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ELECTRON DISCHARGE DEVICE FOR GENERATION OF SPECTRAL RADIATION HAVING AN AUXILIARY DISCHARGE OF LOW CURRENT

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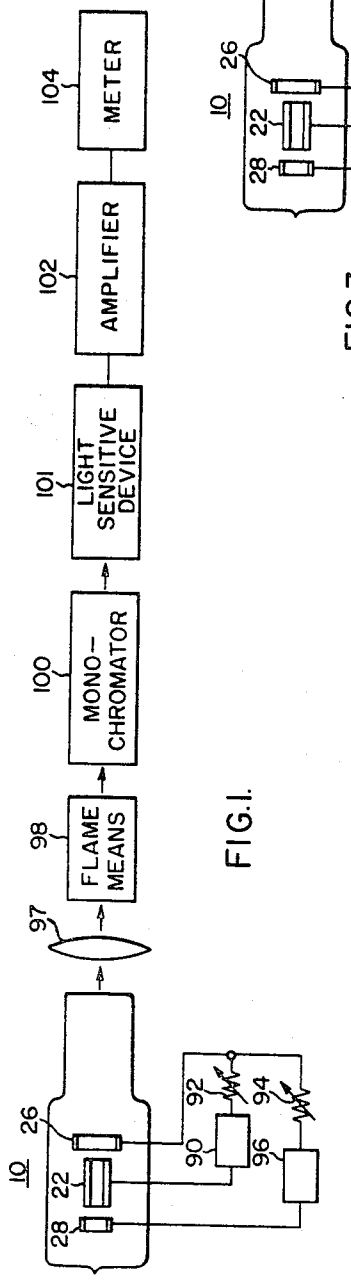


FIG. 1.

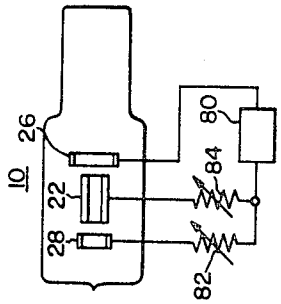


FIG. 3.

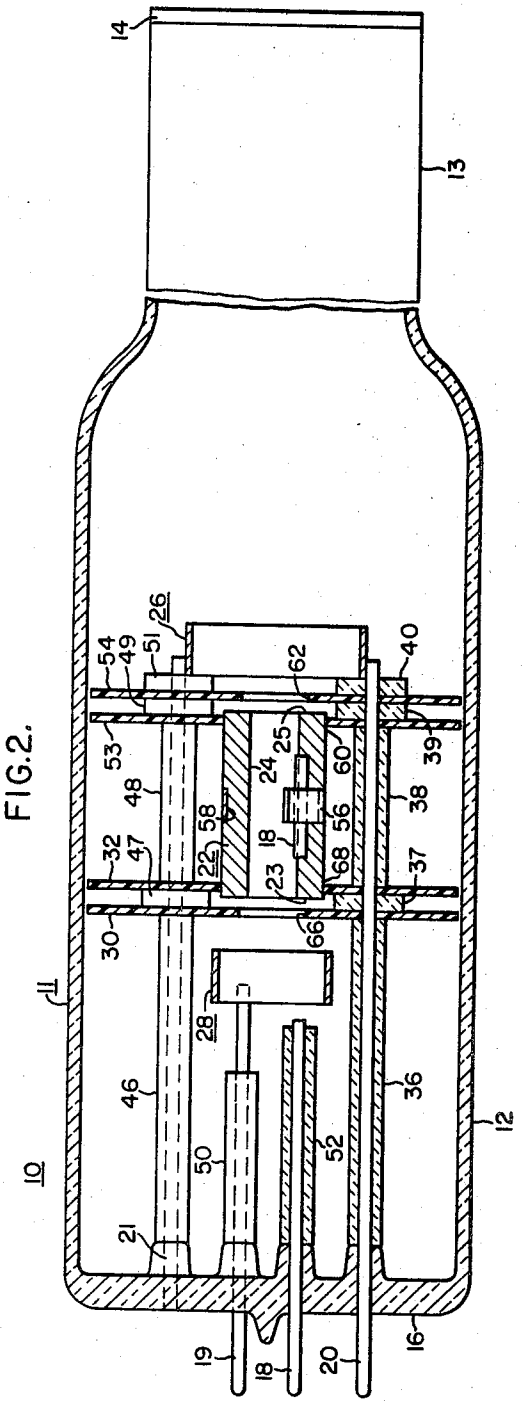


FIG. 2.

