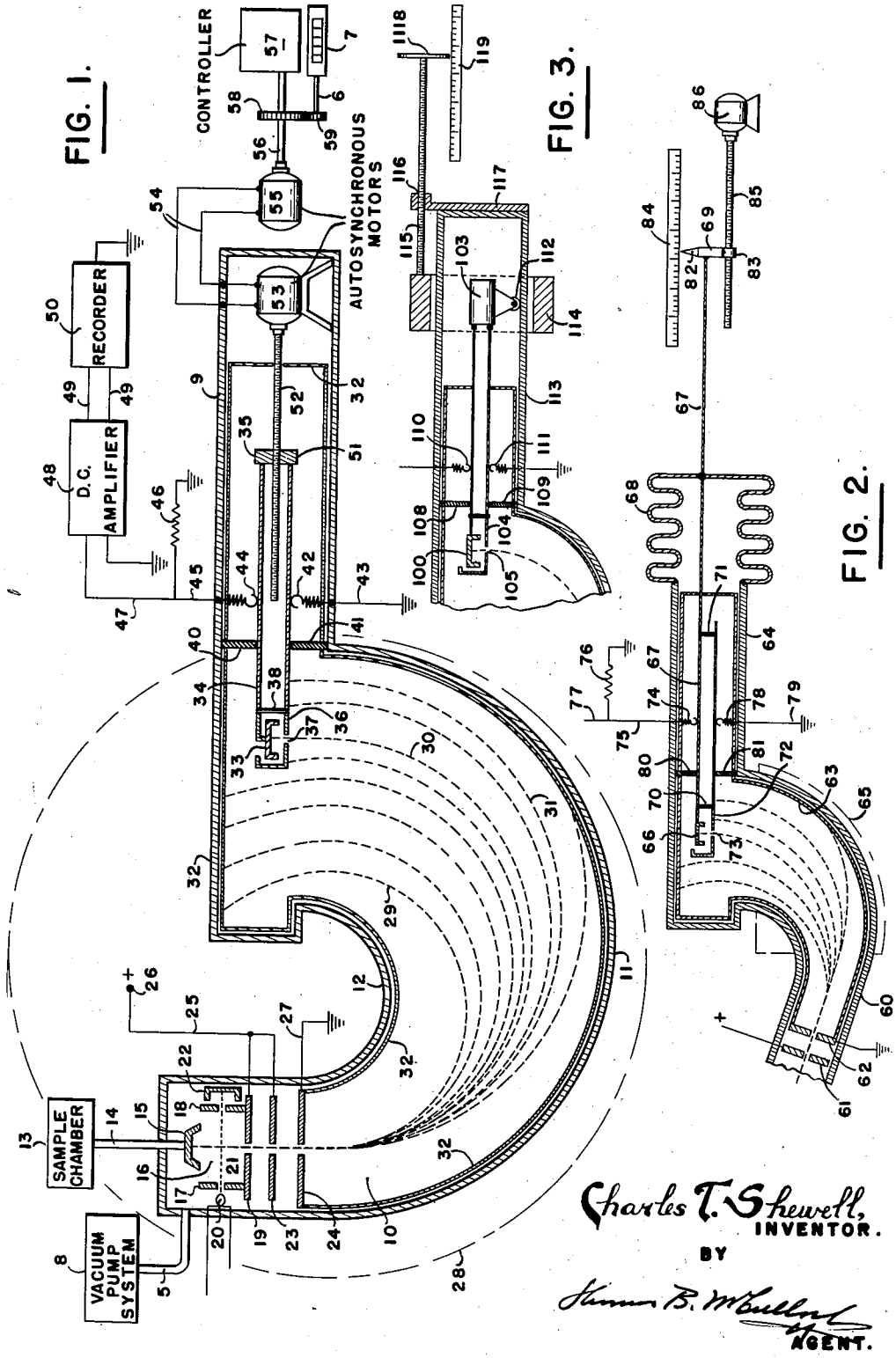


FIG. 1.

FIG. 3.

FIG. 2.

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APPARATUS FOR ANALYSIS BY MASS SPECTROMETRY

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The present invention relates to a method and apparatus wherein ions obtained from substances to be analyzed are effectively resolved and collected.

