Aug. 22, 1967 L. FRIEDMAN ETAL 3,337,728

MASS SPECTROGRAPH ION SOURCE WHEREIN A PULSED ARC IS PRODUCED BY VIBRATING ONE ELECTRODE

Filed Oct. 9, 1964 2 Sheets-Sheet 1

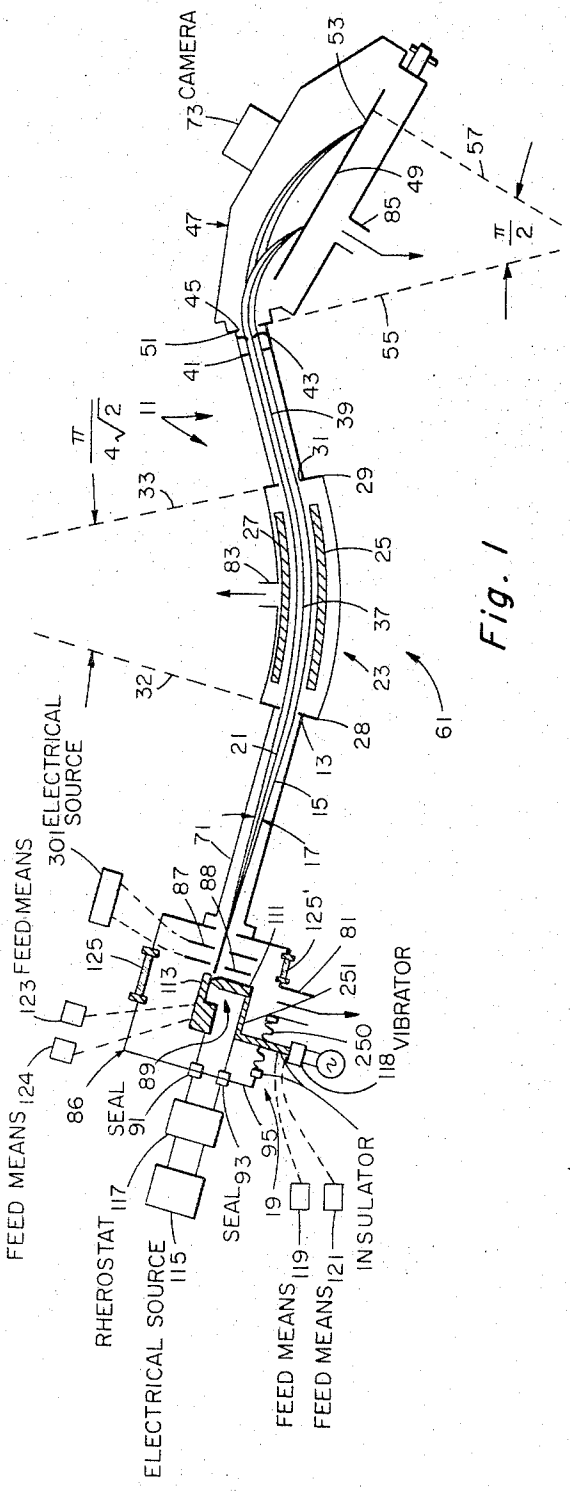


Fig. 1

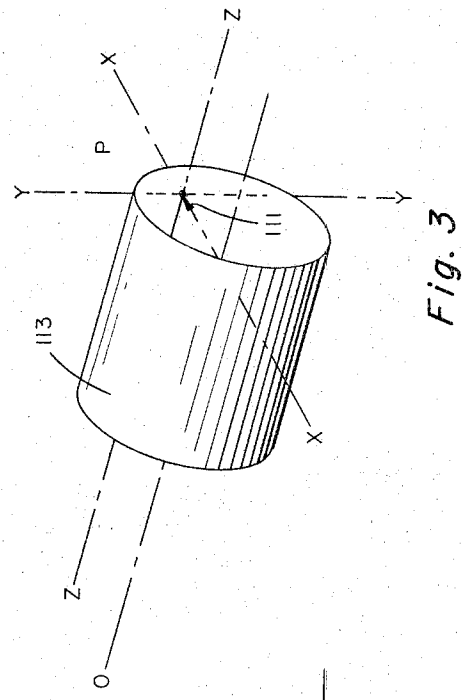


Fig. 3

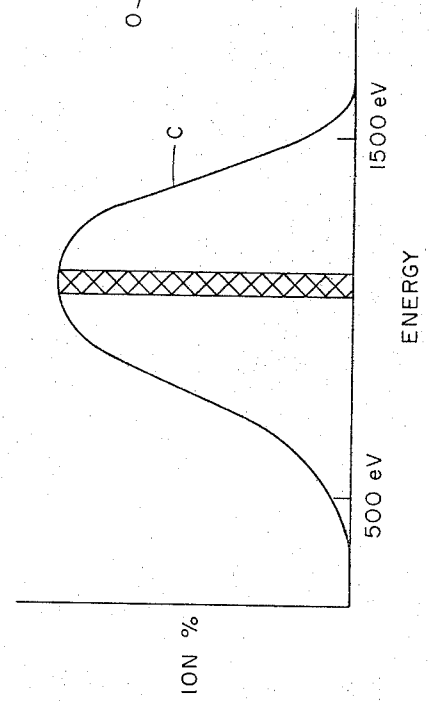


Fig. 2

INVENTOR.
LEWIS FRIEDMAN
BY ADOLPH P. IRSA
Richard A. Gardiner
Attorney

Aug. 22, 1967 L. FRIEDMAN ETAL 3,337,728

MASS SPECTROGRAPH ION SOURCE WHEREIN A PULSED ARC IS PRODUCED BY VIBRATING ONE ELECTRODE

Filed Oct. 9, 1964 2 Sheets-Sheet 2

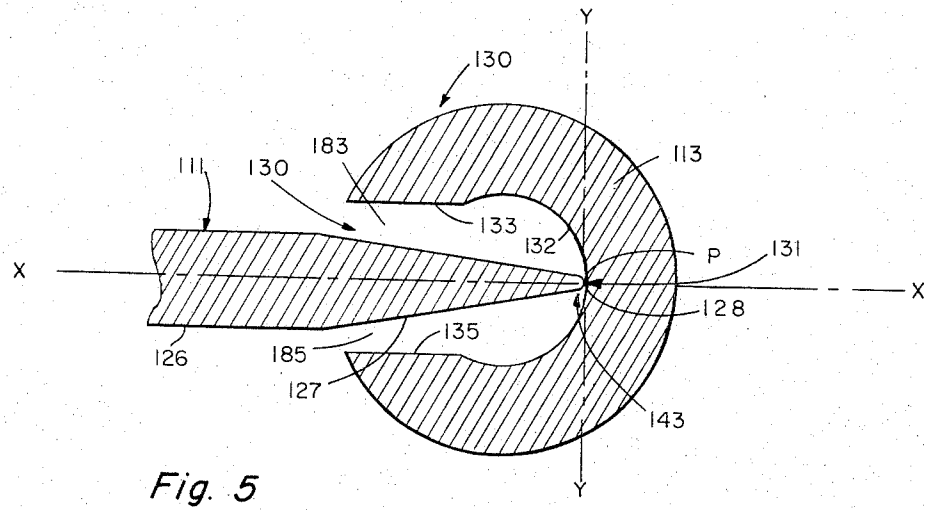


Fig. 5

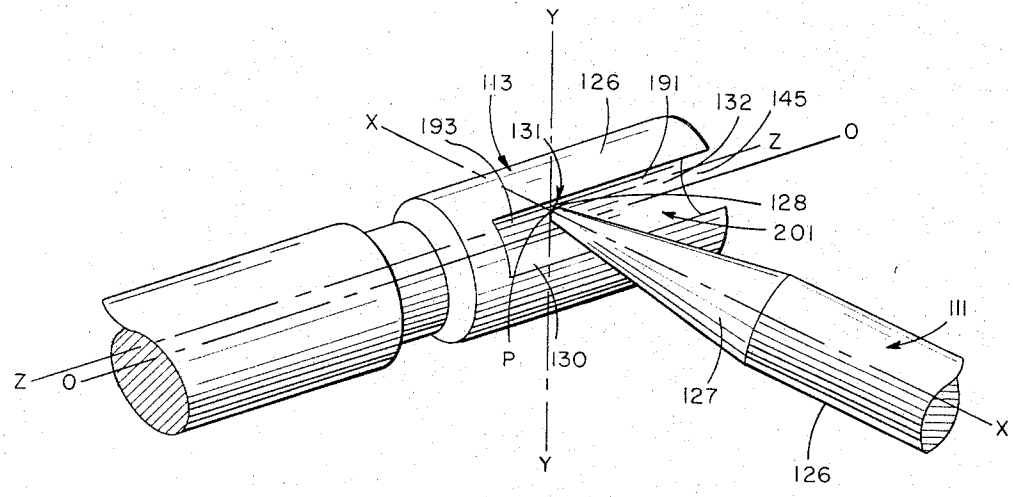


Fig. 4

INVENTOR.
LEWIS FRIEDMAN
ADOLPH P. IRSA

BY

Roland A. Anderson
Attorney

United States Patent Office 3,337,728 Patented Aug. 22, 1967

3,337,728

MASS SPECTROGRAPH ION SOURCE WHEREIN A PULSED ARC IS PRODUCED BY VIBRATING ONE ELECTRODE

Lewis Friedman, Patchogue, and Adolph P. Irsa, Plainview, N.Y., assignors to the United States of America as represented by the United States Atomic Energy Commission

Filed Oct. 9, 1964, Ser. No. 402,980
5 Claims. (Cl. 250—41.9)

ABSTRACT OF THE DISCLOSURE

An ion source for a mass spectrograph having an anode, and a cathode shaped to confine a plasma producing arc so that the plasma that is generated in the arc has only a limited means of escape; the escape means being designed for efficiently extracting ions for the purpose of analyzing samples of limited size. A pointed anode is provided that is vibrated against the inside wall of a well-shaped cathode for extracting the ions in a narrow solid angle along the inside wall of the cathode.

