

method it may be added that the omission of the 1 cc. of sodium hydroxide from the electrolyte works no harm. The volume of sulphide may be reduced to 10 cc. without affecting the result; but then the quantity of alkaline cyanide should be reduced to 2 grams. The reduction of the cyanide to 1 gram without a corresponding reduction of sulphide is apt to give rise to a black border upon an otherwise most satisfactory deposit. If the volume of the alkaline hydroxide be increased to 10 cc., the antimony deposit will be black, powdery and non-adherent.

SEPARATION OF ANTIMONY FROM ARSENIC.

This separation can be carried out with perfect satisfaction when using the rotating anode. The conditions observed in getting the results given below were as follows: A solution of antimony oxychloride in sodium sulphide was made so that 10 cc. of it contained 0.1268 gram of antimony, and to each such portion were added 15 cc. of sodium sulphide (sp. gr. 1.18), 3 grams of potassium cyanide and water to increase the volume of liquid to 70 cc. On applying a current of 6 amperes and 4 volts the antimony was completely precipitated in from fifteen to twenty minutes.

RESULTS.

0.1268 gram of antimony.
0.1267 gram of antimony.
0.1269 gram of antimony.
0.1267 gram of antimony.
0.1269 gram of antimony.
0.1268 gram of antimony.

The deposit of metal was in each instance beautiful, light gray in color, metallic, and perfectly adherent. The arsenic existed in the solution as a sulpharsenate = (0.2000 gram of arsenic).

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, No. 99.]

THE USE OF THE ROTATING ANODE AND MERCURY CATHODE IN ELECTRO-ANALYSIS.

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(SECOND PAPER.)

IN THE previous communication upon this subject zinc, copper, nickel, cobalt, chromium and iron were the metals precipitated

under widely varying conditions with such completeness and surprising rapidity that it was concluded to include still other metals within the scope of the study before turning to an inquiry into certain side reactions, observed from time to time, which tended to draw attention to themselves. These, though most attractive and persistent in their appearance, must remain for more careful and thorough study in the future. Indeed, the side problems in electro-analysis, thus constantly obtruding themselves, have too long been neglected; they call for attention. Their solution will surely solve difficulties encountered by the analyst; remove serious doubts and pave the way for a wider introduction and constant use of the methods of electro-analysis. But, turning to the thought which prefaced this communication, other metals in the form of sulphates were carefully investigated. The results appear in the subjoined paragraphs.

CADMIUM.

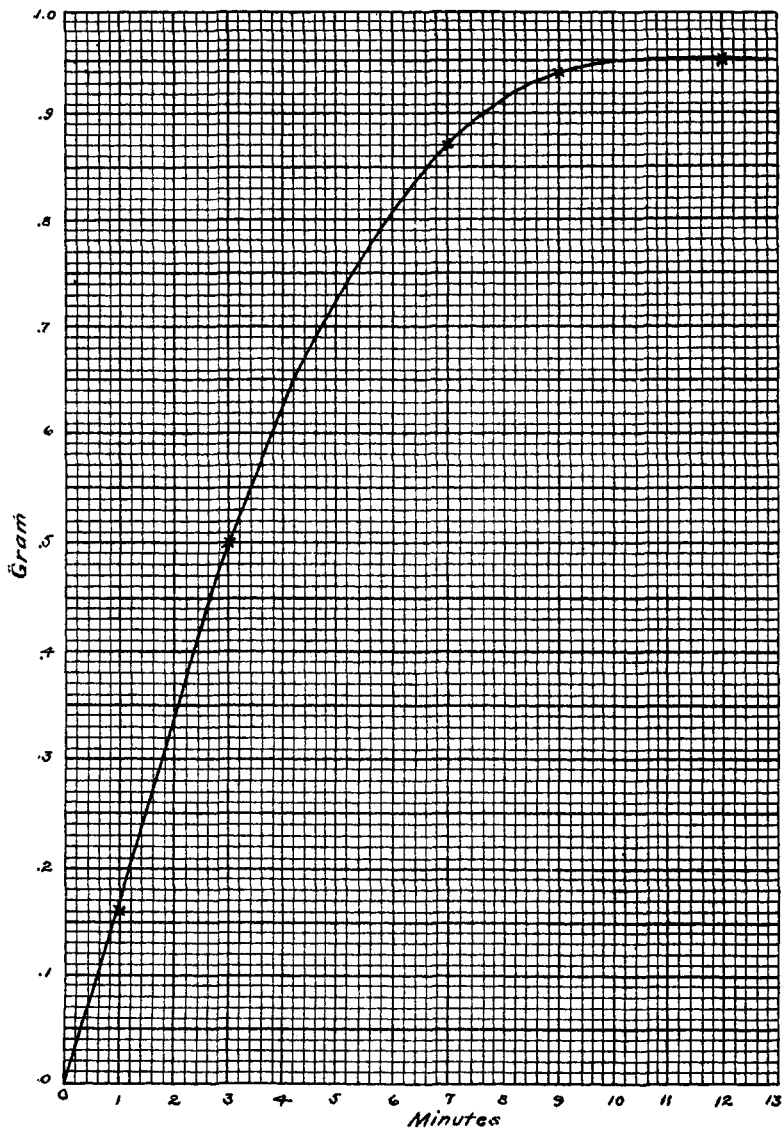
Reference to the literature¹ pertaining to the electrolytic determination of this metal will show that this method of estimating it is in every way superior to the ordinary gravimetric procedures. And only recently Miss Davison, working in this laboratory, has recorded the best electrolytes and the most satisfactory conditions for its estimation with a rotating anode and platinum cathode. To this helpful contribution it is desired to add the data derived from the use of a mercury cathode, supplemented with a rotating anode. The decomposition tube, of the size and arranged as heretofore described, contained from 60 to 70 grams of mercury. Upon this were placed 5 cc. of an aqueous solution of cadmium sulphate, equivalent to 0.9480 gram of metallic cadmium. The current acting upon this solution registered from 1.5 to 3.5 amperes and 10 to 7 volts. It was interrupted at the end of fifteen minutes. The liquid, siphoned from off the mercury, did not show the presence of any cadmium upon the addition of hydrogen sulphide. The metal had entered the mercury completely, the resulting amalgam having much the appearance of zinc amalgam except that it was brighter in color. The anode made 360 revolutions per minute.

