Feb. 16, 1971 J. D. JOHNSON 3,563,655

ELECTRON DISCHARGE DEVICE INCLUDING HOLLOW CATHODE ELEMENT FOR COMBINED EMISSION OF SPECTRAL RADIATION AND RESONANCE DETECTION

Filed Jan. 10, 1968 2 Sheets-Sheet 1

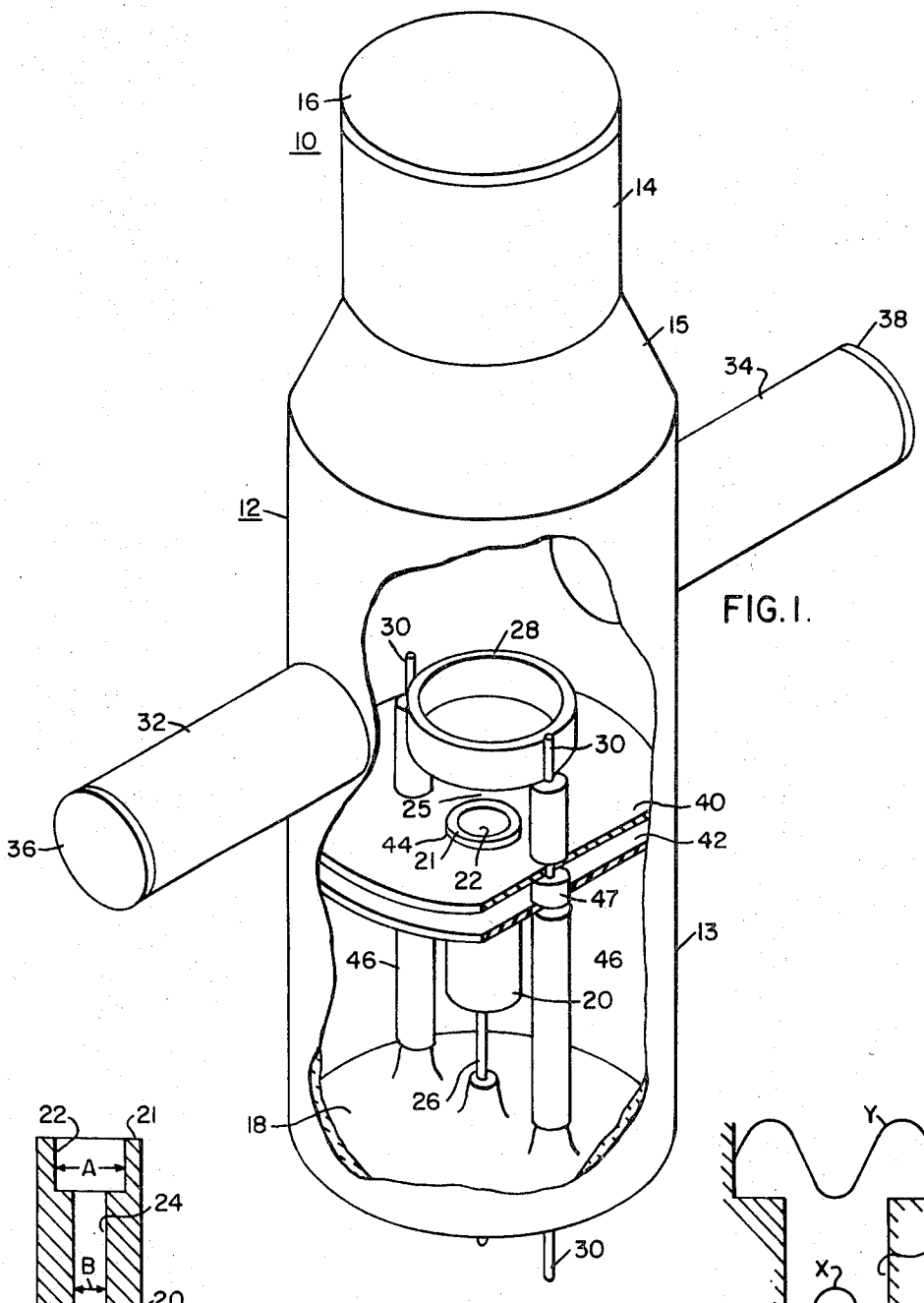


FIG. 1.

