

monia, electrolyzed with concordant percentage results. Platinum was constantly sought for but not found. The anodes were regularly weighed before and after their use, but showed no loss. Copper was successfully separated from iron—the quantity of the former being twice that of the latter. The same occurred when the quantity of iron greatly exceeded that of the copper.

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY.]
**ELECTROLYTIC DETERMINATIONS AND SEPARATIONS WITH THE
USE OF A ROTATING ANODE¹.**

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The following paragraphs contain data obtained by the use of a rotating *dish* anode in the electrolysis of several metallic salt solutions. Curves accompany the various experiments to show more clearly the progressive deposition of metal.

The remarkably short period in which copper, silver, nickel and zinc are precipitated by the use of the *dish* anode leaves no doubt as to the superiority and advantage of electrolytic methods over ordinary gravimetric procedures.

The separations of metals, using the rotating anode, make the rapid methods even more useful. There seems little doubt but that in a short time many of the electrolytic separations now quite satisfactory with stationary electrodes will be further improved by the addition of conditions under which they can be executed with rotating anodes, using increased current and pressure, thereby decreasing the time factor to a minimum.

The spiral anode used and described by Exner has been employed in nearly all the work done in this laboratory on the rapid precipitation of metals in the electrolytic way.

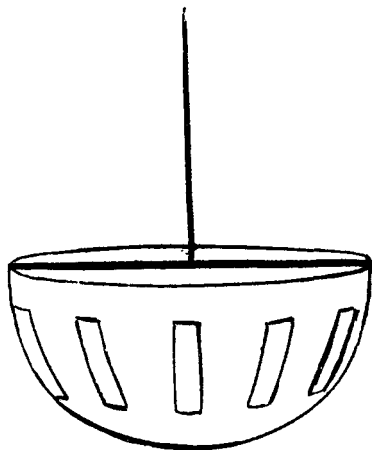
It was with a view of still further reducing the time element that a new form of anode was devised, following a brief description of which, will be recorded a series of experiments illustrating its advantage over the older forms.

The new anode is a platinum dish of the same general form as the cathode (see Figure 1). It is about 7 cm. in diameter and 3 cm. deep. Its sides are provided with ten slits perpendicular to the edge, each slit about 1.8 cm. long, and 0.5 cm. wide. These openings, together with a circular opening 1.3 cm. in diameter in the bottom of the dish, insure free circulation of the liquid.

¹ From the author's Ph. D. thesis, 1906.

It is held in position by a stout platinum rod, and is so adjusted that it is equidistant from the sides of the cathode.

During the rotation of the anode the liquid is all contained within the space bounded by the cathode and the outer surface of the anode, no liquid remaining within the inner dish. It is, therefore, evident that the dilution in this case must be much less than when the spiral anode is employed. The volume of the electrolyte should not exceed 65 cubic centimeters.



Dish Anode.

Fig. 1.

When properly adjusted there is no splashing of the liquid and consequent loss of the electrolyte, as one might at first suppose there would be, nor is there any danger of incomplete precipitation due to liquid adhering to the inside of the anode, the decanted liquid showing no trace of the metal when subjected to tests.

Determinations of Metals.

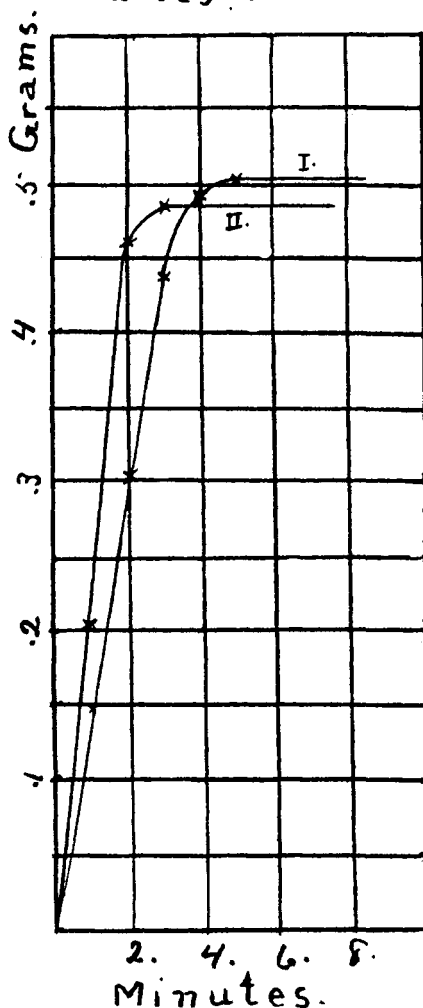
Copper.

