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2,855,820

METHOD OF SPECTROSCOPIC GAS ANALYSIS

Filed June 10, 1955

2 Sheets-Sheet 1

FIG. 1.

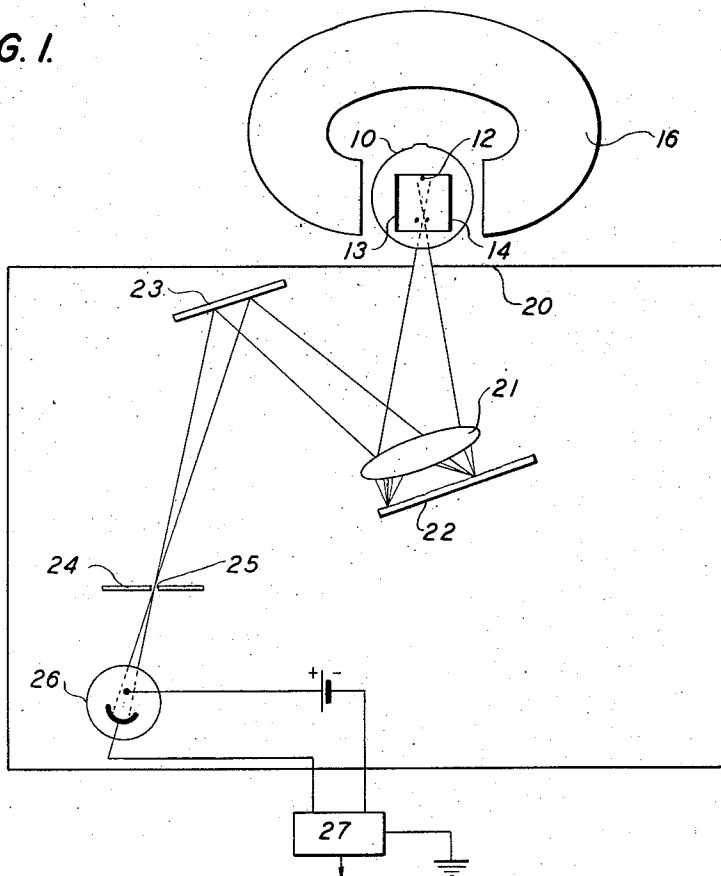
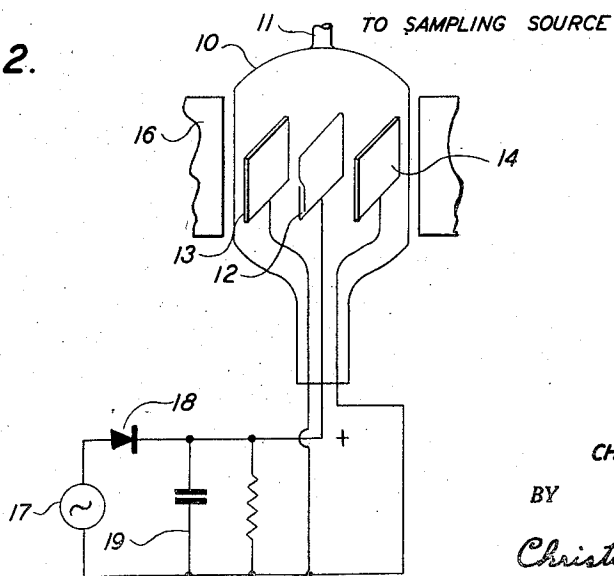


FIG. 2.



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FIG. 3.

