United States Patent [19]

Okagaki

[11] **3,869,643**

[45] **Mar. 4, 1975**

[54] **APPARATUS FOR EMITTING ATOMIC FLOURESCENCE SPECTRAL LINES USED FOR ATOMIC ABSORPTION ANALYSIS**

[75] Inventor: **Hiroshi Okagaki,** Katsuta, Japan

[73] Assignee: **Hitachi, Ltd.,** Tokyo, Japan

[22] Filed: **Jan. 4, 1974**

[21] Appl. No.: **430,943**

[30] **Foreign Application Priority Data**

Jan. 12, 1973 Japan 48-6440

[52] **U.S. Cl.** **315/167,** 313/188, 313/209, 313/216, 313/220, 313/224, 315/172, 315/174, 315/260, 315/334

[51] **Int. Cl.** **H01j 61/04**

[58] **Field of Search** 313/188, 209, 210, 216; 315/167, 172, 174, 260, 334

[56] **References Cited**

UNITED STATES PATENTS

3,089,054 5/1963 Walsh et al. ..... 313/209 X

Primary Examiner—John Kominski
Assistant Examiner—Darwin R. Hostetter
Attorney, Agent, or Firm—Craig & Antonelli

[57] **ABSTRACT**

An apparatus for emitting atomic fluorescence spectral lines used for atomic absorption analysis comprising an envelope containing an inert gas therein and provided with a first hollow cathode, a second hollow cathode disposed in optically coaxial relation with the first hollow cathode and having a slit, a hollow insulator interposed between the first and second hollow cathodes, an anode extending into the hollow space within the insulator, leads connected to the anode and first and second hollow cathodes, and a window for deriving atomic fluorescence spectral lines in a direction different from the direction of the common optical axis of the first and second hollow cathodes.

