Aug. 30, 1949. G. H. DIEKE 2,480,636

OSCILLOGRAPHIC METHOD OF AND SYSTEM FOR SPECTROGRAPHIC ANALYSIS

Filed Feb. 18, 1947 2 Sheets-Sheet 1

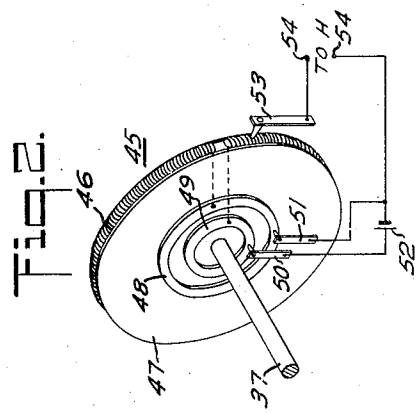



Fig. 2.

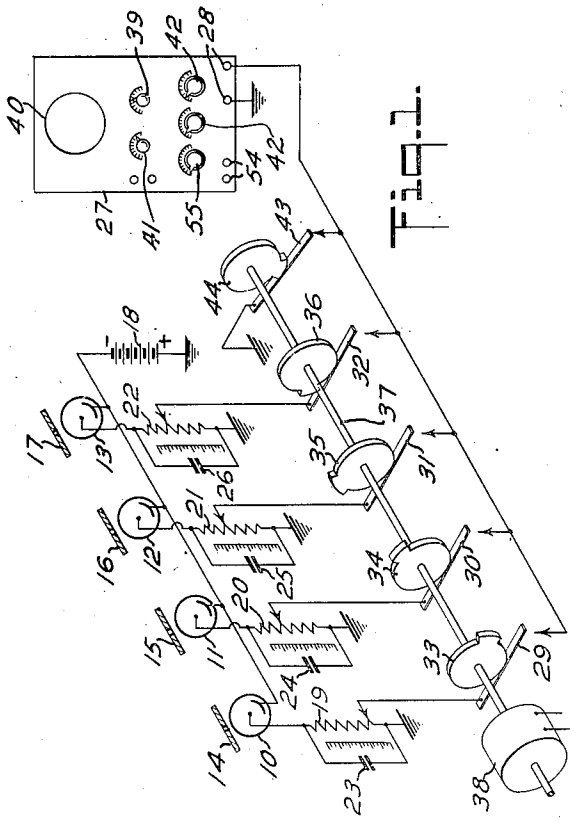



Fig. 1.

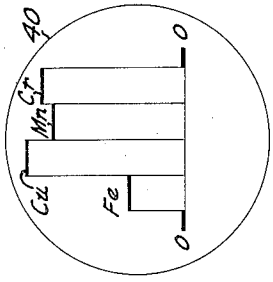



Fig. 3D.

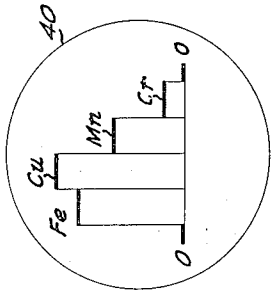



Fig. 3C.

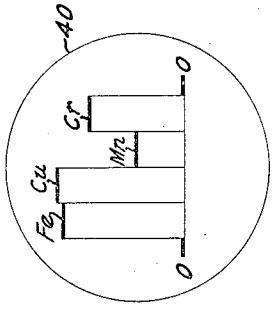



Fig. 3B.

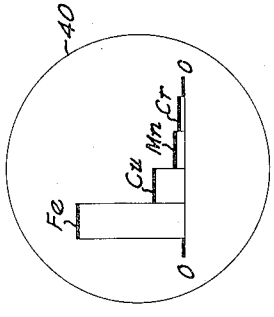



Fig. 3A.

