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[54] EXCITATION SOURCE FOR SPECTROSCOPIC ANALYSIS

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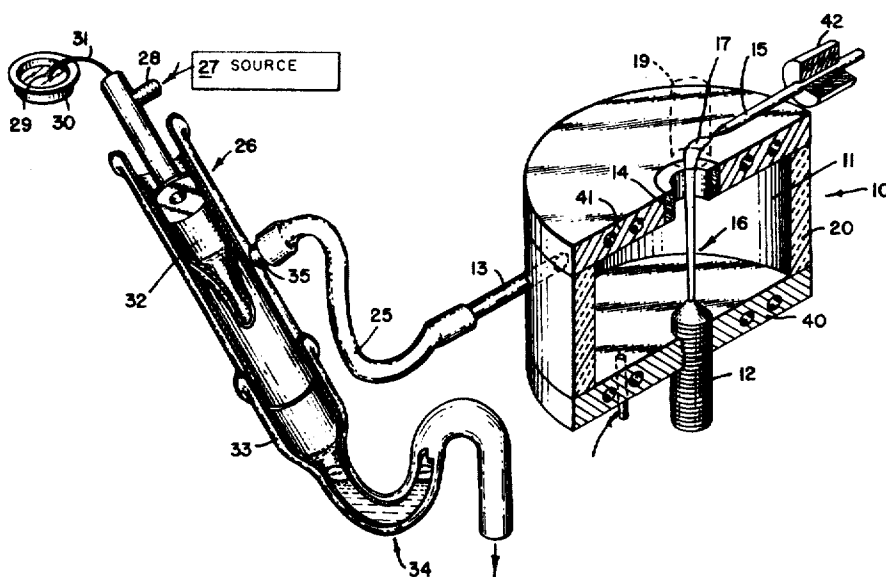
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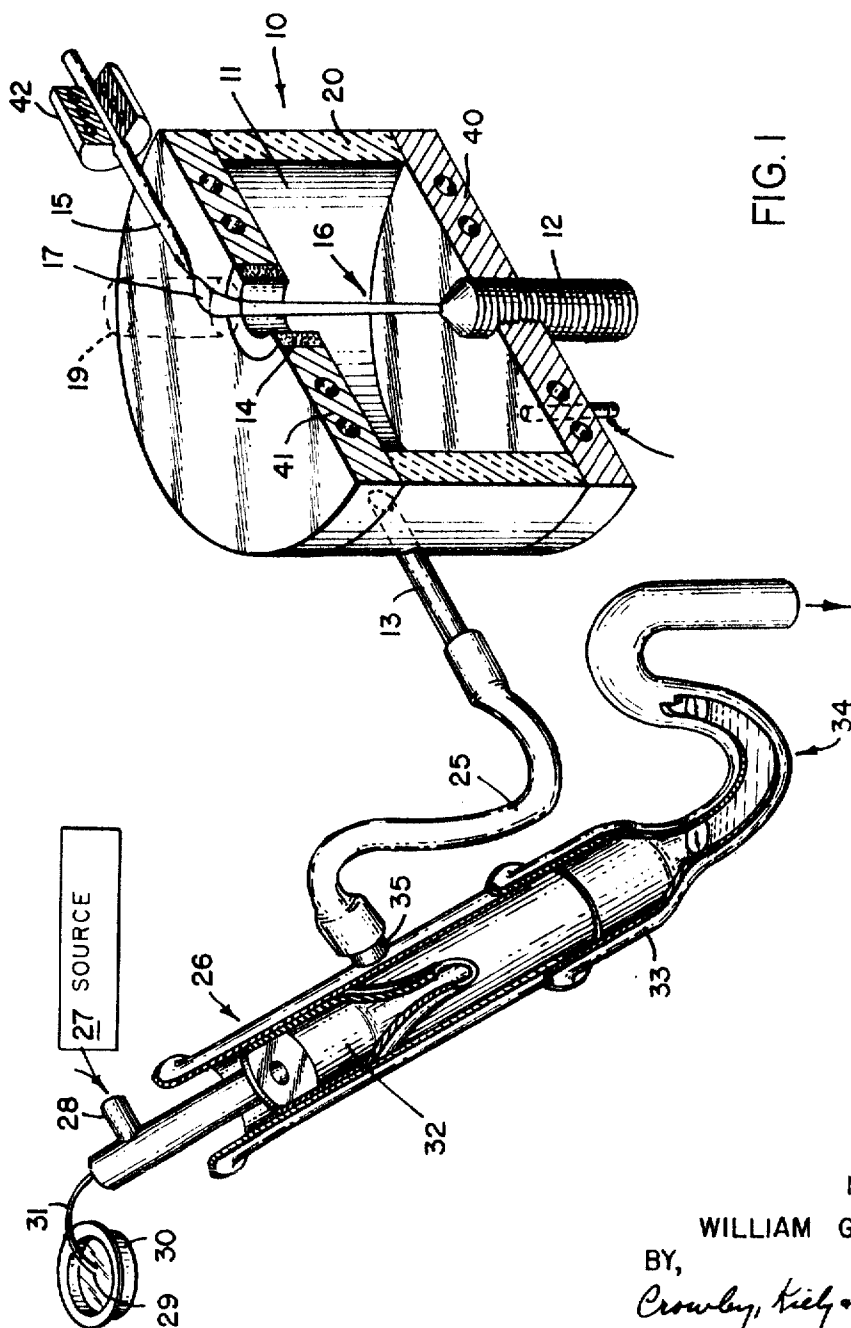
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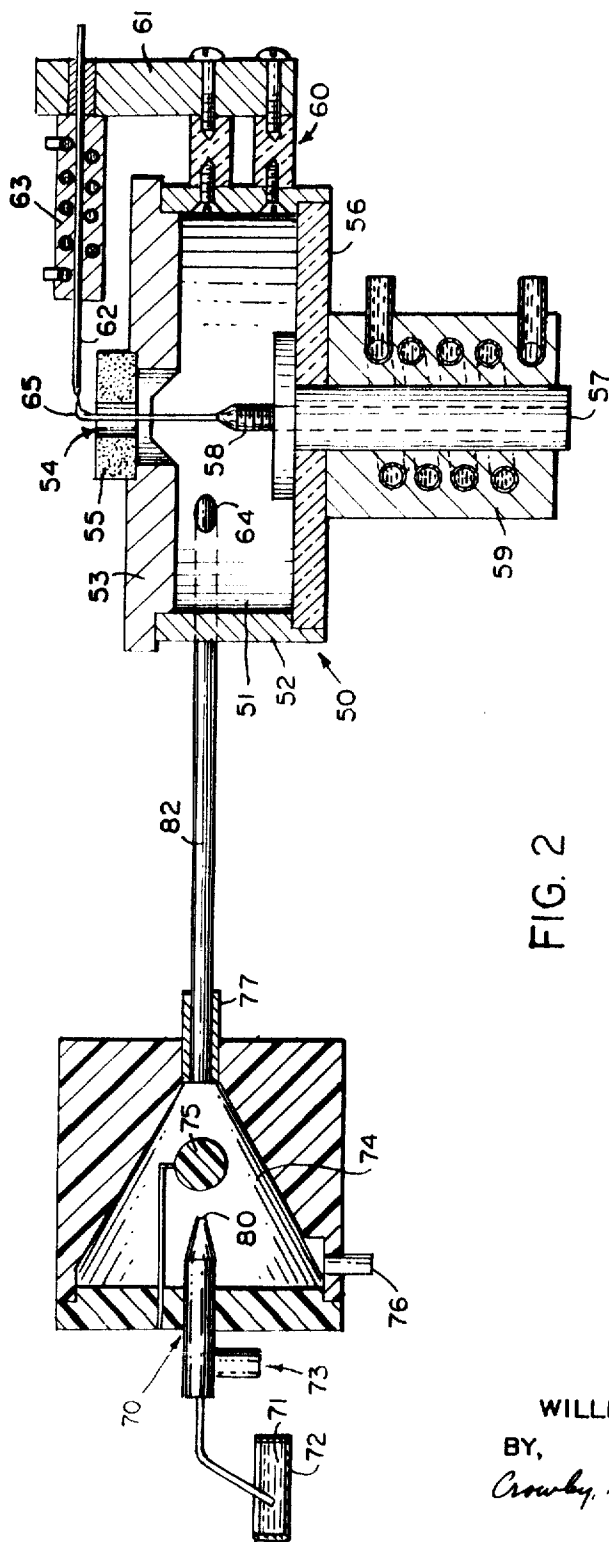
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ABSTRACT: A plasma jet generator is composed of a swirl chamber, an anode within the swirl chamber, means for tangentially introducing a premixed atomized sample and an ionizing carrier gas into the chamber, an exit port for the generated plasma flame located opposite the anode, which exit port preferably has an electrically neutral border surrounding the port, and a cathode outside the chamber, offset from the plasma column and located at an angle to the axis of the anode so that the ionized gas is deflected to the cathode permitting spectrometric observation of any portion of the flame without interference from the ionized gas.





