United States Patent

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[54] RADIO FREQUENCY SPECTRAL EMISSION AND DETECTOR DEVICE

4 Claims, 4 Drawing Figs.

[52] **U.S. Cl.** **315/344,** 313/224, 356/85
[51] **Int. Cl.** **G01j 3/12,** H05b 41/24
[50] **Field of Search** 313/201, 209, 224; 356/85, 86, 87; 315/344

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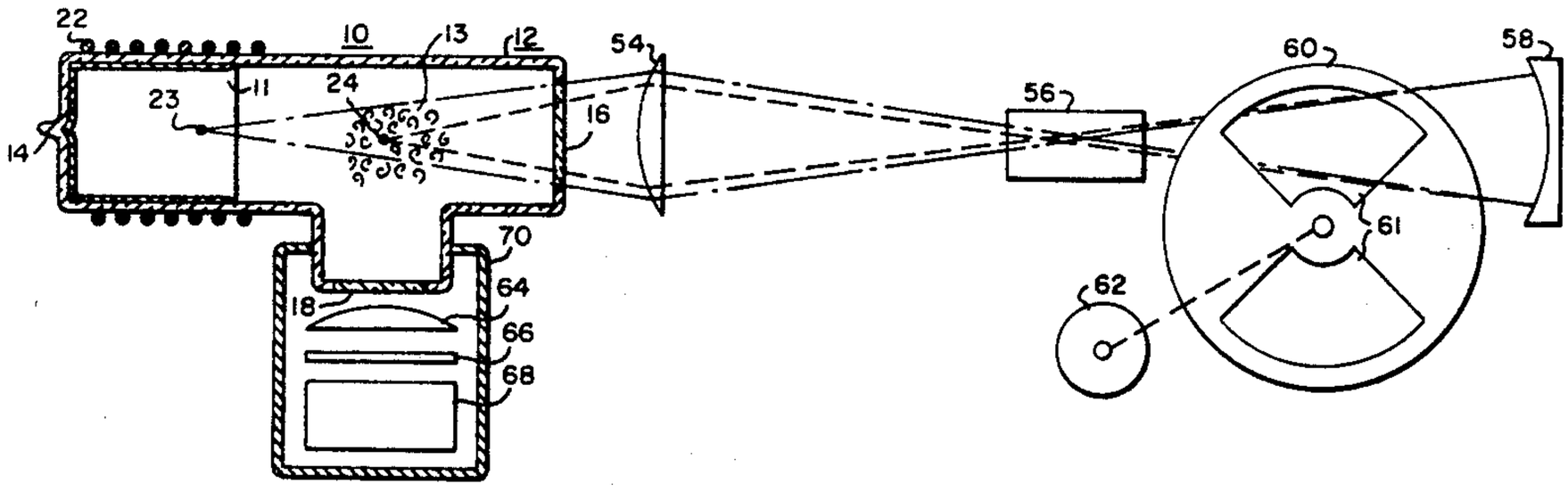
ABSTRACT: This invention relates to a spectral emission and detection device which includes an envelope filled with an inert gas capable of sustaining a discharge under application of radio frequency power. The envelope also includes a metal or metals in a pure state or a chemical compound to produce sharp spectral lines of the atomic spectra of the metal enclosed. The device is capable of emission of light of wavelengths characteristic of the material as well as generation of ground state atoms subject to absorption of radiation and emission of radiant energy at the same or higher wavelength.



