Jan. 31, 1961 H. S. SPACIL 2,970,215

MASS SPECTROMETER

Filed Jan. 10, 1958

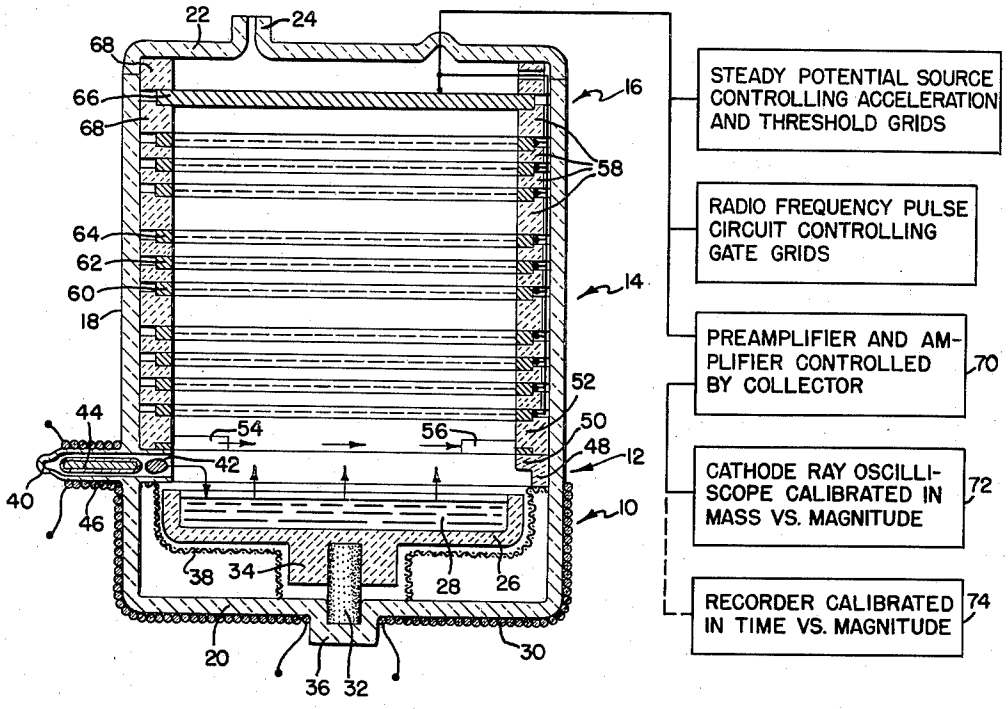


FIG. 1

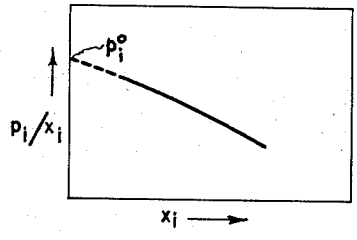


FIG. 2

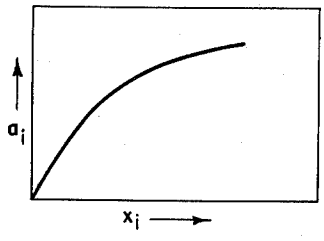


FIG. 3

Henry S. Spacil
INVENTOR
BY Morse & Altman
ATTORNEYS

United States Patent Office 2,970,215
Patented Jan. 31, 1961

2,970,215

MASS SPECTROMETER

Henry S. Spacil, Boston, Mass., assignor to Alloyd Research Corporation, Watertown, Mass., a corporation of Massachusetts

Filed Jan. 10, 1958, Ser. No. 708,323

8 Claims. (Cl. 250—41.9)

The present invention relates to mass spectrometry and, more particularly, to processes and devices for analyzing a chemical sample by electrically charging particles that have been emitted from the sample and by physically separating such particles in an electrostatic and/or magnetic field system that imparts to given particles of selected mass a velocity and/or deflection by which they may be isolated from remaining particles in order to indicate qualitatively and quantitatively the composition of the chemical sample.

