

July 13, 1948.

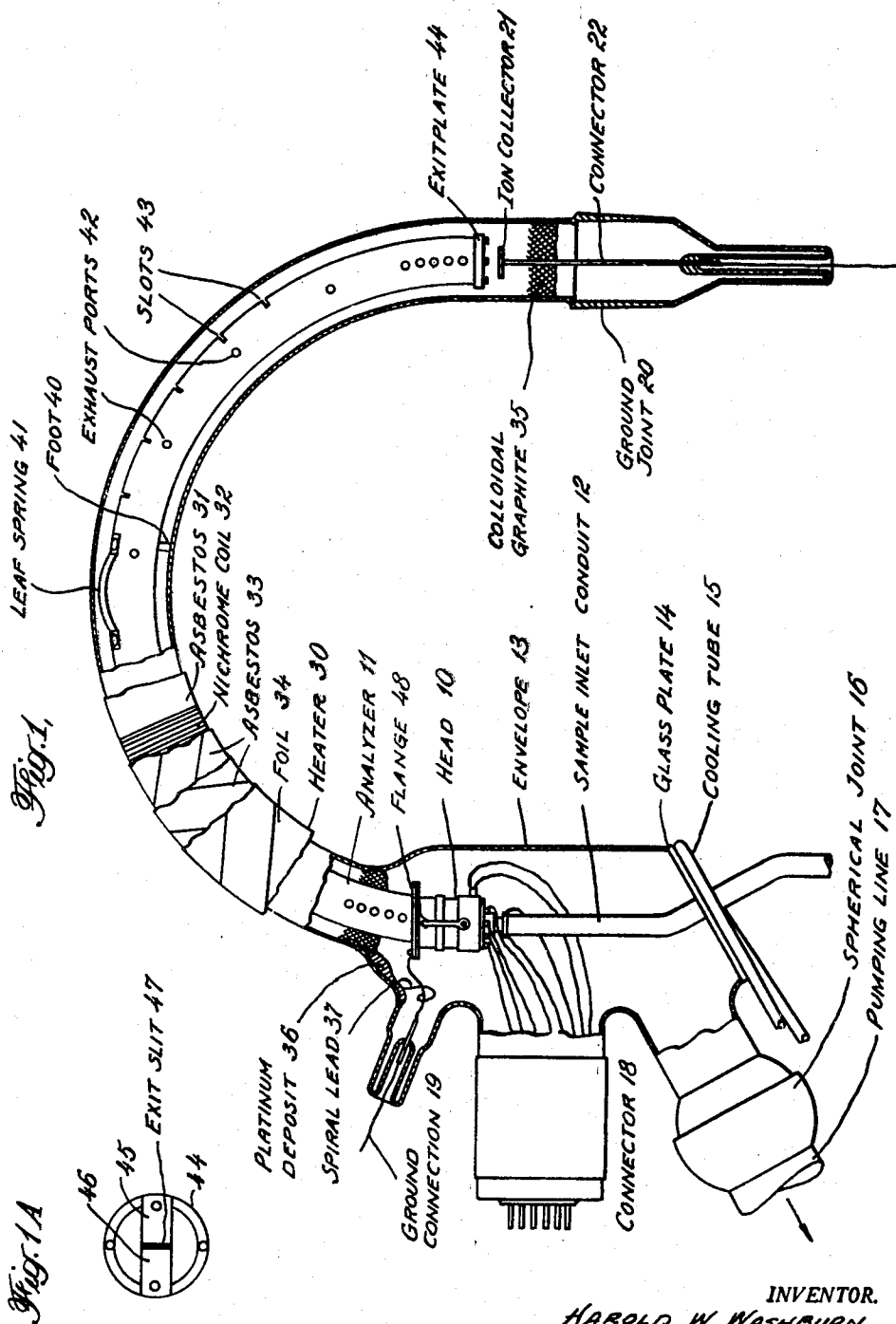
H. W. WASHBURN

2,444,968

MASS SPECTROMETRY

Filed Dec. 9, 1943

2 Sheets-Sheet 1



INVENTOR.
HAROLD W. WASHBURN
BY
Paine, Howe, Munroe & Emmons
ATTORNEYS

July 13, 1948.