This invention relates to mass spectrographs and in particular to novel method and apparatus for efficiently directing a beam of ions into a mass spectrograph.

In trace analysis with a mass spectrograph, particles from an ion source are focused in the spectrograph by electrostatic and magnetic fields. Since the masses of the ions of the different isotopes are different, the trajectories of the ions as they move under the influence of the forces exerted by the fields are slightly different so that the ions of different mass in the incident beam are separated to focus at different spatial positions in the spectrograph's focal plane. If a photographic plate is placed near the focal plane, a mass spectrum will appear in which the distance along the plate corresponds to the mass of the separated ions and in which the blackness of the spectrum lines corresponds to the quantity of material of each particular mass that is separated for recording on the plate.

The electrostatic and magnetic fields are combined to produce double focusing, that is, all the ions of the same mass entering the instrument within a small divergence angle and which have an energy different from the mean energy by a small amount will focus. It is thus apparent that the efficiency of such as instrument will depend upon the proper conduction of a maximum number of ions of the isotopes from the source into the instrument at a high density or small divergence angle beam, particularly when quantitative measurements with a small limit of detection down to a small fraction of a part per million are to be made or where low magnetic fields and low accelerating voltages are used.

Heretofore, the ion source has been a spark source since it has been applicable to a wide range of elements having wide extremes in chemical nature, e.g. xenon and cesium. In this regard although these elements are adjacent on the periodic chart, the xenon is much more difficult to ionize than the cesium. The spark source has thus been particularly important in nuclear transformation determinations where uranium has been bombarded in a nuclear reactor or an accelerator to produce known yields of xenon and cesium. When this sample has been used in the spark ionization source the xenon has produced weaker lines than the cesium but the ratios of intensities have differed only by about a factor of two.

Although the spark ion source has been widely used to introduce ions into spectrograph heretofore, these spark sources have produced ions having significantly wide bands

of directional and velocity spreading, there has been no simple means for directing or confining the ions in a high density beam or a small solid divergence angle beam, the efficiency of the sources has been low, high radiation levels have been required in the ion source or large amounts of the isotope samples have been lost. These problems have been particularly troublesome in trace analysis work e.g. for nuclear transformation determinations, since the samples have often comprised small amounts of different isotopes that have been produced by the bombardment of targets in large and costly reactors and accelerators where many hundreds of expensive man hours have been required in many cases to plan, prepare and execute these bombardments or to produce even small amounts of the different isotopes.