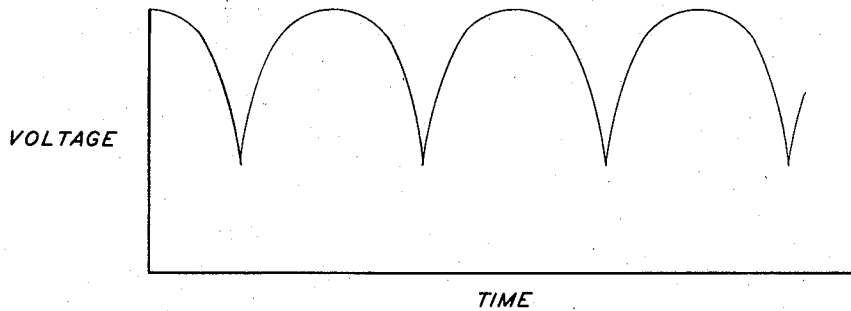
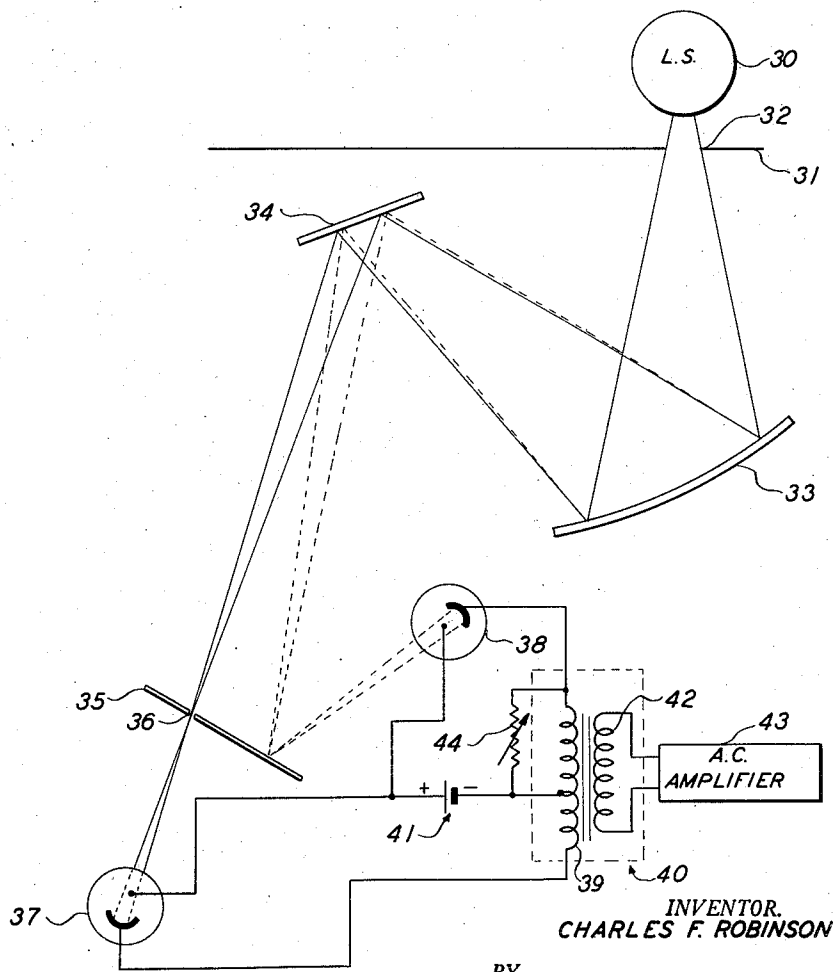


FIG. 4.



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METHOD OF SPECTROSCOPIC GAS ANALYSIS

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3 Claims. (Cl. 88—14)

This invention relates to spectroscopic analysis of gases and vapors and to apparatus for carrying out such analysis.

Ionization of gas may be produced in several ways as for example by electron bombardment. To accomplish ionization, a certain amount of work must be done at the expense of the kinetic energy of the bombarding electron. The amount of work, or the electron energy required to ionize a given molecule is expressed as the ionization potential or the ionization voltage of that molecule. For example, the ionization potential of O_2 is 15 volts. This means that the anode voltage of an electron "gun" employed to develop the bombarding electrons must be at least 15 volts before the electrons emitted will have sufficient energy to ionize any oxygen molecules with which they collide. When an electron collides with a gas atom with insufficient energy to produce ionization, an electron of the atom may be displaced to an energy level different from the one it normally occupies, absorbing a portion of the energy of the colliding electron in so doing. When the displaced electron "falls back" to its normal energy level it gives off the energy it absorbed in displacement in the form of electromagnetic radiation. All atoms have many characteristic discharge frequencies which form the well known line spectra of gases. The energy required to bring about this electron displacement and subsequent radiation is known as the excitation potential. Since it takes less energy to displace an electron into an excited energy level than it does to split-off the electron from the atom, it follows that the excitation potential of a given gas is lower than its ionization potential. Whereas the ionization potential of H_2 is 16 volts, its first excitation potential is only 11.57 volts.

