133
820
THS

SPECTRAL LINE INTENSITIES OF TITANIUM IN STEEL

Thesis for the Degree of M. S.

MICHIGAN STATE COLLEGE
George Parker Koch

1942

MICHIGAN STATE LIBRARIES
3 1293 01771 8317

LIBRARY
Michigan State
University

PLACE IN RETURN BOX to remove this checkout from your record.
TO AVOID FINES return on or before date due.
MAY BE RECALLED with earlier due date if requested.

DATE DUE	DATE DUE	DATE DUE

1/98 c:/CIRC/DateDue.p65-p.14

SPECTRAL LINE INTENSITIES OF TITANIUM IN STEEL

BY

GEORGE PARKER KOCH

A THESIS

Submitted to the Graduate School of Michigan State College of Agriculture and Applied Science in partial fulfilment of the requirements for the degree of

MASTER OF SCIENCE

Department of Chemistry

1942

ACKNOWLEDGEMENT

The author wishes to express his appreciation to Dr. D. T. Ewing under whose direction this work was carried out.

142668

The purpose of this investigation was to find, if possible, one or more titanium lines in the spectra of titanium-steel alloys which might be used as the basis of a procedure for the spectrographic analysis of titanium in steel, and to investigate the suitability of these lines for that purpose.

CHOICE OF LINE

There are many factors which enter into the choice of a line or lines to be used for a spectrographic analysis. Perhaps the most important of these is the position of the line in the spectrum, that is, its wave length. This will determine the type of photographic emulsion which must be used in the analysis, and it is of course obviously simpler to work with a line which falls into an easily accessible photographic region.

The character of the line itself is also of prime importance. It must possess sufficient inherent intensity to avoid a period of exposure which is impractical or which will produce a background of sufficient intensity to alter the density of the line. It must also be separated from adjacent lines by an amount great enough to insure that it will be resolved

from these other lines when the slit of the spectrograph is opened to that width to be used in the analysis.

If the concentration of the element sought is relatively large, and if the intensity of the line is of itself great, the photographic image may suffer reversal unless an extremely short exposure is taken or unless the amount of light entering the instrument is decreased by some means, as for example, by a rotating sector. If on the other hand the concentration of the element sought is relatively small, the use of an intense line is necessary, and in the case of very small concentrations, the use of a line which is both strong and persistent may be in order.

The effect of fluctuations in the excitation conditions on the intensities of the lines to be used for the working line and the internal standard line should also be investigated. This may be done by determining their intensities under various accurately controlled conditions. It is well to choose for the working line and the internal standard line lines which do not vary in intensity for considerable fluctuations in the excitation conditions.

In this connection the use of an homologous pair for the working line and the internal standard line may be advantageous. An homologous pair has been defined as two lines having approximately the same excitation conditions so that for a considerable variation in excitation conditions any change which takes place in one will take place to the same extent in the other. This phase of the problem of choosing a line was not investigated in this thesis.

In choosing a spectrum line to be used in an analysis some attention should also be given to the amount of energy required to produce that line. Under the usual conditions of excitation only those lines coming from neutral or singly ionized atoms are obtained. Sources of unusually high energy are required to obtain lines from atoms in a higher state of ionization.

The first step undertaken in this investigation was to obtain a number of titanium lines which, according to the above requirements, might be suitable as working lines. For this purpose spectra of the titanium-steel containing the largest concentration of titanium were compared

with spectra of a sample of Armco iron of very high purity. Two types of excitation were used, a direct current arc and a condensed spark. The spectrum range covered in each case was roughly from 2300 to 5000 angstroms. The search for titanium lines was greatly facilitated by using a Judd-Lewis comparator, an instrument which makes possible the simultaneous comparison of spectra on two different plates.

The first part of the search for suitable titanium lines was carried out by comparing the spark spectra of the pure Armco iron with the spark spectra of the titanium-steel sample containing the largest per centage of titanium. All the lines appearing in the titanium-steel spectra and not in the pure iron spectra were carefully noted and marked if they appeared to be sufficiently separated from adjacent iron or titanium lines and possessed an appreciable intensity. The wave lengths of the titanium lines which satisfied these requirements were determined by comparing the titanium-steel spark spectra with what may be called an iron arc-spark reference plate. This plate consisted of an iron arc spectrum and an iron spark spectrum photographed in juxtaposition

through a Hartmann diaphragm. The range of wave lengths covered on this plate was the same as that covered by the titanium-steel spark spectra. In determining the wave length of a given titanium line the spark spectra on the two plates were lined up and the wave length of the titanium line determined by interpolation between known lines in the iron arc spectrum. This procedure was necessary because the spectrum charts available listed the wave lengths of the iron spectrum in terms of an arc source and it was found impossible to correlate the iron spark and the iron arc spectra because they were so widely different. Because the maximum resolution was desirable in the determination of the wave lengths, a slit opening of five microns was used.

