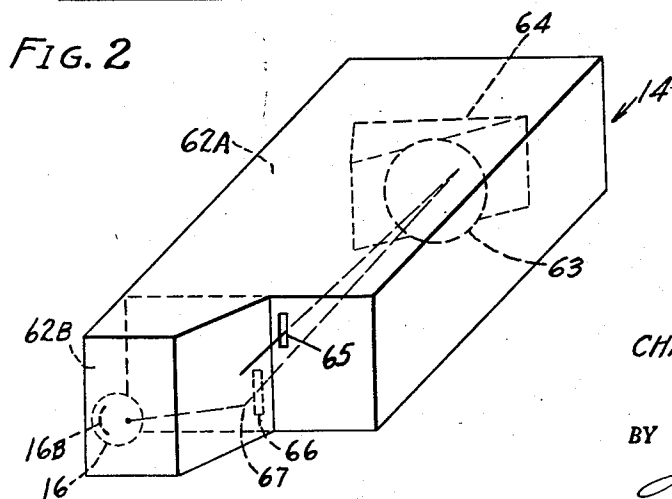
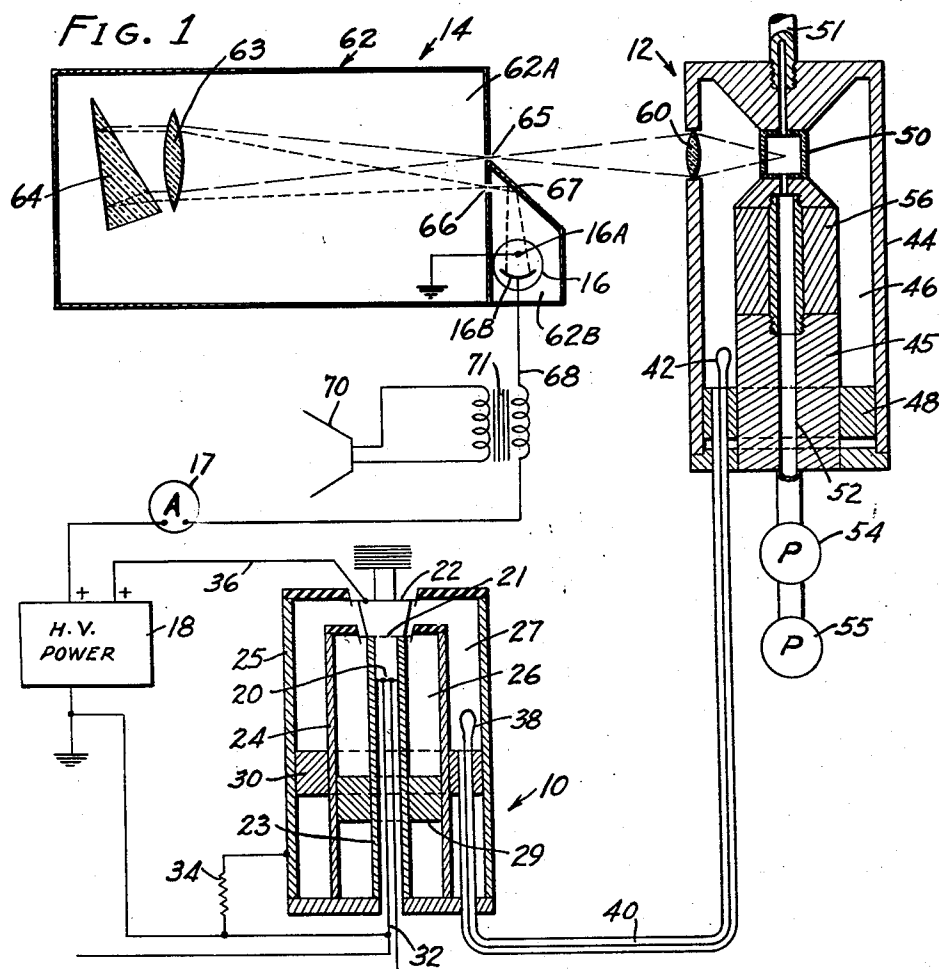


March 2, 1954

C. F. ROBINSON
SPECTROSCOPIC ANALYSIS OF A GAS MIXTURE EXCITED
BY A HIGH-FREQUENCY ELECTRIC FIELD
Filed June 4, 1949

2,670,649



CHARLES F. ROBINSON,
INVENTOR.