The conventional emission spectrograph makes use of the characteristic discharge spectrum of various materials as a means of analyzing gaseous or solid mixtures. The present invention is directed primarily to the analysis of gases and emphasis is accordingly placed on such analysis. In a conventional emission spectrograph a D. C. or low frequency A. C. field is established between two spaced electrodes. A gas sample to be analyzed is introduced between the electrodes and the potential difference is raised above the first excitation potential and generally above the ionization potential of all of the gases suspected of being in the sample. By examining the spectrum of the resultant discharge radiation, the components of the sample can be detected from the appearance of the characteristic frequency lines. However, there are limitations on the scope of emission spectroscopy which can best be made apparent by an example, for instance, detection of traces of helium in other gases.

The problem of detecting extremely small traces of helium as a contamination in other gas has achieved major significance in recent years as a result of the ever increasing use of helium in leak detection. A widely practiced method of detecting leaks in closed vessels or systems is to evacuate the system and to analyze the gases evacuated from the system. By playing a stream of gas foreign

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to the atmosphere within the system over the exterior of the system, the existence and location of leaks can be ascertained by the appearance of such gas in the evacuating system. A recent improvement in leak detection techniques involves the generally reverse procedure of pressurizing the test vessel with a gas constituted in whole or in part of a constituent foreign to the atmosphere surrounding the vessel. By exploring the exterior surface of the vessel with a sampling probe connected to an analyzing system, leaks are detected by the appearance of such constituent in the atmosphere drawn into the probe and analytical instrument connected thereto.

Helium is possessed of several characteristics which make it practically the ideal gas for use as a tracer in leak detection in accordance with either of the methods outlined above. Its natural abundance in air is so low as to be insignificant. It is inert and relatively inexpensive. Moreover, helium resembles hydrogen in that it will leak from vessels which are substantially leakproof with respect to substantially all other gases except hydrogen and helium. This last mentioned property permits detection of leaks which, with respect to other gases, might remain latent until after the vessel had been in service.

Helium, however, in the comparatively small concentrations involved cannot be detected by means of emission spectroscopy as presently being used. The reasons why helium, in low concentrations cannot be detected spectroscopically with conventional instruments are explained as follows:

Helium has a high ionization potential, i. e. 24.5 volts, and a high first excitation potential, i. e. 21.12 volts. In a conventional gas discharge containing a mixture of gases having different ionization potentials, the emission spectra of gases having relatively high ionization potentials tend to be extinguished by a phenomenon known as "collision of the second kind." In such a system, excited atoms such as helium tend to transfer their energy of excitation to atoms of lower ionization potentials such as nitrogen (14.5 volts), oxygen (13.6 volts) or mercury (10.4 volts) in preference to releasing this energy by radiation of their characteristic frequencies. It is this effect which makes the spectroscopic detection of traces of helium in the presence of other gases difficult.

Another impediment to the spectroscopic analysis of helium is the existence of a so-called "metastable" state which the excited helium atom is likely to assume at about 20 volts bombardment energy. Without explaining the mechanism of the metastable state, suffice to say that it accentuates the normal tendency of a gas with a high ionization potential to lose energy to gases of lower ionization potential in preference to radiation. Further, and in the presence of other gases, helium is difficult to ionize because electrons tend to ionize first those gases of lower ionization potential. The foregoing facts, i. e. the tendency toward energy transfer in preference to radiation, the accentuation of this tendency in helium by the existence of a metastable state, and the difficulty of ionizing helium in the presence of gases of lower ionization potential, renders it virtually impossible to detect small amounts of helium by presently practiced spectroscopic means.

If the pressure of the gas being analyzed spectroscopically could be reduced to the point where the probability of collisions between helium atoms and other gaseous atoms or molecules was sufficiently small, the effects of the foregoing facts could be substantially reduced. However, with the conventional D. C. or low frequency A. C. spectroscopy, the pressure cannot be reduced to the desired extent because the mean free path of the electrons cannot be greater than the spacing between the electrodes. If it were otherwise, it would be impossible to obtain a self-sustaining discharge or ionization of the gases.