A solution of copper sulphate was prepared containing about 0.5035 gram of copper in 25 cc., and a series of determinations were made with the *spiral* anode (as described by Exner). The most satisfactory conditions for rapid precipitation were found to be as follows:

To 25 cc. of the copper sulphate solution add 1 cc. of sulphuric acid (dil. 1 : 10), 100 cc. of boiling water, and electrolyze:

No.	Volts.	Amperes.	Time, mins.	Wt. of Cu. in grams.
1	10	6-13	7	0.5038
2	10	5-13	7	0.5037
3	10	6-13	7	0.5034
4	10	5-13	7	0.5035

Copper — Curves I and II.



The perfectly adherent deposits were dark red in color, with a beautiful velvety appearance.

Observing the above conditions the following time curve, (*Curve No. I*) was determined:

Volts.	Amperes.	Time, mins.	Wt. of Cu in grams.
10	5.6	1	0.1493
10	5.6	2	0.3019
10	5.6	3	0.4371
10	5.6	4	0.4925
10	5.6	5	0.5029

Using the *dish* anode, with the same electrolyte, and diluting to about 60 cc., these results were obtained:

No.	Cu present in grams.	Volts.	Amperes.	Time, mins.	Wt. of Cu in grams.
1	0.4884	7+	10-15	4	0.4883
2	0.4884	8	10-16	3	0.4884
3	0.4884	8	10-16	5	0.4887
4	0.4884	8	10	2	0.4634
5	0.4884	8	10	1	0.2010

The character of the deposit was the same as when the spiral was used. *Curve II* is constructed from these results.

When the spiral anode was used and nitric acid added as electrolyte, the best results obtained were those in which $\frac{1}{2}$ cc. of the acid was added to 25 cc. of the copper sulphate solution, and the liquid diluted to 125 cc. with boiling water, (25 cc. of the solution contained about 0.4876 gram of copper). Brilliant, crystalline, adherent deposits were obtained.

No.	Volts.	Amperes.	Time, mins.	Wt. of Cu in grams.
1	8	7	15	0.4878
2	8	7	15	0.4877
3	8	8	15	0.4875
4	8	8	10	0.4875

The following time curve determinations show that ten minutes are required for complete precipitation.