WITNESSES

Theodore F. Wrobel

James F. Young

INVENTOR

George K. Yamasaki

BY R. Lewis Gable

ATTORNEY

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ELECTRON DISCHARGE DEVICE FOR GENERATION OF SPECTRAL RADIATION HAVING AN AUXILIARY DISCHARGE OF LOW CURRENT

George K. Yamasaki, Horseheads, N.Y., assignor to Westinghouse Electric Corporation, Pittsburgh, Pa., a corporation of Pennsylvania

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This invention relates to atomic absorption spectrophotometry and more particularly to electron discharge devices of the hollow-cathode type which are adapted for emitting beams of radiation having sharp spectral lines.

Generally, the constituents of an unknown chemical sample may be discovered by introducing a solution of the unknown sample in the form of a mist into a suitable flame to cause the solution to vaporize. Next, radiation having known spectral lines is directed through the sample of vapor with result that certain spectral lines of the beam of radiation will be absorbed by the atomic vapor. Then, the radiation can be analyzed to find out which spectral lines have been absorbed and the degree to which these lines have been absorbed by the sample vapor to determine the constituents and the concentration of the constituents in the unknown sample.

Typically, beams of radiation with narrow spectral lines are provided by electron discharge devices of the hollow-cathode type. In such devices, the cathode element is usually shaped in the form of a hollow cylinder enclosed at one end. Illustratively, an anode element of an annular, wire or plate configuration may be disposed in the vicinity of the cathode element in a position so as not to prevent the radiation emitted from the hollow portion of the cathode element from being directed to the outside of the electron discharge device. It is noted that the cathode element is generally made of the metal whose spectrum it is required to produce.

In operation, a source of potential is applied between the anode and cathode elements to cause a discharge of electrons therebetween. The discharge of electrons ionizes the gas contained within the envelope of this device. The positive gas ions are attracted to and strike the cathode element. As a result of this gas ion bombardment, atomic particles of the metal of which the cathode element is made are sputtered therefrom into the region of the hollow portion of the cathode element. These sputtered atomic particles are in turn ionized by means of electrons, excited gas atoms, and ion collisions in the electrical discharge between the cathode and anode elements. Due to these collisions, some of the electrons associated with the sputtered atoms absorb energy and are excited from a ground state to a higher energy level. When the excited electrons return to their ground state, some of the energy absorbed by collision is released in the form of radiation having spectral line(s) determined by the material of which the cathode element is made. One of the principal factors which determines the intensity of the spectral radiation emitted from a typical electron discharge device of the hollow-cathode type is the level of the current discharge between the anode and cathode elements. As the electrical discharge current is increased between the cathode and anode elements, a point is reached at which heating effects or excessive sputtering will substantially deform or destroy the cathode element. Thus, it may be seen that if the discharge current between the anode and cathode element is limited, the production of the sputtered ion particles and, therefore, the emission of spectral radiation therefrom is also limited.

Further, it has been suggested in the prior art that an additional auxiliary electrode may be disposed in the vicinity of the hollow portion of the cathode element to

provide a second discharge of electrons to bombard and to excite the particles sputtered from the cathode element. More specifically, such an electron discharge device includes a cathode element having a hollow portion enclosed at one end, and an anode element for establishing electron discharge therebetween. In addition, at least one auxiliary electrode adapted for the emission of electrons is disposed in the vicinity of the hollow portion of the cathode element to emit a stream of electrons across the hollow portion to a fourth electrode acting as the anode element for the auxiliary electrode. The auxiliary electrode takes the form of a heater element having a layer of electron emissive material disposed thereon in order to emit sufficient electrons to achieve the desired enhancement of the emission of spectral radiation. Further, the fourth electrode may be similar in form to the auxiliary electrode and may replace the auxiliary electrode as the emitter of electrons if the auxiliary electrode ceases to operate efficiently. In such a case, the deteriorated auxiliary electrode would then act as the anode element for the fourth electrode.