The slit width was then increased to forty microns and spectra of the titanium-steel and of the reference iron standard taken at this larger slit opening were compared. The purpose of this step was to actually determine if the lines chosen were still resolved from adjacent iron or titanium lines.

The procedure outlined above for the spark was carried out over the same wave length range using a direct current arc, except of course that the use of an iron arc-spark reference plate was not necessary.

Two lines of titanium were found which fitted all the requirements. Their wave lengths according to Harrison are 3361.213 and 3372.800A and their intensities 600 and 400 respectively.(1). The 3361.213 line is a persistent line of titanium. The values of the intensities given are those obtained using a spark source. Because the intensities are appreciably larger in the spark than in the d-c arc it was decided to concentrate on this type of excitation. Both of these lines arise from the singly ionized titanium atom.

Within a range of three angstroms on either side of the titanium line at 3361.213A there are no titanium or iron lines having an intensity of greater than 5 with the exception of the titanium line at 3361.263A. This line would not of course be resolved, but its small intensity(50 as compared to 600) made it improbable that it would affect the intensity of the stronger line to a measureable extent.

Within the same range on either side of the titanium line at 3372.800A there are no titanium or iron lines with an intensity of greater than 30 with the exception of the iron line at 3370.786A having an intensity of 200. This line is resolved from the 3372.800A titanium line at a slit width of forty microns.

CHOICE OF PHOTOGRAPHIC EMULSION

The choice of a photographic emulsion depends upon the wave length of the line which is to be used for the analysis, the range of concentrations over which the analysis is to be made, and the accuracy required in the analysis. The characteristics of three different Eastman photographic emulsions, the Spectrum Analysis No. 1, the 33, and the 40, are expressed in terms of their H & D curves in Fig. I. These curves were prepared by exposing the various plates to visible light through a step density tablet, the steps of which transmit light in known amounts, the ratio between successive steps being the square root of two. The densities of the several steps were determined on an Eastman densitometer which reads directly in

densities.

It can be seen that the Spectrum Analysis No. 1 emulsion would give the greatest accuracy since for a relatively small increase in intensity there would be a relatively large increase in density. However, the range of concentrations over which this emulsion may be used is smaller than that for which either a 33 or 40 emulsion would be suitable.

The H & D curves give no information on the spectral sensitivities of the different emulsions. The Eastman 40 was found to be somewhat more sensitive than the Eastman 33 throughout the region from 2300 to 5000A. The Eastman Spectrum Analysis No. 1 emulsion is less sensitive than either the 33 or 40 in the region from 2300 to 5000A, and much less sensitive in the region from 3500 to 5000A.

In this investigation it was desired to cover the maximum concentration range possible with accuracy a secondary factor. This was the reason for choosing the 40 emulsion.

CALIBRATION OF PLATE

In order to insure that one is working on the straight line portion of the H & D curve of the photographic emulsion, the range of densities

over which there exists a linear ratio between the density and the logarithm of the intensity(or exposure) must be known. The emulsion may be calibrated conveniently and accurately by the use of a logarithmic stepped sector placed in front of the slit. A necessary prerequisite of the use of such a sector is that the slit be evenly illuminated, a condition which was not exactly met in this work. Nevertheless, from the calibration curves prepared the density level at which a linear ratio between the density and the logarithm of the intensity(exposure) was no longer available was evident. It then remained to expose the samples and develop the plate in such a way that the range of densities obtained for the analysis lines did not exceed this value, which was about 1.8. If this was done, however, a considerable amount of background was obtained. It has been shown(2) that a background of sufficient intensity will affect the density of a spectrum line. For this reason the exposure was reduced considerably. An exposure of either 8 or 4 seconds was found to give some continuous background, but presumably not enough to alter the density of the lines. These exposures were

made using a slit width of 60 microns. It may be noted here that a slit width of 40 microns was used in the preliminary work, but this was increased, as stated above, to 60 microns for the analysis. This change was instituted in order that the slit of the density comparator would be more completely covered by the spectrum lines. In this way the line could be scanned effectively. The same conclusions regarding the separation of the working and internal standard lines from adjacent lines which held at a slit of 40 microns are strictly valid at 60 microns.