16 Claims, 17 Drawing Figures

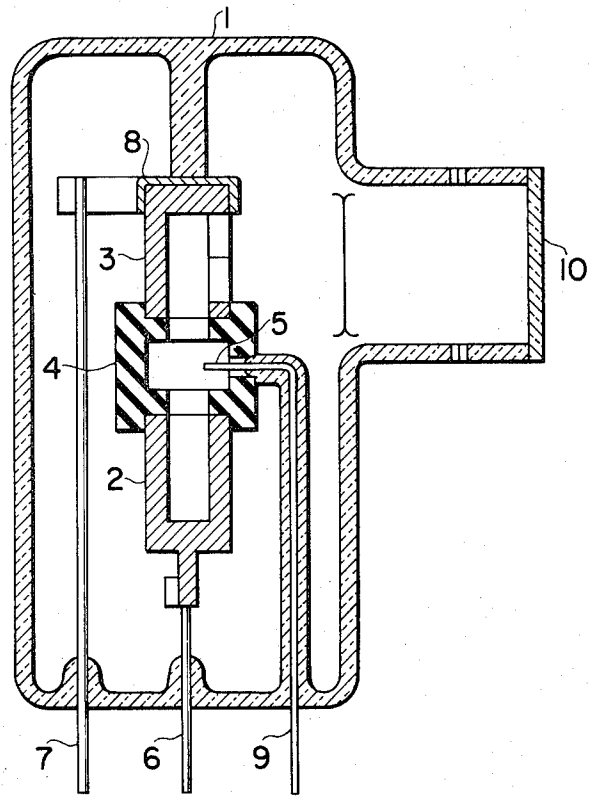


FIG. 1

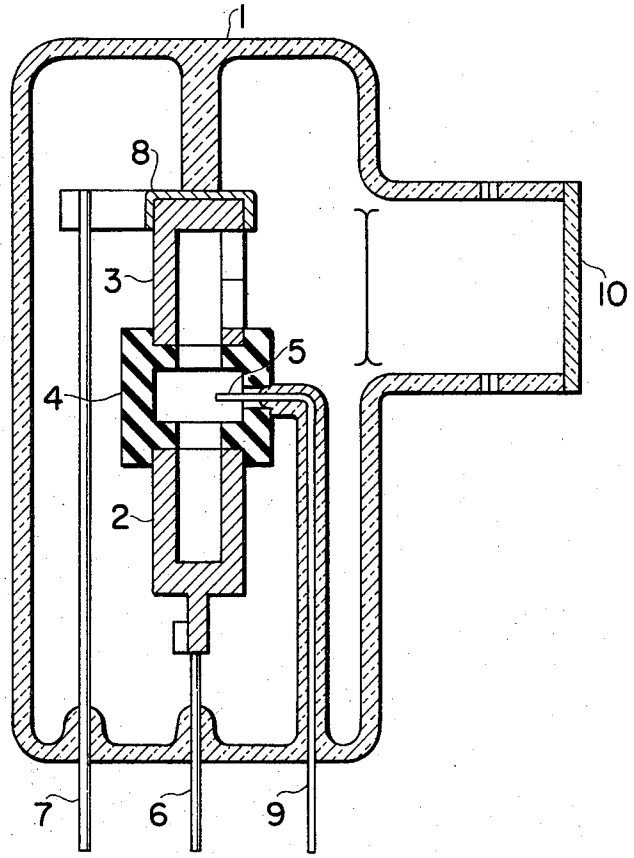


FIG. 2a

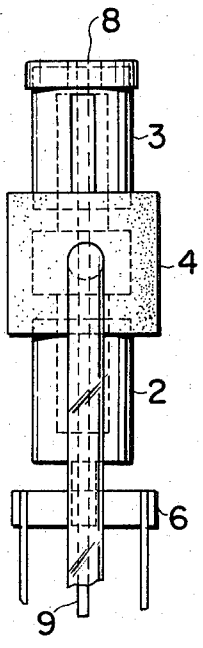


FIG. 2b

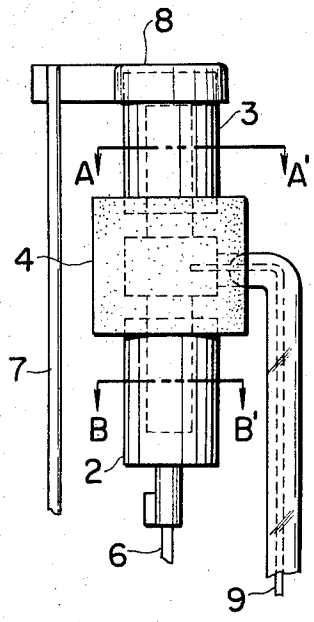
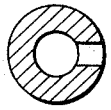


