

# The Spectrograph in the Iron Foundry

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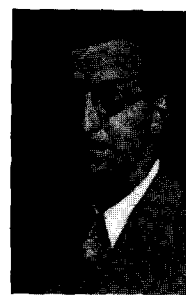
## Rapid and Accurate Control Analysis

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### Introduction

FOR many years the utility of the spectrograph as an analytical tool has been recognized. The discovery that a definite set of spectral lines is a characteristic of each element gave at once a means of determining the elementary constituents of a mixture, a qualitative application which has found considerable use in industry. The appeal of the method has lain in its high sensitivity and its ability to determine the presence or absence of many elements in one operation.

Almost immediately it was noted that if mixtures containing various small concentrations of an element are used in the light source, the spectrum due to that element varies in intensity with the concentration. It appeared that the composition might be determined, quantitatively, from the line intensity, and the spectroscope was hailed as the analyzer to replace all analyzers. The enthusiasm proved somewhat premature and applications led to disappointment. A satisfactory method of analysis needs not only sensitivity but repeatability, and in the early efforts this latter feature was deficient.

The first flurry of optimism, and the resultant chagrin, has been followed by a period of gradual improvement in technique. The contributions of such investigators as de Gramont<sup>1</sup> and Gerlach and Schweitzer,<sup>2</sup> encouraged further efforts to use the spectrograph in industrial problems.

Numerous successful applications were made in the field of extremely small concentrations, where difficulties were experienced with the methods of chemistry<sup>3</sup> and where the demands for precision were not severe.

The use of the spectrograph for rapid and accurate quantitative analysis in the range of concentration from, say, one-tenth percent to five percent is a comparatively new development, and satisfactory technique has been worked out for only a limited number of elements in a few matrices.<sup>4</sup> At present, the spread of the use of the spectrograph in industry is handicapped by the past disappointments arising from the operations of those who have induced industries to try methods of questionable value. The failures have, it is feared, invested the spectrograph with a bad odor which should attach rather to the individuals who have introduced dubious technique in a field where continuous reliability is demanded.

In developing a satisfactory technique for the use of the spectrograph in analysis, special emphasis must be placed on the reproducibility of results—sensitivity is, in general, inherent. The work reported here has been directed almost wholly toward the improvement of reliability, and has resulted in a successful industrial installation.

### The Analysis Problem

During the summer of 1934, the department of engineering research of the University of Michigan undertook to develop for the Campbell, Wyant and Cannon Foundry Company of

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Muskegon, Michigan, a spectrographic method for the analysis of alloy cast iron to determine the elements chromium, copper, manganese, molybdenum, nickel and silicon. The analysis was to provide a production control and not a means of inspection of a finished product. The operation of the foundry is a continuous process in which the level of molten metal is maintained nearly constant in the cupolas by fusion, and in the electric furnaces by additions from a cupola. Ladles of molten iron are drawn off periodically for casting. It was proposed to analyze samples from the ladles, and to post the results as soon as possible, so that drifts in composition might be corrected before they exceeded commercial tolerance. This problem was placed with the authors in the department of physics.

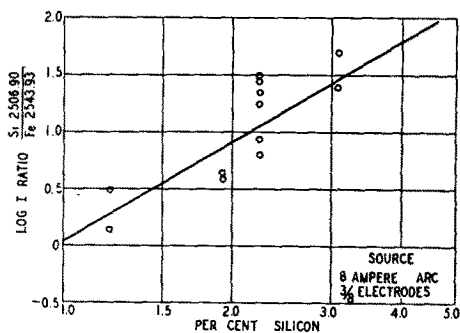


FIG. 1. Analysis with a small open arc. The relative intensity of the selected lines is plotted against the silicon content for several spectra made with the same sample of iron. The six repeats made at 2.2 percent show wide variations, indicating that analyses made with this source are quite unreliable.

It was hoped to develop a method of analysis of a reliability equal to or exceeding that of routine analysis in the chemical laboratory. The elapsed time between the sampling of the iron and the posting of results should be much shorter than that needed for gravimetric chemical methods. The cost of operation should be small, so that analyses might be made more frequently without increasing laboratory expenditures. It has been found possible to realize all these expectations, but it has been necessary to recognize and overcome numerous difficulties.

The accuracy demanded necessitated that the method be completely instrumental with nothing left to the guesswork euphemistically termed "estimate." The speed required provided no

time for cumbersome methods such as those using numerous spectra made from electrodes soaked in solutions. Samples cast directly from the alloy in the pouring ladles have been used throughout. In the matter of the cost of operation, efforts have been made to avoid the use of unreasonable quantities of photographic material, while the high speed attained keeps the expenditure for operators at a very moderate level. Personnel is discussed below.

## Instruments

The early work on this problem was beset with many difficulties. It soon became apparent that the reliability of the work would not exceed that of the instruments employed in the processes. At first, the microphotometer used for instructional purposes was used for analysis work also, but it soon showed itself unreliable to such a degree that its readings were useless for precision work. It was remodelled and its operation improved. It was still necessary, however, to provide a density measuring instrument suitable for use at the foundry.

