- I. Spectrographic Determination of Calcium, Magnesium, Potassium, Manganese, Iron and Phosphorus in Small Samples
- II. Spectrographic Determination of Zinc, Cadmium, Copper and Iron in Concentrated Nickel Sulfate Solutions

By

MABEL FLOREY WILSON

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Chemistry Department

East Lansing, Michigan

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Spectrographic Determination of Calcium, Magnesium, Potassium, Manganese, Iron and Phosphorus in Small Samples

Introduction

The spectrograph is particularly adapted to two types of analysis: first, the determination of traces of metallic substances or impurities, such as manganese in steel; second, the analysis of samples when only very small amounts are available, such as biological ash. This article will be confined to the second type, that is, to the determination of calcium, magnesium, manganese, potassium, phosphorus and iron in samples where the amount is too small to be analyzed by ordinary wet methods.

The method employed is similar to that first used by Nitchie and Standen (Nitchie and Standen, Ind. and Eng. Chem. Anal. Ed., <u>1</u>, 1-7 (1929)), of exposing the spectra of the samples between those of a series of standard solutions containing varying known amounts of the substance being determined. From the densities of the lines working curves were formulated according to

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the method of Twyman and Hitchen (Twyman and Hitchen, Proc. of Royal Soc. of London, Series A, <u>133</u>, 72.) From these standard curves, unknowns were directly determined.

Experimental

Apparatus. A Bausch and Lomb medium quartz spectrograph giving a dispersion of about nine inches for wave lengths of 2000 to 8000 A° was employed in the experimental procedure. The electrodes were held by an adjustable Bausch and Lomb electrode stand. A revolving sector cut down the percentage of light from the arc reaching the slit. Excitation of the samples was obtained by arcing graphite electrodes with direct current furnished by a 15 ampere-300 volt motorblackenings generator. Line densities were determined by means of a Bausch and Lomb density comparator.

Preparation of Electrodes. Acheson graphite rods 5/16 inches in diameter were cut in convenient lengths for arcing. One end of each was drilled approximately seven millimeters deep; one-tenth milliliter of the solution was placed in each crater; the electrodes were dried at 110°, and were used as lower electrodes or anodes. The cathodes consisted of similar lengths broken from the same rod. Special graphite rods very

free of metallic impurities were used in the calcium determinations.

Selection of Base. The first problem to be considered in the preparation of standards was the material for use as a base. This substance serves two purposes: first, as a "filler", giving a greater amount of substance in the electrode; second, as a means of holding back the carbon until volatilization of the sample is complete. Much more even exposures and lighter backgrounds were obtained by employing a base.

Since it is well known that chlorides give much sharper lines than other negative radicals, all determinations were carried out in hydrochloric acid solution. Samples of a type analyzed by this method were found to be readily soluble in hydrochloric acid. Therefore, only chlorides were considered for a base material. Zinc chloride was found to vaporize too readily; lead chloride was too insoluble; sodium chlordde in large amounts caused the arc to flare giving very uneven exposures; very satisfactory arcing conditions and even exposures resulted from the use of ammonium chloride but the spectral lines of the substances desired for use in analysis were not sharp and clear.

A number of mixtures of sodium and ammonium chloride were tried and one consisting of 10% sodium chloride and 90% ammonium chloride was found to give satisfactory results for arcing and for sharpness of lines. Both substances are easily obtainable in very pure condition and dissolve readily. The base solution finally selected consists of five grams of sodium chloride and forty-five grams of ammonium chloride in 4.5% hydrochloric acid solution.

Calcium Standards. No two elements under identical arcing conditions gave the same variation in line densiing ties for an equal change in concentration. Thus it was necessary to try various concentrations until a series of dilutions was obtained which gave a gradation of blackening line densities suitable for analysis.

Enough pure calcium nitrate was dissolved in the base solution to yield 2 grams of calcium per liter. From this, using the base solution for diluting, a series of standards was prepared containing 1.0, 0.5, 0.3, 0.2, 0.1, 0.075, 0.05, 0.03, 0.02, 0.01, 0.005 and 0.0025 grams of calcium per liter.

