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POLAROGRAPHIC STUDIES OF
METALLIC IMPURITIES IN NICKEL
SULFATE SOLUTION

Thesis for the Degree of M. S.
MICHIGAN STATE COLLEGE
Clyde B. Anderson
1941

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POLAROGRAPHIC STUDIES OF METALLIC IMPURITIES
IN NICKEL SULFATE SOLUTION

by
Clyde B. ^{Anderson} Anderson

A THESIS

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INTRODUCTION

The polarographic method of analysis developed by Heyrovsky has been brought into prominence in this country largely due to the work of men like Kolthoff and Lingane.⁽¹⁾ Lingane and Kerlinger⁽⁷⁾ have applied this method to the determination of nickel in alloys. Others such as Muller⁽³⁾ have worked with organic compounds. Recently Lingane and Davis⁽⁶⁾ have determined Vitamin B complexes by the use of the polarograph. This instrument is still being applied in various new fields.

DESCRIPTION OF APPARATUS

The simplified wiring diagram helps explain the method and principles of polarographic analysis. The electrolysis cell containing the solution to be analyzed is denoted by D in the diagram. The cell consists of a dropping mercury electrode as the cathode. This electrode must deliver small drops of mercury at the rate of one drop in every three to four seconds. The tip of this electrode is placed beneath the surface of the solution being analyzed. Two nitrogen inlets are shown. The first inlet N_1 is used to bubble the nitrogen through the solution. This is necessary since the dissolved oxygen would be reduced at the dropping mercury cathode during the analysis, giving troublesome maxima. The second inlet N_2 is used during the actual run. This insures the exclusion of oxygen during the run and also allows the solution to be quiet. An undisturbed solution

is essential since galvanometer readings are affected by disturbances or jarring. The layer of mercury at the bottom of the cell serves as the anode.

This mercury anode is connected to the wire wound cylinder at B by means of a movable disk. Standard resistance wire is wound on the cylinder. If the total voltage of the battery is three volts and if thirty turns of standard resistance wire on the cylinder are just equal to three volts, then each turn would correspond to 0.1 volt. The cylinder is essentially a potentiometric bridge.

By this cylinder arrangement, the applied E.M.F. is increased gradually and uniformly by means of the synchronous motor A. This increasing voltage is synchronized with the moving chart paper. One revolution of the cylinder B, as previously stated, is equal to 0.1 volt, and, by the proper gear ratio, is also made equal to one division of the chart paper. This makes possible an exact knowledge of the applied E.M.F. at any time.

The current passes through a galvanometer whose deflections are mechanically amplified T and transmitted to the inking pen by the automatic recorder R. The displacement of the inking pen is directly proportional to the amount of current flowing. The total range of the recorder varies from two to one hundred microamperes. The recorder range or sensitivity of the system is regulated by varying the shunt resistance S. The larger the shunt resistance, the more sensitive is the system; i.e., a larger fraction of the current is forced through the recorder galvanometer.

Current voltage curves are simply the curves obtained by gradually increasing the applied E.M.F. and noting the current corresponding to each E.M.F. applied. As shown by the diagram, the Leeds-Northrup electro-chemograph makes a permanent record of the current-voltage curve at the time of the analysis. Manually operated polarographic systems can also be used to obtain these curves, which would then consist of a series of points rather than a continuous curve.

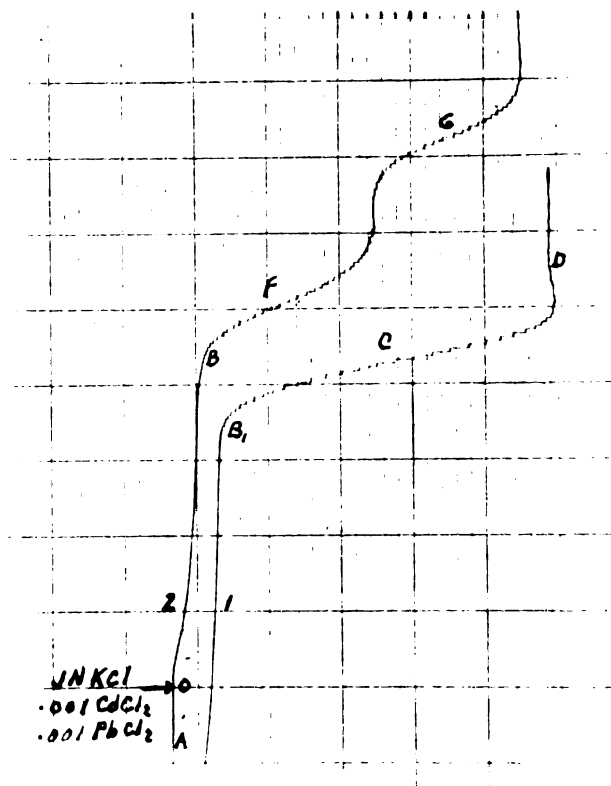


Fig. 1

In this polarogram, curve 1, the applied E.M.F. volts are plotted on the ordinate and the corresponding current on the abscissa. This solution is .002N cadmium

chloride in 0.1N potassium chloride. When the line denoted by A traces a straight line on the ordinate of the graph paper, this is a check that shows the electrical balances have been correctly made. The polarizer was snapped on at point O and the curve started. At first only a small current flowed through the cell and was carried by the potassium chloride. When the decomposition potential of cadmium B was reached, continuous electrolysis began. The cadmium ions were discharged or "plated off" on the cathodic drops of mercury, forming a dilute cadmium amalgam. After the decomposition potential was slightly exceeded, the current carried by the indifferent salt and the cadmium reached a limiting value and became constant. This difference between this limiting current D and the current just before the decomposition potential is reached is directly proportional to the concentration of the reducible substance. This is the basis of quantitative polarography.