BY *James B. Christie*
ATTORNEY.

UNITED STATES PATENT OFFICE

2,670,649

SPECTROSCOPIC ANALYSIS OF A GAS MIXTURE EXCITED BY A HIGH-FREQUENCY ELECTRIC FIELD

Charles F. Robinson, Pasadena, Calif., assignor to Consolidated Engineering Corporation, Pasadena, Calif., a corporation of California

Application June 4, 1949, Serial No. 97,255

5 Claims. (Cl. 88—14)

1

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

2

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 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 more or less 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 leak proof 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 practiced. Accordingly, more complex analytical instruments are 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 factors, i. e. the tendency towards 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 factors could be substantially reduced. However, with the conventional D. C. spectroscope, the pressure cannot be reduced appreciably because the mean free path of electrons cannot be greater than the spacing between the electrodes since, if it were otherwise, it would be impossible to obtain a self-sustaining discharge or ionization of the gases.

I have now found that ultra-high frequency discharges may be maintained under conditions of reduced pressure in which the electron mean free path is much larger than the inter-electrode spacing. With such ultra-high frequency, it is possible to maintain a self-sustaining discharge with only traces of gas present between the electrodes, the discharge being maintained largely by secondary emission alone. Hence it is possible to maintain a sufficiently low pressure so that the probability of collision between helium and other gas molecules is so low as to permit spectrum emission from excited helium. This ultra-high frequency discharge may be maintained under pressures in which collision of the second kind, as well as all other collision processes, are highly improbable. This in turn means that helium will not experience interference from other gases in such a discharge. Accordingly, I have developed an emission spectroscope employing ultra-high frequency discharges which has a sensitivity competitive with other analytical instruments and can be built for a much smaller cost.

In addition to overcoming the factors which prevent helium detection by D. C. emission spectroscopy, my invention has other advantages. I have found that helium ions receive essentially no energy from a high frequency field as they do from a D. C. field, hence, the tendency of helium ions to drift towards the electrodes in a D. C. field is eliminated and there is, under favorable conditions, no migration of the helium except motion due to thermal energies. Additionally, at high frequencies there is developed a so-called space charge trap (net negative space charge), since there are more electrons in the region between the electrodes than there are gaseous ions. This space charge trap further tends

to prevent migration of helium ions towards the electrodes.

Accordingly, the present invention contemplates the method of detecting helium in the presence of other gases which involves subjecting the gas mixture at very low pressures to an ultra-high frequency field, obtaining the emission spectra of the gases subjected to the high frequency field and ascertaining the presence of helium by examination of the spectrum. The invention also contemplates apparatus for carrying out the aforementioned method which comprises a discharge cavity wherein the gas mixture may be subjected at low pressures to a high frequency field, a window in the discharge cavity and an associated optical system and photoelectric or other means for detecting the presence of helium in the gases subjected to the discharge.

Briefly, the apparatus of the invention comprises the combination of an RF oscillator, a discharge cavity containing a discharge bottle through which the gas sample is drawn, an optical system and means for indicating the presence of one or more gases in the gas sample. If the invention is to be used for the detection of helium in leak detection, the optical system may be a fixed focus system and photoelectric means may be coupled with indicating means for signalling the presence of helium in the gas sample. If the apparatus of the invention is to be used for a 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 may be more clearly understood with reference to the following detailed description taken in conjunction with the accompanying drawing in which:

Fig. 1 is a diagrammatic illustration of a fixed focus type of apparatus, in accordance with the invention; and

Fig. 2 is a perspective view of the optical system showing the means of focussing a single frequency on photoelectric detection means.

