April 25, 1967 A. BARDOCZ **3,315,560**

SPECTRUM ANALYSIS WITH TIME-RESOLVED SPARK SPECTRA

Original Filed June 16, 1958 2 Sheets-Sheet 1

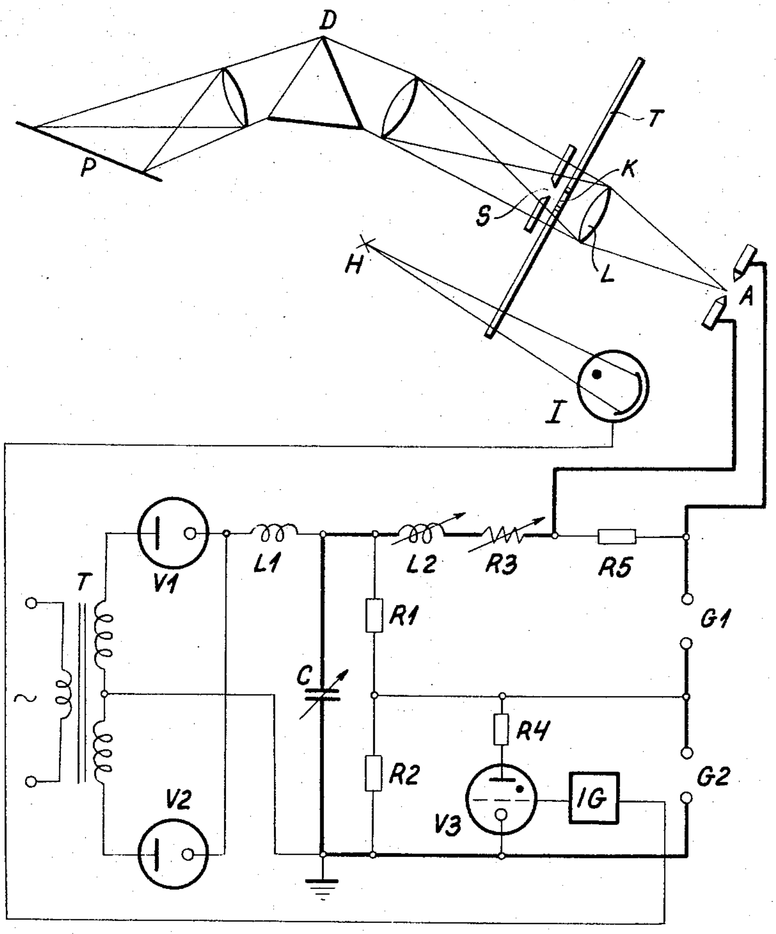

Fig. 1

INVENTOR.
ARPAD BARDOCZ
BY Blum, Moscovitz,
Friedman and Blum
Attorneys

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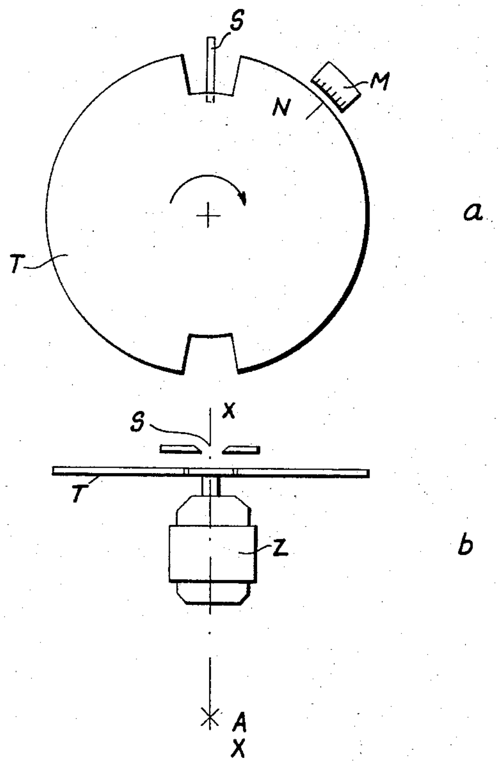