In operation, atomic particles from the cathode element are sputtered by the electron discharge between the cathode element and the anode element, and a partial excitation of the sputtered ionized particles is caused by the principal discharge between the cathode and anode elements. Further excitation of the atomic particles of the cathode element takes place due to the auxiliary discharge between the auxiliary element and the fourth electrode. More specifically, the auxiliary discharge between the auxiliary electrode and the fourth electrode serves to further excite the electrons associated with the sputtered atomic particles and therefore to increase the intensity of the spectral radiation emitted from the hollow portion of the cathode element.

Though increased intensities of spectral radiation have been achieved with the above-described electron discharge device, there are several significant problems associated with this device. First, this device utilizes four electrodes, i.e. a cathode element and an anode element for establishing the primary discharge, and at least one auxiliary electrode for emitting electrons and a fourth electrode acting as the anode element for the auxiliary discharge. Further, such a device requires the use of extensive shields which take the form of tubular members which are disposed about the auxiliary electrode and the fourth electrode for confining the auxiliary discharge between the auxiliary electrode and the fourth electrode to a region in the vicinity of the hollow portion of the cathode element. If these shields were deleted, the resultant device would be inefficient. It may be well understood that the use of four electrodes and the necessary shielding for the auxiliary electrode results in an electron discharge structure which is expensive to manufacture. In addition, it is desired that the current discharge between the cathode element and the anode element and the auxiliary discharge between the auxiliary electrode and the fourth electrode be isolated; as a result, a second source of power may be required to provide the potential for the auxiliary discharge, which of course adds to the expense of operating this electron discharge device.

Therefore, it is an object of this invention to provide a new and improved source of spectral radiation which overcomes the limitations of the prior art.

It is a further object of this invention to provide a new and improved electron discharge device of the hollow-cathode variety capable of emitting radiation of a defined narrow line(s) without the presence of or having reduced intensity of undesired ion lines of the cathode element.

It is a more particular object of this invention to provide a new and improved electron discharge device of the

hollow-cathode variety which is capable of providing intensified spectral radiation with a minimum of electrodes and with a simple, inexpensive construction.

It is another object of this invention to provide a new and improved electron discharge device of hollow-cathode variety capable of emitting an intensified spectral radiation with an auxiliary discharge of low current.

It is a still further object of this invention to provide a new and improved electron discharge device of the hollow-cathode variety capable of emitting spectral radiation of increased intensity by the use of an auxiliary discharge in the region of the hollow portion of the cathode element which requires no additional power sources.

These and other objects are accomplished in accordance with the teachings of the present invention by providing a new and improved electron discharge device including a cathode element having an aperture therethrough and an anode element for establishing a primary discharge therebetween whereby atomic particles are sputtered from the cathode element. More specifically, an auxiliary electrode is disposed to emit an auxiliary discharge through the aperture of the cathode element to the anode element to thereby implement the excitation of the sputtered atomic particles and to thereby increase the intensity of spectral emission from the cathode element. In order to increase the efficiency of the electron discharge device of this invention, suitable shielding means are disposed so as to confine the principal discharge between the aperture of the cathode element and the anode element and further shielding means are disposed to confine the auxiliary discharge between the auxiliary electrode and the anode element to a path through the aperture of the cathode element.

These and other objects and advantages of the present invention will become apparent when considered in view of the following detailed description and drawings, in which:

FIGURE 1 is a diagrammatic view of a system for performing atomic absorption measurements;

FIG. 2 shows a side view, partially broken away and partially in section, of an electron discharge device embodying the present invention; and

FIG. 3 is a diagrammatic view of a further system for supplying appropriate potentials to the electrodes of the device as shown in FIG. 2.

