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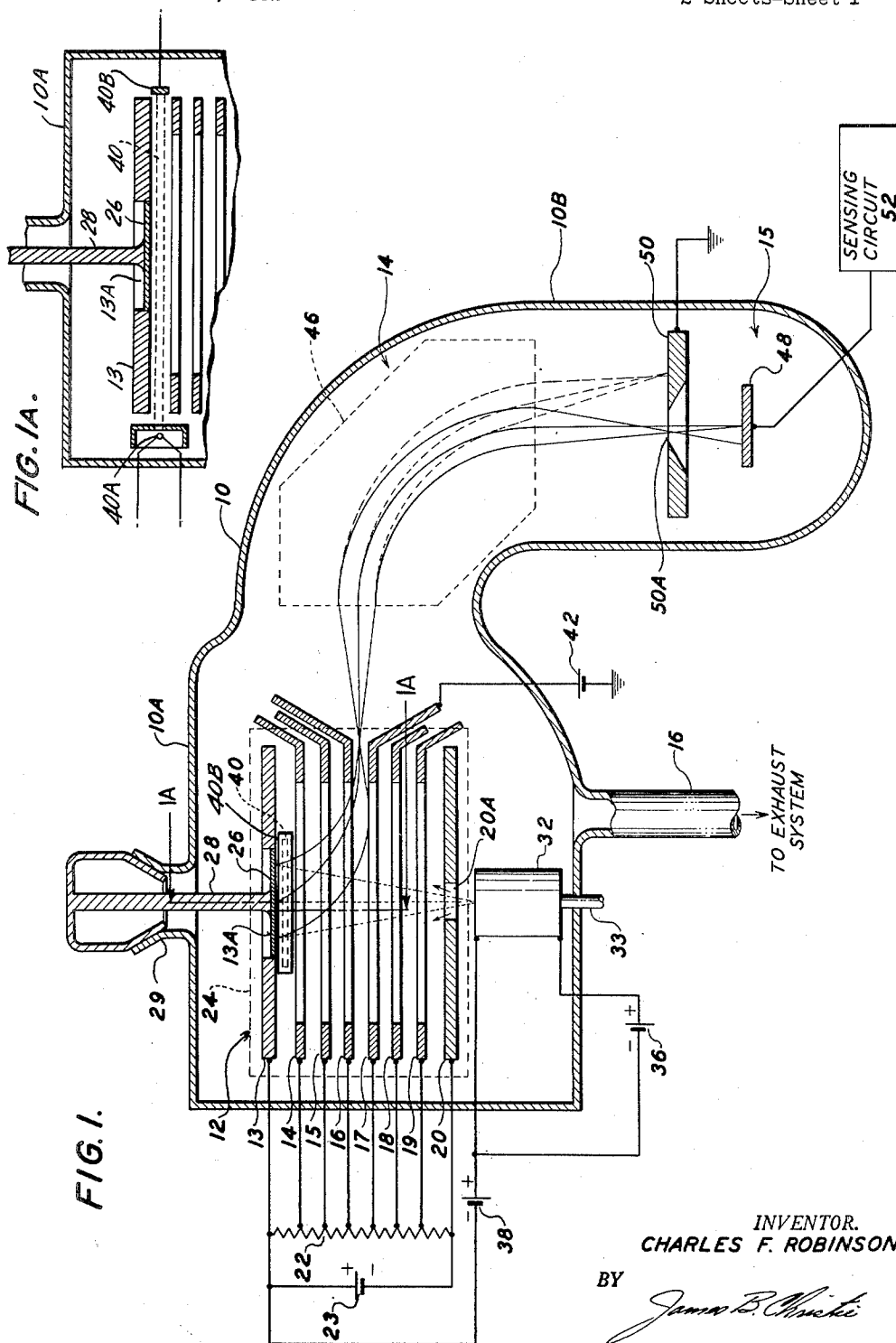
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METHOD AND APPARATUS FOR IONIZATION OF SOLIDS.

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FIG. 2.

