This invention relates to techniques in spectroscopic analysis, and more particularly it relates to a new plasma jet generator so adapted as to accomplish spectroscopic analysis by means of the emission of light obtained by introducing an atomized solution sample into a high-temperature region.

Among the devices in practical use at present as spectroscopic light sources, there are those utilizing electrical discharge and those utilizing chemical flames.

In the case of the former light source, that is, by the electrical discharge method, it is possible to create temperatures as high as 5,000 to 6,000 degrees K. in a relatively easy manner, whereas it is possible to excite almost all elements and cause them to emit light. On the other hand, however, this method has the disadvantage of erosion of the electrodes due to bombardment of electrons or ions, this erosion becoming particularly severe when the electrodes come into contact with such substances as air and water which can react chemically with the electrodes. Since erosion of the electrodes causes instability of discharge and a drop in measurement precision, the introduction of the samples in the discharge excitation method presents a great problem. To date, however, a device fully solving this problem has not been proposed.

In contrast to the above method, the flame photometric analysis method does not require high-temperature electrodes, wherefor it is possible to introduce samples in a relatively easy manner. For example, a common practice is to dissolve a sample in an acid or water to form a solution, to atomize this solution by means of an atomizer, and to introduce the atomized solution into the high-temperature region of a flame. This flame photometric method, however, is disadvantageous in that maximum temperatures of only 2,000 to 3,000 degrees K. can be attained. At such temperatures, the kinds of elements which can be excited thereby are limited. Although this method is relatively sensitive in the case of such substances as alkali metals and alkaline earths, its application is difficult in the case of many heavy metals.

In a recently proposed method, a plasma jet is used as a new light source wherein the high-temperature feature of discharge excitation and the stable characteristic of flame photometry are combined. In this light source, high-temperature plasma created by arc discharge within an inert gas is caused to be ejected from a small hole provided in an electrode, and the high-temperature plasma flame of several thousands to ten thousand degrees Kelvin created thus is used in place of the conventional chemical flame. In the reduction of this analysis technique to practice, it is necessary, ordinarily, to satisfy the following conditions.

(1) In an arc-discharge operation, since the arc feet and particularly the cathode are at a high temperature, it is necessary to provide protective means for preventing erosion of the said cathode. Especially during the introduction of the sample into the high-temperature plasma, this sample must be prevented from contacting the high-temperature electrodes.

(2) In many cases, the arc feet, especially the anode foot, are not fixed in one place but shift to various places on the electrode in an irregular manner with respect to time. Such a shifting of the arc foot causes the discharge to become unstable and lowers the reproducibility of measurement. Accordingly, it is necessary to fix the arc foot by some means.

(3) When the atomized solution of the sample is introduced into the high-temperature plasma, the sample is vaporized and dissociated into atoms, is then excited, and radiates. In order that this process may proceed effectively, it is necessary that the sample penetrate as deeply as possible into the central, high-temperature region of the plasma.

It is very difficult to fulfill all of the above-stated requirements. For example, since the region of maximum temperature of the plasma jet is in the proximity of an electrode, and the temperature at the extreme end of the jet, it is desirable that the sample be introduced into the plasma as closely as possible to the electrode. However, such an introduction of the sample necessarily increases the possibility of the sample contacting the electrode.

The term “arc foot” appearing in this specification is explained as follows:

An arc generated in two electrodes forms an arc discharge column between one point of one electrode, e.g., the anode, and a point on the other electrode, e.g., the cathode. On these two points, a movement of charged particles occurs between the arc discharge column and the respective electrodes. Each of these two contact points between the arc discharge column and the respective electrodes is called an “arc foot.” The contact point created on the anode is called the “anode arc foot” and the one on the cathode the “cathode arc foot.”

In view of the above consideration, it is an object of the present invention to provide a new plasma jet generator having electrodes which are constructionally arranged so as to fulfill in an optimum manner the various conditions which must be met by a plasma jet to be used as a spectroscopic light source.

The nature, principle, and details of the invention will be clearly apparent to those of ordinary skill in the art from the following detailed description of one embodiment when taken in conjunction with the accompanying drawing, which is an elevational view, in vertical section and in diagrammatic form, showing the embodiment of the generator for plasma jet spectroscopic source according to the invention.

Referring to the drawing, the anode is a water-cooled copper anode 1 having formed therein an ejection nozzle 2 for the plasma jet. The upstream part of the nozzle 2 is formed as a hollow chamber within the anode 1, and a cathode 3 in the form of a rod with a tip 4 extends from the bottom of the anode into the said hollow chamber so as to confront the anode 1. During operation, an arc discharge is created with the tip 4 and a point 5 on the peripheral wall of the anode nozzle as foot points.