Referring now to the drawings and particularly to FIG. 1, there is generally shown a system for performing atomic absorption measurement including an electron discharge device **10** of the hollow-cathode variety for providing a beam of radiation having a characteristic spectral line(s). The beam of radiation emitted by the electron discharge device **10** is focused by a suitable optical assembly **97** through a means **98** for evaporating a solution of the unknown vapor into a monochromator **100**. As explained above, certain spectral lines are absorbed by the vapor of the unknown sample from the beam of radiation as it passes through the flame means **98**. By adjusting the monochromator **100** to the wavelength of the spectral lines which are to be absorbed by the sample vapor, a beam of radiation of a narrow bandwidth about the wavelength to be absorbed can be obtained through an opening within the monochromator **100**. The resultant beam of radiation is directed onto a radiation-sensitive device **101** which provides an output signal which is amplified and applied by an amplifier **102** to a meter **104** which in turn provides an indication of the intensity of the radiation directed through the opening of the monochromator **100**. It is contemplated that the degree of absorption may be measured by comparing the indication displayed by the meter **104** when an unknown sample is introduced into the flame **98** and when no sample is introduced into the flame means **98**.

Referring now to FIG. 2, there is shown an illustrative embodiment of the electron discharge device **10** which may be incorporated into the system shown in FIG. 1 to provide an intensified beam of spectral radiation. The electron discharge device **10** includes an envelope **11** made of a suitable insulating material such as glass and having an enlarged portion **12** at one end thereof and a narrowed portion **13** at the other end which is enclosed by a window **14** made of a suitable material transmissive to the radiation produced by this device. The enlarged tubular portion **12** of the envelope **11** is enclosed by a stemheader **16**. The envelope **11** is filled with a suitable gas such as argon or neon at a reduced pressure of approximately 1.0 to 50.0 mm. of mercury. There is disposed within the envelope **11** a cathode (or first) element **22** which is electrically connected to and supported by a strap **56** which is disposed about the cathode element **22** in a recess **58** therein. Further, the strap **56** is connected as by spot welding to a terminal rod **18** which extends through and is supported by the stemheader **16**. The terminal rod **18** is made of an electrically conductive material such as nickel for providing an electrical connection to the cathode element **22** as well as for supporting the cathode element **22** within the envelope **11**. The cathode element **22** is substantially cylindrical in shape and has a central bore or hollow portion **24** extending therethrough from an upper edge **25** to a lower edge **23**.

An anode (or second) element **26**, which is illustratively shown as a ring-shaped member, is disposed within the envelope **11** so as to be substantially concentric with respect to the cathode element **22** and at a point spaced from the upper edge **25** of the cathode element **22**. The anode element **26** may be made of a suitable electrically conductive material such as tantalum, which when operated in reverse mode may serve as a getter for the electron discharge device **10**. The anode element **26** is supported within the envelope by an electrically conductive terminal rod **20** which is secured at one end to the anode element **26** as by spot welding and has the other end extending through and supported by the stemheader **16**. The anode element **26** is further supported as by a rod **21** having one end secured to the anode element **26** as by spot welding and having the other end supported by the stemheader **16**.

In accordance with the teachings of the present invention, an auxiliary or booster electrode **28** is disposed within the enlarged portion **12** of the envelope **11** to establish with the anode element **26** an auxiliary discharge therebetween through the bore **24** of the cathode element **22**. The auxiliary electrode **28** is supported within the envelope **11** by a terminal rod **19** having one end thereof connected to the auxiliary electrode **28** as by spot welding and having the other end extending through and supported by the stemheader **16**. Though both the anode element **26** and the auxiliary electrode **28** could be of the configuration of a plate or a bar, in a structurally preferred embodiment, the anode element **26** and the auxiliary electrode **28** are of an annular or ring configuration. In the illustrative embodiment as shown in FIG. 2, the annular-shaped electrodes **28**, **22** and **26** are disposed concentrically about the axis of the envelope **11** to ensure the substantial symmetry of the electrodes of this device.

In order to provide the desired electrical discharges, a potential source **90** (as shown in FIG. 1) is connected in series with a variable resistive impedance **92** between the cathode element **22** and the anode element **26**. Further, a potential source **96** may be connected in series with a variable resistive impedance **94** between the auxiliary electrode **28** and the anode **26** to establish therebetween an auxiliary discharge. It is noted that the electrical discharges between the cathode element **22** and the anode element **26**, and between the auxiliary electrode **28** and the anode element **26** may be respectively varied by adjusting the resistive impedances **92** and **94**.