A typical mass spectrometer comprises: a vaporizing region in which a rarefied gas is produced; an ionizing region in which particles of the rarefied gas are positively charged by electron bombardment and the resulting ions are accelerated to a kinetic energy of the order of 1,000 electron volts (e.v.); an analyzing region in which the ions are directed through a field system that discriminates between particles of different mass to charge (m/e) ratios; and a collecting region for determining the presence and intensity of beams discriminately produced in the analyzing region. Important related factors in the design of a mass spectrometer are its sensitivity, i.e., its ability to indicate extremely small concentrations of components in a sample being analyzed, and its resolution, i.e., its ability to distinguish between ions of closely similar masses. One purpose of accelerating particles in the ionizing region is to render their kinetic energies substantially uniform. Thus, where the sample is either a gas or a liquid, particles emanate from the sample at energies of a few e.v., more or less, the differences between the kinetic energies of the particles becoming relatively negligible when the particles are accelerated uniformly to kinetic energies of the order of 1,000 e.v. In the analysis of solid samples, however, vaporization by high voltage discharge, for example, produces such a wide energy spread, e.g. of the order of 1 to 100 e.v. among like ions that the sensitivity and resoltuion of the mass spectrometer are adversely affected. Also, in the analysis of solid samples, vaporization by heating has not been feasible because of the difficulty in thermally isolating the relatively high temperature vaporizing region from the relatively low temperature remaining regions while at the same time avoiding condensation of the ions in their path from the vaporizing region into the remaining regions. The present invention contemplates the production, from a solid chemical sample, of ions having closely similar kinetic energies, from which the mass spectrometer may produce monoenergetic ion beams of the type common in the analyses of gases and liquids.

The primary object of the present invention is to provide, for the production of mass spectra, processes and devices that involve dissolving a relatively small quantity of a chemical sample in a relatively large quantity of a known liquified solid in order to produce sample particles of uniform kinetic energies for ionization and analysis. The mass spectrum of particles emitted from the dissolved sample, which posses kinetic energies within the range of from .5 to 5 e.v. and usually of the order of from 1 to 2 e.v., is indicative of the partial vapor pressures of the components of the sample and, in consequence, their chemical identities and proportions.

Another object of the present invention is to provide, for the production of mass spectra, processes and devices, in which particles emitted from a sample in liquified solid solution move in a direct path from the vaporizing region, which is at relatively high temperature, into the remaining regions, which are at relatively low temperature, with a minimum of condensation.

Other objects of the present invention will in part be obvious and will in part appear hereinafter.

The invention accordingly comprises the process involving the several steps and the relation and order of one or more of such steps with each of the others and the device possessing the construction, combination of elements and arrangement of parts, which are exemplified in the following detailed disclosure, and the scope of which will be indicated in the appended claims.

For a fuller understanding of the nature and objects of the present invention, reference should be had to the following detailed description taken in connection with the accompanying drawing wherein:

Figure 1 illustrates, partly in cross-section and partly in diagram, a mass spectrometer embodying the present invention; and

Figs. 2 and 3 illustrate graphs explaining features of processes of the present invention effected in the mass spectrometer of Fig. 1.

The processes of the present invention illustrated specifically herein generally involve determining the composition of an inorganic chemical sample by dissolving a relatively small quantity of the sample in a relatively large known quantity of a liquified known inorganic solid, which contains a material selected from the class consisting of the metals and the metalloids. Particles emanating from the liquified solution, then are transmitted in a mechanically direct or free path, through an ionizing region in which the particles are charged, an accelerating region in which the kinetic energies of the resulting ions are increased to values within the range of from 50 to 1000 e.v., an analyzing region in which an adjustable applied radio frequency potential selectively passes particles moving at a selected velocity to a collecting region. In the collecting region a current is generated, from which the presence and quantity of ions of a selected mass may be determined. By total weight of the liquified solvent and sample solution, the concentration of the overall sample, should be no greater than 10% and the concentration of the major component of the sample preferably should be no greater than 5%. When the sample is in such a minor concentration, as will be more fully discussed below, a selected component of the sample may be considered to be in binary solution with the liquified solid solvent. In consequence, the concentration of the selected component may be calculated from its vapor pressure without consideration of the concentrations of other components. Thus, the current in the collecting region resulting from a beam of ions of any selected mass is a direct indication of the concentration of material of that selected mass in the sample. The liquified solid solvent may be composed of any of a wide variety of low vapor pressure metallic and metalloidal elements and compounds, for example: the metallic and metalloidal elements of groups I, II, III, IV and VIII of the periodic table of chemical elements, e.g. aluminum, gallium, titanium, germanium, tin, and, particularly, the noble metals, including ruthenium, rhodium, paladium, osmium, iridium, gold and silver; and metallic and intermetallic compounds embodying at least in part the aforementioned elements,