FIG. 2.

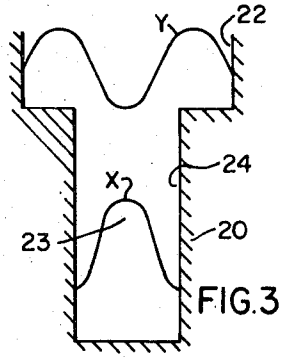


FIG. 3.

WITNESSES:

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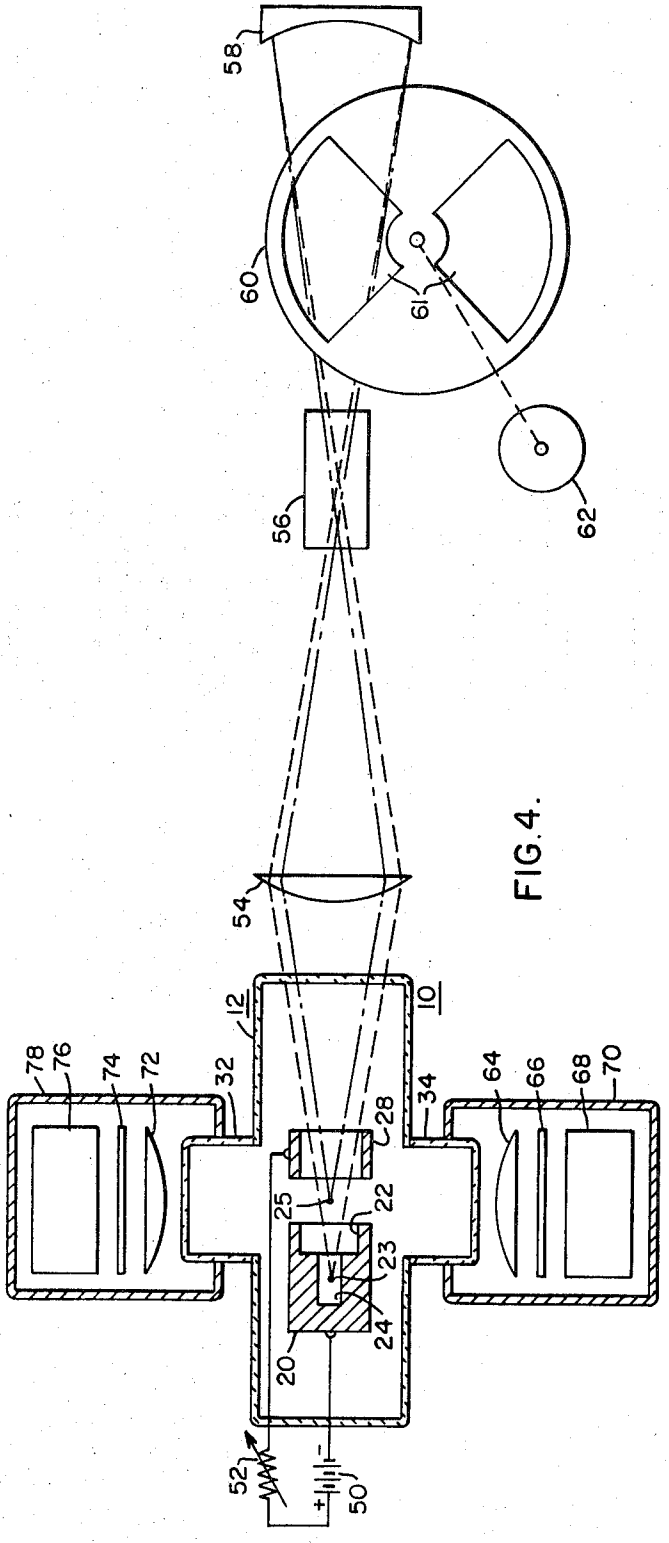


FIG. 4.