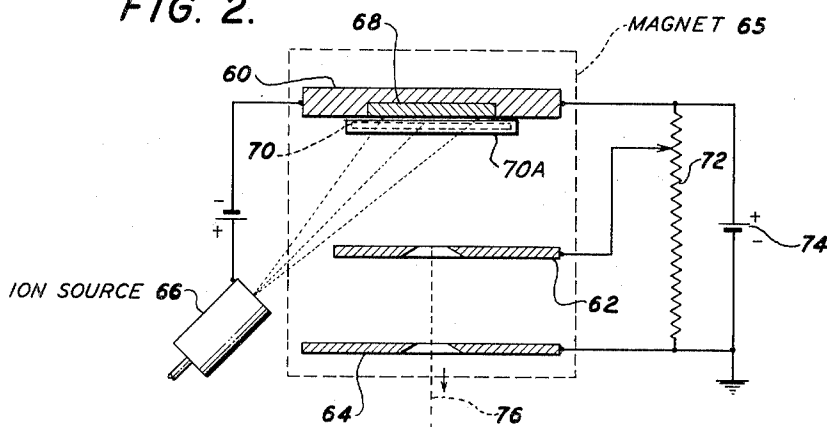
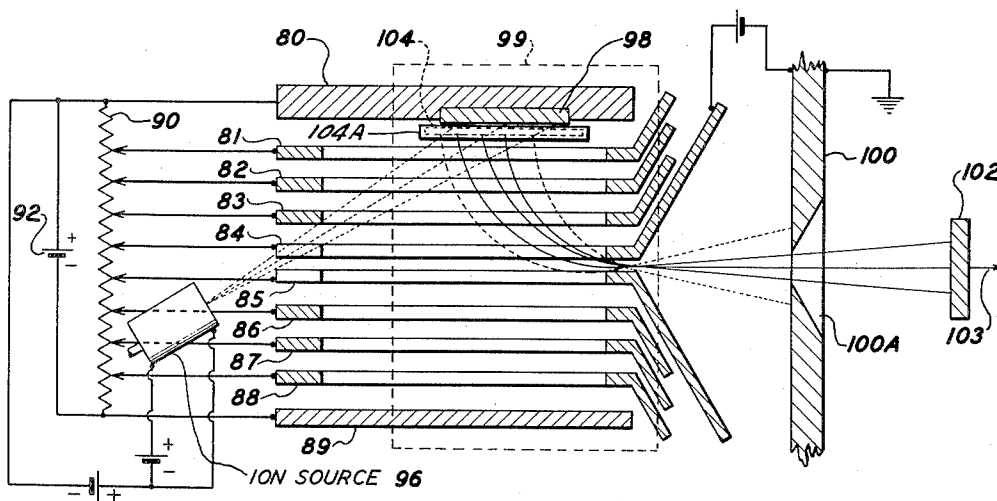


FIG. 3.



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METHOD AND APPARATUS FOR IONIZATION OF SOLIDS

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4 Claims. (Cl. 250—41.9)

The invention relates to method and apparatus for ionizing solid materials to produce a representative quantity of ions and particularly to ionization of solids for purposes of analysis thereof by mass separation.

Although practice of the invention is in no way so limited, a principal interest in ionization of solids is found in the field of mass spectrometry. Mass spectrometry has long been a well established field of analysis particularly with respect to qualitative and quantitative inspection of readily vaporizable fluid mixtures.

Analysis by mass spectrometry involves ionization of a sample under investigation, segregation of the resultant ions in accordance with their specific mass and by virtue of ion behavior in electrical or magnetic fields or both as a function of mass, selective collection and discharge of segregated ion masses and electrical sensing of relative abundance information. These basic operations vary widely in attainment, there being for example a number of electrical and magnetic field configurations suitable for ion segregation as a function of mass.

There is to date no commercially satisfactory application of mass spectrometry to solid materials. The outstanding problem encountered in adapting this form of analysis to solid samples is suitable derivation of ions from such a sample. Bombardment of a sample with an electron beam, as conventionally practiced with vaporized samples, is usually futile as being unproductive of ions. The difficulty attendant upon ionization of a solid sample arises because of the necessity of obtaining from such a sample under investigation an ion beam, (1) the constitution of which bears a reproducible relationship to the composition of the sample, (2) the composition of which will not vary with time, and (3) which is not disproportionately affected by small amounts of impurities in the sample.

It is apparent, therefore, that a mass spectrometer for solid material requires an ion source having the following capabilities and characteristics:

1. A source which will accommodate samples in the form in which they are received or obtained for inspection without need for chemical or physical modification;

2. A source in which the probability of creation of an ion of one kind or another kind depends only upon the relative abundance of the parent particles in the sample and not upon the bulk chemical or physical properties of the material;

3. A source in which extraneous ions (derived from other than the sample) are not randomly introduced by the process of sample ionization; and

4. A source in which the ion current is sufficiently constant with time to permit consecutive scanning of the various mass peaks of interest.