The rate of precipitation of the cadmium was as follows:

0.1531 gram in one minute.

0.4984 gram in three minutes.

¹ Smith's "Electrochemical Analysis," p. 68.



Curve I. Cadmium.

0.8707 gram in seven minutes.

0.9480 gram in nine minutes.

0.9484 gram in ten minutes.

A trace of metal was found in the liquid from the nine-minute experiment, but absolutely none in that from the ten-minute trial. The time (Curve I, page 1529) was drawn from these last results.

As acid was not added to the electrolyte at the start, the current did not exceed 1 ampere, but with the liberation of acid from the salt the current quickly rose to 3.5 amperes, and this strength was maintained in all the subsequent precipitations. Thus, with these conditions, the following quantitative precipitations were made:

Cadmium found. Gram.	Time. Minutes.
0.9480	15
0.9480	10
0.9484	15
0.9481	12
0.9478	12
0.9478	12
0.9479	10
0.9479	10

The quantity of metal present in each determination was 0.9480 gram. Maintaining thus a current of definite strength throughout the decomposition, it next became an object to ascertain the rate of precipitation of metal under such conditions. Accordingly, 5 drops of concentrated sulphuric acid (40 drops equal 1 cc.) were added to 5 cc. of a cadmium sulphate solution, containing 0.9480 gram of metal, and electrolyzed with a current of 3.5 amperes and 10 to 7 volts:

In three minutes 0.6472 gram of cadmium was deposited.

In five minutes 0.9389 gram of cadmium was deposited.

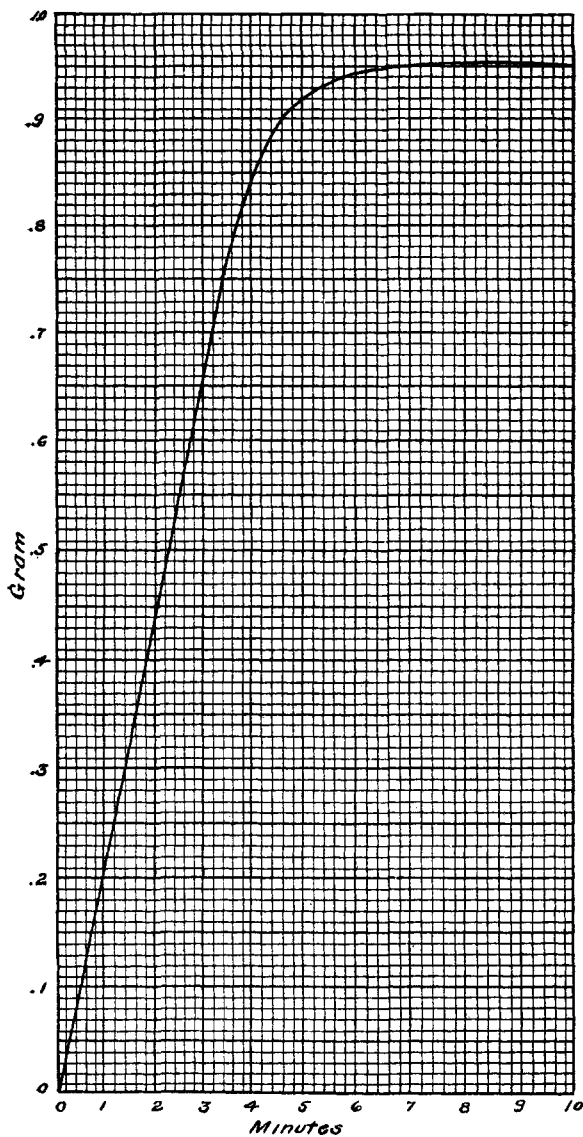
In seven minutes 0.9478 gram of cadmium was deposited.