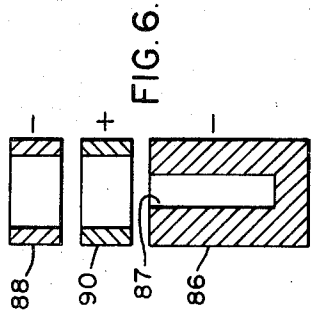


FIG. 6.

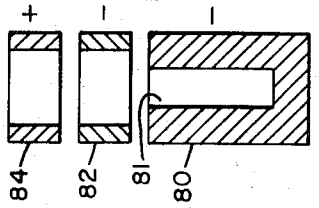


FIG. 5.

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3,563,655

ELECTRON DISCHARGE DEVICE INCLUDING HOLLOW CATHODE ELEMENT FOR COMBINED EMISSION OF SPECTRAL RADIATION AND RESONANCE DETECTION

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Int. Cl. G01j 3/42
U.S. Cl. 356—85 3 Claims

ABSTRACT OF THE DISCLOSURE

This invention relates to a spectral radiation system including an electron discharge device having an anode element and a cathode element for emitting a beam of spectral radiation, a suitable lens for focusing the spectral radiation through a suitable device such as a burner for disassociating the atoms of the sample material to be analyzed into ground state atoms, and a suitable reflecting device for redirecting the interrupted beam of spectral radiation back through the burner and the lens to be focused onto a region in front of the hollow portion of the cathode element. The region in front of the hollow portion is filled with ground state atoms which tend to fluoresce and yield resonance radiation which is sensed by a suitable radiation sensitive device.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to atomic absorption spectroscopy and more particularly to systems including electrons discharge devices of the hollow cathode type which are adapted for emitting spectral radiation having defined spectral line(s) and for resonance detecting beams of radiation.

Description of the prior art

Generally, the constituents of an unknown chemical sample may be detected by introducing a dispersed solution of the unknown sample into a suitable flame or other means to cause the solution to disassociate the sample into its atomic constituents. Radiation having a known spectral characteristic is directed through the vapor of the sample with the result that certain spectral lines of the beam of radiation will be absorbed by the sample material. The radiation can then be analyzed to discover which spectral lines have been absorbed and the degree to which these lines have been absorbed by the sample to determine respectively the constituents and the concentration of these constituents in the unkown sample.

Radiation with specific spectral lines may be 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 having one end thereof enclosed. An anode element illustratively taking the form of a ring or a plate may be disposed to establish an electron discharge between the anode and cathode elements. The conductive cathode element is made of a metal(s) or material containing metal(s), whose spectral lines are to be measured. In operation, a potential is applied between the anode and cathode elements to cause a flow of electrons therebetween. The anode and cathode elements are disposed within an envelope which is sealed at a suitable pressure with a gas which may be positively ionized by the electron discharge. Some of the gas atoms, ionized by the flow of electrons, are attracted to and strike the hollow portion of the cathode element to thereby sputter

atomic particles of the cathode material. The sputtered atomic particles are bombarded by electrons and positive gas ions. Due to the bombardment some of the sputtered atoms are excited from a ground state to a higher energy level. When the sputtered atoms return to their ground state or from a higher energy level to a lower energy level, the energy originally absorbed from the bombarding particles is released in the form of radiation having a spectral line(s) determined by the difference in the energy levels of the atom.

In the process of determining the presence and/or the concentration of the elements in the unknown sample, a beam of radiation having known spectral lines is directed through a vaporized sample of the solution to be analyzed. If the wavelength of the radiation corresponds to that required to excite the vaporized atoms a portion of the intensity of the radiation of that wavelength will be absorbed by the atoms of the vaporized solution thereby indicating the presence and concentration of that element in the sample solution. On the other hand, if the radiation is of a wavelength differing from that required to excite the atoms of the vaporized material, the radiation will not be significantly absorbed thereby indicating that a certain element is not present above the limit of detection in the vaporized solution.