H. W. WASHBURN

2,444,968

MASS SPECTROMETRY

Filed Dec. 9, 1943

2 Sheets-Sheet 2

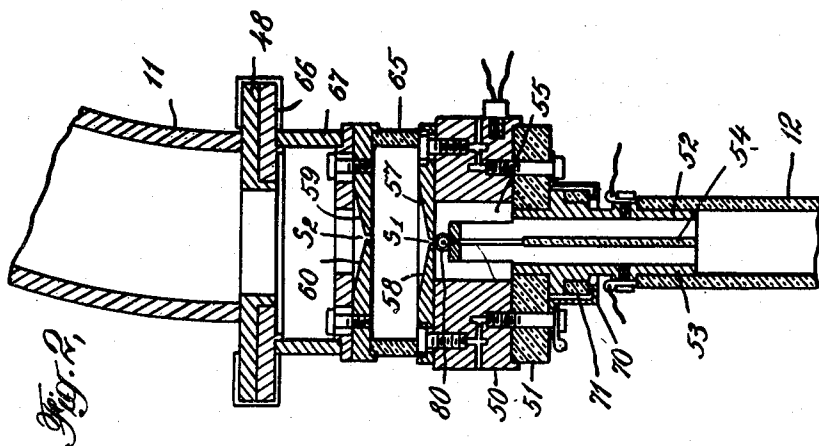


Fig. 2,

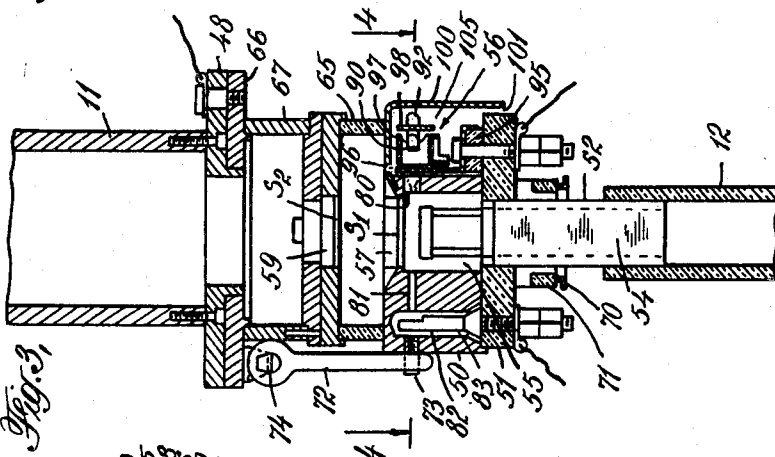


Fig. 3,

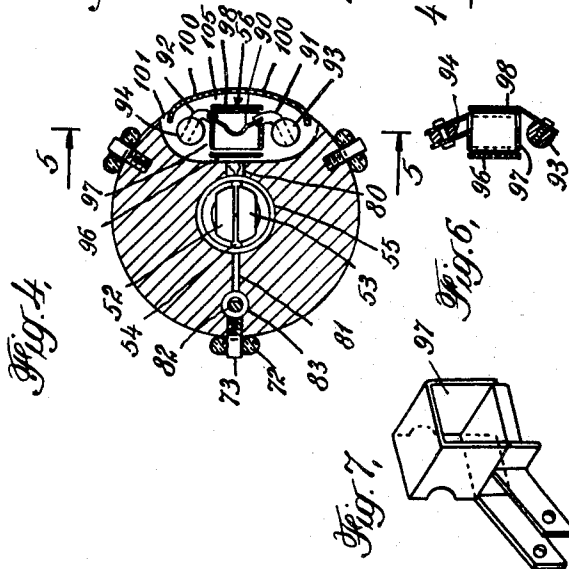


Fig. 4,

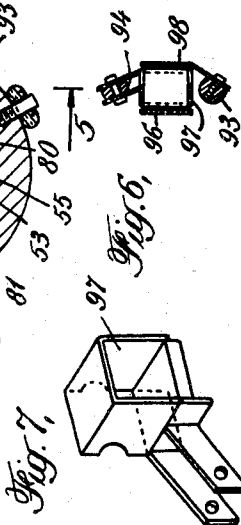


Fig. 5,

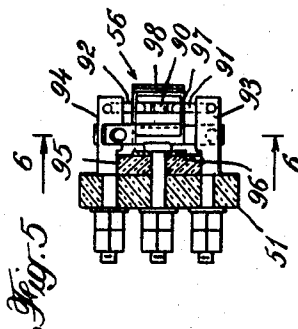


Fig. 6,

INVENTOR.
HAROLD W. WASHBURN
BY
Lawrence H. Brown & Associates
ATTORNEYS

UNITED STATES PATENT OFFICE

2,444,968

MASS SPECTROMETRY

Harold W. Washburn, Pasadena, Calif., assign-
or to Consolidated Engineering Corporation,
Pasadena, Calif., a corporation of California

Application December 9, 1943, Serial No. 513,529

4 Claims. (Cl. 250-41.9)

1

This invention is concerned with mass spectrometers and particularly with spectrometers provided with an ionization chamber and an electron emitting element, such for example as a heated filament, which provides electrons for bombarding molecules in the ionization chamber to convert them to ions.

A mass spectrometer is an ion sorting device which may be employed to ionize molecules and separate the resulting ions according to their specific masses, i. e., according to the ratio of the mass of the ion to the charge which it carries. It may be employed for both qualitative and quantitative analyses of mixtures, particularly gaseous mixtures, as well as for the determination of isotope abundance ratios and other scientific problems. A well known form of mass spectrometer comprises an ionization chamber, means for admitting molecules to be ionized into the chamber, an electron emitting element, means for propelling the emitted electrons against molecules in the chamber to convert them into ions, an analyzer tube (connected to the ionization chamber) in which an electric or magnetic field may be established, electrodes disposed in the neighborhood of the electron emitting element and the ionization chamber for impressing a propelling potential on the ions formed in the ionization chamber to force the ions through the analyzer, and a collector upon which the ions impinge and discharge after travel through the ionization chamber.