Magnesium Standards. Magnesium solutions were prepared in exactly the same manner using magnesium

chloride, giving a final series containing 5.0, 2.5, 1.0, 0.5, 0.3, 0.25, 0.2, 0.1, 0.05, 0.025, 0.01 and 0.005 grams of magnesium per liter.

Manganese Standards. Manganese chloride was dissolved in the base solution to yield 2 grams of manganese per liter. Lower concentrations of 1.0, 0.5, 0.25, 0.1, 0.05, 0.025, 0.01 and 0.005 grams per liter were prepared by combining the manganese solution with proper amounts of base.

Potassium Standards. The behavior of potassium is different than that of magnesium, manganese and calcium. Large amounts of potassium show a marked gradation of line densities. Thus higher percentages may be successfully analyzed directly from the sample without employing a "filler" or dilution of samples. Four groups of potassium standards were prepared in this investigation.

The first group combined potassium and phosphorus in a calcium and magnesium base. Two separate solutions, A and B were prepared. Solution A contained enough potassium chloride and potassium acid phosphate in 4.5% hydrochloric acid solution to yield 4 grams of phosphorus and 96 grams of potassium per liter. Solution

B contained 50 grams each of calcium and magnesium in 4.5% acid. By combining the two solutions in the proper proportions a series containing 48, 40, 32, 24, 16, 12, 8, 4.8, 2.4, 1.2, 0.24 and 0.12 grams of potassium per liter were made up. The phosphorus content was in a ratio of 2 to 48 to the potassium content.

The second group was a duplicate of the first group except for the addition of iron in a concentration equal to that of phosphorus. Since iron was added in the form of ferrous ammonium sulfate which has a tendency to precipitate calcium, special attention was given to the order of addition. The ferrous ammonium sulfate, potassium acid phosphate and potassium chloride were all dissolved separately, the first two combined and slowly added to the third. This combined mixture, 9% acid, was diluted with a calcium-magnesium base containing no acid.

For the third group enough potassium chloride to yield 30 grams of potassium per liter was dissolved in the sodium-ammonium chloride base. Dilutions with the base were made giving a series containing 30, 25, 20, 17.5, 15, 12.5, 10 and 5 grams of potassium per liter.

A fourth group was prepared for those samples in

which the potassium content was low and a greater amount of the substance was necessary. Potassium chloride was dissolved in 9% acid to give 25 grams of potassium per liter. Dilutions were made to yield 20, 15, 12.5, 10, 7.5, and 5 grams of potassium per liter.

Phosphorus and Iron Standards. In addition to the phosphorus and iron standards combined with potassium another series was prepared in the sodium-ammonium chloride base. The iron concentration was 1, 0.5, 0.25, 0.1, 0.05, 0.025, 0.01, 0.005 and 0.0025 grams per liter. The phosphorus content was double that of iron.

Preparation of samples. When ash samples were to be analyzed, 0.05 gram samples were weighed out and treated with 1 milliliter of concentrated hydrochloric acid. This was allowed to stand for an hour; a base of sodium-ammonium chloride solution was then added to a total of 10 milliliters so that the resulting concentration was 5 grams of ash in 4.5% acid, containing 5 grams sodium chloride and 45 grams of ammonium chloride per liter.

Samples for potassium analysis were similarly prepared, but contained 20 grams of ash per liter.

A synthetic ash was prepared for analysis by dissolving the salts in a 4.5% acid solution so that the resulting concentrations were: 0.7 grams of calcium, 0.4 grams of magnesium, 0.01 grams of manganese, 0.15 grams of phosphorus, 0.05 grams of iron and 14 grams of potassium per liter.