STANDARD SAMPLES

A series of standard samples of titanium in steel was obtained from the Bureau of Standards. They were numbered and had the following concentrations:

Number	Titanium %
8	1.19
7	.61
6	.33
5	.004
4	.05
3	.04
2	.00
1	.003

The work inthis particular investigation was concerned only with those concentrations above 0.04% titanium.

The samples as obtained were cylindrical rods 5/8 inches in diameter over 3½ inches of their length and 3/8 inches in diameter over the remainder of their length-1½ inches. The length of the smaller diameter was the part exposed to the action of the spark. The surface was not renewed for successive exposures during the preliminary investigations, but a fresh surface is desirable for greater accuracy, as well as for greater reproducibility.

SPECTROGRAPH AND DENSITOMETER

The spectrograph used in this investigation was a Bausch & Lomb 180 cm. Littrow. It was found that a definite improvement in the sharpness of the spectrum lines on the photographic plate could be obtained by using values of the tilt and focus slightly different from those given by the manufacturers. The improvement is to be noticed chiefly when a series of lines very close together, such as the configuration of iron lines at 3100A, is observed. A more distinct image of the spectrum lines has the effect of increasing the resolution of the instrument.

The densities of the spectrum lines and of the various steps in the step sector patterns were determined on a Bausch & Lomb density comparator. A Leeds & Northrup type R d'Arsonval galvanometer having the following characteristics was used in conjunction with the comparator:

Sensitivity:	0.00047 muA/mm.
Coil Resistance:	500 ohms
C. D. R. X.:	10,000 ohms
Period:	6 seconds

In order to obtain a critical damping of the galvanometer, about 8000 ohms was added in series to the external resistance of the circuit. A deflection of about 70 mm. was then obtained at a distance of two meters as the difference between the clear plate and the black reading. It was possible to read the scale to 0.5 mm.

The densities of the various lines were calculated from the formula

$$D = \log \frac{g - g_0}{g' - g_0}$$

where the g's represent deflections on the scale of the instrument, g the clear plate reading, g_0 the black reading, and g' the line reading.

PROCESSING OF PLATES

All plates were developed in EKC D-19 developer and fixed in EKC acid hypo fixing solution. The 40 plates were developed for five minutes with agitation at fifteen second intervals. They were left in the fixing solution for twice the length of timerequired for complete clearing. When the time required to completely clear the plate reached ten minutes the solution was discarded. A convenient test for the exhaustion of the fixing solution may be made by mixing 50 cc. of the solution with 5 cc. of 4% KI. The formation of a yellow cloudiness indicates that the solution is exhausted.(3).

The effect of the exhaustion of the developing solution on the gamma of the photographic emulsion may be seen in Curves A, Fig. II. Curve (2) is the H & D curve of a plate exposed and developed under the same conditions as the plate whose H & D curve is (1), but which was developed after 28 more plates had been put through the solution. It is evident that the gamma is increased as the solution is used. With the small tank of developer used and the extensive use of the solution by many others, the decrease in the volume of the

solution because of drag-out and evaporation presented quite a serious problem, so much so that it was necessary from time to time to bring the level of the solution back to its original height in order that the photographic plate would be completely immersed. In this connection it was desirable to maintain the potency of the solution as nearly as possible. Curves B and C in Fig. II indicate that the addition of equal parts of fresh developer and water or of water alone accomplishes this purpose. Curve (1) in each case represents the H & D curve of a plate developed before the level of the solution was restored, curve(2) that of a plate developed immediately after renewal of the solution.

In all probability the reason why the addition of water only has the same effect as the addition of equal parts of water and fresh developer is that the water alone was added when a greater degree of exhaustion had been reached. This would indicate, therefore, that the proper proportion of water and developer which should be added to the solution depends upon the degree of exhaustion of the solution, and that the proportion of developer to be used decreases as the exhaustion becomes more complete.

All plates were processed at 18° C, the tanks containing the developer and fixer being maintained at this temperature by a water bath. Between five and ten minutes is required for the solutions in the tanks to reach temperature equilibrium with the water bath after the external temperature is brought either up or down to the standard temperature. A small amount of stirring hastens the attainment of equilibrium.