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EXCITATION SOURCE FOR SPECTROSCOPIC ANALYSIS

BACKGROUND OF THE INVENTION

The employment of a plasma jet for generating excitation energy for the spectrochemical analysis of materials was developed to avoid the inherent difficulties present in the use of flame, which suffers from interference and poor sensitivity for certain elements as a result of too low a temperature, and the electric arc, which often is unstable as a result of sputtering of the electrodes. Such plasma generators are generally composed of a nozzle to atomize the sample as it is introduced into the chamber, and an anode and a cathode to generate the plasma flame. The anode is generally located in proximity to the atomizing nozzle; often the nozzle is located at the center of the anode. The ionizing gas enters the chamber containing the anode and swirls around the anode. The sample is introduced into the plasma from the atomizer. The cathode is generally composed of a ring with a hole in the center in opposed relationship to the anode, thus, permitting the plasma jet to extend beyond the cathode and permit observation of the light emitted from the plasma by a spectrometer or other optical analytical device.

The employment of the ring configuration for the cathode, however, was not entirely satisfactory since the arc striking the cathode often resulted in the deterioration of the cathode because of the excessive heat generation and instability of the plasma flame generally characterized by a wandering flame and a sputtering of the cathode.

Further, the substantial background emission from the ionized gas interferes with the analytical observation of the materials under study.

To provide more stability in the position of the plasma jet and to reduce ablation of the orifice disc, an auxiliary cathode external to the structure has been employed. This has been located with the tip of the electrode directly opposite the orifice with the cathode either parallel to or at a right angle to the anode. Employing the external electrode in this fashion still results in some instability to the plasma jet primarily because of rotational flow of the gas and sample. Interference from the ionized gas is still a problem. Use time of the system is generally a maximum of 30 minutes of continuous use while the electrical and cooling demands are still relatively high.

A novel plasma jet generator for the excitation of samples for spectrochemical analysis has now been found which is not susceptible to the deficiencies of the prior art.

BRIEF SUMMARY OF THE INVENTION

In the novel plasma generator of the present invention, the sample is atomized prior to introduction into the swirl chamber. The anode located in the swirl chamber is positioned opposite an orifice in the roof of the chamber. The cathode for completing the arc is located outside of the swirl chamber, at an angle to the anode offset from the column defined by the plasma flame exiting the orifice whereby the plasma is deflected from its normal path, which is axial to the orifice, to contact the offset cathode. Thus, the plasma jet generated within the swirl chamber leaves the chamber through the orifice and substantially all of the ionized gas is removed from the plasma in a curved fashion thus permitting spectrometric determinations to be made on the plasma flame and the atomic vapor with a minimum of interference from the ionized gas and with the position of the plasma stabilized.