A gas inlet 6 is provided to deliver an inactive gas (a gas here defined as being chemically inactive and harmless, in a practical sense, with respect to the electrodes) into the lower part of the said hollow chamber, becoming a gas current 7 covering the cathode 3 and the inner wall of the nozzle 2, thereby protectively shielding the electrodes 1 and 3. The electrode 1 is cooled by water entering its jacket through an inlet 8 and leaving through an outlet 9.

An important feature of the instant generator is a side tube 10 for introducing samples into the plasma. For this purpose, the sample solution is first placed in an atomizer and atomized by an inactive gas, such as argon, and the mixture of inactive gas and the sample thus formed is injected into the anode nozzle through the side
The opening 11 of this side tube 10 is located at one part of the anode nozzle and is directed toward the high-temperature region at the innermost part of the high-temperature plasma generated by arc discharge, that is, directly at the arc foot at the tip 4 on the rod-shaped electrode 3. Accordingly, the sample is introduced in the most effective manner into the high-temperature plasma.

It is necessary to prevent the sample introduced in the above-described manner from contacting the arc feet, but in the case of the cathode foot at the tip 4, there is little possibility of this contact occurring. That is, the sample flowing out from the opening 11 of the side tube 10 is immediately swept away by the inactive gas current 7 and flows out toward the nozzle 2 above and, although it goes to a point in the close proximity of the arc foot at the tip 4 it does not reach this arc foot. Furthermore, the sample flowing out of the opening 11 is swept away by the plasma jet toward the nozzle 2 before the sample can reach the nozzle foot point 5 on the opposite side. Accordingly, there is little possibility of the sample contacting the anode foot 5.

The fundamental condition for the proper operation in this manner of the generator according to this invention is that the position of the sample must be constant on the side tube opening 11. If, as a supposition, the anode foot 5 should ever shift to a position near the side tube opening 11, the contacting of this anode foot by the sample substance cannot be avoided. However, in the generator according to this invention, the anode foot 5 is pressed by the gas flow flowing out from the opening 11 and is constantly blown against and fixed at the side opposite the opening 11.

In the above-described manner, the auxiliary gas flow containing the sample which is introduced through the side tube 10 fulfills the function of fixing the arc foot 5 and stabilizing the plasma jet as well as the function of introducing the sample substance to a point directly in front of the arc foot at the tip 4 which is the maximum temperature region of the plasma jet.

This auxiliary gas flow, operating in cooperation with the main gas flow 7, which shields the arc foot points 4 and 5, and, at the same time, supplies the ionized gas of the plasma jet, makes it possible to introduce the sample substance into the region of maximum temperature of the plasma flame without causing the said sample substance to contact either of the arc foot points 4 and 5. Thus, it will be apparent that this invention is a device of satisfying all of the aforementioned requirements.

For completely satisfactory operation of the present generator, the flow rates of the gas flows at the side tube opening 11 are extremely important, and when these flow rates are suitably regulated, highly stable operation is obtained.

In order to indicate still more fully the nature of the present invention, the following example of specific construction and operation is set forth, it being understood that this example is presented as illustrative only, and that it is not intended to limit the scope of the invention.

Example

A plasma jet generator with an anode nozzle of 5 mm. throat diameter, and a cathode of 7 mm. diameter was used. For the discharge gas, argon gas was supplied at a flow rate of 7 liters/min. through the inlet 6. As samples to be analyzed, dilute solutions of CaCl₂, MgCl₂, ZnSO₄, and CoSO₄, and other substances were prepared. In the samples, its solution thus prepared was atomized by a separate argon gas current and this argon gas current carrying the atomized sample solution was supplied at a flow rate of 2 liters/min. through the side tube 10.

It was found that, under these conditions, the introduction of the sample had no effect whatsoever on the stability of the operation of the plasma jet. Spectrograms taken of the light emitted by the plasma ejected from the anode nozzle 2 under the above-described conditions clearly show atomic lines of the introduced sample metals to be analyzed, that is, Mg, Ca, Zn, Co, and others. It was found, moreover, that the present generator produced excellent sensitivity in the case of such heavy metals as cobalt and zinc, the detection of which by flame photometry has heretofore been especially difficult.

A significant point which should be fully noted here is that, together with the emission lines of the introduced metal sample, the spectrum of hydrogen atoms produced by the dissociation of the water content of the sample solvent was observed, and each of these lines indicated a large broadening due to the Stark effect. The evidence indicates that the sample had penetrated deeply to the high-temperature region at the center of the plasma.