FIG. 2c

A-A' SECTION



B-B' SECTION

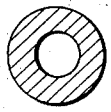


FIG. 3a

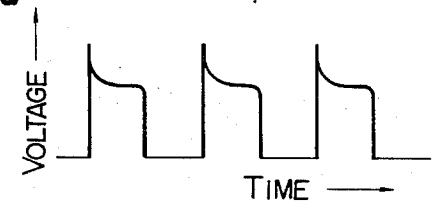


FIG. 3b

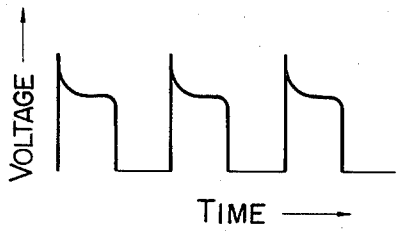


FIG. 3c

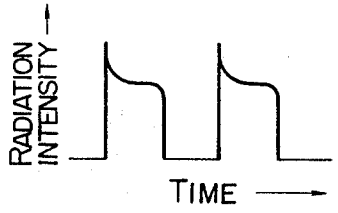


FIG. 3d

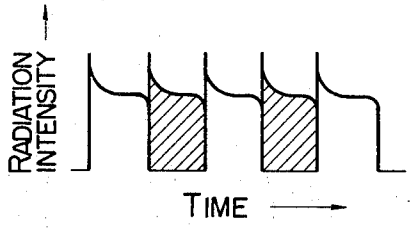


FIG. 4a

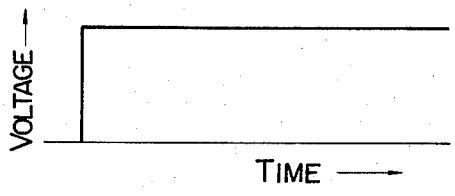


FIG. 4b

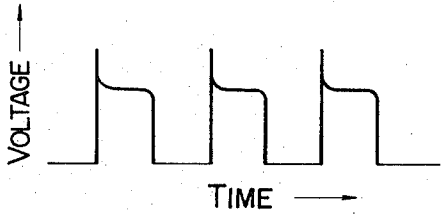


FIG. 4c

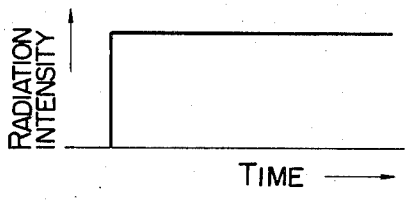


FIG. 4d

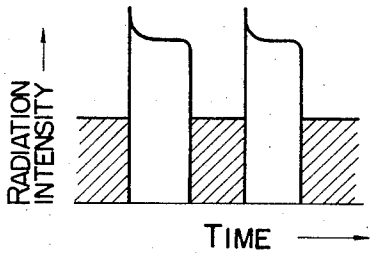


FIG. 5a

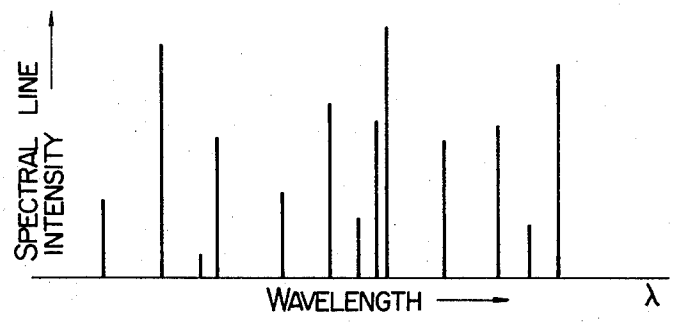


FIG. 5b

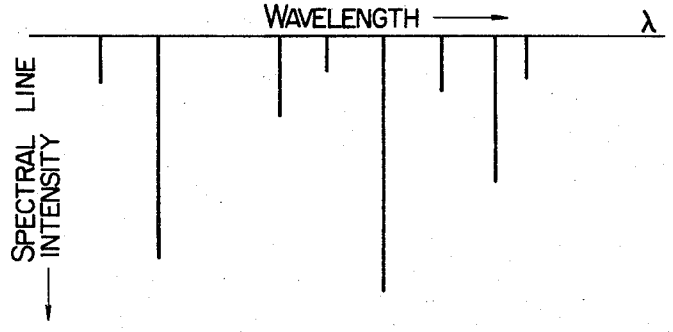


FIG. 5c

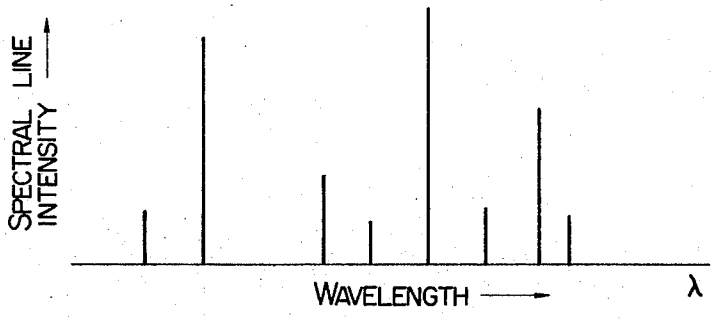


FIG. 6a

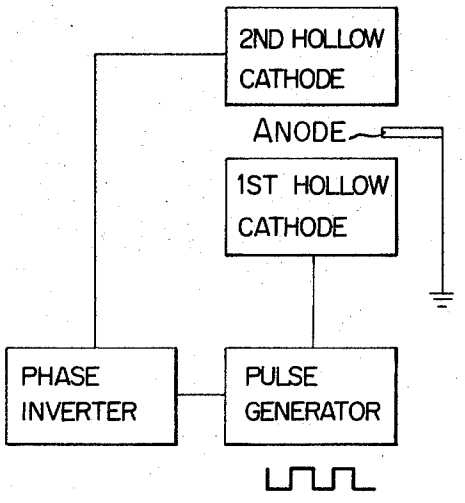
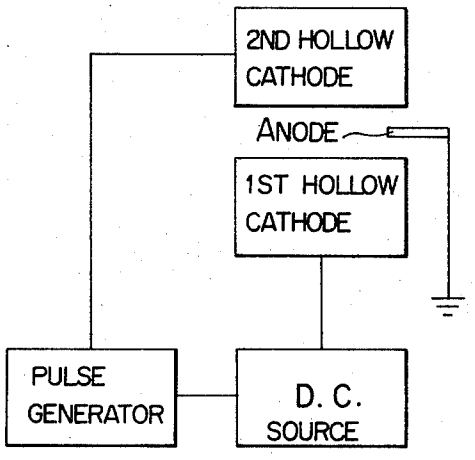


FIG. 6b



APPARATUS FOR EMITTING ATOMIC FLOURESCENCE SPECTRAL LINES USED FOR ATOMIC ABSORPTION ANALYSIS

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to apparatus for emitting spectral lines used for atomic absorption analysis and more particularly to an apparatus for emitting atomic fluorescence spectral lines used for such analysis.