The orifice or control ring is preferably surrounded by a material which is resistant to the temperatures generated in the chamber. Cooling gases from the chamber surround the flame as it passes through the orifice providing stability to the flame, preventing "wandering." Thus, two concentric columns leave the chamber through the orifice; an inner column constituting the plasma flame and an outer column surrounding the inner column consisting of cooling gases. The cathode may overhang the edge of the orifice that is in the

zone of the cooling gases, provided the cathode does not extend into the column of the plasma flame.

Preferably, the sample is atomized and mixed with the ionizing carrier gas prior to introduction into the swirl chamber.

Thus, the possibility of large droplets being introduced into the swirl chamber is eliminated and a very fine mist of the sample, well mixed with the ionizing gas, is introduced into the swirl chamber. This arrangement also serves to sweep the chamber clean of any preceding sample as each succeeding sample is introduced, thus, minimizing the possibility of interference in the analysis of the materials and further serves to prevent contamination of the anode.

As stated above, it is preferred that the anode located in the swirl chamber have a conical construction.

The cathode, which is external to the chamber, is preferably given a conical tip and its axis is preferably perpendicular to the axis of the plasma and is located radially with respect to the control ring.

By means of the plasma generator of the present invention, the electrically neutral radiation from the sample continues in a substantially straight line path from the anode while a curvature is provided to substantially all of the plasma as a result of the greater attraction of the ionized carrier gas particles to the cathode.

As stated above, because of the separation of the ionized carrier gas, there is a higher ratio of the recombining atoms to be analyzed in the plasma jet with respect to the concentration of carrier ions. Because the temperature gradient at the curve is relatively well defined, different locations on or above the curve may be observed to enhance selectivity among materials being analyzed. Preferably, the outer periphery of the visual limits of the curved plasma is employed. It is possible, however, to discriminate against those elements which have relatively low excitation temperatures, such as sodium, by using this portion of the plasma flame. Such elements, however, may be readily observed in the plasma jet above the curved portion of the plasma.

Neither the anode nor cathode is within the field of view of the analytical instrument, thus, there is essentially no thermal continuum.

The flow rate of the ionizing gas and the electrical requirements are relatively low compared with conventional units. In addition, the plasma generator of the present invention has been operated for periods of 8 hours or longer without detriment to the apparatus and without any loss of sensitivity in the analytical observations of the plasma jet.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a side elevational view of the novel plasma generator of the present invention with an atomizer connected thereto; and

FIG. 2 is an alternative embodiment of the plasma generator of the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Turning now to the drawings;

FIG. 1 shows a side elevational view of plasma generator 10 and atomizer 26.

Plasma generator 10 is composed of a swirl chamber 11 having therein a graphite, conical tipped anode 12. The walls 20 may be composed of teflon (polytetrafluoroethylene), ceramic, or other equivalent material. If the wall material is not normally resistant to high temperatures, e.g., teflon, then cooling means should be employed. In the embodiment shown, the graphite anode is threaded through the bottom floor of the chamber and is connected to a power supply. Alternatively, the anode may be separately introduced into the chamber without connection to the floor of the chamber. The anode is located directly opposite control ring 14, in this case, an electrically neutral graphite ring. The graphite control ring 14 defines an orifice through which the generated plasma passes. The control ring 14 is electrically neutral, thus, would

have no effect on the plasma passing therethrough. It should be understood that any electrically neutral material can be employed for the control ring as well as graphite.

Alternatively, the control ring could be electrically connected to the cathode. However, this operation of the generator is not substantially different since the plasma column is essentially isolated from the control ring by the cool gas surrounding it and the external cathode exercising greater attraction for the plasma than the control ring.

Because of the constricted opening through which the plasma passes, a "pinching" of the plasma jet by cooling gas occurs which holds the plasma in a compact configuration, preventing the instability and "wandering" which characterizes prior art generators when the control ring is also the cathode.