It is well known to the art to analyze subtances by means of a mass spectrometer. One conventional procedure comprises bombarding substances with low energy, high speed electrons such that the substance is converted into ions of different masses. The ions are then caused to move into a conduit wherein they are resolved into ion beams of selected masses. The ion beams are then focused by suitable means through a slit in one end of the conduit and onto an ion collecting means to produce a signal which is a function of the number of ions striking the collecting means per unit of time. The electric signal may be amplified and recorded by a suitable recording device. As a general rule, the ions prior to resolution are accelerated from the ionization chamber into the resolution chamber by means of an ion accelerating field. The resolution of the ions into beams of selected masses is accomplished by imposing thereon a magnetic or electrostatic field which deflects ions having different masses by different amounts. The magnitudes of the magnetic field and/or the accelerating voltage are usually changed successively to focus an ion beam representing only one mass on the collecting means.

Several disadvantages result from the use of the above mentioned type of apparatus. Hysteresis and/or drift of the magnetic field frequently occurs as a result of rapid changes in the magnitude of the magnetic field. If the magnetic field tends to drift to any appreciable extent, it may be necessary to recalibrate the instrument frequently in order to obtain accurate analysis. Slight variations in the magnitude of the accelerating field also cause variation in the location of the desired ion mass.

It has been known to analyze substances quantitatively by ionizing a substance, resolving the ions into beams of selected masses and focusing the various beams simultaneously on a photographic plate. The location of lines obtained on the developed photographic plate gave some indication of the masses present and in a semi-quantitative way may be used for analysis of the substance. This procedure has not proven to be satisfactory for obtaining a precise, quantitative analysis of the substance to be analyzed. It would, therefore, be desirable to employ a mass spectrometer that could be used for the precise analysis of substances which would be at the same time overcome the operating and apparatus limitation mentioned above.

It is one of the main objects of the present invention to disclose a method and apparatus suitable for the precise analysis of various substances.

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It is a further object of the present invention to disclose a new and rapid method for the analysis of the substances by mass spectrometry employing constant accelerating voltage and intensity of resolving field over a wide range of ion masses.

Further objects of the present invention will become apparent from reading the ensuing description of the invention taken with the drawings, in which:

Figure 1 is a side sectional view of a preferred embodiment of an apparatus of the present invention showing a mass spectrometer tube containing a means for ionizing the substance to be tested, a moving collecting means, and apparatus for moving the collecting means;

Figure 2 shows a side sectional view of another type of mass spectrometer tube containing a collecting means and apparatus for inducing the movement thereof; and

Figure 3 shows another modification of collecting means and apparatus for the movement thereof.

Briefly, the present invention involves forming ions of various masses from a substance to be tested, resolving the ions into beams having selected masses, and passsing a collecting means transverse the path of the resolved ion beams to produce successively signals which are a function of the magnitude of the several ion beams collected.

The apparatus of the present invention includes a mass spectrometer tube having a shape similar to a truncated cone which may be curved such that the interior radius of curvature of the tube is somewhat less than the radius of curvature of the path followed by the lightest ion to be detected and the outer radius of curvature of the tube is somewhat greater than the radius of the curvature of the path followed by the heaviest ion to be detected under the particular operating conditions to be employed. At the small end of the tube is provided an ionization chamber to form ions of various masses from a substance to be analyzed. The ions are then passed through an entrance slit into a resolving field, such as a magnetic field with ions passing at right angles to the magnetic lines of force, such that the ions will resolve into beams of selected masses and are curved through the mass spectrometer tube to the large end thereof. The collecting means such as a Faraday cage is provided at the large end of the tube and is connected through suitable means to a prime mover adapted to move the collecting means transversely across the path of the resolved ions. For optimum resolution of

the ion beams, the collecting means should move on a path which is a straight line defined in direction by the entrance slit and the center of the resolving field. Only one beam at a time is passed through an exit slit in the shield of the Faraday cage and impinges on the cage. The Faraday cage is grounded through a resistance and a current of ions flows to the cage to neutralize the ions impinging thereon. This current, which may be amplified and measured by a suitable galvanometer, is proportional to the number of ions of a given mass striking the cage per unit of time.