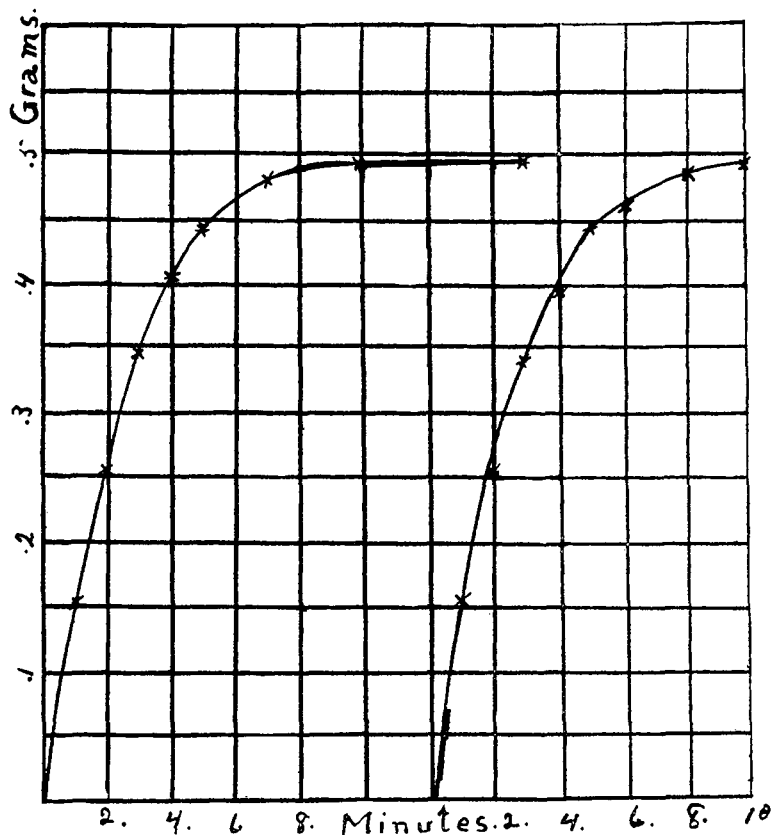
No.	Volts.	Amperes.	Time, mins.	Wt. of Cu in grams.
1	8	7-8	1	0.1507
2	8	7-10	2	0.2518
3	8	7-11	3	0.3418
4	8	7-11	4	0.3960
5	8	7-11.5	4	0.4486
6	8	7-12	6	0.4654
7	8	7-12	8	0.4852
8	8	7-12	10	0.4875

See *Curve III* for graphic representation.

Using the *dish* anode with the same electrolyte, the deposition of 0.4817 gram of copper was complete in six minutes, with a pressure of 8 volts and 16 amperes.

When 25 cc. of copper sulphate solution, containing 0.4967 gram of copper, to which was added 1.2 grams of ammonium nitrate and 25 cc. of ammonia, were diluted to 125 cc., heated to boiling, and electrolyzed, complete precipitation, using the *spiral* anode, required about fifteen minutes, as per table below and *Curve IV*.

Copper — Curves III and IV.



No.	Volts.	Amperes.	Time, mins.	Wt. of Cu in grams.
1	8	9	1	0.1508
2	8	9	2	0.2520
3	8	9	3	0.3455
4	8	9	4	0.4023
5	8	9	5	0.4422
6	8	9	7	0.4802
7	8	9	10	0.4914
8	8	9	15	0.4963

The deposits were bright and adherent.

With the same electrolyte 0.4824 gram of copper was deposited in six minutes with six volts and a current of 17 amperes, using the *new* anode.

The *dish* anode was also employed in depositing copper from a cyanide solution. A slight excess of potassium cyanide was added above that required to precipitate the copper and redissolve the precipitate. To that solution were added 10 cc. of ammonia, and in six minutes, using 7 volts and 15 amperes, 0.4883 gram of copper was deposited in a beautiful bur-nished form.

Silver.

Silver gave the most satisfactory results. The silver from a nitrate solution was precipitated and redissolved in potassium cyanide, and an excess of two grams of potassium cyanide added in each determination, the solution diluted as usual, heated almost to boiling, and electrolyzed.

The following table and corresponding curve (No. V) show results obtained by the use of the *spiral* anode.

No.	Volts.	Amperes.	Time, mins.	Wt. of Ag in grams.
1	5	2.8	1	0.2046
2	5	2.8	2	0.3391
3	5	2.8	3	0.4858
4	5	2.8	4	0.5043
5	5	2.8	5	0.5225
6	5	2.8	7	0.5270
7	5	2.8	10	0.5301