It is thus an object of this invention to provide for the prevention or continual correction of the conditions described above and greatly to increase the efficiency of the spectrograph and its ion source;

As a further object, this invention involves the establishment of an ion source utilizing directional collimation;

Still another object is the provision for the deposition, re-ionization, and direction of ions for achieving an efficient beam source for a spectrograph;

It is also an object of this invention efficiently to utilize electrical and mechanical means for providing an incident beam source of ions for a mass spectrograph;

An additional object is to provide an efficient ion nozzle for an ion source for a mass spectrograph;

A still further object is to provide very low limit, spectrograph detections for nuclear transformation determinations.

By this invention, there is provided method and apparatus for providing and collimating a beam of ions from a trace element sample for nuclear transformation determinations. The method and construction involved in this invention utilizes standard and well known techniques and apparatus and is highly flexible for a wide range of applications, isotope separations, resolutions, limits of detection, isotope samples, sample sources and spectrographs. More specifically, this invention involves the use of systems of electrodes which form and collimate the beam of ions to be separated. The systems of electrodes are arranged in one embodiment, with a vibrating electrode and a stationary electrode which contact each other in a confined area formed by said electrodes to provide and direct ions from a small spark source in a high density or narrow divergence angle beam and to provide deposition and re-ionization of said isotopes for direction in said beam. With the proper selection of electrodes, voltage, and positioning of the sparks, as hereinafter to be more particularly described, it is possible by this invention efficiently to provide the desired beam.

The above and further novel features and objects of this invention will appear more fully from the following detailed description when the same is read in connection with the accompanying drawings. It is expressly understood, however, that the drawings are not intended as a definition of the invention but are for the purpose of illustration only.

In the drawings where like parts are marked alike:

FIG. 1 is a partial cross-sectional view of a mass spectrograph incorporating the source apparatus of this invention;

FIG. 2 is a graphic illustration of the energy spread of ions in the spectrograph of FIG. 1;

FIG. 3 is a partial schematic representation of the principles of this invention;

FIG. 4 is a partial three directional view of the source apparatus of FIG. 1 embodying the principles illustrated in FIG. 4;

FIG. 5 is a partial cross-sectional view of the apparatus of FIG. 5.

Referring to FIG. 1, a mass spectrograph **11** is shown in which the method and apparatus of this invention are utilized. This spectrograph **11** employs the Mattauch-Herzog geometry, which utilizes the double focusing principle. This type spectrograph his high sensitivity for constituents having low concentrations, and in accordance with this invention, an incident high density beam is provided for determinations having a low limit of detection, e.g. down to 0.01 parts per million atomic particles. A more detailed description of this geometry is found in FIG. 24 in Chapter V, of "Mass Spectroscopy" 1958, Cambridge Press, by H. E. Duckworth.

Stop **13** has a predetermined, small entrance opening to receive a small cross-section ion beam **15** in a small angle **17** through exit slits in an ion source **19** along a straight axis **21**. This stop **13** is in one end of an electrostatic sector **23**, which has a positively charged side **25**, a negatively charged side **27** and ends **28** and **29** forming entrance slit **13** and an exit slit **31** like in area with stop **13**. Converging lines **32** and **33** drawn from these ends **28** and **29** form an angle

$$\frac{\pi}{4\sqrt{2}}$$

The beam **15** is bent in sector **23** along a first curved axis **37**, travels along a straight axis **39** after exiting from sector **23** and enters an annular magnet shunt **41** having beam monitor electrodes **43** and a small energy resolving opening **45** formed by the entrance to magnetic sector **47**.

The paths of the charged particles are bent in magnetic sector **47** and focused thereby in focal plane **49**, having between magnetic sector ends **51** and **53**, a photographic plate mask. Converging lines **55** and **57** drawn from ends **51** and **53** form an angle $\pi/2$.

As is conventional, separate vacuum chambers are provided for the sectors of the analyzer **61**, comprising the electric sector **23** having an entrance chamber **71** and magnetic sector **47** having a photographic system **73**. To this end each sector has a liquid nitrogen cold trap and oil diffusion pump. Also, suitable valves and connecting pipes **81**, **83** and **85** between the source chamber **86** and analyzer **61**, and between the source chamber and source pumping system, permit the ion source to be vented and rough pumped without disturbing the analyzer vacuum. The differential pumping between the source slits **87** and **88** is accomplished by separate pumping systems to provide a very low pressure in the analyzer **61** during sparking. Slit **88** is at a first or ground potential and slit **87** is at a potential of between 15 to 20 kilovolts.