Following absorption, the beam of radiation is directed into a device known in the art as a monochrometer which acts as a filter to isolate radiation of a specific wavelength emitted by the hollow cathode device. It may be understood that there are many other wavelengths of radiation that may be contained in the beam to be analyzed. For example, the flame required to vaporize the solution produces an undesired radiation, and the hollow cathode device, itself, may produce radiation of a wavelength other than that of particular interest. By adjusting the monochrometer to the wavelength which is to be absorbed by the sample vapor, radiation of a narrow bandwidth about the wavelength to be absorbed can be obtained and directed onto a suitable device for measuring the intensity of the spectral radiation. The degree of absorption may be measured by comparing the intensity of the beam of radiation when unknown samples are introduced into the burner and when no sample is introduced.

Recently, a second process of analyzing the radiation directed through the vaporized sample has been used in place of the monochrometer described above. These devices typically known as resonance detectors are based upon the phenomena of resonance radiation. Specially designed hollow cathodes or low pressure thermal emitters are operated to generate a field of ground state atoms of the desired element. The radiation to be analyzed is directed into the field of ground state atoms. If the radiation is of a wavelength corresponding to the energy state of the ground state atoms in the detector, these atoms will be excited to emit resonance radiation. This phenomena is also known as atomic fluorescence. If the radiation to be analyzed has wavelengths not corresponding to the quantum of energy required to excite the ground state atoms to fluoresce, no atomic fluorescence or resonance radiation will be produced. Suitable radiation detectors such as photocells are used to sense the resonance radiation to thereby determine the relative intensity of the resonance radiation. A resonance detector acts as a means for isolating radiation of a specific wavelength(s) emitted by the hollow cathode device. Typically a mechanical interrupter or chopper is positioned in the beam of radiation to be analyzed to discriminate between resonance radiation and general scattered and incandescence radiation. However, the resonance detectors of the prior art have utilized a separate device for producing the ground state atoms and have required addi-

tional power supplies for exciting and disassociating the atoms.

It is therefore an object of the present invention to provide a new and improved spectral device having the dual function of emitting a beam of spectral radiation and also serving as a resonance detector to measure the effect of atomc absorption.

SUMMARY OF THE INVENTION

These and other objects are accomplished in accordance with the teachings of the present invention by providing a new and improved spectral system including a hollow cathode device containing within a single envelope an anode and a dual function cathode for emitting a beam of spectral radiation of a defined line(s) and for providing a cloud of ground states atoms, a suitable device such as a burner for disassociating the sample to be analyzed, a suitable reflecting means, and a suitable optical assembly for interrupting and directing the beam of spectral radiation through the excited atoms of the sample material onto the reflecting means. Further, a suitable radiation detector such as a photocell is provided to detect the resonant radiation caused by the interrupted and reflected radiation exciting the ground state atoms of the element of interest.

DESCRIPTION OF THE DRAWINGS

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

FIG. 1 is a perspective view, partially broken away and partially in section, of the electron discharge device embodying the present invention;

FIG. 2 is a sectioned view of an illustrative embodiment of the cathode element incorporated in the device of FIG. 1;

FIG. 3 is a graphical representation of the population state of excited atoms as provided by various portions of the cathode element of FIG. 2;

FIG. 4 is a diagramamtic view of a system for performing atomic absorption measurement including the dual functioning device of FIG. 1; and

FIGS. 5 and 6 are sectioned views of other electrode arrangements which may be incorporated into the device of FIG. 1.

DESCRIPTION OF THE PREFERRED EMBODIMENT

Referring now to the drawings and in particular to FIG. 1, there is shown an illustrative embodiment of an electron discharge device **10** in accordance with the teachings of the present invention. The electron discharge device **10** includes an envelope **12** made of a suitable insulating material such as glass, and having an enlarged tubular portion **13** and a smaller tubular portion **14**, which portions are interconnected by a transition portion **15**. The tubular portion **14** is sealed off at one end by a window **16** which is made of a suitable material efficiently transmissive to radiation of the wavelength(s) produced by this device. The enlarged portion **13** is sealed off by a stem header **18** having a tipped off exhaust tube (not shown) in a manner well known in the art.