2. Description of the Prior Art

In an atomic absorption analysis, cathode sputtering occurring in the glow discharge region of a hollow cathode discharge tube is utilized to emit spectrum lines of atoms and an atomized sample is irradiated with the spectral lines to obtain required absorption lines. Due to the fact that the spectrum emitted from the hollow cathode discharge tube includes a plurality of spectral lines peculiar to the element constituting the cathode, a spectral line having a high absorption sensitivity among these spectral lines has been selectively obtained by means of a monochrometer in prior art practice to use such specific spectral line for the atomic absorption analysis. However, it is difficult to derive the specific spectral line by the monochrometer due to the limited dispersive power of the dispersing element, and the specific spectral line to be absorbed includes other non-absorbed spectral lines resulting in poor analytical precision. An attempt to improve the precision of analysis by further reducing the width of the slit in the monochrometer results in a weakened intensity of the spectral line. An increase in the tube current in an effort to increase the intensity of the spectral line results in a widened profile of the spectral line, and thus, a spectral line having a high sensitivity suitable for analysis is difficult to obtain. Further, the optical system including the monochrometer used in the atomic absorption analysis involves such a problem that it shows a sharp response to variations of ambient temperature resulting in remarkable variations of the intensity of the spectral line derived from the system.

In another prior art apparatus for emitting atomic fluorescence spectral lines used for atomic absorption analysis, an anode and a cathode are disposed in suitably spaced relation in an envelope containing an inert gas and means are provided for applying a voltage across these electrodes for causing discharge thereacross and directing light to the atom vapor produced by sputtering so as to derive fluorescent radiation and absorbed radiation from the atom vapor. However, due to the small absolute quantity of the atom vapor thus produced and due to the presence of atoms in an excited state, the emission intensity is considerably weak and it is very difficult with such an apparatus to derive solely a specific spectral line.

It will be seen from the above description that, with prior art discharge tubes used for atomic absorption analysis, it is essentially nearly impossible to derive solely required spectral lines.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide a novel apparatus for emitting atomic fluorescence spectral lines used for atomic absorption analysis, which can emit solely such spectral lines which are required for the atomic absorption analysis and contribute to the absorption.

Another object of the present invention is to provide an apparatus for the kind above described which can easily increase the intensity of spectral lines to be absorbed.

Still another object of the present invention is to provide an apparatus of the kind above described which can remarkably improve the precision of analysis.

In accordance with a preferred embodiment of the present invention, there is provided an apparatus for emitting atomic fluorescence spectral lines used for atomic absorption analysis comprising an envelope, first means for emitting spectral lines of atoms in a first position within said envelope, second means for generating vapor of atoms at ground state in a second position within said envelope, said second position lying on the optical axis providing the path for said spectral lines of atoms, and third means for directing atomic fluorescence spectral lines obtained by irradiation of the atom vapor with said spectral lines of atoms in a direction different from the direction of said optical axis thereby deriving said fluorescence spectral lines from said envelope.

Other objects, features and advantages of the present invention will become more apparent from the following description taken in conjunction with the accompanying drawing.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 is a longitudinal section of an embodiment of the apparatus according to the present invention.

FIGS. 2*a*, 2*b* and 2*c* are a front elevation, a side elevation and partial sections respectively of the hollow cathode portion in the apparatus shown in FIG. 1.

FIGS. 3*a* to 3*d* and 4*a* to 4*d* show the relation between the voltage applied to the apparatus of the present invention and the intensity of spectral lines emitted thereby.

FIGS. 5*a* to 5*c* show the relation between the absorption spectral lines and the atomic fluorescence spectral lines.

