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REPORT NO. 122/4-1

SPECTROGRAPHIC QUANTITATIVE ANALYSIS
OF
MOLYBDENUM IN STEELS

INDEXED

By

J. Sterner
Asst. Phys. Science Aide
September 18, 1936

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WATERTOWN, MASS.

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SPECTROGRAPHIC QUANTITATIVE ANALYSIS
OF
MOLYBDENUM IN STEELS

By

J. Sterner

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Report No. 122/4-1
Watertown Arsenal

September 18, 1936

SPECTROGRAPHIC QUANTITATIVE ANALYSIS
OF
MOLYBDENUM IN STEELS

By J. Sterner, Asst. Phys. Sci. Aide

Purpose

Description of a practical method of quantitative analysis for molybdenum in gun and armor plate steels by means of the spectrograph.

Conclusions

A method utilizing a condensed spark discharge between solid electrodes has been found both convenient and reliable. A detailed description of the procedure involved is given. Brief comments on the various factors entering into the problem are included for the benefit of future investigators.

A. Introduction and Preliminary Investigations.

Quantitative spectrographic work was initiated at Watertown Arsenal by Lieutenant R. H. Coombs who, in 1935, carried out a thesis (toward a degree at Massachusetts Institute of Technology) entitled "Spectrographic Method for the Determination of the Diffusion of Molybdenum in Weld Metal."*

There were several difficulties with which Lieutenant Coombs had to contend. The laboratory was new at the time, containing much equipment quite unsuitable for accurate quantitative work. Again, he was not equipped with adequate standard steels of known molybdenum content. Much difficulty was encountered in using the recording photodensitometer due to lack of personnel trained in its operation and to mechanical maladjustment of the machine.

In spite of these handicaps, the work indicated quite clearly that, with precision equipment and careful manipulation, a method of quantitative analysis for molybdenum might be practical. Lieutenant J. W.

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*Watertown Arsenal Report #840/2

Fig. I

Chemical Molybdenum Analyses of Homogenized Steels (4 Laboratories).

Laboratory A - Colorimetric (each value given is an average of four determinations)

Laboratory B - Both colorimetric and gravimetric

Laboratory C - Colorimetric

Laboratory D - Gravimetric (routine analyses)

MOLYBDENUM STANDARDS

	A	B		C	D
1	.044 .034	.025 .025	.024 .020	.01	.03
✓ 2	.13 .13	.110 .112	.116	.13	.07
✓ 3	.21 .21	.192	.198	.31	.205
4	.30 .30	.28 .28	.29	.16	.18
✓ 12 AP	.25 .25	.254 .254	.25	.26	.27
✓ 13X AP	.55 .55	.56 .56	.556	.59	.49
✓ 13 AP	.48 .47	.41 .41	.417	-	.33
✓ 17 AP	.41 .43	.42 .42	.42 .427	-	.39
✓ 17X AP (marked 32 AP)	.61 .66	.662 .662	.65 .66	.67	.47
✓ 8 AP	.70 .74	.71 .71	.715	.78	.62
✓ 15 AP	.93 .96	.97 .97	.98	.99	.88
✓ 19 AP	.97 .97	.98 .97	.98	1.01	.89
✓ 25 AP	1.09 1.09	1.15 1.15	1.13	1.13	1.04
✓ 26 AP	2.07 2.07	2.16 2.18	2.14 2.10	1.32	2.08

Fig. I

Hansborough carried out, at the same time, a thesis entitled "The Quantitative Analysis of Molybdenum in Steel by Means of the Spectroscope".* He was beset by the same troubles which Lieutenant Coombs encountered, in addition to the fact that he attempted to use an electric arc as a source rather than a spark.

With all these things in mind a series of carefully homogenized steels with varying molybdenum content were sent to the Bureau of Standards and each of two outside industrial laboratories for check analyses. The results are included in Figure I along with Watertown Arsenal analyses.

In connection with these figures, one of the interesting points to note is the fact that two of the four laboratories made individual check analyses which proved each laboratory to be extremely consistent within itself; but agreement between even these two laboratories

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*Watertown Arsenal Report #122/2

showed no such consistency. In Laboratory B, the first column gives colorimetric analytical results, the second, gravimetric. In Laboratory A, each figure quoted is an average of four colorimetric determinations. Laboratories C and D made only single determinations, the former colorimetric, the latter gravimetric. It is to be noticed in many cases, especially in the steels of low molybdenum content, that variations amounting to over a hundred per cent from the mean occur. Bearing these analyses in mind, it was decided that the spectrographic method should give reproducibility within 10% for single determinations in order to compare favorably with chemical results. If this accuracy could be attained, it would be cheaper and quicker to run molybdenum analyses in the spectrographic laboratory.

Actual work was commenced in January, 1936. The first problem was to decide on the most suitable method to use. The electric arc discharge was first tried, being in many ways the most direct. In this method a 220 volt electric arc is struck between bar electrodes cut from the steel to be analyzed. After considerable experimentation, including efforts to stabilize the arc with various types of hoods and air blasts, the method was discarded as undesirable. Figure IIa shows typical

Fig. IIA

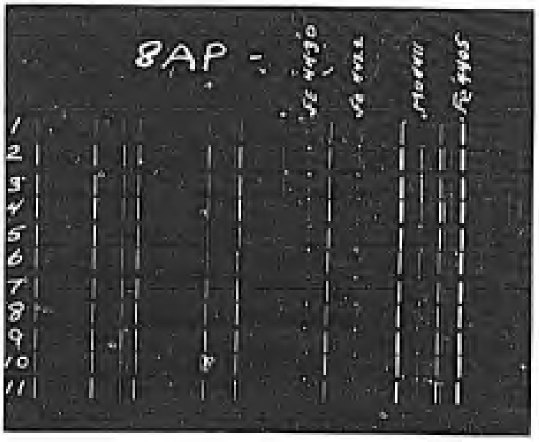
Erratic Behavior of an Electric Arc

Successive spectra were photographed of one of the homogenized standard steels (8 AP). Note the lack of constancy in the relative heights of the iron and molybdenum lines. Incidentally, these are third order spectra, dispersion 1.3 Å/mm.

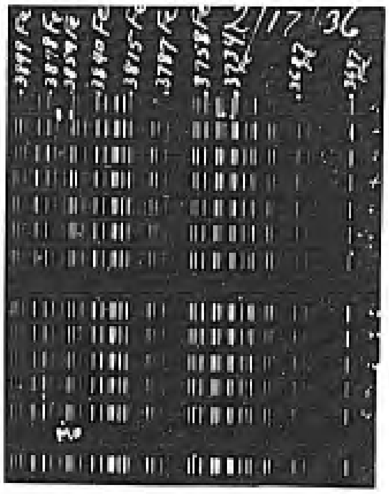
Fig. IIB

Stability of a Condensed Spark Source

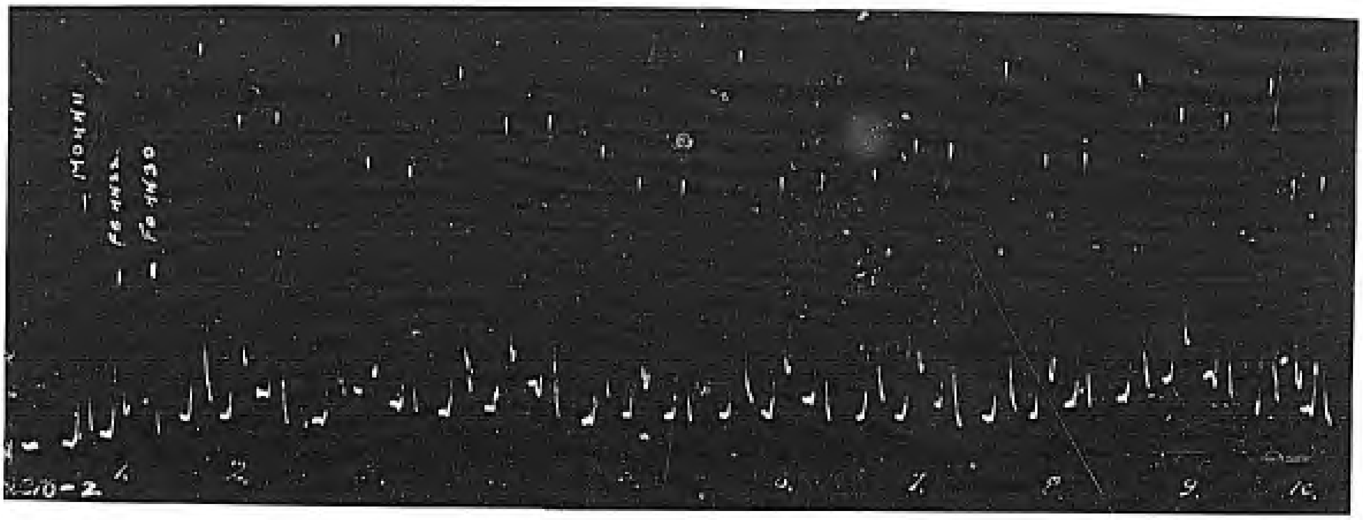
Again successive exposures were made, this time using a condensed spark as a source. A homogenized steel was again used (13X AP). The discrepancy in spectrum #6 is due to a bad scratch on the film. Note the consistency obtained even though conditions were not very carefully controlled.