The limiting current is often called a diffusion current. Lingane⁽¹⁾ states that "when an indifferent electrolyte is used the current is practically entirely carried by the indifferent ions and the electrical forces on the reducible ions is nullified. Under the^{se} conditions the reducible ions reach the electrical surface only by diffusion and hence the limiting current is called a diffusion current." After the limiting current is reached the cadmium ions are reduced as fast as they reach the mercury drop by diffusion, and the effect is then a constant effect.

The identifying parts of curve 1 are first the decomposition potential B. This is characteristic for each element and for cadmium in this solution it is $-.64$ volts. Many workers use the half-wave potential C rather than the decomposition potential as the identifying method.

The half wave potential is less affected by such factors as the capillary used and the drop time⁽¹⁾. The half wave potential as used throughout this thesis is the value of the applied E.M.F. of the dropping mercury electrode at that point on the current voltage curve where the current is one half of its limiting value.

Curve 2 shows the simultaneous determination of $.001N$ lead chloride and $.001N$ cadmium chloride in $0.1N$ potassium chloride. The first diffusion current F is for the lead ions and the second diffusion current G is for the cadmium ions. The decomposition potential of cadmium is the same in each case. The diffusion current G is half that shown in curve 1. This is in direct agreement with their concentrations.

PROCEDURE

The general procedure for the run for the .002N cadmium chloride solution is as follows. The electrical balances are made as specified by the Leeds-Northup Co. Enough mercury was poured into the electrolyzing cell to form a layer at the bottom. A measured volume of the cadmium chloride solution was pipetted into the cell. Next nitrogen was bubbled through the solution by inlet 1 as shown on the diagram for a period of 10 minutes. The incoming nitrogen was changed to inlet 2 and the first inlet stoppered. The dropping electrode was next introduced, its tip being placed 3 mm. below the surface of the solution. The cell was then connected to the electrical system and allowed to come to equilibrium over a period of five minutes. During this time the drop rate of the mercury electrode was checked. The drop rate must be between three and four seconds as the time per drop. After this check the polarizing unit was snapped on and the resulting current-voltage curve obtained. At the completion of the analysis the polarizing unit was snapped off, the outside glass of dropping mercury electrode was cleaned. Then the tip was immersed in pure mercury and thus kept free from contamination until the next analysis.

PREPARATION OF MATERIALS

The mercury was purified according to the following procedure. Very fine drops of mercury from the capillary stem of a funnel reservoir were allowed to fall through

a glass tube 150 cms in length that contained a 40% nitric acid solution. Next the mercury was electrolyzed with mercury as the anode. A 4% nitric acid solution was used with a current density of two amperes per square decimeter for a period of twelve to sixteen hours. After electrolysis, the mercury was dried and distilled under vacuum.

The nitrogen used was taken from a commercial nitrogen pressure tank. This nitrogen was bubbled through two separate flasks each containing alkaline pyrogalllic acid to remove oxygen. Then the gas was bubbled through a flask containing water to remove the vapors of pyrogalllic acid. From this flask the nitrogen was introduced into the electrolyzing cell.

DETERMINATION OF METALLIC IONS IN NICKEL SULFATE

The nickel sulfate solution used throughout the research was made by dissolving 479.3 grams of nickel sulfate in two liters of water. This is equivalent to two pounds of nickel sulfate per gallon and is the concentration often used in plating solutions. Sulfate solutions are commonly used in the determination of cadmium.

Cadmium was the first ion tried in the nickel sulfate solution. Excellent current-voltage curves were obtained as shown by Fig. 2. The amount of cadmium or of any other metallic ion will be expressed in mg. per liter throughout this thesis.

For cadmium the simple conversion was made:

$$\frac{\text{At. Wt. Cd (112.41)}}{\text{Mol. Wt. CdCl}_2 \cdot 2\text{H}_2\text{O (219.4)}} \times \frac{877.6}{\text{Wt. CdCl}_2 \cdot 2\text{H}_2\text{O mg per liter}} = \frac{449.6}{\text{mg Cd per liter}}$$

Cadmium at the above concentration was added to nickel sulfate solutions at various pH's. The nickel sulfate solutions of pH 1.22 and 2.85 were acidified by the addition of C.P. hydrochloric acid. The nickel sulfate solution of pH 6.70 was obtained by the addition of 0.125N sodium hydroxide drop by drop using a mechanical stirrer. The pH 6.70 was considered as the upper limit since above this pH nickel precipitated in appreciable amounts.