FIGS. 6*a* and 6*b* are block diagrams of circuits preferably used in the apparatus according to the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Referring to FIG. 1 showing an embodiment of the present invention, a gas-tight envelope 1 contains therein a rate gas such as neon or argon at a pressure of several Torr. A first hollow cathode 2 is disposed in a first position within the envelope 1 so as to contribute to emission of spectral lines of atoms. A second hollow cathode 3 is disposed in a second position within the envelope 1 so as to contribute to the generation of atomic vapor at substantially ground state. This second position lies on the optical axis along which the spectral lines of atoms emitted from the first hollow cathode 2 are directed toward the second hollow cathode 3. An insulator 4 of material such as a ceramic material, mica, or glass is interposed gas-tight between the first hollow cathode 2 and the second hollow cathode 3 which are arranged to each other in optically coaxial relation. This insulator 4 acts to prevent undesirable discharge across a common anode 5 of the first and second hollow cathodes 2, 3 and the exterior of the first and second hollow cathodes 2, 3. A lead 6 is connected to the first hollow cathode 2, and another lead 7 is con-

nected to the second hollow cathode 3 through a cap 8 covering a portion of the second hollow cathode 3. Another lead 9 is connected to the anode 5 and may be insulated as required. An exit window 10 of material such as quartz is fixed to a part of the envelope 1 so as to derive atomic fluorescence spectral lines from the envelope 1 in a direction perpendicular to the optical axis. As shown in FIG. 2*c* in which a section taken on the line A—A′ in FIG. 2*b* is illustrated, the second hollow cathode 3 is formed with a slit for deriving the atomic fluorescence spectral lines from the window 10 of the envelope 1 in a direction perpendicular to the optical axis.

FIGS. 3*a* to 3*d* show the waveforms of power supply voltage applied to the apparatus of the present invention and the waveforms of emission spectral lines and atomic fluorescence spectral lines emitted in response to the application of the power supply voltage. FIG. 6*a* is a block diagram of a circuit preferably used in the present invention. More precisely, FIG. 3*a* shows the relation between time and the waveform of a pulse voltage applied to the first hollow cathode 2 and FIG. 3*b* shows the relation between time and the waveform of another pulse voltage applied to the second hollow cathode 3. It will be seen that these pulse voltages are 180° out of phase from each other. FIG. 3*c* shows the relation between time and the intensity of the emission spectral lines emerging from the first hollow cathode 2, and FIG. 3*d* shows the relation between time and the intensity of the emission spectral lines and atomic fluorescence spectral lines (hatched portions) emerging from the second hollow cathode 3. The vertical axis in FIGS. 3*a* and 3*b* represents the voltage value, while that in FIGS. 3*c* and 3*d* represents the spectral line intensity, and the horizontal axis in FIGS. 3*a* to 3*d* represents time.

Referring to FIG. 6*a*, a pulse voltage generated by a pulse generator is passed through a phase inverter so that pulse voltages having a suitable phase difference of, for example, 180° can be applied to the first and second hollow cathodes 2 and 3 respectively. In response to the application of the pulse voltage to the second hollow cathode 3, spectral lines are emitted from the second hollow cathode 3, and at the same time, the metal forming the second hollow electrode 3 is vaporized to produce vaporized metal atoms by the sputtering action occurring in the inert gas atmosphere enclosed within the envelope 1. The vaporized metal atoms are restored to ground state in a period of time of 10^{-8} to 10^{-7} second and remain stable. When the pulse voltage which is 180° out of phase from the pulse voltage above described is applied to the first hollow cathode 2 while the vaporized metal atoms restored to the ground state exist in the second hollow cathode 3, spectral lines are emitted from the first hollow cathode 2 and impart energy to the vaporized metal atoms of the ground state existing in the second hollow cathode 3. Consequently, the energy level of the vaporized metal atoms is raised to a high level by absorption. However, since the state of the vaporized metal atoms raised to a high level is unstable, the absorbed energy is discharged in the form of spectral lines and the stable ground state is restored again. The spectral lines emitted during the restoration to the stable ground state are called atomic fluorescence spectral lines which differ from ordinary emission spectral lines in that the same spectral lines as the absorbed spectral lines only are emitted and non-absorbed spectral lines are not included therein. The manner of emission of such spectral lines will be described with reference to FIGS. 5*a* to 5*c*. FIG. 5a shows spectral lines emitted from the first hollow cathodes 2 and it will be seen that these spectral lines are relatively close to each other. FIG. 5*b* shows spectral lines to be absorbed and it will be seen that specific emission spectral lines are absorbed by the atoms of the metal forming the second hollow cathode 3. Consequently, the second hollow cathode 3 emits fluorescence spectral lines which are the same as the absorbed spectral lines as seen in FIG. 5*c*. In FIGS. 5*a* to 5*c*, the vertical axis represents the spectral line intensity and the horizontal axis represents the wavelength.

