

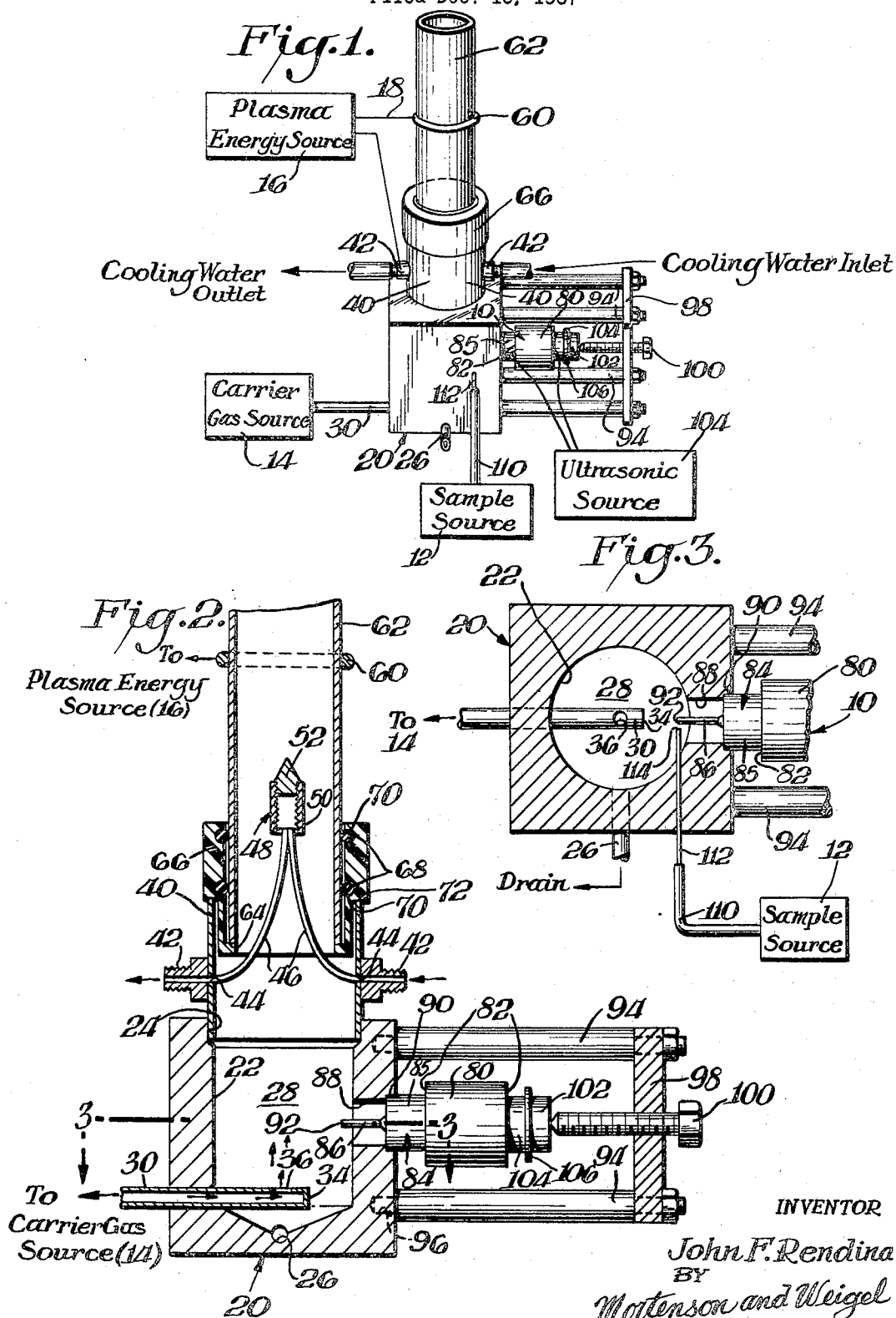
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J. F. RENDINA

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PLASMA ATOMIC VAPOR GENERATOR