One suitable double focusing spectrograph having a high resolution and a low limit of detection with the source **19** of this invention, is the model 21–110B Mass Spectrometer made by the Consolidated Electrodynamics Corporation, Pasadena, Calif. This spectrograph is particularly adapted for analysis of solids from a spark ion source having small round or rectangular exit slits **87** and **88** and is adapted to provide a mass spectrum covering a mass range of 36:1, thus permitting for example, recording from lithium through uranium, all the sample solids in the periodic table in a single photographic exposure in focal plane **49**. A typical schematic comparison of an incoming ion energy spread (area under curve *c*) vs. the end energy spread (cross-hatched area) for this spectrograph is shown in FIG. 2.

Typical source samples **89** comprise trace elements from an elemental metal target, such as uranium that has been bombarded in a nuclear reactor, an accelerator or in other means to produce various nuclear transformations forming characteristic quantities of certain isotopes. After bombardment, the metal target is treated chemically to separate the trace elements, which are applied in solution to heated electrodes to evaporate the solution and adsorb the trace element solute on the electrodes.

In general, such trace element samples have been ionized in a vacuum by a spark, provided heretofore by a radio-frequency power supply that developed a peak voltage of about 100 kilovolts between two large, wedge-shaped electrodes between which this supply caused sparks to jump. It has been necessary to pulse this supply to reduce the duty cycle of the spark because electrode heating has been a problem. Typically the electrodes were held in fixed vises conected to the source through vacuum tight connections **91** and **93** in the wall **95** of source chamber **86**. The fixed position of these electrodes has required frequent and time consuming adjustments as well as high voltage supplies or highly radioactive samples **89**. Also, these sources have not vaporized all the sample constituents non-preferentially, kept the bulk of the sample cool, or efficiently directed a large number of the constituents into the analyzer section **61**. Moreover, it has been difficult or impossible to provide a simple high efficiency, high density, or small solid angle beam source with this or any of the other source systems known heretofore.

In order to explain how the method and apparatus of this invention accomplish the function of concentrating ions, such as the described metal ions, and directing them in a high density beam or in a small solid angle coinciding with the small entrance angle of the analyzer **61**, reference is made to FIG. 3 wherein is illustrated a horizontal *x*—*x* axis coresponding to the axis of a first longitudinally extending first pointed electrode at right angles to a vertical *y*—*y* axis. The *o*—*o* axis is at right angles to *x*—*x* and *y*—*y* represents the central axis of a cylindrical second electrode **113**. The *z*—*z* axis represents an axis parallel to *o*—*o* on the inside wall of the electrode **113** formed by the intersection of the inside wall with a plane passing through the *o*—*o* axis. Point P is at the intersection of the *x*—*x*, *y*—*y* and *z*—*z* axes. It will be seen that a spark at point P will produce a high pressure plasma which is ejected out the open end **145** of electrode **113** in a filled high density beam whose maximum divergence angle depends on the position of point P with relation to the open end **145**.

It is also seen that the plasma will be produced and concentrated substantially instantaneously in a high pressure, high density plasma beam by a very low voltage source. This may be explained by the fact that increased plasma pressure facilitates the spark formation at low voltages. Moreover, this high pressure region will eject the ions at high energies along the P–Z axis while the potential difference between slits **87** and **88** extracts the ions and injects them into the analyzer **61**. These energies are low enough to keep the ions from being imbedded too deeply in the electrodes or too far from the spark so that they are lost or difficult to re-ionize. Thus some of the ions will be deposited for immediate spontaneous re-ionization and ejection in the beam along the P–Z axis or deposited on the inside of the electrode **113** and re-ionized and ejected in the beam by intermittent sparks between electrodes **111** and **113**. Also, the energy spread of the ions produced by this low voltage source is low so that a majority of these ions are ejected in a well defined low energy spread, high intensity beam along the P–Z axis. Additionally, the low voltage prevents the undue heating of the spark electrodes while providing a localized hotter spark.