e.g. antimony antiminide and aluminum phosphide. Preferably the liquified solid has a low oxide stability that precludes the formation of an oxide film on its free surface. In the foregoing system, particles are emitted from the free surface of the solution at uniformly low energies within the range of from 0.5 to 5.0 e.v. in a steady flux that is substantially devoid of short term variations. In general the minimum temperature of the solution is that required to give a high evaporation rate. The upper temperature limit, approximately 4000° C. as a practical matter is limited only by the nature of refractory material of the crucible containing the solution. Although the solution thus is maintained at a temperature considerably higher than that of the other components of the mass spectrometer, condensation upon or interaction with these other components by particles emanating from the solution is avoided by operating at such a low pressure, of the order of 10^{-7} to 10^{-6} millimeters of mercury (mm. Hg), that the mean free particle path is many times greater than the dimensions of the various regions of the mass spectrometer.

Figure 1 discloses, in accordance with the present invention, a mass spectrometer providing a vaporizing region **10**, an ionizing region **12**, an analyzing region **14** and a collecting region **16**. The components of these regions are confined by and supported within a hermetically sealed jacket having a vertical tubular portion **18**, a base portion **20** integral with the tubular portion and a removable cover portion **22**. Tubular, base and cover portions **18**, **20** and **22**, for example, are composed of a glass or metal that is sufficiently strong and impermeable to permit the production of a high vacuum within the jacket by rapid and continuous exhaustion, for example, through an outlet **24** in cover portion **22**. This exhaustion may be effected by a multistage mercury diffusion pump.

The components of vaporizing region **10** include a crucible **26** containing a predetermined quantity of an inorganic solid to serve as a liquified solvent, a radio frequency current in induction coil **30** ranges from **28** to the liquid state and agitating it to ensure that it dissolves the sample rapidly and completely in a manner to be described below. Preferably the radio frequency curernt in induction coil **30** ranges from 10×10^3 to 10×10^6 cycles per second, lower frequencies being conducive to increased agitation. Crucible **26** is composed of a material that melts at a higher temperature than does liquifiable solid **28**, for example, is composed of a refractory metal such as platinum, tungsten or tantalum or a ceramic, for example, a refractory oxide such as zinc oxide or beryllium oxide. In order to isolate crucible **26** thermally from adjacent remaining components of the system, which are at relatively low temperature, crucible **26** is supported by a rod **32**, the upper end of which projects into a hub **34** depending from the base of the crucible and the lower end of which projects into a well **36** depending from base portion **20** of the jacket. Rod **32**, which is either similar to or different from crucible **26** in composition, serves as an insulating support to prevent the conduction of heat from crucible **26** to base **20**. A radiation screen **38** that blocks radiation directed outwardly from crucible **26** to the jacket, has a dished conformation that generally surrounds crucible **26**. The upper free edges of the conformation are outwardly flanged for the purpose of centering the conformation in the container and the base of the conformation has a circularly flared opening through which rod **32** may be seated in well **36** and hub **34** may be seated on rod **32**. Shield **38** is characterized by an interrupted metallic portion, for example, has a spiral strip construction, of which the successive substantially isolated convolutions provide only short electrically conducting paths. Thus, shield **38**, although substantially unheated by eddy currents generated by induction coil **30**, is capable of reflecting the bulk of thermal radiation emanating from liquifiable solvent **28**.