There is disposed within the portion **13** a conducting cathode element **20** which is made of or contains a selective material(s) which yields the wavelength(s) of interest emitted from the electron discharge device **10**. For example if it is desired to emit spectral lines corresponding to a material such as nickel, the cathode element **22** will be made of nickel or a material containing nickel. On the other hand, the cathode element may be made of an alloy of several materials such as brass; an electron discharge device including an alloyed cathode element has been further described in U.S. Pat. No. 3,183,393 entitled Discharge Device by James E. Paterson and assigned to the

assignee of the present invention. As shown in FIGS. 1 and 2, the cathode element **22** may illustratively be of a cylindrical configuration, having an opening extending from an edge **21** of the cathode element **20** facing toward the window **16** into the cathode element **20**. In one illustrative embodiment of this invention as shown in FIG. 2, the cathode element **20** has a first hollow portion **22** receding from the surface **21** into the element **20**, and a second hollow portion **24** disposed remotely from the edge **21**. Illustratively, the opening or hollow portion **22** may be of a cylindrical configuration disposed concentrically about the axis of the element **20** and having a diameter A, and the hollow portion **24** may be of a cylindrical configuration disposed concentrically about the axis of the element **20** and having a diameter B less than the diaameter A. In one illustrative embodiment, the diameter A was set at $\frac{3}{16}$ inch and the diameter B set at $\frac{3}{32}$ inch. Illustratively, the cathode element **20** is supported by a lead **26** made of a suitable electrically conductive material such as nickel. One end of the lead **26** may be affixed to the cathode element **20** and the other end may extend through the stem header **18** to the exterior of the envelope **12**. The lead **26** not only serves to support the cathode element **20** in optical alignment within the envelope portion **13**, but also serves to provide an electrical connection thereto.

An anode element **28**, which is illustratively shown to be of an annular configuration, is spaced from the upper edge **21** of the cathode element **20** to provide a fluorescing region **25** therebetween. The anode element **20** is made of suitably electrically conductive material such as tantalum, nickel or tungsten and is supported, in an illustrative embodiment, within the envelope **12** by means of two insulated support rods **30**. At least one of the support rods **30** is made of an electrically conductive material, for example, the same material as that of the cathode lead **26**. One end of the support rods **30** is secured to the anode element **28** as by welding and the other end extends through the stem header **18** to the exterior of the envelope **12** to thereby provide means by which a potential may be applied to the anode element **28**.

As shown in FIG. 1, the envelope **12** includes a pair of arm portions **32** and **34** of an approximately cylindrical configuration disposed about an axis passing through the axis of the cylindrical envelope portion **13**. As will be explained later, radiation will be emitted from the region **25** and the arm portions **32** are disposed so that a suitable sensor may view the region **25**. The arm portions **32** and **34** respectively include windows **36** and **38**, which are made of a material efficiently transmissive to the radiation emitted in the region **25**. As will be explained later, this system may be used to detect more than one wavelength of radiation, and the windows **36** and **38** may be made of different materials to be particularly transmissive to different wavelengths of radiation.

As shown in FIG. 4, a source **50** of potential is connected in series with a variable, resistive impedance **52** between the cathode element **20** and the anode element **28** to provide an electrical discharge therebetween. The electrical discharge between the cathode element **22** and the anode element **28** occurs in a gaseous medium such as helium, neon or argon capable of supporting the electrical discharge. The electrical discharge excites the atoms of the gas to produce ions which, in turn, are drawn to and bombard the cathode element thereby sputtering atoms of the cathode material. In order to limit the path of electrical discharge between the cathode element **20** and the anode element **28**, suitable shielding means is provided which illustratively includes as shown in FIG. 1 two insulating disks **40** and **42**. The insulating disks **40** and **42** are disposed in a spaced, parallel relationship about the cathode element **20**. The insulating disks **40** and **42** have apertures **44** of a diameter substantially equal to the outside diameter of the cathode element **20**. The cathode element **20** is disposed through the apertures