Referring to the drawing, the apparatus includes an RF oscillator 10 of the cavity resonator type, a discharge cavity 12, an optical system 14, a photocell 16, indicating means 17 and a power supply 18.

Oscillator 10 is a conventional RF oscillator comprising a cathode 20, a grid 21 and an anode or plate 22 mounted respectively in the ends of concentric tubes 23, 24, 25. Conveniently this assembly comprises a triode vacuum tube of the "lighthouse" type, of which many forms are commercially available, mounted in the cavity tubes 23, 24, 25 according to well known means. Alternatively the vacuum tube may be a "lighthouse tetrode" of a type commercially available. The tubes 23, 24, 25 form an annular grid cavity 26 and an annular plate cavity 27. Tuning plugs 29, 30 provide means for tuning the grid and plate cavities respectively. Heating wires 32 are carried through the axial tube 23 to the cathode 20 and a grid resistor 34 is connected between the grid 21 and the cathode 20 according to methods well known in the construction of RF oscillators.

The high voltage power supply 18 includes a source of voltage which may be unregulated, of suitable voltage and current, which may be approximately 800 volts and 100 milliamperes and which is connected through a lead 36 to the

plate 22 of the oscillator. A coupling loop 38 is mounted in the plate cavity 27 and is connected by means of a coaxial cable 40 mounted through the tuning plug 30 to the discharge cavity 12. This loop is for the purpose of abstracting RF power from the oscillator and may be replaced by a capacitive pickup or other well known and conventional means.

The discharge cavity 12 includes a tubular housing 44 having a coaxial central column 45 forming an annular resonant cavity 46. A tuning plug 48 provides means for tuning the cavity 46. A coupling loop 42 is mounted in the cavity on the end of the coaxial cable 40 which projects through the tuning plug 48. A space is provided between the upper end of column 45 and the top of the discharge cavity in which is mounted an axially perforated glass discharge bottle 50. The bottle 50 is connected through a passageway 51 in the top of the discharge cavity to a source of gas to be analyzed, say a sampling probe in a leak detector, and through a coaxial passageway 52 in the column 45 to an evacuating system which may include pumps 54, 55. The central column 45 is preferably spring-loaded within the housing 44 to seal the discharge bottle. The desirability of the glass bottle will vary from one application to another depending on the nature of the gas to be analyzed and on the relative convenience of maintaining vacuum seals around the glass bottle or the cavity itself. Usually the glass bottle will be convenient but it is not necessary to the invention.

The discharge cavity 12, as shown, is provided with a permanent magnet 56 mounted in the central column 45. I have found that magnet 56 serves to increase the electron density in the region in which the discharge bottle is located. However, the magnet is not a necessary feature of the invention, the apparatus operating entirely satisfactorily without it. A lens 60 is mounted in a wall of housing 44 in alignment with the discharge bottle 50.

The optical system 14 includes a light-tight box 62 comprising two compartments 62A, 62B. A lens 63 and a back-silvered prism 64 are enclosed in compartment 62A and the photocell 16 in compartment 62B. The box is mounted in line with lens 60 in the discharge cavity. A first slit 65 in the outer face of the box opens into compartment 62A and admits radiation passing through lens 60 into this compartment. The radiation passes through lens 63 through prism 64, and is reflected back through prism 64 and lens 63 to a second slit 66 opening from the compartment 62A into the compartment 62B. A mirror 67 deflects the rays passing through the second slit to the photocell 16. The photocell 16 is conveniently a conventional photomultiplier tube.

The cathode 16A of the photocell is grounded and the anode 16B is connected through lead 68 to the high voltage power supply 18. This power supply in the illustrated embodiment includes a source of 1000 volt 1 milliamperere current preferably 1% regulated and limited to 1.5 milliamperes maximum current which is supplied through line 68 to the anode 16B of the photocell. An ammeter 17 connected in series in line 68, indicates the appearance of helium in the gas sample by signaling the periods of conductivity of the photocell.