Projecting through tubular portion **18** of the jacket is a tube **40** composed of the same material as is the container. The outer end of tube **40** normally is sealed. The inner end of the tube, which is open, projects substantially to a point in superposition above the edge of crucible **26**. At the open inner end of tube **40** may be placed a specimen **42**, the composition of which is to be determined. In the remainder of tube **40** is a magnetic slug **44**, which when actuated by a solenoid **46**, propels specimen **42** from the open end of tube **40** into liquifiable solid **28** for dissolution. Slug **44** is encased in glass for the purpose of preventing any chemical activity between the slug and the remainder of the system. Particles thermally escaping from the free surface of the solution in crucible **26** are directed generally upwardly into ionizing region **12**, analyzing region **14** and collecting region **16**, now to be described.

Resting upon the upper flanged edges of shield **38** are the lower edges of an annulus **48** suitably cut away in the vicinity of tube **40**. Annulus **48** is inwardly flanged at **50** to support an annulus **52** that mounts an electron emitter **54** and an electron collector **56**. Emitter **54** and collector **56**, respectively, present opposed horizontally elongated emitting and collecting surfaces that generate a planar electron beam of a sufficiently broad horizontal extent to substantially cover the circular opening defined by flange **50** of annulus **48**. Details of the filament and accelerating grids of emitter **54** and of the anode and secondary electron shield of collector **56**, which are designed in accordance with known techniques, need not be discussed in detail. A proportion of the particles emitted from liquifiable solid **28**, become ionized upon passing through the planar electron beam generated between emitter **54** and collector **56**. Particles so ionized are selectively transmitted, in accordance with their mass to charge ratio, through analyzing region **14**, now to be described.

The components of analyzing region **14** include ten accelerating, control and threshold grids to be described in detail below. Accelerating grids are designated by **60**, control grids by **62** and threshold grids by **64**. These grids are positioned in horizontal planes by spacers **58**, composed for example of aluminum oxide, that are supported one above the other upon annulus **52** and present central circular openings each equal in extent to the opening presented by annulus **52**. Spacers **58** are centered with the aid of projections that are integral therewith and that extend to the inner surface of tubular portion **18**. Steady negative potentials are applied to accelerating grids **60** for the purpose of imparting to the positively ionized particles a selected kinetic energy usually within the range of from 50 to 1,000 e.v. Radio frequency signals are applied to control grids **62** and positive steady potentials are applied to threshold grids **64**. Grids **62** and **64** coact to transmit or reject ions in accordance with their m/e ratio in the following manner. Ions of mass greater than a predetermined magnitude will not acquire a sufficient velocity from an accelerating grid **60** to reach a control grid **62** until after the brief accelerating portion of the radio frequency cycle has been terminated. On the other hand, ions of mass smaller than this predetermined magnitude will acquire so great a velocity that they will reach the control grid **62** before the brief accelerating portion of the radio frequency cycle is initiated. The arrangement is such that ions which are either too heavy or too light will not have sufficient energy to overcome the positive repelling voltage on a threshold grid **64**.

Ions that succeed in passing through analyzing region **14** impinge upon a collector plate **66**, which is mounted upon a spacer **68**, of the type described above. The resulting current through collector plate **66** is applied

to an amplifying circuit **70**, which applies a control signal either to a cathode ray oscilloscope **72** or a continuous recorder **74**. Cathode ray oscilloscope **72**, for example, is calibrated in units representing mass vs. current. This arrangement is particularly useful when an overall mass spectrum indication is desired. Recorder **74**, for example, is calibrated in units representing time vs. current. This arrangement is particularly useful when a precise indication of the concentration of a particular mass is desired. In either case, the calibration will depend upon functional relationships between the vapor pressure of particles emitted by the solution (the number of ions collected per unit time in collecting region **16** is determined by this vapor pressure) and the concentration of the component of that mass in the solution, as will become apparent in the following discussion.