DISCUSSION

The results obtained in this study are shown in Figs. III and IV. The ratios of the densities of the two titanium lines used as working lines tothe density of the iron line 3570.10A, the internal standard line, are plotted against the logarithms of the per cent titanium in the standard samples. The possibility of using the titanium lines 3361.213 and 3372.800 in a spectrographic analysis is clearly indicated.

In the curves shown it can be seen that the densities obtained for the same lines and the same exposures are not equal. This difference would be corrected for in any analytical method by referring the densities of the lines to a standard calibration curve or by using the differences in the densities of the working and internal standard lines as the basis for the working curve.

The regular decrease in the intensities of the 3361.213 and 3372.800A titanium lines as the concentration of titanium decreases is apparent in Fig. V.

Since the concentrations obtained from the working curves constructed were only within

30 % of the concentrations given for the standard samples, the results could not properly be called quantitative. An error of this magnitude could, however, be tolerated in a survey analysis.

The same two titanium lines used in this study have been used for the estimation of titanium in steel by the internal comparison method.(4)

The relation between the intensity of the titanium line at 3380.30A and the concentration of titanium in titanium-steels has been investigated by Brody.(5). The iron line at 3369.549A was used as the internal standard line.

SUMMARY

Curves showing the ratio of the densities of the titanium lines 3361.213 and 3372.800A to the density of the iron line 3570.097A as a function of the concentration of titanium in steel have been presented. The results indicate that the titanium lines given could be used in a method for the spectrographic analysis of titanium in steel.

REFERENCES

(1) "M. I. T. Wavelength Tables," George R. Harrison, Ed. pp. 270, 272. John Wiley & Sons, Inc., New York, 1939

(2) L. W. Strock, "Spectrum Analysis with the Carbon Arc Cathode Layer," p. 39. Adam Hilger, Ltd., London

(3) C. B. Neblette, "Photography, Its Principles and Practice," Ed. 3, p. 342. D. Van Nostrand Company, Inc., New York, 1939.

(4) F. G. Barker, J. Iron Steel Inst., 139, 211 (1939)

(5) J. K. Brody, "Spectral Line Ratios of Iron-Nickel and Titanium-Iron." Thesis for the degree of M. S., Michigan State College, 1941.