A further refinement in the apparatus includes a speaker 70 connected through a transformer 71 to line 68. By including a small (say 5%) A. C.

component in the voltage source supplying line 68 and the photocell, the speaker 70 will emit an audible signal when the photocell conducts. Since the arrangement is such that the photocell will conduct only when helium appears in the discharge bottle, the signal will be emitted from the speaker only at such time.

The optical system 14 is a fixed focus system. That is, the prism 64 is oriented within the box 62 so that only a selected characteristic frequency of the helium spectrum will be passed through the second slit 66 and be reflected by mirror 67 onto the photocell.

The operation of the apparatus is as follows: Power is supplied to the RF oscillator wherein a signal of from about 250 to about 750 megacycles is developed. This oscillating current in the plate cavity of the oscillator induces a like oscillating current in the coupling loop disposed in the cavity. This induced current flowing in the companion coupling loop in the discharge cavity sets the discharge cavity into oscillation, which gives rise to a high frequency field across the gap occupied by the discharge bottle.

A gas to be analyzed is drawn into or through the discharge bottle at a pressure of approximately 10^{-3} to 10^{-4} mm. Hg. It is usually necessary to admit a burst of gas to raise the pressure initially to perhaps $2-3 \times 10^{-2}$ mm., after which the pressure may be reduced to the lower value without extinguishing the discharge. Although the discharge may be maintained at pressures as high as 1 mm. Hg, the advantages of this type of excitation are not realized at such high pressures. In order to minimize intermolecular and ion-molecular collisions, it is desirable to maintain the pressure as low as possible. Since the pressure is very low, the chance of an excited helium atom undergoing collisions with other atoms and subsequent energy transfer is reduced appreciably and helium radiation is obtained. The light from the gas discharge is admitted to the optical system wherein the prism and lens arrangement is such as to focus a single one of the characteristics helium frequency lines on the mirror and photocell. When there is no helium in the gas passing through the discharge bottle, no light will fall on the phototube. When helium is present, the phototube will conduct, this state being registered by deflection of the ammeter or an audible sound from the speaker.

The frequency range in which the method and apparatus of the invention are effective in detecting traces of helium in other gases has a lower limit determined by the point at which oscillatory electron travel is lost. It has been determined by experiment that the lower limit for practical purposes is about 200 megacycles. Lower frequencies, say of about 100 megacycles, may be used but tend to require discharge chambers of excessive volume. As the frequency is increased, the power requirements likewise increase in order to maintain the necessary kinetic energy for ionization of helium. The relationship can be expressed mathematically as follows:

$$T_{\max} = \frac{q^2 E_0^2}{2mw^2} (1 + |\cos \theta|)^2$$

where:

T = kinetic energy.

$E = E_0 \sin (wt + \theta)$.

q = charge on particle.

m = mass of particle, generally an electron.

$w = 2 \pi$ (frequency in cycles/sec.).

To maintain T at a given minimum value for discharge, any increase in w must be accompanied by an increase in E_0 . For this reason, 1000 megacycles appears to be a practical upper frequency limit.

The operating pressure, i. e. the gas pressure within the discharge bottle is selected so that the mean free path (MFP) of helium ions will exceed the largest internal dimension of the discharge bottle. The MFP of helium at a pressure of 1 mm. of mercury is approximately .18 cm.; at 10^{-3} mm. about 20 cm. and at 10^{-4} mm. of Hg about 200 cm. Selecting a discharge bottle of any given size, say for example 6.0 cm. inside dimensions, a pressure of less than about 3×10^{-3} mm. Hg is employed.

By operating at or below a pressure at which the MFP of helium ions exceeds the inside dimension of the discharge bottle, the probability of inter-ionic collisions is small. In the high frequency field employed, however, the helium ion oscillates within the field and is not lost by migration. In the conventional D. C. discharge the ionic MFP must be considerably smaller than the spacing between the electrodes to achieve a self-sustaining discharge. This requires operation at pressures where inter-ionic collisions effectively extinguish or suppress the helium spectrum as above described.