Microphotometers available on the market did not appear entirely satisfactory for a number of reasons. A density comparator was supplied on memorandum through the courtesy of the



FIG. 2. The end of an electrode burned in a direct-current arc showing evidence of subsurface boiling.

Bausch and Lomb Optical Company of Rochester, New York, and with their cooperation, this was developed into a microphotometer of the required speed and accuracy. A new Littrow spectrograph purchased from the same company to replace the old model used

in the early work proved to have excellent optical characteristics. Some improvement in its baffle system was needed to minimize internal reflections.

## Light Sources

### Small d.c. Arcs

However, the principal problem was always the source to be used for the vaporization and

excitation of the alloy. Small direct-current arcs were tried with cylindrical electrodes cast in permanent molds. These electrodes were three-eighths inch in diameter and the arc currents ranged up to eight amperes, beyond which point molten material dripped from the electrodes. Results were not encouraging, as may be seen from the typical observations shown in Fig. 1.

Here, as in other methods involving internal control, analysis is to be performed through establishing, by the use of samples of known composition, the percentage content of an alloy as a function of the relative intensity of selected lines arising from the element and matrix, respectively, and using this relationship to evaluate the composition of samples of unknown content. Obviously, it is imperative that the functional relationship be monotonic so that the correspondence between relative intensity and percentage content is unique. When a single sample yields successive values of relative intensity of such divergence as those shown in the figure, the correspondence is far from unique and gross errors may be anticipated.

Several possible reasons for the inconsistencies experienced with the small open arc present themselves. A picture of the end of an electrode used in an arc is shown in Fig. 2. The slag has been ground away to expose the underlying metal, and it is clearly indicated that subsurface boiling may occur. This would lead to a random area of disengaging surface, and no equilibrium could be established. Since the arc was open, fluctuations in ambient conditions might influ-

ence the electrode and discharge temperatures. There is also the possibility that the composition of the sample varied from point to point, and that the portion burned was not representative.

It appeared that any or all of the conditions mentioned above might influence the results obtained, and it was decided to try some modification. The obvious way to minimize the effect of variation in composition is to burn up a sufficient amount of the material during analysis, but it immediately became apparent that inconveniently large currents would be required to vaporize any considerable quantity of iron. It was decided to try sampling the material under analysis.

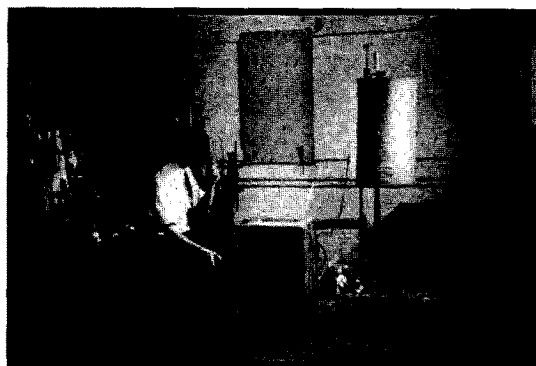


FIG. 4. Arc for sampling material in a molten form. The illustration shows the driving motor, the electrode spindle and the adjusting lever in the hand of the operator. Continuous adjustment of the electrode is necessary to maintain the arc length.

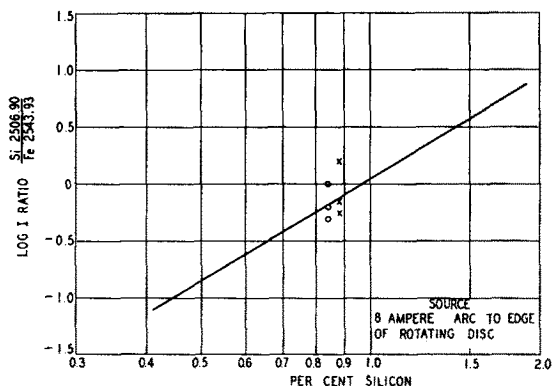


FIG. 3. Sampling by a slow continuous motion of the material under investigation. The reliability of analyses made with a small arc is little, if any, improved by these means.

Tests of repeatability were made on an arc between a pencil of graphite of spectroscopic purity and the edge of a cast iron disk rotated at a slow constant speed, such that it made slightly less than one revolution for each exposure. The results of this test are shown in Fig. 3. It appears doubtful that any improvement was effected.