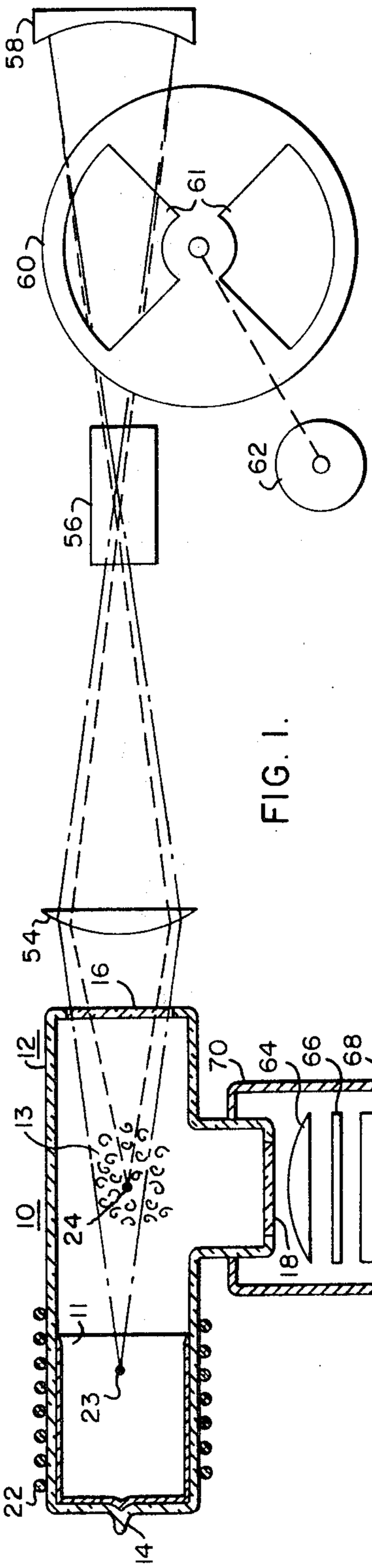


FIG. 1.

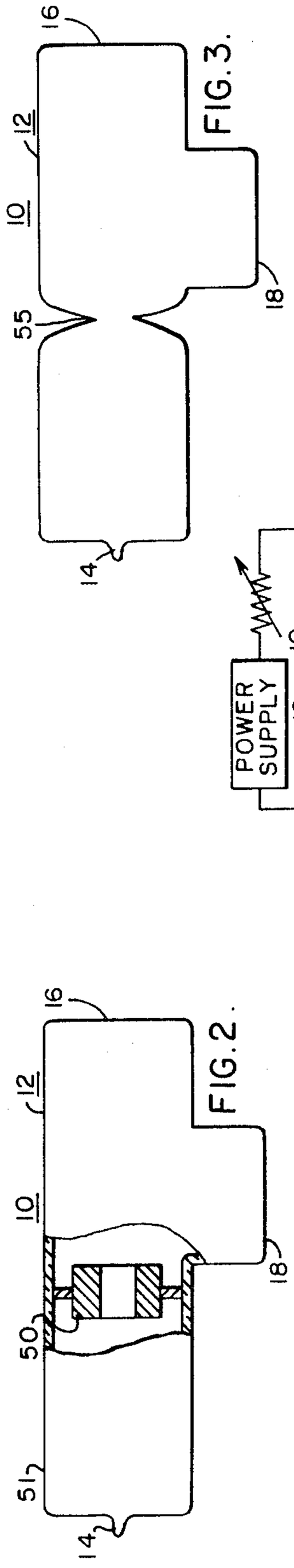


FIG. 3.

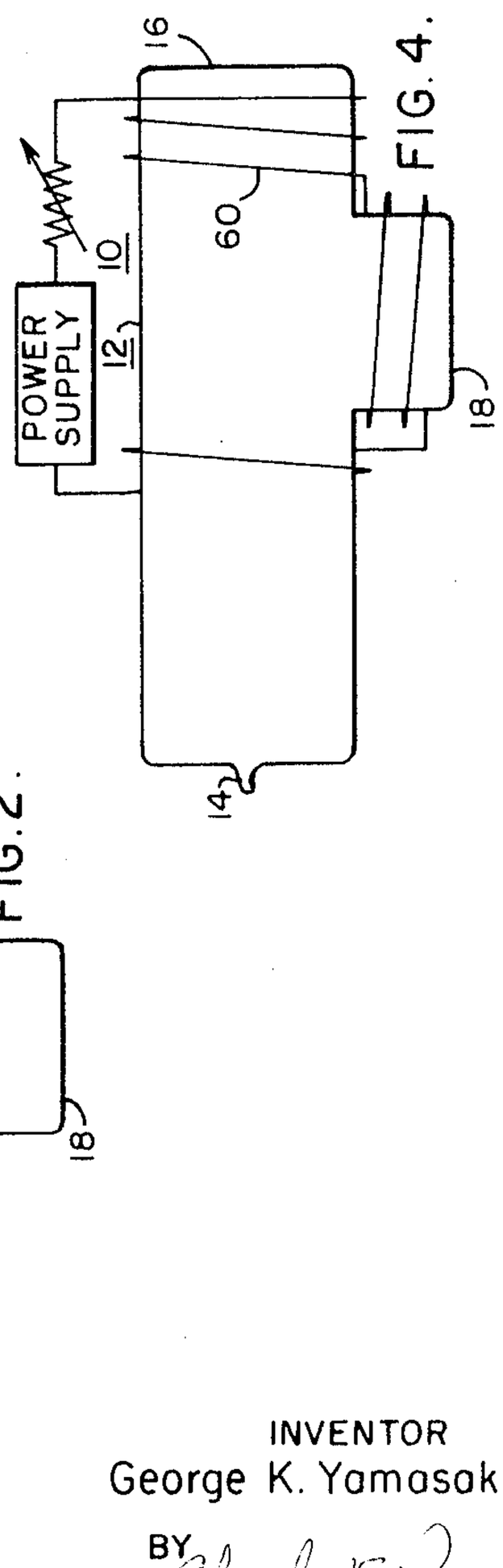


FIG. 4.

