# A DIRECT READING ANALYTICAL SPECTROSCOPE*

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## ABSTRACT

A system of spectroscopic analysis is described which eliminates measurement of wave lengths and reference to tables by direct comparison of the spectrum of the sample with master spectra of the several elements. Master films are built into a spectroscope having an optical system that projects two continuous spectra adjacent to the spectrum of the sample, and the master films are illuminated in their true colors for comparison line by line with the observed spectrum. Elimination films select out the lines of major constituents so the lines of other constituents are apparent for comparison with identification films. The master spectra are classified by index charts.

The spectroscope operates on 115 volts alternating current. The sample is placed on a dispensable refractory hearth adjustably mounted below a horizontal arc. Progressive heating permits successive excitation of the spectra of the component elements and facilitates their identification.

Applications to specific examples of mineral analysis are given.

## INTRODUCTION

In the May–June, 1947, issue of *The American Mineralogist* Messrs. Peterson, Kauffman and Jaffe, of the U. S. Bureau of Mines, published a paper setting forth the advantages to the mineralogist of the spectroscope as a simple, direct and positive means of determining the constituent elements of a mineral sample.[2]

That paper was timely and appropriate. The present writer has used the spectroscope for this purpose for many years and found it indispensable. The purpose of the present paper is to describe a greatly simpified technique of spectroscopic analysis which is believed to be novel, and an apparatus especially designed for making this technique available to mineralogists and to those who want to get a result quickly and positively without the intricate and exacting process of measuring spectrum lines and searching through tables to decipher them.

This result is accomplished by the use of master standard spectra of the several elements, recorded on films and built into the spectroscope, where they are compared directly with the observed spectrum of the sample.

The instrument thus reads directly in terms of the constituent elements of the sample, without measurements or tables, without the time-

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* Letter describing the apparatus and photograph of a direct reading analytical spectroscope, Model No. 3, mailed Aug. 26, 1947. Complete text of manuscript, mailed April 27, 1948.

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[2] *Am. Mineral.*, **32**, 322–335 (1947).

consuming process of photographic recording, and without the necessity of specialized training in spectroscopic technique. The apparatus is self-contained and includes everything necessary for making an analysis. It is designed for operation on an alternating current of 115 volts, without the use of motor-generators or other auxiliary apparatus, so that it may be plugged into an ordinary electric power outlet. It is light and portable enough to be carried in a car for field tests.

## The Apparatus

The apparatus used is shown in Fig. 1. *A* is an arc holder, with a dispensable refractory hearth on which the sample is placed. *S* is a switch for turning the arc on and off. *C* is an eyepiece by which the spectrum is magnified and viewed. *D*, *D*, are films on which the master spectra are recorded, placed on both sides of the observed spectrum for direct comparison. *E*, *E*, are knobs for turning the spools on which the master spectrum films are wound.

All the rest is inside the box where the operator can forget it. The optical system is simple. The parts are rigidly mounted on pedestals on a substantial base casting and do not require adjustment. The spectrum is formed by a concave reflection grating of short focus, which not only makes the apparatus compact and simple, but forms a spectrum of great brilliance which is sensitive to elements present in small amounts. The focal length was chosen to give resolution sufficient for the separation of any elements likely to be found in mineralogical work, including minor constituents in irons which, as every spectroscopist knows, require care and precision when the ordinary spectroscopic methods are used.

Referring to Fig. 1, it will be noted that the points of the carbon electrodes of the arc are arranged in a horizontal plane, not vertically as in the usual spectroscopes and spectrographs. The sample is not placed in a hollow of the electrode, as is customary, but on a dispensable refractory hearth below the electrodes. The hearth adjacent to the electrodes has the effect of conserving and concentrating the heat of the arc. The hearth has a vertical adjustment for height, which permits control of the rate of "burning" of the sample, so that the spectra of the several component elements may be excited progressively and studied one by one instead of being all mingled together in confusion.