Conditions of Exposure. Eastman "33" commercial plates were used for all analyses except those in which iron interfered with potassium. Wratten - Wainwright Process Panchromatic plates gave satisfactory results in this case. The "33" plates were chosen because their characteristics were suitable for the particular conditions required for such analyses. Both types of plates were developed in Eastman developer formula D-11 for five minutes at 18°.

The method of "continuous exposure" extensively employed by this laboratory for some time was used to determine the behavior of the six substances upon volatilization. The plate was placed in readiness for exposure, the slit opened and the electrodes adjusted. Each fifteen seconds from the instant of arcing, the plate was moved rapidly, allowing the arc to burn continuously for four or five minutes. In this manner the comparative amounts of each substance volatilized

in any fifteen second interval could be determined as well as the time required for the volatilization of each to proceed to a point where no effect was shown on the photographic plate under the conditions of exposure employed.

From the data obtained on such a plate the time for exposure of each substance was found. The amount of light used was also found experimentally. Enough light was used so that the heaviest lines to be used for analysis were well under maximum blackening. In this blackening way a gradation of line densities was obtained for the lower concentrations. The amount of light reaching the slit was regulated by the adjustable revolving sector. The following table shows the conditions of exposure used for each substance when a current of ten amperes was carefully maintained.

TABLE I

Substance	Seconds Time	% Light	Sector
Potassium in 9% acid in NH ₄ -Na base in Ca-Mg base	40 40 60	5 5 6.25	1/10 1/10 1/8
Iron and Phosphorus in NH ₄ -Na base in Ca-Mg base	60 90	5 6.25	1/10 1/8
Iron (alone)	60	2	1/25
Magnesium	40	3.125	1/16
Manganese	40	2	1/25
Calcium	40	1.625	1/32

Slight variations were made when only the higher or lower concentrations of a series were used.

Evaluation of Plate Densities. The densities of the proper lines from the various analyses were read on the density comparator. Only plates free of fogging were used; any which were slightly fogged or not entirely clear were discarded. A reading for blackness when no light entered the slit was taken first. Each line was read independently until an accurate check was obtained. The plate was then moved to a clear background in the same region. This reading was recorded as the "background". The differences between the density of the line and absolute blackness and also between the background and absolute blackness were calculated. The ratios of these differences wereplotted against the logarithms of concentrations to obtain the working curve or "standard curve", the method of Tyman and Hitchen line blackening previously cited. The density ratios for the unknowns were located on the standard curve and the corresponding concentrations read directly from the curve. NO attempt was made to calibrate the plates as the standard curve and unknowns to be determined were all placed on one plate. Duplicate plates were made to check results.

Results

"Continuous Exposure." The behavior of each of the six substances upon volatilization was individual.

Potassium, although present in the largest amount, volatilized most rapidly and disappeared in forty-five seconds.

Phosphorus also volatilized to an extent that no effect could be observed on a photographic plate. It was unique in behavior, volatilization beginning slowly, gradually increasing to a peak and then slowly decreasing. About two minutes were required, although the bulk of it vaporized in sixty seconds, the time of exposure used for analysis.

Manganese volatilized very rapidly at first, most of it disappearing in forty-five seconds. A faint trace remained for forty-five to sixty seconds longer.

Magnesium did not volatilize completely. As in the case of manganese, forty-five seconds were sufficient for the greater portion to burn out. After that time the amount volatilized in each interval gradually decreased and finally reached a constant.

Calcium acted somewhat similar to magnesium, except that it behaved very erratically when only a trace remaind.

Iron was found to be the most persistent of any of the six substances under investigation. However, very consistent results were obtained when sixty second exposures were used.

Figure 1 shows graphically how the substances compare in speed of volatilization and in the amounts of each volatilized in any time interval. Line densities are plotted as ordinates against time intervals as abscissae. Potassium has the steepest slope; magnesium.



3.	Iron - 3020.65 A		4. N	anganese	-	2576.12	A
5.	Calcium - 3158.87	A	6. F	otassium	-	3447.38	٨

manganese and iron behave somewhat alike; calcium shows a slower rate of volatilization; and the erratic behavior of phosphorus is very evident.