The diffusion current of cadmium at the same concentration was the same regardless of the acidity as shown by curves f or these three pH's.

The diffusion current at each pH was directly proportional to the amount of cadmium present over the range of 12 to 450 mg of cadmium per liter. Current voltage curves are shown in Fig. 2. Acidity had no definite effect on either the decomposition potential or the half-wave potential as shown by Table 1.

Table 1.

Decomposition Potential in Volts

Conc. Cd mg/liter	pH 1.22	pH 2.85	pH 6.70
449.6	-.65	-.65	-.64
228.8	-.65	-.69	-.66
114.4	-.66	-.69	-.66
57.2	-.68	-.68	-.66

Half-Wave Potential

Conc. Cd mg/liter	pH 1.22	pH 2.85	pH 6.70
449.6	-.76	-.76	-.76
228.8	-.74	-.78	-.74
114.4	-.73	-.74	-.73
57.2	-.72	-.73	-.72

Drop time: 3.2 seconds

Shunt Resistance: 50,000 and 22,222 ohms

Range: 0 to -3 volts

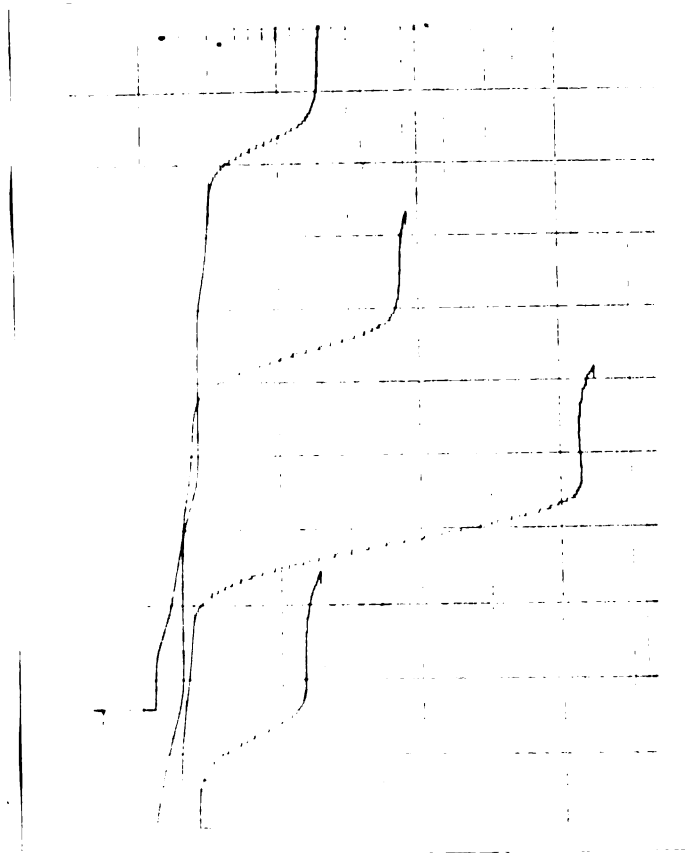


Fig. 2

Stannous sulfate was next added to the nickel sulfate solution at the rate of 473 mg of tin per liter. The curves obtained as shown by Fig. 3 were not satisfactory. The solution containing the stannous sulfate clearly showed increasing amounts of precipitate upon standing. This was also evident in the current-voltage curves since the amount of stannous ion shown was much less than the 1:1 dilution used.

The difficulty in the determination of stannous sulfate in the nickel sulfate solution was overcome by the use of an acid solution of nickel sulfate (pH 2.21). Again 473 mg

of tin per liter were added as stannous chloride, using the same method as before the runs were made. The current-voltage curves Fig. 4 show the improvement in the determination of tin and also well-defined decomposition potentials on the curves. Tables 2 and 3 show the comparative results in each case.

Table 2

Stannous sulfate in nickel sulfate (pH 4.83)

Tin mg per liter	Diffusion current microamperes	Half-wave potential	Decomposition potential
473.0	.69	-.35	-.25
236.5	.31	-.36	-.28
118.2	.08	-.38	-.31
59.1	.04	-.45	-.40

Table 3

Stannous sulfate in nickel sulfate (pH 2.21)