It will thus be seen that specific spectral lines are absorbed due to the fact that the energy level of the metal atoms produced by the sputtering action in the hollow space of the second hollow cathode 3 is the ground level. More precisely, those spectral lines whose energy is equal to the difference (energy difference) between the ground level and the high level of the metal atoms among the spectral lines emitted from the first hollow cathode 2 impart energy to the metal atoms existing in the hollow space of the second hollow electrode 3 (that is, metal atoms of the ground state) to raise the energy level of the metal atoms of the ground state to the high level by absorption and the so-called atomic fluorescence spectral lines are emitted when the energy level is restored to ground level. In the case of other spectral lines emitted from the first hollow cathode 2 due to transition between the excited levels, these spectral lines are transmitted merely in the direction of the optical axis of the second hollow cathode 3 and no energy transfer is done due to the fact that the metal atoms in the hollow space of the second hollow electrode 3 have solely the ground state.

The atomic fluorescence spectral lines emitted in the manner above described pass through a slit which is formed in the second hollow cathode 3 in such a position that the atomic fluorescence spectral lines can be derived in a direction perpendicular to the optical axis of the second hollow cathode 3. The atomic fluorescence spectral lines emerging from the slit pass through the window 10 of quartz fixed to the envelope 1 to be directed toward, for example, an atomized sample portion of an atomic absorption analyser. Since the metal atoms in the atomizer sample portion of the atomic absorption analyzer are at ground level and do not have any other levels, the atomic fluorescence spectral lines used for analysis provide spectral lines including solely absorption lines.

It will be understood that the atomic fluorescence spectral lines emitted from the apparatus embodying one form of the present invention do not include any other non-absorbed spectral lines. Thus, not only the intensity of the absorption spectral lines can be easily increased but also the precision of analysis can be remarkably improved.

In the embodiment of the present invention above described, emission spectral lines emerge also from the slit of the second hollow cathode 3 during sputtering for producing the vapor of metal atoms, but such undesirable spectral lines are eliminated by electrical means (not shown) or optomechanical chopper means (not shown).

The above description has referred to the case in which pulse voltages 180° out of phase are applied to

the first and second hollow cathode 2 and 3 respectively. An effect similar to that above described can be attained by applying a d.c. voltage to the first hollow cathode 2 and a pulse voltage to the second hollow cathode 3 as shown in FIGS. 4*a* and 4*b*. FIG. 4a shows the waveform of the D.C. voltage applied to the first hollow cathode 2 and FIG. 4b shows the waveform of the pulse voltage applied to the second hollow cathode 3. FIG. 4c shows the relation between time and the intensity of the emission spectral lines appearing from the first hollow cathode 2, and FIG. 4d shows the relation between time and the intensity of the emission spectral lines and atomic fluorescence spectral lines (hatched portions) appearing from the second hollow cathode 3. FIG. 6*b* is a block diagram of a circuit preferably used for this purpose.

It will be understood from the foregoing detailed description of the present invention that atomic fluorescence spectral lines contributing to absorption for atomic absorption analysis can be solely obtained without using any optical means such as a spectroscope and the intensity of the absorption spectral lines can be easily increased thereby remarkably improving the precision of analysis.

I claim:

1. An apparatus for emitting atomic fluorescence spectral lines used for atomic absorption analysis comprising an envelope, first means for emitting spectral lines of atoms in a first position within said envelope, second means for generating vapor of atoms at ground state in a second position within said envelope, said second position lying on the optical axis providing the path for said spectral lines of atoms, and third means for directing atomic fluorescence spectral lines obtained by irrediation of said atomic vapor with said spectral lines of atoms in a direction different from the direction of said optical axis thereby deriving a said fluorescence spectral lines from said envelope.

2. An apparatus as claimed in claim 1, wherein said first means includes means for continuously emitting said spectral lines of atoms, and said second means includes means for generating said atomic, vapor in a pulsed fashion.

3. An apparatus as claimed in claim 1, wherein said first means includes means for emitting said spectral lines of atoms in a pulsed fashion, and said second means includes means for generating said atomic vapor in a pulsed fashion, the pulse signals applied from said first and second means having a suitable phase difference therebetween.