A sample to be analyzed, say a gaseous mixture, is admitted to the ionization chamber and there bombarded by the electrons so that ions are formed. These ions are forced by the propelling potential out of the ionization chamber and through the analyzer tube, where (under the action of the field) they are separated into diverging beams of ions according to their specific mass, each beam comprising a stream of ions having the same specific mass. By sweeping these beams successively over the collector, or by moving the collector into the paths of the several beams, a series of charges is collected. Measurements of the amounts of these charges represent the mass spectrum of the gas subjected to ionization. This spectrum is a measure of the amounts of the several kinds of ions collected and, under certain operating conditions, can be a measure of the amounts of the several kinds of molecules in the original mixture from which the ions were derived. In short, under proper operating conditions, a quantitative analysis of the mixture can be obtained from the mass spectrum.

2

The propelling potentials exerted by the electrodes which force the ions from the ionization chamber into the analyzer usually are high, of the order of several hundred volts or more, and create an electric field which may affect the electron emission, with a consequent effect upon the mass spectrum.

In accordance with my invention, this effect is minimized by interposing one or more metallic shields adjacent the electron-emitting element and between it and the electrodes. Preferably, means are provided for maintaining a potential difference between the shield and the element which is independent of any potential difference between the element and the electrodes. For example, means may be provided for maintaining a constant potential difference between the shield and the filament.

In the preferred form of my invention, the metallic shield, which may comprise several sections maintained at different potentials, surrounds the electron emitting element substantially completely, i. e., is disposed on all six sides of the element, but is provided with an aperture for the emission of an electron beam. In this preferred form the electron emitting element (filament) is mounted externally of the ionization chamber, and the insulators on the leads which supply current to the filament are protected by one or more metallic shields interposed between the insulators and the filament, so that metal vaporized and emitted by the filament is deposited on the shields instead of on the insulators.