8AP -
Fe 4430
Fe 4422
Mo 4411
Fe 4405
1
2
3
4
5
6
7
8
9
10
11

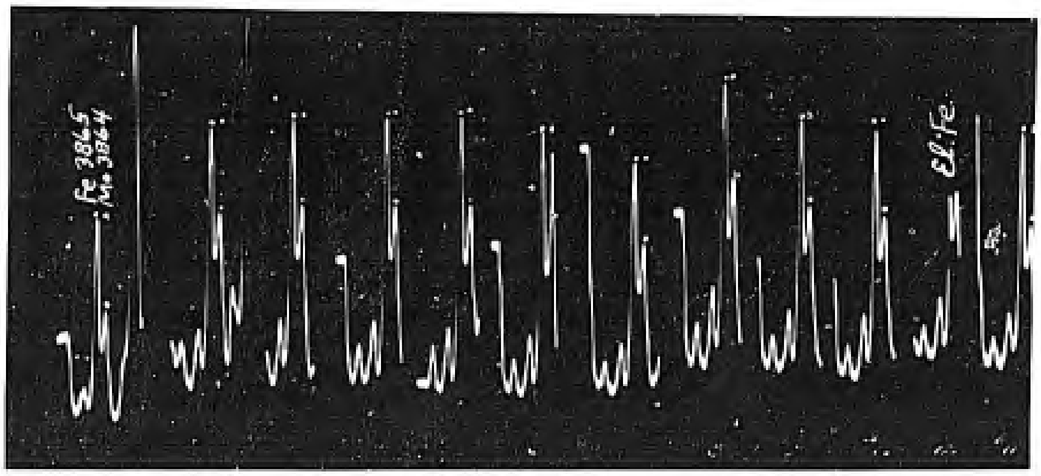
A


3899 Fe
3878 Fe
3859 Fe
3840 Fe
3815 Fe
3787 Fe
3758 Fe
3734 Fe
2/17/36
Mo

B


Mo 4411
Fe 4422
Fe 4430
2510-2
1
2
6
7
8
9
10

A


Fe 3865
Mo 3864
El. Fe

B

FIG 11

results of a series of runs made with the same pair of electrodes. It will be seen that in some cases the molybdenum line is denser, in some cases lighter than the iron line. This erratic behavior seems very difficult to control, occurring even when the physical appearance and electrical conditions of the arc seem to be constant. This situation is probably caused by a number of factors such as the uncontrollable formation of an oxide cloud surrounding the arc, varying resistance in the air gap due to air currents and temperature changes, and the natural tendency of an arc cathode spot to wander and seek regions of the electrode which have the lowest potential barrier (very often regions higher or lower in inclusions or alloying elements than the base metal). The arc method might possibly be further developed if a special housing were constructed to minimize air currents, if the specimens were arced in a nitrogen atmosphere and if the electrodes were kept at a constant temperature by water-cooling.

To take these precautions was not considered practical, wherefore it was decided to consider another source. All "solution" methods were discarded without a trial as possessing many of the disadvantages of and no advantages over chemical analysis. The next logical choice was the condensed electric spark. This type of source, unlike the arc, is a high potential discharge (10,000 - 25,000 volts per cm. gap) and is oscillatory in nature (frequency of the order of .1 megacycles). Much better reproducibility, in general, was obtained as can be seen by Figure IIb. The following studies were made to determine the optimum conditions for analysis:

(1) Proper choice of iron and molybdenum lines: certain lines are more sensitive to chemical composition than others. However, due to the richness of the iron spectrum (one of the factors which makes ferrous analysis much more difficult than nonferrous) only a few molybdenum lines could be found which were sufficiently isolated to be usable. These were investigated, and the line 3864Å chosen as most suitable for the purpose at hand. This line should not be used in steels where the vanadium content is large due to the nearby presence of a weak vanadium line. This latter, however, has a completely negligible effect on the analysis of ordinary steels which have well below .5% Vanadium. (Our specific problem is to analyze gun steels and armor plate, none of which exceed .30 Vanadium)

(2) Proper shape of electrode and optimum values of applied potential and power input: besides ascertaining what seemed to be the best spectrum lines to use, it was

necessary to consider various types of electrodes and seek optimum electrical conditions. It should be emphasized that the literature on quantitative analysis is of practically no use in determining such details as these. Authors seem to use their own individual techniques, and very few of them give detailed descriptions of their work. Furthermore, very little has been published on analysis of ferrous alloys due to the highly dispersive apparatus necessary.

As might have been suspected, it was soon found that the electrodes should have no sharp corners or edges. We were using, as most convenient to prepare, 1/4" bars for specimens. Unless the edges were very carefully rounded, the spark tended to branch, seeking always a path in the direction of a maximum potential gradient. Any rough or jagged spots on the surface would also focus the discharge and, the obtrusions being of small cross-sectional areas would have high resistance, resulting in a so-called "hissing" or "burning" spark. This is most unsuitable as a large proportion of the available energy is expended in local heating at the electrode surface instead of producing radiation in the spark gap. Furthermore, what radiation is produced comes from a relatively low potential field and is, therefore, more "arc-like" in its spectral characteristics.

Another effect which is very important and which has been neglected by many authors is the "spark etching effect" discussed by Gerlach and Schweitzer, Triche, and Richardson, and mentioned by several other authors. Lieutenant J. A. Barclay* experimented with the effect recently, in the case of Monel Metals, in a thesis performed in this laboratory. The effect consists essentially of a tendency for a high tension spark to follow the grain boundaries of a metallic specimen, thus giving a spectrum in which any materials segregated at the boundaries predominate unduly. Obviously then, a discharge between two plane electrodes wherein a large surface is covered by the spark is not desirable unless one assumes the same "grain boundary effect" for both standards and unknowns. This might be an undesirable assumption where the steels under consideration may have been subjected to various heat treatments and may have quite different compositions.

With all these things in mind we concluded that an electrode with tip shaped not unlike the head of a bullet, should give most satisfactory results. Considerable experimentation has substantiated this conclusion.

It was found that a potential of 30,000 volts/cm. with a 3 mm. gap seemed most suitable. If a higher potential gradient is used, small grinding marks and other

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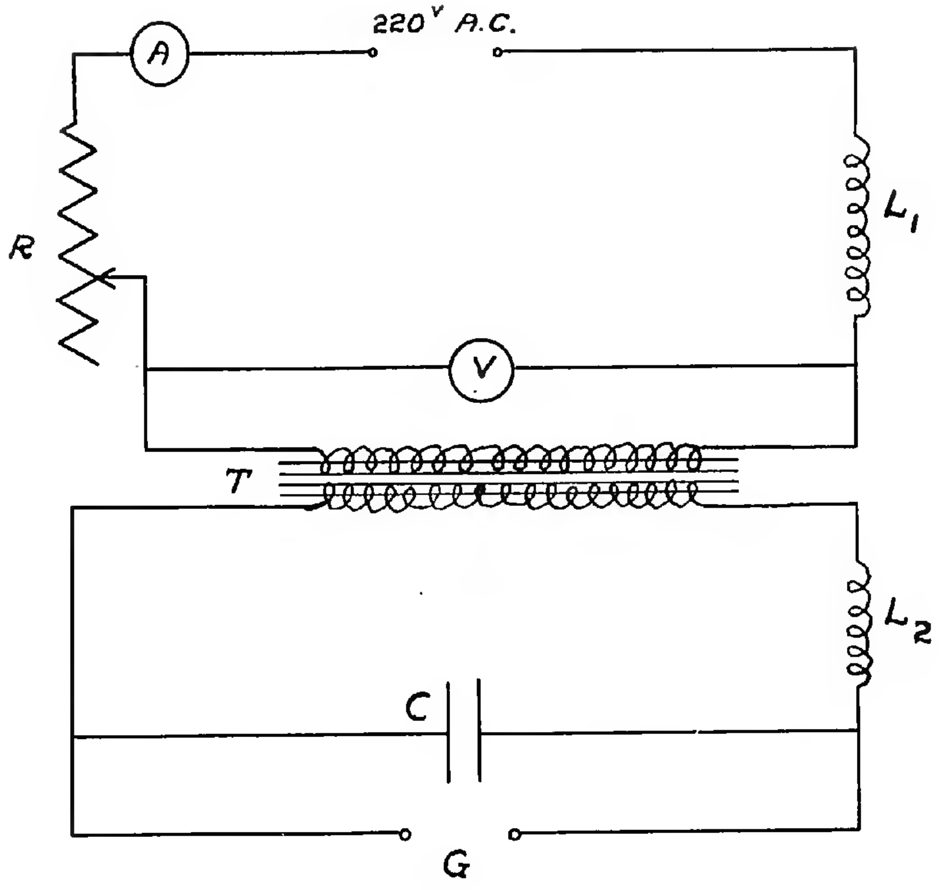
*Watertown Arsenal Report No. 122/4

Fig. III

Electric Spark Circuit

A diagrammatic sketch. Actually the circuit is such that some of the same equipment can be used interchangeably for both arc and spark sources.