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John F. Rendina, R.D. 3, Kennett Square,

Red Clay Valley, Pa. 19348

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19 Claims

ABSTRACT OF THE DISCLOSURE

A plasma generator, for converting a sample to be analyzed into an atomic vapor capable of absorbing and/or emitting electromagnetic radiation, includes a vertically disposed cylindrical discharge cavity. A ring electrode connected to a source of high frequency R.F. energy is positioned about the discharge cavity and a replaceable electrode is positioned within the discharge cavity to form a high frequency electric field between the ring electrode and the replaceable electrode. The discharge cavity is coaxially positioned adjacent the hollow cylindrical receptacle in which the sample is nebulized and entrained in a carrier gas for passage through the discharge cavity. A horn-type ultrasonic transducer is positioned in a side wall of the receptacle with its nebulizing surface essentially parallel to the direction of carrier gas flow through the discharge cavity. The carrier gas is introduced into the bottom portion of the receptacle such that the carrier gas flows past the nebulizing surface of the transducer, thereby to entrain the sample and thence carry it upwardly through the high frequency electric field in the discharge cavity where the atomized sample is exposed to the plasma. The sample fluid is directed through a horizontally positioned small tube to a point immediately adjacent the nebulizing surface.

This invention relates to an apparatus for generating an atomic vapor and, more particularly, to an apparatus for effectively nebulizing a sample vapor and passing the sample vapor through a plasma discharge for conversion to free atoms essentially at the ground state energy level.

BACKGROUND OF THE INVENTION

Since the time of Fraunhofer, it has been known that if a substance is converted into an atomic vapor it will absorb radiation of the same wave lengths as are emitted by the same substance when electrically or thermally excited. It is known also that if a given substance is heated sufficiently its vapor will emit certain predetermined characteristic radiation. These principles have been used to great advantage in the development of what is now known as atomic absorption spectroscopy. Usually, in atomic absorption spectroscopy, radiation from a characteristic line or other conventional source is passed through an atomic vapor of the sample under test. The extent or degree of absorption of the characteristic radiation by the atomic vapor is a measure or indication of the presence of atoms having the same characteristic lines as the source. This type of spectroscopy is used to measure and detect the presence of various metals in substances although the technique in theory is not limited to metals alone.

To detect the presence of a particular metal or element in a sample, it is necessary to have a source of radiation which produces wave lengths of light which are characteristic of the element atoms under test. One such source is a metallic halide discharge tube of the type described in U.S. Patent 3,319,119 issued to John F. Rendina on May 9, 1967. Another is the so-called hollow cathode lamp. Whatever the source, characteristic radiation therefrom is passed through a medium in which free

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atoms are available. These free atoms are obtained by dissociation of molecules of a sample of the substance under test.

Various means have been employed to dissociate the sample. These have included conventional chemical combustion flames. Unfortunately, flames are limited in the heat or energy that they are able to impart to the sample and hence the sensitivity of such a system is rather severely limited. Some substances require relatively high dissociation energies. More recently plasmas have been employed to excite the sample under test for emission spectroscopy. One such plasma is described in U.S. Patent 3,242,798 issued Mar. 29, 1966 to Yamamoto. Even plasma sources are not perfect. In their present state of development, they often introduce errors into and decrease the sensitivity of the system, particularly when used in atomic absorption spectroscopy.

Regardless of the system employed to impart energy into the sample, it is generally desired to nebulize or atomize the liquid sample and sweep the resulting fog into the reaction zone of the flame, arc, plasma, or other energy means using a gas stream. As the energy is transferred to or absorbed by the individual droplets comprising the fog, some of the more volatile components are evaporated leaving a solid particle. Absorption of additional energy by the solid particles results in the particle reaching the boiling or sublimation point—it then becomes independent molecules (a gas). Further absorption of energy by the molecules produces chemical bond splitting resulting in free atoms in their ground or unexcited state which are capable of absorbing electromagnetic radiation of a resonant frequency. It is this fog or atomic vapor of ground state free atoms which produces the absorption necessary to the atomic absorption process. For emission spectroscopy, additional energy must be imparted to the free atoms to raise them to an excited state necessary to yield emission spectra.