If several solutes are present in a solvent, the interaction of these with each other can be neglected if the solution is dilute. Thus each of the solutes can be considered, to the exclusion of the other solutes, as being in binary solution in the solvent. The activity of the *i*th solute in the solvent is defined by the expression

$$a_i=\frac{p_i}{p_i^0}$$

where p_i is the vapor pressure of the *i*th solute in the solvent, and p_i^0 may be defined in any convenient way. One preferred way will be considered below. The activity of the *i*th solute is related to the composition of the *i*th solute by the expression

$$a_i=f_ix_i$$

where f_i is the activity coefficient of the *i*th solute, and x_i is the composition of the solution in terms of the *i*th solute. For example, x_i may be the weight percent or the atomic fraction. In the case of dilute solutions, it is convenient to specify that the activity coefficient becomes equal to unity as the solution becomes infinitely dilute, or

$$\lim_{x\to 0} f_i=1.0$$

The value of p_i^0 may be determined by introducing the activity coefficient, as above defined, into the expression for activity, thus:

$$f_ix_i=\frac{p_i}{p_i^0}$$

This expression can be solved for p_i^0 to yield

$$p_i^0=\frac{1}{f_i}\frac{p_i}{x_i}$$

Now, by specifying, as above, that the activity coefficient f_i, becomes equal to unity as the solution becomes infinitely dilute, p_i^0 can be specified mathematically as

$$p_i^0=\frac{1}{1}\lim_{x_i\to 0}\frac{p_i}{x_i}$$

In practice, p_i^0 is obtained by measuring p_i at known values of x_i and plotting a curve of p_i/x_i as a function of x_i. This curve then is extrapolated to $x_i=0$ in order to obtain p_i^0, as shown in Fig. 2. Once p_i^0 has been determined as above, measurements of p_i at known values of x_i are used to produce a chart of a_i as a function of x_i, as shown in Fig. 3. Such a chart is plotted for each solute to be analyzed.

If such a chart of activity vs. composition is available from prior calibration for a solute or solutes of interest, measurement of the vapor pressure of the solute may be used to obtain the activity since

$$a_i=\frac{p_i}{p_i^0}$$

The value of activity thus obtained, is used to read the concentration of the solute directly from the curve of activity vs. composition. When the solute is introduced into the solvent as a small solid or liquid sample, if the weights of the solvent and the sample are known, the composition of the sample may be calculated.

In an exemplary mass spectrometer of the type herein specifically described: thermal evaporation takes place from a liquified metal solvent of 10 cm.^{2} free surface area; the included angle from the normal to the solvent surface, within which evaporating atoms or molecules are collected is 60 degrees; 10% of the evaporating atoms or molecules are singly ionized; and of the ten linearly superposed grids, each produces a 5% transmission loss. Under these conditions, the number of ions per second passing to collector plate **66** (with suitable settings of grid potentials) is given by:

$$N_i=1.3\times 10^{21}E_i\frac{p_i}{(M_iT)^{1/2}}$$

where M_i is the molecular weight of particles being analyzed; T is the solvent temperature expressed in ° K/100; p_i is the vapor pressure of the particles at the surface of the solvent in mm. Hg; and E_i is the overall current efficiency of the mass spectrometer. As stated above, the concentration of a particular component of the sample is derived from the vapor pressure of that component as indicated by the intensity of its associated ion beam impinging upon collector plate **66**.