One or more of the above requirements effective preclude the possibility of ion acquisition by any of the following procedures:

1. Vapor phase sample introduction and electron beam bombardment;

2. Vaporization of a solid sample in the ion source by

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application of heat and ionization of the vapor by electron bombardment;

3. Incorporation of the sample in an electrode of an electric arc or spark system; or

4. Chemical reformation of the sample to a more readily vaporizable form.

All of the foregoing suggest themselves as possible methods of approach, but each can be shown to be unsatisfactory from economic and practical considerations.

The present invention contemplates a method of ionizing a solid which comprises forming a beam of positive ions and impinging the ion beam against a surface of the solid sample. Principal merit of the invention is the use of a bombarding ion beam to vaporize a mixed solid sample bit by bit in order to provide a beam of ions from the sample, the composition of which will not change with time and which accurately reflects the relative abundance of the various components of the sample. Refinements in the method of the invention and apparatus suitable for practicing the invention are described in detail hereinafter.

The ionizing ion beam involves a highly local process for the ionization of the solid sample. All "bulk" effect, such as that attendant upon thermal heating, is minimized. It is apparent that vaporization by thermal heating inevitably results in differentiation based not solely on abundance but also on relative vapor pressures, etc. and therefore is incapable of developing a representative sample of ions. The destructive effect of a positive ion beam is well known, as is also the lack of dependence of this effect on the melting or boiling points of the components of a target material. In accordance with the present invention I have made use of both of these known properties of an ion beam providing a method of ionizing a solid sample to develop a representative beam of ions therefrom.

The heat of vaporization of tungsten, for example, is 2.23×10^5 calories per mole or 3.68×10^{-19} calories per atom. This amounts to 9.67 electron volts of energy per atom. Hence the bombardment of tungsten by 10-volt ions can just result in the ejection from the tungsten sample of one atom for each incident ion if 100% efficient energy transfer is assumed.

The spacing of atoms in a crystal lattice tends to lie somewhere in the region of 10^{-8} centimeters. Although no definite means is available for determining the size of an ion, the de Broglie wave length may be assumed to give a clue to the effective dimensions. The de Broglie wave length λ associated with a helium nucleus is

$$\lambda = \frac{h}{mv} = \frac{h}{\sqrt{qmW_0}} = 2.8 \times 10^{-9} / \sqrt{m^1 W_0} \text{ (cm.)}$$

where

$h = 6.5 \times 10^{-27}$ (Planck's constant)

$m =$ ion mass, gram

$m^1 =$ ion mass, atomic weight units (4 A. W. U.)

$v =$ ion velocity

$q =$ charge of ion, and

$W =$ energy of the ion in electron volts.

Since the effective dimension of the ion can be made less than the spacing of atoms in a crystal lattice by a factor of approximately 10, it is apparent that the bombardment of tungsten by helium ions is the highly local process required for representative ionization of a solid sample. There is no possibility for the incident helium ions to deliver their energy to so many tungsten atoms simultaneously that their energy is degraded into heat. Aside from variations in ejection efficiency associated with variations in relative mass of impinging and

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recipient particles, the probability of ejection of a particular atom in a crystal lattice depends therefore only on whether the particular atom in question happens to be the one struck by the impinging ion. This in turn is a function solely of relative abundance.

The destructive effects of helium ions are relatively slight, and as a consequence heavier ions are preferred as the impinging medium. Ions derived from such heavy atoms as sodium or mercury show considerably greater destructive effects than the helium ions and are highly effective for the purpose under discussion, although it is in no way intended to rule out the lighter atoms such as helium or hydrogen for this purpose.

It is important to consider the small amounts of thermal energy which are delivered to the solid sample under bombardment. A positive ion beam of one milliamper at 1,000 volts delivers only one watt. By comparing the heat requirements for vaporization of a welding electrode it will be shown that the above postulated ion beam would have to be concentrated on a focal spot of approximately 0.14 millimeter in diameter in order to achieve a comparable heating effect. In practice the positive ion beam is preferably spread over an area five to ten times this diameter on the surface of the solid sample so that bulk heating effects are effectively avoided.

Although not so limited, the method of ionizing solids in accordance with the invention is particularly adapted to mass spectrometry as facilitating for the first time the analysis by mass separation of solid samples in a practical manner.