The alternating current in the arc is stabilized by a fixed ballast which does not require adjustment. For exceptional samples of highly refractory material an additional ballast is provided and snapped on by a switch, giving higher temperature in the arc. The optical system is designed to bring the spectrum of the sample to a focus in a curved band 3 mm. wide in the slot *B* between the films *D*, *D*, across which the characteristic lines

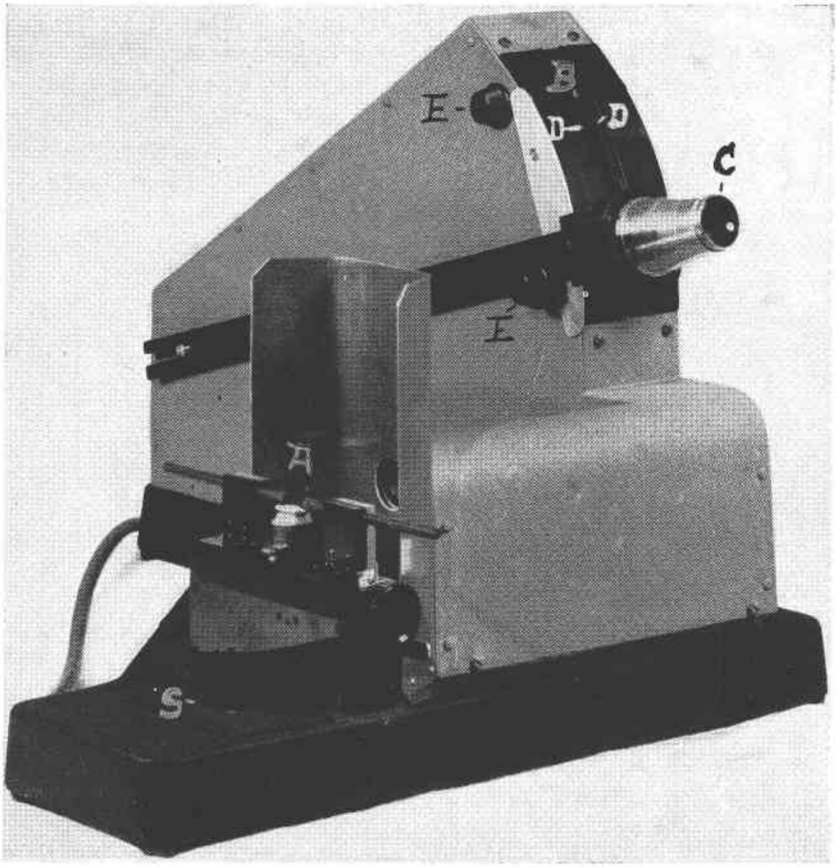


FIG. 1. The Direct Reading Analytical Spectroscope.
A. Arc holder with hearth.
B. Spectrum slot.
C. Eyepiece.
D, D. Master films.
E, E. Film control knobs.
S. Starting switch.

of the component elements appear, like rungs of a ladder, magnified by the eyepiece *C*. The lines are seen in the full brilliance of their colors against a dark background, free from dimming by any continuous spectrum.

The optical system also projects at the same time two continuous spectra, on opposite sides of the line spectrum of the sample and immediately adjacent to it. The films *D, D,* carrying the master standard spectra are arranged parallel to and on opposite sides of the spectrum of the sample, and are illuminated by the two continuous spectra. The master standard films are photographic positives, so that the lines of the standards, each illuminated by the correct part of the spectra, appear in their true spectral colors. They may thus be compared directly with the corresponding lines of the observed spectrum. When the spectrum of the sample and the standard are matched the lines appear continuous and unbroken across the spectrum of the sample and the master film, so that any departure from the standard is immediately apparent.

By this means, not one but all the lines characteristic of an element can be matched against the standard with a precision greater than could be expected by the measurement of the wave lengths of the lines, one by one, by any feasible scale. By the multiple coincidences of all the lines of the spectrum of an element, its identification is assured with precision and positiveness. If there are any lines in the spectrum that do not match, they are recognized at once as belonging to another element or elements, which are thus marked for identification in their turn.