R	-	500^W variable resistor - "stove" type
L_1	-	Iron core stabilizing choke
L_2	-	1 m.h. variable solenoid inductance
C	-	.004 μ F. Dubilier mica condensers, Navy type (three in series)
G	-	Electrode spark gap
A	-	10^a A.C. - D.C. ammeter
V	-	300^V A.C. - D.C. voltmeter

Fig. III

protruberances become of importance, tending to give sparks which "hiss" at times and therefore yield erratic results. Careful grinding would permit the use of higher voltages but this is hardly expedient for routine work and is, as we shall see, unnecessary.

The power input to the primary of our transformer is in the neighborhood of 1/4 kw. (at 220 v.). The electrical circuit is shown diagrammatically in Fig. III. New condensers have been purchased to replace the old, home-made, glass-plate ones hitherto in use. Their constancy has in no small part contributed to the success of our analyses. They are "Navy-type" Dubilier Mica condensers, .004μ F each, three being placed in series to insure sufficiently high breakdown voltage. A 1 m.h. inductance is used in the secondary circuit to damp out oscillations and reduce the "continuous background" or "air spectrum" to a negligible factor.

(3) Proper Sampling

Test specimens are obtained from the same "cups" which furnish "chips" for chemical analyses. The dimensions of the test cup are about 1 1/2" x 4" x 1"; it is shaped like an inverted loaf of bread. Chemical chips are obtained from the first "slice", if we may be permitted to continue the analogy. The spectrographic test bar is cut along the length of the "loaf" about 1/8" in

Fig. IV

Segregation Analysis

Typical results of a study of molybdenum segregation in the test-cup ingot from which both chemical "chips" and spectrographic electrodes are obtained. The upper pictures represent vertical sections through the ingot; the lower represent longitudinal bars, such as are used as spectrographic specimens. No marked segregation was observed in any of the tests made.

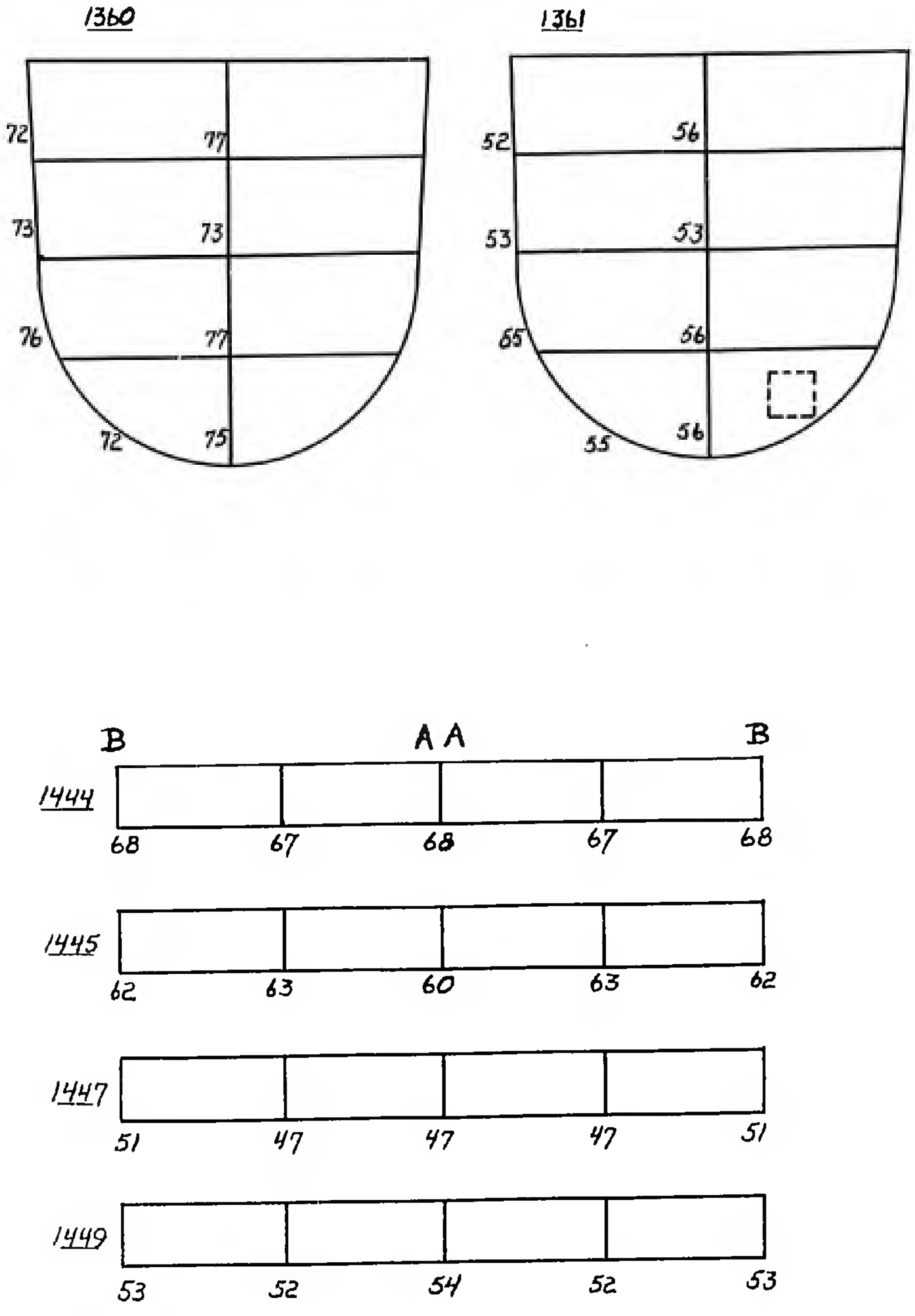


Fig IV

W.A.639-431

from the side and 1/8" up from the bottom. It is then cut in half providing two 1/4" x 1/4" x 2" electrodes.

Before deciding upon this choice of location, several ingots were cut into sections and studied spectrographically to ascertain whether or not segregation occurred within the test ingot. Fig. IV gives typical results. The upper two diagrams represent "slices" from the ingot. The lower four represent spectrographic test bars taken, of course, in a direction perpendicular to the "slices" and in the position indicated by the dotted square.

As might be suspected in the case of such a small casting, there is no evidence for segregation, at least, macroscopically speaking. A variation of 2 or 3 points is well within the error of our measurements. However, as a precaution against trouble from large scale segregation occurring in a particular casting, it was decided that each specimen should be analyzed at two points in the test bar. This gives us an additional advantage in that any error in procedure produces disagreement between the two values obtained and leads to a check analysis. Such a disagreement occurs in about 5% of all analyses for one reason or another.

B. Analytical Procedure as Adopted

(1) Taking Spectrograms

A detailed account of the particular technique used in molybdenum analyses in the laboratory at Watertown Arsenal is given so that the work can be continued by new personnel with a minimum of duplication of effort.

The apparatus used is a Johns Hopkins 3m. concave grating with a Paschen mounting. The spark is focussed on the entrance slit by a 25 cm. focal length quartz lens. An enlarged image is used so that only the center of the spark is imaged on the slit*. The slit height is adjusted so that the images of the electrodes themselves are cut off, a precaution which minimizes background and exposes the plate to light from atoms which are essentially in a constant field. The spark is about 150 cm. from the slit.

