

March 23, 1965

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3,174,393

EXCITATION SOURCE FOR EMISSION SPECTROSCOPY

Filed June 29, 1961

3 Sheets-Sheet 2

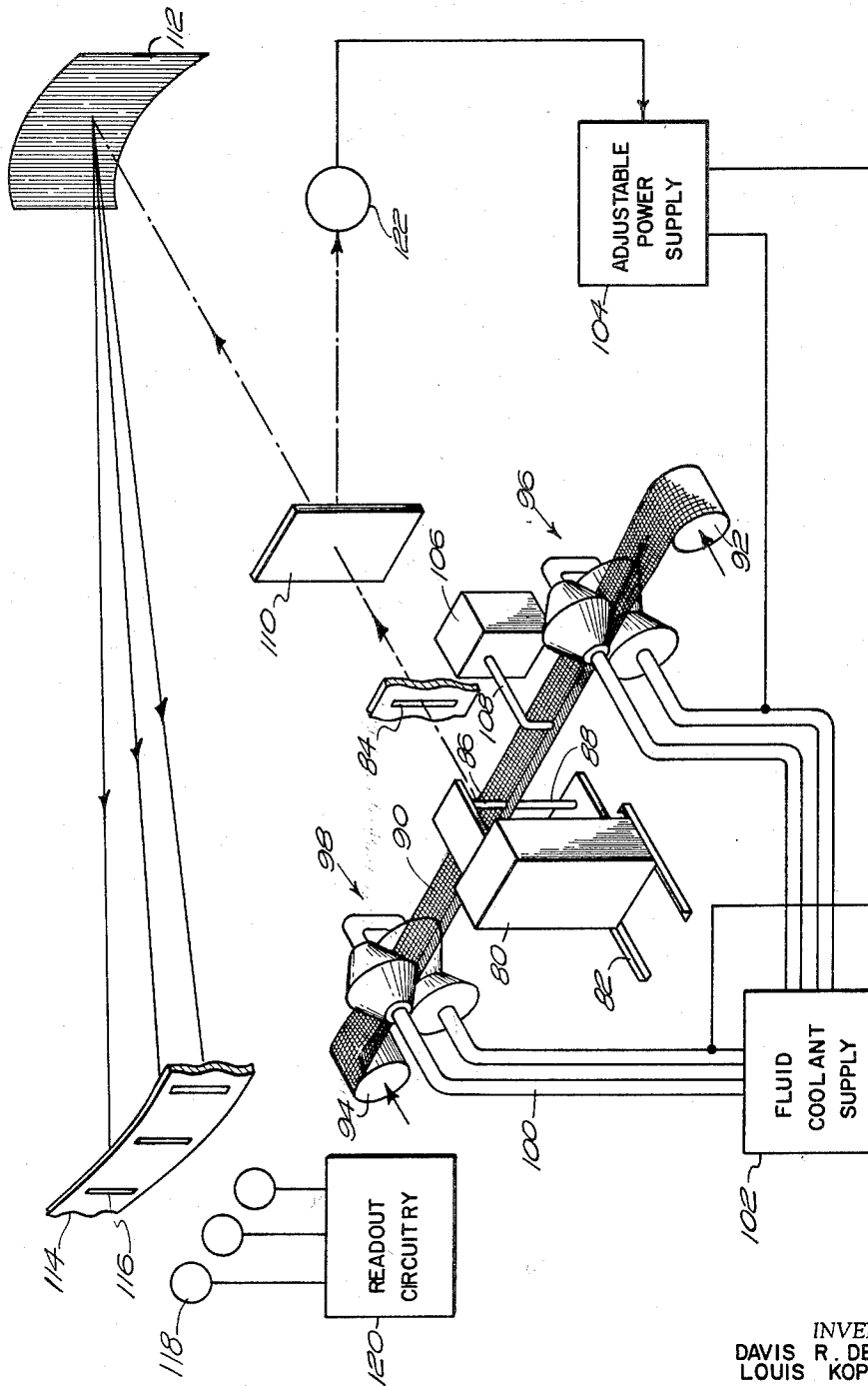


FIG. 6

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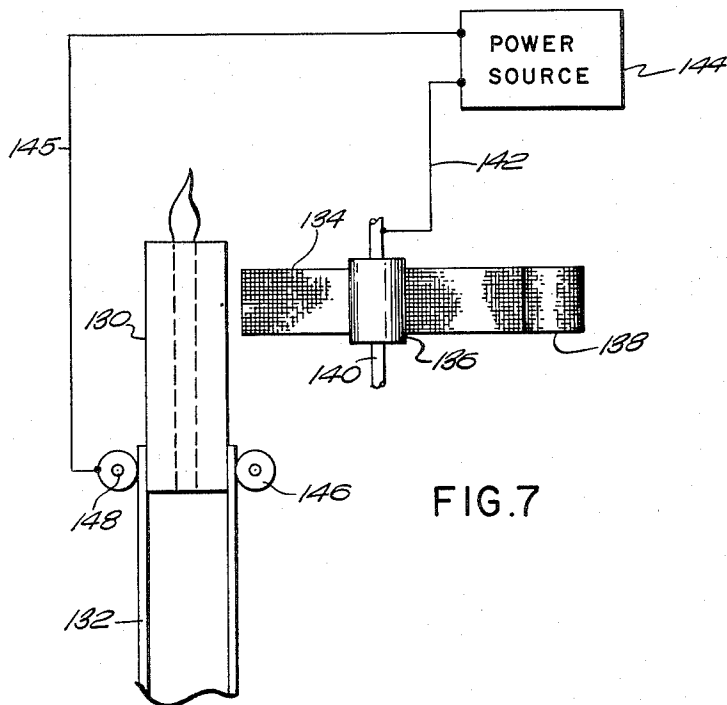


FIG. 7

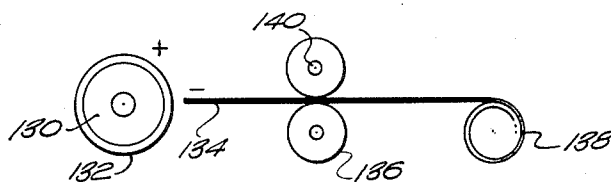


FIG. 8

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EXCITATION SOURCE FOR EMISSION SPECTROSCOPY

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15 Claims. (Cl. 83-14)

This invention relates in general to emission spectroscopy and more particularly concerns the use of graphite cloth as a source of excitation of emission spectra in spectrochemical analysis.

Emission spectroscopy is recognized as an extremely useful method for analyzing specimens both qualitatively and quantitatively in that the technique is relatively quick and the apparatus used in quite sensitive. However, practical applications of emission spectroscopy have been hampered to some extent because the range of operation of existing instruments is somewhat limited. The utility of flame photometers, for example, is restricted because the excitation energies from the flame are too low for many elements. An ordinary air-gas flame of the Bunsen type produces a temperature of about 1700° C. which is sufficient to excite only about a dozen elements, chiefly the alkali and alkaline earth metals. Although mixtures of hydrogen or acetylene with oxygen produce a much hotter flame (about 3050° C.), with correspondingly greater excitation, the temperature level is such as to excite the spectra of only half the metals and a few non-metals. While cyanogen-oxygen flames are capable of producing temperatures over 4500° C., the complications in handling the gases and venting the combustion products negate the basic simplicity of flame photometry.

Other radiation generating sources such as arcs, sparks and discharge tubes are efficient within certain limits but are generally lacking in flexibility. Arcs, for instance, produce a rich spectrum but satisfactory reproducibility is difficult to achieve, mainly because the zone of burning is not distributed over the whole area of the electrode tip with the result that the arc has a certain amount of instability. While the condensed spark is superior to the arc in reproducibility and versatility, it is lacking in sensitivity and its use is not recommended when the concentration of the analyzed element is below 0.1%.

Accordingly, it is an object of the present invention to provide an improved source for excitation of emission spectra in spectroscopic instruments.

Another object of this invention is to provide a spectrochemical analyzer which is capable of generating a wide range of temperatures.