### Large Sampling Arc

Efforts made to sample the iron in a molten state resulted in the apparatus shown in Fig. 4. A relatively large arc was maintained between a cathode of graphite of spectroscopic purity and a three-eighths inch cylinder of the cast iron to be analyzed. The arc was vertical, with the negative electrode above the positive. The anode was rotated by the motor shown at the right. As the

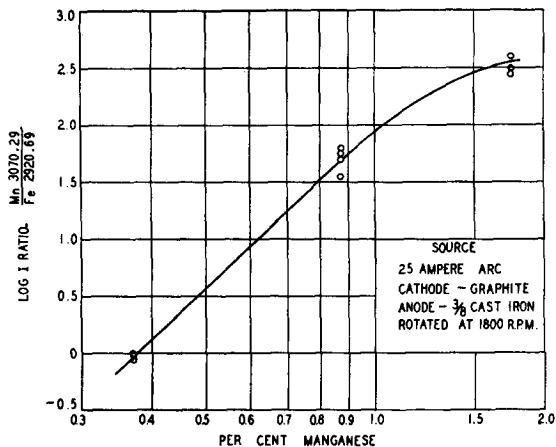


FIG. 5. Results obtained with arc shown in Fig. 4. Four readings are plotted for each sample. The improvement in constancy of the log  $I$  ratio may be noted by comparison with Fig. 1.

iron melted, it was forced outward by centrifugal force, and escaped from the edge of the anode in small drops. About two inches of the length of the casting was consumed per minute, and it was necessary to feed the anode slowly into the arc to maintain its length. It was difficult to enclose the arc and maintain the required visibility while, if the drops of molten iron were permitted to fly about, the destruction to trousers was considerable. The box shown in the illustration represents a scientific advance over the traditional barrel.

Typical results obtained with this arc are shown in Fig. 5, where four readings are plotted for each sample. It is readily observed that the new source shows considerable improvement in precision over the small stationary arc. It may be that the improvement is due in some measure

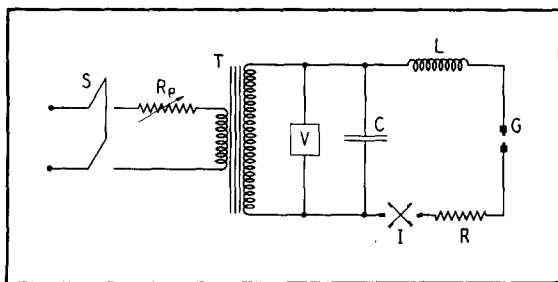


FIG. 6. Circuit diagram of condensed spark source, comprising  $S$ , line switch;  $R_p$ , adjustable primary resistor;  $T$ , high voltage transformer;  $V$ , electrostatic voltmeter;  $C$ , condenser;  $I$ , synchronous interrupter;  $R$ , resistor;  $G$ , sample gap;  $L$ , inductance.

to the sampling action which permits the consumption of fairly large quantities of the alloy, but more recent experiments indicate that the homogeneity of the iron is very good. It is thought that the benefit arises largely, if not wholly, from the tendency of the equilibrium, established between viscosity and centrifugal force, to maintain a constant temperature at the surface where the evaporation takes place, and, hence, a more constant vapor pressure in the discharge.

The accuracy of the analyses which could be performed with this arc was not ideal, but might be sufficient for the problem in hand. However, all the lines available and resolved for the important element, silicon, showed saturation at percentages lower than the normal content of several of the irons. The obvious solution of this

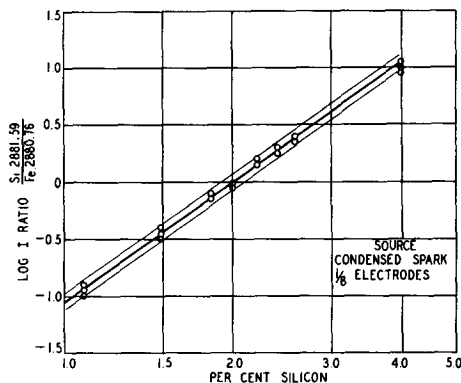


FIG. 7. Graph of results obtained with the spark source shown in Fig. 6. Four readings are plotted for each sample, the outer lines showing variations of  $\pm 5$  percent of the amount of silicon present.

problem appeared to be dilution of the alloy before analysis, and samples were cast in tubes of Armco ingot iron. This material is so nearly pure iron that it was thought that the probable variation in its content of the elements under investigation would contribute no difficulties.

The tube and cast core were burned together with results as consistent as those shown in Fig. 5, and the relative intensity of the silicon lines was reduced. The saturation point, however, remained virtually unchanged. It is not quite certain why the dilution failed so completely to produce the desired results. Among the effects to be considered are the higher melting point of the ingot iron, and the possibility of

reduction in cross section of the part of the arc column containing silicon.

Other difficulties were experienced also. If the arc was to carry a fairly large current, it appeared desirable to use graphite for the upper electrode since it produces few lines and has no liquid phase to cause dripping. When a new rod of graphite was installed in the arc the relative intensity of a fixation pair—an arc line and a spark line—would fluctuate erratically, and no reliable analysis could be performed. Numerous methods of treatment of the graphite were tried, but none was thoroughly satisfactory. Continued use of the graphite in the arc would eventually put it in a condition such that the results would be repeatable.

### The Spark Source

While the reliability of the rotating arc might be made satisfactory, it did not permit analysis for silicon over the required percentage range. Several other types of source were set up and tested briefly. Among these was a source described by Feussner,<sup>6</sup> for which he claimed a high degree of accuracy. The precision was found to be, in fact, quite good, but, in view of the complexity of quenched gaps and multiple resonances involved in the circuit, it did not seem certain

that the apparatus would maintain its reliability over long periods of routine operation with infrequent checks. The results obtained with the Feussner spark, which burned a very small amount of material, indicated that the lack of homogeneity in the sample would not be a major problem, so it was decided to attempt to construct a spark source of such simplicity that reliable operability over long periods might be anticipated.