4. An apparatus as claimed in claim 1, wherein said third means includes means for deriving said atomic fluorescence spectral lines obtained by irradiation of said atomic vapor with said spectral lines of atoms through an exit window forming a part of said envelope in a direction perpendicular to the direction of said optical axis.

5. An apparatus for emitting atomic fluorescence spectral lines used for atomic absorption analysis comprising an envelope, a first hollow cathode disposed in a first position within said envelope for contributing to the emission of spectral lines of atoms, a second hollow cathode disposed in a second position within said envelope on the same optical axis as that of said first hollow cathode for contributing to the generation of vapor of atoms in a ground state, a hollow insulator interposed between said first and second hollow cathodes, an anode disposed within the hollow space of said insulator in common to said first and second cathodes, lead connected to said anode and said first and second cathodes, and a window forming a part of said envelope so that atomic fluorescence spectral lines obtained by irradiating said atom vapor with said spectral lines of atoms can be derived from said envelope in a direction different from the direction of said optical axis.

6. An apparatus as claimed in claim 5, wherein a D.C. voltage is applied to said first hollow cathode for continuously emitting said spectral lines of atoms, and a pulse voltage is applied to said second hollow cathode for generating said atomic vapor in a pulsed fashion.

7. An apparatus as claimed in claim 5, wherein a first pulse voltage is applied to said first hollow cathode for emitting said spectral lines of atoms in a pulsed fashion, and a second pulse voltage is applied to said second hollow cathode for generating said atomic vapor in a pulsed fashion, said first and second pulse voltages having a suitable phase difference therebetween.

8. An apparatus as claimed in claim 5, wherein a slit is formed in said second hollow cathode for deriving said atomic fluorescence spectral lines in a direction different from the direction of the optical axis of said second hollow cathode.

9. An apparatus as claimed in claim 6, wherein a slit is formed in said second hollow cathode for deriving said atomic fluorescence spectral lines in a direction different from the direction of the optical axis of said second hollow cathode.

10. An apparatus as claimed in claim 7, wherein a slit is formed in said second hollow cathode for deriving said atomic fluorescence spectral lines in a direction different from the direction of said second hollow cathode.

11. An apparatus for emitting atomic fluorescence spectral lines used for atomic absorption analysis comprising an envelope charged with an inert gas and having a first hollow cathode contributing to the emission of spectral lines of atoms, a second hollow cathode connected gas-tight to said first hollow cathode on the same optical axis with a hollow insulator interposed therebetween for contributing to the generation of a vapor of atoms in a ground state, said second hollow cathode being provided with a slit for directing atomic fluorescence spectral lines obtained by irradiation of said atomic vapor with said spectral lines of atoms in a direction perpendicular to the direction of said optical axis, an anode disposed within the hollow space of said insulator in common to said first and second hollow cathodes, leads connected to said anode and said first and second hollow cathodes, and a window for deriving said atomic fluorescence spectral lines from said envelope to direct same to the exterior.

12. An apparatus as claimed in claim 11, wherein a D.C. voltage is applied to said first hollow cathode for continuously emitting said spectral lines of atoms, and a pulse voltage is applied to said second hollow cathode for generating said atomic vapor in a pulsed fashion.

13. An apparatus as claimed in claim 11, wherein a first pulse voltage is applied to said first hollow cathode for emitting said spectral lines of atoms in a pulsed fashion, and a second pulse voltage is applied to said second hollow cathode for generating said atomic vapor in a pulsed fashion, said first and second pulse voltages having a suitable phase difference therebetween.

14. An apparatus as claimed in claim **1**, wherein said first means includes means for emitting said spectral lines of atoms in a pulsed fashion, and said second means includes means for generating said atomic vapor in a pulsed fashion, the pulse signals applied from said first and second means having a phase difference of 180° therebetween.

15. An apparaturs as claimed in claim **5**, wherein a first pulse voltage is applied to said first hollow cathode for emitting said spectral lines of atoms in a pulsed fashion, and a second pulse voltage is applied to said second hollow cathode for generating said atomic vapor in a pulsed fashion, said first and second pulse voltages having a phase difference of 180° therebetween.

16. An apparatus as claimed in claim **11**, wherein a first pulse voltage is applied to said first hollow cathode for emitting said spectral lines of atoms in a pulsed fashion, and a second pulse voltage is applied to said second hollow cathode for generating said atomic vapor in a pulsed fashion, said first and second pulse voltages having a phase difference of 180° therebetween.

* * * * *