Yet another object of this invention is to provide a source for spectral excitation that is easily controlled, possesses good reproducibility characteristics and which may be used independently or in conjunction with conventional excitation sources.

More particularly, this invention features a spectroscopic instrument in which graphite fabric woven or felted, serves as a source for excitation of emission spectra. The graphite material is capable of converting applied electrical energy into thermal energy with high efficiency and may be utilized to provide the necessary excitation by itself or may be energized in conjunction with a conventional source of excitation such as a flame in a flame photometer. In addition to its primary function as a

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source of excitation, the graphite material may also be employed to support the specimen in a spectrometer. Still further, the material may serve as an electrode in an arcing flame photometer.

But these and other features of the invention, along with further objects and advantages thereof, will become more readily apparent from the following detailed description taken in connection with the accompanying drawings in which:

FIG. 1 is a partly mechanical, partly electrical assembly and schematic view of a flame photometer embodying the present invention,

FIG. 2 is a perspective view of the graphite cloth dome shown in FIG. 1,

FIG. 3 is a view in perspective showing another arrangement for embodying graphite cloth in a flame photometer,

FIG. 4 is a perspective showing the underside of the FIG. 3 device,

FIG. 5 is a view in perspective showing multiple layers of mesh graphite cloth forming a head assembly for a flame photometer,

FIG. 6 is a view partly perspective and partly schematic showing the invention embodied in a direct reading spectrometer,

FIG. 7 is a view in side elevation, partly in section and somewhat diagrammatic showing the invention as applied to an arcing flame photometer, and,

FIG. 8 is a top plan view of the FIG. 7 embodiment.

Referring now to the drawings generally, there are illustrated several different emission type spectroscopic instruments, each adapted to employ a conventional source of thermal excitation as well as electrically energizable graphite fabric. The graphite cloth components featured in this invention are fabricated from woven or felted graphite material sold commercially under the trade designation "Graphite Cloth" by the National Carbon Company. The material is formed from fibers of high purity graphitic carbon having a tensile strength in the 50,000 to 100,000 p.s.i. range and characterized by high thermal conductivity and good electrical conductivity. The graphite fibers may be produced by processing carbonaceous materials at temperatures up to 5400° F. Typically, such fibers are composed of approximately 0.04% ash composed principally of magnesium and aluminum with traces of calcium, iron, manganese, silicon, boron, copper, nickel and sodium. The material sublimates at approximately 6600° F. (3650° C.) without melting.

The filaments have an average diameter ranging from 0.00005 to 0.001 inch. The fabric has a thread count per inch ranging from 20 to 30, a gage ranging from 0.01 to 0.04 and a filament count per ply ranging from 1 to 2000. The woven fabric is quite supple but can be provided with good lateral stability by forming a lamination composed of woven and felted graphite fabrics.

The graphite cloth displays many desirable attributes that make it particularly useful in spectroscopic applications. For example, the fabric is not wet by most molten metals and is resistant to practically all corrosives over a wide temperature range. The fabric is easily handled and its strength increases with temperature. Although the material oxidizes in air at temperature over 600° F., the rate of oxidation is so slight that it can be disregarded for all practical purposes.

Referring now more particularly to FIGS. 1 and 2, there is illustrated a flame photometer in which a hollow dome 10 of woven graphite cloth has been mounted on the top

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of a burner tube 12. In practice, the burner tube is provided with a bottom inlet connection 14 for introducing a combustible gas and a side inlet connection 16 for the introduction of an aerosol mixture. The gas and aerosol combine within the tube and, when ignited, the water or other solvent in the aerosol is vaporized, leaving minute particles of dry salt. The heat of the flame causes the dry salt to vaporize also, and part or all of the gaseous molecules are progressively dissociated to give neutral atoms which are the potentially emitting species.

Some of the free metal atoms unite with other radicals or atoms present in the flame gases. The vapors of the neutral metal atoms, or of the molecules containing the metal atom, are then excited by the thermal energy of the flame. Ionization of the neutral atoms may also occur to some extent. From the excited levels of the atom, molecule or ion, a reversion takes place to the ground state. When this reversion occurs, energy in the form of radiation is liberated. Since the energy of the atom or molecule exists in a discrete integral number of levels, a whole series of radiations, each with a distinct wavelength, may result, corresponding to transitions between the various levels. Such radiations form an emission spectrum that is characteristic of the atoms and molecules.