Cathode 15, which is preferably composed of tungsten, is located outside the swirl chamber offset from the orifice in the control ring and preferably perpendicular to the plane of the plasma jet. It is only, however, necessary that the cathode be sufficiently set back from the center axis of the orifice to be out of the plasma column. The plasma jet 16 is generated within the swirl chamber and passes through the orifice in control ring 14. Plasma 17 is curved as a result of the attraction of the cathode for the ionized gas. The atomic vapor of the sample does not bend and can be viewed in area 19. Thus, a relatively large observation region 19 is provided, any portion of which can be focused on a suitable analytical device, for example, the entrance slit of a spectrometer. Depending upon the particular material desired to be analyzed, various portions of the plasma jet can be employed; generally depending upon the temperature of excitation of the material which is desired to be studied.

As shown in the drawing a graphite control ring is employed in the top of the swirl chamber. As desired, a ceramic top can be employed.

The heat output of the plasma generator of the present invention is particularly low compared with prior art plasma generators. Roughly a factor of 10 with respect to decrease in heat output has been observed in the present invention as opposed to prior art devices. Therefore, while no cooling is necessary with the plasma generator of the present invention if relatively high temperature resistant materials are used, e.g., ceramic or stainless steel, if desired, water cooling can be applied to the cathode and the anode to prolong the life of the electrodes. The drawing indicates the optional cooling means for the chamber as water circulation lines 40 and 41 as well as water cooled holder 42 for the cathode.

As stated above, it is preferred that the sample, either liquid or solid, be atomized and combined with the carrier gas prior to introduction into the swirl chamber. Any suitable atomizing apparatus can be employed. However, FIG. 1 also illustrates a novel, highly effective device for providing the sample mist in the carrier gas.

Atomizer 26 is composed of a mixing chamber 32 which feeds into trap chamber 33. Carrier gas, e.g., argon, helium, or other suitable ionizing gas known to the art, is fed into mixing chamber 32 through inlet 28 from source 27. A sample 29 is introduced from source 30 into mixing chamber 32 through conduit 31. Various means are employed for introducing the sample mist into the mixing chamber, for example, by pumping, gravity feed, or by suction created by the introduction of the carrier gas into the mixing chamber. A very fine mist of the sample is introduced into mixing chamber 32 and mixed with the ionizing carrier gas. The carrier gas and sample mist is then passed into trap chamber 33 where any large droplets are passed onto pressure trap 34. Outlet 35 is located above the opening from the mixing chamber 32 so that only the mixture of the carrier gas and the atomized sample can pass through the outlet 35 through conduit 25 into inlet 13 in the swirl chamber.

The aforementioned configuration minimizes the contamination of the anode. In addition, the mixing chamber 32 is swept clean of the preceding sample by the subsequent introduction of a new sample.

FIG. 2 shows a side elevational view of the preferred embodiment of the present invention.

Plasma generator 50 is composed of walls 52, floor 56 and roof 53 and which defines swirl chamber 51. In the embodiment shown, the walls 52 are composed of stainless steel and contain therein inlet 64 for tangentially introducing the sample and ionizing gas into the swirl chamber. Roof 53 contains therein orifice 54 defined by control ring 55. The floor of the swirl chamber is composed of a ceramic disc having an orifice therein to support a stainless steel anode holder post 57 supporting anode 58. Cooling collar 59 is also shown for applying circulating water or gas to the anode 58 for cooling. Anode 58 is preferably a pointed graphite anode and is located opposite orifice 54. In the embodiment shown, the cathode is supported by ceramic standoffs 60 on wall 52. The cathode support 61 carries cathode 62 and cooling collar 63. The cathode is preferably pointed, is preferably composed of tungsten and is offset from orifice 54. The plasma jet 65 generated by the anode passes through orifice 54 in control ring 55 and is bent to cathode 62.