473.0	1.30	-.44	-.29
236.5	.63	-.43	-.32
118.2	.28	-.39	-.31
59.1	.14	-.39	-.33

Drop time: 3.5 seconds
Shunt resistance 22,222 ohms
Range 0 to -3 volts

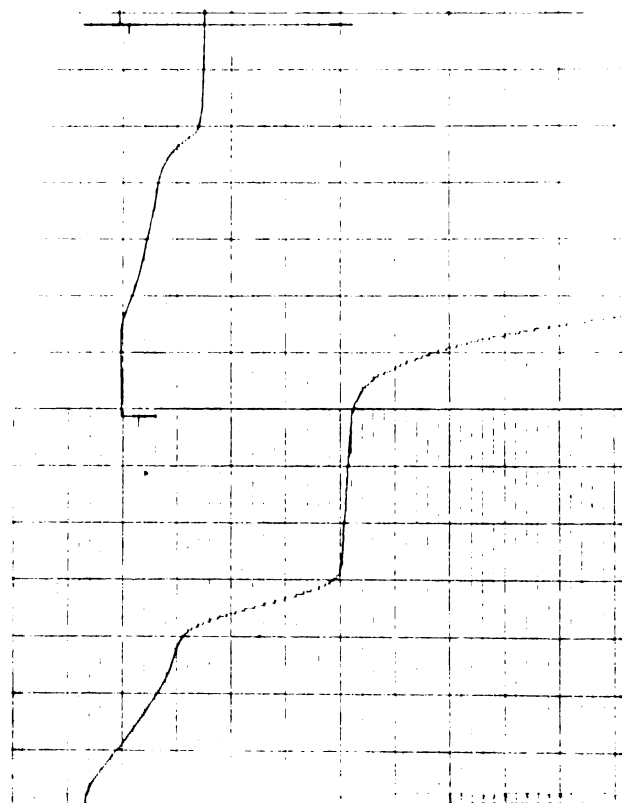


Fig. 3

Tin 236.5 mg/liter curve 1
Tin 118.2 mg/liter curve 2

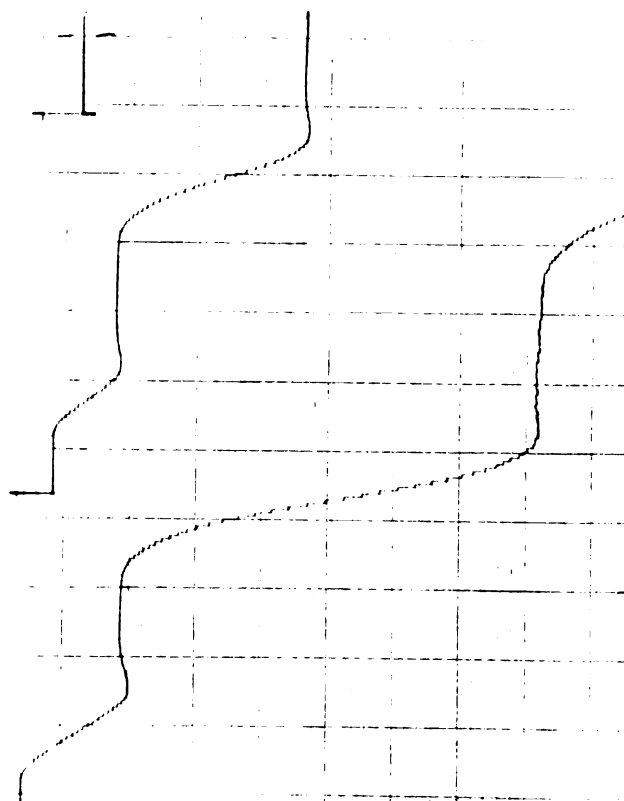


Fig. 4

Tin 236.5 mg/liter curve 1
tin 118.2 mg/liter curve 2

Copper was also determined in nickel sulfate solution. A known amount of cupric sulfate, .0499 grams per 100 milliliters, was added to the nickel sulfate solution. Again the conversion to mg of copper per liter was made.

The following table 4 shows the summary of results. In each case it was necessary to run a blank determination on the nickel sulfate solution due to the copper already present in the solution. The amount of copper as determined in the blank was then subtracted in each case.

This use of blanks could be very useful. In cases where the increase in the amount of copper present is important, the increase could be shown by polarographic determinations.

Likewise by adding a known amount of copper and noting the increase due to the copper added, the amount of copper originally present can be calculated. As starred on the table, 7.93 mg of copper has a diffusion current of .44 microamperes. Then .60 microamperes, diffusion current of the blank, would equal 10.80 mg. of copper per liter. This is the amount originally present.

As shown by table 4 and in spite of the presence of copper in the original solution, the amount of copper can be determined to 2 mg per liter. This is considerably lower than in the case of cadmium.

Cadmium and copper both have approximately the same "current carrying" ability but cadmium has the larger atomic weight which is the determining factor. Table 5 and Fig. 5 show the comparative result for cadmium and

copper in the same solution.

Table 4 Diffusion Current in Microamperes

Cu in Mg/liter	S 22,222	S 22,222 50,000	S 200,000	400,000
127.0	6.78	6.94		
63.5	3.40	3.30		
31.75	1.66	1.62		
15.87	1.20	.78	.92	.89
9.93			.44*	.43
3.96			.20	.21
1.98			.13	.10
.99			.01	.07
Blank	.58	.64	.60	.59

Table 5

Cu Mg/liter	Microamperes	Cadmium mg/liter	Microamperes
127.00	6.74	224.80	7.06
63.50	3.14	112.40	3.33
31.75	1.47	56.20	1.57
15.87	.62	28.10	.81

Drop time: 3.0 seconds

Range: 0 to -3 volts.

Shunt resistance for table 6: 22,222 ohms.