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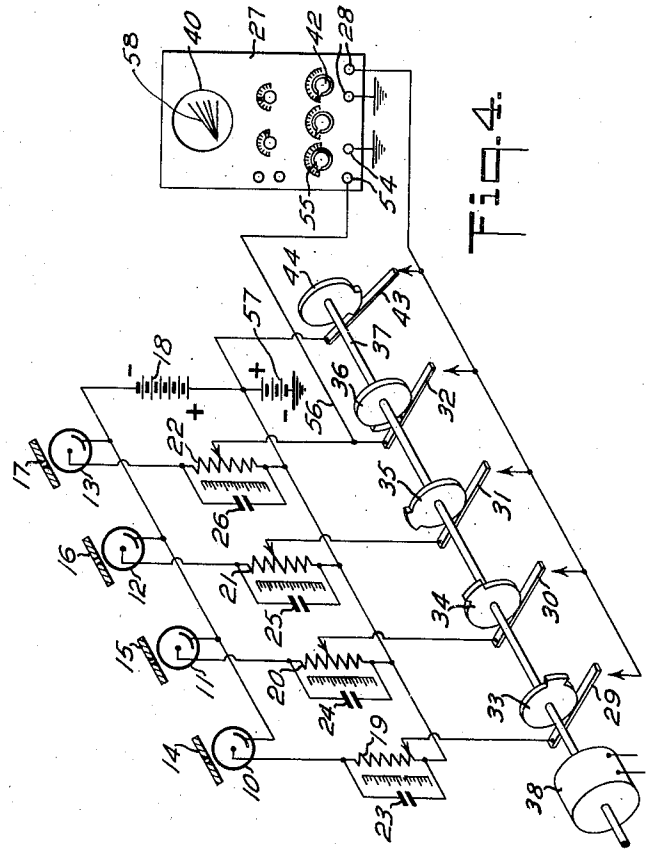


Fig. 4.

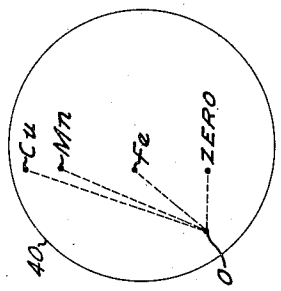



Fig. 5-D.

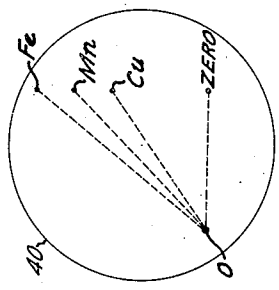



Fig. 5-C.

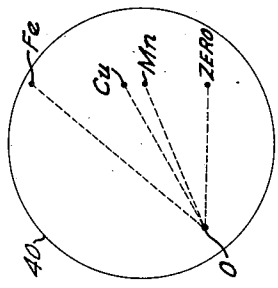



Fig. 5-B.

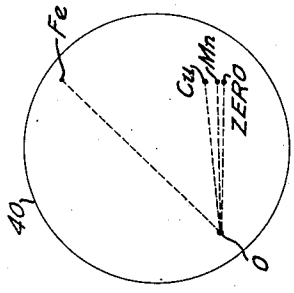



Fig. 5-A.

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## OSCILLOGRAPHIC METHOD OF AND SYSTEM FOR SPECTROGRAPHIC ANALYSIS

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Application February 18, 1947, Serial No. 729,272

13 Claims. (Cl. 315—26)

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This invention relates to spectrochemical analysis and particularly to systems and methods suited to needs of industry where speed and simplicity of operation are of greater importance than extreme accuracy.

The present most commonly employed method of spectrochemical analysis involves the use of a photographic plate which is exposed to the spectrum produced by an arc or spark discharge between electrodes of material whose composition is to be determined. Aside from variable factors, such as non-uniform sensitivity of photographic plates and films, the temperature, concentration and age of the developing solution and action of the fixing bath, all of which affect its accuracy, the photographic method has the further disadvantage that a relatively long time is needed for the development, washing and drying of the photographic plate or film. Because of inherent slowness of the photographic method, it is not suited for close control of the composition of a furnace charge or melt, for example, or for other industrial processes where time is of essence either because of production demands or because the material analyzed substantially changes in composition between time of withdrawal of a sample of it for analysis and the time when the results of the analysis are available.