44 and the insulating disks 40 and 42 extend from the cathode element 20 to the interior periphery of the envelope 12. It is noted that the insulating disk 40 is illustratively recessed from the edge 21 of the cathode element 20 in order to not obstruct the view of the fluorescing region 25 through the region 25 through the arm portion 32 and 34. For a similar reason the support rods 30 are disposed in a plane perpendicular to the axis of the arm portions 34 and 36. In addition, the shielding means includes a pair of insulating sleeves 46 disposed about the support rods 30 extending between the stem header 18 and the insulating disk 42. Two pair of insulating rings 47 and 48 are disposed about the support rods 30 between the insulating disks 42 and 40, and between the insulating disk 40 and the anode element 28, respectively. The anode element 28 abuts against the insulating rings 48 and serves to hold the insulating disks 40 and 42, the insulating rings 46 and 47, and the insulating sleeves 48 axially in place. In another embodiment, it may be desired that the insulating disk 40 be disposed on the cathode element surface 21 with an aperture less than diameter A to reduce extraneous radiation as will be explained.

Referring now to FIG. 4, there is shown a system for measuring the concentration of an element in an unknown sample by analyzing the degree of absorption of the beam of radiation generated by the device 10. The potential applied by the source 50 between the cathode element 20 and the anode element 28 establishes a flow of electrons through the gas contained within the envelope 12. Due to the flow of electrons, the gas is partially ionized and the positive ions are drawn into the second hollow portion 24 of the cathode element 20. The positive ions bombard the interior surface of the portion 24 to sputter cathode particles into an emission region 23. The sputtered cathode particles are excited by other positive gas ions and the flow of electrons to emit spectral radiation having the characteristic wavelength(s) of the material(s) of which the cathode element 20 is made. Referring now to FIG. 3, the second hollow portion 24 is chosen to be of a diameter B which is sufficiently narrow to concentrate the bombardment of the sputtered particles by positive gas ions and electrons to excite atomic particles from a ground (or a first energy) state to a higher energy level. As is well understood in the art, the particles on relaxation to the ground state emit radiation characteristic of the sputtered particles. As shown in graphical form in FIG. 3, the central portion of the second hollow portion 24 has a relatively high population state of excited particles.

Radiation emitted from the region 23 is focused by a suitable optical assembly (as indicated by dashed lines) or lens 54 into a sample region 56. Disassociated atoms of the material to be analyzed are generated within the region 56. Illustratively, the sample material may be placed in solution and then vaporized in the region 56. The vaporized solution may be heated as by a premixing laminar flow or direct consumption burner to disassociate the atoms of the sample material to thereby provide a cloud of atoms at a ground state level. Other means of disassociating the atoms of the sample include high temperature furnaces, are plasmas, and high frequency gas plasmas. The beam of radiation emitted by the device 10 contains a specific spectral wavelength(s) which may be effectively absorbed by the vapor. More specifically, if the energy states of the disassociated atoms within the region 56 corresponds to the wavelength of the spectral radiation, the atoms will be excited thereby absorbing energy from the emitted spectral radiation. As shown in FIG. 4, the radiation passes through the region 56 and is reflected by a concave mirror 58 along a path denoted by a dash-dot line back through the region 56 into the device 10. A particular advantage of this invention is that the beam of spectral radiation is passed twice through the region 56 thereby absorbing a greater portion of the beam of radiation.

A suitable mechanical interrupter or chopper is provided in this system and includes a rotating sector 60 which is driven by a motor 62. As shown in FIG. 4, the sector 60 has portions 61 which allow the radiation to pass therethrough and to be reflected by the mirror 58. The other portions of the sector 60 intercept the radiation during the other portion of the rotation of the sector 60. It may be understood that there exists spurious and extraneous sources of radiation which may include scattered flame emission from the burner, fluorescence from scattered particles within the device 10, and resonant emission from the hollow cathode region 25 of spectral wavelengths which are not absorbed in the region 56. During a portion of the rotation of the sector 60, the beam of radiation is allowed to be reflected back through the region 56 and the total radiation effect is detected. During the blocked part of the cycle of the rotation of the sector 60, detection will be made of the spurious sources of light. The amplitude of the alternating signal thus generated is a measure of the specific atomic absorption effect occurring in region 56.