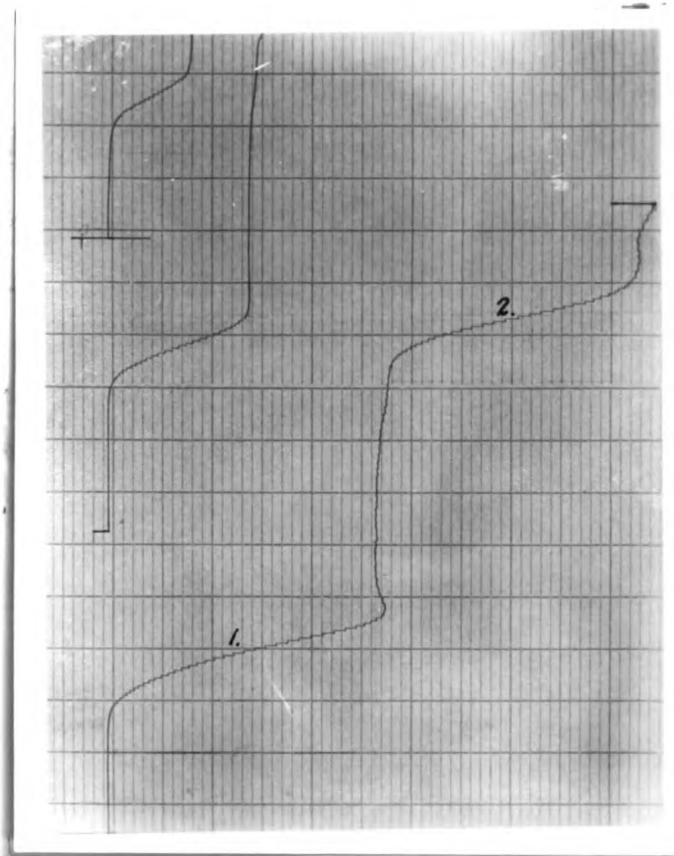


Fig. 5
Copper 127.8 mg/liter curve 1
Cadmium 224.8 mg/liter curve 2

Copper present alone in the nickel sulfate solution was also determined by the oxidation reaction. The dropping electrode was made the positive electrode and the range of +1 to -2 volts was used.

The range for the determination of copper by this method is very small. Large concentrations of copper changed the current reading of the system so much that at the zero applied E.M.F. the current reading was outside the range of the graph paper. Large external shunts had the same effect on analysis of the dilute copper solutions.

The same solutions were used as in the determination of copper by the reduction method. Again a blank was run

to determine the copper originally present and the the correction made.

Table 6

Copper mg per liter	Diffusion Current in Microamperes	Half-wave potential	Decomposition potential
31.75	2.44	+ .23	+ .31
16.89	1.20	+ .23	+ .31
7.56	.54*	+ .23	+ .30
Blank	.76*		

Drop time: 3.5 seconds
 Shunt Resistance: 22,222 ohms
 Range: +1 to -2 volts.

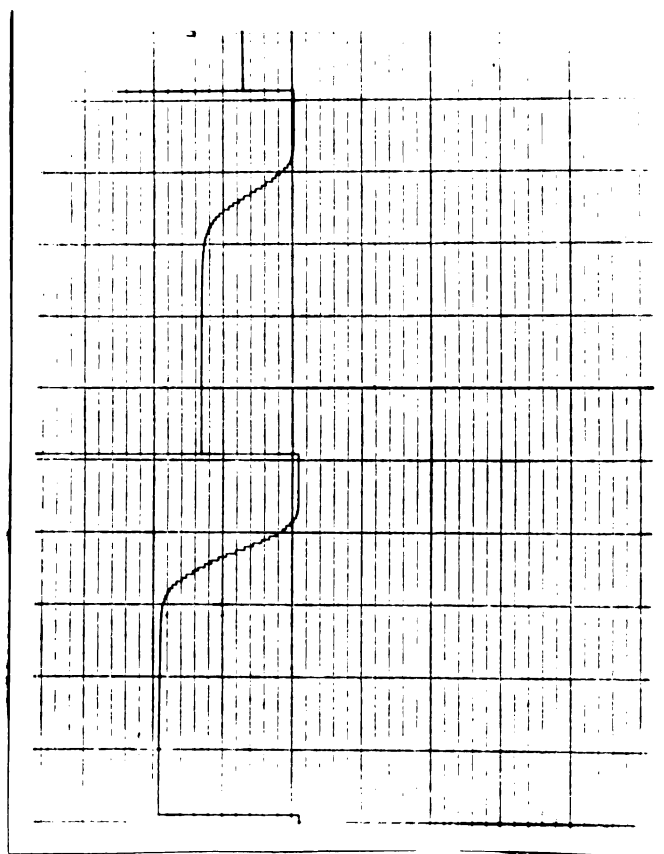


Fig. 6
 Copper 16.89 mg/liter curve 1
 Copper 7.56 mg/liter curve 2

By comparing table 6 with table 4, it is evident that the same number of mg of copper by the oxidation method results in a larger diffusion current. The constancy of the amount of copper present can again be shown by the calculation of the copper in the blank. By this method, using the starred value in the table and the blank, the amount of copper originally present will be 10.64 mg per liter. This is in excellent agreement with value 10.80 mg as found by the reduction method and well within the limit of accuracy of the electro-chemograph.