The apparatus of the present invention is advantageous in that a constant accelerating voltage and magnetic field may be used in order to form ion beams of a number of different masses which focus on a common straight line determined by the location of the entrance slit and center of curvature of the resolving field. The collecting means may be moved transversely across the path of the beams of ions at a desired speed and the entire spectrum may be scanned without making any changes in the accelerating voltage or resolving field.

Referring now to Figure 1, the numeral **10** designates a circular, crescent-shaped mass spectrometer tube which is a modification of the so-called 180° type commonly used. It is noted, however, that the outer wall **11** of tube **10** has a much larger radius of curvature than the inner wall **12** of the tube. The small, upper portion of tube **10** is enclosed and defines the apparatus used for ionizing the substance to be analyzed as will be explained in more detail hereinafter. The large, upper portion of the tube defines a space through which a collecting means **33** moves and is rigidly attached to a housing **9** which encloses a portion of apparatus used to move the collecting means.

Line **14** passing through the small, upper end of tube **10** connects outer sample chamber **13** and an inner pusher electrode **15**. Vacuum pump system **8** is fluidly connected through line **5** to the upper portion of tube **10** and maintains the tube at extremely low pressure such as from 10^{-3} to 10^{-6} millimeters of mercury absolute pressure. Ionization zone **16** is defined by electrodes **17**, **18**, and **19** which are electrically connected to a focusing electrode **23**, and to a source of high potential **26** (with respect to ground) through lead **25**. Electrode **24** below electrode **23** is grounded through lead **27**. Electrodes **19**, **23** and **24** contain aligned slits directly below the pusher electrode **15**. Also, included in the ionization chamber is electron generator **20** which comprises a tungsten filament or the like connected to a suitable power supply not shown and an electron collector **22**.

Spectrometer tube **10** is provided with an internal nonmagnetic shield **32** which extends from electrode **24** to the large, upper end of the tube and a portion of housing **9**. This shield is grounded through electrode **24** and other grounding connections as desired. Tube **10** is also provided with an outer magnet such as electromagnet **28** regulated by suitable power supply not shown. Movable Faraday cage **33** is shown as being positioned in the upper right end of tube **10** and is supported by electrically conducting member **34** which in turn is connected to and electrically insulated from traveller **35**. Collector **33** is shielded by shield **36** which, likewise, connects to and is insulated from traveller **35**. Shield **36** contains exit slit **37** in front of collector **33**. This shield is sufficiently wide to prevent ion beams

from reaching either collector **33** (except through exit slit **37**) or support member **34**. Member **34** is maintained in position by and is slidable on insulated support **40** rigidly affixed to housing **9**, and shield **36** is, likewise, slidable on insulated support **41**. Flexible contact member **42** is grounded through a spring and lead **43**, lead **43** being sealed through the wall of housing **9**. Shield **36** is slidable on contact **42** such that good electrical connection is maintained between these members. Shield **36** and member **34** are connected by insulated support **38**.

Member **34** is slidable on contact **44** which is also connected through a spring and lead **45** to grounded resistance **46** and through lead **47** to suitable D. C. amplifier **48**. Amplifier **48** is, likewise, connected by leads **49** by a suitable galvanometer and/or recorder **50**.

Traveller **35** contains a central screw-threaded portion **51**, through which passes screw-threaded shaft **52** connected to an autosynchronous motor **53**. Motor **53** is supported at the extreme right hand portion of housing **9** and is electrically connected through leads **54** to autosynchronous motor **55**. The autosynchronous motors **53** and **55** are conventional and are described, for example, in "Chemical Engineer's Handbook," edited by Perry, second edition, McGraw-Hill Publishing Company (1941) on page 2026 or in "Instruments for Measurement and Control" by Rhodes, McGraw-Hill Publishing Company, first edition (1941) on page 368. Since the autosynchronous motors can transmit high torques and are reversible, they are ideally suited in the practice of the present invention. It is noted that shield **32** extends around the inner, lower edges of housing **9** and in front of motor **53**. Motor **55** is connected through shaft **56** to controller **57**. Controller **57** may comprise a synchronous motor or other type of motor or may be a manually operated device for turning the armature of the driver motor.