Second order spectra are being used at present since the large dispersion obtained (2.6 Å/mm.) permits the use of a wide slit (.3 mm.) and gives broad lines which are easy to run spectrophotometrically. As used at present, 15 seconds exposures are required. This is a convenient value, inasmuch as it is a compromise between very long exposures with adequate "sampling" and very short ex-

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*Note should be made here of the fact that the lens is uncorrected for axial chromatic aberration so that the ultra-violet focus is several centimeters in back of the focal region for visible light.

exposures with an appreciable saving of time.

Inasmuch as grinding a test bar to a bullet-shape is tedious and expensive, it was found that corners of the bar, with careful technique, could be quickly ground to approximate this shape. The test bars are marked so that the ends which were on the outside and inside, respectively, of the cup-ingot, can be distinguished from each other. Two spectra are then run for each steel: one, using corners of the two inside ends A (Fig. IV); the second, using corners of the two outside ends B. In this way chance macroscopic segregations or experimental errors are unable to pass unnoticed, as already pointed out in the preceding chapter. In addition, on each plate are placed five spectra of standard steels (mentioned in Section A) ranging from .25% to 2.1% Mo.

A voltmeter placed across the primary of the transformer is found to give the most sensitive indication of proper sparking conditions. When the discharge shows any tendency toward "hissing" the voltage drop rises markedly. The electrodes are then reground or readjusted until proper conditions are obtained. On the other hand, the voltage seems to drop at times probably due to the fact that segregation regions containing the more volatile elements are reached - perhaps surrounding a small crack or blowhole; or else the electrode separation

Fig. V

Types of Electrodes Used

Illustrating the two types found most satisfactory for condensed spark specimens:

- (a) Electrode tips as cut from test-cups
- (b) Electrodes after grinding corners
- (c) Electrodes after grinding to a bullet-shape

Below is shown the first type as set up in electrode-holder ready for sparking. Note rough 45° symmetry found quite essential for reproducible results.

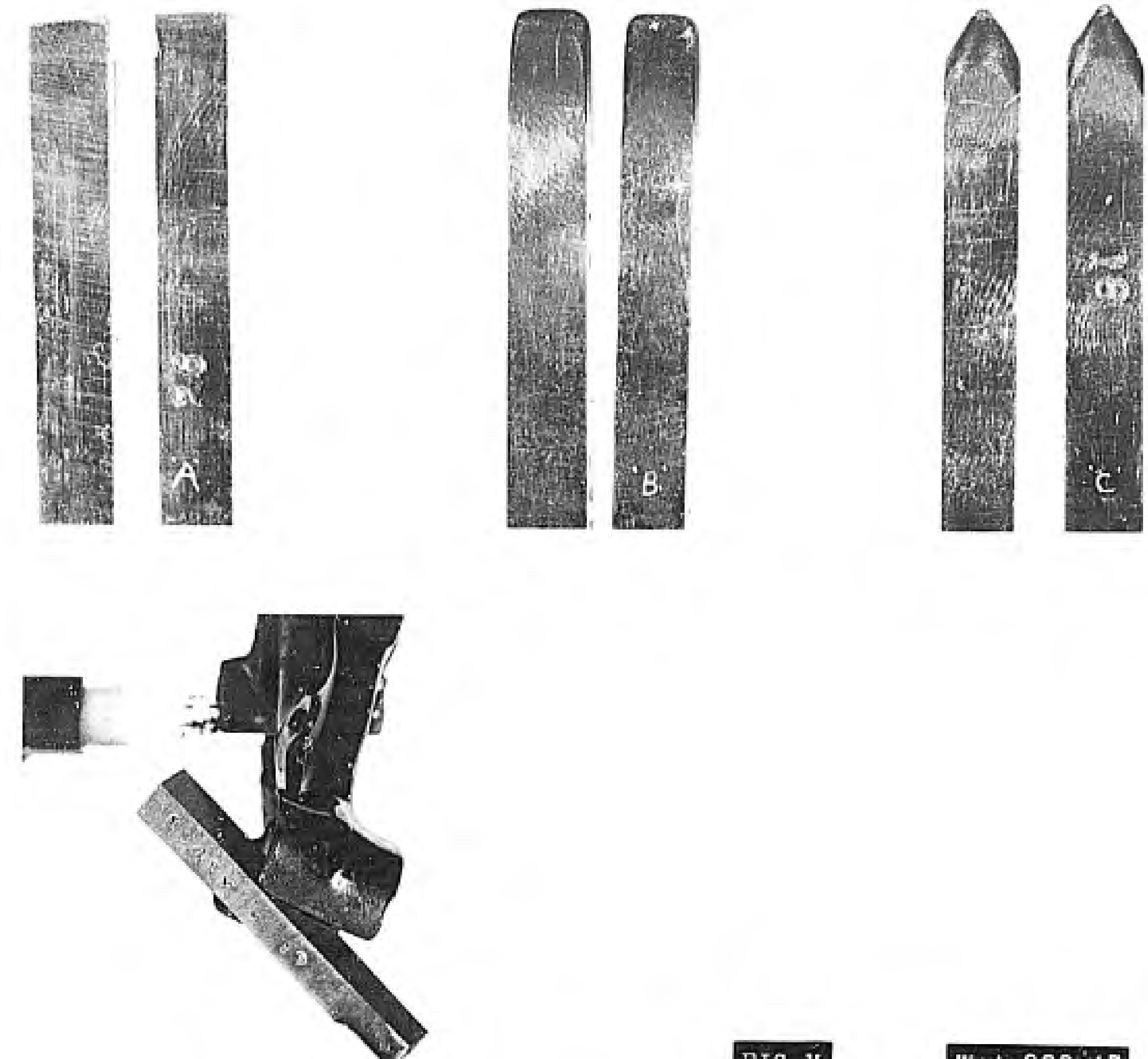

FIG. V

W.A.922-47

is too small due to wearing away of the corners (the electrode separation seems, however, to be much less critical than other factors. This experimentally proven fact is in disagreement with many authors, but may be due to the fact that we are using relatively higher voltages).

The spark is always allowed to run for about 15 seconds before an exposure is made. During this period small protruberances, inevitably left by the grinding wheel, have a chance to burn off, leaving the corner well rounded and considerably steadying the voltage drop across the gap. This pre-sparking also serves to burn out material from the surface grain boundaries of the corners being analyzed and thus to minimize the "grain boundary effect". Fig. V gives photographs of typical electrodes illustrating method of grinding and position in electrode-holder during sparking.

(2) <u>Photographic Materials</u>:

Eastman "40" plates, 4" x 10", are found to give a wide latitude, fair contrast, and satisfactorily linear density-log intensity relation. Inasmuch as latitude is much more important than contrast in the particular problem at hand, we have found that best results are obtained with a development somewhat under gamma unity. A certain amount of background is unavoidable due to scattering at the grating, continuous radiation from oxide vapors, etc.... D61a has been found to be a satisfactory developer, though Eastman Kodak recommends D19 for extremely fine grain development. Plates have been found to be much more satisfactory than films in the fact that they lie in the spectrophotometer holder without necessitating the use of auxiliary glass plates with additional scattering surfaces. It might be noted here, however, that film is very satisfactory for qualitative and semi-quantitative work; of many films tried, Eastman "Commercial" obtainable in 8 x 10" size was found spectrographically most suitable. Eastman "F" plates are used for work in the longer wavelength regions of the visible spectrums.

(3) Spectrophotometry:

The method used in this laboratory depends on the assumption that, over a considerable region of densities, the familiar "S-curve" equation holds:

$$(1) \quad D = k \log E$$

where D is density and E exposure which is very closely proportional to the product:

$$(2) \quad E \propto It$$

where I is the intensity of the light source and t the time of exposure. Careful experimentation by a large number of authors has shown that none of these equations hold exactly; but we have found that the errors involved lie well within the experimental accuracy of our measurements and are quite negligible.

Now the assumption is always made and seems to agree with experiment, that the concentration of an impurity or alloying element is proportional to the relative intensity of the radiation which it emits compared with that emitted by the base material, or:

$$(3) \quad C_x = g \frac{I_x}{I_a}$$

where g is a constant. Of course this is only true where the total percentage of alloying elements is small, and that of the base element large. A logical procedure would appear to be:

(1) Before developing a spectrogram, place thereon a "photographic wedge" or "intensity calibration," taking care to use a source similar to the one which is to be analyzed.

(2) Measure the opacity of the various steps of the wedge with a densitometer* and plot it against the logarithm of exposure.