Suitable Lines for Analysis. Very few "raies ultimes" are suitable for use in quantitative analysis using the method of arc excitation as they show maximum blackening in comparatively low concentrations. A line used effectively must show two characteristics: first. it must be persistent even in very low concentrations: and second, it must show a definite change in line blackening density for a small change in concentration. Lines which fulfill these requirements give very satisfactory standard curves over a short range of concentrations. Many lines of each substance were investigated and those selected which were found to be most satisfactory under the conditions of excitation and exposure employed. They are as follows:

> Potassium 3446.37 and 3447.38 A° Magnesium 2776.71 and 2779.85 A° Calcium 3158.87 and 3179.33 A° Iron 2598.08 and 2599.40 A° Phosphorus 2536.38 A° Manganese 2576.12 and 2605.69 A°

In special cases other lines had to be employed. In the case of high iron content, the calcium line at $3179.33 \text{ A}^{\circ}$ was not satisfactory. For the same reason, the potassium lines mentioned above were unsatisfactory. In that case the potassium line at 5782.6 $\stackrel{\circ}{A}$ was employed. This necessitated the use of Wratten-Wainwright Process Panchromatic plates. For high concentrations of iron the doublet mentioned did not show satisfactory gradation and the unresolved doublet at 3021.08 and 3020.65 $\stackrel{\circ}{A}$ was used.

Table II shows a typical set of data from which the standard curve for potassium and the concentrations of the unknowns are obtained.

g/l of K	3446.37 Á	Background	Ratio
25 20 15 (1) unknown 12.5 10.0 7.5 5.0 (2) unknown	29.0 26.7 24.6 22.4 23.3 22.3 22.3 22.2 23.4 23.6	15.8 16.4 16.4 16.5 16.7 16.7 17.3 17.9 16.3	.35 .48 .59 .70 .66 .71 .74 .70 .63
Complete blackr	less: 36.2		

TABLE II

A sample calculation of ratios is shown below.

$$36.2 - 29.0 = 7.2$$
$$36.2 - 15.8 = 20.4$$
$$\frac{7.2}{20.4} = .3529$$

Figure 2 shows the standard curve for potassium plotted from the data given in Table II, and the determination of the concentrations of two unknowns.

Figure 3 gives typical standard curves for phosphorus, iron, manganese, magnesium and calcium, all plotted from experimental data.

Table III shows the results obtained by the application of these methods to the analysis of a synthetic ash of definite composition in grams per liter.





TABLE III.

Substance	Spectrographic	Chemical	% Erro r
Magnesium	0.370	0.400	7.5
	0.400	0.400	0
	0.390	0.400	2.5
Manganese	0.0112	0.0100	12.0
	0.0103	0.0100	3.0
	0.0099	0.0100	6.0
Phosphorus	0.148	0.150	1.3
	0.148	0.150	1.3
	0.153	0.150	2.0
Potassium	15.00	14.00	6.7
	14.25	14.00	1.7
	13.00	14.00	6.7
	14.00	14.00	0
Iron	0.048	0.05	4.0
	0.052	0.05	6.0
Calcium	0.68	0.7	3.0
	0.68	0.7	3.0

Figure 4 is taken from an analysis for phosphorus and iron. The phosphorus line 2536.38 \mathring{A} and the iron doublet 2598.08 and 2599.40 \mathring{A} are shown dotted. The gradations of both are apparent to the eye.

Figure 5 shows two analyses of a sample, one for magnesium and one for manganese. The magnesium group of five lines in the region of 2780 Å is marked and also three manganese lines in the region of 2600 Å.