The presence of a shield (say the shield 97) between the ionization chamber and the filament is desirable because this shield can be used to create a space charge around the filament to protect it from the effect of positive ions and minimize fluctuations in electron emission due to fluctuations in filament current. These results can be obtained without affecting the energy of the electron beam entering the ionization chamber. The electrode arrangement shown in this application is described and claimed in my copending patent application, Serial No. 513,525, filed December 9, 1943, now Patent No. 2,378,962.

These and other features and advantages of my invention will be more thoroughly understood in the light of the following detailed description, taken in conjunction with the accompanying drawings in which:

Fig. 1 is a sketch of a mass spectrometer assembly, including an ionization chamber assembly or "head," an analyzer and a collector all disposed within an envelope.

Fig. 1A is a plan of the exit plate of the analyzer tube of Fig. 1;

Figs. 2 and 3 are longitudinal sectional views of the head of Fig. 1, taken through the axis of the assembly and, respectively, perpendicular and parallel to a magnetic field impressed on the ionization chamber and analyzer tube by a magnet (not shown);

Fig. 4 is a section through the head of Figs. 2 and 3 taken along the line 4—4 of Fig. 3 of the apparatus;

Fig. 5 is a section through the filament assembly of Fig. 4 taken along the line 5—5;

Fig. 6 is a section through the filament assembly taken along the line 6—6 of Fig. 5; and

Fig. 7 is a sketch showing the box-shaped shield of the filament assembly.

In the type of mass spectrometer herein described, the envelope and the elements which it encloses are normally mounted in a horizontal plane between the poles of an electromagnet (not shown).

General assembly in the envelope

By reference to Fig. 1, it will be seen that the instrument is provided with a head 10, which includes an ionization chamber, connected at one end to a semi-circular analyzer tube 11 and at the other end to a glass conduit 12 through which a gas sample to be analyzed may be admitted. The head and analyzer tube are enclosed within a glass envelope 13. The end of the envelope at which the head is positioned is enlarged and has a flat section 14 at the very end thereof through which the gas introduction conduit passes. This flat section is in the form of a glass plate which is secured to the envelope with wax. This wax is kept from melting during the operation of the mass spectrometer by means of a cooling fluid which is circulated through a copper tube 15 in contact with the glass plate adjacent the wax joint.

The enlarged section of the envelope has three side branches. One of these is terminated in a spherical point 16 which is adapted for connection to a pumping line 17. The second side branch is terminated by an electrical connector 18 having plug terminals for supplying various currents and voltages to electrodes in the ionization chamber. In the third branch there is sealed a lead 19 which may be used as a ground connection. The second and third branches are spaced apart considerably in order to insulate the ground lead from the plug terminals since these are operated at a voltage which may be either positive or negative with respect to ground but which in either event may differ greatly from ground potential.

The end of the envelope remote from the enlarged section has a tapered ground joint surface 20 on the outside. A metal disc 21 acting as an ion collector is mounted on a rod or connector 22 coaxial with the ground joint and within the envelope. This rod extends through a glass seal at the end of the envelope and makes an electrical connection to the grid of an amplifying tube contained in an evacuated metal tube (not shown) which fits over the ground joint.

A heater 30 is provided for heat treating or baking out the envelope assembly, and comprises the following layers which are wrapped successively about the semi-circular portion of the envelope between the enlarged section and the ground joint:

A layer of asbestos 31;

A coil of Nichrome wire 32 adapted to be heated by electric current;

Two layers of asbestos 33; and

A layer of metal foil 34.

In order to provide against the accumulation of any electrical charges on the inside wall of the envelope, it is coated with a layer 35 of colloidal graphite which is maintained at ground potential through a platinum deposit 36 on the wall and a spiral lead 37 which is connected to the ground lead within the envelope.

The asbestos layers serve to insulate the coil from the foil and also to distribute the heat from the coil over the surface of the glass envelope. The foil aids in heating the assembly by reducing outward radiation of heat from the coil.

The analyzer tube is centered within the glass envelope with the aid of feet 40 extending outwardly from the walls of the analyzer tube and flexible curved leaf springs 41 secured to the outside of the analyzer tube. These centering springs are secured at one end rigidly to the analyzer tube and are held in axial alignment with the tube by means of screw heads at the other end which overlap slotted parts of the spring.