Also shown in FIG. 2 is an alternative preferred embodiment for mixing the sample and ionizing gas and introducing it into the swirl chamber. Nebulizer 70 receives sample 71 from sample cup 72 by means of the suction created by the introduction of the ionizing gas through inlet 73. As stated above, however, other equivalent means may be employed for introducing the sample into the nebulizer. The thus-mixed sample and gas is sprayed from nozzle 80 into conical chamber 74. Ball 75 condenses the larger droplets which fall to the floor of the chamber and leave the chamber through drain 76. The more highly atomized particles admixed with the gas pass from chamber 74 through outlet 77 into conduit 82 and into swirl chamber 51 through inlet 64. The chamber and ball may be composed of any suitable material which is stable and noncorrosive to the particular sample materials employed. As examples of suitable materials, mention may be made of nylon, teflon (polytetrafluoroethylene), stainless steel and the like. Similar materials may also be used on conduit 82 which carries the sample to the swirl chamber. In an alternative embodiment, heat may be applied to conduit 82 to prevent the condensation or collection of droplets therein.

In a particularly preferred embodiment, the swirl chamber walls are uncooled and thermally conductive, preferably stainless steel. Such a structure substantially prevents the condensation of sample droplets in the chamber and the attendant fouling of the chamber.

One of the reasons for the extremely low rate of attack on the cathode results from the relatively low electrical requirements. Thus, the present invention generally employs 25 to 50 volts at 2 to 10 amperes whereas the prior art generally employs 100 volts or more at 15 to 25 amperes. From the foregoing figures, it can be seen that while cooling would be necessary, even essential, with the prior art systems, it will not be necessary with the low current requirements for the present invention and would be employed only at the option of the operator. Further, as the art has stated that the life of the electrodes varies as a function of current and time, it can also be seen that the current requirements are one factor for the greatly extended life of the electrodes in the present invention. Still further, it has been noted that the flow rates of the ionizing gas of the prior art systems has been relatively high. As compared with the flow rates of the ionizing gas in the plasma generator of the present invention, it has been found that five times the flow rate of the present invention is necessary with prior art devices. Thus, while the present invention employs flow rates of the order of magnitude of 3 to 10 cubic feet per hour with a stable plasma in terms of geometric configuration, the prior art requires flow rates of 20 to 40 cubic feet per hour with the aforementioned higher current requirements. The present invention, therefore, can be employed with standard arc lamp power supplies and standard electrical circuits unlike the prior art which requires special electrical circuitry.

Still another advantage achieved in the present invention is the substantial elimination of the sound which is peculiar to

plasma generators. In prior art devices, the concern has been with decreasing the intensity to a point where then noise can be tolerated by the operators for a reasonable period of time. In the present invention, the device can be operated substantially indefinitely without hardship to the operator.

Thus, it will be seen that in the present invention, a relatively simple system which does not require the nozzle of the prior art which requires only a single ionizing gas which requires substantially lower flow rates with the ionizing gas, which requires very low electrical current requirements, and which can be operated substantially indefinitely and without substantial deterioration of the anode and the cathode and which provides a more stable plasma jet with a greater flexibility for analysis than heretofore has been obtained can be provided by the novel device of the present invention.

The swirl chamber has been defined above primarily in terms of a cylindrical structure. It should be understood that, while a cylindrical structure is preferred, other shapes such as elliptical, rectangular, or square are also contemplated by the present invention. Similarly the orifice through which the plasma jet exits the chamber is preferably circular, but may be other shapes depending upon the symmetry desired in the flame and depending upon the particular shape of the electrodes used.

In still further embodiments, the ionizing gas is heated prior to mixing with the sample to further assist in vaporizing the sample. In an alternative embodiment, the mixing chamber is not employed and the sample and gas are aspirated directly into the swirl chamber with the gas.