FIGURE 5





Discussion

Variation of Line $\frac{Bkackening}{Densities}$ Due to Other Substances. In an article dealing with the analysis of solutions by means of the spectrograph by Duffendach, Wylie and Owens (Duffendach, Wylie and Owens, Ind. and Eng. Chem., Anal. Ed., 7, 410-413, (1935)) it was found that magnesium, calcium, sodium and potassium affected the relative intensity of the spectral lines of each of the other elements with regard to the spectral intensity of an internal standard. They also found that the addition of 2% sodium had the effect of eliminating further variations due to the other elements.

The effect of calcium, potassium and sodium on the blackening of magnesium was measured and found to be well within the range of experimental error for the conditions of exposure employed. The addition of sodium chloride in the base material would also eliminate slight variations due to small amounts of other substances.

No attempt was made to remove any substance from the ash before analyzing for the six substances determined. As shown by the graph resulting from a continuous exposure, all substances were vaporized concurrently.

Phosphorus. The possible exception to the general rate of volatilization is phosphorus. However, an increase in the time of exposure compensated for the difference in rate. The fact that 0.148 of the 0.150 grams of phosphorus in the synthetic ash were regained by this method points to its feasibility. The error was only 1.3%. However, the range within which phosphorus can be determined is limited. No attempt to show it in less than 0.01 gram per liter was successful. In cases where the phosphorus content was low, the sample was not diluted as much. Even in instances where phosphorus was not at first shown to be present, a concentration of the ash solution yielded a positive phosphorus determination. The solutions for phosphorus vielded a very satisfactory standard curve between the limits of 0.01 and 10 grams per liter, making determinations of unknowns with a high degree of accuracy. There were no lines of any substances used or impurities occurring in the region of the phosphorus line, namely 2536.38 Å and no background to interfere. The line was easily read on the density comparator and gave a smooth curve when plotted.

Iron. Iron had the advantage of having a number of lines which showed a definite gradation of line blackening, density, yielding satisfactory standard curves. The

unresolved doublet at 3020.65 and 3021.08 Å gave a usable curve for concentrations of iron from 0.05 up to 20 grams per liter. This doublet would be more effective on an instrument with higher resolving power. The pair at 2598.38 and 2599.40 Å are the most satisfactory over a long range. From a range of 2 gram per liter down to as low as 0.0005 grams per liter, a standard curve can be made. However, it has less change blackness in density for a small change in concentration than does the doublet at about 3020 \AA . When only iron is being determined, the latter is to be preferred except in extremely low concentrations. In conjunction with phosphorus, the pair at 2598.38 and 2599.4 Å were most extensively used. They occur in a region clear of background, free of interfering lines and are brought out satisfactorily under the same conditions used for phosphorus. It is well, however, in a series of analyses to use the same line throughout. An accuracy of 6% was found in the case of iron in a concentration of 0.05 grams per liter.

Manganese. Two lines, mainly 2576.12 and 2605.69 Å give standard curves for manganese over a range of 0.001 to 5.0 grams per liter by varying the amount of light. In the case of an analyzed synthetic ash containing 0.01 grams per liter, the error was estimated at

5 to 10%. As the manganese was found to contain a small amount of iron, the error was not extreme. The curve for manganese was very smooth, giving both the shoulder and toe of the curve as well as the straight portion. Determinations of higher concentrations are more easily made, being on a straight part of the curve.

Magnesium. Magnesium was the easiest to analyze of any of the six substances. The curves obtained from the lines at 2776.71 and 2779.85 Å more nearly resembled Hurter and Driffield curves than any of the others handled. Over the comparatively short range of 0.01 to 1.0 gram per liter a complete curve was obtained by proper exposure. Results on magnesium showed also, the smallest percentage of error. In a group of five analyses, the average error was 3%. Magnesium may be determined very satisfactorily in a range of 5.0 down to 0.001 grams per liter. Also, it is probably the most accurate of the six analyses.

Potassium. The most difficult to obtain successfully by the method employed was potassium. Many different errors enter into such a determination. In the first place, the range is very limited. Gradation of line densities may be obtained only between 1.0 and 50 grams per liter, and only with great difficulty under

5 grams per liter. The sample must be heavy in potassium to be analyzed at all; this is scarcely feasible in most cases, as the advantage of the general method is to utilize very small samples.