Iron was determined in the nickel sulfate solution in the form of the ferric ion. In order to prevent the precipitation of ferric ion as ferric hydroxide, the nickel sulfate solution was made strongly acid (pH 0.8) with C.P. sulfuric acid. To this acid solution 0.1 g of anhydrous ferric sulfate per 100 mls was added. The current-voltage curves were obtained in the usual manner. However 1:1 dilution was not used. The results are tabulated.

The maximum that is very marked for this ion was not suppressed by glue. The maximum is more pronounced with increasing concentration of the reducible ion.⁽¹⁾ Current voltage curves Fig. 7 show this effect. Heyrovsky attributes the maxima to an adsorption of the electroreducible ion on the drops of mercury.

Table 7.

Iron mg per liter	Diffusion current Microamperes		
	S 10,526	S 22,222	S 200,000
279.30	8.76	8.60	
139.65	4.52	4.34	
46.55		1.54	1.50
34.91		1.20	1.11
27.93		.86	.85

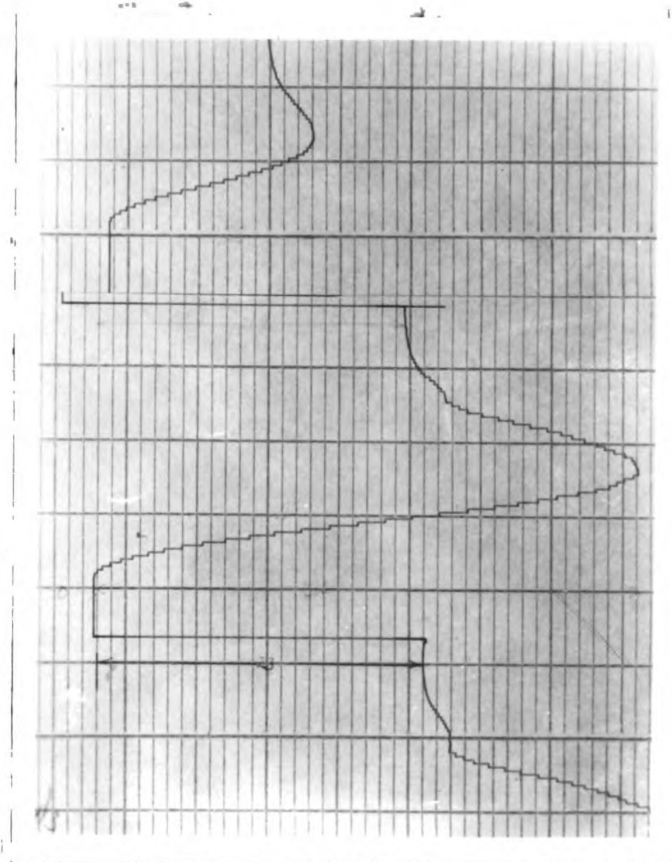


Fig. 7
 Iron 279.3 mg/liter curve 1
 Iron 139.6 mg/liter curve 2

DETERMINATION OF VITAMIN B COMPLEXES

The determination of vitamins is of the utmost importance. This undoubtedly resulted in Lingane's determination of the vitamin B complexes. Lingane found that riboflavin gave good polarographic waves and that its diffusion current was directly proportional to its concentration.⁽⁶⁾ The current-voltage curves that were made by the writer are similar to those of Lingane. The various modifications are specifically mentioned as such.

The vitamin B complexes used are the controlled products of Parke Davis Co. Thiamine hydrochloride was determined in 0.1 N potassium chloride. Weighed samples of 1 mg each were dissolved in a known amount of the indifferent salt solution. These sample weights were then converted into parts per million (ppm). This procedure was followed for each complex. Also dilution was 1:1.

The current-voltage curve Fig. 8 depicts the results for 200 and 100 ppm of thiamine hydrochloride. The following curve Fig. 9 shows the simultaneous determination of thiamine hydrochloride and riboflavin.

The reduction of the nicotinic acid when dissolved directly in 0.1 N potassium chloride did not appear on the current-voltage curve. However by the use of 0.1N sodium bicarbonate fairly good waves were obtained. The sodium bicarbonate solution neutralizes the nicotinic acid and also acts as a buffer.⁽⁶⁾ Lingane, by first neutralizing the nicotinic acid with sodium hydroxide, was able to obtain well-defined curves in 0.1N potassium chloride. By the

use of the bicarbonate, the nicotinic acid can be determined directly. These results are quantitative as shown by the current voltage curves Fig. 10 and by the Table 9.

Pyridoxine was found to be quite difficult to work with and obtain satisfactory results. Various supporting electrolytes were tried. The best results were obtained using potassium thiocyanate as the indifferent salt. In this solution, pyridoxine produced curves with pronounced maxima, Fig. 11. No satisfactory method for the suppression of the maxima was found. Methyl red was the best of the suppressors used. Glue was found to interfere with the diffusion current in the case of the vitamins and could not be used.