In operation, a primary electrical discharge is caused between the cathode element **22** and the anode element **26** to sputter atomic particles of the material of which the cathode element **22** is made. The particles sputtered from the cathode element **22** are excited by electrons, excited

gas atoms, and ion collisions in the electrical discharge between the cathode element **22** and the anode element **26**. As a result of the collisions, the electrons associated with the sputtered atomic particles are excited to a higher level of energy. When the electrons associated with the excited ions return to their ground state, the energy absorbed due to the collisions is released in the form of spectral radiation which is characteristic of the material of which the cathode element **22** is made. As explained above, the degree of excitation by the primary electrical discharge between the cathode element **22** and the anode element **26** is limited by the current flow through the cathode element **22**. At a certain point, the current of the primary discharge may be increased to an extent where the cathode element **22** will be heated to extreme temperatures, or will be excessively sputtered, and therefore may be deformed or destroyed. Thus, in order to enhance the excitation of the positive ions sputtered from the cathode element **22**, an auxiliary discharge is established between the auxiliary electrode **28** and the anode element **26**. It is particularly noted that the auxiliary discharge does not increase the current flowing through the cathode element **22** but rather acts to further increase the excitation of the sputtered atoms of the cathode elemen and to thereby increase the intensity of the spectral radiation. Illustratively, a potential difference in the approximate range of 100 to 400 volts may be maintained between the cathode element **22** and the anode element **26**, whereas a potential difference in the approximate range of 100 to 500 volts may be maintained between the auxiliary electrode **28** and the anode element **26**. It is believed that a more efficient operation may be achieved by disposing the auxiliary electrode at a negative potential with respect to the anode element. It appears that if the auxiliary electrode is maintained at a positive potential with respect to the anode element that an undesired discharge may be established between the auxiliary and cathode elements.

Tests were conducted to compare the intensities of radiation from devices incorporating an auxiliary discharge in accordance with the teachings of this invention and from devices without an auxiliary discharge. In these tests, the current supplied to all of the cathode elements was maintained at approximately 15 ma. It was found that the relative intensities of beams of radiation derived from devices having cathode elements of Zn–Cu, Cu and Ni and to which approximately 50 ma. was supplied to auxiliary electrodes were increased respectively 40, 3 and 4 times as compared with devices having identical cathode elements and without an auxiliary discharge.

Though the electrodes **26** and **22** have been described respectively as an anode element and as a cathode element, it is noted that the potential source **90** may be a source of alternating current or pulsed current. In such an embodiment, the cathode element would be the principal source of electrons and a radiation output would occur when the anode element is disposed at a positive voltage with respect to the cathode element. In addition, the potential source **96** could in certain embodiments be a source of alternating current or pulsed current so that either of the electrodes **28** or **26** would alternately act as the source of electrons, depending upon the instantaneous polarity of the source **96**.

Various sources of distortion may be found in the system as described with respect to FIG. 1. More specifically, a noise may be introduced in this system due to the radiation emitted by the flame of the means **98** for vaporizing the sample to be analyzed. The flame of the means **98** provides radiation which is sensed by the light sensitive device **101**. The monochromator **100** and amplifier **102** may not be able to filter out the radiation from the flame and as a result an error may be introduced into the reading from the meter **104**. This extraneous error (or noise) may be eliminated by operating the amplifier **102** as an A.C. device which will amplify only the alternating or pulsed spectral output of the electron discharge device **10** so that the meter **104** monitors only the radiation generated within the cathode element **22** and not the random radiation of the flame means **98**.

Another advantage of the use of an auxiliary electrode is the improved spectrum obtained from such an electron discharge device. It may be understood that the radiation emitted from the cathode element of such an electron discharge device includes a plurality of lines, all of which are not desired. More specifically, it is normally desirable to emphasize those lines known as ground state lines which result from excited atoms and to de-emphasize those lines which result from ionized atoms of the cathode element. It has been found that the use of an auxiliary discharge and, more specifically, the use of an auxiliary discharge as passing through the bore or aperture of the cathode element **22** does in fact reduce the intensity of the aforementioned spectral ion lines, whereas the intensity of the ground state lines is greatly intensified.