Iron in any concentration greater than 0.1 grams per liter interferes with the unresolved doublet at 3446.37 and 3447.38 Å making the employment of these lines for analysis impossible. An attempt to cut down on the exposure and use the pair at 4044.16 and 4047.22 Å was only partially successful. Potassium lines are accompanied by a continuous background in the same region greatly increasing the background reading, resulting in very small ratios much less mensitive than for other substances. Another line obtainable on special red-sensitive plates, 5782.6 Å, can be used between limits for approximations but has too much continuous background to be used for formulating a standard curve.

The standard curve obtained for potassium using 3447.38 \AA in a range of concentrations from 5 to 30 grams per liter is very easily obtained and satisfactory for concentrations within that range when iron is absent or present in an amount less than 0.05 gram per liter. A spectrograph giving a greater resolution of

the doublet, thus freeing it from interference by iron, would yield very satisfactory results.

Results obtained on four samples of potassium containing less than 0.05 grams of iron per liter, and known to contain 14 grams of potassium, gave the results of 15.0, 14.25, 13.0 and 14.0 grams per liter, an average of about 5% error.

Calcium. Calcium is present in an appreciable amount in most graphite rods ordinarily used for analysis. It was necessary for consistent and reliable results to use very pure carbons. Calcium gives a standard curve with a slope nearly horizontal. Although a series of standard solutions give a smooth curve, blackness there is very little change in density for a large change in concentration, due to the extreme persistence of calcium even in very minute amounts. Thus the determination of unknowns is much less accurate for calcium than, for example, magnesium. Only two lines of calcium were found to yield satisfactory standard curves; 3158.87 and 3179.33 $\overset{\circ}{\mathtt{A}}$. Between the concentrations of 0.001 and 5 grams per liter, smooth standard curves were obtained and successful determinations made. However, the percent error was higher for calcium than for magnesium, manganese, iron or phosphorus, particu-

larly when the concentration of the unknown was very low.

Actual applications of the methods just discussed were made in the analyses of plant ash tissues for the Botany department under the direction of Dr. R. P. Hibbard. The results will appear in a forthcoming publication of that department.

Summary

Calcium, magnesium, manganese, potassium, phosphorus and iron may be determined in a solution of their salts by means of the spectrograph by the methods just described. Under the conditions of exposure and arcing used, a definite range of concentrations for each element was found satisfactory; they are:

(1) For calcium, 0.001 to 5 grams per liter.

(2) For potassium, 1 to 50 grams per liter.

(3) For iron, 0.0005 to 2 grams per liter.

(4) For magnesium, 0.001 to 5 grams per liter.

(5) For manganese, 0.001 to 5 grams per liter.

(6) For phosphorus, 0.01 to 10 grams per liter.

Lines satisfactory for the analysis of the ranges just mentioned under the conditions of exposure employed are as follows:

Calcium	3158.87	and	3179.33	° A
Potassium	3446.37	and	3447.38	° A
Iron	2598.08	and	2599.40	° A
Magnesium	2776.71	and	2779.85	Å
Manganese	2576.12	and	2605.69	Å
Phosphorus	2536.38	Å		

II

Spectrographic Determination of Zinc, Cadmium, Copper and Iron in Concentrated Nickel Sulfate Solutions.

Introduction

It has been found that small amounts of zinc, cadmium, copper and iron materially affect the physical properties of nickel when electrolytically deposited from sulfate solution. Ordinary chemical methods of analysis for these metals when present in amounts of a few milligrams per liter of solution are difficult, tedious and not very accurate. The spectrographic method is very rapid and accurate even for these exceedingly small amounts.

In the procedure followed in this investigation the solutions are placed in hollow graphite electrodes, arced and the spectra photographed. The density of the lines of the metal to be determined is compared with the density of the corresponding lines made by the standard solutions and the results rapidly interpreted.