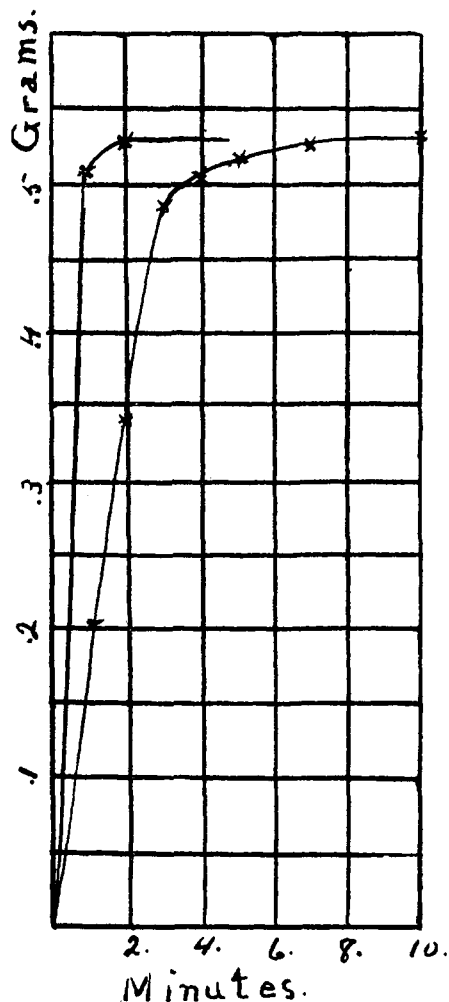
The precipitation was complete in ten minutes.

The deposits were chalk-white, and spongy in the bottom of the dish, but adherent. With the *new* anode, using a portion of the same solution, and adding three grams of potassium cyanide, the 0.53 gram of silver was deposited in two minutes, all but a very small quantity of which was precipitated during the first minute. See *Curve VI* constructed from the results which follow:

No.	Volts.	Amperes.	Time, mins.	Wt. of Ag in grams
1	5	10	4	0.5304
2	5	6	4	0.5306
3	5	8	3	0.5306
4	5	9	2	0.5304
5	5	9	1	0.5116

The great differences in current strength in the above series are due mainly to the variation in distance between the electrodes, a small decrease in distance causing a large rise of the current, the pressure being kept constant.

Silver— Curves V and VI.



Nickel.

A few determinations of nickel from a solution containing ammonium sulphate show that half a gram of that metal may be precipitated in five minutes using the *dish* anode.

To 25 cc. of the nickel solution, containing 0.5004 gram of the metal, were added 3 grams of ammonium sulphate dissolved in water and 20 cc.

of ammonia, the solution then diluted to 60 cc. and heated almost to boiling.

No.	Volts.	Amperes.	Time, mins.	Wt. of Ni in grams.
1	6	11-16	6	0.5005
2	6.5	11-14	5	0.5002

Zinc.

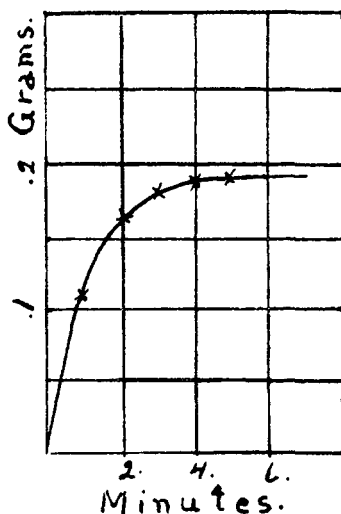
This metal was also tried, and it was found that a quarter of a gram of the metal could be deposited in three minutes, using the *dish* anode, with the conditions indicated in Experiment No. 2.

No.	NaOH added.	Volts.	Amperes.	Time, mins.	Wt. of Zn in grams.
1	5 grams	5	10	6	0.2472
2	4 ..	6	13	3	0.2476
3	8 ..	5	13	8	0.2472

Platinum.

Platinum has long been known to be completely precipitated by means of the electric current, and, while the ordinary electrolytic methods for its determination are very satisfactory, they require considerable time,—four to five hours for the precipitation of 0.1 to 0.2 gram. By agitating the electrolyte, the complete deposition of the same amount may be accom-

Platinum — Curve VII.



plished in a few minutes, as shown by the following experiments, in which a solution of potassium chloroplatinate was used, 25 cc. of the solution

containing about 0.0953 gram of platinum. The metal was deposited on a silver-coated dish. The *dish* anode was employed and made to rotate during the electrolysis.