These efforts resulted in the apparatus shown in Fig. 6. The transformer charges a condenser which discharges through a series network comprising a synchronous interrupter, a resistor,

an inductance, and the sample gap. The peak voltage imposed is 40,000 volts, and the elements are balanced to produce the lines desired at suitable intensities. The results obtained have been uniformly gratifying. A typical set of analyses for silicon is shown in Fig. 7, where four independent determinations are plotted for each sample against a careful analysis by the best chemical means. The outer lines indicate errors in analysis of plus and minus five per cent of the amount present. It may be noted that, in the working range of from one percent to three percent of silicon, all values fall within these

outer lines. Likewise, in routine operation at the foundry it has been found possible to maintain a limit of error certainly not exceeding plus or minus five percent of the amount present.

The possibilities offered by the spark source in the control of relative intensities and saturation of lines make its use highly desirable. Spark spectra, taken of iron containing silicon, are shown in Fig. 8, where the silicon line at 2881.59A is easily recognized. Both spectra were taken from samples of identical composition, but at different discharge temperatures. For the upper spectrum, a large inductance was used in the discharge circuit, while the

lower spectrum was taken with a much smaller inductance. The variation in the strength of the silicon line is quite apparent in the illustration, and since intermediate values of intensity are obtained at intermediate temperatures of the discharge, control of relative intensities may be effected over wide limits.

With a suitable selection of spectral lines the apparatus proved capable of effecting analysis for the six elements required, the following ranges of composition being covered simultaneously in a single spectrum: Cr, 0.10 percent to 1.00 percent; Cu, 0.20 percent to 0.80 percent; Mn, 0.40 percent to 1.00 percent; Mo, 0.10 per-

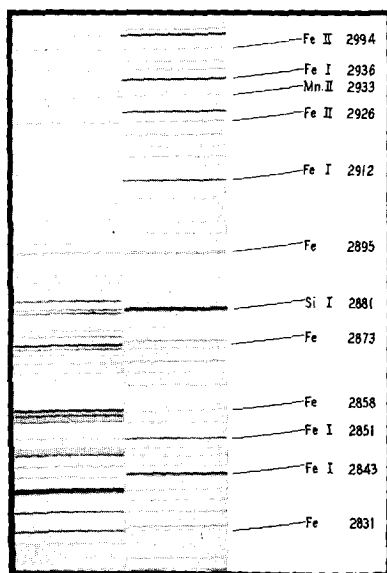


FIG. 8. Change of relative intensity of spectral lines with discharge temperature.

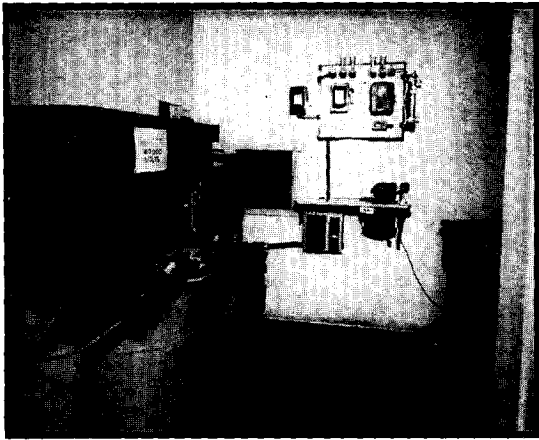


FIG. 9. The source room. The spark source operates from the power lines through a motor-driven voltage regulator. Controls are seen in the background. The sample gap is protected by a cover operating a safety switch.

cent to 1.50 percent; Ni, 0.15 percent to 1.25 percent; and Si, 0.50 percent to 4.00 percent. These ranges do not include all compositions for which analysis could be made with the lines chosen, but only those portions of interest to the problem in hand. Analyses for all six elements could be performed for most of the irons but for a few alloys containing larger amounts of copper and nickel the necessary percentages were not covered. More recent work detailed below has resulted in extensions to include all compositions of current production.

### The Foundry Laboratory

Routine analyses are made at the foundry in a laboratory especially constructed for spectro-

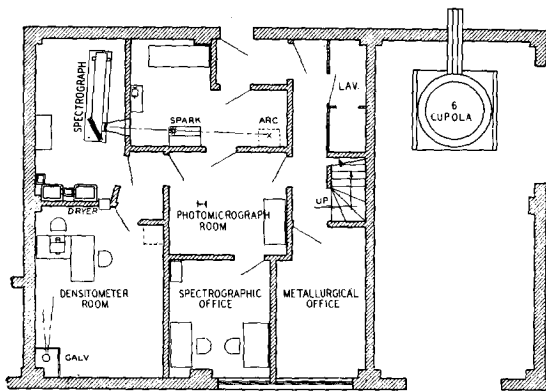


FIG. 10. The spectrographic laboratory at the Campbell, Wyant and Cannon Foundry Company. Note proximity to the line of furnaces whose output is analyzed.

graphic work. The floor plan and views of the equipment are shown in Figs. 9, 10, 11 and 12.