In ten minutes 0.9477 gram of cadmium was deposited.

In twelve minutes 0.9481 gram of cadmium was deposited.

These data gave Curve II (page 1531).

The liquid poured off from the mercury in the seven-minute period showed only the slightest yellow tinge when it was treated with hydrogen sulphide. Other trials conducted with conditions similar to those first mentioned gave these results in metallic



Curve II. Cadmium.

cadmium: 0.9484, 0.9479, 0.9478, 0.9477, 0.9483, 0.9481, 0.9484 gram.

To learn the time necessary to precipitate smaller quantities of metal, a solution was made up containing 0.1600 gram of cadmium in 5 cc. On acting upon this last volume with a current of 3.5 amperes and 7 to 4 volts, the entire quantity of metal (0.1600 gram) was completely precipitated in three minutes. The following rates of deposition are shown in Curve III:

In one minute 0.1370 gram of cadmium was deposited.

In two minutes 0.1577 gram of cadmium was deposited.

In three minutes 0.1602 gram of cadmium was deposited.

In four minutes 0.1596 gram of cadmium was deposited.

Other results, obtained in three minutes, showed cadmium as follows: 0.1598, 0.1600 and 0.1601 gram.

The rate of deposition of metal from a solution, containing 0.3250 gram of cadmium in 5 cc., was also studied with these results:

In one minute 0.1945 gram of metal was deposited.

In two minutes 0.2835 gram of metal was deposited.

In three minutes 0.3150 gram of metal was deposited.

In four minutes 0.3217 gram of metal was deposited.

In five minutes 0.3249 gram of metal was deposited.

Cadmium was found in the residual liquor from Expt. 4, but absolutely none in that from the fifth experiment.

The preceding results gave Curve IV. From a solution containing 0.4740 gram of cadmium all of the metal was precipitated in five minutes:

In one minute 0.3706 gram was deposited.

In three minutes 0.4633 gram was deposited.

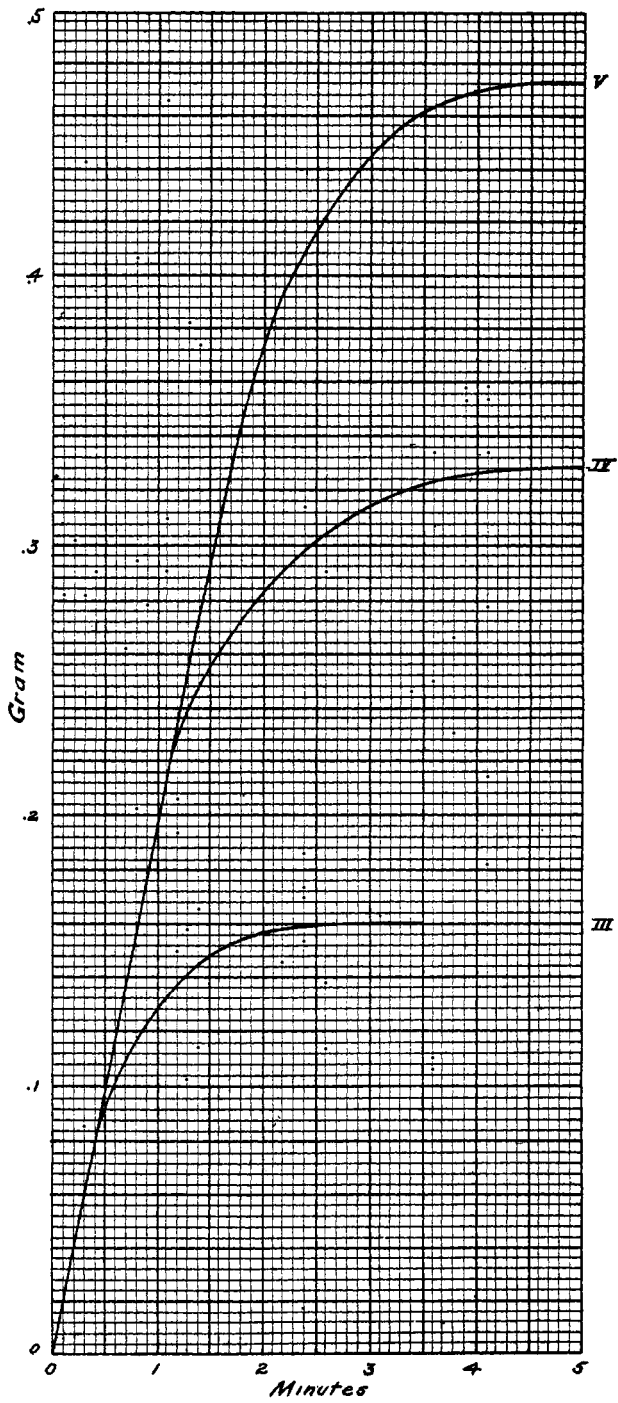
In five minutes 0.4743 gram was deposited.