No.	H ₂ SO ₄ (dil. 1:10) in c.c.	Volts.	Amperes.	Time, mins.	Wt. of Pt. in grams.
1	5	7	14	4	0.0956
2	5	8	14	3	0.0907
3	5	7	14	1	0.0821
4	5	5	10	7	0.0953
5	5	6	17	3	0.0932
6	2.5	10	16	3	0.0952
7	2.5	10	17	2	0.0926

In numbers 1, 4 and 6 the precipitation was complete. The deposits were dark gray in color and perfectly adherent. The great difference in voltage and amperage in the above experiments is due to variation in electrode distance.

Reproducing the conditions of 6 and 7, doubling the amount of the solution, and diluting to 60 cc., the following experiments gave the results from which *Curve No. VII* was constructed.

No.	H ₂ SO ₄ (dil. 1:10) in c.c.	Volts.	Amperes.	Time, mins.	Wt. of Pt. in grams.
1	2.5	10	16	3	0.1855
2	2.5	10	18	4	0.1904
3	2.5	10	17	5	0.1973
4	2.5	10	18	2	0.1734
5	2.5	10	17	1	0.1158

The platinum was completely precipitated in five minutes.

Palladium.

This metal was precipitated from a solution of palladammonium chloride, Pd(NH₃Cl)₂. A quantity of the salt was dissolved in ammonia and diluted so that 10 cc. of the solution contained about 0.268 gram of palladium.

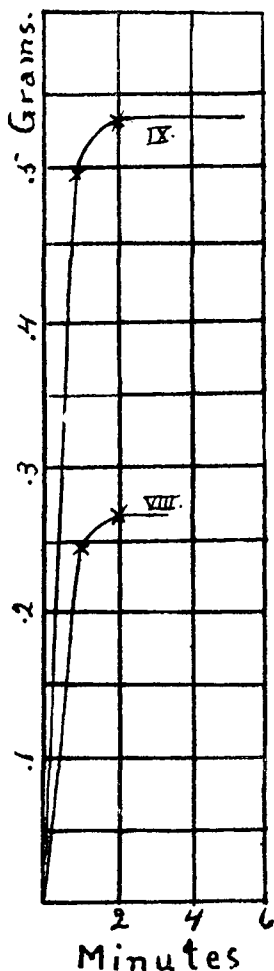
The deposits were usually made on silver-coated dishes, and the rotating *dish* anode was employed.

To 10 cc. of the palladium solution were added 20 cc. of boiling ammonia, and the whole diluted to 60 cc. with boiling water and electrolyzed.

No.	Volts.	Amperes.	Time, mins.	Wt. of Pd. in grams.
1	5-6	2+	18	0.2682
2	11	5	10	0.2680
3	17	7	5	0.2682
4	17	10	3	0.2678
5	17	10	2	0.2678
6	17	9	1	0.2476
7	17	10	2	0.2683
8	17	10	2	0.2680
9	17	10	2	0.2681

The precipitation was complete in all except the sixth experiment. The deposits were gray and perfectly adherent. In the last three the metal was

Palladium—
Curves VIII and IX



deposited directly on the platinum dish, and was removed by a warm mixture of chromic acid and potassium chloride.

Another series of determinations was made by doubling the amount of the palladium solution.

No.	NH ₄ OH in c.c.	Dilution.	Volts.	Amperes.	Time, mins.	Wt. of Pd. in grams.
1	20	60 c.c.	15	14	3	0.5358
2	20	60 c.c.	17	14-20	2	0.5357
3	20	60 c.c.	17	14-20	1	0.4966

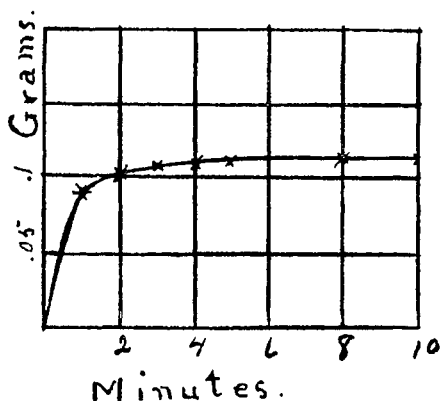
These determinations of palladium speak for the accuracy of the method. With no other metal does the rapid electrolytic determination give more satisfactory results. The character of the deposit is excellent, the time element almost annihilated, and the range of conditions within which the complete precipitation is possible, is large; a high current, however, being necessary for the speediest deposition. *Curves VIII and IX* were constructed from the preceding data. Another series of experiments in which no ammonia was added also resulted well as to time and character of deposits.