The spark apparatus, built in the instrument shop of the university, is capable of handling a sample per minute. The pencils of iron to be analyzed are loaded into the spark gap in a jig which expedites accurate positioning. A trap with a safety switch covers the sample gap, and all other high voltage parts are enclosed in the housing. A voltage regulator, shown in the background, eliminates excessive fluctuations of line voltage. The convenience of design and arrangement of the spark equipment contributes materially to the high speed attained in the analysis.

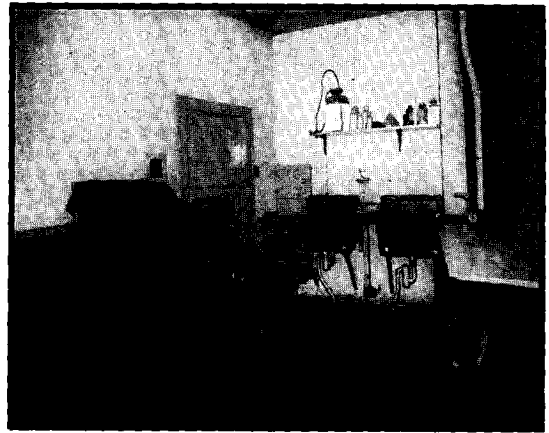


FIG. 11. The darkroom. The inclusion of the spectrograph in the darkroom saves many steps.

The inclusion of the spectrograph in the darkroom saves many steps, and conveniences such as oscillating trays and a hot-air dryer are supplied to hasten the processing.

As has been stated, the microphotometer used is a remodelled Bausch and Lomb density comparator. The resolution has been decreased and a new photo-cell installed to permit the use of a critically damped galvanometer having a period of two seconds. The galvanometer, on a Julius suspension, is protected from drafts by the chimney shown in the background. New parts have been added to the plate carriage to permit motion from one spectrum to another without loss of proper alignment of the plate. Reading is greatly facilitated by a slow motion, comprising a worm drive, which engages the original rack and

pinion motion through a clutch. The clutch may be thrown out for rapid motion between readings. Readings may be made of the opacities of five or six spectral lines per minute, with an error not exceeding one percent at normal densities.

The laboratory has been in operation for about a year and its general arrangement has been found to be very satisfactory. Less than two man-minutes elapsed time is required per analysis, if spectra of eight samples are recorded on the same photographic plate. Experience at the foundry indicates that similar analyses in the chemical laboratory would entail three times the personnel charge.

### Reliability

The question of precision in analysis is of fundamental importance and no pleas including the well-worn "lack of homogeneity" serve to make useful for production control a method of analysis which will not indicate very nearly the same composition if the sample is run a second time.

The reliability demonstrated by the condensed spark source in laboratory tests has been shown in Fig. 7, a graph of results obtained on samples analyzed chemically by the best analytical methods by expert analysts. The comparisons about to be presented do not stand on such a complete scientific basis. It is true that during several months of operation numerous check readings between chemical and spectrographic

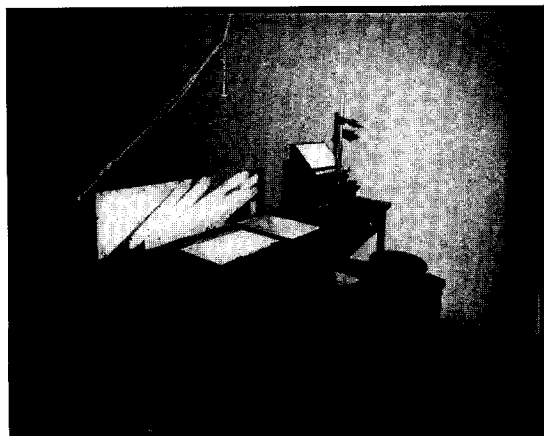


FIG. 12. The microphotometer equipment.

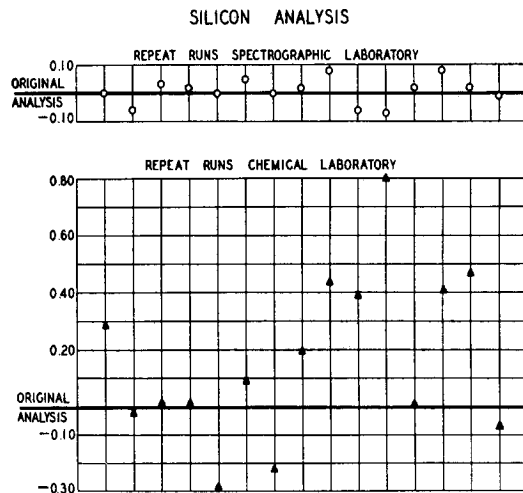


FIG. 13. Comparative reliability. Production records at the foundry indicate that the spectrographic analysis is more reliable than analysis performed in the chemical laboratory. The original analysis is the heavy line, and repeat analyses, the points shown. The silicon content is in all cases about two percent.

analyses have been obtained. Samples to be analyzed in both laboratories are supposed to be poured from the furnace at the same time, but it is not possible to guarantee that the two laboratories had in all cases samples of exactly the same composition. The comparisons are with routine-control chemical analysis which is, perhaps, somewhat more hurried than the best analytical determinations. In general, the press of arrival of new samples prohibited efforts to compose small differences in analysis. However, if the discrepancies were sufficiently great, one laboratory or the other might find time for a check run.