In addition, the plasma jet temperature was measured by a spectroscopic method and was found to be approximately 7,000 degrees Kelvin at the outlet of the anode nozzle when the arc current was 100 amperes. Furthermore, the spectrum of the anode material did not appear in the spectrograms clearly indicating that the sample was not eroding the high-temperature arc foot point. The anode foot was disassembled after a long period of operation, and the electrodes were examined, whereupon it was found that neither the cathode nor the anode exhibited any signs of erosion whatsoever.

Thus it will be seen that the present invention provides a plasma jet generator having a highly sensitive and stable operation.

Although this invention has been described with respect to a particular embodiment and example of application thereof, it is not to be so limited as changes and modifications can be made therein which are within the full intended scope of the invention, as defined by the appended claims.

What is claimed is:

1. A plasma jet generator comprising a hollow electrode having a nozzle portion, a rod-shaped electrode disposed around the central portion of the said hollow electrode and pointed toward the said nozzle portion, a first means for creating an arc discharge between the tip of the said rod-shaped electrode and the inner wall surface of the said hollow electrode, a second means for introducing a first inactive gas current into the space between the said two electrodes in the direction toward the said nozzle portion, a third means, pointed toward the said tip of the said rod-shaped electrode, for introducing a second gas current in a direction opposite to the said first inactive gas current such as to cause suppression of fluctuation of the path of the said arc discharge, thereby effecting the mixture of said first with said second gas current to the hottest point in the arc.

2. A plasma jet generator comprising, in combination, a hollow electrode substantially cylindrical at its bottom, tapering conically in the upward direction and ending in a nozzle; a rod-shaped electrode disposed within said hollow electrode having a tip which ends near the top of the conical taper in said hollow electrode; means for creating an arc discharge between said tip and the inner wall surface of said hollow electrode substantially at the point where taper and nozzle meet; an inlet for an inactive gas leading into the cylindrical part of said hollow electrode; a sample inlet leading from the top of said generator substantially the beginning of said nozzle and being connected thereto; said sample and inactive gas meeting from opposite directions above said arc discharge point of said generator, thus avoiding contact of said sample with the arc foot points; and cooling means for said generator.

3. In a plasma jet generator including a hollow electrode; a rod-shaped electrode disposed therein; means for creating an arc discharge between the tip of said rod-shaped electrode and the inner wall surface of said hollow electrode; an inactive gas inlet; a sample inlet; a nozzle in said hollow electrode; and cooling means for
said generator; the improvements which comprise said hollow electrode being substantially cylindrical at its bottom, tapering conically in the upward direction up to contact with said nozzle; the tip of said rod-shaped electrode being disposed near the top of the taper of said hollow electrode; said arc discharge having a foot point at the meeting of taper and nozzle in said hollow electrode; said inactive gas inlet heading into said cylindrical part; said sample inlet leading from the top of said generator to substantially the point at which said nozzle starts and being connected to said nozzle; said sample and said inactive gas meeting from opposite directions above said arc discharge thus avoiding contact of said sample with the arc foot points.

4. In a plasma jet generator including a hollow electrode substantially cylindrical at its bottom, tapering conically in upward direction and ending in a nozzle; a rod-shaped electrode disposed in said hollow electrode; means for creating an arc discharge between the tip of said rod-shaped electrode and the inner wall of said hollow electrode; an inactive gas inlet leading into said cylindrical part; a sample inlet; and cooling means for said generator; the improvements which comprise said arc discharge having a foot point substantially at the meeting point of nozzle and taper in said hollow electrode; said sample inlet leading from the top of the generator at an angle with the generator axis to substantially the point where said nozzle starts and being connected thereto; said sample and inactive gas meeting from opposite directions above said arc discharge at substantially the hottest point of said generator thus avoiding contact of said sample with the arc foot points.

5. A plasma jet generator comprising, in combination, a hollow electrode substantially cylindrical at its bottom, tapering conically in the upward direction and ending in a nozzle; a rod-shaped electrode disposed within said hollow electrode having a tip which ends near the top of the conical taper in said hollow electrode; means for creating an arc discharge between said tip and the inner wall surface of said hollow electrode substantially at the point where taper and nozzle meet; an inlet for an inactive gas leading into the cylindrical part of said hollow electrode; a sample inlet leading from the top of said generator at an angle with the generator axis to substantially the beginning of said nozzle and being connected thereto; said sample and inactive gas meeting from opposite directions above said arc discharge at the hottest point of said generator, thus avoiding contact of said sample with the arc foot points; and cooling means for said generator.

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