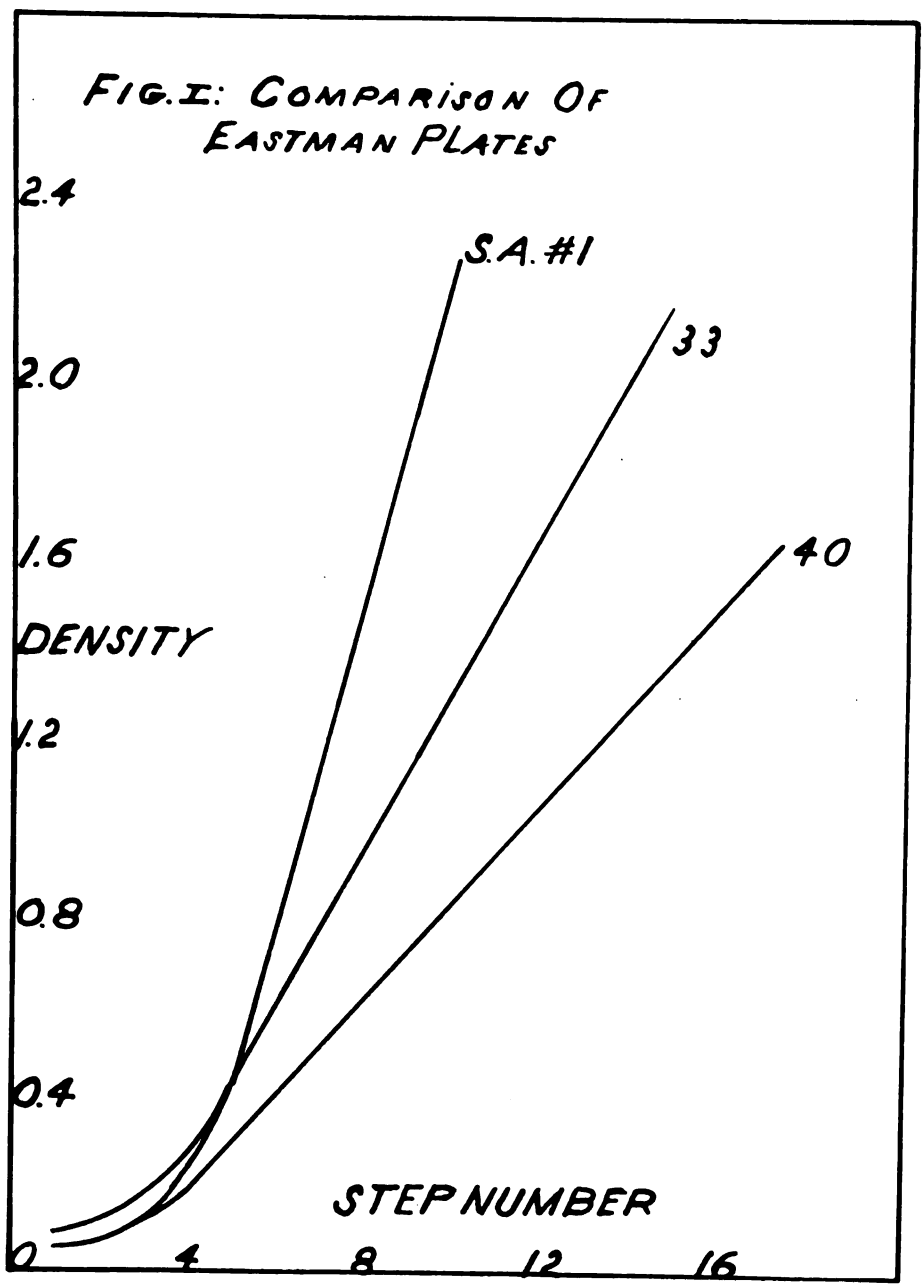


FIG. I: COMPARISON OF EASTMAN PLATES
2.4
2.0
1.6
DENSITY
1.2
0.8
0.4
0
4
8