Referring to FIGURES 4 and 5, in a practical arrangement for accomplishing the desired concentration and direction of the ions, first and second electrodes **111** and **113** provide a nozzle utilizing mechanical boundaries for collimating the ions. These electrodes connect in a circuit to a conventional constant power source **115** having a variable rheostat **117** for energizing the electrodes at a uniform constant level to produce sparks therebetween. Electrode **113**, for example, is at ground potential and electrode **111** is at a higher potential. One electrode has

a vibrationing means **118** for vibrating the electrodes into and out of contact to produce intermittent sparks. In this system the sparks are formed at a point P and the spark is extinguished as electrode **111** moves away from this point P by stretching the spark into a thin cross-section that cannot jump the gap formed by the movement of electrode **111** away from electrode **113**.

Initially a suitable threaded feed means **119** biases electrode **111** into point contact with the inside of cylindrical electrode **113** at right angles to the *z*—*z* axis of electrode **113**. The arrangement and position of this contact point are so related to the arrangement and position of electrodes **111** and **113** and the source slits **87** and **88** and the direction stop **13** along the axis **21** of analyzer **61**, that the maximum divergence angle of the plasma beam from this point corresponds with the maximum line of sight angle from point P through slits **87**, **88** and stop **13** along the P–Z axis, this axis coinciding with the axis **21** of these slits. In this regard threaded feed means **121** moves electrode **111** backward or forward parallel with the axis *z*—*z* of electrode **113**. Also, threaded feed means **123** biases electrode **113** in both directions parallel with axis *z*—*z* and threaded feed means **124** moves electrode **113** in and out at right angles to axis *z*—*z* of electrode **113**. Windows, such as windows **125** and **125'** provide visual viewing of the electrodes **111** and **113** and their sparks. This permits adjustment so that there is no back spark along axis *z*—*z* away from analyzer **61**.

The first electrode **111** has a longitudinally extending, uniform, cylindrical portion **126** and a uniformly tapered portion **127** forming a pointed end **128** on the electrode axis *x*—*x* at point P. This axis *x*—*x* of electrode **111** coincides with the mid-plane of uniform cylindrical electrode **113** passing through axes *o*—*o* and *z*—*z* and the center of slot **130** in electrode **113**. The contact point of these electrodes **111** and **113** thus form a first confining zone providing confining forces in the *x*—*x* direction in a larger second confining zone formed by electrode **113** providing forces along the *z*—*z* axis equivalent to forces in the *y*—*y* direction. The cross-sectional area of these forces is large due to the large areas of the electrode surfaces relative to the small cross-section of the spark formed between the electrodes. This leads to the high efficiency of these electrodes in directing ions therefrom in a high density or small solid angle beam. The taper of electrode **111**, however, makes a small angle with its axis *x*—*x* extending from the inside surface **132** of electrode **113** past the opposite surfaces **133** and **135** of slot **130** so as to have a clearance from the sides **133** and **135** of slot **130** sufficiently small to prevent arcing across this slot **130** and large enough effectively to block the emergence of ions through slot **130**.

It will be understood, from the above that the movement of electrode **111** toward surface **132** of electrode **113** causes a spark between tip **128** of electrode **111** and surface **132**. This spark is small in cross-section and substantially corresponds to a point spark that ionizes the isotopes on tip **128** to provide a point ion source in nozzle **131** between the two electrodes. Thus this spark is effectively blocked in the first small zone **143** between the electrodes from all the openings in electrode **113** except open end **145** thereof. It will be seen, for example, that tip **128** blocks the direct line of sight from point **128** through openings **183** and **185** in FIG. 5. Also, tip **128** blocks the direct line of sight from point **128** through openings **191** and **193** forming the rest of slot **130** in FIG. 4, and leaves a line of sight opening from point **128** through open end **145** of electrode **113** whose maximum divergence angle is determined by the position of the tip **128** (point P) relative to the open end **145**. Also, it will be understood that electrode **111** is locally heated much more than electrode **113** and as material is slowly eroded from the electrode **111** this electrode is biased toward inside surface **132** of electrode **113** continually to provide simultaneous substantially equal forces which confine the ions and eject them along the axis P–Z and its continuation axis **21**. Additionally, some isotopes are deposited on the inside **132** of electrode **113** and the automatic vibration of electrode **111** along axis *z*—*z* of electrode **113** corresponding to axis **21** of the analyzer **61** automatically re-ionizes and ejects these isotopes out end **145**. Thus the nozzle **131** forms a first opening between electrodes **111** and **113** whose distance from the second opening **145** is adjustable.

