

A CRITICAL STUDY OF THE COPPER SPARK  
METHOD OF SPECTROGRAPHIC ANALYSIS

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JOHN EDWARD VARNER

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METHOD OF SPECTROGRAPHIC ANALYSIS

Approved:

*W. M. K. I.*  
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*W. M. K. I.*  
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*W. M. K. I.*  
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## DEFINITION OF TERMS

Standard Deviation. The random differences between spectrographic and chemical analyses are measured by the standard deviation, S, which is defined mathematically as

$$S = \sqrt{\frac{\sum(x - \bar{x})^2}{n - 1}}$$

where  $x$  = the value of an individual spectrographic results  
 $n$  = number of comparisons  
 $\bar{x}$  = arithmetic mean of the spectrographic results

Coefficient of Variation. The coefficient of variation is simply the standard deviation expressed as a percentage of the arithmetic mean, i.e.

$$V = \frac{100 S}{\bar{x}}$$

Mean Deviation. The mean deviation is defined as the arithmetic mean of the deviations from the mean, all taken with the positive sign.

$$M.D. = \frac{\sum|x - \bar{x}|}{n}$$

Index Point. The index point is defined as the percentage read on the spectrographic working curve where the ratio is equal to unity.

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I PURPOSE OF THE INVESTIGATION

The use of copper electrodes in spectrographic laboratories has been known for a number of years, the principle advantage being to avoid interference from cyanogen bands. Therefore, while the principle of the copper spark method as an analytical procedure is not new, the question of the accuracy of the method, as a quantitative spectrochemical technique, has not been sufficiently explored.

Russell<sup>1</sup> reports that the copper spark method is useful for the analysis of solutions if a high degree of accuracy is not necessary and states that the procedure is capable of detecting on the order of 0.001 mg. of an element with an error of  $\pm 10\%$ . However, Russell offers no data to substantiate his estimation of the error to be expected and, hence, further work on this important question was felt necessary. Since one of the chief features of the method is its universality, the question of the accuracy to be expected is of considerable interest. Therefore, the purpose of the present work is to make a critical study of the method with respect to precision and accuracy. In order to do this, it was decided to prepare stock solutions of nickel in an iron solution and analyze these by the copper spark method. The accuracy obtained in this way was to be compared

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<sup>1</sup>R. G. Russell, "Emission Spectroscopy in an Oil Laboratory", Analytical Chemistry, 20: 296, (1948)



with the accuracy obtained by analyzing for nickel in steel using National Bureau of Standards samples. The latter determination was to be carried out by the conventional spectrochemical method and is considered to be one of the most precise of all spectrochemical determinations.<sup>2</sup>

Therefore, the objectives to be gained in undertaking this study of the copper spark method are two fold. The first objective is to find those experimental conditions which yield the most precise results. The second objective is to obtain an estimation of the accuracy and precision of this method as compared with that obtained in a very favorable case, namely, the determination of nickel in National Bureau of Standards steel samples.

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<sup>2</sup>M. F. Hasler and J. W. Kemp, "Spectrochemical Analysis of Metals with the Multisource Unit", Journal Optical Society of America, 34: 21 (1944)

## II INTRODUCTION

The copper spark method of spectrochemical analysis under investigation in this work was first proposed by Fred, Nachtrieb, and Tomkins.<sup>3</sup> The purpose of these authorities in suggesting this method was to present a means by which any sample can be successfully analyzed using standard spectrographic equipment. The only requirement necessary in applying this technique is that the sample under investigation must be obtainable in a hydrochloric acid solution.

Essentially, the method consists of evaporating a given small volume of solution on the tip of pure copper electrodes. After complete evaporation has taken place, the electrodes are then sparked in such a fashion that the evaporated film on the electrodes is volatilized and excited.

Therefore, this procedure offers an easy method for the rapid analysis of solutions while in no way sacrificing the sensitivity of the spectrum obtained. This means that very small samples can be handled. However, the extreme sensitivity of the method proves to be a disadvantage from the point of view of contamination. This is especially true for many of the more common elements such as calcium, magnesium, and sodium. In order to successfully analyze for these elements, elaborate precautions must be taken to eliminate contamination. The sensitivity of the method is discussed in the article by Fred, Nachtrieb, and Tomkins.<sup>4</sup>

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<sup>3</sup>Fred, Nachtrieb, and Tomkins, "Spectrochemical Analysis by the Copper Spark Method", Journal Optical Society of America, 37: 279, (1947)

<sup>4</sup>Loc. cit.

## III APPARATUS

The grating spectrograph,<sup>5</sup> Multisource unit,<sup>6,7</sup> and comparator-densitometer<sup>8</sup> used in this work were those manufactured by A. R. L.-Dietert. The spectrograph covered the range from 2300 A to 4300 A with a uniform dispersion of 7 A per mm. in the first order. The Multisource was adjusted to spark excitation and the exposures were made under the following conditions:

	Condition #1	Condition #2
Charge vs discharge	180 degrees	180 degrees
Initiator switch	continuous	continuous
Initiator knob	high power	high power
Capacitance	2 microfarads	5 microfarads
Resistance	0.4 ohms	10 ohms
Inductance	50 microhenries	100 microhenries
Slit setting	60 microns	60 microns
Output voltage	960 volts	960 volts

The upper electrode was negative in all cases.