In order to improve the efficiency of the electron discharge device, the primary discharge between the cathode element **22** and the anode element **26** should be confined to the bore **24** of the cathode element and, further, the auxiliary discharge between the auxiliary electrode **28** and the anode element **26** should be confined to a path through the bore **24** of the cathode element **22**. It may be understood that if either the auxiliary or primary discharges are allowed to be dissipated as by striking the peripheral portions of the cathode element **22** or the various support or terminal rods, that the intensity of the auxiliary and primary discharges may be dissipated, and therefore the intensity of the spectral emission will be reduced. In particular, the primary discharge between the anode element **26** and the cathode element **22** is limited to the bore **24** by the use of discs or insulating members **53** and **54** which are made of a suitable insulating material such as mica. As shown in FIG. 2, the insulating disc **53** has an aperture **60** therein through which the cathode element **22** extends in a close fit. Further, the insulating disc **53** extends from the periphery of the cathode element **22** to the interior of the envelope **11**. The second insulating disc **54** is disposed in a parallel, spaced relation with the insulating disc **53** to confine the primary discharge to the bore **24** of the cathode element **22**. The insulating disc **54** has an aperture **62** of a diameter slightly larger than that of the bore **24** and is disposed so as to abut or to be closely spaced from the upper edge **25** of the cathode element **22**.

Further, the auxiliary discharge through the bore **24** of the cathode element **22** is confined by the use of a pair of insulating discs or members **30** and **32**. More specifically, the insulating disc **32** has an aperture **68** therein through which the cathode element **22** is disposed in a tight fitting relation. The insulating disc **30** is disposed in a parallel, spaced relation from the insulating disc **32** so as to abut or to be closely spaced from the lower edge **23** of the cathode element **22**. Further, the insulating disc **30** has an aperture **66** therein of slightly greater diameter than the bore **24** to thereby prevent the electrical discharge from the auxiliary electrode **28** from striking substantial portions of the edge **23** of the cathode element **22**. It may be understood that the primary discharge between the cathode element **22** and anode element **26** is prevented by the insulating discs **30** and **32** from being directed through the bore **24** to the exterior portions of the cathode element **22**. In a similar manner, the auxiliary discharge between the auxiliary electrode **28** and the anode element **26** is prevented by the insulating discs **53** and **54** from being directed to the exterior portion of the cathode element **22**.

In order to substantially isolate the various elements from each other, it is also desirable to place suitable insulating members about the terminals associated with the various electrodes. More specifically, an insulating

sleeve 36 made of a suitable insulating material such as aluminum oxide is disposed about the terminal rod 20 and extends between the stemheader 16 and the insulating disc 30. A ring 37 of a suitable insulating material is disposed about the terminal rod 20 between the insulating discs 30 and 32. Further, an insulating sleeve 38 is disposed about the terminal rod 20 and extends between the insulating disc 32 and the insulating disc 53. A pair of insulating rings 39 and 40 are disposed about the terminal rod 20, respectively, between the insulating discs 53 and 54, and between the insulating discs 54 and the anode element 26. The insulating discs and rings associated with the terminal rod 20 are held axially in place by the anode element 26 which is secured to one end of the terminal rod 20 to abut against the insulating ring 40. In a similar manner, the support rod 21 which is connected to the anode element 26 is isolated from the other electrodes of this device by an insulating sleeve 46 which is disposed about the support rod 21 and extends between the stemheader 16 and the insulating disc 30. Further, an insulating ring 47 is disposed about the terminal rod 21 between the insulating discs 30 and 32. An insulating sleeve 48 is disposed about the terminal rod 21 and extends between the insulating disc 32 and insulating disc 53. Further, a pair of insulating rings 49 and 51 are disposed about the support rod 21, respectively, between the insulating discs 53 and 54 and between the insulating disc 54 and the anode element 26. It may be understood that the anode element 26 serves to axially position the insulating rings and sleeves disposed about the support rod 21 and is secured to the support rod 21 so as to abut the insulating ring 51.