The current efficiency, E_i, depends inversely upon the resolving power of the mass spectrometer, that is, upon the ability of the spectrometer to reject ions which are not of a selected *m/e* ratio. Resolving power may be defined as

$$R=\frac{M_i}{M_{i+1}-M_{i-1}}$$

where M_i is the molecular weight of ions passing through the mass spectrometer, and M_{i+1} and M_{i-1} are the molecular weights of heavier and lighter ions, respectively. These heavier and lighter ions do not pass through the grid system to the collector plate. Once the resolving power required by the problem has been determined, the required current efficiency is indicated by

$$E_i=\frac{10}{16R}$$

Example I

In one process performed in the above described mass spectrometer, magnesium is dissolved in gallium to the extent of one part per million (p.p.m.) at 350° C. The molecular weight of magnesium is about 24. The mass spectrometer must exclude sodium, molecular weight 23, and aluminum, molecular weight 27. Accordingly, the required resolving power is

$$R=\frac{24}{27-23}=6$$

Thus the required current efficiency is

$$E_i=\frac{10}{(16)(16)}=0.10$$

The ion current is the number of ions per second arriving at the collector plate multiplied by the charge per ion, or

$$I_i=\frac{(1.6\times 10^{-19})(1.3\times 10^{21})(10^{-1})}{[(24)(6.2)]^{1/2}}p_i=1.7p_i$$

At 350° C., the vapor pressure of pure magnesium is 3×10^{-4} mm. Hg. Thus $p_i=3.0\times 10^{-10}$ mm. Hg, so that the net ion current is

$$I_i=5.1\times 10^{-10}\text{ amps.}=510\ \mu\mu\text{a.}$$

This current is detectable with reasonably sensitive electrical instrumentation.

Example II

In another process performed in the above described mass spectrometer, lead is dissolved in nickel to the extent of one p.p.m. at 1500° C. The molecular weight of lead is about 207. The mass spectrometer will have to exclude bismuth, molecular weight 209, and thallium, molecular weight 204. Accordingly, the required resolving power is

$$R=\frac{207}{209-204}=41.5$$

Now the required current efficiency is

$$E_i=\frac{10}{(16)(42)}=1.5\times10^{-2}$$

The ion current is

$$I_i=\frac{(1.6\times10^{-19})(1.3\times10^{21})(1.5\times10^{-2})}{[(207)(17.7)]^{1/2}}p_i=3.2\times10^{-2}p_i$$

At 1500° C., the vapor pressure of pure lead is 200 mm. Hg. Thus

$$p_i=2\times10^{-4}\text{ mm. Hg}$$

so that the ion current is

$$I_i=6.4\times10^{-6}\text{ amps.}=6.4\ \mu\text{a.}$$

This current is readily detectable with instrumentation of only moderate sensitivity.

In operation, the components of the mass spectrometer of Fig. 1 initially are removed from the container and cleaned. Thereafter, in sequence, shield **38** is placed in position, slug **44** and specimen **42** are inserted into tube **40**, rod **32** is inserted into well **36**, and hub **34** is seated upon rod **32**. Next, the crucible is provided with a predetermined quantity of solvent to be liquefied. Thereafter grids **60**, **62** and **64**, with the aid of spacers **58**, are placed in registered relation in superposed planes within the container and their leads extended through an opening in cover **22**. This opening is sealed by heating. Then, induction coil **30** is energized to liquify liquifiable solid **28** and solenoid **44** is actuated to propel specimen **42** into solvent **28**. Finally, information about the mass spectrum of the various components of the sample **42** is presented on cathode ray oscilloscope **72** or recorder **74** by varying the radio frequency applied to control grids **60**.

Since certain changes may be made in the above processes and devices without departing from the scope of the invention herein involved, it is intended that all matter contained in the above description or shown in the accompanying drawings shall be interpreted in an illustrative and not in a limiting sense.

What is claimed is:

1. A mass spectrometer for determining the composition of an unknown specimen of relatively small mass, said mass spectrometer comprising a jacket and components within said jacket providing, in sequence, a vaporizing region, an ionizing region, an analyzing region and a collecting region, said ionizing region and said analyzing region providing a path between said vaporizing region and said collecting region, the components of said vaporizing region including a crucible containing a known solid liquifiable at relative high temperature to provide a bath of relatively large mass, said specimen being soluble in said bath, said crucible being thermally isolated from adjacent portions of said jacket and preventing said bath from flowing to said adjacent portions of said jacket, said adjacent portions of said jacket being at relatively low temperature.