Fig. 13 shows a comparison of original and repeat analyses for the chemical and spectrographic laboratories at the foundry. The readings shown here include, with no omissions, all the repeat runs made on silicon analysis in certain types of iron during the period March 1 to May 20, 1936. The original analyses lie on the heavy line and departures of the repeat analyses from the original are shown by the distribution of the points. The silicon content is, in all cases, about two percent, and it is apparent that no repeat spectrographic determination differs from the original by more than eight points, or four percent of the silicon content, and that the

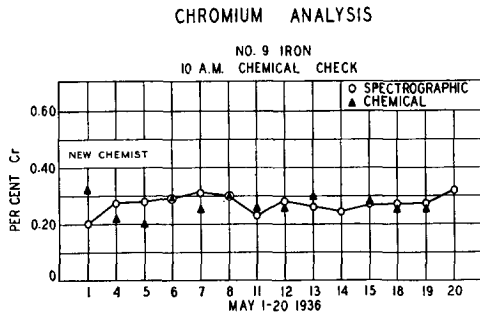


FIG. 14. Comparison of spectrographic and chemical analyses. New analyst at first of month shows rapid improvement in accuracy.

limit of error from the mean does not exceed plus or minus two percent of the amount of the element present. It is thought that a limit of error of plus or minus five percent of the content is sufficiently liberal to include such systematic errors as may be anticipated. It is important to note that this is an unselected list of repeat analyses from an actual routine-control installation, that it covers an elapsed time of nearly three months and is not a quotation of results obtained on a single photographic plate in a development laboratory.

The repeat runs made in the chemical laboratory for the same element and the same irons over the same period show considerably wider departures. This graph does not, of course, represent the average chemical accuracy, since check readings were taken only in cases where the initial determination appeared questionable, either through failure to check the spectrographic result on the same sample, or because the com-

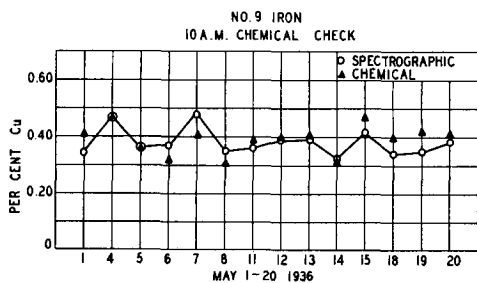


FIG. 15. Comparison of spectrographic and chemical analyses of copper. Segregations, which cause considerable difficulty in the chemical analysis of this element, are avoided by the high chill of the cast used for spectrographic analysis samples.

position appeared to differ from the expected value. Perhaps the best view to take of this figure is that the departures show the relative probability of something's going wrong with the method. In any case, the spectrographic determinations show superior reliability. The analysts in the spectrographic laboratory previously worked in the chemical laboratory so the difference in personnel is negligible.

Figs. 14 to 19, inclusive, show a comparison, for each of the six different elements, of routine spectrographic and chemical analyses performed on irons in production at the foundry. In general, analyses were made in the spectrographic laboratory at much more frequent intervals than

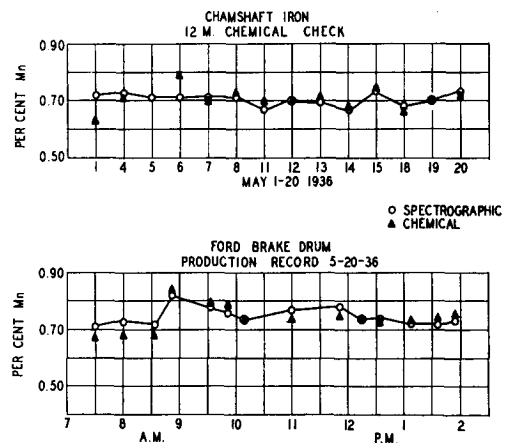


FIG. 16. Comparison of spectrographic and chemical analyses for manganese.

in the chemical laboratory. The figures show all chemical results posted, and the corresponding values obtained by the use of the spectrograph. The period selected for comparison is random and covers a sufficient time to be representative. The graphs show small differences in analysis but none of important proportions. It must be borne in mind that the exact composition is not known and that it cannot be guaranteed that the samples were of precisely the same composition. In view of Fig. 13, which demonstrates relative repeatability, and Fig. 14, which shows the beneficial effect on the chemical laboratory of spectrographic treatment of new analysts, perhaps no large part of the small variations



observed should be assessed as errors in the spectrographic determinations.