Fig.2

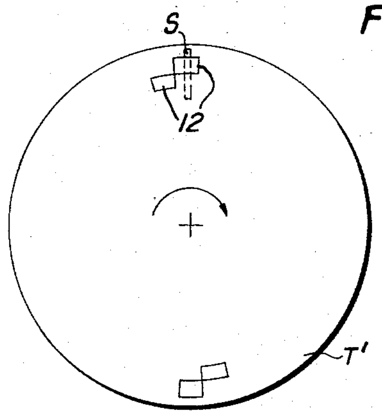

Fig.3

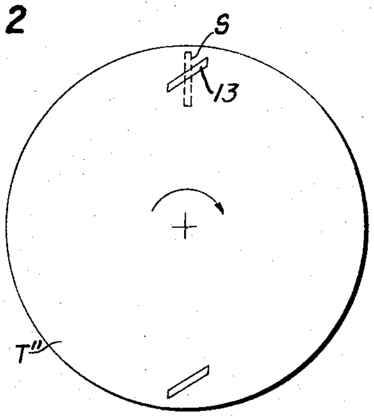

Fig.4

INVENTOR.
ARPAD BARDOCZ
BY Blum, Moscovitz, Friedman and Blum
Attorneys

3,315,560
Patented Apr. 25, 1967

3,315,560

SPECTRUM ANALYSIS WITH TIME-RESOLVED SPARK SPECTRA

Arpad Bardocz, 28–30 Attila Korut,
Budapest, Hungary

Original application June 16, 1958, Ser. No. 742,360. Divided and this application Jan. 10, 1962, Ser. No. 168,303
1 Claim. (Cl. 88—14)

This invention relates to spectrum analysis with time-resolved spark spectra and, more particularly, to improved apparatus for such spectrum analysis. This application is a division of my copending application Ser. No. 742,360, filed June 16, 1958 which is, in turn, a continuation-in-part of my copending application Ser. No. 688,688, filed Oct. 7, 1957, and now both abandoned.

With the invention apparatus, the radiation arising at different time intervals of transient electrical discharges, or from respective time ranges thereof, can be separated and the thus separated radiation can be investigated.

It is well known that, when using ignited and self-ignited low voltage and high voltage sparks, as well as A.C. interrupted arcs, as spectroscopic light sources, there is a large variation in conditions with respect to time so that there is a consequent large variation in the light emitted by the spark in point of time. Thus, the optical conditions prevailing in the electric spark and in the interrupted arc may be studied only by reference to time-resolved spectra. Investigations show that the spectrum emitted by the electric spark during the initial stage of the discharge is mainly of a spark-like character and contains the spark lines of the elements as well as background. The easily excitable arc lines arise during the later stage of the spark discharge, when the level of the excitation energy is low. In this later stage of the spark discharge, the spark spectrum is completely free of background, and it is primarily the arc lines appearing during this later stage which are used in spectrochemical analyses.

The invention apparatus produces spectra resolved in time, and comprises, as main components, an electronically controlled periodic light source (excitation source) operating with high precision in time, a screen moving in synchronism with the light source, an electric trigger generator, and a spectrograph.

Generally speaking, the apparatus of the invention operates in the following manner. A moving screen such as a rotating, vibrating, oscillating, or reciprocating screen, is positioned in the path of light emitted from a high precision electronically controlled light source and directed into a spectrograph. The screen is moved in synchronism with the light source and has, for one of its purposes, the blocking of light arising during one portion of the active period of the light source and the passing of light arising during the remaining active period of light source. However, the apparatus may also be used to direct into the spectrograph light arising from two or more different time periods of activity of the light source. In this case, different spectra will correspond to different time ranges of the active period of the light source. If the light is divided into only two parts, then one part will comprise radiation arising during the initial time range of the discharge and the other will comprise radiation arising only during a later time range of the discharge.