---

*The terms "densitometer" and "photodensitometer" are misnomers as the quantity actually measured is "opacity", which is related to density by the following relationship:

$$D = \gamma \log O$$

(3) Measure, for each of a series of spectra of standard alloys, the opacities of two selected spectrum lines, one of the base metal A, the other of the alloying element X.

(4) From the calibration curve, obtain the values of the logarithms of the relative exposures which produced these lines and plot the difference $\log I_a - \log I_x$ against the logarithm of the concentration of X in A.

(5) From this curve analyses could be made simply by measuring the opacities of the base and impurity lines of the unknown alloys.

This is an "absolute" method and is undoubtedly desirable whenever one wishes to make analyses over a wide range of impurity content. It is very much like the one which Duffendack* describes; however, his treatment is incorrect due largely to a confusion of the terms "opacity" and "density."

The above described procedure involves a considerable amount of computation and graphical work which can be eliminated. In the first place, in most of our routine work, analyzing for molybdenum in gun castings and armor plate steels, we know that the content will

---

* U.S. Pat. #1,979,964 Nov. 6, 1934.

fall within certain definite limits (as a matter of fact between .40 and .90%). Making use of this fact and the fundamental laws of photometry as discussed on page 13, we are able to greatly simplify the problem.

Let us consider the photographing of two spectrum lines, one molybdenum, the other, iron; let us assume that their intensities in the source are I_{Mo} and I_{Fe}. Then, according to equation (1)*

$$(4) \begin{cases} D_{Mo} = k \log I_{Mo} \\ D_{Fe} = k \log I_{Fe} \end{cases}$$

since t, the exposure time is the same in each equation and can be included in the constant k. Subtracting, we have:

$$(4a) \quad D_{Mo} - D_{Fe} = k \log \frac{I_{Mo}}{I_{Fe}}$$

Now from (3) it follows that:

$$C_{Mo} = g \frac{I_{Mo}}{I_{Fe}}$$

So that (4a) becomes:

$$(4b) \quad D_{Mo} - D_{Fe} = k (\log C_{Mo} - \log g)$$

It should be pointed out here that the above equa-

---

*We have omitted the additive constant (k log i) where i is the "inertia" of the photographic emulsion, inasmuch as it cancels from all our calculations.

Fig. VI

Log I_{Mo}/I_{Fe} vs. Log C Plot

For Standard Steels

This is the type of curve which is obtained in general for homogenized steels. The values used as ordinates are obtained by averaging the results of the four chemical laboratories (omitting analyses obviously in disagreement with the majority). By means of the spectrograph, specimens of ingot 17X were discovered to have been mixed with those of #33 AP (not sent out for check analysis). A chemical recheck of 17X yielded an analysis of .47% Mo but consistent spectrographic analyses indicate that .55% is a better value.

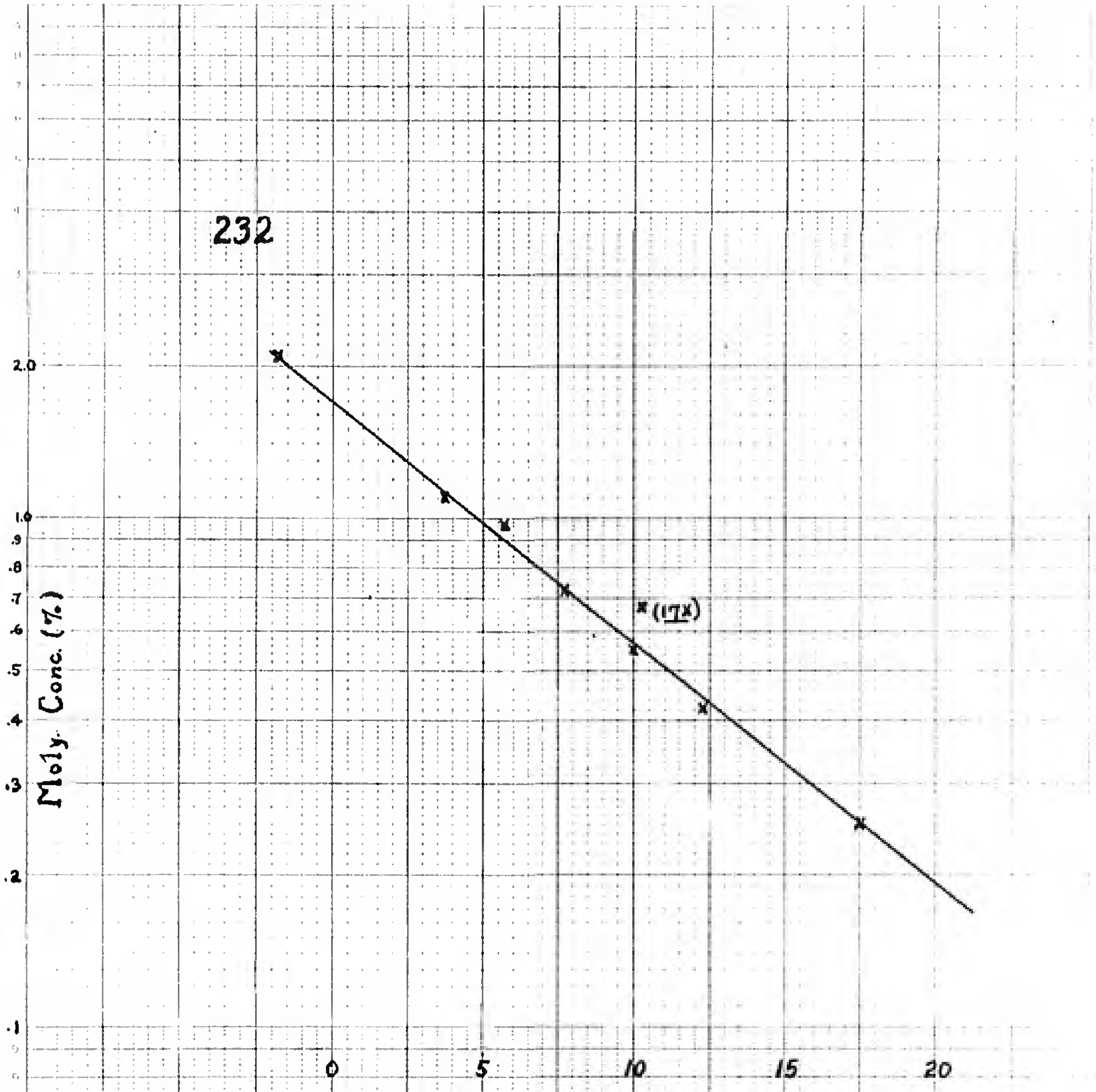

Fig VI

tions apply strictly only in the absence of "background radiation." We should not expect concentration to be proportional to the quantity $\frac{I_{Mo} + I_B}{I_{Fe} + I_B}$, where I_B is the intensity of the "continuous" radiations which we term "source background." Experimentally we try to maintain I_B below the point where its effect becomes comparable with other errors.

Now in making densitometer measurements we shine a light source of intensity J through the lines and measure the transmitted intensities J_{Mo} and J_{Fe}. The opacities of the lines are J/J_{Mo} and J/J_{Fe} so that

$$(5) \quad \begin{cases} D_{Mo} = k' \log J/J_{Mo} \\ D_{Fe} = k' \log J/J_{Fe} \end{cases}$$

and subtracting:

$$(5a) \quad D_{Mo} - D_{Fe} = k' \log \frac{J_{Fe}}{J_{Mo}}$$

Equating (5a) and (4b) we obtain:

$$(6) \log C_{Mo} = \frac{k'}{k} \log \frac{J_{Fe}}{J_{Mo}} + \log g$$

The densitometer readings d_{Mo} and d_{Fe} are directly proportional to J_{Mo} and J_{Fe} so that:

$$(6a) \quad \log C_{Mo} = K \log \frac{d_{Fe}}{d_{Mo}} + K' .$$

Therefore, if we plot the concentration against the ratio of densitometer readings on log-log paper, we should expect a linear relationship. It should be emphasized that this argument holds only when the densities are such that they fall within the straight line portion of the density-log I curve.

There are several reasons why it is undesirable to make absolute densitometer readings, as would be necessary in order to measure the ratio d_{Fe}/d_{Mo}. In the first place it would be necessary to make "zero" readings on the densitometer, which would considerably increase the running time. In the second place there would be a certain amount of calculation necessary before plotting data.