The filters used with the solutions were numbers 1 and 6 which allowed approximately 32% of the light produced to enter the spectrograph. The exposure time used under these conditions was 14 seconds.

The filters used with the National Bureau of Standards samples were numbers 1 and 5 which allowed 85% of the light to be utilized. The exposure time, including 5 seconds prespark, was 20 seconds.

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<sup>5</sup> M. F. Hasler and R. W. Lindhurst, "Spectrograph for Rapid Industrial Application", Metal Progress, 30: 59, (1936)

<sup>6</sup> M. F. Hasler and H. W. Dietert, "A New Spectroscopic Source Unit", Journal Optical Society of America, 33: 218, (1943)

<sup>7</sup> M. F. Hasler and J. W. Kemp, "Spectrochemical Analysis of Metals with the Multisource Unit", Journal Optical Society of America, 34: 21, (1944)

<sup>8</sup> H. W. Dietert and J. A. Schuch, "A New Projection Comparator-Densitometer", Journal Optical Society of America, 31: 54, (1941)

For the purpose of facing the electrodes, a lathe was used at the beginning of the experimental work. This, of course, was a very effective means for cutting a smooth face on the electrodes. However, this procedure was disadvantageous from the stand point of the time required for cutting 28 electrodes. Therefore, in order to save time, it was imperative that another method be found for this operation.

A unique device was constructed for this purpose which proved to be quite rapid while in no way was there a loss in the smooth surface obtained on the electrodes. This device consisted of a 1/4 horsepower motor equipped with an adapter for holding a disc operating on a 1/2 inch shank. The disc was 3/8 inches thick with a diameter of 4 inches. On the disc was attached 1/0 sandpaper with the aid of Casco Casein glue.

The motor was mounted on a 1 inch by 6 inch cold-rolled steel plate. A right angle piece, on which a tongue had been cut, was allowed to slide on the plate by means of a T-slot. The right angle piece was held in place in the T-slot with the aid of a T-headed bolt and a wing nut.

In order to hold the electrodes in place, a 1/4 inch hole was reamed in the center of the right angle piece in such a way as to strike the center of the disc. In this way, the electrodes could be moved from the outer end of the disc to the center as the sandpaper was consumed. Once the sandpaper had been consumed, it was readily removed from the disc by wetting the surface with water. New sandpaper could be quickly attached to the disc with the glue mentioned above.

By using this device, approximately twenty minutes could be saved in facing the 28 electrodes.

The only possible objection which might arise to the above mentioned apparatus is if a qualitative determination of silicon is desired. It is obvious that traces of silicon are almost sure to be deposited on the face of the electrodes as they come in contact with the sandpaper. Therefore, this device is not recommended when an analysis of a sample containing silicon is to be performed. However, it might be pointed out that this objection did not arise in connection with the work contained in this report.

## IV PHOTOGRAPHY

Eastman spectrum analysis No. 1 film was used to photograph the ultraviolet spectrum. The film was developed for 3 minutes in Eastman D-19 developer, immersed in a 3% acetic acid solution short-stop for 30 seconds, fixed in Eastman X-ray fixing bath for 1 minute, and washed for 5 minutes in circulating water. Mechanical agitation for processing the film was provided in the A. R. L.-Dieter film developing machine.<sup>9</sup>

The film was calibrated by use of the two-step filter, preliminary curve method.<sup>10</sup>

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<sup>9</sup>J. Schuch, "Film and Plate Processing Equipment", Journal Optical Society of America, 32: 116, (1942)

<sup>10</sup>J. R. Churchill, "Techniques of Quantitative Spectrographic Analysis", Industrial Engineering Chemistry, Analytical Edition, 16: 653, (1944)

## V PREPARATION OF SOLUTIONS

Solutions containing nickel and iron in varying amounts were prepared. "Baker's Analyzed"  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and  $\text{Ni}_2\text{O}_3$  were used as the source of iron and nickel respectively. A nickel solution containing 0.001 gm. Ni per ml. was prepared by dissolving a weighed amount of nickelic oxide in 0.1 N hydrochloric acid. An iron solution was prepared in a like manner, but due to the hygroscopic nature of the ferric chloride used, a chemical analysis was felt necessary to determine its true composition.

The chemical analysis of the iron solution was performed by making duplicate quantitative determinations. Each sample of the iron solution, which was subjected to the chemical analysis, contained 10 ml. each. These samples were then diluted with sulfuric acid, and were evaporated to fumes of sulfuric acid to remove any chloride ions that might interfere with the subsequent titration. After this operation had been completed, the iron was reduced from the ferric to the ferrous state with the aid of 20 mesh zinc. After complete reduction had taken place, the samples were diluted with water, more sulfuric acid added in order to make the solution acidic and, finally, titrated with permanganate solution which had been standardized as 0.0943 N. For the two samples analyzed in this work, 14.60 and 14.80 ml. of permanganate solution was required. With this information, appropriate calculations revealed that the iron content of the samples under investigation contained 0.00770 and 0.00780 gm. Fe per ml. respectively. An average of these two figures was taken, and the final figure of 0.00775 gm. Fe per ml. was used in determining

the percentage composition of the solutions described below.