In the general field of spectroscopy, including emission, as well as absorption spectroscopy, there are many additional requirements imposed upon the sample introduction system. The sample introduction system must have a low sample hold up volume. In other words, it is highly desirable that any changes in the sample consistency be readily observable. The sample feed rate should be capable of being varied independently of the other parameters of the system. Additionally the sample introduction system should be so isolated that the sample contacts only inert materials. A maximum amount of the sample should actually reach the plasma itself, i.e., if a high proportion of the sample is lost during the introduction phase, gross inaccuracies result.

One problem often encountered when an ultrasonic transducer is employed as the nebulizing element is that which results from the condensation of the nebulized sample on the walls of the plasma generator. Once condensed, the sample fluid runs down the walls and often drips upon the horn tip of the transducer. This can load the transducer such that its frequency changes thus producing a non-uniform fog. The fog should be uniform in order to reach the limits of the sensitivity theoretically possible using the atomic absorption process.

It is, therefore, an object of this invention to obviate many of the disadvantages inherent in the prior art plasma generators for spectroscopic analysis.

Another object of this invention is to provide an improved apparatus for introducing a fluid sample into the plasma generator for spectroscopic analysis.

SUMMARY OF THE INVENTION

A preferred embodiment of this invention provides an improved apparatus for uniformly converting a fluid sample into a fog or mist and entraining such fog in a

carrier gas for passage through an energy source and subsequent conversion into free atoms at the ground state energy level. This apparatus includes a fluid sample introduction chamber in which the fluid sample is passed through a small tube to the tip of an ultrasonic horn type transducer. The sample introduction tube and the horn transducer are disposed in a horizontal plane at right angles to each other such that the nebulizing surface of the horn transducer directs the nebulized sample into the central portion of the sample chamber. A carrier gas, introduced at the bottom of the sample chamber, flows upwardly past the nebulizing surface of the horn type transducer so as to entrain the nebulized sample and carry it upwardly through a tube into a high frequency electric field. In the high frequency electric field the carrier gas is converted to a plasma which in turn transfers energy to the sample droplets for their dissociation into free atoms.

This particular apparatus has many advantages. The fog is relatively uniform. If any of the sample fog condenses on the walls of the quartz tube or sample chamber, it tends to run to the bottom of the chamber and thence to a drain. It is not able to run onto the horn type transducer and impair the transducer's operating efficiency. Furthermore, the small tube through which the sample is introduced to the transducer has a relatively low hold-up volume. Finally, since the sample is nebulized directly adjacent the energy source, a highly uniform fog reaches the plasma. The sample may be introduced at a constant rate to the nebulizer and hence the sample rate is relatively unaffected by sample viscosity. Further, since the nebulized sample is directed into the stream of carrier gas, for immediate entrainment and introduction into the plasma zone, very little of the sample is lost.

DESCRIPTION OF THE DRAWINGS

The novel features of this invention which are considered characteristic are set forth with particularity in the appended claims. The invention, itself, however, both as to its organization and method of operation, as well as additional objects and advantages thereof, will best be understood from the following description when read in connection with the accompanying drawings, in which:

FIGURE 1 is a part block and part pictorial view of a plasma atomic vapor generator constructed in accordance with this invention;

FIGURE 2 is a cross-sectional elevation view of the plasma generator illustrated in FIG. 1; and

FIGURE 3 is a cross-sectional, plan view of the plasma generator illustrated in FIG. 1 taken along the section line 3—3 to illustrate the details of the nebulizer and carrier gas introduction system.