FIG. 2.

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RADIO FREQUENCY SPECTRAL EMISSION AND DETECTOR DEVICE

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a radio frequency-type spectral emission source and detector and associated system primarily for utilization in atomic absorption spectroscopy.

2. Description of the Prior Art

In copending application Ser. No. 696,761 filed Jan. 10, 1968 entitled "An Electron Discharge Device Including Hollow Cathode Element For Combined Emission of Spectral Radiation and Resonant Detection" by John D. Johnson and assigned to the same assignee as this invention, there is described an atomic absorption spectroscopy system which utilizes a hollow type cathode device for generating spectral emission characteristic of the cathode of the device and also exhibiting the property of detection of resonant radiation directed onto the discharge device to reemit radiation proportional to the intensity of the resonant lines in the exciting radiation directed thereon by external systems. The hollow cathode-type device is commonly used in present atomic absorption spectroscopy primarily because of the narrowness of the atomic absorption spectral lines generated by the hollow cathode discharge device. Another class of highly desirable spectral emission sources are those commonly referred to as radio frequency discharges and in this type of device the source draws the energy from an electrical field which excites and ionizes inert gas atoms which in turn excite the metal or compound included in the device for generation of spectra characteristic of the metal. A common class of this radio frequency type spectral source is that referred to as an electrodeless discharge lamp.

In the application of these devices in atomic absorption spectroscopy, radiations from a suitable spectral source such as the hollow cathode discharge device give off a spectral emission characteristic of the cathode. This spectral emission by the cathode is accomplished by ionizing the inert gas within the hollow discharge device by means of an electrical discharge between the cathode and anode. The gas atoms ionized by the electrons are attracted and strike the hollow portion of the cathode causing the sputtering of atomic particles of the cathode into the region of the cathode. These sputtered atomic particles are bombarded and a portion are excited from a ground state to a higher energy level. When these excited sputtered atoms return to their lower ground state level, energy originally absorbed from the bombarding particles is released in the form of radiation having spectral lines characteristic of the material of the cathode. This beam of spectral radiation is then directed through a vaporized sample of the solution or material to be analyzed. If the wavelength of the radiation from the spectral source corresponds to that required to excite the vaporized atoms which are ground state, a portion of the intensity of the spectral radiation will be absorbed by the atoms of the vaporized solution thereby absorbing the spectral radiation. If the radiation is of a wavelength differing from that required to excite the atoms in the vaporized material, the radiation will not be significantly absorbed. The normal practice is then to direct the radiation, after transmission through the unknown sample, to a monochromator which is selective to the wavelength of the initial radiation from the source. A suitable detector is associated therewith which measures the amount of absorption of that passing through the sample and without passing through the sample so as to arrive at a determination of the amount of spectral radiation absorbed within the unknown sample. This technique is well known in the art.

Recently, another method of analyzing the radiation after passing through the unknown has been described. This includes a device referred to as a resonance monochromator or detector. This resonant detector provides a cloud of atoms by cathodic sputtering or direct heating of a similar element as that of the spectral source to create an atomic vapor of ground

state atoms. The direction of the radiation, after transmission through the unknown, into such an atomic vapor results in the absorption of this transmitted radiation and excitation of the ground state atoms. Resonance radiation characteristic of the element is emitted upon the return of the excited ground state atoms to their ground state energy. This emitted radiation is referred to as atomic fluorescence.

In the previously mentioned copending application this system is more thoroughly described and particularly with regard to the utilization of a hollow cathode discharge device.

It is accordingly a general object of this invention to provide a new and improved spectral radiation source having a dual function of emitting a beam of spectral radiation and also serving as a resonance detector to measure the effect of atomic absorption.