The matching of the standard to the spectrum is assured by using the two *D* lines of sodium as a datum, to which the film is adjusted by means of the knobs *E*, *E*. The *D* lines are recorded on each master standard film and indicated by a marker and, since the *D* lines appear in practically every observed spectrum, the adjustment of the standard to this datum is easy. The *D* lines are exceedingly sensitive and are produced by less than 0.001% of sodium in the sample or the carbons.

## ANALYTICAL PROCEDURE

A sample is taken, in the amount of something like 25 milligrams, powdered in a mortar and placed on a hearth. The hearth is dispensable. A fresh hearth is used for each sample. Several refractory materials have been found suitable for hearths. For most mineralogical work slips of porcelain may be used if the determination of aluminum or titanium is not required. The china clay used in most porcelains contains a substantial amount of titanium. For exacting work hearths especially made of a purified material are preferable. Hearths of graphite are useful for highly refractory samples.

With the sample in place on the hearth, which is lowered, the switch *S* is turned on and the carbon points brought into contact, then separated, drawing an arc. The hearth is then raised gradually until spectrum lines are seen through the eyepiece. This gradual heating of the sample is a valuable feature, since the several elements vary greatly in their response to excitation. Mercury and antimony appear immediately and are soon volatilized and disappear. The alkalis, sodium, potassium, lithium, etc., appear quickly. In some combinations they inhibit the excitation of other elements until they are gone. The heavy metals appear with various degrees of heating. Zinc and cadmium appear soon. The metals of the platinum group require strong heat. The rare earths are slow to appear.

Applying the heat gradually by raising the sample slowly into the arc makes it possible to develop the spectra of the several components successively and pick them out one by one, without confusion. When a pattern of spectrum lines appears, if it is not recognized by the observer, reference is made to an index chart on which all the spectra of the master standards are recorded. When the desired pattern is found on the chart the corresponding master film is rolled into place by the knobs *E, E,* and its lines matched against the lines of the spectrum. The identification of that element is then complete and positive. Other components are likewise identified one by one, as they appear, by their line patterns.

This simple system of identifying elements by the patterns of their spectrum lines is in marked contrast with the laborious process usually employed of measuring the wave lengths of individual lines and looking them up in tables. It saves much time, labor, and specialized study. It is more positive and more accurate.

No two elements have the same spectral pattern. Their patterns are distinctive in arrangement and in color, and once learned they can usually be identified by inspection. The comparison of the observed pattern with its master film makes the identification complete. It is like fitting a key into a lock. Each notch of the key corresponds to a tumbler of the lock. So with the spectrum. Each coincidence of a line of the spectrum with an immediately adjacent standard line is highly accurate in itself. When such coincidences are multiplied the possibility of error is eliminated.

## THE MASTER FILMS AND INDEX CHARTS

The character of the master films may be understood by reference to the index charts used as a guide to the selection of the desired identification film. Figure 2 is a reproduction of one of the index charts. This chart shows the most significant line groups in the spectra of 16 more important metals. The spectra are arranged in the order of the positions of the prominent line patterns in the spectrum, ranging, for this chart, from the violet to the yellow; lead, with its strong violet line, being first on the left and molybdenum, with its yellow triplet, being last on the right.