The results for the determination of pyridoxine are tabulated, Table 10.

Table 8 Thiamine Hydrochloride

ppm	Microamperes		Half Wave Potential		Decomposition Potential	
	S 22,222	S 50,000	S 22,222	S 50,000	S 22,222	S 50,000
200	3.78	3.83	-1.34	-1.35	-1.19	-1.15
100	1.80	1.87	-1.31	-1.34	-1.21	-1.18

Table 9 Nicotinic Acid

ppm	Microamperes		Half Wave Potential		Decomposition Potential	
	200,000	50,000	200,000	50,000	200,000	50,000
200	1.05	1.01	-1.78	-1.75	-1.66	-1.67
100	.53	.49	-1.75	-1.74	-1.67	-1.68
50	.24	.18	-1.74	-1.76	-1.67	-1.71

Table 10 Pyridoxine

ppm	Microamperes		Half Wave Potential		Decomposition Potential	
	50,000	10,526	50,000	10,526	50,000	10,526
181	4.02	3.64	-1.38	-1.36	-1.16	-1.25
95	2.06	1.76	-1.36	-1.35	-1.15	-1.27

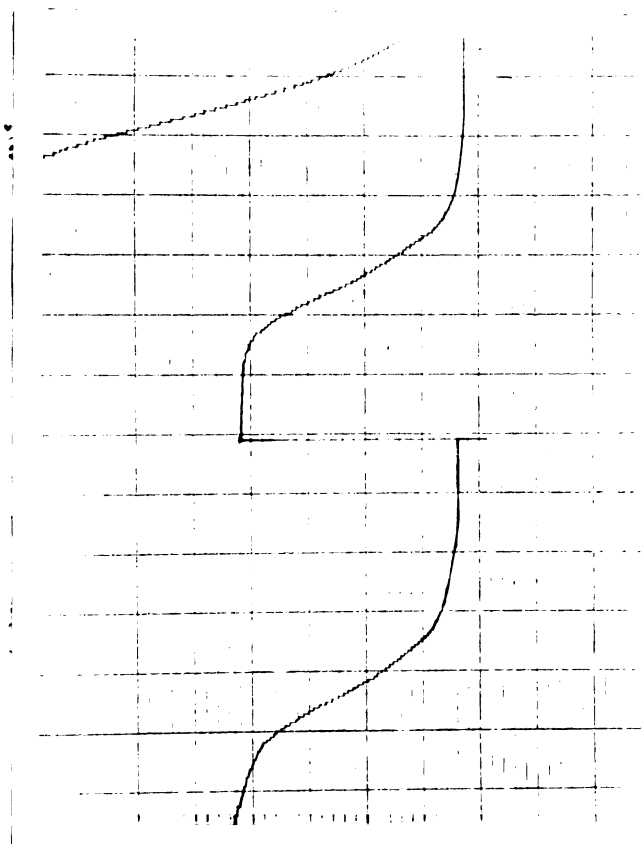


Fig. 8

Thiamine Hydrochloride 200 ppm, S 22,222, curve 1
 Thiamine Hydrochloride 100 ppm, S 50,000, curve 2