The nickel solution was diluted with nine volumes of 0.1 normal hydrochloric acid making the resultant concentration of the solution 0.0001 gm. Ni per ml.

It was desired to mix the two solutions described above in such a way as to produce stock solutions containing from 0.100% to 0.400% Ni. This was done by taking 32.30 ml. of iron solution and adding varying amounts of the nickel solution as shown below.

Percent Nickel in Sample	Volume of Fe Solution	Volume of Ni Solution
0.100%	32.30 ml.	2.50 ml.
0.150	32.30	3.75
0.200	32.30	5.00
0.250	32.30	6.25
0.300	32.30	7.50
0.350	32.30	8.75
0.400	32.30	10.00

The approximate concentration of hydrochloric acid in the final solutions was 0.1 normal. This was the concentration recommended by Fred, Nachtrieb, and Tomkins.<sup>11</sup>

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<sup>11</sup>Fred, Nachtrieb, and Tomkins, loc. cit.



## VI EXPERIMENTAL TECHNIQUE

The electrodes used in this work were quarter inch copper rods cut into lengths of approximately three inches each. In order to decrease the danger of oxidation, the freshly cut electrodes were placed in a jar containing enough benzene to keep the tips well covered. The electrodes were kept in this manner until it was convenient to use them, but in no case were the electrodes allowed to stand for longer than a twelve hour period before use.

For the purpose of evaporating the solutions on the copper electrodes, a hot plate was found most convenient. In order to hold the electrodes in a vertical position on the hot plate, a steel plate 4 by 4 inches and 1/2 inch thick in which were drilled 16 holes of slightly greater than 1/4 inch diameter was used. By making use of this arrangement, a solution could be evaporated on 16 electrodes simultaneously. With the hot plate set on the low position, a temperature of 140 degrees centigrade was registered at the tip of these electrodes. This information was obtained in the following way. First, a hole was drilled into the face of an electrode which was big enough to allow the bulb of a thermometer to enter. Next, this hole was filled with enough mercury to completely surround the thermometer bulb. The electrode was then placed on the hot plate, the thermometer fixed in the correct position, and a reading of 140 degrees centigrade recorded.

Immediately after placing each electrode on the hot plate, its tip was covered with the solution under investigation. In general, this will require about one thirty-fifth of a ml., and this amount can be most

conveniently placed on the electrodes by means of a medicine dropper. For the 0.100% nickel solution prepared in this work, one thirty-fifth of a ml. will contain only 0.07 mg. of iron and 0.00007 mg. of nickel. That this small amount can be detected emphasizes the extreme sensitivity of the copper spark method. This is especially true in view of the fact that the filters used allowed only 32% of the light produced by the sparking to be utilized.

For the present work, each electrode was heated for exactly 14 minutes before being removed. This allowed sufficient time for the solution to completely evaporate and the deposit to become thoroughly dry. In general, the drop of solution placed on the electrodes would evaporate slowly with little tendency to boil or run over the sides.

The spectrum lines chosen for study in this work were the iron line at 3370.786 Å and the nickel line at 3414.765 Å. These particular lines were chosen since they fall near the middle of the spectrum photographed, were free from interference, and were close together. These two lines can also be classified as arc lines as can be seen by reference to the well known M. I. T. Wave Length Tables.<sup>12</sup> This information from the M.I.T. Tables is given below.

Wave Lengths	Intensities	
	arc	spark
3370.786 Å (Fe)	300	200
3414.765 Å (Ni)	1000	50

After each film had been properly exposed and developed, the

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<sup>12</sup>G. R. Harrison, Massachusetts Institute of Technology Wave Length Tables (New York: John Wiley & Sons, 1939)

transmission readings of the iron line and nickel line, as measured with the aid of the comparator-densitometer, were recorded. With the information made available in this manner, the ratio of the iron line to the nickel line was determined by making use of the film calibration curve. These ratios were then subjected to statistical tests.

Background corrections on the transmission readings mentioned above were not significant except when using the two step filter while investigating the National Bureau of Standards samples. In this case, background corrections were made by subtracting the background intensity from the total intensity.<sup>13</sup>

When the results from more than one film were to be combined, care was taken to run all these films on the same day. This was done in order to eliminate any error introduced into the final data as a result of a possible shift in the working curve.

The humidity in the spectrograph room was kept constant at all times except during the final week of this research when the effect of a change in humidity was under investigation. For this purpose, a Carrier air conditioning machine was used. This machine maintained the temperature at a constant value of 76 degrees fahrenheit, and the humidity was fixed at 78%.

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<sup>13</sup>W. C. Pierce and N. H. Nachtrieb, "Photometry in Spectrochemical Analysis", Industrial Engineering Chemistry, Analytical Edition, 13;744, (1941)

## VII RESULTS AND DISCUSSION

The following results were obtained for the two objectives of this research, with the interpretations given below.