It will be apparent at once that each element has its own distinctive pattern of lines. It will be noted also that there are certain resemblances as well as differences between the several patterns. The most conspicuous pattern of all, which everybody knows, is the brilliant yellow doublet of

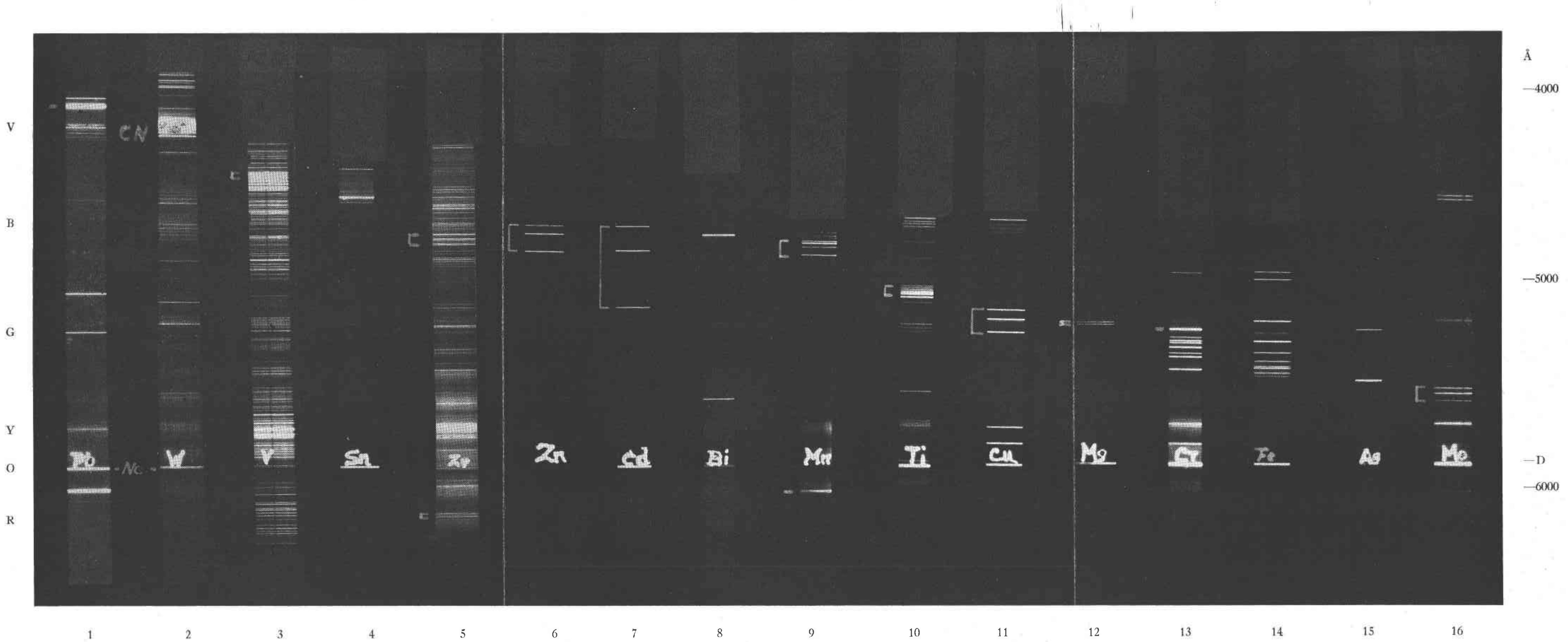


Fig. 2. Index chart of the identification films of 16 metallic elements. Prominent line groups are indicated by brackets.

sodium, the *D* lines of Fraunhofer. These lines, used as the datum for orienting the spectra, are recorded on every master film. They are indicated by the letters identifying the element on each of the films. Sodium has also several weaker doublets, one in the green, one in the red and one in the blue, which are not strong enough to appear in this chart. Potassium likewise, which is listed on another index chart, has a pair of strong lines in the deep red and another pair in the high violet. Aluminum is noted for its several doublets in the ultra violet.