In accordance with another aspect, therefore, the invention contemplates a method of mass separation of a normally solid sample which comprises developing a beam of positive ions at a point spaced from the sample, impinging the beam against a surface of the sample to expel ions from the material representative of the composition of the material, subjecting the expelled ions to a field in which ions have a characteristic motion as a function of specific mass and collecting ions of a given specific mass.

Ions assume characteristic patterns of motion in electrical or magnetic fields as well as in combined electrical and magnetic fields as exemplified by various previously disclosed forms of mass spectrometry. The within method is not limited to the particular forces employed to accomplish ion segregation as a function of specific mass as will be readily apparent from the description of the several illustrated embodiments of apparatus for carrying out the above defined method. The term "field" as used herein is therefore assumed to include electrical or magnetic fields or a combination thereof.

One particularly interesting manner of accomplishing the desired mass separation is by means of transverse electrical and magnetic fields established in the region of ion formation. Under the influence of such a field the ions move in cycloidal paths from their point of origin, the curvature of which paths is a function of ion mass. This is a convenient way of discharging the ions from the source itself whereupon they may be subjected to further stimulus to effectuate the desired mass separation. Other methods may be employed to propel the ions from the source as for example conventional propelling electrical fields.

Transverse magnetic and electrical fields provided in the region of ion formation may be employed, not only to expel ions from the source as above described but also to effectuate mass separation independent of supplemental stimulus and by reason of the dependent relationship between specific mass and radii of travel in such a field. A mass spectrometer involving this principle is described and claimed in my co-pending application Serial No. 277,773, filed concurrently herewith. The mass spectrometer described in the aforementioned co-pending application is not limited in its usefulness to mass separa-

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tion of solid materials, and is not therefore included in the scope of the present disclosure. Full disclosure of the present invention requires some discussion of the disclosures of said co-pending application.

5 The invention will be more clearly understood by reference to the following detailed description of the apparatus devised for carrying out the method of the invention as illustrated in the accompanying drawing, in which:

10 Fig. 1 is a schematic sectional view of a mass spectrometer embodying a solids ion source in accordance with the invention;

Fig. 1A is a partial transverse section taken on the line 1A—1A of Fig. 1;

15 Fig. 2 is a sectional diagram of an alternative form of solids ion source; and

Fig. 3 is a sectional diagram showing the use of the ion source of the invention as a mass spectrometer in accordance with the teaching of the aforementioned co-pending application.

20 Referring to Figs. 1 and 1A, the mass spectrometer there shown comprises an envelope 10 in two sections 10A, 10B, an ion source 12 disposed within section 10A, and an analyzer 14 and a collection system 15 disposed within section 10B. An opening 16 in the envelope provides means for connection to an exhaust system (not shown) for evacuating the envelope.

25 The particular ion source shown in Fig. 1 comprises a series of grids 13, 14, 15, 16, 17, 18, 19 and 20, the grids 14 through 19, lying between the outer grids 13 and 20, being open centrally and serving only to define the boundaries of the field established thereby. These intermediate grids may be apertured plates, annular or square disks or even wire loops to provide a uniform electric field in the area defined thereby. The several grids 13 through 20 are separately connected to a voltage divider 22 which is in turn connected across a voltage source 23 so as to develop a uniform field across the grid system. A transverse magnetic field is established by magnet means (not shown), the transverse field being represented by the dotted rectangle 24.

30 The grid 13 is provided with an opening 13A through which a solid sample 26 may be inserted into the source, as for example on the end of a probe 28 sealed through a wall of the envelope 10 by means of a conventional seal 29. An auxiliary ion source 32 is mounted within the envelope section 10A and on a projection of the axis of electrical field. The source 32 may be any one of a number of conventional sources and is provided with an inlet 33 by means of which ionizable media are introduced thereinto. Suitable ionizing and accelerating potentials are provided to the source 32 from voltage sources 36, 38. The grid 20 is apertured at 20A to admit into the grid system an ion beam propelled from the auxiliary source 32.

35 An electron beam 40 is preferably developed within the grid system adjacent the surface of the solid sample by a conventional electron gun 40A (Fig. 1A), the beam traveling parallel to the magnetic field in a conventional manner to strike an anode or electron target 40B located opposite the gun 40A.

40 Each of the grids 14 through 19 is shaped adjacent the right-hand end as viewed in the drawing to form baffles so as to preclude egress of ions except between the center grids 16 and 17. Grid 17 is grounded through an auxiliary voltage source 42. In the analyzer 14 a transverse magnetic field is established by magnet means, one pole 46 of such a magnet being shown in dotted lines. The transverse magnetic field deflects ions entering the analyzer with the radius of curvature of the ions being a function of their specific mass. A collector electrode 48 is mounted adjacent the end of the envelope section 10B and is preceded by a barrier electrode 50 provided with a resolving aperture 50A. The collec-

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tor electrode is connected to an external sensing circuit 52 which may be of any conventional type.