Curve V was deduced from these figures.

The addition of 20 drops of sulphuric acid (or 0.5 cc.) to the solution, retaining the current conditions previously mentioned, produced no ill effect as 0.1591 gram of cadmium, instead of 0.1600 gram, was precipitated in three minutes. One cubic centimeter (40 drops) of concentrated acid, however, retarded the deposition, since only 0.1507 gram of metal was thrown down into the mercury in three minutes.

TIN.

While this metal has been determined quite often in the elec-



Curves III, IV, V.—Cadmium.

trolytic way the method does not appear to have gained such recognition as it justly deserves. It was thought that it would be well to learn how its solutions deported themselves when electrolyzed under the conditions prevailing in this and the previous communication to which it serves as a sequel. Accordingly, stannous hydrate was dissolved in sulphuric acid, the solution being so made up that 5 cc. of it contained 0.4106 gram of metallic tin and 0.2 cc. of concentrated sulphuric acid. A current of 2 to 4 amperes and 5 to 4 volts acted for ten minutes upon 5 cc. of this solution. The mercury increased 0.4109 gram in weight and the liquid poured off from it showed no tin upon examination. The addition of sulphuric acid seemed in no way to arrest the precipitation of metal, for the following masses of it were obtained with a current of 4 amperes and 5 volts:

In two minutes 0.2898 gram.

In four minutes 0.3890 gram.

In five minutes 0.4068 gram.

In six minutes 0.4106 gram.

From them Curve VI was drawn.

Even in the presence of a smaller amount (0.5 cc.) of acid, almost identical results were obtained:

In two minutes 0.2997 gram of tin was deposited.

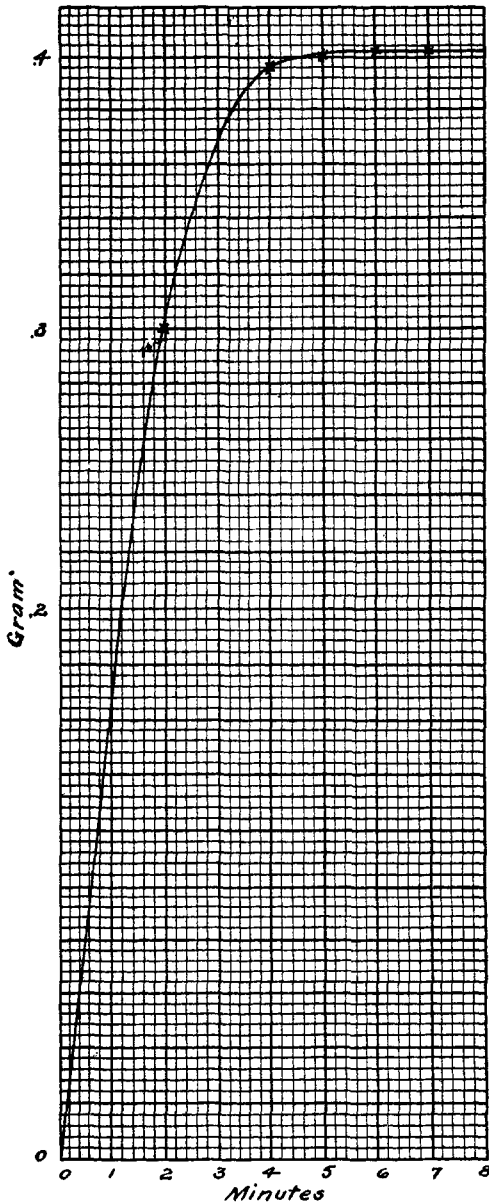
In four minutes 0.3974 gram of tin was deposited.

In five minutes 0.4060 gram of tin was deposited.

In six minutes 0.4106 gram of tin was deposited.

It was found advantageous to let the solution heat up quietly in order that the condensed steam might wash down the sides of the tube, otherwise traces of basic sulphate separated on the walls of the decomposition cell. With a current of 5 amperes and 5 to 4 volts it was possible to precipitate 0.8212 gram of tin (10 cc. of solution) in eight minutes.