Preparation of Materials

All substances used in the determinations were first analyzed spectrographically for traces of the metals to be determined and were found to be sufficiently free of contamination.

Sufficient zinc sulfate to make a solution containing one gram of zinc per liter was dissolved in distilled water. To 70 milliliters of this solution were added 30 grams of nickelous sulfate and the resulting solution made up to 100 milliliters volumetrically. Similarly, other solutions were prepared so that the final range of concentrations was 700, 350, 300, 250, 200, 150, 100 and 50 milligrams of zinc per liter of solution containing also 62.7 grams of nickel.

A stock solution of nickel sulfate giving a concentration of 62.7 grams of nickel per liter was prepared with distilled water. Another solution containing enough cadmium sulfate to yield 1400 milligrams per liter of cadmium was also prepared. From these two stock solutions a series of dilutions was made yielding a final range of 1400, 700, 350, 200 and 50 milligrams per liter of cadmium in a solution of nickel sulfate containing 62.7 grams of nickel per liter.

Enough copper sulfate to yield 200 milligrams of copper per liter was dissolved in 100 milliliters of the stock solution of nickel sulfate. To 10 milliliters of this solution were added 90 milliliters of the nickel solution yielding one containing 20 milligrams per liter of copper. Similarly, one was prepared containing 2 milligrams of copper per liter.

In exactly the same manner, using ferrous ammonium sulfate, three solutions containing 200, 20 and 2 milligrams of iron per liter were prepared.

Re-graphitized Acheson graphite rods were cut into convenient lengths for arcing. One half were drilled at one end to make craters for the solution; the other half were filed wedge shaped.

One tenth milliliter portions of the solutions were pipetted into the pre-ignited craters while the carbons were still warm. After being thoroughly dried in an electric oven at 100 they were ready for arcing.

Procedure

Eastman "33" plates were used on a medium quartz spectrograph giving a nine inch dispersion covering wave lengths from approximately 2100 to 5000 angstrom units.

The electrodes containing the solutions were made the anodes and were arced using 300 volts D.C.

The length of the exposure depended upon the metal to be determined. In the case of zinc, one minute exposures were made at nine amperes. The light from the arc was cut down to 1 percent by a rotating sector after passing through a lens. Metallic zinc was flashed on to give the R.U. lines for quick identification. One minute exposures of each zinc sample were made, beginning with the greater concentration and ending with nickel solution free of zinc.

The method of determining the amount of zinc in commercial baths consists of exposing three known concentrations of zinc in nickel; one of a concentration just equal to the "safety" point, one greater and one less. The spectrum of the sample to be analyzed is placed between these spectral standards using as nearly as possible the same conditions of blackenings exposure. By a comparison of line densities the unknown can be very rapidly determined as falling between definite limits.

In the case of cadmium the same procedure may be employed except that the length of exposure may be shortened to forty-five seconds as cadmium volatilizes more rapidly. Solutions containing 1400, 700, 350, 200 and 50 milligrams of cadmium per liter were used.

Neither iron nor copper will vaporize to the point of not affecting a photographic plate and thus the method for their determination depends entirely upon uniform exposure. Thirty seconds are sufficient for copper. Iron requires a slightly longer time. Very small amounts of both are readily discernible in nickel solutions.

Although the gradations of varying amounts of these metals are apparent to the eye, precision measures blackening were made of the densities of the lines with the density comparator.

Readings on both lines and backgrounds were repeated until satisfactory checks were obtained. A reading of the galvanometer when no light reached the cell was also taken and termed the "zero" reading. The difference of both the line and background readings from zero were calculated. The ratios of these differences were plotted as ordinates against the logarithms of the concentrations as abscissae. The resulting curve resembles an Hurter and Driffield curve closely, and is termed the standard curve.

Tabulation of Data

Typical sets of readings and calculated ratios for the standard curves of zinc and cadmium are shown in the following tables.