Determination of Precision. The first objective of the present research on the copper spark method was to find those experimental conditions which, after statistical tests had been applied, could be considered as yielding the most precise data. In order to obtain this information, certain variables were altered, and the resultant data, accumulated under the changed conditions, were examined. The solutions were first run just as they were prepared. Next, the effect of dilution was determined. Various reagents were used for this purpose, such as water, hydrochloric acid, and ammonium chloride. The effect of changing the conditions under which the spark was obtained was also studied as well as the effect of a change in humidity.

The stock solutions, containing from 0.050% to 1.000% Ni were first run just as they were prepared, and the results obtained are shown below.

Solution	No. of Runs	Average Ratio(Fe/Ni)
1.000%	10	1.774
0.800	12	1.310
0.600	14	1.160
0.400	9	1.010
0.200	9	0.860
0.100	10	0.342
0.050	8	0.196

The ratios shown above are those using the 3268.236 A iron line and the 3414.765 A nickel line. Background corrections were made in every case. The ratios obtained in this manner were then plotted on log-log paper in the hope that a straight line might be obtained. A straight line

was not obtained, and this result was, perhaps, not too surprising in view of the fact that there were wide discrepancies in the individual ratios for the same solution. The fact that a straight line was not obtained might be attributed to a number of causes. First of all, the 3268.236 Å line used for iron was later shown to be a bad choice since a copper line at 3268.278 Å might well cause interference. The second possible reason why a straight line was not obtained might conceivably be due to an insufficient number of runs having been made. In other words, additional runs on the solutions might have changed the average ratios obtained and given a more accurate approach to the true value. A final reason might lie in the possibility that the solutions were inaccurately prepared causing the true composition to be entirely different from the values used to plot the curve.

It might be added that, at this early stage of the research, no attempt was made to heat each electrode an equal length of time. Later, it was discovered that the manner in which the electrodes were treated while on the hot plate had a marked effect on the ratios obtained. Disregard of this fact, undoubtedly, was the main cause for the wide discrepancy obtained in the individual ratios.

In any event, a new line had to be selected for iron to avoid interference from copper. After a thorough search was made, the line at 3370.786 Å was decided upon as being the most suitable since no interference occurred at this wave length. Furthermore, the intensity of this line was suitable, with the given exposure time, to obtain a reasonable ratio when compared to the nickel line. This line had the additional

advantage of lying close to the chosen nickel line. For these reasons, the 3370.786 Å iron line was used in all subsequent work.

To eliminate the possibility of improperly prepared solutions, new solutions were prepared and subjected to chemical analysis to determine their concentration.

The possibility of the existence of impurities in the copper rods, either inherent in the rods or introduced on the lathe, was not overlooked. However, an analysis of the rods, before and after they were cut on the lathe, showed no trace of iron or nickel impurities.

The effect of a change in variables on the precision obtained was best determined by applying statistical tests. The tests used in this work are those outlined by Mandel<sup>14</sup> and Davies,<sup>15</sup> and involved the computation of the standard deviation and the coefficient of variation.

The results obtained by changing the variables involved and applying the statistical tests are best shown by means of Table I given in the Appendix. As can be seen from this table, the solutions involved were analyzed by diluting with various amounts of distilled water and 0.1 N hydrochloric acid. Furthermore, from an examination of the standard deviation and coefficient of variation obtained, it is readily seen that the solution diluted with four volumes of 0.1 N hydrochloric acid can be considered as giving the most precise results.

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<sup>14</sup>J. Mandel, "Efficient Statistical Methods in Chemistry", Industrial Engineering Chemistry, Analytical Edition, 17: 201, (1945)

<sup>15</sup>O. Davies, Statistical Methods in Research and Production (London: Oliver & Boyd, 1947)

For comparison purposes, the standard deviation and coefficient of variation obtained by running the National Bureau Of Standards steel sample #411 is included in the above mentioned table. It is readily seen that a high degree of precision is reached in this determination. This was, of course, according to expectations. In order to check this determination for normal distribution of data, the difference between the individual ratios and the average ratio showed that 70% of the data was included in one standard deviation and 95% was included within two standard deviation. According to Churchill,<sup>16</sup> this definitely establishes the existence of a normal distribution.

An attempt to dilute the solution with ammonium chloride eliminated the iron and nickel lines from the spectrum with the exception of the persistent lines. In addition, an attempt to change the Multisource setting from condition 1 to condition 2, as recommended by Nachtrieb, gave no improvement in the precision obtained. That this is true can be readily seen from an examination of Table I.

Using the information obtained above, it was felt that the first objective of this research had been attained, and the solutions were diluted with four volumes of 0.1 N hydrochloric acid in all subsequent work.

Determination of Accuracy. The second objective of this research was to construct a suitable working curve so that the accuracy of the copper spark method as a quantitative spectrochemical technique might be determined.

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<sup>16</sup>H. V. Churchill and J. R. Churchill, "Evaluation of Spectrographic Analytical Data", Industrial Engineering Chemistry, Analytical Edition, 17: 751, (1945)

For this purpose, a series of runs were made on the solutions to cover the range from 0.150% nickel to 0.400% nickel. The results of this work is shown in Table II. These values were then plotted on log-log paper, and the working curve obtained is shown in Figure 1. The working curve is seen to be a straight line which is, of course, as it should be.