Small exhaust ports 42 are drilled into the analyzer tube at numerous points throughout its length at the front and back thereof.

Slots 43 are cut into the outside circumferential edge of the analyzer tube. Metal baffles (not shown) may be inserted into these slots to aid in the elimination of "ghosts" (which may arise because of the reflection of ion beams at the inner wall of the analyzer tube).

At the outlet end of the analyzer tube there is secured an aperture plate 44 on which (see Fig. 1A) are mounted two slidable jaws 45, 46, the sharp edges of which define an exit slit 47 through which ions are projected from the analyzer tube onto the collector.

At the inlet end of the analyzer tube, there is a flange 48 to which the head 10 is secured by pivoted clamps.

Head, including ionization chamber

Details of the head are shown in Figs. 2, 3, 4, 5, 6 and 7. By reference to these figures it will be seen that the head comprises a block 50 in the form of a thick-walled metal cylinder, a quartz disc 51 secured to the inlet end of the block, a pair of pusher segments 52, 53 separated by a quartz insulator 54 and extending into the block bore 55 through the quartz disc, an electron gun 56 (Fig. 3) mounted on the quartz disc, a pair of jaws 57, 58 positioned at the outlet side of the block to define a first slit S₁, a second pair of jaws 59, 60 separated from the first pair of jaws by a Pyrex insulating ring 65 and defining a second slit S₂, and a head mounting flange 66 spaced from and electrically connected to the second pair of jaws by means of a copper spacer 67.

The pusher segments are secured to the block by means of a pusher clamp 70 (which cover a Pyrex pusher locking ring 71 surrounding the two pusher segments) screwed to the block through the quartz disc. The block and first pair of jaws, the Pyrex insulating ring, the second pair of jaws, the copper spacer, and the head mounting flange are held together by quartz links 72 each of which has an eye at one end (which is positioned over a link-stud screw 73 which extends outwardly from the side of the block wall) and at the other end a second eye perpendicular to the first eye. The second eye is secured to the head mounting flange by means of spring link clips 74.

5

On one side of the block, there is a cut-away section in which the elements of the electron gun are mounted. Electrons from this source are projected through a slotted insert 80 in the wall of the block into the ionization chamber and thence through a concentric bore 81 in the other side of the block onto an electron catcher 82 which is supported by the quartz disc and extends into a bore 83 drilled part way into the block perpendicular to the bore 81.

The block, the pusher segments, the central part of the quartz disc and the first pair of slit jaws form a substantially enclosed space that serves as an ionization chamber.

The entire assembly is so arranged that the adjacent but spaced edges of the pusher segments, the axis of the electron beam, the axes of slits S₁ and S₂, and the axis of the exit slit of the analyzer tube are all parallel to each other and to lines of force of the magnetic field in which the entire envelope assembly is to be placed.

Electron beam source

A filament 90 which acts as an electron source in the gun is supported by two L-shaped filament supports 91, 92 which in turn are fastened to filament posts 93, 94 mounted on the quartz disc and perpendicular thereto. Changes in the position of the filament are prevented in part by means of a square quartz locking plate 95, two edges of which rest against locking flaps cut into the sides of the filament posts. An apertured electron accelerating electrode 96 is mounted intermediate the filament and the slotted insert or "gun barrel" 80 through which electrons are to be propelled into the ionization chamber. A box-shaped shield 97 open at opposite ends is disposed around the filament and supported by one of the filament posts with the planes defined by its open ends perpendicular to the axis of the electron beam. A rear filament shield 98 is supported by the other filament post and is disposed in the open end of the box-shaped shield opposite the electrode 96.

The electron accelerating electrode, the box-shaped shield, and the rear filament shield are insulated from each other. Together, they prevent metal evaporated from the filament from striking the quartz disc, for such metal strikes one or the other of the members and condenses before it reaches the quartz insulator.