SUMMARY OF THE INVENTION

This invention is directed to a dual function device for special emission and radiation detection which is responsive to a radio frequency field. The excitation field may also be applied to the RF discharge device by capacitive coupling by placing the RF device between or in close proximity to a set of closely spaced conductive plates which are energized with RF power.

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 diagrammatic view of a system embodying the present invention for performing atomic absorption measurements;

FIG. **2** illustrates a modification of the radio frequency spectral device which may be incorporated into FIG. **1**;

FIG. **3** is another modification of a spectral device which may be incorporated in FIG. **1**; and

FIG. **4** is another modified spectral device which may be incorporated into FIG. **1**.

DESCRIPTION OF THE PREFERRED EMBODIMENT

Referring in detail to FIG. **1**, an atomic absorption system is illustrated which incorporates the spectral device **10**. The spectral device **10** is a tubular envelope **12** which is tipped off at one end to provide a tip-off portion **14** and the other end of the tubular member **12** is closed by a spectral emission face plate **16** capable of transmission of the radiations generated by the spectral device **10**. A suitable material for the window **16** is quartz. Any other suitable transmissive glass or material may be used. In addition, a second detection radiation window **18** is provided which may also be of quartz or any other glass or material which is transmissive to the resonance radiation to be detected. The spectral device **10** includes the envelope **12** which is filled to a pressure of 1 to 2 millimeters of mercury of a suitable gas such as argon, neon, helium or xenon. The gas pressure may range from 0.1 millimeters of mercury to 300 millimeters of mercury. In addition, a small quantity of a pure metal or a chemical compound of a metal such as a salt of the metal or a halide is also provided within the envelope **12**. For example, if the characteristic emission of arsenic was desired then the envelope **12** may have a length of about 10 centimeters and a diameter of about 1.0 centimeter. A composition of about 10 milligrams of arsenic and 10 milligrams of iodine would be introduced into the envelope **12**. The material is indicated as item **11**. A suitable method of preparing the device is to seal the two windows **16** and **18** into the envelope **12** and then place the envelope **12** on a vacuum system. A few milligrams of the metal or compound is then placed in the envelope **12** and the tube placed on the vacuum system. The tube is then outgassed by heating and finally an inert gas such as argon at a pressure of about 1 to 5 millimeters of mercury is emitted in this system and the lamp is tipped off at the tip-off section **14**. The gas filling is indicated in the drawing as item **13**.

A source of radio frequency energy is positioned about the envelope and is illustrated as a coil 22. The radio frequency filed may also be applied to the envelope by means of capacitive means or also within a microwave source. In the case of the microwave source, the frequency might be of the order of 2,450 megacycles with a wattage of less than 100 watts. Any high frequency oscillator with several watts input will operate the spectral device. The application of this radio frequency field causes a high voltage field to be produced within the envelope 12 exciting and ionizing the inert gas atoms of the fill 13 in the device. These gas atoms in turn collide and excite the metal atoms in the coating 11 included in the device resulting in emission of a sharp line spectra of the metal upon deexcitation of these metal atoms to the ground state. In addition, the RF heating will heat the device so that the vapor pressure of the metal coating 11 is increased in the device during operation and thereby increases a population of the metal atoms in the vapor state further improving the probability of excitation and emission of spectral light. In addition to the excited metal atoms there is a large cloud of metal atoms in the unexcited or ground state atoms which are generated and located in the region 24 of the envelope. The returning light directed onto the region 24 causes these ground state atoms to become excited and on return to ground state will emit resonant radiation which can be detected through the window 18.

Referring now to FIG. 1, 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 to the coil 22 causes the emission of spectral light corresponding to the metallic element in coating 11, such as arsenic. Simultaneously with the generation of the light emission from the region 23, a large number of unexcited arsenic atoms is generated in the ground state and located generally in the region 24.

Radiation emitted from the region 23 is focused by a suitable optical assembly as indicated by the dash lines and illustrated as lens 54 into a sample region 56. Disassociated atoms of the material to be analyzed are generated within the region 56. For example, the sample material which we assume includes arsenic is placed in solution and vaporized in the region 56. The vaporized solution may be heated by any suitable means such as premixing laminar flow or direct consumption burner to disassociate the atoms of the sample material to thereby provide a cloud of atoms at ground state level. The beam of radiation emitted by the device 10 contains a specific spectral wavelength characteristic of arsenic which may be effectively absorbed by the vapor in region 56 if arsenic is in the sample. More specifically, if the energy states of the disassociated atoms within the region 56 correspond to the wavelength of the spectral radiation, the atoms will be excited thereby absorbing energy from the emitted spectral radiation from the device 10. The radiation after passing through the region 56 passes through to a mirror 58 along a path denoted by the dash dot lines and then back through the region 56 into the device 10. 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. 1, the sector 60 has portions 61 which allow the radiations to pass therethrough and to be reflected by the mirror 58. The other portions of the sector 60 intercept the radiations during the other portion of the rotation of the sector 60. There exists spurious and extraneous sources of radiation which may include scattered flame emission from the region 56, fluorescence from scatter particles within the device 10 and resonant emission from the device 10 of spectral wavelength 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 block part of the cycle of the rotation of sector 60, detection will be made of the spurious sources of light. The amplitude of the alternating signal thus derived from the system is a measure of the specific atomic absorption effect occurring in the region 56.