In order to test the accuracy of the copper spark method as a rapid quantitative procedure, immediate use was made of the working curve. Two solutions were selected as unknowns. Additional runs were made on these unknowns, and the ratios obtained in the usual manner were converted into percentage composition with the help of the working curve. The two solutions, used as unknowns, contained by chemical analysis, 0.200% nickel and 0.350% nickel. The figures obtained by the copper spark method of spectrochemical analysis were identical to those obtained by the chemical analysis. This was true, of course, after an average was taken of fifty repeat runs on the unknown solutions. The standard deviation of the 0.200% nickel solution was found to be 0.01744 with a coefficient of variation of 8.72%. For the 0.350% nickel solution, the standard deviation was found to be 0.02621 and the coefficient of variation was 7.48%.

Bureau of Standards Steel Samples. The final step necessary, in carrying out the objectives of this research, was to select suitable samples of nickel in steel from those obtainable from the National Bureau of Standards. In selecting these samples, it was desired to cover the same range as that covered by the solutions. However, this range could only be approximately duplicated as shown in Table IV.



These samples were run in exactly the same way as were the solutions with the exception of the fact that five seconds prespark was allowed. In addition, filters one and five plus a number nine, two step filter was used. This set of filters allowed 85% of the light to enter the spectrograph. The exposure time, including the prespark time, was twenty seconds.

The purpose of the two step filter was to furnish a means of obtaining an index point. In other words, it was immediately obvious that the index point would not be reached, using the above mentioned samples, if continued use was made of the 3370.786 Å iron line and the 3414.765 Å nickel line. This result may seem surprising in view of the fact that an index point was reached with the solutions which contained approximately the same percentage of nickel. However, if reference is made to the table given on page 11 of this report, it is readily seen that the nickel line is more arc like than the iron line. Also, it must be kept in mind that when the evaporated film on the copper electrode is excited, vapors will accumulate during the discharge and, consequently, the conditions are more favorable for the production of the arc lines. No such effect is achieved when running the steel samples and, as a result, the discharge is less arc like in character. Therefore, it would be expected that the transmission readings on the nickel line will be less for the solutions than for the steel samples. Hence, the ratio of the iron line to the nickel line will be different even though the same percentage of nickel exists in both cases.

The only way that an index point could have been reached under the

old conditions was either to select a new set of lines, or to use samples of a higher nickel percentage composition. Neither of these procedures was felt to be desirable since a suitable nickel line, that might prove useful for this purpose, could not be found near the chosen iron line, and the next National Bureau of Standards samples that were available contained over 1% nickel. Therefore, the decision was made to use the two step filter. This technique was not, however, without some disadvantages. For example, the number of films used were necessarily increased two fold. However, the biggest disadvantage lay in the fact that the background intensities of the iron line and nickel line were different. This meant that a correction for background became a necessity. The procedure for making the background correction is not difficult to apply.<sup>17</sup> Nevertheless, it is time consuming.

After the decision had been made to apply the above mentioned experimental technique to the samples involved, repeat runs were made with the results shown in Table III. The working curve obtained is shown in Figure 2, and it is readily seen that the desired straight line is obtained.

It is interesting to note that a straight line was obtained for these National Bureau of Standards samples in spite of the fact that the average composition of each sample was different from the others. However, sample #405, also containing 0.15% nickel, did not fall on the straight line obtained above. This failure was attributed to the fact that sample

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<sup>17</sup>W. C. Pierce and N. H. Nachtrieb, loc. cit.

405 contained 1.38% manganese while the other samples involved contained less than 1.0% manganese. Sample # 405 was, therefore, not used. An analysis of these samples is shown in Table IV.

Another interesting fact that was noticed in running these samples is that the spectrum obtained, using both ends of the same rod, were not always identical. This can only mean that the state of aggregation of the various constituents were different at the two ends of the sample.

Another important experimental result that must be mentioned is the fact that the intensity of the lines obtained, using the same exposure time, depended upon the temperature of the sample at the time of sparking. It was very noticeable that the intensity obtained during the first run was quite different from that obtained after the sample had been sparked several times. However, since this phenomenon had no effect on the ratios obtained, this point was not investigated further.

Sample #413, containing 0.18% nickel, was selected as the unknown and additional runs were made. The ratios obtained, after background corrections had been made, were converted into percentage of nickel in a manner similar to that used for the solutions. The spectrochemical analysis carried out in this way, indicated that the percentage of nickel contained in the sample was 0.181%. The standard deviation was 0.008956, the mean deviation was 0.007524, and the coefficient of variation was found to be 4.94%. This information was determined with the help of fifty three repeat runs on the same sample.

Effect of a Change in Humidity. As a final step in the present re-  
search on the copper spark method, the effect of a change in humidity  
was felt desirable. In order to perform this part of the research suc-  
cessfully, the air conditioning machine was cut off, the windows opened,  
and the room allowed to stand in this way for several days. At the end  
of this time, those samples which had been used as unknowns in previous  
work, when the temperature and humidity were held constant, were run  
again under the changed conditions. These unknowns were the 0.200% nickel  
solution, the 0.350% nickel solution, and the National Bureau of Standards  
sample #411. The data accumulated for these unknowns, allowing the humidity  
and temperature to vary, are given in Tables VIII, IX, and X, for the 0.200%,  
the 0.350%, and the sample #411, respectively. For purposes of comparison,  
the same data, accumulated while the temperature and humidity were held  
constant, is presented in Tables V, VI, and VII for the 0.200%, the 0.350%,  
and the sample #411, respectively. The ratios shown in these tables are  
those calculated in the usual way, namely, the ratio of the transmission  
reading taken on the nickel line to that taken on the iron line. The per-  
centages were obtained with the aid of the working curves made available  
by earlier work already described. Statistical tests were applied to the  
data accumulated in this way, and the results are shown in Table XI.