The beam of spectral radiation is reflected back through the region 56 and is focused by the lens 54 into the fluorescing region 25 lying between the cathode element 20 and the anode element 28. Illustratively, the reflecting mirror 58 may be slightly displaced so that the return beam of radiation denoted by the dot-dash lines will be focused in the region 25 in front of the cathode element 20. It is noted that the lens 54 is normally not capable nor is it desired to precisely focus the return beam of spectral radiation, but generally focus it within a region denoted by the numeral 25.

Referring to FIG. 3, there is shown graphically the population state indicated by the curve Y of the population state of excited atomic particles within the first hollow portion 22. The curve Y indicates that the population of excited particles at the center portion of the first hollow portion 22 decreases. This decrease is believed due to the increased diameter of the first hollow portion 22 relative to the mean free path of the sputtered ions. As a result, a portion of the sputtered atoms derived from the portion 22 remain in their ground state and will drift randomly into the fluorescing region 25 where they are subjected to the incident, reflected beam of spectral radiation. A portion of the ground state particles in the region 25 will be caused by the reflected radiation to fluoresce and emit resonant radiation having defined spectral wavelength(s) characteristic of the sputtered cathode material. More specifically that portion of the radiation reflected into the region 25 having a spectral wavelength corresponding to that required to excite the ground state particles in the region 25 will cause the ground state particles to become excited and upon relaxation, the excited particles will emit a resonant radiation. The other portion of the reflected radiation not having the defined spectral line(s) will not excite the ground state particles by atomic fluorescence to yield resonance radiation.

As explained above, the resonance radiation may be observed through either of the arm portions 32 or 34 of the envelope 12. A suitable radiation sensor 68 such as a photocell may be of use to observe the region 25. More specifically, a lens assembly 64 is used to focus the radiation derived from the region 25 onto the sensor 68 through a filter 66. It is noted that the sensor 68 may be exposed to reflected radiation from the hollow cathode element 20 or that the fluorescent radiation from the region 25 may contain lines which are not of immediate interest and may be removed by means of the filter 66. In order to eliminate ambient radiation, the sensor 68 may be disposed within a container 70 which presents a black, matted surface to absorb ambient radiation.

As mentioned above, the cathode element 20 may be made of one or more materials to thereby provide a spectral beam of radiation having more than one defined line. As a result, the sample to be analyzed within the re-

gion **56** may contain more than one element to be analyzed and to absorb the radiation directed therethrough. Further, the region **25** may contain ground state atoms of more than one element and the return beam of radiation may cause each of these different atomic species to fluoresce. The sensor **68** and the filter **66** may thus be selected to detect a resonance radiation of a first element, whereas a second radiation sensor **76** may be disposed to detect resonance radiation of a second element. The resonance radiation of the second element is focused by a lens **72** onto the radiation sensor **76**. A filter **75** is inserted between the lens **74** and the sensor **76** to allow only the resonance radiation of the second element to be directed onto the sensor **76**. A shielding container **78** is disposed about the sensor **76** to present a matted black surface to ambient radiation. Although not shown in FIG. 4, the device **10** may be disposed in a box having separate compartments corresponding to the containers **70** and **78** for shielding the remaining portion of the tube **10** from ambient radiation. Such a container would have only a small opening to allow the beam of spectral radiation to be focused onto the region **56** and to be reflected back by the mirror **58**.

Referring now to FIG. 5, there is shown an alternative embodiment of the electrode structure which may be disposed within the electron discharge device **10** of FIG. 1. In FIG. 1, there was shown a unitary cathode element **20** which was capable of producing both excited particles for emitting a beam of spectral radiation and also for generating ground state particles which will fluoresce in response to the reflected beam of radiation. In an alternative embodiment as shown in FIG. 5, a first cathode element **80** is provided with a hollow portion **81** of a diameter designed to emit a beam of spectral radiation. A second cathode element **82** is disposed adjacent the first cathode element **80** and has an inner diameter of a dimension greater than that of the hollow portion **81**. The cathode element **82** could illustratively be made of a wire and be disposed in a plane at an angle of 45° with respect to the axis of the device to allow the fluorescing radiation to be more readily observed. An anode element **84** would then be provided for establishing suitable flows of electrons between the anode element **84**, and the first and second cathode elements **80** and **82**. It is believed that the use of a separate cathode element **82** to provide the ground state particles would allow separate voltages to be applied to the first and second cathode elements **80** and **82** to thereby maximize their separate functions.