Shaft **56** contains gear **58** which meshes with gear **59** connected to shaft **6** of counter **7**. Gears **58** and **59** may have any desired ratio such as one to ten, depending on the accuracy desired.

In the operation of the device shown in Figure 1, a small amount of an ionizable substance in vaporized form is introduced into ionization chamber **16**, wherein it is bombarded by low energy, high speed electrons traveling as beam **21** from filament **20**, and through apertures in electrodes **17** and **18** to electron collector **22**. A portion of the substance is ionized into ions of various masses, and, by maintaining a small potential difference between pusher electrode **15** and electrodes **19** and **23**, positive ions are slowly moved through the slits in these electrodes. The accelerating field existing between electrodes **19** and **23** at high potential and electrode **24** at grounded potential causes the ions to be accelerated to high speeds and passed through the entrance slit in electrode **24** into the resolving portion of mass spectrometer tube **10**. The ions of many different masses that enter the curved portion of the conduit pass through a magnetic field at right angles to the magnetic lines of force wherein a sorting of the particles, according to their masses, occurs. Since the radius of curvature of the path of any particular ion in the magnetic field is proportional to the square root of its mass, ions of any one mass will follow a path having a radius of curvature different from the radius of curvature of the path of ions of any other mass. The ions are thus resolved

into ion beams of selected masses as represented by dotted line 29 which represents a beam composed of ions of low mass, dotted line 30 which represents a beam of ions of intermediate mass, and dotted line 31 which represents a beam of ions of high mass.

It is noted that Faraday cage 33 is positioned so that a single ion beam passes through exit slit 37 in shield 36 and impinges thereon. The charges given up by the ions striking Faraday cage 33 cause a current of electrons to flow through grounded resistance 46, lead 45, slidable contact 44 and supporting member 34 to cage 33 for their neutralization, giving a signal transmitted through lead 47 to amplifier 48 wherein it is amplified to a current amenable to measurement in a suitable galvanometer and/or recorder 50. At the time ion beam 30 is being measured other ion beams are grounded either by striking shield 32 on the inside wall of tube 10 or collector shield 36.

When the suitable measurement has been made, controller 57 is rotated a sufficient amount to move the armature of the autosynchronous motor 55 and at the same time the armature of the autosynchronous motor 53 will assume an in-phase position. The rotation of the armature in motor 53 will cause shaft 52 to turn and cause traveller 35 to be moved to another position. The movement of traveller 35 at the same time longitudinally moves collector 33 and shield 36 to another position in the path of an ion beam composed of ions of a different mass. Again the ions striking collector 33 will be neutralized by a flow of current and measured. The extent to which it is desired to move collector 33 across the path of ions is determined by the number of revolutions of shaft 56 as indicated by counter 7. Counter 7 may be calibrated in terms of the various ion masses such as from one to 60 that are to be measured.

By having counter 7 carefully calibrated such that collector 33 may be precisely positioned at any desired point in the path of various ion beams and by maintaining the acceleration field between electrodes 19 and 23 and electrode 24 and the strength of magnetic field 28 constant, an ion beam of a given mass will always focus at the same position in the exit portion of the mass spectrometer tube. This feature of my invention has several advantages, the chief of which being, as previously mentioned, the fact that small drifting of the magnetic field or hysteresis effects do not occur which necessitate frequent calibration of the instrument.

It should be mentioned that several different ranges of ion masses may be determined at any one setting of the accelerating field and magnetic field providing counter 7 is properly calibrated for each setting. Thus, it may be desired to set the accelerating fields at one desired magnitude such that ions have masses from about 1 to 25 focusing on the line through which collector 33 passes, suitable values being noted on counter 7 for determining where each mass is located. Another setting of the accelerating and magnetic fields could be made so that ions having masses of from about 25 to 60 would focus in the proper position, suitable calibration likewise being made on counter 7 for their location. If desired, a third strength of accelerating and/or magnetic fields could be used to focus ions having masses from about 60 to 100 on the line through which collector 33 passes.