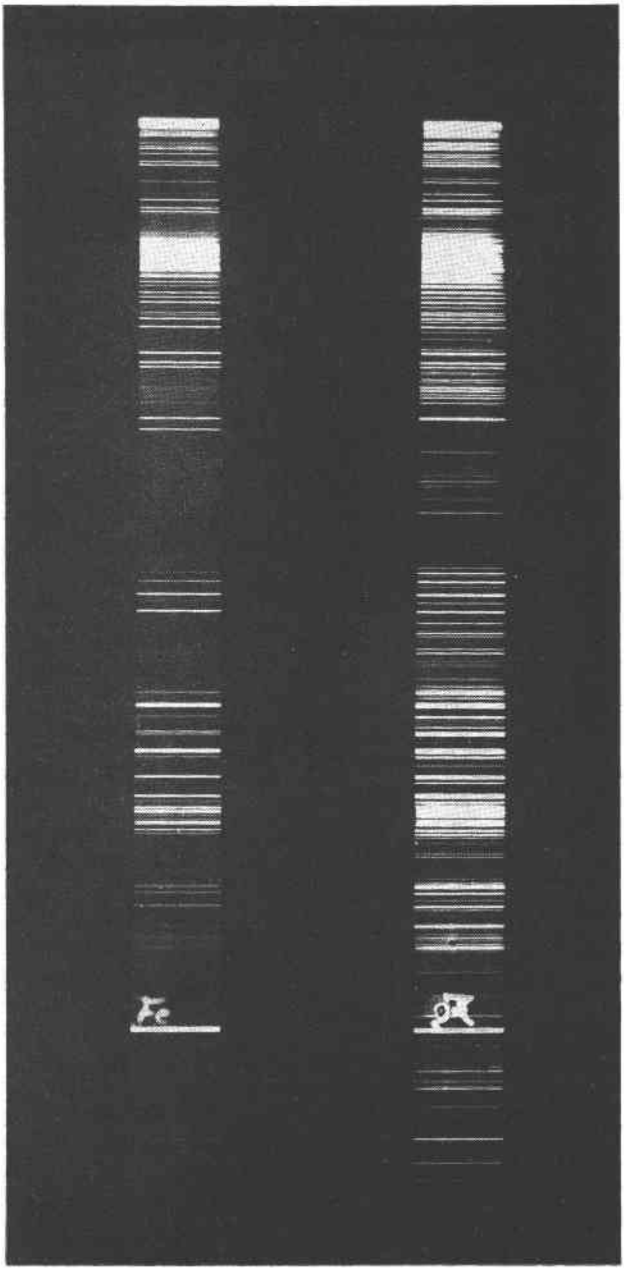
There are physical reasons for these and other line groups in the arrangement of the electrons in the atom, but that is outside the scope of this discussion. We shall find it convenient to use the patterns empirically for identifying the elements.

Referring again to the chart, Fig. 2, it will be noted that there are several groups of three lines, differing in spacing and in color. Zinc (spectrum No. 6) has three bright blue lines. Copper (No. 11) has three similar lines, but they are a vivid green. Cadmium (No. 7) has three blue lines with a wider spacing. Molybdenum (No. 16) has a closer group of three yellow lines. Magnesium (No. 12) has a still closer group of three green lines. Manganese (No. 9) has a triplet of red lines that appear in the reproduction as a single broadened line but are clearly resolved by the instrument into the three components. Manganese has also a vivid group of blue lines. Chromium (No. 13) has a close green triplet with a separation of only 1.5 and 2.4 Å, which shows in the figure as a broadened bright line. It is resolved by the instrument and is the first group to appear when there is a trace of chromium present. When chromium is present in larger amounts the pattern of other green lines appears below the close triplet. Zirconium (No. 5) has a spectrum of many lines, but it is readily distinguished by a group including a bright green triplet, and by another still brighter triplet in the red.

These and other similar groups are valuable because they can be seen at a glance and are unmistakable. They are especially useful in detecting their elements from complex samples. As they flash in and out with variations in the light of the arc they are immediately distinguished as separate from the surrounding lines, and comparison with the master film establishes their identification.

This is an outstanding advantage of the present system of visual analysis over the conventional method of spectrography, where everything is jumbled together and has to be laboriously unscrambled.