The operation of the instrument illustrated in Fig. 1, and above described, is as follows: The solid sample to be investigated is inserted into the receptacle provided in grid 13 in the illustrated manner. The auxiliary ion source is energized and is provided with an ionizable medium whereby a beam of positive ions is directed from the auxiliary source through the grid system normal to the magnetic field to impinge on the solid sample, voltage source 38 being of such magnitude that the impinging ions are comparatively unaffected by the electric and magnetic fields in the source 12. This ion beam is indicated by diverging dotted lines extending from the auxiliary source to the solid sample. By the mechanisms above explained, impingement of the positive ions on the solid sample results in the emission of uncharged as well as ionized particles therefrom. The ions of the beam originating in the auxiliary source discharge for the most part at the sample.

The uncharged particles emitted from the sample are ionized by the juxtaposed electron beam 40. The sum total of the ions developed at the sample will follow cycloidal trajectories under the influence of the transverse electrical and magnetic fields with the result that a portion of the ions will assume paths which direct them out of the influence of the fields through the virtual resolving slit or outlet aperture formed by the adjacent centrally located grids 16 and 17. The ions issuing from the ion source pass into the analyzer region where they are resolved in a manner conventional in the mass spectrometer art and are focused and discharged at the collector electrode 15. Ions issuing into the analyzer region other than the particular ion or ions of interest do not focus through the resolving aperture 50A of the barrier electrode 50 and as a consequence discharge at the electrode.

An alternative form of ion source is shown diagrammatically in Fig. 2 and involves electrodes 60, 62, 64 immersed in a magnetic field established by magnet pole 65 and a corresponding opposite pole not appearing in the illustration. The ion source illustrated in Fig. 2 is somewhat similar to the presently conventional ion source in provision of a repeller electrode 60 and linearly spaced apertured accelerating electrodes 62, 64. As in the foregoing embodiment the ion source of Fig. 2 is provided with an auxiliary ion source 66 by means of which a positive ion beam is developed and directed against a solid sample 68 carried by or mounted on or adjacent electrode 60. Again an electron beam 70 is directed across the chamber parallel to the magnetic field and adjacent the surface of the solid sample 68. The electron beam is formed by a conventional electron gun (not shown) and is directed across the chamber to discharge at an anode or target electrode 70A. The magnetic field is optional in this embodiment and is used principally to facilitate collimation of the electron beam.

The electrodes 60, 62 and 64 are connected to a voltage divider 72 which is in turn connected across voltage source 74, the result being that ions developed at the sample 68 are propelled through and collimated by the apertured electrodes 62, 64 to issue therefrom as an ion beam 76. The beam 76 may be resolved in any desired fashion, as for example in the conventional 180° mass analyzer.

An ion source as shown in Fig. 3 is capable of effecting mass resolution without application of additional segregating stimuli, and in this respect is also a mass spectrometer. The source is similar to that of Fig. 1 in the provision of boundary grids 80, 89 with intervening apertured grids 81, 82, 83, 84, 85, 86, 87 and 88, the several grids being connected across the voltage divider 90 and to a voltage source 92 to provide a uniform electrical field across the source. A transverse

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magnetic field represented by the dotted area 99 is provided by magnet means not shown.

In this particular embodiment an auxiliary ion source 96 is disposed to the side of the grid system and grids 84, 85 are perforated in the proper plane to pass an ion beam from the auxiliary source to a solid sample 98 located adjacent grid 80. The orientation of the auxiliary ion source in the manner shown in Fig. 3 is not necessarily characteristic of the apparatus of this figure and may be employed, as for example, in the ion source shown in Fig. 1. Similarly the structure of Fig. 3 may be provided with an axially disposed auxiliary source as in Fig. 1.

In this instance the ion source itself is used for mass resolution by combining therewith a barrier grid 100 provided with a resolving slit 100A giving access to a collector electrode 102. The collector electrode is connected through a lead 103 to a sensing circuit (not shown). The entire grid system, auxiliary ion source, resolving grid and collector electrode are immersed in an evacuated envelope (not shown). An auxiliary ionizing electron beam 104 disposed adjacent the surface of the sample again is a preferred feature, the beam being developed by electron gun means (not shown) and is directed across the chamber from such means to strike target electrode 104A.