It would be difficult to reach any definite conclusion regarding  
the effect of humidity from the information given in the table indicated  
above. However, much can be said in favor of maintaining the temperature  
and humidity constant since it can be readily seen that in this case, the  
spectrographic analysis of the unknowns is identical to the chemical

analysis. Furthermore, the statistical tests indicate that the data are more precise in all cases with the exception of the National Bureau of Standards sample #411.

Attention is called to the fact that, with the temperature and humidity varying, a curve shift is obtained with the 0.200% nickel solution and sample #411. However, it is hardly possible to account for this by holding the change in humidity and temperature as responsible. This is true since no curve shift occurred with the 0.350% nickel solution. The data on each unknown was collected on different days, and with the exception of the change in humidity and temperature in those cases indicated, no other change was made. Therefore, the reason for the curve shift in the two cases indicated is too obscure for an explanation to be given.

## VIII CONCLUSIONS

In conclusion, it might be restated that the copper spark method of spectrochemical analysis offers to the chemist an excellent means for the rapid analysis of any sample that can be obtained in a hydrochloric acid solution. The extreme sensitivity claimed for this method was clearly shown in the present work since only 0.00007 mg. of nickel was used while running the 0.100% solution. This small amount was easily detected in spite of the fact that only 32% of the light produced by the sparking was utilized. Therefore, the use of copper electrodes in place of the conventional graphite is highly recommended for the detection of small traces of an element, while at the same time avoiding interference from cyanogen bands. Furthermore, a quick and easy method will be provided for obtaining a smooth surface on the electrodes if use is made of the electrode cutting device described in this report. Thus, the difficulty of machining the electrodes is eliminated.

The practicability of the copper spark method as a quantitative analytical technique has been demonstrated for nickel-iron solutions. Suitable working curves were obtained, and the results of the spectrographic procedure for analyzing unknown solutions has been shown to be identical to that of a chemical analysis. However, it must be pointed out that an average of a large number of repeat runs must be made in order to reach this degree of accuracy. For example, the average percentage composition calculated by using only the first twenty readings shown in Tables V, VI, and VII is 0.205%, 0.347%, and 0.1794% for the

0.200% nickel solution, the 0.350% nickel solution, and sample #411. For this reason, at least fifty repeat runs are recommended as the minimum required for best results.

When compared with the National Bureau of Standards steel samples, it is readily seen that the data accumulated by the copper spark method is less precise. However, it must be remembered that the analysis of nickel in these steel samples is considered to be one of the most precise of all spectrochemical determinations.<sup>18</sup> Therefore, in spite of the fact that the degree of precision reached is not the maximum obtainable in the spectrographic laboratory, the copper spark method remains an important analytical procedure. This is due to the fact that the method is not limited to those samples obtainable only in the form of alloys. The scope of the samples that may be analyzed by this technique is very general in nature, and can be applied to any sample obtainable in a hydrochloric acid solution.

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<sup>18</sup>M. F. Hasler and J. W. Kemp, loc. cit.

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## APPENDIX

TABLE I: Statistical Data on Solutions

Sample	No. of Runs	Mean Ratios*	Standard Deviation	Coefficient of Variation
1	49	1.340	0.1160	8.7
2	40	0.834	0.0288	3.4
3	40	0.827	0.0235	2.8
4	56	0.948	0.0253	2.6
5	33	0.936	0.0308	3.3
6	30	0.921	0.0305	3.3
7	50	0.883	0.0279	3.2
8	56	0.641	0.0173	2.7
9	56	0.752	0.0256	3.4

\*arithmetic mean of the ratios of the nickel line intensity to the iron line intensity.

The identity of the samples as well as the temperature, humidity, and Multisource setting under which the above data was accumulated is indicated in the table below.

Sample (Identity)	Temp.	Humidity	Multi-source
1(0.200% soln as originally prepared)	76 F	74.5%	Cond 1
2(0.100% soln as originally prepared)	74	78.0	Cond 1
3(0.100% soln diluted with 2 vol distilled water)	74	78.0	Cond 1
4(0.100% soln diluted with 4 vol 0.1 N HCl)	75	78.0	Cond 1
5(0.100% soln diluted with 6 vol 0.1 N HCl)	75	78.0	Cond 1
6(0.100% soln diluted with 5 vol distilled water)	75	78.0	Cond 1
7(0.200% soln diluted with 4 vol 0.1 N HCl)	75	78.0	Cond 1
8(National Bureau of Standards Sample #411)	75	78.0	Cond 1
9(0.200% soln diluted with 4 vol 0.1 N HCl)	78	75.0	Cond 2