However, as previously indicated, the degree of excitation required to produce an emission spectrum varies quite widely depending upon the molecular and atomic structure of a particular substance and it is therefore desirable that the instrument be capable of producing sufficient thermal energy to excite as wide a range of elements as possible. To this end the dome 10 of graphite cloth has been incorporated into the flame photometer. This dome generally encompasses the flame issuing from the tube 12 and may be energized or not depending upon the particular substance being analyzed. The dome 10 is a wedge shaped affair and is truncated across the top to provide a normal outlet for the flame. The dome may be connected by its base to the burner tube 12 by means of an annular bracket 18. Electrical connections are made through carbon elements 20 and 22 both of which have been formed with a central passage 24 and 26 to accommodate a flow of a suitable cooling medium such as water. The two carbon elements 20 and 22 are connected by leads 28 and 30 to a variable power source 32 which is also connected to a detecting element such as a photo cell 34.

Typically, an array of filters 36 is mounted on a rotatable disc 38, the indexed position of which is controlled by a selector 40. With the selected filter in position, the detector 34 will respond according to the intensity of the particular wavelength passed by the filter. A galvanometer 40 or other suitable instrument, will provide a visual display of the detector output.

In the event that the temperature of the flame is too low to excite the material under analysis, the graphite dome 10 may be energized and the temperature raised to any desired level below the sublimation point of the cloth.

In the event that the graphite cloth is to serve as the sole source of thermal energy, the inlet connection 14 will be disconnected from the combustible gas supply and coupled to a supply of one of the noble gases such as argon, or a stable, non-oxidizing gas such as CO₂ or N₂. This gas will thus serve as a carrier for the aerosol mixture.

In FIGS. 3 and 4 there is illustrated a modification of the apparatus shown in FIGS. 1 and 2. In this instance, the dome assembly has been replaced by a fence 50 of graphite cloth in strip form. The fence 50 surrounds an opening 52 formed in a platform 54 which supports the fence, a number of carbon rollers 56 and two spools 58 of graphite cloth, one for feed and one for take-up. The platform 54 is mounted on top of the burner tube 12 by means of an annular bracket 60 attached to the underside of the platform as shown in FIG. 4. All of the rollers 56 are provided with cooling tubes 62 and electrical connections preferably should be made through the carbon rollers 56 adjacent to the spools so that the entire section

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of cloth that forms the fence 50 will be energized.

As in the principal embodiment, the graphite cloth fence may be used alone or in conjunction with a combustible gas. In either event, the aerosol and gas mixture will rise up through the burner tube and pass out the opening 52. There the heat generated by the cloth will excite the elements in the aerosol mixture causing an emission of a spectrum characteristic of the elements contained therein.

In FIG. 5, there is shown an attachment for a burner in a flame photometer wherein the flame or inert gas and aerosol mixture are passed through multiple layers of graphite cloth to provide a gradient increase in thermal excitation of the flame. The attachment includes a triangular platform 70 having a central aperture 71 for the passage of gas. At each corner of the platform there is an upright stack of tubular carbon elements 72, each stack provided with a tube 74 for a cooling medium. Three triangular sections 76 of mesh graphite material are mounted in spaced relation between the upright stacks and directly over the aperture 71. As before, appropriate electrical connections may be made where convenient so that each section 76 may be energized over its entire area.