The beam of spectral radiation reflected back through the region 56 is focused by the lens 54 into the ground state region 24. This reflected radiation into the region 24 is absorbed by the ground state atoms of arsenic and the mixed resonant radiation characteristic of the arsenic. The ground state atoms will be excited by this reflected radiation to a higher energy and then on return to ground state will emit radiations which may be detected through the window 18, a suitable radiation sensor 68 such as a photocell may be of use to observe the region 24. More specifically, a lens assembly 64 is used to focus the radiation derived from the region 24 onto the sensor 68 through a filter 66. The sensor 68 may be exposed to undesired radiation wavelengths and the filter 66 removes these undesired radiation wavelengths. In order to eliminate ambient radiation, the sensor 68 may be disposed within a container 70 which presents a black matter surface to absorb ambient radiations.

In the event that the device 10 includes more than one metallic material to therefore provide a spectral beam of radiation from more than one element the region 24 will contain ground state atoms of more than one element and the return beam of radiation may cause each of these different atomic species to reemit radiation. The sensor 68 and filter 66 may thus be selected to detect a radiation of a first element whereas a second radiation sensor may be disposed to detect resonant radiation of a second element. This second radiation system could be disposed near the output window 18 or an additional window might be provided for this additional determination.

The presence of a bright radio frequency discharge in the forward region of the device 10 may interfere with the detection of resonant light from the region 24. For best resonant detection, the presence of free atoms without the presence of ionized or excited atoms is therefore desirable. In FIG. 2, a shield member 50 is provided to contain the discharge in the lower region 51 of the device and away from the side window 18. FIG. 3 illustrates another possible modification in which the tubulation is provided with a neck down portion 55 to contain the discharge in the lower region of the device away from the side window.

If the distance from the discharge region 23 of the device 10 becomes too great from the output window 16, the front end of the device 10 will run cooler in temperature and the population of the atomic vapor necessary for resonant detection becomes lower. In this case, an auxiliary heating means such as a coil or a resistance heating wire or an oven may be required. In FIG. 4, an auxiliary heating means is illustrated as a coil 60 wrapped around the portion of the envelope adjacent the output window 16 and the side window 18. If the window area is too cool in temperature, the metal and salt vapor may leave the discharge area and condense on these cooler surfaces. This would of course result in poor spectral light formation because of the decreased atom population for excitation of the RF radiation and the coating on the window would reduce transmission of the light.

It is also obvious that rather than utilizing the side windows that a front window may be utilized with an associated mirror so as to reflect the radiations onto a detector located off axis of the device. In addition, the envelope of the device may be made of suitable transmissive type material so that the side window is not necessary.

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 dual purpose, spectral analysis device comprising an elongated envelope, said envelope having a metallic material and an inert gas therein, means provided at one portion of said envelope to provide a radio frequency field within a first region of said envelope to generate a first radiation within said

first region containing spectral lines characteristic of said metallic material and also provide a cloud of ground state particles in a second region of said envelope, and spaced from said first region, said envelope having a first portion transmissive to said first radiation, said envelope having a second portion transmissive to the wavelengths of said first radiation and disposed to permit viewing of said cloud of ground state particles in said second region of said envelope without substantial interference from said first radiation.

2. The device set forth in claim 1 in which shielding means is provided in said envelope between said first and second regions to contain the generation of said first radiation to said first region.

3. The device set forth in claim 1 in which means are provided within said envelope to substantially isolate the region of said spectral emission within said envelope from the region of said ground state particles to permit viewing of resonant radiation from said ground state particles without substantial interference of said spectral emission.

4. The device set forth in claim 1 in which means are provided for localized heating of portions of said envelope surrounding said second region to enhance said ground state population.