Rhodium.

The rapid precipitation of rhodium was found to be best accomplished from a solution of sodium rhodium chloride, Na₂RhCl₆, to which a few drops of sulphuric acid had been added.

See *Curve X* for plotted results.

Rhodium —
Curve X.



In the first four determinations 10 cc. of the rhodium solution (about 0.0576 gram of rhodium), acidified with 2.5 cc. of sulphuric acid (dil. 1:10), were diluted to 105 cc. with boiling water, and electrolyzed, using a *spiral* anode; while in the last three, using the *dish* anode, the solution was diluted to about 60 cc. The metal was deposited on a silver-coated dish.

No.	Volts.	Amperes.	Time, mins.	Wt. of Rh. in grams
1	7	8	15	0.0577
2	7.5	8	10	0.0580
3	8	9	10	0.0575
4	8	9	7	0.0576
5	8	15	4	0.0573
6	6	11	4	0.0563
7	7	14	4	0.0567

In all but the sixth and seventh experiments the precipitation was complete. The deposits were adherent and almost black in color.

Doubling the quantity of the rhodium solution the following time curve determinations were made using the *dish* anode.

No.	Volts.	Amperes.	Time, mins.	Wt. of Rh. in grams.
1	7	15	1	0.0896
2	7	15	2	0.1006
3	7	15	3	0.1104
4	7	15	4	0.1128
5	7	15	5	0.1141
6	7	15	8	0.1152
7	7	15	10	0.1153

SEPARATIONS.

Gold from Platinum.

As the cyanide electrolyte affords a means of separating gold from platinum, it was thought probable that a rapid separation might be possible from the same electrolyte. In the following determinations 5 cc. of gold chloride solution, containing about 0.0462 gram of gold, and 25 cc. platinum solution, containing about 0.094 gram of platinum, were employed. A *spiral* anode was used. The solution was diluted to about 125 cc. and heated almost to boiling in each case.

No.	Au Sol. in cc.	Pt. Sol. in cc.	KCN in grams.	Volts.	Amperes.	Time, mins.	Wt. of Au
1	5	10	1.5	6	2	15	0.0464
2	5	10	1.5	6	2	20	0.0462
3	5	10	2	6+	2.5	12	0.0464
4	10	25	2	6	2.5	20	0.0931
5	10	25	2	6	2.5	15	0.0930
6	10	25	2	6	2.5	10	0.0932
7	20	25	2	6	2.5	15	0.1863

Gold from Palladium.

Gold was separated from palladium from a cyanide solution containing about equal amounts of the two metals. The solution was diluted to 125 cc. with boiling water and electrolyzed. The following three determinations show satisfactory conditions for the separation.

No.	Au sol. in cc.	KCN in grams.	Volts.	Amperes.	Time, mins.	Wt. of Au
1	5	1	6	2	10	0.0464
2	5	1	6	2	30	0.0462
3	10	1.5	6	2	30	0.0932

Copper from Platinum.

A series of determinations showed that copper can be precipitated free from platinum in a solution containing the two metals, when 3 grams of potassium cyanide and 10 to 20 cc. of ammonia are added. When the ammonia was omitted a faint trace of platinum was deposited with the copper.

No.	Cu Sol. in cc.	Cu present in grams.	KCN in grams.	NH ₄ OH in cc.	Volts.	Amperes.	Time, mins.	Wt. of Cu
1	10	0.1290	3	10	5	3.5	35	0.1290
2	10	0.1290	3	10	5	3	30	0.1295
3	10	0.1290	3	20	5	3	30	0.1291
4	10	0.1290	3	20	5	3	60	0.1294

In the fourth determination, in which the current was passed through the solution for a whole hour, a very slight trace of platinum was detected in the deposit.