Further, the terminal rod 18 associated with the cathode element 22 is isolated from the auxiliary electrode 28 by an insulating sleeve 52 which is disposed about the terminal rod 18 and extends between the stemheader 16 and the insulating disc 30. In addition, an insulating sleeve 50 may be disposed about a portion of the terminal rod 19 between the stemheader 16 and the auxiliary electrode 28. Thus, as shown in FIG. 2, the electron discharge device of this invention utilizes a shielding structure and an electrode structure which is significantly less complex and less expensive to manufacture than that required by the prior art. More specifically, the number of electrodes is minimized and would not normally require the presence of a fourth electrode. Further, the complicated insulating shielding of the prior art is replaced by the use of easily manufactured insulating discs and sleeves.

Referring now to FIG. 3, there is shown a significant advantage resulting from the construction of the electron discharge device of this invention. In particular, the potentials required to establish the auxiliary and principal discharges may be supplied by a single potential source 80 which is connected illustratively in series with a variable resistive impedance 84 between the cathode element 22 and the anode element 26. Further, a variable resistive impedance 82 is connected between the cathode element 22 and the auxiliary electrode 28. A significant advantage of this invention resides in lowered levels of current required by the auxiliary discharge between the auxiliary electrode 28 and the anode element 26. More specifically, experimental measurements that have been made upon the device of this invention have shown that only approximately 10 to 100 milliamps of current is required for the auxiliary discharge between the auxiliary electrode 28 and the anode element 26 of this invention, whereas approximately 200 to 400 milliamps has been reported and is believed to be required for the auxiliary discharge of the devict of the prior art described above. Since the magnitude of the auxiliary discharge and the principal discharge of the device of this invention are approximately equal, a single potential source may be used to establish both of these discharges. In contrast, the normal practice employed where the auxiliary and primary discharges are of substantially different magnitudes may require the use of two potential sources. Further, where the auxiliary discharge is of the lower level as described above, it is no longer necessary to use a thermionic cathode in order to supply the high levels of current for the auxiliary discharge. These advantages are believed to be due to the very simple configuration of the electrodes and shielding means suggested by this invention wherein the path of the auxiliary discharge is rather simple, i.e. directly between the auxiliary electrode 28 and the anode element 26 through the aperture of the cathode element 22.

Since numerous changes may be made in the above-described apparatus and different embodiments of the invention may be made without departing from the spirit thereof, it is intended that all matter contained in the foregoing description and shown in the accompanying drawings shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. A spectral radiation source comprising first and second electrodes for establishing a first electrical discharge therebetween, said first electrode having an aperture therethrough and including a material for providing a beam of characteristic spectral radiation, and an auxiliary electrode for establishing a second electrical discharge between said auxiliary electrode and said second electrode through said aperture of said first electrode to thereby intensify said beam of characteristic spectral radiation.

2. A spectral radiation source as claimed in claim 1, wherein said first electrode is disposed about an axis of said source, said second and said auxiliary electrodes being of an annular configuration and disposed at either end of said first electrode concentrically about said axis.

3. A spectral radiation source as claimed in claim 1, wherein there is provided shielding means for confining said first electrical discharge to a path between said second electrode and said aperture of said first electrode and for confining said second electrical discharge to a path between said auxiliary electrode and said second electrode through said aperture of said first electrode.

4. A spectral radiation source as claimed in claim 3, wherein said first, second and auxiliary electrodes are disposed within an envelope, said first electrode having first and second edges with said aperture disposed therebetween, said means for confining including at least first and second insulating members having openings therein, said first insulating members disposed between said first electrode and said second electrode in proximity to said first edge, said opening of said first member disposed concentrically about said aperture of said first electrode, said first member extending to the interior periphery of said envelope, said second insulating member disposed between said first electrode and said auxiliary electrode in proximity to said second edge of said first electrode, said opening of said second insulating member disposed concentrically about said aperture of said first electrode, said second insulating member extending to the interior periphery of said envelope.

5. A spectral radiation source as claimed in claim 4, wherein there is included electrical terminals connected to said first, second and auxiliary electrodes and extending through said envelope, said means for confining further including insulating sleeves disposed about said terminals to thereby isolate said terminals from each other and from the first, second and auxiliary electrodes.

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JAMES W. LAWRENCE, *Primary Examiner.*

R. JUDD, *Assistant Examiner.*