And it so happens that, by measuring merely the difference in height between the densitometer peaks ($d_{Mo}-d_{Fe}$), at the same time observing certain fundamental restrictions, we are able to make reliable analyses. This step requires justification:

Equation (6a) may be rewritten:

$$(6b) \qquad \log C_{Mo} = K' - K \log \frac{d_{Mo}}{d_{Fe}} \quad .$$

Now it is a mathematical fact that:

$$(7) \qquad \log \frac{d_{Mo}}{d_{Fe}} \xrightarrow[(d_{Mo} \to d_{Fe})]{\text{lim.}} \frac{d_{Mo} - d_{Fe}}{d_{Fe}}$$

since both sides vanish at $d_{Mo} = d_{Fe}$. Furthermore, in general, if one plots $\log \chi$ vs. $(\chi - 1)$, one obtains a curve whose slope changes but very little for a considerable distance around $\chi = 1$. It has been found by calculation that the substitution of equation (7) is an excellent approximation in the range $d_{Mo}/d_{Fe} = .7 \rightarrow 1.5$ and a fair one considerably beyond. Physically, this means that in assuming:

$$(8) \quad \log C_{Mo} = K'' (d_{Fe} - d_{Mo}) + K'$$

we are making an excellent approximation around the region where the iron and molybdenum lines are homologous. The constants of equation (8) are such that we have found, experimentally, that we obtain the linear relationship expressed therein over a range of concentrations from .4% Mo to 2% Mo using 3864 Mo and 3865 Fe (homologous at 2% Mo). Since we are interested in gun steels only in concentrations in the neighborhood .40 - .60%, we have found 3866 Fe to be even more satisfactory (homologous at .25% Mo). An ideal iron line would, of course, be one homologous at .50%, but at present other errors far outweigh those introduced by non-linearity in our plotting. As a working rule we have adopted the following criterion: <u>linearity may be assumed over a region of intensities in which the two lines compared differ by no more than a</u>

factor of two. Such is the case in our molybdenum analysis. Wherever it is desired to extend the range of concentrations other iron lines can be used which are homologous at different values. In this way practically all ranges of concentration can be analyzed by the use of a single spectrum line of the alloying element.

The analysis consists then merely: of plotting opacity differences against logarithms of known concentrations for our standard steels; then reading the concentrations of our unknowns from the straight-line curve thus obtained. If we are not working on the straight-line portion of the S-curve, log C vs $(d_{Mo} - d_{Fe})$ does not plot as a straight line and the plate is discarded. In actual routine practice, with conditions standardized, this rarely occurs. To help obviate difficulty from this source we make use of an S-curve of log C vs. opacity. This, it should be pointed out is different from the more familiar S-curve of log C vs. density but for obvious reasons is desirable in our method. As a matter of fact the straight-line ranges of intensity for the two curves overlap over a considerable region. The procedure for obtaining the S-curve will be described below.

The flexibility of this method cannot be overemphasized. Having once obtained a few standards in the desired concentration range the usable specification bracket could be easily extended in both direction.

Developing procedure does not have to be controlled carefully since standards are placed on each spectrogram. It is felt that so little time is required to record a few standards on a plate that it is hardly worthwhile to use standard curves and suffer annoyance of trying to control development time, temperature, and age, and having to bother about homogeneity of different batches of emulsion.

Although obtaining a calibration curve is quite unnecessary in this method, it has been found convenient to put a sensitometric wedge on each spectrogram. This is done, incidentally, with the aid of a rotating disc sensitometer built chiefly for studying different types of photographic materials. The instrument consists of nothing more than an incandescent light source in a housing, a rotating sectored disc with logarithmic steps and a plate-holder behind the disc. Since the opening of each sector of the disc is double that of the preceding, and since each is given an equal spacing radially, the densitometer in making a record of the wedge automatically plots an "S-curve". By glancing at the densitometer record while still in the developer, one can immediately tell whether or not the spectra are far from the straight line portion of the curve or not. If then the series must be rerun, no time is wasted. Of course, in borderline cases only actual plotting of the standard curve determines acceptability of results.

Let it be stressed that no measurements are made with this wedge. It affords merely a rapid visual check and is found convenient in connection with the particular problem at hand where washing and drying of films consume a large proportion of the time for making an analysis. In fact, when several pictures are taken in succession, the wedge is often omitted from all but the first plate. Indeed it would be grossly incorrect to use our wedge for obtaining a calibration curve such as Duffendack uses. In the first place we do not have the same kind of source excitation; secondly, we are not using light of the same wavelength as that which is to be studied. Harrison* and others have pointed out that the "S-curve" varies considerably when these factors are changed. However, we have confirmed experimentally the fact that our sensitometer gives us an "S-curve" near enough to the correct one to be used for our rough visual check. We might liken its use to the engineers' "rules of thumb", which are extremely useful and time saving though very often not at all quantitative. Fig. VII gives a typical plate, densitometer record and curve to illustrate points discussed in the preceding paragraphs.

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* Jl. Opt. Soc. Am. 24 (1934) 59

Fig. VIIA

Effects of Over and Under Exposing

Extreme examples. Plate #280 was over exposed by a factor of two. Note that upper point is most affected. Plate #317 was similarly under-exposed this time with lower point most affected, as would be expected. Note that both plates give, in general, more erratic results than plate #333 which is typical of proper exposure. If the standard iron line does not fall on the straight line portion of the "S-curve", any variation in exposure or procedure affects the analysis.

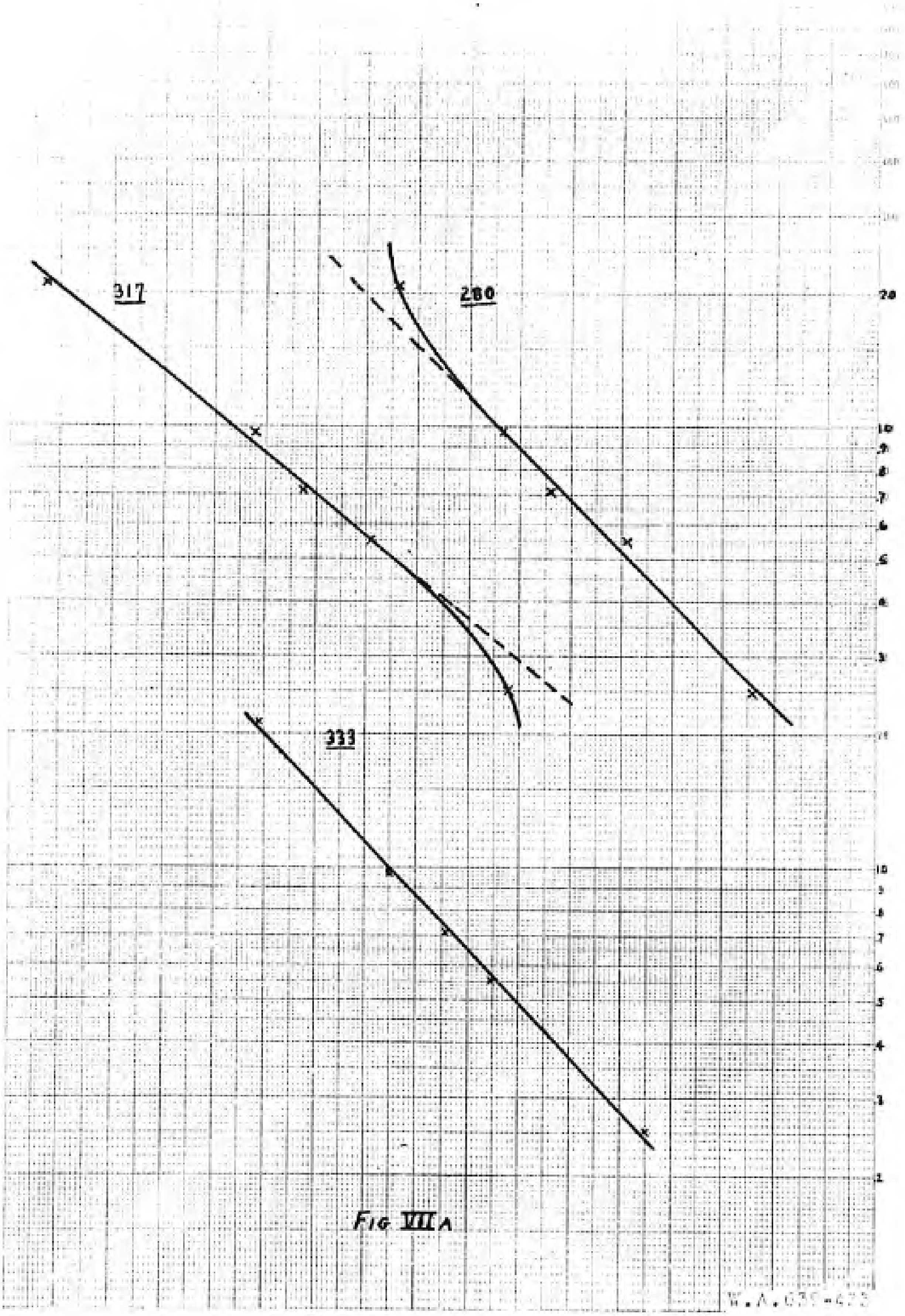
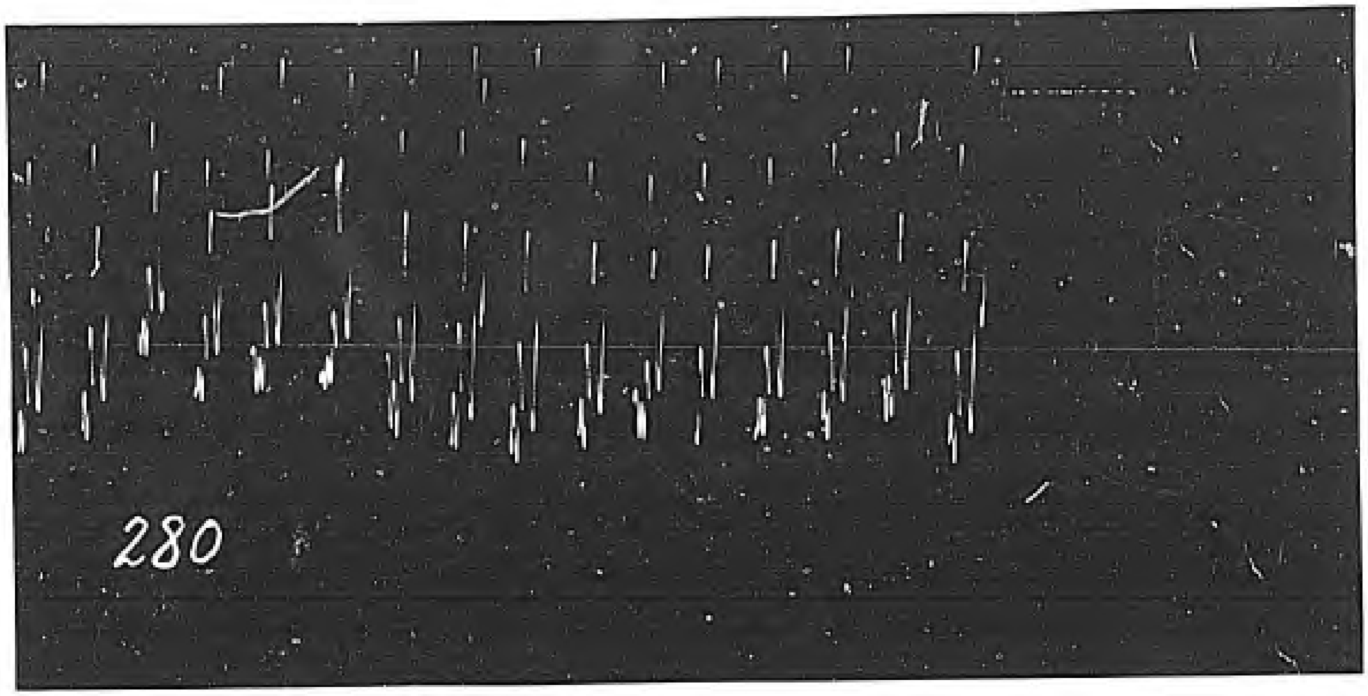