Turning now to Figure 2, the apparatus shown

comprises a mass spectrometer tube 60 which is a modification of the 90° type frequently used. In this case the ion source portion of the tube is of smaller diameter than the upper portion of the tube through which the ion collector passes. Focusing electrode 61 is shown as being connected to a source of high potential, and grounded electrode 62 is shown as being connected to an inner non-magnetic shield 63 which extends through curved portion of tube 60 and through a portion of housing 64, which is rigidly attached to the upper end of the mass spectrometer tube. The curved portion of tube 60 is placed within suitable magnetic field 65.

Collector 66 is connected to supporting member 67 which extends through housing 64 and expansion bellows 68 to traveler 69. Collector 66 and member 67 are connected through insulated connections 70 and 71 to shield 72 containing exit slit 73. Flexible electrical connector 74 on which member 67 is slidable is electrically connected through 75 to grounded resistance 76 and line 77 connecting to an amplifier and recording system not shown. Shield 72 is slidable on flexible electrical connector 78 which is grounded through lead 79. Member 67 and shield 72 are slidable on rigid, insulated supports 80 and 81, respectively. Expansion bellows 68 may be constructed of suitable metallic material having sufficient flexibility to contract and expand through a distance of from 10 to 15% of its total length. Suitably it should have a diameter of from 3 to 4 inches or more in order to contract and expand a sufficient distance. Bellows 68 may be suitably sealed to housing 64 by a conventional glass to metal seal that is well known to the art.

Traveler 69 containing pointer 82 and threaded opening 83 is connected to the outer end of supporting member 67. Pointer 82 is positioned below a calibrated scale 84. Threaded shaft 85 of suitable variable speed motor or other prime mover 86 passes through threaded opening 83 of traveler 69.

In the operation of the apparatus shown in Figure 2, a substance is partially ionized as discussed in connection with the description of Figure 1, and the ions of various masses are introduced into the curved portion of conduit 60 through the slit in electrode 63. The ions of vairous masses are resolved into ion beams, each having distinct paths, by means of magnetic field 65. Scale 84 has previously been calibrated so that each mark on the scale will correspond to a specific ion mass. Motor 86 actuates shaft 85 which, in turn, moves traveler 69. The traveler induces movement of collector 66 either to the right or left depending on the desired position to be obtained. An ion beam of the desired mass passes through exit slit 73 is shield 72, is collected and an electric signal is formed that is amplified and recorded. Ion beams that are not being collected impinge on and are neutralized by grounded shields 63 or 72.

When it is desired to measure the intensity of another ion beam, motor 86 is again rotated in the desired direction to move collector 66 to the desired position.

The modification of Figure 2 is advantageous, in that ion collector 66 is displaced positively from one position to another; hence, there is no necessity for recalibration of scale 84 at frequent intervals. It may be desired to move collector 66 through a path of about 5 to 10 inches across the diameter of the upper portion of tube 60, and in

order to obtain the desired amount of expansion and contraction of the bellows expansion bellows 63 should have a length of from about 50 to 80 inches more or less. Although glass may be used in the construction of the bellows, the flexibility of glass expansion bellows is somewhat less than those made from metal; hence, the length of a glass bellows required to move collector 66 through a given distance is considerably greater than it is for a metal bellows.

Turning now to Figure 3, a collection portion of a mass spectrometer tube is shown with another modification for actuating the collector. Collector 100 is movably positioned in the large end of a mass spectrometer tube of the type discussed in conjunction with Figures 1 or 2 or other similar types of mass spectrometer tubes. Collector 100 is connected to an electrically conducting support 101 which in turn is connected to and insulated from a magnetizable armature 103. Armature 103 may be a soft iron core of suitable dimensions or may be a permanent magnet, if desired. Shield 104 containing exit slit 105 is constructed of an electrically conducting material and is likewise connected to and insulated from armature 103. Member 101 and shield 104 are connected by insulated connector 107. Support 101 is slidable on insulating member 108 rigidly affixed to the walls of the mass spectrometer tube, and shield 104 is likewise slidable on insulating member 109. Support 101 is also slidable on contactor 110 leading to a suitable grounded resistance and amplification system, as previously described, and shield 104 is slidable on grounded connector 111. Armature 103 may be supported on wheel 112 which may roll along the lower portion of housing 113.