DESCRIPTION OF THE PREFERRED EMBODIMENT

In the drawing of FIG. 1 there is seen a spectroscopic analysis apparatus including a plasma-atomic vapor generator constructed in accordance with this invention. The plasma-atomic vapor generator includes an ultrasonic transducer 10 for nebulizing a sample introduced from a sample source 12. The fog of the nebulized sample is swept by a carrier gas from a carrier gas source 14 upwardly in the drawing into a plasma. The plasma imparts energy into the sample so as to dissociate the sample molecules into either free atoms at a ground state energy level for atomic absorption spectroscopy purposes or into excited atoms in the free state for spectroscopic emission studies. Energy for generating the plasma is derived from a plasma energy source which in this instance is denoted by the block 16 with the connection 18 leading to the upper portion of the plasma generator. The plasma energy source 16 may be either a source of high frequency oscillations or it may be a source capable of producing a D.C. arc, both being known mechanisms for transferring

energy to a plasma. For purposes of illustration, a high frequency light source is shown.

The details of the transducer illustrated in FIG. 1 are perhaps more clearly depicted in the cross-sectional views of FIGS. 2 and 3. Referring to these FIGS. 2 and 3, the plasma light source is seen to include a base member 20 which may be constructed from suitable stainless steel bar stock. The base member 20 is formed to have a bore 22 therein which opens generally upwardly, in the drawing, and a counter bore 24 at the uppermost portion (in the drawing) thereof. The lower portion of the bore 22 is generally conical in shape and at the lower most portion thereof a radial bore 26 provides a drain for the mixing cavity 28 formed by the bore 22. A tube 30 is inserted into the lower part of the mixing cavity 28 immediately above the drain 26 through a second radial aperture formed in the side wall of the base member 20. The tube 30 may be any suitable tubing, typically $\frac{1}{8}$ " is adequate for this purpose, and it is connected to be fed by the carrier gas source 14 (FIG. 1). The end of the tube 30 which extends into the cavity 28 is closed as at 34 and a radial orifice 36 in the side wall of the tube 30 opens upwardly to permit the flow of carrier gas upwardly and out of the mixing cavity 28.

Mounted within the counter bore 24 is a short tubular section 40 having substantially the same inner diameter as does the cavity 28. The tubular section 40 may be formed of any suitable material such as stainless steel which is generally less chemically reactive to the sample mixtures that are introduced in the mixing cavity 28. A pair of threaded male tubing connectors 42 are attached as by welding at different peripheral points on the tubular section 40 to permit the attachment thereto of a female tubing connector supplying water or other cooling fluid to be introduced as will be described. A pair of apertures 44 are formed in the wall of the tubular section 40 to permit small tubes (typically $\frac{1}{16}$ " stainless steel tubing is satisfactory) to run from the tubing connectors 42 up into a water cooled replaceable electrode 48. The water cooled electrode 48 includes a hollow cylindrical tip holder 50 fed with cooling fluid by the stainless steel tubes 46. The tip holder 50 is hollow and internally threaded to permit a replaceable tip 52, which is generally conical in shape, to be screwed into the tip holder 50. The replaceable tip 52 may be formed of aluminum, rhodium clad copper, or any other suitable material having a relatively high heat conductivity. Cooling water may thus enter through one of the connectors 42 and travel through one of the tubes 46 into the tip holder 50 and thence be withdrawn through the remaining tube 46 and its connector 42.

Thus constructed the replaceable electrode 48 may form one electrode which is particularly adapted for use with a radio frequency (R.F.) plasma generator. To complete the R.F. plasma generator portion, an R.F. induction ring or ring electrode 60 is placed slightly above the replaceable electrode 48 and is mounted on a tube or chimney 62 which confines the plasma and carrier gases flowing upwardly from the mixing cavity 28 and is a part of the discharge cavity. To complete the discharge cavity, the tube 62 is mounted upon an internally protruding annular flange 64 formed at the bottom of a stepped ring section 66. The inner wall of the ring section 66 has internal grooves 68 formed therein which accommodate O-rings 70 to aid in maintaining a seal between the tube 62 and the ring section 66. The O-rings may be formed of any suitable elastomer. The stepped ring section 66 includes a stepped portion 72 which rests upon the upper portion of the short tubular section 40. This completes the discharge cavity in which the plasma is formed to dissociate the sample molecules. The tube 62 may be formed of quartz, fused silica, or other suitable material which is relatively inert and capable of withstanding relatively high temperatures. The stepped ring section 66 may be formed of any inert plastic such as that sold under the

trade name Teflon or for that matter may be formed of stainless steel.