FIG VII A

Fig. VIIB

Illustrating Use of Wedge

Showing densitometer records of plates #280 and #317 discussed in the preceding figure. Though the wedge cannot be used for quantitative measurements, a quick glance at these two plates shows that the exposures are incorrect without necessitating the plotting of data.


280

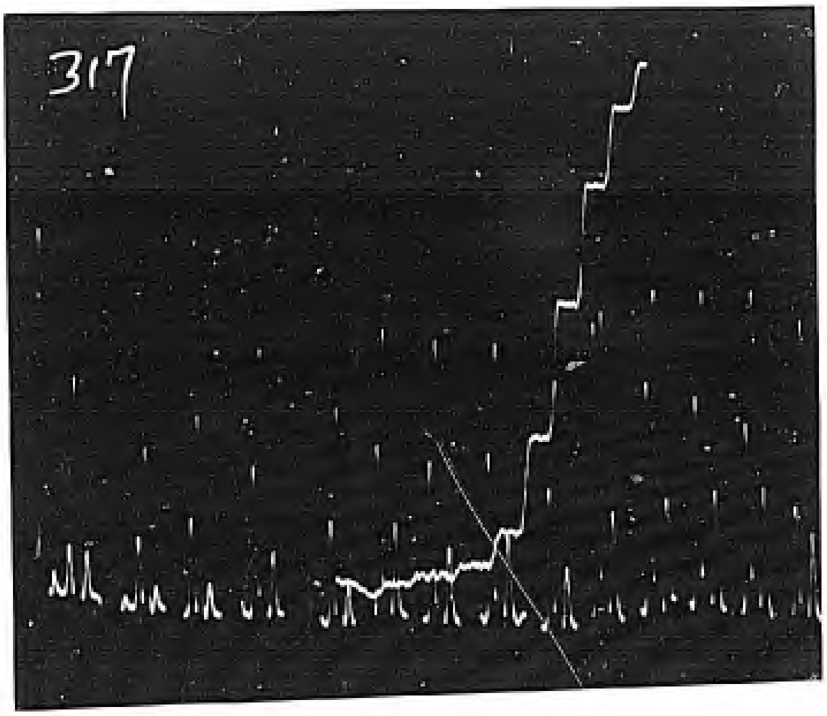
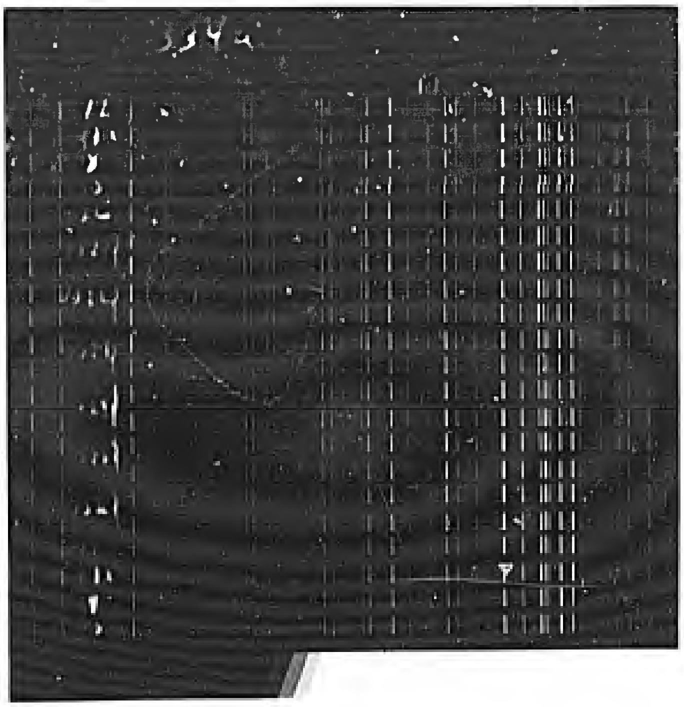
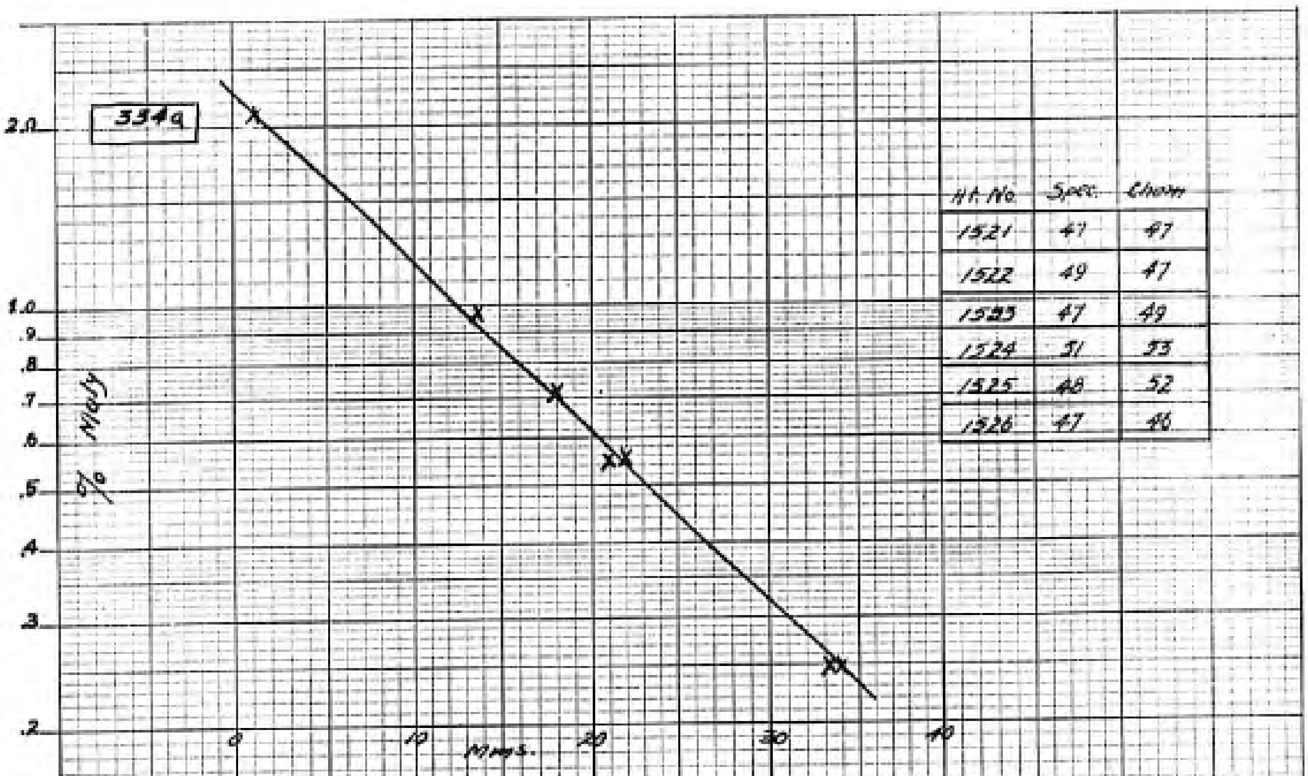