The apparatus of Fig. 3 may be operated as a mass spectrometer by suitable adjustment of the magnetic field strength and electrical field distribution whereby only ions of a comparatively narrow mass range in pursuing their characteristic cycloidal trajectories pass through the initial resolving aperture defined by the centrally oriented grids 84, 85. Those ions which emerge from the grid system with a direction of travel substantially parallel to the grids will pass through the resolving aperture 100A, whereas those emerging from the grid system with an angular deflection from the parallel axis will strike the barrier grid 100. Since the angle of emergence from the source is mass dependent, the apparatus provides means for mass separation.

It will be immediately recognized that the type of mass spectrometer shown in Fig. 3 is not limited to solid samples, that the cycloidal travel of ions originating in the illustrated grid system may be employed to achieve resolution independent of the actual source of the ions, and that ions derived from a vaporizable material and introduced into or formed in the system at approximately the location of the solid sample 98 will be subjected to the same resolution. This type of mass spectrometer is covered separately in my co-pending application referred to above, and is illustrated herein as an example of another form of solids ion source and the adaptability of such a source to this particular form of mass separation.

Each of the illustrated embodiments of the invention include means for directing an electron beam across the ionization chamber and adjacent the bombarded surface of the solid sample. Since impingement of a positive ion beam on this surface generates both charged and uncharged particles, the electron beam increases sensitivity by ionizing the uncharged particles. However, where high sensitivity is not an important consideration, such an electron beam may be eliminated without interfering with the operation of the source.

I claim:

1. An ion source for ionizing a solid sample comprising an evacuable envelope, means for supporting the solid sample within the envelope, a secondary ion source adapted to develop a beam of positive ions, means for impinging the beam of positive ions against the surface of the solid sample whereby ions are emitted therefrom, a series of parallel arranged grids disposed in the envelope adjacent the means for supporting the solid sample, a voltage source connected across the grids to form a

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uniform electrical field, magnet means disposed to develop a magnetic field normal to the electrical field whereby ions emitted from the sample pursue cycloidal trajectories from the point of origin with a consequence that a part thereof is expelled from the source between the grids.

2. An ion source for ionizing a solid sample comprising an evacuable envelope, means for supporting the solid sample within the envelope, a secondary ion source adapted to develop a beam of positive ions, means for impinging the beam of positive ions against the surface of the solid sample whereby ions and unionized particles are emitted therefrom, means for directing an electron beam parallel to and adjacent the surface of the sample, a series of parallel arranged grids disposed in the envelope adjacent the means for supporting the solid sample, a voltage source connected across the grids to form a uniform electrical field, magnet means disposed to develop a magnetic field normal to the electrical field whereby ions emitted from the sample pursue cycloidal trajectories from the point of origin with a consequence that a part thereof is expelled from the source between the grids.

3. An ion source for ionizing a solid sample comprising an evacuable envelope, means for supporting the solid sample within the envelope, a secondary ion source, means for introducing an ionizable fluid into the secondary source, means for ionizing the ionizable fluid in the secondary source, means for propelling ions formed in the secondary source as a beam directed to impinge on the solid sample whereby ionized and un-ionized particles will be emitted therefrom, means for developing a second ionizing electron beam, means for propelling the second electron beam across the ion source adjacent and parallel to the surface of the solid sample, a series of parallel-arranged grids disposed in the envelope adjacent the means for supporting the solid sample, a voltage

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source connected across the grids to form a uniform electrical field, magnet means disposed to develop a magnetic field normal to the electrical field whereby ions admitted from the sample and ions formed by the second ionizing electron beam pursue cycloidal trajectories from the point of origin with the consequence that a part thereof are expelled from the source between the grid.

4. Apparatus for ionizing a solid material comprising an evacuable envelope, a primary ion source within the envelope and including electrode means defining the source for expelling ions produced from the solid material from the primary ion source and means for supporting the solid sample within the region defined by the electrode means, means for developing an electron beam, means for propelling the electron beam through the primary ion source adjacent and parallel to the surface of the solid sample, a secondary ion source disposed in the envelope outside the region defined by the electrodes of the primary source, means for introducing an ionizable fluid into the secondary source, means for ionizing the fluid in the secondary source, and means for propelling ions formed in the secondary source as a beam directed to impinge on the solid sample whereby ionized and unionized particles will be emitted therefrom.

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