An ultrasonic nebulizer is employed to nebulize the sample. The nebulizer includes a transducer 80, which may be any suitable piezoelectric crystal having a pair of electrodes 82 on either side thereof. The piezoelectric crystal may be formed of a natural piezoelectric crystal material such as quartz, or it may be a man made, polarized ceramic such as one of the lead ziconate-lead titanate (PZT) polycrystalline materials or a barium titanate polycrystalline material. As used herein the term "crystal" refers to both the natural and synthetic materials. The electrodes 82 make actual physical contact with either of the side faces of the transducer 80. They (the electrodes 82) may be formed by a thin coating of conductive painting applied to the crystal surfaces just prior to assembling the unit. The paint should be wet when the components comprising the complete transducer are assembled. A suitable paint for this purpose is a silver paint No. 4922 available from E. I. du Pont de Nemours & Company, Wilmington, Del.

To complete the nebulizer and amplify the longitudinal vibrations produced thereby, a stepped or other displacement amplifying horn 84 is mechanically clamped to the transducer 80. The small diameter horn portion, which produces the amplified uniform longitudinal vibrations, is introduced through an aperture 88 formed in the side wall of the cavity 28. Actually, the outer portion of the aperture 88 may have a shallow counterbore at 90 to facilitate the mounting of a stepped horn 84. As is known, the stepped horn is formed of a large segment 85 and an extension or smaller segment 86 to provide a displacement amplification of the longitudinal vibrations of the transducer 80. The amplification is directly related to the ratio of the area of the large segment face to the area of the small segment face 92 (FIG. 3).

The means of mechanically clamping the stepped horn 84 to the transducer 80 includes four supporting rods 94 each of which has a threaded end stud, as seen for example at 96, which is inserted at one end into tapped holes formed in the side wall of the base member 20 and at the other end to a support plate 98. The support plate 98 holds a pressure adjusting screw 100. The pressure adjusting screw has a pointed tip applied to a pressure plate 102 which is separated from a backup plate 104 by an electrical insulator 106 of any suitable elastic non-conductive material. The ultrasonic nebulizer is seen to comprise a sandwiched array of the stepped horn 84, the transducer 80, the backup plate 104, the insulator 106, the pressure plate 102, and the pressure screw 100. When the pressure screw 100 is tightened, the single point pressure reduces the possibility of misalignment or cocking of the various components of the sandwiched array.

It is understood of course, that the transducer 80 may be by a crystal of any suitable size—that is to say, it may be approximately the size of the large horn section or it may be smaller or larger than the largest portion of the stepped horn 84. As is known, the acoustical properties of the horn and the inherent properties of the crystal must be taken into account in their assembly. The size and the shape of the horn and crystal, as well as the choice of material from which the horn is formed, may be varied to obtain a predetermined frequency at the nebulizing surface or face 92.

Thus, if a desired frequency is to be used as the ultrasonic frequency to nebulize a sample, a source of ultrasonic frequency, denoted by the box 104, applies an alternating electrical signal of that frequency to the electrodes 82 of the crystal. The crystal is sized to be some multiple of one-half of the wave length of that frequency. In like manner, the axial length of both of the smaller and larger sections of the stepped horn 84 are each some multiple of one-quarter of the wave length of the selected frequency. The combined sandwich of the pressure plate 102, insulator 106 and backup plate 104 desirably is

some multiple of one-quarter of the wave length of the selected wave length, whereas the distance along the pressure screw between the pressure plate 102 and the support plate 98 should be some multiple of one-half of the wave length of the selected frequency. In this manner, the acoustic energy of the crystal is transmitted to the atomizing tip 92 of the stepped horn 84 and yet little or no energy is transmitted back to the support plate 98 since it is at a node point of the wave pattern setup in the system. These particular design considerations need not be elaborated on further since they are known techniques. The nebulizing surface 92 faces radially, inwardly of the cavity 28 and is disposed so as to be substantially parallel to the longitudinal axis of the gas flow directed upwardly from the orifice 36.