Although the invention has been described with particular reference to analysis of helium, it is not so limited, the emphasis on helium being because of its importance in leak detection technology and the inability to detect small amounts of this gas by conventional spectroscopic means. Any gaseous mixture can be analyzed in accordance with the invention. Furthermore, the particular apparatus shown is not essential. Other forms of oscillators, discharge cavities etc. may be used provided only that the requirements of frequency and pressure can be met.

I claim:

1. In a method for analyzing a gas mixture which involves producing radiation to be spectroscopically analyzed, the improvement which comprises producing in a discharge chamber in which the mixture is contained a pressure less than that at which the mean free path of gas ions produced in the mixture equals the greatest dimension of the chamber, disposing the gas in the chamber at said pressure in an alternating electrical field having a frequency substantially in excess of 100 megacycles whereby radiation is produced and spectroscopically analyzing said radiation to determine spectral components of the mixture.

2. In spectroscopic analysis, the improvement which comprises passing a stream of gas through a chamber at a pressure below that at which the mean free path of helium equals the maximum dimension of the chamber, producing in the gas in the chamber at said pressure an alternating electrical field having a frequency of about 200 megacycles to about 1000 megacycles, thereby producing a gas discharge having a spectrum, spectroscopically analyzing the spectrum and examining the analyzed spectrum for lines characteristic of helium.

3. In a method of analyzing a gas mixture which involves producing radiation to be spectroscopically analyzed, the improvement which comprises producing in a discharge chamber in which the mixture is contained a pressure less than that at which the mean free path of gas

ions produced in the mixture equals the greatest dimension of the chamber, disposing the gas in the chamber at said pressure in an ultra high frequency alternating electrical field whereby radiation is produced and spectroscopically analyzing said radiation to determine spectral components of the mixture.

4. In a method for analyzing a gas mixture for helium which involves producing radiation to be spectroscopically analyzed, the improvement which comprises producing in a discharge chamber in which the mixture is contained a pressure less than that at which the mean free path of helium ions equals the largest inside dimension of the chamber containing the mixture, establishing in the chamber an alternating electrical field having a frequency of from about 200 megacycles to about 1000 megacycles and of a field strength sufficient to impart at least 25 electron volts to an electron whereby radiation is produced and spectroscopically analyzing the radiation to determine the presence of spectral lines characteristic of helium.

5. In a method for analyzing a gas mixture which involves producing radiation to be spectroscopically analyzed, the improvement which comprises detecting helium in the mixture by creating in the mixture at a pressure below that at which the mean free path of a helium ion is equal to the greatest dimension of the chamber an alternating electrical field having a frequency of at least 200 megacycles and thereby producing an electrical discharge accompanied by radiation, and spectroscopically analyzing that radiation to determine the presence of lines characteristic of the helium spectrum.

CHARLES F. ROBINSON.

References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
1,871,226	Skala	Aug. 9, 1932
2,047,930	Linder	July 14, 1936
2,121,460	Waters	June 21, 1938
2,189,279	Bitner	Feb. 6, 1940
2,285,622	Slepián	June 9, 1942
2,333,762	Bertrand	Nov. 9, 1943
2,344,719	Nusbaum et al.	Mar. 21, 1944
2,395,850	Colman	Mar. 5, 1946
2,486,199	Nier	Oct. 25, 1949
2,525,624	Stahl et al.	Oct. 10, 1950
2,538,062	Touvet	Jan. 16, 1951
2,559,688	Touvet	July 10, 1951

FOREIGN PATENTS

Number	Country	Date
588,844	Great Britain	June 4, 1947

OTHER REFERENCES

Spectroscopy. Text by Baly; vol. II, page 200. Published by Longmans, Green & Co., 55 Fifth Ave., New York, 1927.

Ricerche Spettroscopiche; vol. 1, February 1946, No. 7, pages 204 through 209 and 3 plates between pages 204 and 205. Printed in Vatican City Laboratories Astrofisico.

Experimental Spectroscopy by Sawyer, pages 25, 26 and 27. Published by Prentice-Hall Inc., New York, 1946.

Practical Spectroscopy, Harrison et al., pages 190, 191 and 192; 1948. Published by Prentice-Hall Inc., New York, New York.