In accordance with the present invention, the spectrochemical analysis of a sample is effected substantially instantaneously by impressing the radiation from selected lines of the spectrum upon a corresponding number of photoelectric cells which, in predetermined sequence, are rapidly and recurrently connected to an oscillograph. The intensities of the lines and therefore the concentrations of the corresponding elements may be read directly from the resulting visual pattern, or alternatively, the deviations from standard concentrations may be determined by noting the extents to which it is necessary to adjust calibrated coupling networks of the tubes in order to make the visual pattern match with a standard pattern.

More particularly and in one form of the invention, the photocells are successively connected, for example, to the vertical-deflection circuit of a cathode-ray tube during each traverse of the screen of the tube by the cathode spot as effected by a saw-tooth sweep voltage or current applied to the horizontal-deflection circuit. With this arrangement, the pattern is composed of a series of parallel lines or traces each having a position transversely of the screen which identifies a particular element and whose position

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vertically of the screen is indicative of the concentration of that element.

In another form of the invention, the photocells are sequentially connected to the vertical-deflection circuit as before but no sweep voltage is applied to the horizontal-deflection circuit. Instead, there is connected thereto one of the photocells which views that one of the spectrum lines selected as a reference. Assuming the light source and the current supply for the tubes are steady, the resultant pattern is a series of vertically spaced spots each having a position which depends upon the respective intensities of the reference spectrum line and a particular one of the other selected lines. If the light source and/or the current source for the cells are unsteady, the spots are more or less elongated traces; all, however, directed toward a common point if the coupling networks of the tubes are selected or adjusted to have the same time constant. The slope of a selected trace then corresponds with the relative intensities of the corresponding spectrum lines notwithstanding the aforesaid unsteadiness of the light source or power supply.

The invention further resides in methods and systems having features herein disclosed and claimed.

For more detailed understanding of the invention and for illustration of preferred forms thereof, reference is made to the accompanying drawings, in which:

Fig. 1 schematically illustrates a spectrographic analyzer using phototubes and a conventional cathode ray oscillograph or oscilloscope;

Fig. 2 is a detail view of an external sweep generator;

Figs. 3A–3D are examples of patterns obtained with the system of Fig. 1;

Fig. 4 illustrates a modification of the system of Fig. 1; and

Figs. 5A–5D are examples of patterns obtained with the system of Fig. 4.

Referring to Fig. 1, the tubes 10—13, each associated with one of the slits 14—17, are disposed along the focal curve of the spectrum produced by a light source, for example, an arc whose electrodes are comprised of material to be analyzed. Each cell is disposed continuously to view a selected line or region of a spectrum to be analyzed. Assuming it is desired to analyze steel samples for their copper, manganese and chromium contents, a spectrum line of each of those elements is selected and also an iron line to serve as a reference line. For example, the cells 10—13 may be disposed respectively to view the spectrum lines

Cr 4254, Mn 4823, Cu 5218, and Fe 4528. The intensities of these lines are measured by connecting the cells 10—13 sequentially in circuit with an oscillograph in such rapid sequence that due either to the persistence of vision or to the persistence of the cathode-ray screen, the intensities of all of these lines are immediately visually apparent. The oscillograph may be of conventional type having an internal sweep-generator, a synchronizing network and variable gain amplifiers for the horizontal and vertical deflection circuits.

To afford coupling between the photocell tubes and the oscillograph, each cell or tube circuit includes a resistance traversed by the output current of the tube and all or a selected fraction of the voltage drop across this resistance is intermittently impressed upon the vertical-deflection circuit of the oscillograph. More specifically, the cathodes of all of the tubes 10 to 13 are connected to the negative terminal of a suitable source of direct current 18 and between the anodes of the tubes and the other terminal of source 18 are respectively connected the resistors 19—22, each preferably shunted by one of the condensers 23—26 for reasons which hereinafter appear. The common terminal of the resistors 19—22 is connected to one of the terminals 28 of the vertical-deflection circuit of the oscilloscope 27 and the other terminal of this deflection circuit is connected to the fixed contacts of timing switches 29—32, whose movable contacts are respectively connected to the adjustable contacts of the resistors 19—22 in the photocell circuits. These switches are closed in succession by the cams 33—36 mounted upon shaft 37 and driven by motor 38 or equivalent device.