Circular magnet 114 extends around the outer portion of housing 113 and has a length of armature 103. Magnet 114 is rigidly affixed to threaded rod 115 which, in turn, passes through threaded opening 116 of bracket 17. Micrometer wheel 118 rigidly attached to rod 115 may be used to adjust the position of magnet 114. This may be done manually or by a suitable mechanical device. Wheel 118 is marked on its outer edge with suitable divisions adjacent to scale 119.

The operation of the device in accordance with Figure 3 is carried out by moving magnet 114 to a desired position along housing 113 which, in turn, will cause armature 103 to assume a corresponding position inside housing 113. The movement of armature 103 positively positions collector 100 and exit slit 105 in the path of the desired ion beam. Micrometer 118 and scale 119 may be calibrated so that the desired portion of outer magnet 114 will be known to correspond to the desired position of exit slit 105 to collect a specific ion beam.

The apparatus in accordance with Figure 3 is most applicable to the measurement of ion beams having masses in the lower range, i. e., from about 1 to 30 or 40 since there is a greater distance between the resolved beams having lower masses than there is between those having masses of 50 to 100 or thereabouts. It will be obvious to one skilled in the art that the practice of my invention can be carried out in the different types of mass spectrometer tubes and collector actuating devices. The mass spectrometer tube itself may be a suitable straight conduit or a curved conduit of the 60, 90, 180° or other types of tubes with the ionization portion of the tube having a somewhat smaller diameter than the collecting portion of the tube. The movable ion collecting means may be actuated by any number of devices that will permit accurate location of the collecting means at the desired point in the mass spectrometer tube.

Although one of the chief advantages of my invention is the feature of maintaining the magnitude of the ion accelerating field and of the resolving field at constant values during an analysis, it may be desired in some instances to supply variable sources that may be adjusted to focus successively certain desired ranges of masses in the collecting portion of the tube. For example, the accelerating and/or magnetic voltages will be set at one value to project ion beams having masses from about 1 to 25 in the path of the movable ion collector with a suitable calibrated scale being available for this range of masses. Another adjustment of ion accelerating field and/or magnetic field could be made to focus ion beams of from about 25 to 60. In this manner, the accelerating voltage and/or magnetic field would be fixed for a certain desired range of ion beams and after all readings have been made for that particular range, the adjustment could be made to cover another wide range of ion beams.

The nature and objects of the present invention having been fully described and illustrated, what I wish to claim as new and useful and to secure by Letters Patent is:

1. A mass spectrometer which comprises, in combination, a mass spectrometer tube, means within said tube for producing ions of different masses from a substance, means adjacent the tube for resolving ions in the tube into beams of selected masses, movable carriage means in said tube adapted to move transversely across the resulting paths of resolved ion beams, shielded movable collecting means within the tube for collecting ions of said resolved ion beams and forming an electric signal mounted on said movable carriage means for movement transverse to the path of said resolved ion beams and actuating means for moving the carriage transverse to paths of resolved ions which includes a first auto-synchronous motor mounted in the tube and electrically connected to a second auto-synchronous motor mounted outside the tube.

2. A mass spectrometer which comprises, in combination, a mass spectrometer tube, means within said tube for producing ions of different masses from a substance, means adjacent the tube for resolving ions in the tube into beams of selected masses, movable carriage means in said tube adapted to move transversely across the resulting paths of resolved ion beams, shielded collecting means mounted on said carriage for collecting ions of said resolved ion beams and for forming an electrical signal, an actuating means for moving said carriage and collecting means, which actuating means includes a screw-threaded traveller, a first auto-synchronous motor having an elongated shaft screw-threadedly engaging said traveller and aligned transverse to the paths of the resolved ions, said traveller, shaft and motor being mounted within the tube, and a second auto-synchronous motor outside the tube and electrically connecting with said first motor.

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REFERENCES CITED

The following references are of record in the file of this patent:

Straus, Physical Review, March 1, 1941, volume 59, pages 430–433.