Other elements have quintuplets. Titanium (No. 10) has such a group of five blue-green lines, almost equally spaced, which are immediately evident. Vanadium (No. 3) has a closer violet quintuplet of 5 Å spacing



I E

FIG. 3. Identification Spectrum, I, and Elimination Spectrum, E, of iron.

that readily distinguishes its otherwise complex spectrum. Every spectroscopist knows the famous ultra-violet quintuplet of magnesium. The triplet of magnesium here employed is equally distinctive.

Some elements have distinctive pairs of lines more widely spaced. Silver (No. 15) has a green line and a yellow line. The latter has a weaker component 6 Å below it. Bismuth (No. 8) has a wide pair, one blue and the other yellow. Lead (No. 1) has a green pair, not so strong as its outstanding violet line. Tungsten (No. 2) has a closer green pair, besides stronger violet lines.

These and other distinctive line groups and *raies ultimes* are charted on a graduated scale included in the film of master spectra, as a supplementary guide to the master films and index charts, and as a guide for finding suspected elements in the spectrum.

There remains the spectrum of iron, No. 14. Iron has one of the most intricate of metallic spectra. The ordinary working tables of the spectroscopist list some 2500 lines of iron, whose wave lengths are determined with an accuracy of one part in a million or better and are used by spectroscopists as a standard of reference. Its lines are closely spaced over the entire range of the visible and ultra-violet spectrum.

For the purpose of our identification film the number used is reduced to about 25 prominent lines that are visible when iron is present in small amounts. One of these, a strong green line of $\lambda = 5{,}371.493$ Å, is visible when a small trace of iron is present in a sample, and six others near it form a distinctive pattern that is readily identified when any substantial amount of iron is present. Larger amounts bring out a group of blue lines and still larger amounts a group of red lines. Thus identification of iron and a rough estimate of the amount present is readily made by inspection.

When iron is a major constituent, innumerable fine lines appear. To pick out the lines of other constituents of an iron mineral by the conventional method of wave length measurements is a highly exacting problem. By the present method of master standards an elimination film is used. This is shown on a larger scale at *E* in Fig. 3, though much of the fine detail is lost in reproduction. The identification film of Fig. 2, No. 14 is shown on the same scale next to it, at *I*. The elimination film is mounted on one side of the spectrum and the identification film on the other side. By matching the lines of the elimination film against the lines of the sample, any lines that do not match are at once apparent as belonging to a different element and are identified by matching against the appropriate identification film.

Similar identification films of other elements are included so that complex spectra including many elements may be analyzed.