In the particular arrangement shown, and as used, the motor-driven cam shaft 37 may make a revolution in about one-fifth of a second and the dwell of each of the cams 33—36 is such that each photocell is connected in turn to the vertical-deflection circuit of the oscillograph for one twenty-fifth of a second. The period or frequency of the horizontal-sweep generator within the oscilloscope 27 is adjusted by the control knob 39 so that the cathode spot traverses the screen 40 once for each revolution of the motor 38, and as usual the synchronizing control 41 is adjusted to lock-in the sweep generator at that frequency. For any given setting of the gain control 55 for the horizontal-deflection amplifier, the successive traces produced by each of the photocells therefore always have the same position laterally of the tube, the vertical position of each trace depending upon the intensity of the radiation received by the particular phototube, the setting of the gain control 42 for the vertical amplifier and by the magnitude or setting of the associated anode resistor. Condensers 23—26 are provided in shunt to the resistors 19 to 22 to increase the time constant of the coupling networks formed thereby and so eliminate the adverse influence of short-period fluctuations of the light source upon steadiness of the cathode-ray pattern on screen 40.

Preferably and as shown, there is also provided an additional switch 43 operated by a cam 44 on shaft 37 so that once for each revolution of the motor 38 there is applied to the vertical-deflection circuit a fixed voltage, which may be zero, thus to establish a definite base line 0—0, Figs. 3A–3D, from which the vertical distances to the several stages or portions of the pattern may be measured as from a scale in front of or upon the screen 40 of the tube.



The usual oscillograph, to adapt it for a wide variety of uses, is provided with an internal saw-tooth generator whose frequency may be varied over a wide range and with arrangements for locking the generator in synchronism with a periodic input signal, but such complexity is unnecessary for the present purposes and, as shown in Fig. 2, a suitable synchronized saw-tooth wave may be simply provided by rotating with shaft 37 a circular slidewire 46 mounted upon a disc 47 suitably attached to the shaft 37. The ends of the slidewire are connected, as by the rings 48, 49 and brushes 50, 51, to a suitable source of direct current 52. The terminals 54 of the horizontal-deflection circuit of the oscilloscope 27 are connected respectively to one terminal of the source 52 and to the stationary contact 53 which bears against the slidewire 46. Consequently, for each revolution of the motor 38 there is applied to the horizontal-deflection circuit a sweep voltage which increases from zero to a maximum and then abruptly returns to zero near the end of the revolution. This external sweep generator 45 has the additional advantage of offering no problems in synchronization because should the speed of motor 38 vary, the sweep voltage of necessity automatically correspondingly changes and so there is maintained the proper synchronism without need for any manual adjustment.

The patterns shown in Figs. 3A–3D are typical of those obtained in use of the system of Fig. 1; the pattern of Fig. 3A is that of an electrolytic iron; that of Fig. 3B a chromium steel having copper .06%, manganese .65% and chromium .91%; that af Fig. 3C a manganese steel having copper .12%, manganese 1.4%, and chromium .18%; and that of Fig. 3D a stainless steel having copper .59%, manganese 4.1% and chromium 20%. Particularly when the various elements are anticipated to be present in widely different percentages, there is no single suitable setting of the vertical gain control 42 and the effective values of the resistors 19—22 must be so chosen or adjusted that the cathode spot will not go off scale and yet will have reasonably large vertical deflection. Assuming the apparatus is to be used for checking samples whose compositions do not differ widely, permanent scales, one for each of the photocells, may be attached at proper position on screen 40. Preferably, however, a standard specimen is first used in the light source and a desired standard pattern obtained by setting the contacts of the various resistors 19—22. These settings correspond with calibration points of scales associated with the several resistors so that in checking future samples the extent of displacement of any of the contacts necessary to match the actual pattern with the standard pattern is a measure of the deviation of concentration of a particular element in the sample from the desired or standard value.

With the arrangement shown in Fig. 1, if the light source is subject to large fluctuations, the whole pattern may shift up and down on the screen but in first approximation holding the relative position of the traces. Consequently, all traces should be evaluated in terms of the iron concentration if the sample is predominantly iron. The dancing of the pattern, however, makes observation difficult and the arrangement shown in Fig. 4 is for that and other reasons preferred.