In U. S. Patent 2,670,649 issued to me on March 2, 1954, I disclosed a process for spectroscopic analysis of helium by means of a very high frequency discharge. I have now discovered that helium and other gases can be spectroscopically detected with a D. C. or low frequency discharge of the cold cathode type providing the pressure of the gas in the discharge space is lower than that at which the mean free path of the gas to be detected is equal to a major dimension of the discharge space. In a simple two-electrode discharge tube it is impossible to maintain a self-sustaining discharge at such low pressures, but it is possible to provide a certain three-electrode array which, in combination with an appropriate magnetic field, will permit such operation. This kind of cold cathode discharge has been used in ionization gauges for some time wherein the magnitude of the total discharge current which is the sum of the positive ion current to the cathode and the electron current from the same electrode is used as a measure of the pressure of gas present.

I have now found that such a cold cathode discharge can be utilized to permit the spectroscopic analysis even of helium, providing the pressure in the region of the electrodes is lower than that at which the mean free path of the helium ion or the ion of the gas to be measured is less than the spacing between these two electrodes.

In a preferred form of the invention and for the purpose of increasing the sensitivity of the spectroscopic analysis, the potential on the electrodes is modulated at such a frequency that the period of oscillation is long compared to the transit time of ions in the discharge. the modulating voltage is preferably unipolar and may, for example, vary between about 1000 and from 2000 to 3000 volts in the mentioned frequency range. It is important that this modulating voltage be maintained sufficiently high at all times to prevent the discharge from being extinguished in order to achieve stable operation at very low pressures.

By modulating the potential on the electrodes it is possible to detect the output of the associated spectroscope with a tuned amplifier thereby cancelling stray light, dark current and noise from the photometer.

If the invention is to be used for the detection of helium in leak detection, the optical system may be a fixed focal system and means may be associated with the output for signaling the appearance of helium in the discharge. If the apparatus is to be used for more complex analysis the optical system may be a variable focus system and recording means may be provided for recording the spectrum obtained. Fixed focus and variable focus optical systems are well known in the spectroscopic art.

The invention will be more clearly understood from the following detailed description taken in conjunction with the accompanying drawings, in which:

Fig. 1 is a schematic diagram of one form of apparatus for practicing the invention;

Fig. 2 is a diagram of a cold cathode discharge tube with means for modulating the potential on the electrodes;

Fig. 3 is a graph of the modulating potential wave; and

Fig. 4 is a schematic diagram of an optical system differing from that shown in Fig. 1.

Referring to Figs. 1 and 2 of the drawing, the apparatus shows a cold cathode discharge tube 10 having an inlet nipple 11 for connection to a source of gas to be analyzed. A cathode 12 is supported in the tube and in a preferred embodiment is formed as a split ring as illustrated. This permits spectroscopically viewing the discharge at a point between the split ends of the ring giving a maximum brilliance to the optical system. A pair of anodes 13 and 14 are supported on either side of the cathode, the tube being immersed at a magnetic field produced by a magnet 16. The magnetic field is parallel to the direction of electron travel between the cathode and anodes whereby the electrons are caused to

oscillate for a period of time between the two anodes before striking and discharging at the cathode.

As previously mentioned, the preferred form of the invention involves modulating the potential applied to the cathodes and anodes of the tube, and means are shown in Fig. 2 for accomplishing such modulation. The voltage source in this instance comprises an A. C. source 17 connected through a rectifier 18 and across a filter network 19. The output of the modulation source is connected between the cathode 12 and the two anodes 13 and 14, as illustrated. The A. C. output of the alternating current source 17 is rectified at 18 to produce a unipolar low frequency alternating field as shown in the graph of Fig. 3 in which time is the ordinate and voltage the abscissa. The frequency of alternation may be any frequency such that the period of oscillation is long compared to the transit time of ions in the discharge. Conveniently available line frequency is satisfactory.