Experi- ment.	Tin present. Gram.	Volume. cc.	Sulphuric acid. cc.	Current. Amperes.	Volts.	Time. Minutes.	Tin found. Gram.	Error. Gram.
1	0.4106	5	0.2	2-4	5	10	0.4109	+0.0003
2	0.4106	5	0.2	4	5	9	0.4114	+0.0008
3	0.4106	5	0.2	4	5-4.5	9	0.4109	+0.0003
4	0.4106	6	0.5	4	5	6	0.4106
5	0.4106	5	0.25	4	5	6	0.4106
6	0.8212	10	0.5	6	5.5	9	0.8210	-0.0002
7	0.4106	10	0.75	5	5	8	0.4107	+0.0001
8	0.4106	7	0.05	5	5	7	0.4106
9	0.4106	7	0.25	5	5	10	0.4107	+0.0001

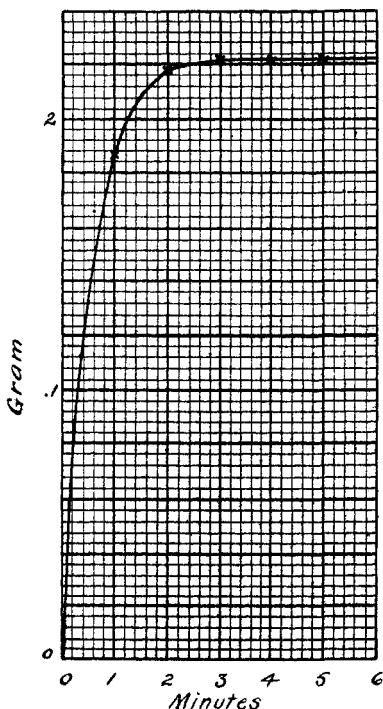


Curve VI. Tin—4 amperes, 5 volts.

SILVER.

There is nothing really to be added to the electrolytic methods proposed for this metal, and it would perhaps not have been included in our experiments had not the question arisen—as to whether nitrates could be used with a mercury cathode, the thought being that possibly they might be reduced to ammonia and the latter then enter the mercury. But the electrolysis of nitric acid and nitrates under the conditions prevailing in the experiments here recorded, *viz.*, with high current density and voltage, never resulted in this way, and, therefore, enables the analyst to employ this class of salts in metal determinations with a mercury cathode and rotating anode. In confirmation of these statements silver, mercury and bismuth nitrates were thus electrolyzed and the results therefrom are given in the succeeding paragraphs.

The conditions observed with silver nitrate were:



Curve VII. Silver—4 amperes, 6 volts.

Volume of solution, 5 cc. (equal to 0.2240 gram of Ag).

Nitric acid 5 drops (30 drops equaled 1 cc.).

Current, 4.5 to 3 amperes.

Volts, 6.5 to 6.

The anode made 1200 revolutions per minute.

Results:

In one minute 0.1874 gram of silver was deposited.

In two minutes 0.2178 gram of silver was deposited.

In three minutes 0.2207 gram of silver was deposited.

In four minutes 0.2240 gram of silver was deposited.

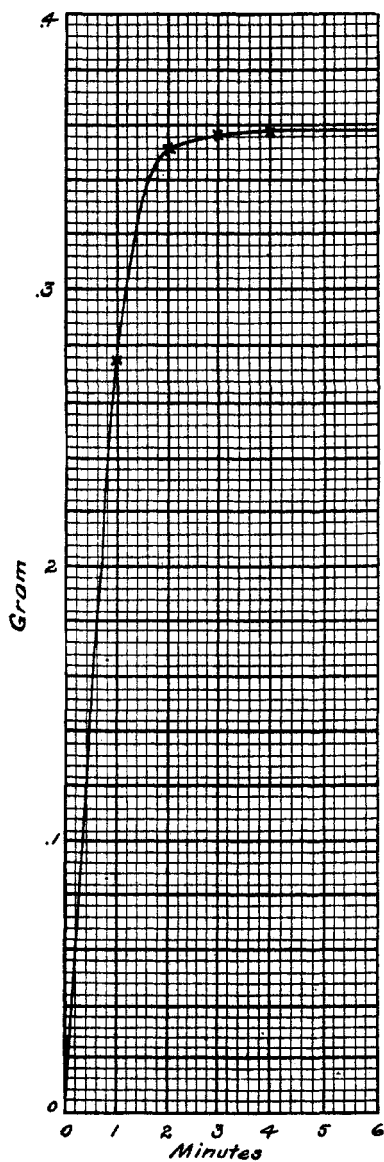
These gave Curve VII.

As might be expected, working with a nitric acid solution, there was an anodic deposit. At the end of one minute this was quite heavy but when two minutes had expired it was almost entirely gone, and in three minutes the anode was perfectly clean. Silver is precipitated quite rapidly, hence the anode was given high speed to insure agitation of the mercury and thereby render the silver absorption more rapid. It is not advantageous to have a greater concentration than 0.3500 gram of silver in 5 cc.