The system shown in Fig. 4 is similar to that of Fig. 1 except that instead of connecting an internal or external sweep generator to the hori-

zontal-deflection circuit, the output of one of the cells, for example that of cell 13 which views the iron line in the example given above, is connected by conductor 56 to the horizontal-deflection circuit of the oscilloscope. Preferably, in addition there is applied a fixed voltage derived from battery 57 or equivalent source to displace the zero position 0 of the cathode spot, for example, toward the left and below the center of the screen, so that the maximum area of the screen is usable rather than merely one-quadrant.

Typical patterns resulting from this mode of connection to the deflection circuits of the cathode-ray tube are shown in Figs. 5A–5D, respectively, corresponding to Figs. 3A–3D. As in this instance, Figs. 5A–5D, the chromium line is absent, the contact on resistor 19 is adjusted to its zero position. In this system, and as apparent from Figs. 5A–5D, the intensities of each of the lines viewed by the phototubes is plotted as a vertical-deflection against the concurrent horizontal deflection due to phototube or cell 13; that is, the measurement is that of the relative intensity of the line viewed by the cell 13 to that of the lines viewed by each of the other cells in succession.

With this arrangement, if the light source remains constant, the intensity of each of the spectrum lines corresponds with a spot appearing on the cathode-ray screen 40 and all spots lie on the same vertical line. If the source fluctuates, each of the spots moves along a line going through the common zero or origin point 0. When the networks 19—23 to 22—26 have equal time constants, each of these points moves along a straight line directed towards the origin 0 and the slope of each line is therefore a measure of the intensity of the spectrum and concentration of the corresponding particular element. Alternating-current light sources commonly available can therefore be used with the system of Fig. 4 whereas this would ordinarily be impossible with the system of Fig. 1.

When the time constants of the several coupling networks have been adjusted or selected to effect equality, this relation is not upset by adjustment of the adjustable contacts of the resistors 19 to 22 effectively to vary the signal gain from the photocell to the oscillograph, providing that the resistors are used as potential dividers, as shown, rather than as rheostats.

The relative intensities or concentrations may be read directly from the cathode-ray screen 40, Fig. 4, or from a suitable angularly graduated transparent scale 58 attached thereto or disposed in front of it. Alternatively, a standard pattern on a transparent sheet may be disposed in front of the cathode-ray screen and the contacts of the several resistors 19—22 adjusted to effect match of the actual pattern therewith, the deviation of the concentration of the several elements then being read directly from scales associated with the several resistors. In either case, the concentrations can be read to within five per cent accuracy or better, comparable with that obtained by the much slower photographic method.

If a complete analysis is required for a sample having many constituents, the pattern on the screen becomes too complicated to be easily interpreted. However, even under such condition, the traces of the several elements can be identified by pulsing them at different characteristic rates.

In both systems, Figs. 1 and 4, the photoelectric tubes 10 to 13 are preferably of the photomultiplier type, such as the IP 28, 931A and the IP 21 tubes manufactured by the Radio Corporation of America, because of their high sensitivity and linear response characteristic.

It shall be understood the invention is not limited to the particular systems disclosed and that changes and modifications may be made within the scope of the appended claims.

What is claimed is:

1. A system affording substantially instantaneous analysis of selected lines of a spectrum comprising photocells for respectively continuously viewing said selected lines of the spectrum, an oscillograph, and switching means for connecting said cells to said oscillograph in rapidly recurring sequence to produce a pattern concurrently showing the intensities of said lines.

2. A system affording substantially instantaneous analysis of selected lines of a spectrum comprising photocells for respectively continuously viewing said selected lines of the spectrum, an oscillograph including a cathode-ray tube, a sweep generator in circuit with one pair of deflection plates of said tube, and switching means operating in synchronism with said sweep generator sequentially to connect said cells in circuit with another pair of deflection plates of said tube.