Silver from Platinum.

This separation is best accomplished from a solution containing 1.5 grams of potassium cyanide. The silver present in solution in the following determinations was 0.1183 gram.

No.	Volts.	Amperes.	Time, mins.	Wt. of Ag
1	3	0.25-0.05	20	0.1181
2	3	0.25-0.05	20	0.1180
3	3	0.25-0.05	25	0.1180
4	3	0.25-0.05	20	0.1182
5	3	0.25-0.05	20	0.1138

Silver from Copper.

It was found that silver and copper may be separated with ease from a cyanide solution by means of the rotating anode. Two grams of potassium cyanide should be added.

No.	Volts.	Amperes.	Time, mins.	Wt. of Ag
1	2.5	0.35-0.1	15	0.1184
2	2.5	0.4 -0.1	20	0.1184
3	2.5	0.4 -0.1	20	0.1183

Silver and Copper from Platinum.

From a mixture of the three metals, in a solution containing 2 grams of potassium cyanide, the silver may first be removed and then the copper. In each of the following experiments the solution contained about 0.1314 gram of copper and 0.1183 gram of silver.

No.	Volts.	Amperes.	Time, mins.	Wt. of metal found
1	2.5	0.40-0.08	15	0.1183 g. silver
	5	3	35	0.1311 g. copper
2	2.5	0.45-0.08	15	0.1182 g. silver
	5	3	35	0.1320 g. copper

The silver deposits were free from copper and the copper deposits showed no trace of silver or platinum.

Silver from Nickel.

Two separations were made from solutions containing 1.5 grams of potassium cyanide.

No.	Volts.	Amperes.	Time, mins.	Wt. of Ag.
1	2.5	0.4-0.07	20	0.1184
2	2.5	0.4-0.07	20	0.1185

Silver from Zinc.

A solution of the two metals containing 2.5 grams of potassium cyanide was used. Only two determinations were made.

No.	Volts.	Amperes.	Time, mins.	Wt. of Ag.
1	3	0.35-0.08	20	0.1187
2	3	0.3	20	0.1185

Silver from Copper in Coin.

The ease with which silver may be separated from copper by means of the rotating anode suggested the rapid analysis of a silver coin by the same method.

A dime was cleaned and cut into four parts. One part was then weighed (0.7070 gram), dissolved in the least possible amount of nitric acid, the excess of acid evaporated, and the residue dissolved in water and diluted to 100 cc. To 25 cc. of this solution was added $\frac{1}{2}$ gram of potassium cyanide. The silver was first removed with a low current, and the decanted liquid after evaporation electrolyzed for the copper. The conditions and results obtained are tabulated below.

No.	Volts.	Amperes.	Time, mins.	Wt. of metal.	% of metal.
1	3-2.5	0.4-0.06	35	0.1539 g. Ag	89.90% silver
	10	5	10	0.0177 g. Cu	10.01% copper
2	3-2.5	0.4-0.06	45	0.1588 g. Ag	89.84% silver
	10	6	10	0.0180 g. Cu	10.18% copper

The complete analysis, including the weighing of the coin and the final weighing of the deposits, required about two and a half hours.

If two portions are taken, depositing the metals together in the one, and the silver alone in the other, the complete analysis can be made in an hour and a half, providing two dishes are available. One determination was made in that way. The coin weighing 0.5638 gram was dissolved in a small amount of nitric acid (less than 1 cc.). The excess of acid was evaporated. Two grams of potassium cyanide were then introduced and the solution diluted to 100 cc. 25 cc. of this solution diluted to about 125 cc. were electrolyzed for the silver and copper combined, and a second portion for the silver alone.

Volts.	Amperes.	Time, mins.		
7	0.2	18	0.1409 combined wt. of Cu and Ag	99.94%
2.5	0.5-0.07	25	0.1268 weight of silver	90.00%