Experiment.	Silver present. Gram.	Volume. cc.	Nitric acid in drops. $30 \equiv 1$ cc.	Current. Amperes.	Volts.	Revolutions of anode per minute.	Time. Minutes.	Silver found. Gram.	Error. Gram.
1	0.2240	5	5	1	6	1400	7	0.2240
2	0.2240	5	5	3.5	6-5	1360	5	0.2241	+0.0001
3	0.2240	5	5	4-2	6-5	1360	5	0.2246	+0.0006
4	0.2240	5	2	3-2.5	7-6	1360	5	0.2236	-0.0004
5	0.2240	5	5	4.5-3	6.5-6	1200	4	0.2240
6	0.2240	5	1	3-2	5-4	200	5	0.2238	-0.0002
7	0.4480	10	5	2.5	5.5	1200	8	0.4472	-0.0008
8	0.2240	5	5	2.5	5.75	1080	5	0.2244	+0.0004
9	0.4480	10	10	3.5	6	1440	6	0.4471	-0.0009
10	0.4480	10	5	3.5	6	1440	6	0.4475	-0.0005
11	0.3720	5	2	2.5-3	8-6	1200	5	0.3719	-0.0001
12	0.3720	5	3	2.5-3	8-6	1200	4	0.3723	+0.0003
13	0.3720	5	10	3	8	1200	5	0.3713	-0.0007

MERCURY.

A solution of mercurous nitrate was used. It contained 0.3570 gram of mercury in 5 cc. Sufficient nitric acid was also present to prevent the formation of a basic salt. A current of



Curve VIII. Mercury—3 amperes, 7.5 volts.

3 amperes and 7 to 5 volts decomposed the salt at the following rate:

In one minute 0.2777 gram of mercury was deposited.

In two minutes 0.3542 gram of mercury was deposited.

In three minutes 0.3572 gram of mercury was deposited.

Curve VIII was constructed from these values.

The effect of dilution upon the rate of deposition was learned by adding water to 5 cc. of the solution just mentioned until its volume became 25 cc. It was then exposed to a current of 3 amperes and 13 to 7.25 volts. When it was found that eight minutes were necessary to completely precipitate the metal present, the masses deposited were:

In two minutes 0.2796 gram of mercury,

In five minutes 0.3488 gram of mercury,

In seven minutes 0.3552 gram of mercury,

In eight minutes 0.3570 gram of mercury,

from which was constructed Curve IX.

It was found that the addition of free nitric acid tended to retard the rate of precipitation unless the pressure was maintained at 5.5 volts, the current strength sometimes then rising to 8 amperes. Even in the presence of 1 cc. of the acid all of the mercury was deposited in three minutes:

In two minutes 0.3498 gram of mercury.

In three minutes 0.3569 gram of mercury.

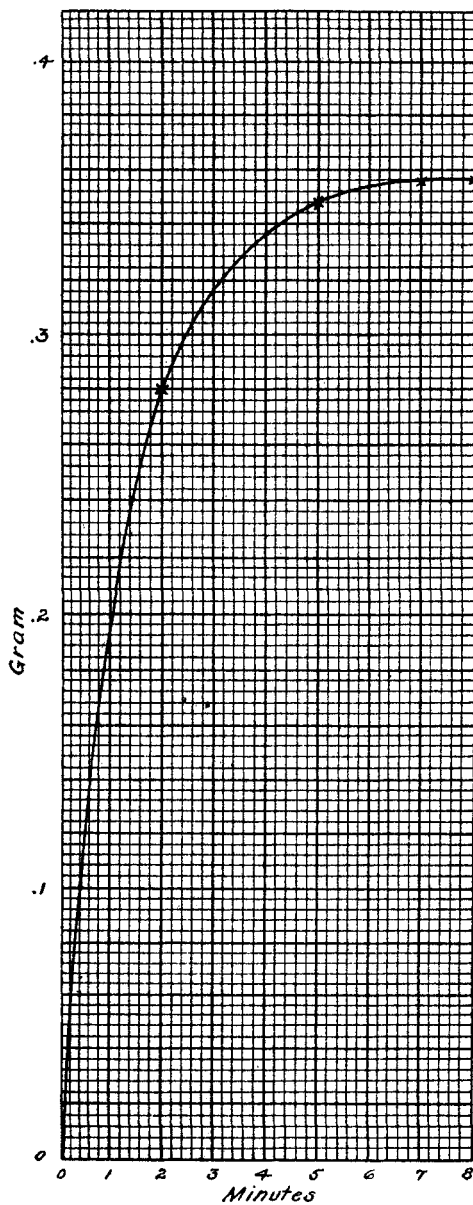
In four minutes 0.3569 gram of mercury.

The total quantity of mercury present equaled 0.3575 gram.