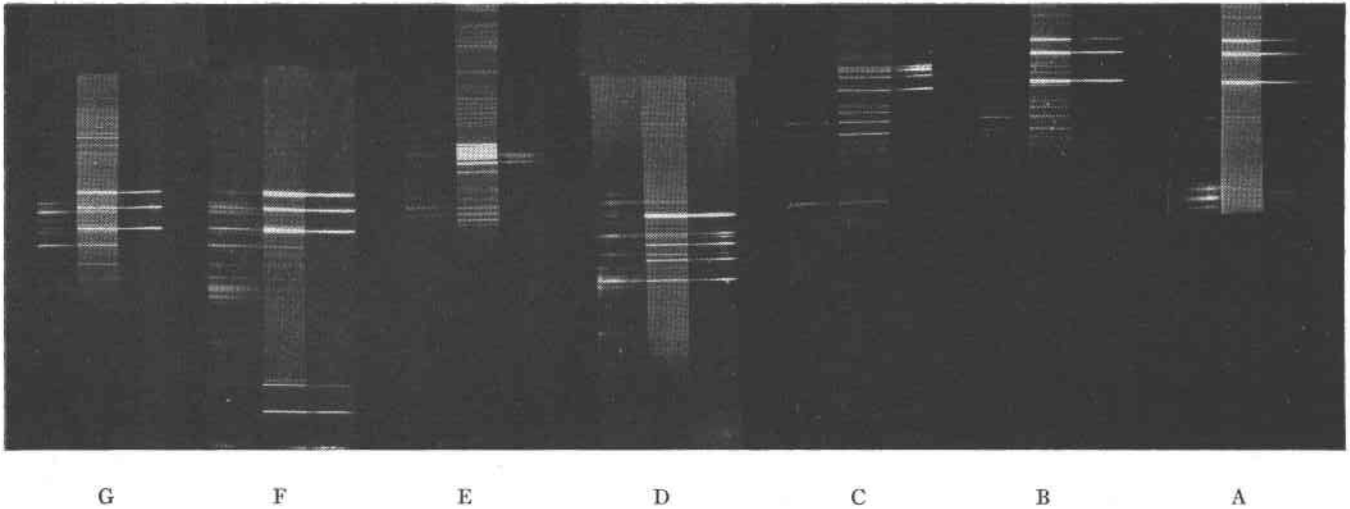


FIG. 4.—Spectra of four iron minerals matched against master films. Photographed as seen by observer.

A, B, C—Three aspects of franklinite.
A—Early phase. Zn matched by identification film, right.
B—Later phase. Zn matched right, Fe left, Mn unmatched, weak.
C—Final phase. Mn matched right, Fe left, Zn finished.
D—Chromite. Cr matched right, Fe left.
E—Ilmenite. Ti matched right, Fe not yet developed.
F—Chalcopyrite. Cu matched right, Fe (weak) left.
G—Chalcopyrite, later phase. Cu matched right, Fe left, Ti visible and unmatched.

The procedure in practice is illustrated for several iron minerals in Fig. 4. Each of the figures, A, B, C, D, E, F, G, is a photograph of a part of the spectrum of a sample, made with a camera whose lens was substituted for the eye piece of the spectroscope. The photographs are limited in scope and detail because of the curvature of the field.

A, represents the spectrum of franklinite at the beginning of the "burning." Zinc only has been excited at this time and its three brilliant blue lines are seen matched against the identification film of zinc at the right of the spectrum. The elimination film of iron is shown in part at the left but its lines are not matched in the spectrum. The iron spectrum has not been developed.

B, shows the spectrum of the same sample as it appeared a little later. The zinc lines are still bright. The spectrum of iron is partly developed and its lines are matched against the lines of the iron film on the left. Intermingled with the zinc lines are five other blue lines that do not match either film and so are known as belonging to another element.

C, shows the final stage. The zinc lines have almost disappeared and the five other blue lines, now stronger, are matched against the film of Mn and thus identified. The iron spectrum is well developed and its lines matched against the film on the left.

D, shows the spectrum of chromite. The pattern of chromium green lines is well developed and matched against the film on the right. The spectrum of iron is still weak but the lines that are visible are matched against the iron film on the left.

E, shows the spectrum of ilmenite. The pattern of titanium is well developed including not only the conspicuous blue-green quintuplet, matching the film on the right, but also other less sensitive lines that are not included in the identification film. Titanium is thus shown to be a large constituent. The iron spectrum is not yet developed.

F, shows the spectrum of chalcopyrite in an early stage, with the copper spectrum matched at the right, including its three green lines and two yellow lines in full strength. The iron spectrum is beginning to appear.

G, shows a later stage. The copper lines are weaker and the iron stronger. Titanium is visible faintly as a small constituent.

Without going into unnecessary detail, it may be said that index charts similar to Fig. 2 are made with the elements arranged in groups having natural affiliations, such as the alkali elements, Li, Na, K, Rb, Cs; the elements of the calcium group, Mg, Ca, Sr, Ba; the elements of the platinum group, Ru, Rh, Pd, Os, Ir, Pt; the rare earths elements, etc.

This arrangement is convenient since the elements of each group are often associated in minerals and also because the spectra of the several groups have certain general characteristics in common. The alkali elements, with their single valence electron, have relatively simple spectra with very strong lines, and are quick to appear. The elements of the calcium group, with two valence electrons, have more complex spectra, with strong lines and slower to develop.