In operation, a small voltage is applied to electrodes **111** and **113** of about 10 volts for carbon electrodes **111** and **113**. Soft metal electrodes, such as copper, however, require only 3 volts for sparking therebetween. Advantageously the source **115** is a conventional 60 cycle source having a voltage control, such as rheostat **117** and a 120 cycle/sec. vibrator **118** for moving electrode **111** into and out of contact with electrode **113** to produce intermittent sparks that ionize the sample **89** on the end **128** of electrode **111**. The majority of these ions leave the nozzle **131** formed by these electrodes in the mid-plane between the electrodes **111** and **113** corresponding with the *y*—*y* axis and the majority of the ions directed toward opening **145** are ejected through the opening in a high energy (200 to 5000 electron volts) high intensity, narrow angle beam whose maximum divergence angle from point P in the *y*—*y* direction is determined by the position of point P relative to opening **145**. This position of point P is so located that the ejected beam from opening **145** substantially corresponds with the small solid angle of incidence through slits **87**, **88** and **13** from point P.

Some isotope particles are deposited on the inside of electrode **113** near the spark between electrodes **111** and **113** and the vibration of electrode **111** back and forth a short distance from point P in the mid-plane of electrode **113** passing through axes *o*—*o*, *x*—*x* and slot **130** has the advantageous effect of rapidly re-ionizing these particles and ejecting them from open-end **145** of electrode **113** in a high energy, high intensity, small, solid angle beam corresponding to the required small incident angle of analyzer **61**. The isotope is thus removed from electrode **111** and efficiently introduced into analyzer **61** for quantitative and qualitative isotope determinations. The apparatus is then ready for the beginning of a new cycle with the same or a new electrode **111** having a newly adsorbed isotope sample thereon.

This new cycle is begun by bringing the electrodes **111** and **113** in contact to produce sparks at the proper point to achieve the required small incident ion beam angle. In this regard, the electrodes **111** and **113** are freely movable as described. In this regard, moving electrode **111** back away from analyzer **61** makes the ion solid angle smaller while moving this electrode toward analyzer **61** makes the ion solid angle larger. Movement of electrodes **113** toward and away from the analyzer has the opposite effect on the solid angle of the ion beam and suitable adjustment is made so that the beam O.D. just passes inside the edge of slits **87**, **88** and **13**.

In one actual example of this invention electrode **111** was heated to about the boiling point of water, and trace elements chemically separated from a sample containing 2 milligrams of U_{235}, which had been bombarded in the Brookhaven Graphite Research Reactor, was applied to the tip of electrode **111** with an eye dropper, whereupon the solution was evaporated to leave the sample **89**. Electrodes **111** and **113** were energized to 10 volts while electrode **111** was brought into contact with the inside wall of electrode **113** in the mid-plane through axes *o*—*o*, *x*—*x* and slot **130** in a vacuum of 10^{-6} torr. Means **119**, **121**, **123** and **124** operate by moving a bellows and bellows arms connected to the respective electrodes. Means **119** and **121**, for example, move bellows **250** and bellows arm **251** connected to electrode **111**. The end of vibrating means **118** butts up against the end of threaded feed means **121** thereby simply to vibrate electrode **111** in the

same direction that means **121** moves the electrode i.e. in the mid-plane through axes *o—o*, *x—x* and slot **130**. By butting the vibrator **118** up against means **119**, **123** or **124** the electrode vibration will correspond to the direction of movement of the electrodes by those means. One advantageous means **118** is a hand engraving tool. As is conventional with such tools, it operated on the vibrating reed or door-bell principle, and the vibration was readily felt by hand although not readily seen by the naked eye. This produced ionizing sparks which ejected Ce, Xe, Tb and other ions in a high density, narrow angle means which passed inside the edges of slits **87**, **88** and **13**. The potential difference between round slits **87** and **88** is adjusted to between 15–20 kilovolts by means of adjustable source **301**. By making the potential between slits **87** and **88** big enough and the sparks back far enough from open end **145**, the beam can be extracted through slits **87** and **88** in a maximum divergence angle of as low as 1°. The actual dimensions of the electrodes in inches were—