For an understanding of the principles of the invention, reference is made to the following description of typical embodiments thereof as illustrated in the accompanying drawings. In the drawings:

FIG. 1 is a schematic illustration of the electrical and optical system used in spectrographic analysis in accordance with the invention, the optical system and the screen being shown substantially in plan;

FIG. 2, part *a*, is an elevational view of the screen and a phase adjusting scale system cooperable therewith, and part *b* is a plan view of the screen and its driving means; and

FIGS. 3 and 4 are elevational views of alternative embodiments of a rotating screen or disk.

FIG. 1, in its lower part, illustrates one example of a circuit diagram of a high precision electronically controlled spark source, as a periodic light source, and in its upper part illustrates the optical arrangement embodying the invention. Referring to the lower portion of FIG. 1, a condenser C supplies the excitation energy and is known as the "working condenser." Condenser C is charged from a high voltage transformer T through diodes V1 and V2. That portion of the circuitry to the left of the condenser C in FIG. 1 is the charging therefor, and that part to the right of the condenser C is the discharge circuit thereof.

The discharge circuit of condenser C includes an analytical spark gap A shunted by a resistance R5. A pair of controlling spark gaps are illustrated at G1 and G2, the self-induction of the discharge circuit is indicated at L2, and the ohmic resistance thereof is illustrated at R3, these several elements controlling the operating conditions of the discharge circuit. Voltage dividing ohmic resistors are indicated at R1 and R2 to distribute the charge voltage of condenser C uniformly across the symmetrically adjusted twin control spark gaps G1 and G2. An electron tube V3, or its equivalent, has a resistance R4 in its anode or plate circuit and is blocked with a negative bias on its grid.

The twin controlling spark gaps G1 and G2 are so adjusted that, except when condenser C is fully charged, there is no breakdown across these spark gaps. If, under such conditions, a positive signal voltage is applied to the grid of tube V3, this tube will conduct and the charging voltage of condenser C will appear entirely across the spark gap G1 so that the latter will break down and condenser C will begin to discharge through inductance L2, ohmic resistances R3 and R5, controlling spark gap G1, ohmic resistance R4, and tube V3. Since the breakdown of the spark gap G1 results, in effect, in substantial short circuiting thereof, almost the total charge voltage of condenser C will appear on the terminals of resistances R4 and R5. Accordingly, either control spark gap G2 or analytical spark gap A will break down according to which one thereof is shunted by the higher resistance. If, as is customary in practice, resistance R5 has a higher value than resistance R4, analytical spark gap A will break down after the break down of spark gap G1. When spark gap G1 breaks down, the discharge path of condenser C will include inductance L2, ohmic resistance R3, spark gap A, spark gap G1, ohmic resistance R4, and tube V3. At this time, the charge voltage of condenser C will appear on the terminals of ohmic resistance R4 and thus across the spark gap G2. Thus, spark gap G2 breaks down after which condenser C discharges along a path including inductance L2, ohmic resistance R3, spark gap A, spark gap G1 and spark gap G2 to supply the excitation energy. This discharge is indicated in FIG. 1 by a relatively heavy line.

One optical system embodying the invention is shown in the upper part of FIG. 1, wherein light from the analytical spark gap A is imaged by the lens L through the collimator slit S of the spectrograph, and directed to the collimator lens of the spectrograph. The prism of the spectrograph is indicated at D, and the photographic plate, or, in the case of direct reading, the position of the photocells, at P.

By way of example, in FIG. 1 a rotating disk T is placed in the light path and is secured to the shaft of a synchronous motor. In FIG. 1, the disk T is shown in side elevation. This disk is provided with suitable apertures, such as slots or notches therein, through which light may pass to reach the spectrograph. In FIG. 1, the axis of rotation of disk T is substantially beneath the slit S of the spectrograph in order that the cut or slit in disk T will be positioned in alignment with the slit S. The operative relationship between the light source and the optical system is established in the example shown in FIG. 1, by a photocell I. Light from an auxiliary light source H impinges on the photocell I through one of the apertures of disk T. The photo current supplied by the photocell I, and amplified by amplifier 1G, provides the positive control or trigger signal to the grid of electron tube V3. Illumination, synchronous with the rotation of disk T and directed upon the photocell I, may be so directed by the light from source H impinging upon a rotating mirror which then reflects the light to photocell I.