Referring now to FIG. 6, there is illustrated a direct reading spectrometer in which the source of thermal excitation is provided either by an electrical arc or by a belt of graphite cloth or by both. The apparatus is organized about an electrical arc generator 80 which is mounted on tracks 82 for horizontal adjustment of the arc, to or away from a slit 84. The arc generator 80 includes a pair of coaxial electrodes 86, 88 spaced slightly from one another to define a gap through which a belt 90 of graphite cloth is stretched. The belt 90 may be fed from one spool 92 and wound up on another spool 94. Two sets of carbon rollers 96, 98 are provided to support the belt on either side of the arc generator 80. Each roller set is composed of a lower roller and an upper roller with the lower roller being tapered inwardly toward its center to form a roller with a restricted midsection. The upper roller is tapered outwardly towards its center portion so as to mate with the lower roller. With this configuration of the rollers, the section of the belt 90 extending between the two sets of rollers will assume a longitudinal trough in which the specimen to be analyzed may be carried. Cooling tubes 100 pass through the axes of the several rollers and are connected to a coolant supply station 102. The tubes 100 also serve as electrical conductors between the rollers 96, 98, the graphite cloth belt 90 and an adjustable power supply 104. The particular substance which is to be analyzed may be manually deposited in the trough of the belt or, if in liquid form, may be metered onto the belt from a dispensing station 106 through a discharge tube 108.

As will be readily understood, the specimen will be carried by the belt into the gap between the electrodes 86, 88. When the specimen has reached this position, either the arc generator 80 or the belt 90 or both will be energized as desired. The radiation emitted by the excited specimen will pass through the slit 84, a beam splitter 110 and against an arcuate reflective grating 112. From the grating 112 the light from the excited specimen will be diffused into a spectrum and directed against a curved screen 114 having a series of slits 116 formed therein. An array of photodetectors 118 is located behind the screen 114 and responds according to the character and intensity of the spectrum. The output of the photodetectors may then be fed a suitable readout system 120 which will present visual information as to the ingredients of the specimen.

Associated with the spectrometer is a feedback system for maintaining the thermal output of the belt 90 at a constant level. The primary component of the feedback is a temperature controlled pyrometer 122 which is located in the path of a beam divided from the main beam by the beam splitter 110. The output of the pyrometer is fed to the adjustable power supply 104 and the two

components cooperate to automatically regulate the thermal excitation of the specimen.

A further modification of the invention is shown in FIGS. 7 and 8 and concerns the application of graphite cloth in an arcing flame photometer. In this embodiment a graphite tubular rod 130 extends coaxially from the top of a burner tube 132 through which an aerosol mixture is fed along with a combustible or inert gas. The combined aerosol and gas pass up through the passage in the rod 130 into the atmosphere where a resulting flame will provide a spectral emission.

In order to increase the excitation of the atoms and molecules of the specimen under analysis and present in the flame, an electrical arc may be introduced to heat the rod 130 to temperatures above those available from chemical combustion. The arc is formed between the rod, which may serve as the cathode, and the free end of a belt 134 of graphite cloth, which may serve as the anode. The belt end is spaced slightly from the side of the rod to define a gap between the two conducting elements. The belt of graphite cloth may be fed through a pair of carbon rollers 136 from a supply spool 138. A cooling conduit 140 passes through each of the rollers 136 and serves as an electrical conductor between a lead 142 from a power source 144 and the graphite material 134 through the roller 136. A second lead 145 is connected to a carbon annulus 146 mounted at the top of the tube 132 and also is provided with a cooling tube 148.

It will be appreciated that the incorporation of graphite cloth into spectroscopic instruments greatly enhances the utility of the instruments and widens their scope of operation. The graphite cloth is relatively inexpensive and may be added to existing devices with very little modification. The fabric may be conveniently energized to any selected black body temperature by merely altering the flow of electrical energy. Reproducibility characteristics are excellent since all of the variable factors may be precisely controlled.

While the invention has been described with particular reference to the illustrated embodiments, it will be understood that many modifications may be made by those skilled in the art without departing from the scope and spirit of the invention. It will also be understood that all matters contained in the above description or illustrated in the accompanying drawings shall be interpreted as illustrative and not in a limiting sense.

Having thus described the invention, what we claim and desire to obtain by Letters Patent of the United States is:

1. A spectroscopic apparatus, comprising a section of graphite fabric, means for locating a specimen in close proximity to said fabric, an electrical power source, conductive elements for forming a circuit between said power source and said fabric, said fabric when energized being adapted to convert electrical energy from said source into thermal energy for spectrally exciting said specimen and means for dispersing the light emitted from the excited specimen into its component wave lengths.