2. A mass spectrometer apparatus for determining the composition of an unknown specimen of relatively small mass, said mass spectrometer apparatus comprising a jacket and components within said jacket providing, in vertical sequence, a vaporizing region, an ionizing region and a collecting region, said ionizing region and said analyzing region providing a straight line path between said vaporizing region and said collecting region, the components of said vaporizing region including a crucible containing a known solid liquifiable at relatively high temperature, said crucible being thermally isolated from adjacent portions of said jacket and preventing said bath from flowing to said adjacent portions, said adjacent portions being at relatively low temperature.

3. The mass spectrometric apparatus of claim 2 wherein the components of said analyzing region include a series of superposed grids.

4. The mass spectrometric apparatus of claim 2 wherein the path of particles from the free surface of said liquifiable solid through said vaporizing region, said ionizing region, said analyzing region and said collection region, is of substantially uniform cross-sectional extent, said cross-sectional extent being substantially equal to the extent of said free surface of said liquifiable solid.

5. A mass spectrometric apparatus for determining the composition of an unknown specimen of relatively small mass, said mass spectrometer apparatus comprising a jacket and components within said jacket providing, in vertical sequence, a vaporizing region, an ionizing region, an analyzing region and a collecting region, said ionizing region and said analyzing region providing a substantially straight path between said vaporizing region and said collecting region, the components of said vaporizing region including a crucible containing a known solid liquifiable at relatively high temperature, said crucible being thermally isolated from adjacent portions of said jacket and preventing said bath from flowing to said adjacent portions, said adjacent portions being at relatively low temperature, the path of particles from the free surface of said liquifiable solid through said vaporizing region, said ionizing region, said analyzing region and said collecting region being of substantially uniform cross-sectional extent, said cross-sectional extent being substantially equal to the extent of said free surface of said liquifiable solid.

6. The mass spectrometric apparatus of claim 5 wherein the components of said analyzing region include a series of superposed accelerating, radio frequency control and threshold grids.

7. A mass spectrometer for determining the composition of an unknown specimen of relatively small mass, said mass spectrometer comprising a jacket and components within said jacket providing, in sequence, a vaporizing region, an ionizing region, an analyzing region and a collecting region providing a path between said vaporizing region and said collecting region, the components of said vaporizing region including a container, a known solid liquifiable at relatively high temperature within said container, means for heating said known solid to said relatively high temperature to form a bath of relatively large mass for receiving said specimen of unknown composition, said liquifiable solid comprising a materail selected from the class consisting of elements and compounds containing metal and metalloids, said specimen constituting less than ten percent of the total weight of said bath and said specimen.

8. A mass spectrometric apparatus comprising a jacket and components within said jacket providing, in vertical sequence, a vaporizing region, an ionizing region, an analyzing region and a collecting region, said ionizing region and said analyzing region providing a straight line path between said vaporizing region and said collecting region, the components of said vaporizing region including a crucible containing a solid liquifiable at relatively high temperature, said crucible being thermally isolated from adjacent portions of said container, said adjacent portions being at relatively low temperature, the path of particles from the free surface of said liquifiable solid through said vaporizing region, said ionizing region, said analyzing region and said collecting region being of

substantally uniform cross-sectional extent, said cross-sectional extent being substantially equal to the extent of said free surface of said liquifiable solid, means adjacent to said crucible for projecting said specimen into said liquifiable solid, said liquifiable solid being of known composition, said specimen being of unknown composition, said liquifiable solid being of relatively large proportion, said specimen being of relatively small proportion, said liquifiable solid being composed of a material selected from the class consisting of elements and compounds containing metals and metalloids, said specimen

constituting less than 10% of the total weight of said liquified solid and said specimen.

References Cited in the file of this patent

UNITED STATES PATENTS

2,703,843	Cameron	Mar. 8, 1955
2,715,682	Lawrence	Aug. 16, 1955
2,721,271	Bennett	Oct. 18, 1955
2,768,301	Bennett	Oct. 23, 1956
2,818,507	Britten	Dec. 31, 1957