In order to illustrate better the operation of the invention, and particularly of the optical system thereof, in parts *a* and *b* of FIG. 2, the rotating disk T of FIG. 1 is shown both in front elevational view and in top plan view. In part *b* of FIG. 2, *x*—*x* is the optical axis, and the analytical spark gap is indicated at A. Disk T is fastened to the shaft of a motor Z and is positioned in advance of the collimator slit S of the spectrograph. The passage of light through the slit S is controlled by one of the apertures or notches in the disk T. By proper adjustment of the rotational phase position of disk T with respect to the slit S of the spectrograph, it can be assured that light will enter the spectrograph from only a portion of the light period before or after a predetermined point during the discharge time of the spark gap.

The setting of such rotational phase position of disk T with respect to slit S of the spectrograph can, for example, be effected in the following manner. As shown best in part *a* of FIG. 2, the circumference of disk T is illuminated directly or through a lens by the light of the analytical spark gap A. A mark N is provided on the circumference of disk T. Controlling of the electronically controlled high precision spark source is effected either by means of a rotating mirror driven by the shaft of motor Z of disk T and a photocell, or by using the trigger signal produced by the combination of the light interrupted by the rotating disk T and the photocell I. In either case and in both cases, the time between the appearance of the triggering signal produced by the photocell and the initiation of the spark discharge can be adjusted or varied. Since there is synchronism between the rotating disk T and the initiation of the spark discharge, during operation of the apparatus the mark N on the rotating disk T appears to be standing still. If the time betwen the appearance of the signal voltage of the photocell and the initiation of the spark discharge is varied, the apparent standing position of the mark N on the circumference of disk T will shift. A gauge or scale M is placed opposite the mark N, and the relative displacement of the apparent position of the mark N can be read with respect to the scale M. The system can be calculated in such a manner that spectra may be used corresponding to different positions of the mark N with respect to the gauge or scale M, and thus by adjusting the relative positions of the mark N and the scale M to indicate the particular portion of the spectrum desired to be used, the required spectrum can always be produced.

The essential feature of the electronically controlled high precision light source of FIG. 1 is that, with respect to the trigger signal given to the grid of tube V3 of the spark source, the breakdown of the analytical spark gap A occurs with only a very small time scatter or "jitter." This time scatter is one microsecond or less. This means that, in other words, the separation of the time ranges by means of the rotating disk T of FIGS. 1 or 2 can be performed with very high precision. This is an important factor if light emitted by electric discharges of short duration is to be investigated.

In place of the disk T of FIGS. 1 and 2, the disk T′ shown in FIG. 3 may be used in advance of the slit S in the spectrograph. The disk T′ is formed with two pairs of quadrilateral openings **12**, the pairs being displaced by 180 degrees with respect to each other. These double apertures **12** are effective to define the light arising from transient discharges into two parts. Besides providing for correct rotational phase setting with respect to the collimator slit S of the spectrograph, the provision of the double apertures **12**, **12** can provide that radiation arising from the initial portion of the time range of the spark discharge will enter the spectrograph through the radially outer aperture of each pair, whereas radiation arising from a later portion of the time range of the arc discharge will enter the spectrograph through the radially inner aperture of each pair. This disk T′ can be used also for eliminating the background.

Positioning the rotating disk of FIG. 2 so that its circumference extends over a certain portion only of the slit S of the spectrograph, so that all of the slit S is not covered by the disk T, results in that radiation containing the background also will enter the spectrograph. In this manner, a double spectrum is obtained similarly to the effect obtained using the disk T′ of FIG. 3.

If it is desired to investigate the light emitted by discharges of relatively long duration in time resolution, then the rotating disk T″ of FIG. 4 can be used in advance of the slit S of this spectrograph. The disk T″ has two relatively elongated apertures or slots **13** which are displaced 180 degrees from each other and are oblique with respect to a radius of the disk T″. As disk T″ rotates, radiation from different time ranges of the discharge is permitted to enter the slit S by means of the oblique apertures or slots **13**. In this way, a spectrum resolved continuously in time can be reproduced.