317

Fig. VIIC

A Typical Quantitative Analysis

Showing analysis of a series of gun steels. Above is seen the spectrum plate; below the curve of our standard steels and a table showing comparative spectrographic and chemical analyses of the unknown steel specimens.





Ht. No.	Spec.	Chem.
1521	47	47
1522	49	47
1523	47	49
1524	51	53
1525	48	52
1526	47	46

FIG. VII c

W.A.639-434

(4) Equipment:

It would be superfluous to include in this report details of the physical equipment of the spectrographic laboratory at the Arsenal. In previous reports* details of both spectrograph and recording densitometer have been given. Doctor W. S. Baird has made several minor improvements in the densitometer as originally described. When in proper working condition and in the hands of competent personnel it is now capable of yielding results which are reproducible to within 1% to 2%.

In certain cases a nonrecording densitometer is far more advantageous than a recording one. If properly constructed it may be used in a fully lighted room; also, it presents the double advantage of permitting more than one setting to be made on a given line and eliminating the processing of a second film. For these reasons it was considered advisable to have both types available to the laboratory and a new instrument is now in process of construction.

C. Work in Progress and Suggestions for Future Investigation:

(1) Discussion

Two problems of considerable importance to quantitative spectrographic analysis in general, have not been adequately treated in the literature.

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*Watertown Arsenal Reports #840/2; 122/2; 160/2; 160/5

The first concerns the effect of heat treatment on the "binding" forces existing between an alloying element and its base metal. To be specific, the following question arises in our investigations. Does the relative "volatility" of molybdenum with respect to iron in a given specimen vary in accordance with the heat treatment to which the specimen has been subjected? Apparently, judging from the accuracy of our analyses, no serious difficulty from this source has arisen thus far. However, it is extremely important to know whether or not this is incidental to the fact that our specimens are in general all subjected to essentially the same treatment.

To find out more about this subject, a number of "as cast" ingots have been obtained, each having a half dozen quarter-inch protruding "tits". It is planned to subject these castings to various heat treatments, knocking off and analyzing one "tit" after each operation. If positive, this method might later be developed to attempt correlation between interatomic binding forces and physical properties.

The second problem which seems to be of primary importance concerns the possible effect which various alloying elements can exert on each other. A program is contemplated for the near future (probably to be carried out as a Master's Thesis by a student officer) in which specimens of the same composition, except for one element, are used. The effect of varying this one element (chromium, for example) on our molybdenum analysis will be observed. The greatest difficulty connected with this study will be found in the obtaining of suitable specimens; therefore, steps are now being taken to collect a series to fit the problem.

Results of these studies should tell us definitely whether or not we would be justified in extending our present method of molybdenum analysis to apply to steel specimens of widely different compositions and heat treatments, using a single set of standards.

A question naturally arises regarding the possibility of extending the present method to the analysis of other elements. In this connection it seems only fair to point out one or two obvious limitations of quantitative spectrographic analysis.

The most important of these is the fact that the spectroscopist deals always with "percentage" errors, while the chemist obtains "absolute" errors. In other words, if the spectroscope yields 5% accuracy (which is excellent at the present time), an analyst would report an alloying element 4.0% ± .2% being unable to state definitely whether it was 3.8% or 4.2%. Such a determination would horrify an analytical chemist. On the other hand, it is only fair to state, a report of .040% would be defined within the limits of .038% and .042%, a determination which would be difficult to excel chemically.

In other words we may state that wherever specification limits are narrow, the spectroscope is, in general, not useful for analyzing elements which constitute greater than 1% of the alloy. This figure is, of course, purely arbitrary. Furthermore, it is hoped that greater accuracy will be obtained in the future as more reliable sources of excitation are developed and as alloys improve in homogeneity.

The latter statement suggests a second and exceedingly important limitation of the spectrographic method: namely, inadequate sampling. Whereas the chemist can use a large sample which represents fairly well the average content of the alloy under consideration, in the spectrographic light source no more than a few milligrams of material are expended during an exposure. For this reason, it is probable that the electric arc which utilizes considerably more material than the spark will be developed in the near future to the point where it will yield satisfactory quantitative results.

An extremely important point which must be considered before attempting to perform routine analyses of a given element in the spectrographic laboratory, even where the content is low, is the relative ease of analyzing for that element in the chemical laboratory.

In certain cases a chemical analysis can be made in a very few minutes. Unless the determination of that element spectrographically is purely incidental to the analysis of other elements, the method cannot be economically applied. Furthermore, due to the paucity of available alloy lines in ferrous analysis, very little headway has been made to date in solving the problem of analyzing for several elements on a single photographic plate. Such is not the case for nonferrous materials; so that, eventually, it seems obvious, the more difficult ferrous problem will be solved.

Molybdenum was chosen as the first element to work with here at the Arsenal because it is one of the most difficult ones to analyze by the wet method and requires the most time. Vanadium undoubtedly should appear next on the list and should yield better "absolute" accuracy due to the fact that it is present in lower concentration than is molybdenum in our steels.

(2) Conclusion

Indeed preliminary work by S. Vigo, Assistant Chemist, on the spectrographic quantitative analysis of vanadium indicates that, in a very short time, it will be possible to make both molybdenum and vanadium analyses simultaneously working with the first order spectrum. Further details of this work, which is still in progress, will be given in a later report.

In conclusion, the author wishes to acknowledge the advice and cooperation received from the entire laboratory staff at Watertown Arsenal; particularly, his co-worker S. Vigo who took active part in the preliminary investigations of the present problem and has since offered many suggestions; Captain D. J. Crawford who initiated spectrographic work at the Arsenal and without whose support and advice this development would have been impossible; and Mr. A. Sloan, Chief Chemist, under whose supervision the spectrographic laboratory has recently been placed and whose check analyses have been invaluable in helping establish the spectrograph here on a firm foundation.

May we express our thanks to the Climax Molybdenum Company, the Union Carbon and Carbide Company and the Bureau of Standards at Washington for so generously extending to us the cooperation of their chemical laboratories for check analyses. Mr. David Low made most of the densitometer records.

In a companion report will be found results of a chemical-spectrographic correlation test involving forty gun and armor plate steels which completely justify the adoption of the method of analysis herein described.

Respectfully submitted,

J. Sterner

J. Sterner,
Asst.Phys.Science Aide

Note: Since this report was written, spectrographic vanadium analysis was developed to the point where it was ready for production.

As we go to the publications office, the spectrographic laboratory is in its second week of making routine production molybdenum and vanadium analyses under the direction of Mr. S. Vigo of the Chemistry laboratory.

First order spectra are used with an auxiliary filter, making possible simultaneous analyses of both elements on a single plate.