An external filament shield 100 having a general L-shape is mounted with one flat side in contact with the block at the side remote from the quartz disc, and with the other side of the L generally concentric with the block. This shield thus encloses the electron gun except for an evacuation slot 101. Thus, the apparatus is provided with an enclosed electron gun chamber 105 which may be evacuated through the slot.

Electrical elements

Considered from an electrical standpoint, the block and first jaws represent a first ion accelerating electrode, and the jaws forming the second slit comprise a second ion accelerating electrode. The two pusher segments are pusher electrodes.

The voltages of the filament, the electron accelerating electrode, the block and the pusher electrodes may be controlled independently. In normal operation, when interested in the analysis of positive ions, these electrodes are all at high positive potentials with respect to the second ion accelerating electrode, which is at ground.

The rear filament shield is at the same potential

6

as one end of the filament, and the box shield is at the potential of the other end of the filament. The outer filament shield is at the same potential as the block and hence at the same potential as the first ion accelerating electrode. The outer filament shield and the wall of the block provide an equipotential surface which shields the filament from stray fields that might arise because of any high potential applied between the first ion-accelerating electrode and the second ion-accelerating electrode. Any residual stray field that might leak toward the filament because of the presence of the slot and the non-conductive insulating surface of the quartz disc at the bottom of the electron gun chamber is prevented from doing so by the presence of the potentials existing on the box-shaped guard disposed around the filament and comprising the electron-accelerating electrode, the open-ended box-shaped shield and the rear filament shield.

Operation

A gas mixture, say a mixture of hydrocarbons, may be analyzed by introducing it at low pressure into the ionization chamber through the sample inlet conduit 12. Thus the gas enters the ionization chamber in the head 10 through a passageway between the two pusher segments 52, 53.

In the ionization chamber, the molecules of gas are bombarded by an electron beam originating at the filament of the electron gun and passing through the gun barrel 80. An electrical potential is impressed between the pusher electrode (i. e., the interior ends of the two pusher segments) and the jaws 57, 58 which define the slit S₁. This potential pushes the ions through the slit S₁ as a heterogeneous ion beam. This beam is further accelerated by a potential impressed between the jaws defining the slit S₁ and the jaws 59, 60 which define the slit S₂. The two slits act as a collimator and the heterogeneous ion beam or ribbon is projected through the slit S₂ into the analyzer tube. In the analyzer tube the ions are acted upon by a magnetic field which separates them according to their specific masses into a plurality of curved homogeneous ion beams which diverge from each other and are focused at different points within the analyzer, for example on the exit plate. By varying the magnetic field the radii of the curving ion beams may be changed so that the beams are swept successively across the exit slit 47 of the instrument. In this fashion the several beams may be brought to focus successively on the ion collector and there discharged. The currents thus formed constitute the mass spectrum of the gas mixture and, if amplified and recorded, produce a mass spectrogram.

The propelling potential which is impressed between the pusher electrodes and the electrodes 57, 58 (which define the slit S₁) is relatively high, and the potential impressed between the slits S₁, S₂ (i. e., between the ion accelerating electrodes) may be very high—of the order of several hundred volts. These potentials create an electric field which may affect the emission of electrons by the electron gun, with a serious effect upon the mass spectrum. The effect of electric fields created by the propelling potentials in the head of the mass spectrometer is minimized by the metallic shields which are disposed around the ion emitting filament. Thus in the apparatus illustrated, the filament 90 is substantially surrounded by a metallic shield comprising the box-shaped shield 97, the rear shield 98 and the electron accelerating electrode 96, which has the aperture

through which the ion beam is projected. The leads, i. e., the supporting posts which hold the filament are insulated by the quartz plate and this plate is protected by the shields, so that metal vaporized and emitted by the filament is deposited on the shields instead of on the insulator.

I claim:

1. In a mass spectrometer provided with an ionization chamber, means for admitting molecules to be ionized into the chamber, an electron emitting element, means for propelling the emitted electrons against molecules in the chamber to convert the molecules into ions and electrodes disposed in the neighborhood of the electron emitting element and the ionization chamber for impressing a propelling potential on the ions thus formed, the combination which comprises a plurality of metallic shielding elements surrounding the electron emitting element and adjacent thereto, one of these elements being provided with an aperture for the emission of the electron beam, and means for maintaining another of these elements at the same potential as one end of the electron emitting element.