2. In combination with a flame photometer in which an ignited combustible gas serves as a spectral excitation source for a specimen included in the gas, an alternate source of excitation, comprising a section of graphite cloth located in close proximity to the ignited gas, an electrical power source and conductive elements for forming a circuit between said power source and said fabric, said fabric when energized being adapted to convert electrical energy from said source into thermal energy for spectrally exciting said specimen.

3. A flame photometer, comprising a tubular burner body having an outlet formed therein, means for introducing a combustible gas and a specimen into said body for discharge through said outlet, said gas when ignited serving as one source of spectral excitation for said specimen, graphite cloth located in close proximity to said outlet, an electrical power source, conductive elements

for forming a circuit between said source and said graphite cloth, said graphite cloth when energized serving as another source of spectral excitation for said specimen and optical means for analyzing according to wavelength the light emitted by the excited specimen.

4. A flame photometer according to claim 3 wherein said graphite cloth is in the form of a hollow dome and mounted over said outlet.

5. A flame photometer according to claim 3 wherein said graphite cloth comprises a length of graphite cloth extending about the edges of said outlet.

6. A flame photometer according to claim 3, wherein said graphite cloth comprises a plurality of graphite cloth sections mounted in parallel spaced array over said outlet.

7. Spectroscopic apparatus, comprising a pair of electrodes spaced from one another to define a gap therebetween, means for positioning a specimen within said gap, a first electrical power source connected to said electrodes and adapted to generate an electrical arc across said gap, said arc serving as one source of spectral excitation for said specimen, of graphite cloth located in close proximity to said electrodes, a second electrical power source connected to said graphite cloth, said graphite cloth when energized serving as another source of spectral excitation of said specimen and optical means for analyzing according to wavelength the light emitted by the excited specimen.

8. Spectroscopic apparatus according to claim 7 wherein said graphite cloth is in the form of a belt extending through said gap and adapted to support said specimen.

9. Spectroscopic apparatus according to claim 8 including holder elements for supporting said belt, said elements having contoured belt supporting portions for imparting a longitudinal trough into said belt.

10. Spectroscopic apparatus, comprising a graphite tube, means for delivering a gaseous specimen through said tube, a length of graphite cloth having a free end thereof extending towards said tube and defining a gap therebetween, an electrical power source connected to said cloth and said tube and adapted to generate an electrical arc across said gap to thereby heat said tube and spectrally excite said specimen, and optical means for analyzing according to wavelength the light emitted by the excited specimen.

11. Spectroscopic apparatus, comprising a pair of electrodes spaced from one another to define a gap therebetween, a belt of graphite cloth extending through said gap, holder elements for supporting said belt, dispensing apparatus located adjacent said belt for depositing a specimen thereon, means for moving said belt whereby said specimen may be carried into said gap, a first power source connected to said electrodes and adapted to generate an arc across said gap, said arc serving as one source of spectral excitation for said specimen, a second power source connected to said belt, said belt when energized serving as another source of spectral excitation for said specimen and optical means for analyzing according to wavelength the radiant energy emitted by the excited specimen.

12. Spectroscopic apparatus according to claim 11 including a monitoring device located in the path of said radiant energy, said device being operatively connected to said second power source and adapted to maintain said belt at a constant level of thermal excitation.

13. Spectroscopic apparatus according to claim 11 wherein said holder elements comprise rollers arranged in pairs on either side of said electrodes, each pair of rollers being profiled to define a V bight whereby that portion of the belt supported between said pairs of rollers will assume a longitudinal trough.

14. Spectroscopic apparatus according to claim 11 including a cooling system for said holder elements comprising a cooling medium source and conduits connecting said source to said elements.

15. Spectroscopic apparatus comprising a section of

graphite fabric, an electrical power source connected to said fabric and adapted to thermally excite said fabric to any desired black body temperature, means for locating a specimen in close proximity to said fabric whereby said specimen may be spectrally excited and optical means for analyzing according to wavelength the radiant energy emitted by the excited specimen. 5

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