Errors may creep into chemical analysis in many ways, one of which is illustrated in Fig. 20. At 8:30, 10 and 1 o'clock the chemical analysis showed a high silicon content, which was not verified by the spectrographic laboratory. During the analysis of the 2:30 sample it was noticed that, in the silica to be weighed, there were several pieces of surface scale. These were removed with, perhaps, some silica adhering, and the result was a bit low. A more careful repeat on the samples, which had originally shown high silicon, agreed very well with the spectrographic values. Other cases could be cited.

It has been demonstrated that, in the hands of routine operators of the class customarily used in chemical laboratories, the spectrographic technique developed by the authors has shown a high degree of reliability. The whole process is instrumental and does not require continuous concentration on all details as do chemical methods. This may account for the fact that it appears to be continuously reliable, and entirely free from even occasional gross errors.

The claims of spectroscopists in development laboratories sometimes fail to be realized when routine operation in a manufacturing plant is attempted. It is hoped that it has been made adequately clear that the analyses shown in Figs. 13 to 20, inclusive, were taken from the production records of the Campbell, Wyant and Cannon Foundry Company and represent actual results obtained in an industrial spectrographic laboratory doing industrial work.

### New Developments

As a result of recent work on the system of analysis, several changes are being instituted at this time. While no data under routine operating conditions are available, tests at the university laboratory indicate that the alterations proposed will extend the percentage range over which analysis may be effected, expedite the work, and yield improved accuracy in the determinations.

Changes in source temperature and the choice of a new set of spectral lines have led to the extension of the analysis range, so that the following percentages may be read simultaneously from

a single spectrum: Cr, 0.01 percent to 1.50 percent; Cu, 0.20 percent to 3.00 percent; Mn, 0.30 percent to 1.25 percent; Mo, 0.07 percent to 1.50 percent; Ni, 0.15 percent to 2.00 percent; Si, 0.50 percent to 4.00 percent. All the irons in current production by the company

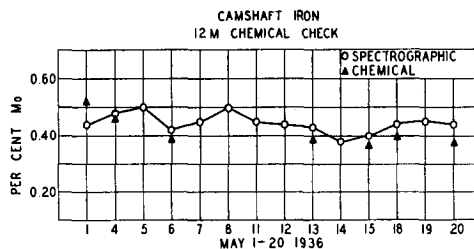


FIG. 17. Comparison of spectrographic and chemical analyses for molybdenum.

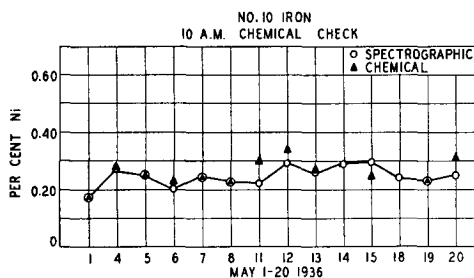


FIG. 18. Comparison of spectrographic and chemical analysis for nickel.

fall within these ranges and it is thought that further extensions are easily possible.

Through the cooperation of Dr. C. J. Staud of the Eastman Kodak Company of Rochester, New York, tests have been made on a number of types of photographic plates to determine their suitability for this work. The type 144-0 plate has been chosen to replace the polychrome plate previously used. Numerous experiments have been made on processing solutions to reduce the time which must elapse between the completion of the exposure and the beginning of microphotometer readings. It now appears possible from the dry exposed plate to produce a dry processed plate in less than nine minutes. For a given change of composition of the alloy the change in microphotometer reading has been increased two to threefold. The reproducibility of relative opacities appears as good as before and further increases in accuracy are indicated.

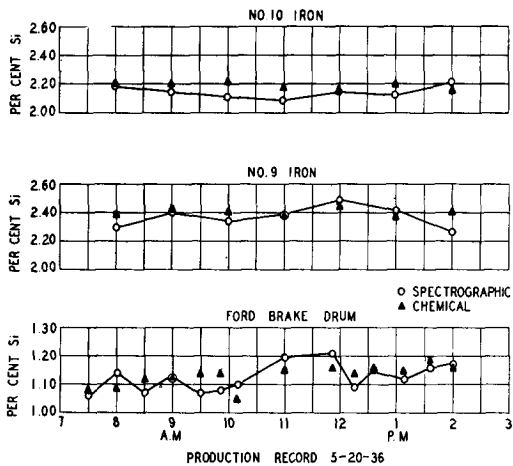


FIG. 19. Comparison of spectrographic and chemical analysis for silicon.

The methods of handling the various processes involved in an analysis have passed through several phases. Mention in detail of these processes has been postponed to this point since it was felt that only the most recent need be described. The samples used are cast in a permanent mold from the molten iron tapped off from the furnace. The form of the sample is cylindrical, one-eighth inch in diameter by one inch long. Electrodes of this small size have been found convenient and rapid to handle; the intense chill of the casting discourages segregation and equilibrium in the source is established almost instantly. Two sets of clamps hold two such cylinders in vertical coaxial alignment, the nearer ends being separated by one-quarter inch. The discharge crosses this quarter-inch gap and produces the light to record the spectrum. While the adjustment of the gap length is not at all critical, a loading jig is used for speed and convenience.