Electrode **111**:
- Outside diameter tapered from .02 to .120
- Length .700
- Tip length .300
- Tip angle ~20°
- Tip distance to slit **88** ¼ to ⅜ for beam passing through slits **87** and **88**
- Vibration rate 120 cycles/sec.
- Vibration distance (of the order of a few thousandths of an inch)

Electrode **113**:
- Outside diameter .120
- Inside diameter .070
- Length .700
- Slot width .035
- Slot length .115
- Wall thickness .050

The ability to detect Ce isotopes was shown in an actual example of this invention where the total sample was 8×10^{13} Ce atoms and Ce-136 corresponding to 2×10^{11} atoms was detectable.

In another embodiment, the electrode **111** comprising a solid conducting material to be tested for trace constituents. In one example, this material is uranium metal, but any conducting solid could be used.

The source in this invention has the advantage of efficiently providing a high intensity, high energy, small solid angle beam of ions and finds utility for directing ions into a high resolution, double focusing spectrograph for qualitative and quantitative isotope determinations. Actual tests, for example, have shown the source of this invention to have very high efficiency in providing low detection limits for traces of Xe and rare earths, such as Ce, Tb, etc. Moreover, the source and nozzle of this invention are simple, inexpensive and durable and permit the use of a simple, conventional low voltage source while preventing overheating of the source electrodes and providing ion beam with a relatively low energy spread. Additionally, the system of this invention permits low radiation sources, whereas the samples required heretofore had radiation levels over a curie. Thus this invention decreases the health hazards to the operators while increasing the utility of spectrographs for small amounts of sample material, e.g. from reactor and accelerator bombardment, and high sensitivity for quickly determining nuclear transformation reactions.

What is claimed is:

1. In an ion source for a mass spectrograph having an ion extraction means at one end thereof, the improvement comprising, a first and solid pointed anode having a first axis, a slitted, hollow, cylindrical cathode forming an inside wall around a uniform diameter well having a second axis at right angles to said first axis, said cathode forming a slit in said inside wall parallel with said second axis for inserting said anode from one side of said well to the other side thereof transverse to said second axis, means for energizing said anode and cathode at low voltage for producing ions from solid material in an arc between said pointed anode and the inside wall of said cathode at the point of intersection of said first axis and said wall opposite to said slit, and means for vibrating said anode back and forth in a first plane passing through said slit and intersecting said second axis and the inside wall of said cathode, the direction of said vibration being at right angles to said second axis whereby said arc is pulsed at right angles to said second axis to provide a pulsed jet of ions that is shaped by said anode and cathode to limit the escape thereof in a small solid angle into said ion extraction means along a third axis corresponding to the intersection of said first plane and the inside wall of said cathode in a direction at right angles to the directions of said vibration of said anode and the pulsing arc produced thereby.

2. The invention of claim **1** in which the point of said anode is tapered through said slit to a pointed tip adjacent the inside wall of the cathode to provide a small cross-section arc and to prevent arcing in the cathode slit while blocking the emergence of ions therefrom.

3. The invention of claim **1** in which said vibration is at a rate of about 120 cycles/second over a small distance to produce a high density jet of ions having a relatively high energy in a narrow velocity band.

4. The invention of claim **4** having means for moving said anode in said first plane relative to said cathode during said vibration thereof for maintaining said pulsing and for providing for re-ionization of material deposited on said cathode from said jet.

5. The invention of claim **1** having means for moving said anode in said first plane relative to said ion extraction means during said vibration for providing a jet of ions having an adjustable solid angle relative to said ion extraction means.

References Cited

UNITED STATES PATENTS

2,724,056	11/1955	Slepian	250—41.9
2,736,809	2/1956	Bacon	250—41.9
2,848,620	8/1958	Backus	250—41.9

RALPH G. NILSON, *Primary Examiner.*

W. F. LINDQUIST, *Assistant Examiner.*