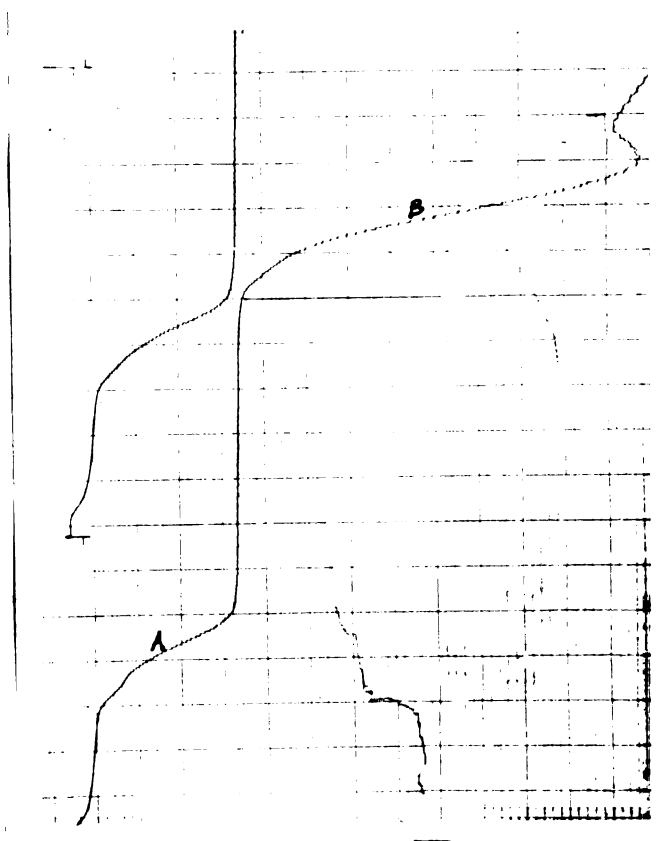


Fig. 9
 Riboflavin A
 and
 Thiamine Hydrochloride B

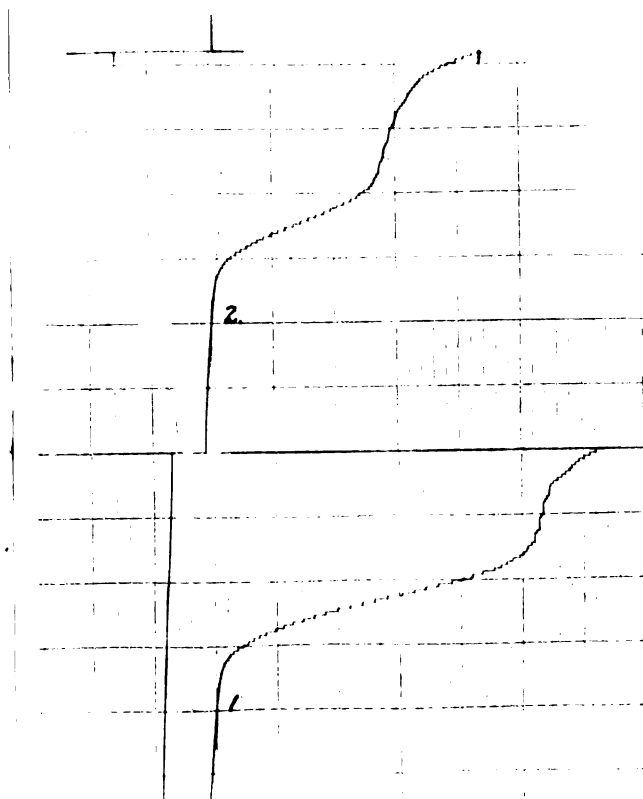


Fig. 10
 Nicotinic Acid 200 ppm curve 1
 Nicotinic Acid 100 ppm curve 2

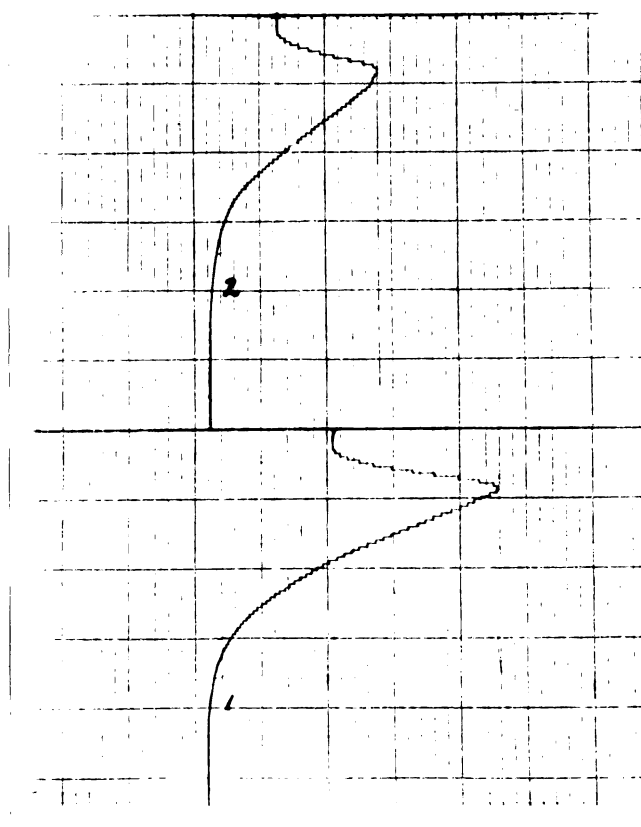


Fig. 11
 Curve 1:
 Pyridoxine 181 ppm
 Curve 2:
 Pyridoxine 95 ppm

SUMMARY

Cadmium, stannous, cupric, and ferric ions may be determined in nickel sulfate solution. Cadmium may be quantitatively determined at various pH's. The stannous and ferric ions must be determined in an acid solution. The cupric ion may be determined either by oxidation or by cathodic reduction. The latter is the more practical.

The vitamin B complexes can be determined polarographically. Thiamine hydrochloride and riboflavin can be determined separately or together in 0.1 N potassium chloride. Nicotinic acid can be determined directly in 0.1 N sodium bicarbonate. Pyridoxine can be determined directly in 0.1 N potassium thiocyanate. The simultaneous determination of these four complexes was not accomplished.

LITERATURE

- (1) Kolthoff and Lingane; Chemical Reviews, 24, 1 (1939)
- (2) Borchardt; J. Am. Chem. Soc., 59, 2171 (1937)
- (3) Muller; Chemical Reviews, 24, 95 (1939)
- (4) Adkins and Cox; J. Am. Chem. Soc., 60, 1151 (1938)
- (5) Lingane and Kerlinger; Ind. and Eng. Chem. Analytical Edition, 12, 750 (1940)
- (6) Lingane and Davis; J. Biol. Chem., 137, 567 (1941)
- (7) Lingane and Kerlinger; Ind. and Eng. Chem. Analytical Edition, 13, 77 (1941)
- (8) Lingane, J. Am. Chem. Soc., 61, 2099 (1939)

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