To complete the system, the sample from the sample source 12 must be introduced to the nebulizing surface. Sample from the source 12 is injected through a suitable flexible tubing 110, which connects the sample source 12 to a small piece of stainless steel tubing or hypodermic needle 112. The needle 112 passes through a hole formed in the block 20 and extends into the cavity 28 to a point immediately adjacent the atomizing surface 92 of the stepped horn 84. The tube 112 is horizontally disposed and is positioned preferably a millimeter or less from the side of the small diameter portion 86 of the stepped horn 84. Actually, the end 114 of the tubing 112 may be positioned at or slightly beyond the end of the small diameter portion 86 of the stepped horn 84. It is preferred, however, that it be immediately at the end but not extending beyond the end face or nebulizing face 92 of the small diameter portion 86. A positive displacement pump or motor driver hypodermic may be used to continuously and evenly feed the sample to the nebulizing surface.

In this manner, as the sample is introduced into the system and the transducer 80 activated, the nebulizing surface 92 causes a continuous fog of the sample injected through the tubing 112. Because of the horizontal positioning, the fog is continuous and free of undulating variations which normally occur in ultrasonic vibrators of this type. The aperture 88 prevents any condensate which forms on the interior walls 22 of the chamber 28 from running down the walls and dropping on the small portion 86 or the nebulizing face 92. Thus, there is no loading of the horn tip as occurs in many systems. The system disposed in this horizontal array has been found to be less critical of any loading on the horn tip which is advantageous in producing a more uniform fog.

The direct injection of the sample fog into the flowing carrier gas at the lower portion of the cavity 28 results in a relatively small hold up volume and little loss of the atomized sample before it is transported upwardly into the plasma formed between tip 52 and the electrode 60. Furthermore, by forming the tube 62 to have a relatively small diameter, the plasma may be tightly confined so as to impart a maximum amount of its energy into the sample for dissociation.

The system thus described permits the use of relatively low gas velocities so that the sample fog stays in the reaction zone of the plasma for a longer period of time. The positive displacement feed assures that a sample be introduced at a constant rate regardless of its viscosity. The sample is not contaminated by chemically active materials since it touches essentially only relatively chemically inert parts. The replaceable tip on the electrode can be replaced quickly and easily as is necessary.

Although the system has been illustrated as utilizing an R.F. excited plasma, it is to be understood that direct current (D.C.) arcs could also be used to establish the plasma if desired. D.C. arcs of this type have long been used to excite plasmas and require no more than a pair of electrodes disposed on opposite inner walls of the tube 62 so as to establish an arc across the diameter of the tube through which the entrained sample fog must pass.

It will be obvious that various modifications may be made in the apparatus and in the manner of operating it. It is intended to cover such modifications and changes as would occur to those skilled in the art, as far as the following claims permit and as far as consistent with the state of the prior art.

What is claimed is:

1. Apparatus for dissociating a sample to be analyzed into free atoms comprising:

tubular means defining a discharge cavity having a first axis and first and second ends, said first end being formed from an electrically insulating material,

plasma generating means for forming a plasma contiguous said first end of said cavity, said second end having a radially disposed transducer means and a nebulizing surface adapted to oscillate at an ultrasonic rate,

a fluid conduit means disposed in said second end adapted to deliver said sample to said transducer means to be nebulized, and

means disposed in said second end for directing a stream of carrier gas along said first axis through said discharge cavity, thereby to sweep said nebulized sample into said plasma for dissociation into free atoms.

2. Apparatus according to claim 1 wherein said nebulizing surface is planar and lies in a plane substantially parallel to said first axis, thereby to direct said nebulized sample into said carrier gas flow, and said second end also includes means defining an aperture in which said transducer is coaxially disposed.