The photocell controlling the analytical light source can be illuminated in synchronism with the spark discharge by permitting the illuminating light to reach the photocell through the apertures of the disk T, T′, or T″. Thus, the light will reach the photocell only when one of the apertures passes through the light rays directed toward the photocell from the auxiliary light source H.

The zero position of the rotating disks of FIGS. 2, 3 and 4, or the position in which the path of the light rays passes through one of the apertures of the disk, can be most easily determined with the aid of a further photocell included in the spectrograph. In such case, and using the disk of FIG. 2 for example, the disk will be rotated slowly with the aid of the photocell in the spectrograph, so that the rotational phase position of the disk can be noted and read from the scale M at a position where the slit or aperture just opens. For direct reading devices, this setting alone can be used. The setting can also be effected by observing the opening of the slit of the spectrograph by means of the naked eye and from the direction of the focal plane of the spectrograph.

The fact that the background of the spark spectrum can be separated in the above-described manner has many advantages from the point of view of spectrochemical analysis. In the first place, the sensitivity is greatly increased because weak lines will not disappear in the background. On the other hand, the working curves will be straight lines because they will not need the background correction. Furthermore, the separated background of the spectrum can be usefully employed in the following manner.

Modern spectrochemical analysis is based on the so-called internal standard method. The essence of this method consists in that the determination of the impurities of the material or of alloying constituents is effected by providing the intensity ratios of a spectrum line of the impurity or alloying element to be determined and that of the matrix element, which, when brought into relation with the percentage quantity of the respective element, provides a quantitative determination. This method can be practiced effectively if, in the spectrum, there is near to the spectrum line of the impurity, or of the alloying element to be determined, a comparison line corresponding to the matrix element. If these comparative spectrum lines were spaced further from each other and if they were recorded by photographic plates, then, owing to the different sensitivity of the photographic emulsion for light of different wave lengths, the comparison of the two lines is not a simple task.

Thus, and as an auxiliary help, such comparative lines should be derived from the spectrum of another material, in which the spectrum line intensity ratio is known. This method is called the external standard method and, owing to the fact that it is cumbersome, it is very seldom used. In most cases, it is also a particular condition that the matrix element should be present in a generally higher percentage. The satisfaction of these conditions in practice is an exception rather than a rule. In practice, further, cases occur in which the matrix element does not have corresponding comparison lines. In such cases, the problem can be resolved by utilizing the material to be investigated in adequate amounts mixed in the form of a powder or a solution, the lines of which will form the internal standard.

As against this, a spectrochemical analytical method is possible with the invention in which neither an internal nor an external standard is needed. For the analysis, the comparison standard is the background separated from the rest of the spectrum. The lines of the alloying elements or the impurity elements in the spectrum, without the background, are compared with the part of approximately identical wave lengths of the continuous spectrum present in the total length of the spectrum in the direction of dispersion.

While specific embodiments of the invention have been shown and described in detail to illustrate the application of the principles of the invention, it will be understood that the invention may be embodied otherwise without departing from such principles.

What is claimed is:

Spectrographic apparatus comprising, in combination, a periodic light source; a spectrograph having a collimating slit; and a substantially circular screen disk, rotatable in synchronism with the activation of said light source, positioned in the path of light rays from said source to said spectrograph collimating slit and formed with aperture means, said aperture means including at least one aperture in said disk adjacent the perpihery thereof and extending generally radially of the disk and cyclically moveable across such path and each aperture in said disk comprising at least a pair of adjacent openings therein which are spaced at different distances radially of said disk and angularly of said disk so that one opening immediately follows the other opening; each opening uncovering a different portion of the length of said collimating slit; and means, including a trigger signal generator operable in synchronism with said screen disk, effective to activate said light source cyclically at precisely timed intervals for precisely timed period of light duration.

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JEWELL H. PEDERSEN, *Primary Examiner.*

J. L. CHASKIN, R. L. WIBERT, *Assistant Examiners.*