What I claim is:

1. A plasma flame generator comprising:

- a. a chamber, one wall thereof having an orifice therein;
- b. an anode disposed in said chamber and located opposite said orifice;
- c. means to introduce an atomized sample to be analyzed and an ionizing carrier gas into said chamber whereby a plasma flame is generated in the chamber and the plasma flame exits the orifice in a plasma column, said column aligned along an axis passing through the orifice and the anode; and
- d. a cathode located externally to and spaced from said chamber and at an angle to the axis of the plasma column, said cathode being offset from said plasma column whereby the plasma flame after exiting said chamber through the orifice is bent at an angle to the axis of the plasma column to contact said cathode.

2. The device as defined in claim 1 wherein said anode is graphite, said orifice is an electrically neutral ring of graphite, and said cathode is tungsten and said cathode is substantially perpendicular to the axis of said plasma column.

3. The device as defined in claim 1 which includes means to introduce said sample and said gas tangentially into said chamber.

4. The device as defined in claim 1 which includes a second wall spaced apart from the wall having the orifice therein and wherein the walls of said chamber are uncooled and thermally conductive.

5. The device as defined in claim 1 wherein said sample introducing means includes an atomizer located externally to said chamber.

6. The device as defined in claim 5 wherein said atomizer comprises a mixing chamber and a trap chamber wherein a sample to be analyzed and an ionizing carrier gas are introduced under sufficient pressure to atomize said sample, orifice means for passing the contents of the mixing chamber into

the trap chamber, means in said trap chamber for communicating with said plasma chamber located above the inlet to said trap chamber from said mixing chamber whereby any droplets are retained within said trap chamber and only atomized sample and carrier gas pass from said trap chamber to said plasma chamber.

7. The device as defined in claim 5 wherein said atomizer comprises a conical chamber; a nozzle for introducing into said conical chamber said sample and said ionizing gas under sufficient pressure to atomize said sample; means in opposed relationship to said nozzle for collecting relatively large droplets of said sample from the atomized mist, and means communicating with said plasma chamber from said conical chamber, whereby only highly atomized droplets are introduced into said plasma flame.

8. The device as defined in claim 1 wherein cooling means are associated with said anode and said cathode.

9. The device as defined in claim 1 wherein said orifice is an electrically neutral ring composed of a ceramic and constitutes substantially the entire wall of said chamber.

10. The device as defined in claim 1 wherein the second wall is the floor of said chamber and said floor is composed of a ceramic and the chamber includes sidewalls which are stainless steel.

11. The device as defined in claim 1 wherein said anode and cathode are connected to a power supply of about 25 to 50 volts at 2 to 10 amperes.

12. A method for generating a curved plasma flame which comprises:

- a. introducing an atomized mixture of a sample to be analyzed and an ionizing gas into a chamber;
- b. applying a voltage to an anode and a cathode to generate a plasma flame, the anode disposed within the chamber and substantially in line with an exit orifice, and the cathode located external to the chamber and orifice and offset from said orifice;
- c. flowing the plasma flame through the orifice in the chamber;
- d. exiting the plasma flame from the orifice as a plasma column, said column substantially aligned with the axis passing through the anode and the orifice; and
- e. bending the plasma flame from the plasma column to engage the cathode at an angle to the axis of the plasma column and to a position offset from said plasma column.

13. The method of claim 12 which includes introducing tangentially the atomized mixture into the chamber.

14. The method of claim 12 wherein the plasma flame exiting the orifice as a plasma column comprises an ionized gas and a sample in the form of atomic vapor and which includes: bending substantially all of the ionized gas from the plasma column to engage the cathode, and flowing the atomic vapor substantially in line with the axis passing through the anode and the orifice.

15. The method of claim 12 which includes:

surrounding the plasma flame with cooling gases as it exits the orifice to define a second column of cooling gases surrounding the plasma column.

16. The method of claim 15 which includes:

flowing the plasma flame and the surrounding column of cooling gases through a constricted orifice; and pinching the plasma as it flows through the orifice to prevent wandering.

17. The method of claim 12 wherein the carrier gas is argon.

18. The method of claim 12 wherein the carrier gas has a flow rate of 3 to 10 cubic feet per hour.