3. Apparatus according to claim 1 wherein said transducer means includes a piezoelectric crystal and a displacement amplifying horn having a larger diameter portion and a smaller diameter portion coaxially disposed along a second axis intersecting said first axis substantially at a right angle.

4. Apparatus according to claim 3 wherein said nebulizing surface is planar, is disposed at the free end of said small diameter portion, and lies in a plane substantially parallel to said first axis, thereby to direct said nebulized sample into said carrier gas stream.

5. Apparatus according to claim 4 wherein said fluid conduit means has a discharge orifice located contiguous to the periphery of said small diameter portion adjacent said nebulizing surface.

6. Apparatus according to claim 5 wherein the center of said orifice and said second axis lie in a plane substantially perpendicular to said first axis.

7. Apparatus according to claim 5 wherein said discharge orifice is positioned at substantially the same elevational level as said nebulizing surface.

8. Apparatus according to claim 1 wherein said first axis is vertically oriented, said second end of said tubular means being tapered to a low point and which apparatus includes means defining a drain aperture communicating with said low point.

9. Apparatus according to claim 8 wherein said nebulizing surface is planar and lies in a plane substantially parallel to said first axis, thereby to direct said nebulized sample into said carrier gas stream.

10. Apparatus according to claim 8 wherein said transducer means includes a piezoelectric crystal and a stepped horn having a large diameter segment and a small diameter segment coaxially disposed along a second axis intersecting said first axis substantially at a right angle, said nebulizing surface is planar and is disposed at the free end of said small diameter segment and lies on a plane substantially parallel to said first axis, and said fluid conduit means has a discharge orifice located contiguous to the periphery of said small diameter segment adjacent said nebulizing surface.

11. Apparatus according to claim 1 wherein said discharge cavity is formed of fused silica.

12. Apparatus according to claim 1 wherein said plasma generating means includes means for establishing a high frequency electric field within said cavity.

13. Apparatus according to claim 12 wherein said means for establishing high frequency electric field includes a ring electrode disposed about the first end of said cavity and a second electrode positioned within said cavity along said first axis.

14. Apparatus according to claim 13 wherein said second electrode is hollow and has means for circulating cooling water therethrough.

15. Apparatus according to claim 13 wherein said nebulizing surface is planar and lies in a plane substantially parallel to said first axis, thereby to direct said nebulized sample normal to said first axis.

16. Apparatus according to claim 13 wherein said transducer means includes a piezoelectric crystal and a stepped horn having a large diameter segment and a small diameter segment coaxially disposed along a second axis intersecting said first axis substantially at a right angle, said nebulizing surface being planar and positioned at the free end of said small diameter segment and lies in a plane substantially parallel to said first axis, and said fluid conduit means has a discharge orifice located contiguous to the periphery of said small diameter segment adjacent said nebulizing surface, thereby to direct said nebulized sample into said carrier gas stream.

17. Apparatus according to claim 1 wherein said first axis is vertically oriented.

18. Apparatus according to claim 16 wherein said nebulizing surface is planar and lies in a plane substantially parallel to said first axis, thereby to direct said nebulized sample normal to said first axis.

19. Apparatus according to claim 16 wherein said nebulizing surface is planar and lies in a plane which intersects said first axis at an angle of other than ninety degrees.

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JAMES W. LAWRENCE, Primary Examiner

R. F. HOSSFELD, Assistant Examiner

U.S. Cl. X.R.

313—231; 356—85

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,484,650

December 16, 1969

John F. Rendina

It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

In the heading to the printed specification, lines 3 and 4, "John F. Rendina, R. D. 3, Kennett Square, Red Clay Valley, Pa. 19348" should read -- John F. Rendina, Kennett Square, Pa., assignor to Hewlett-Packard Company, Palo Alto, Calif., a corporation of California --.

Signed and sealed this 27th day of October 1970.

(SEAL)

Attest:

Edward M. Fletcher, Jr.

Attesting Officer

WILLIAM E. SCHUYLER, JR.

Commissioner of Patents