Experi- ment.	Mercury present. Gram.	Volume.	Nitric acid. cc.	Current. Amperes.	Volts.	Time.	Mercury found. Gram.	Error. Gram.
1	0.3575	5	0.02	3	7-5	4	0.3576	+0.0001
2	0.3575	5	0.02	3	7-5	3	0.3572	+0.0003
3	0.3575	5	0.02	3	7-5	4	0.3573	+0.0002
4	0.3575	5	0.02	3	7-5	3	0.3573	+0.0002
5	0.3575	5	0.02	3	7-5	3	0.3566	-0.0001
6	0.3575	5	0.02	3	7-5	3	0.3574	+0.0001
7	0.3575	25	0.02	3	13-7.25	8	0.3575
8	0.3575	6	1	8-7	5.5	4	0.3569	-0.0006
9	0.3575	6	1	8-7	5.5	3	0.3569	-0.0006

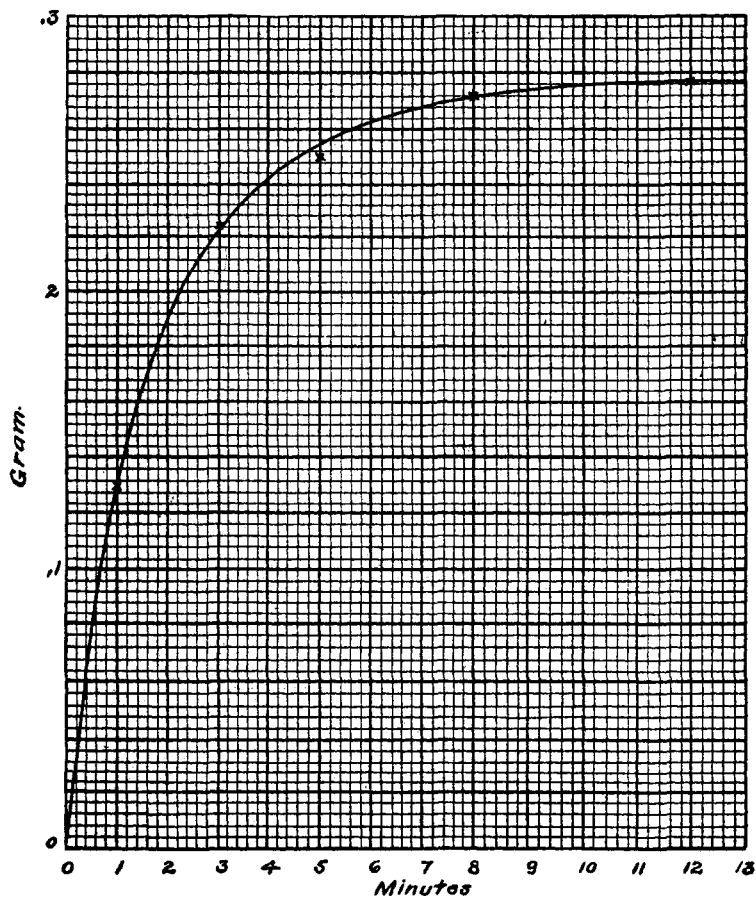
BISMUTH.

This metal, as is well-known, has always presented difficulties when determined electrolytically, so that the successful conditions which have been offered must be strictly observed in order



Curve IX. Mercury—25 cc.—3 amperes, 13-7 volts.

that the results may be satisfactory. The formation of peroxide on the anode simultaneously with the precipitation of metal on the cathode has been the problem. To prevent the anodic deposit has called forth numerous suggestions which need not be given here. The addition of a glycerol mixture did not entirely