Referring now to FIG. 6, a first cathode element **86** is provided having a hollow portion **87** of such a diameter to efficiently emit a beam of spectral radiation. Next, there is provided an anode element **90** for establishing an electron flow with the first cathode element **86** and with a second cathode element **88**. The second cathode element **88** is disposed at a negative potential with respect to the anode element **90** and has an inner diameter of such a magnitude to efficiently generate ground state atomic particles. With regard to the embodiment of FIG. 6, it is believed that the disposing of asecond cathode element **88** remote from the first cathode element **86** will avoid an interaction between the electron flows to cathode elements and also provide better stability of operation. The embodiment of FIG. 5 may have the advantage that the return beam of spectral radiation may be more accurately focused onto the fluorescing region between the second cathode element **82** and the anode element **84**.

Referring again to FIG. 4, if a Cassegrain type collimator is substituted for the lens **54**, an ideally parallel beam of radiation may be passed through sample region **56** by a plane reflecting mirror (in place of the concave mirror **58**). If the plane mirror may be placed upon the blocking portion of sector **60** and portion **61** remains an aperture, the reflected radiation completes the system as has been described. In addition, the radiation passing through portion **61** can be further analyzed with a monochrometer and detector or with yet another remote resonance detector as may be desired. It is noted that this alternating signal is 180 degrees out of phase with the alternating signals from sensors **68** and **76**.

Thus there has been described an electron discharge device having the dual function of emitting a beam of spectral radiation and of producing within a single envelope ground state particles, which may be caused to fluoresce by the reflected beam of spectral radiation. Such a device would have the advantage over the prior art of being able to pass the beam of radiation twice through the sampling region and also the economies of requiring only a single power supply to energize the device. Further simplification and economy is achieved through the use of a device having a single envelope and a fewer number of electrodes. Furthermore, significant increases in measurement precision may result from the use of a single power supply.

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 or shown in the accompanying drawings shall be interpreted as illustrative and not in a limiting sense.

I claim:

1. A spectral analysis system including cathode and anode means disposed within a single envelope filled with a gas for establishing an electron flow therebetween, said cathode means having a hollow portion for establishing a spectral light source within said hollow portion and emitting a beam of spectral radiation containing a spectral line characteristic of a substance to be analyzed and for providing a cloud of ground state particles in a region exterior of said hollow portion of said cathode, first means for disassociating the atomic particles of a substance to be analyzed, second means for directing said beam of spectral radiation onto the atomic particles of said substance, third means for directing the spectral beam of radiation as acted upon by said atomic particles into said cloud of ground state particles in the region exterior of said cathode and spaced therefrom and fourth means for viewing said region exterior of said cathode for detecting the fluorescing radiation emitted from said cloud of ground state particles in response to said spectral beam of radiation after being acted on by said atomic particles to be analyzed.

2. A spectral analysis system as claimed in claim **1**, wherein said cathode means takes the form of a single electrode having a first hollow portion for emitting said beam of spectral radiation and a second hollow portion having a diameter greater than that of said first hollow portion for providing said ground state particles in a region exterior of said cathode.

3. A spectral analysis system as claimed in claim **1**, wherein said third means is positioned to redirect said beam of spectral radiation derived from said second means through said first means.

References Cited

UNITED STATES PATENTS

2,433,809	12/1947	Clapp	313—209
3,475,099	10/1969	Yasuda et al.	356—87X
3,489,942	1/1970	Walsh et al.	313—209
3,503,686	3/1970	Walsh et al.	356—85

FOREIGN PATENTS

1,389,897	1/1965	France	356—98
1,481,541	5/1967	France	356—87

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