12
16
STEP NUMBER
S.A. #1
33
40

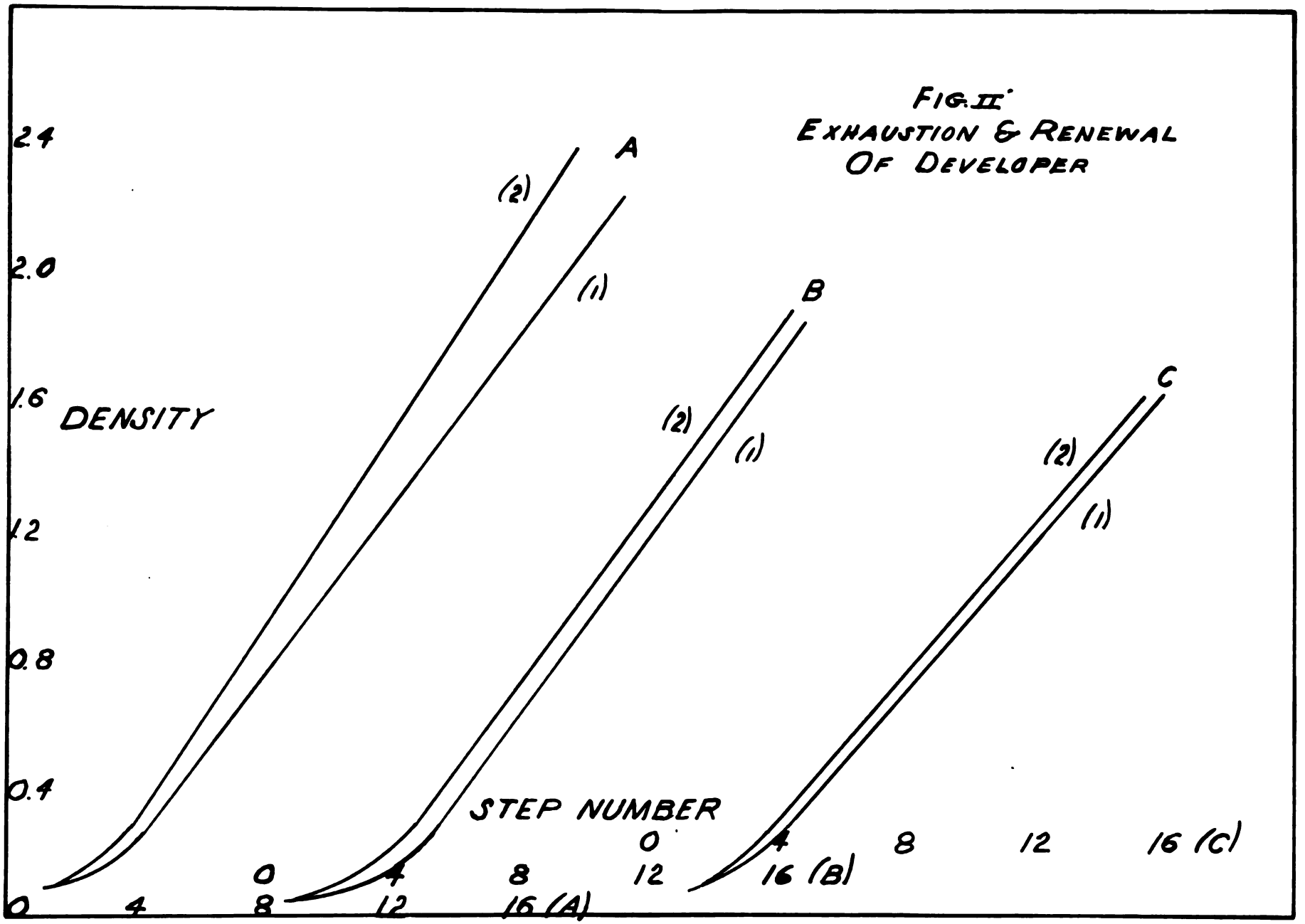
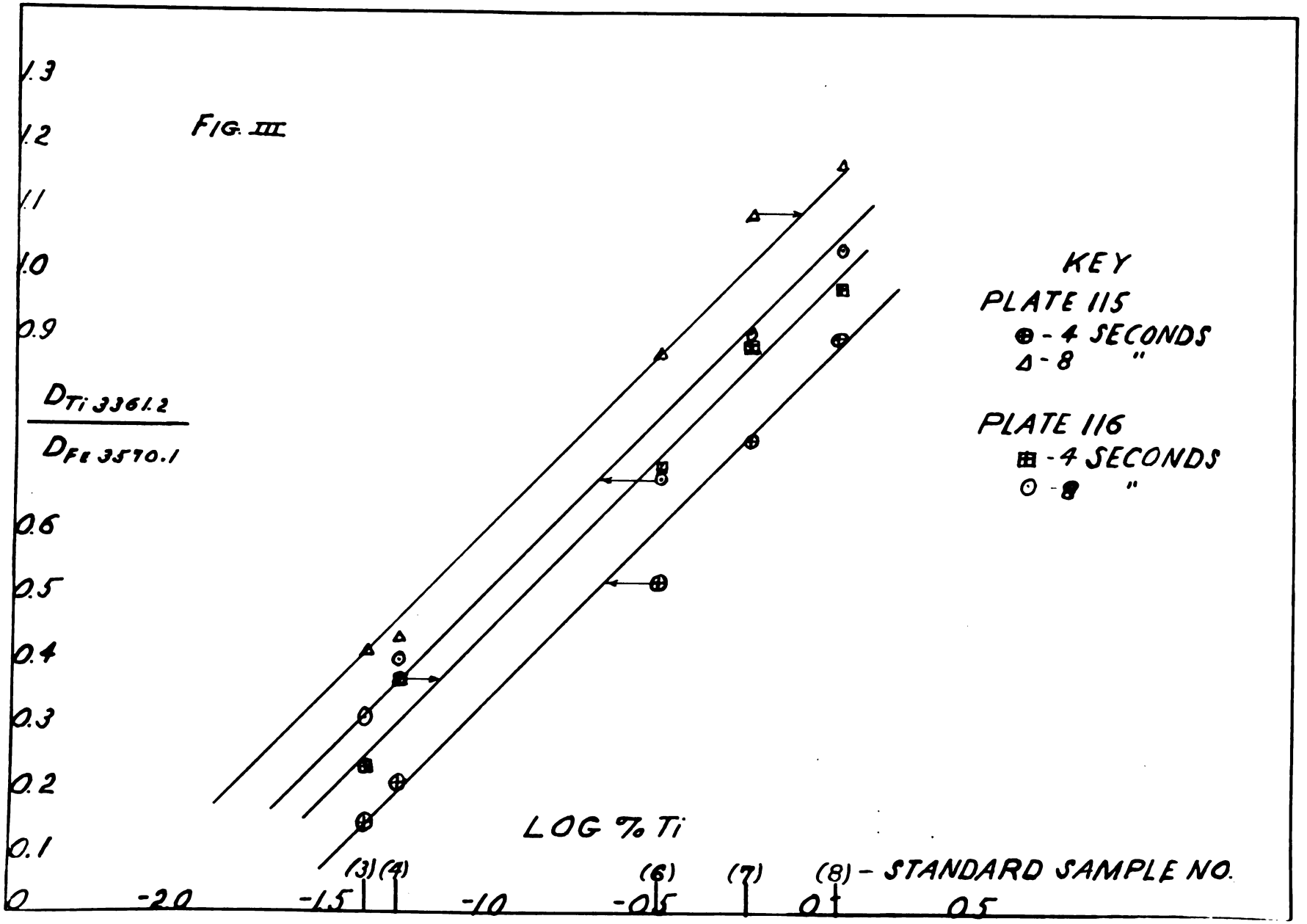