The optical system as shown schematically in Fig. 1 includes an apertured shield 20, a lens 21, a diffraction grating 22, a reflecting mirror 23, a shield 24 with a resolving aperture 25, and a photocell 26. The inlet aperture in the shield 20 is aligned with the mid-point between the opposing ends of the split cathode 12 so that light from the most intense portion of the discharge passes through the inlet aperture. Admitted light passes through lens 21, is broken into its spectrum and reflected by the diffraction grating 22 back through the lens 21 and again reflected by mirror 23 in such a manner that the desired spectrum line is focused on the resolving aperture 25. The output of photocell 26 is, in a preferred embodiment, connected to a tuned amplifier 27, the output of which may be connected to any conventional detecting means.

It is important to note that although a modulated discharge is preferred, for reasons explained, the invention may be carried out with a steady D. C. discharge in which the voltage source connected between the cathode 12 and anodes 13 and 14 may be any D. C. source, such as a battery. In this event, the tuned amplifier may be replaced by any conventional D. C. amplifier. The term "low frequency discharge" as used throughout the specification and claims is intended to mean a discharge at any frequency including D. C. or zero frequency such that the period of oscillation is long compared to the transit time of ions in the discharge.

A typical instrument as illustrated schematically in Figs. 1 and 2 may have an anode spacing of from about one-half to about one inch and may be operated in a magnetic field of 1000 gauss or more, at a field strength in excess of about 1000 volts and at reduced pressures of from about 10^{-3} to about 10^{-8} mm. of Hg.

An alternative optical system is shown in Fig. 4. This system may be used to replace the optical system of Fig. 1, and for this reason a light source 30 is shown purely schematically. A shield 31 provides an inlet aperture 32 for admitting light to a concave diffraction grating 33 by means of which a spectrum is formed and is reflected to a mirror 34 to be focused on an apertured mirror 35. The mirror 35 has a resolving aperture 36 giving access to a first photocell 37. A second photocell 38 is positioned to pick up light reflected from the mirror 35. By focusing the wave length of interest on the resolving aperture 36 it may be sensed by the photocell 37 while any background or spurious radiation is picked up by the photocell 38. In this embodiment it is the ratio between the outputs of photocells 37 and 38 which is sensed, and any change in total light admitted to the optical system for any reason will not affect the measurement of the wave length of interest since the ratio between the output of photocells 37 and 38 will remain constant. However, any change in the absolute proportion of the component responsible for the wavelength of interest will result in a change in the relative output of photocells 37 and 38 and can thus be selectively detected.

A suitable detection circuit is shown schematically in the figure. The anodes of photocells 37, 38 are connected in opposition across primary 39 of a transformer 40. The cathodes of the two photocells are connected in common to the center tap of the primary through a battery 41. Secondary 42 of the transformer feeds the difference signal to an A. C. amplifier 43. A balancing resistor 44 may be connected as shown. The illustrated circuit for an A. C. system may obviously be modified for D. C. application by the simple and obvious expedient of chopping the D. C. output of the two photocells.

The advantages of a cold cathode type discharge for spectroscopic analysis, particularly of gases like helium which are difficult to analyze by this method, are substantial. A considerable reduction in cost as compared to either mass spectrometry or ultra-high frequency spectroscopy is realized by reason of the comparative simplicity of instrumentation. In addition, there is an important improvement in reliability since such a cold cathode discharge is self-sustaining over a much wider range of conditions than is a ultra-high frequency discharge, and the entire equipment is undamaged by being vented accidentally to atmospheric pressure.

I claim:

1. The method of detecting the presence of a component of a gas mixture which comprises introducing the gas mixture to a discharge space defined by two anodes on opposite sides of a cathode, maintaining the space at a pressure lower than that at which the mean free path of the component is equal to a major dimension of the discharge space, applying a low frequency voltage to the cathode to sustain a glow discharge, maintaining a magnetic field across the discharge space, and detecting the presence of a characteristic line of the spectrum of the component in the resultant radiation.

2. The method of detecting the presence of a com-

ponent of a gas mixture which comprises introducing the gas mixture to a discharge space defined by two anodes on opposite sides of a cathode, maintaining the space at a pressure lower than that at which the mean free path of the component is equal to a major dimension of the discharge space, applying a modulated low frequency unipolar voltage to the cathode to sustain a glow discharge, maintaining a magnetic field across the discharge space, and detecting the presence of a characteristic line of the spectrum of the component in the resultant radiation.

3. A method according to claim 2 wherein the period of oscillation of the modulated voltage is long compared to the transit time of ions in the discharge.

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