The elements of the transitional group, including the metals shown in Fig. 2 and the metals of the platinum group, are not so readily generalized, but each has a distinctive line pattern.

Gallium, indium, and thallium each have individual lines of outstanding brilliancy. Silicon and beryllium have visible arc lines but they are not strong. These elements are best determined in the ultra-violet. The rare earth elements, with their incomplete $N$ shells having different numbers of electrons, are in a class by themselves spectroscopically, as they are chemically. They have spectra of many lines that are slow to develop by which they may be recognized as a group. Since they are practically always mixed in nature, their separate determination by the conventional methods is difficult. By the present method, the elimination films weed out at a glance the lines of the more common elements, such as cerium and lanthanum, leaving the lines of the other constituents clearly marked for identification.

Of the elements of negative valency, P, As, S, Se, Te, F, Cl, Br, I do not produce lines in the visible arc spectrum that are favorable for identification. Some of them, notably fluorine, produce molecular bands that are useful for this purpose, but it is not the purpose of this paper to go into that rather specialized field except for certain examples of unusual interest to mineralogists.

## Molecular Band Spectra

One element that is common in minerals, aluminum, has its most prominent lines high in the violet, near the limit of visibility, but it has also a characteristic molecular band spectrum that is useful in identifying it. Like other molecular bands, this consists of many fine lines whose spacing is concentrated toward a series of band heads, which are sharply defined limits of the bands. The element is recognized by the pattern of these band heads on the master film, as in the case of line spectra.

The principal lines of boron are high in the ultra-violet but it also has a band spectrum by which it is identified. Fluorine does not form a line spectrum by arc excitation, but CaF has a brilliant band spectrum in the yellow and red. When F is present without Ca, a little of a calcium compound mixed with the sample produces the band spectrum and shows the presence of fluorine.

The bright bands shown on some of the spectra in Fig. 2, on the violet end, are molecular bands of CN, formed by the combination of carbon of the electrodes with nitrogen of the air. The fine structure is lost in the reproduction but the pattern of band heads can be seen.

There are many other band spectra that are of interest to specialists but they may usually be disregarded in the analysis of minerals.

## Conclusion

The spectroscope here described is designed primarily for qualitative analysis. It is specialized for that purpose. The use of master standards for direct comparison with the visible spectrum, combined with the feature of progressive excitation which causes the elements to appear in succession, greatly facilitates the determination of the constituent elements of the sample, whether simple or complex.

It does not pretend to be a quantitative instrument. However, it is adapted for the semi-quantitative estimation of the relative amounts of the elements present in a sample, by comparison of the spectrum with the identification films and the elimination films, as indicated in the case of iron in Fig. 3.

In general it may be said that a major constituent should show all the lines of the elimination film; a minor constituent, the strongest of those lines; a small percentage, the lines of the identification film; and a trace, only the most prominent lines. These four classes may differ, roughly, by a factor of ten. One may thus distinguish between essential components of a mineral, minor constitutents or isomorphous substitutions, and impurities.

The system is especially adapted to finding the minor constituents of a complex sample. It is useful for the detection of titanium in irons, silver in galena, barium in feldspars, manganese in calcite, hafnium in zircon, cesium, rubidium and thallium in lepidolite, etc; also in such problems as the relation of impurities to color and fluorescence.

It is useful in prospecting for the immediate examination and selection of numbers of samples, and as a guide to detailed assays. In this field it is a great time and labor saver, as well as a guide to the assayer or chemist. It has an advantage over an assay in its ability to locate the presence of an element in small, selected parts of a specimen without destroying the specimen. In the study of rocks, it is not unusual to detect as many as ten or a dozen elements in a single sample.

This system is not a substitute for precise chemical or spectrographic analyses. The writer has made some contribution in the latter field. It is believed, however, that it fits in a niche that is all its own and is not occupied by any system otherwise available.