No condensing lens is interposed between the source and the spectrograph slit. The use of such a lens has not appeared desirable for a number of reasons; additional equipment involves additional hazard of variation in adjustment; the source produces sufficient light to record a spectrum in less than one minute, so no important saving of time could be accomplished; small variations in the position of the spark may lead to important errors if the spark is imaged on the slit.

A section of the spectrum extending from about 2220A to 2950A is recorded on a photographic plate eleven and one-half inches long in a special plate holder constructed in the physics instrument shop. The demands for speed in the operation of the microphotometer make desirable the production of a spectral line of appreciable area; a slit width of seventy microns and a line length of seven millimeters are used. Nine spectra may be recorded on a four-inch plate with sufficient separation and margin, while the precision is such that only one spectrum is required for the analysis of each sample.

### Calibration

The photographic plate is processed and, when dry, is installed in the microphotometer. Attempts to read wet plates have been uniformly discouraging. Readings are made of the opacities of several selected lines due to the matrix, in this case iron. Arbitrary values of exposure have been assigned to these lines in such a way that if the lines are of moderate densities a plot of galvanometer reading against log exposure is linear. The selected line due to the element to be analyzed is measured, and the log of the ratio of its equivalent exposure to that of a selected iron line is read from the arbitrary scale mentioned above. This is done with a graduated set of samples whose compositions are known from careful chemical analysis, and the relation between log exposure ratio and percentage content is established. At this point the standard samples may be laid aside, and need be used further only for occasional checks. To analyze a sample of unknown composition, the log exposure ratio is determined as above,

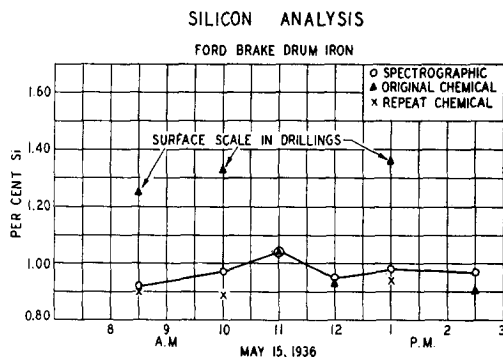


FIG. 20. An error in chemical analysis.

and the percentage content of the element is read from the curve of their relationship.

It is apparent that the method involves internal control with interpolation between lines of the matrix, and, hence, follows directly the suggestions of Gerlach and Schweitzer. Obviously, other methods of interpolation might be used with equal success: no especial virtue is claimed for the one outlined above except that it appears direct and effective. If several spectra are recorded on a single plate, it is considered necessary to read the whole set of matrix lines for the first spectrum only. For succeeding spectra, the opacity of the whole set of lines is known from reading any one of them.

Six analyses may be performed, to determine the percentage content of the elements mentioned, on a single sample in fifteen minutes elapsed time. Normally, spectra for forty-eight analyses on eight samples are recorded on each plate and the posting of results may be completed in thirty-five minutes. The speed and precision attained has exceeded expectations. Operating expenses are very reasonable, and the personnel demand small for the number of analyses performed. The technique developed is capable of extension to many other elements and matrices, if such extensions are, or become, of interest to industry.

### Summary

To obtain the rapid analysis necessary for rigorous composition control in routine production, satisfactory spectrographic technique has been developed, and an installation put in operation in a large Michigan foundry, which produces alloy cast iron. Spectra are recorded, on a photographic plate, from the condensed discharge across a one-quarter inch gap between the ends of two cast cylindrical electrodes one-eighth inch in diameter. After the plate has been processed and dried, opacity measurements of selected lines are made on a microphotometer, and the percentage composition is read from calibration charts. The condensed-spark source developed in this laboratory gives excellent reproducibility. Its principal features are the control of the damping in the oscillatory circuit, and the use of a synchronous interrupter to maintain the discharge potential. The normal speed of recording spectra is one sample per minute. A suitable choice of photographic emulsion and of processing solutions and technique permit the processing and drying of the plate to be completed in slightly less than nine minutes. The microphotometer has been remodelled for rapid operation, and permits the

measurement of five to six spectral lines per minute. Calibration is effected by the use of a series of samples of known composition, the relative intensity of lines due to element and matrix, respectively, being plotted against percentage content in accordance with internal control methods. Analyses for six elements are obtained from a single spectrum, the percentage ranges covered being as follows: Cr, 0.01% to 1.50%; Cu, 0.20% to 3.00%; Mn, 0.30% to 1.25%; Mo, 0.07% to 1.50%; Ni, 0.15% to 2.00%; and Si, 0.50% to 4.00%. Other ranges may be obtained by variation of the discharge conditions. Six analyses for a single sample may be completed in fifteen minutes; or if spectra of eight samples are recorded together on a plate, the forty-eight analyses may be completed in about half an hour. In routine operation at the foundry, the method of spectrographic analysis described has shown itself more reliable than chemical wet methods. The average accuracy of a single determination deviates from the actual amount present by not more than  $\pm 1\%$  of the amount of the element present, and the maximum errors observed amount to less than five times the average uncertainty.

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