TABLE II: Data for Solution Working Curve

Solution	No. of Readings	Mean Ratio
0.150% Ni	20	0.800
0.200	50	0.883
0.250	20	0.965
0.300	20	1.017
0.350	50	1.080
0.400	20	1.125

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Index Point: 0.280%

TABLE III: Data for National Bureau of Standards Working Curve

Sample	Percent Nickel	No. of Readings	Mean Ratio
410	0.13	20	0.501
407	0.15	21	0.592
413	0.18	53	0.747
403	0.23	21	1.007
411	0.29	21	1.332

Index Point: 0.23%

TABLE IV: Analysis of National Bureau of Standards Samples

Sample	Mn	Si	Cu	Ni	Cr	V	Mo	Al
411	0.65	0.14	0.065	0.29	0.91	0.003	0.15	-
403	0.89	0.25	0.16	0.23	0.28	0.045	0.060	0.005
413	0.67	0.22	0.25	0.18	0.055	0.007	0.006	-
407	0.79	0.29	0.09	0.15	1.15	0.19	0.035	0.055
410	0.38	0.30	0.11	0.13	2.30	0.004	0.97	-
405	1.38	0.19	0.12	0.15	0.18	0.010	0.010	-

Standards in the 400 series are rods  $7/32$  inch in diameter, 4 inches long

TABLE V: Data on 0.200% Nickel Solution (Humidity Constant)

Ratio	Percent Nickel	Ratio	Percent Nickel
0.910	0.217	0.885	0.201
0.895	0.207	0.910	0.217
0.895	0.207	0.950	0.243
0.875	0.195	0.880	0.198
0.925	0.227	0.870	0.192
0.915	0.221	0.855	0.182
0.895	0.207	0.905	0.213
0.875	0.195	0.887	0.202
0.890	0.204	0.865	0.188
0.905	0.213	0.865	0.188
0.905	0.213	0.895	0.207
0.890	0.204	0.880	0.198
0.890	0.204	0.845	0.177
0.892	0.205	0.815	0.159
0.850	0.179	0.835	0.171
0.830	0.168	0.875	0.195
0.875	0.195	0.850	0.179
0.945	0.241	0.840	0.174
0.895	0.207	0.890	0.204
0.860	0.185	0.905	0.213
0.880	0.198	0.925	0.227
0.898	0.209	0.875	0.195
0.885	0.201	0.870	0.192
0.880	0.198	0.908	0.216
0.850	0.179	0.840	0.174

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Mean Percentage : 0.200%  
 Mean Deviation : 0.0135  
 Standard Deviation : 0.0174  
 Coefficient of Variation: 8.7%

TABLE VI: Data on 0.350% Nickel Solution (Humidity Constant)

Ratio	Percent Nickel	Ratio	Percent Nickel
1.140	0.406	1.110	0.377
1.140	0.406	1.120	0.387
1.100	0.368	1.050	0.323
1.080	0.350	1.050	0.323
1.090	0.359	1.080	0.350
1.045	0.318	1.110	0.377
1.080	0.350	1.050	0.323
1.110	0.377	1.085	0.354
1.020	0.299	1.060	0.332
1.090	0.359	1.090	0.359
1.045	0.318	1.065	0.336
1.060	0.332	1.050	0.323
1.080	0.350	1.075	0.345
1.050	0.323	1.065	0.336
1.000	0.280	1.100	0.368
1.080	0.350	1.095	0.363
1.065	0.336	1.110	0.377
1.030	0.307	1.080	0.350
1.100	0.368	1.070	0.340
1.110	0.377	1.040	0.314
1.065	0.336	1.090	0.359
1.105	0.372	1.090	0.359
1.130	0.396	1.080	0.350
1.075	0.345	1.115	0.381
1.135	0.401	1.040	0.314

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Mean Percentage : 0.350%  
 Mean Deviation : 0.0212  
 Standard Deviation : 0.0262  
 Coefficient of Variation: 7.5%

TABLE VII: Data on National Bureau of Standards Sample 413(0.18% Ni)  
(Humidity Constant)

Ratio	Percent Nickel	Ratio	Percent Nickel
0.775	0.1865	0.690	0.1700
0.817	0.1950	0.725	0.1770
0.725	0.1770	0.730	0.1780
0.757	0.1834	0.710	0.1740
0.740	0.1795	0.695	0.1705
0.735	0.1790	0.817	0.1950
0.720	0.1755	0.820	0.1955
0.710	0.1740	0.698	0.1710
0.712	0.1742	0.770	0.1855
0.710	0.1740	0.745	0.1800
0.740	0.1795	0.717	0.1753
0.695	0.1705	0.732	0.1784
0.810	0.1935	0.780	0.1880
0.770	0.1855	0.730	0.1780
0.755	0.1830	0.723	0.1765
0.705	0.1730	0.773	0.1865
0.715	0.1750	0.768	0.1850
0.710	0.1740	0.697	0.1710
0.680	0.1680	0.768	0.1850
0.780	0.1880	0.788	0.1890
0.715	0.1750	0.785	0.1885
0.700	0.1720	0.748	0.1805
0.655	0.1625	0.817	0.1950
0.735	0.1790	0.835	0.1980
0.705	0.1730	0.850	0.2100
0.780	0.1880	0.830	0.1970
0.790	0.1895		