3. A system affording substantially instantaneous analysis of selected lines of a spectrum comprising photocells for respectively continuously viewing said selected lines of the spectrum, an oscillagraph including a cathode-ray tube and a sweep generator in circuit with one pair of deflection plates thereof, switches each in circuit with one of said cells and the other pair of deflection plates of said tube, and motor-driven cam structure for actuating said switches sequentially to connect said cells to said other pair of plates each for a predetermined portion of the cycle of said generator.

4. A system affording substantially instantaneous analysis of selected lines of a spectrum comprising photocells for respectively continuously viewing said selected lines of the spectrum, resistance-capacitance networks respectively in circuit with said photocells, an oscillograph having a horizontal-deflection circuit and a vertical-deflection circuit, a generator for introducing a sweep voltage into one of said deflection circuits, and switching means operating in synchronism with said generator sequentially to include in the other of said deflection circuits voltages respectively derived from said networks.

5. A system affording substantially instantaneous analysis of a spectrum comprising photocells for respectively viewing selected lines of the spectrum, an oscillograph having a horizontal-deflection circuit and a vertical-deflection circuit, a generator for introducing a sweep voltage into one of said deflection circuits, and switching means operating cyclically in synchronism with said generator sequentially to connect said cells to the other deflection circuit and in each cycle to apply a voltage establishing the base line of the pattern resulting from aforesaid sequential connection of the cells.

6. A system affording substantially instantaneous analysis of a spectrum comprising photocells for respectively viewing selected lines of a spectrum, an oscillograph having a horizontal-deflection circuit and a vertical-deflection circuit, switching means for connecting said cells sequentially to one of said deflection circuits, and means for connecting a selected one of said cells to the other of said deflection circuits.

7. A system affording substantially instantaneous analysis of a spectrum comprising photocells for respectively viewing selected lines of a spectrum, resistance-capacitance networks respectively in circuit with said photocells, an oscillograph having horizontal-deflection and vertical-deflection circuits, switching means in predetermined and rapidly recurring sequence introducing into one of said deflection circuits voltages respectively derived from said networks, and means for introducing into the other of said deflection circuits a voltage derived from a selected one of said networks.

8. A system affording substantially instantaneous analysis of a spectrum comprising photocells for respectively viewing selected lines of a spectrum, an oscillograph having horizontal and vertical-deflection circuits, and switching means operating cyclically to connect said cells in rapidly recurring sequence to one of said deflection circuits and in each cycle to apply a voltage establishing the base line of the pattern resulting from aforesaid sequential connection of the cells, and means for connecting one of said cells to the other of said deflection circuits.

9. The method of spectrochemically analyzing a specimen which comprises the steps of continuously producing voltages respectively corresponding with the intensities of selected regions of the spectrum of the specimen, and repeatedly and in predetermined sequence applying said voltages to an oscillograph.

10. The method of spectrochemically analyzing a specimen which comprises the steps of continuously producing voltages respectively corresponding with the intensities of selected regions of the spectrum of the specimen, applying a periodic sweep voltage to one deflection circuit of an oscillograph, and in synchronism with said sweep voltage repeatedly applying said first named voltages in predetermined sequence to another deflection circuit of said oscillograph.

11. The method of spectrochemically analyzing



a specimen which comprises the steps of producing voltages respectively corresponding with the intensities of selected regions of the spectrum of the specimen, applying one of said voltages continously to one deflection circuit of an oscillograph, and repeatedly and in predetermined sequence applying the other of said voltages to another deflection circuit of the oscillograph.

12. A spectographic system comprising photocells, each associated with a spectrographic slit, for respectively continuously viewing selected lines of a spectrum, potentiometers respectively in circuit with said photocells, an oscillograph, and switching means for connecting the adjustable contacts of said potentiometers to said oscillograph in rapidly recurring sequence to produce a pattern determined by the intensities of said lines and the setting of said contacts.

13. The method of spectrochemically analyzing a specimen which comprises the steps of continuously producing voltages respectively corresponding with the intensities of selected regions of the spectrum of said specimen, repeatedly and sequentially applying a selected fraction of each of said voltages to an oscillograph, and varying the fraction of the individual voltages which is applied to said oscillograph to match the actual oscillograph pattern with a standard pattern.

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