2. In a mass spectrometer provided with an ionization chamber, means for admitting molecules to be ionized into the chamber, an electron emitting element, means for propelling the emitted electrons against molecules in the chamber to convert the molecules into ions, and electrodes disposed in the neighborhood of the electron emitting element and the ionization chamber for impressing a propelling potential on the ions thus formed, the combination which comprises a separate chamber in which the electron emitting element is mounted, a conduit connecting the separate chamber to the ionization chamber to permit the emitted electrons to enter the ionization chamber comprising an aperture in one of the electrodes, a shield at the side of the electron-emitting element opposite the last-mentioned electrode, and means for maintaining said shield and the last-mentioned electrode at substantially the same potential.

3. In a mass spectrometer provided with an ionization chamber, means for admitting molecules to be ionized into the chamber, an electron emitting filament, means for propelling the admitted electrons against the molecules in the chamber to convert the molecules into ions, and electrodes disposed in the neighborhood of the electron emitting element and the ionization chamber for impressing a propelling potential on the ions thus formed, the combination comprising a six sided metal shield substantially enclosing the electron emitting filament, the front side of the shield being part of the means for propelling the emitted electrons and being insulated from the other sides of the shield, the rear side of said shield opposite said front side also being insulated from the remaining sides of the shield, means for maintaining the rear side at the potential of one

end of the filament and means for maintaining the remaining sides at the potential of the other end of the filament.

4. In a mass spectrometer provided with an ionization chamber, means for admitting molecules to be ionized into the chamber, an electron emitting filament, means for propelling emitted electrons against molecules in the chamber to convert the molecules into ions and electrodes disposed in the neighborhood of the electron emitting filament and the ionization chamber for impressing a propelling potential on the ions thus formed, the combination which comprises a four sided box disposed around the filament and open at opposite ends, an electrode for propelling the emitted electrons so disposed as to substantially close one end of the box and being insulated therefrom, a shield substantially closing the opposite end of the box and being insulated therefrom, means for maintaining the shield at the potential of one end of the filament and means for maintaining the box at the potential of the other end of the filament.

HAROLD W. WASHBURN.

REFERENCES CITED

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

UNITED STATES PATENTS

Number	Name	Date
2,221,467	Bleakney	Nov. 12, 1940
2,331,189	Hipple	Oct. 5, 1943

OTHER REFERENCES

Technical Publication, "A Mass Spectrum Analysis of the Products of Ionization by Electron Impact in Nitrogen, Acetylene, Nitric Oxide, Cyanogen and Carbon Monoxide," by John T. Tate et al., pp. 525-531, Physical Review, vol. 48, 2nd series, Sept. 15, 1935. (Photostat copy in Division 36, U. S. Patent Office.) 73-51 Mass. Spec.

Technical Publication, "The Ionization Potential of Molecular Hydrogen," by Walter Bleakney, pp. 496-501 of Physical Review; vol. 40, 2nd series, May 15, 1932. (Photostat copy in Division 36, U. S. Patent Office.) 73-51 Mass. Spec.

Technical Publication, "A Mass Spectrometer for Routine Abundance Measurements," by Alfred O. Nier, pp. 212-216, Review of Scientific Instruments, vol. 11, No. 7, July 1940. (Photostat copy in Division 36, U. S. Patent Office.) 73-51 Mass. Spec.

Technical Publication, "Primary and Secondary Products of Ionization in Hydrogen," by H. D. Smith, pp. 452-459 of Physical Review, vol. 25, 1925. (Photostat copy in Division 36, U. S. Patent Office.) 73-51 Mass. Spec.

Technical Publication, "An Experimental Mass Spectrometer," by N. D. Coggeshall et al., pp. 125-129, Review of Scientific Instruments, vol. 14, No. 5, May 1943. (Photostat copy in Div. 36, U. S. Patent Office.) 73-51 Mass. Spec.