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Mean Percentage : 0.181%  
Mean Deviation : 0.00752  
Standard Deviation : 0.00896  
Coefficient of Variation: 4.9%



TABLE VIII: Data on 0.200% Nickel Solution (Humidity Varies)

Ratio	Percent Nickel	Ratio	Percent Nickel
0.835	0.171	0.833	0.170
0.835	0.171	0.855	0.182
0.785	0.144	0.868	0.190
0.800	0.150	0.847	0.178
0.805	0.153	0.825	0.165
0.820	0.162	0.880	0.198
0.860	0.185	0.830	0.168
0.853	0.181	0.845	0.177
0.823	0.164	0.870	0.192
0.840	0.174	0.850	0.179
0.820	0.162	0.835	0.171
0.850	0.179	0.885	0.201
0.810	0.156	0.865	0.188
0.860	0.185	0.835	0.171
0.830	0.168	0.863	0.187
0.860	0.185	0.830	0.168
0.780	0.141	0.865	0.188
0.835	0.171	0.815	0.159
0.853	0.181	0.790	0.147
0.815	0.159	0.835	0.171
0.885	0.201	0.855	0.182
0.900	0.204	0.875	0.195
0.835	0.171	0.855	0.182
0.870	0.192	0.845	0.177
0.835	0.171	0.865	0.188
0.840	0.174	0.820	0.162
0.775	0.139	0.820	0.162
0.878	0.197		

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Mean Percentage : 0.174%  
 Mean Deviation : 0.0124  
 Standard Deviation : 0.0156  
 Coefficient of Variation: 8.9%

TABLE IX: Data on 0.350% Nickel Solution (Humidity Varies)

Ratio	Percent Nickel	Ratio	Percent Nickel
1.160	0.420	1.015	0.293
1.110	0.377	1.000	0.280
1.080	0.350	1.055	0.327
1.100	0.368	1.025	0.303
1.060	0.332	1.005	0.284
1.040	0.314	1.040	0.314
1.020	0.299	1.070	0.340
1.085	0.354	1.090	0.359
1.150	0.381	1.105	0.372
1.190	0.441	1.065	0.336
1.160	0.420	1.090	0.359
1.170	0.427	1.065	0.336
1.105	0.372	1.090	0.359
1.110	0.377	1.100	0.368
1.070	0.340	1.060	0.332
1.120	0.387	1.065	0.336
1.045	0.318	1.045	0.318
1.060	0.332	1.040	0.314
1.150	0.413	1.050	0.323
1.100	0.368	1.000	0.280
1.150	0.413	1.070	0.340
1.140	0.406	1.045	0.318
1.100	0.368	1.090	0.359
1.090	0.359	1.005	0.284
1.085	0.354	1.120	0.387
1.095	0.363	1.060	0.332
1.075	0.345	1.025	0.303
1.115	0.381		

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Mean Percentage : 0.350%  
 Mean Deviation : 0.0308  
 Standard Deviation : 0.0387  
 Coefficient of Variation: 11.0%

TABLE X: Data on National Bureau of Standards Sample 413(0.18% Ni)  
(Humidity Varies)

Ratio	Percent Nickel	Ratio	Percent Nickel
0.638	0.1590	0.698	0.1710
0.650	0.1615	0.715	0.1750
0.644	0.1605	0.705	0.1730
0.663	0.1645	0.678	0.1670
0.650	0.1615	0.675	0.1665
0.678	0.1670	0.630	0.1575
0.698	0.1710	0.723	0.1765
0.750	0.1815	0.715	0.1750
0.733	0.1790	0.688	0.1695
0.673	0.1665	0.728	0.1777
0.680	0.1680	0.665	0.1645
0.688	0.1695	0.678	0.1670
0.638	0.1590	0.693	0.1705
0.683	0.1685	0.620	0.1555
0.688	0.1695	0.690	0.1700
0.725	0.1770	0.750	0.1815
0.680	0.1680	0.720	0.1755
0.750	0.1815	0.663	0.1645
0.715	0.1750	0.690	0.1700
0.695	0.1705	0.655	0.1625
0.688	0.1695	0.665	0.1645
0.677	0.1670	0.690	0.1700
0.698	0.1710	0.713	0.1745
0.678	0.1670	0.688	0.1695
0.730	0.1780		

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Mean Percentage : 0.169%  
Mean Deviation : 0.00483  
Standard Deviation : 0.00630  
Coefficient of Variation: 3.7%

TABLE XI: Statistical Data on Unknowns

Sample	Humidity Constant			Humidity Varies		
	0.200%	0.350%	#411	0.200%	0.350%	#411
No. of Runs	50	50	53	55	55	49
Mean Percentage Ratio	0.200	0.350	0.181	0.174	0.350	0.169
Temperature (°F)	75	75	77	82-84	81-83	80-82
Humidity (%)	78	78	78	76-80	76-80	79-80
Mean Deviation	0.0135	0.0212	0.00752	0.0124	0.0308	0.00483
Standard Deviation	0.0174	0.0262	0.00896	0.0156	0.0387	0.00630
Coefficient of Variation	8.7	7.5	4.9	8.9	11.0	3.7