TABLE I

mg	Zinc line	Zinc line	Back	Rat	ios
Zn/l	3302.6 Å	3345.0 Å	Ground	3302.6 Å	3325.0 Å
700	26.4	28.5	20.7	.61	. 47
350	25.6	27.6	20.3	.65	. 52
300	25.7	27.8	20.8	.67	. 52
250	25.0	27.1	20.7	.73	. 57
200	24.4	26.8	20.5	.74	. 58
150	23.5	25.8	20.0	.77	. 63
100	21.6	24.2	19.9	.89	. 72
50	21.7	23.9	21.0	.95	. 80
Complet	te blackness	: 35.5			

ZINC IN NICKEL SULFATE SOLUTION

TABLE II

mg Cd/1	Line 3261.05 Å	Back Ground	Ratio	Line 4799.91 Å	Back Ground	Ratio
1400 700 350 200 50	30.9 30.4 30.0 28.8 26.6	19.4 19.5 19.3 18.3 18.8	. 29 . 32 . 34 . 39 . 53	30.5 29.4 26.4 24.0 22.7	21.5 21.5 21.6 20.4 20.4	. 36 . 37 .65 . 76 . 85
Comple	te blackne	ss: 35.5				

CADMIUM IN NICKEL SULFATE SOLUTION

The density comparator gives very sensitive and accurate measurements not apparent to the eye. For all accurate quantitative work it should be used, but for control work, that is to say, between definite limits, the line densities do not need to be measured. Care must be taken not to reach the point of complete blackening of the lines or the differences in density due to change in concentration are not apparent.

Figure 1 shows four typical curves obtained by (inc blackening) plotting ratios of densities against the logarithms of concentration; (1) and (2) are for zinc and (3) and (4) are for cadmium. The two curves for zinc are very nearly parallel, the line of the greater intensity lying above the lighter line.



Logarithms of Concentration

FI	GURE 1.	STANDARD	CURVES			
1.	Zinc -	3302.6 🛦	2.	Zinc -	3325.0 A	
3.	Cadmium	n - 3261.09	5 🛦 4.	Cadmiun	n - 4799.91	

The two cadmium lines shown are from different regions of the spectrum. The one above (3261.05 \mathring{A}) is very nearly maximum blackening and gives only the upper part of the standard curve. The lower line (4799.91 \mathring{A}) gives a typical curve for correct exposure.

Figure 2 is a print of the plate from which readings on the density comparator were made and recorded in Table I. The two used in preparing the standard curves are shown dotted on the plate. A peculiar phenomenon was observed on this plate. A line just to the right of 3302.60 Å appeared to increase in intensity as the zinc line decreased. However, upon measuring it on the density comparator, it was found to be constant and merely an optical illusion. The line was identified as an iron line, 3305.978 Å, iron occurring as an impurity in the zinc.

Figure 3 shows the plate from which lines of cadmium were selected to make the standard curves shown in figure 1. The two lines of cadmium marked are 3261.05 and 4799.91 Å.

Figure 4 shows how iron may be detected in nickel in very small amounts. The doublet 2598.377 and 2599.4 Å was found to be most satisfactory for very







small emounts of iron. The upper spectrum represents 200 milligrams per liter, the second 20 milligrams per liter and the third 2 milligrams per liter. The last one is pure nickel.

Copper analyses were made in the same manner as those for iron.

Although the methods were worked out using a medium quartz spectrograph, it has been adapted in this laboratory to the use of an instrument of less dispersion. The results will be set forth in a forthcoming publication.

Summary

Very small amounts of zinc, cadmium, iron and copper in nickel sulfate solutions were readily determined by spectrographic methods using solutions in graphite electrodes.

Lines of each substance were selected which showed definite gradations of density for small changes in concentration, and which were persistent in very low concentrations. Such lines are: zinc, 3302.60 and 3345.60 Å; cadmium, 3261.05, 4799.91 and 2763.9 Å; iron, 2598.36 and 2599.39 Å; and copper, 3273.96 Å.