FIG. II
EXHAUSTION & RENEWAL
OF DEVELOPER
DENSITY
2.4
2.0
1.6
1.2
0.8
0.4
0
A
B
C
(1)
(2)
STEP NUMBER
0
4
8
12
16 (A)
16 (B)
16 (C)

FIG. III


1.3
1.2
1.1
1.0
0.9
$\frac{D_{Ti\ 3361.2}}{D_{Fe\ 3570.1}}$
0.6
0.5
0.4
0.3
0.2
0.1
0
-2.0
-1.5
-1.0
-0.5
0
0.5
(3) (4)
(6)
(7)
(8) – STANDARD SAMPLE NO.
LOG % Ti
KEY
PLATE 115
⊕ - 4 SECONDS
Δ - 8 "
PLATE 116
⊞ - 4 SECONDS
⊙ - 8 "

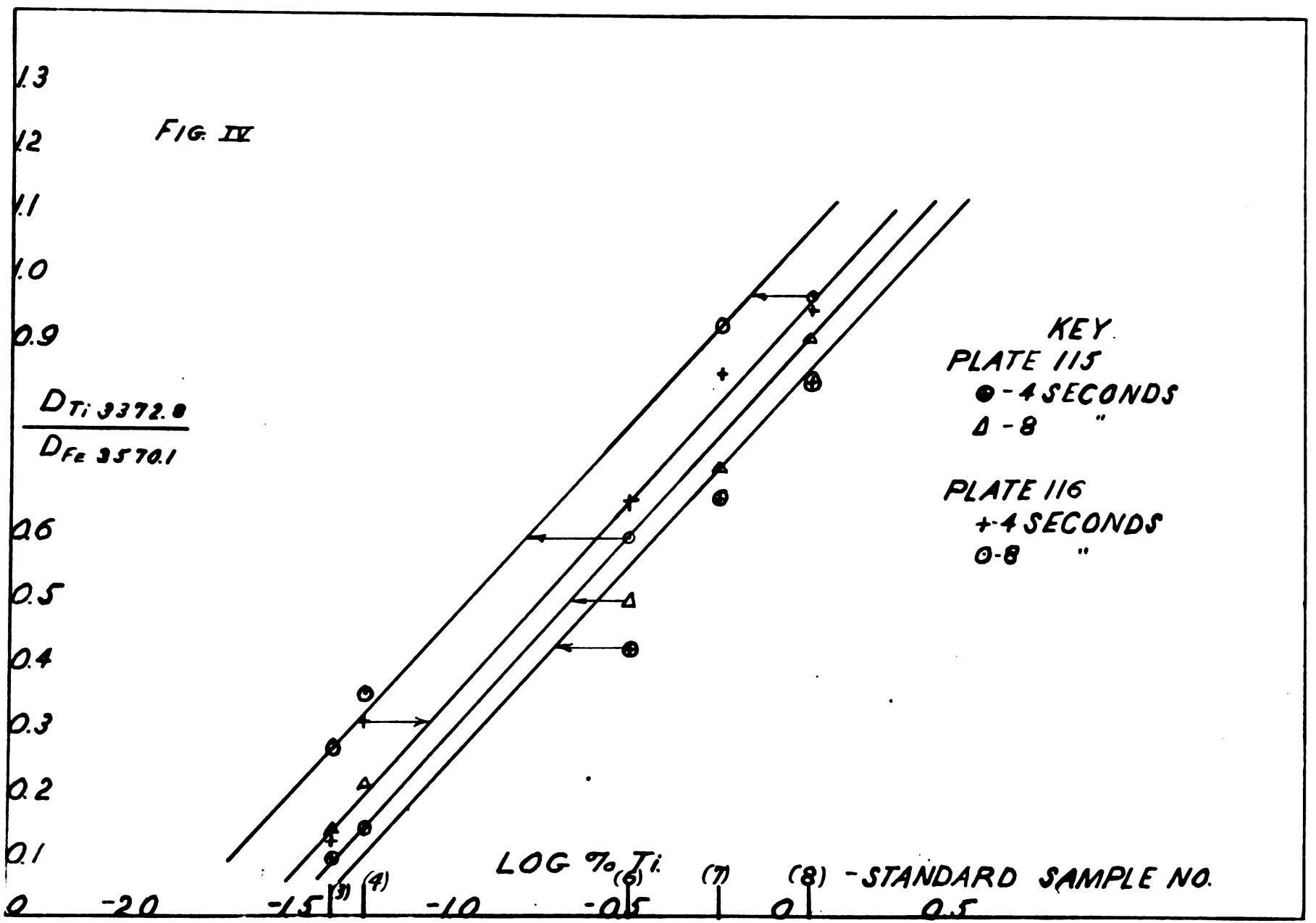
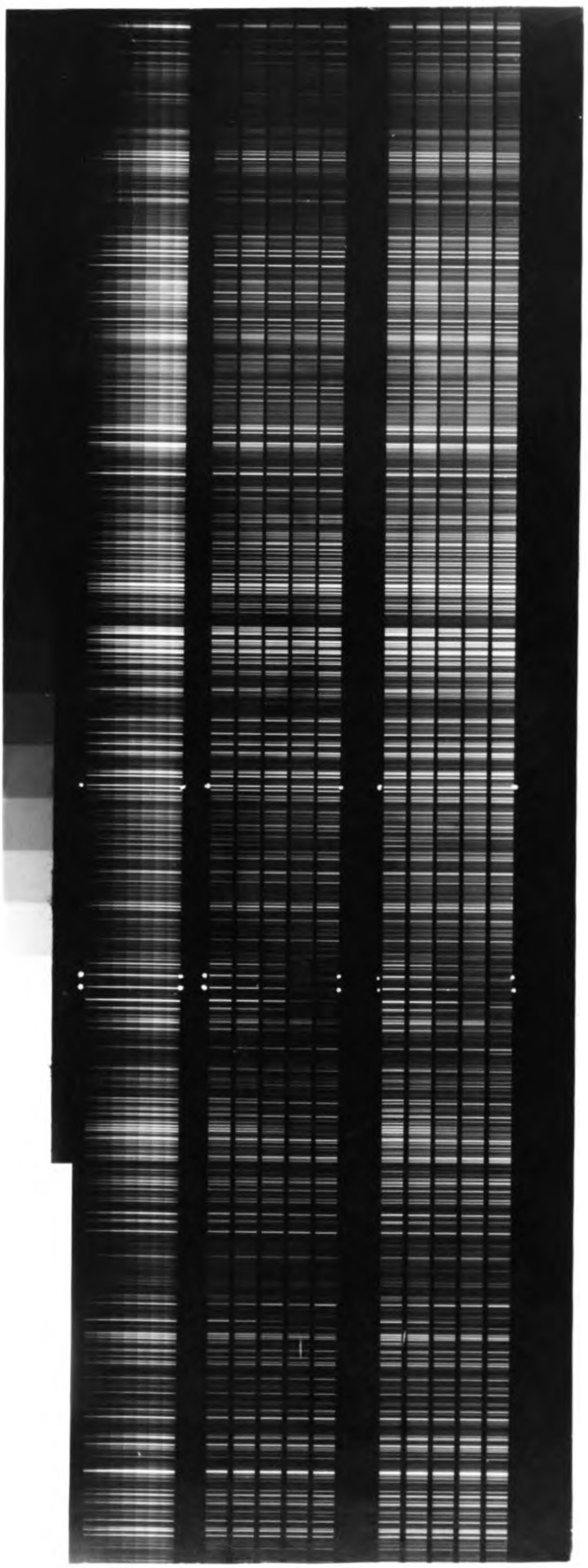


FIG. IV
1.3
1.2
1.1
1.0
0.9
$\frac{D_{Ti\ 3372.8}}{D_{Fe\ 3570.1}}$
0.6
0.5
0.4
0.3
0.2
0.1
0
-2.0
-1.5
-1.0
-0.5
0
0.5
(3)
(4)
(6)
(7)
(8)
LOG % Ti.
STANDARD SAMPLE NO.
KEY
PLATE 115
● - 4 SECONDS
Δ - 8 "
PLATE 116
+ - 4 SECONDS
⊙ - 8 "

FIG. V.



MICHIGAN STATE UNIV. LIBRARIES
31293017718317