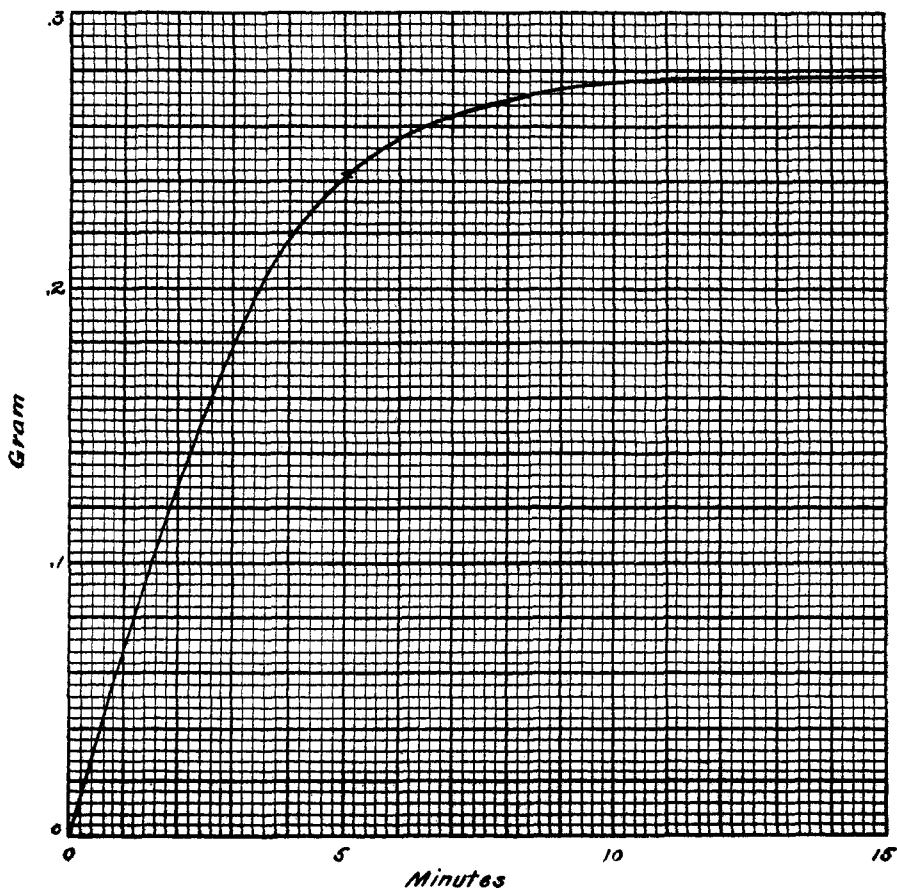


Curve X. Bismuth—3 amperes, 5 volts (nitric acid).

prevent the peroxide formation, nor did the reduction of the current, after it had acted awhile, produce the beneficial effect noticed in the electrolysis of bismuth solutions with a platinum cathode.

A solution containing 0.2777 gram of bismuth in 12 cc., with 0.5 cc. of concentrated sulphuric acid, was electrolyzed with a

current of 4 amperes and 5 volts. Consecutive experiments showed that 0.2777, 0.2779, 0.2770, 0.2773 and 0.2767 gram of metal was precipitated in twelve minutes. The liquid removed from each of these deposits gave no test for the metal upon examination. There was not a trace of anodic precipitation at the completion of any one of these experiments. In the earlier stages of the decompositions the peroxide appeared on the anode wire but rapidly redissolved. Smooth wire should be used for the anode. If its surface is rough, the deposit, if there be any, will disappear very slowly. The anode should rotate rapidly, so



Curve XI. Bismuth—3 amperes, 5-4 volts (0.5 cc. sulphuric acid).

that the mercury may take up the metal which is deposited quickly, as it often collects in a black mass beneath the anode.

As bismuth solutions generally contain considerable free nitric acid, 0.5 cc. of the latter was added to each of six experiments in which a current of from 3 to 4 amperes and 5 volts acted for twelve minutes, precipitating 0.2778, 0.2769, 0.2768, 0.2775, 0.2776 and 0.2772 gram of bismuth respectively, at the rate of 0.1305 gram of metal in one minute.

0.2274 gram of metal in three minutes.

0.2515 gram of metal in five minutes.

0.2732 gram of metal in eight minutes.

0.2751 gram of metal in ten minutes.

0.2775 gram of metal in twelve minutes.

From these results Curve X was constructed.

The substitution of sulphuric for nitric acid appears to make little difference in the rate of the precipitation as may be seen from the following figures:

In five minutes 0.2409 gram of bismuth was deposited.

In ten minutes 0.2764 gram of bismuth was deposited.

In fifteen minutes 0.2770 gram of bismuth was deposited.

These gave Curve XI.

Experi- ment.	Bismuth present. Gram.	Volume. cc.	Sulphuric acid. cc.	Current. Amperes.	Volts.	Time. Minutes.	Bismuth found. Gram.	Error. Gram.
1	0.2273	12	0.5	3	5	15	0.2777	+0.0004
2	0.2273	12	0.5	3-4	5	15	0.2779	+0.0006
3	0.2273	12	0.5	4	5	12	0.2770	+0.0003
4	0.2273	12	0.5	3	5.5	15	0.2773
5	0.2273	12	0.5	3	5	15	0.2767	-0.0006
6	0.2273	11.5	0.5	3	5	15	0.2770	-0.0003
			Nitric acid. cc.					
7	0.2273	11.5	0.5	4	5	12	0.2778	+0.0005
8	0.2273	11.5	0.5	4	5.75	12	0.2769	-0.0004
9	0.2273	11.5	0.5	4	5	12	0.2768	-0.0005
10	0.2273	11.5	0.5	4	5	12	0.2775	+0.0002
11	0.2273	11.5	0.5	4	5	12	0.2776	+0.0003
12	0.2273	11.5	0.5	4	5	12	0.2772	-0.0001
13	0.2273	11.5	0.5	4	5	12	0.2772	-0.0001

The many determinations given in the present communication as well as in the one which preceded it demonstrate beyond question that metallic sulphates and nitrates may be successfully electrolyzed with the mercury cathode and the rotating anode, the results in all instances being as satisfactory as with stationary

electrodes, it being possible also to determine the acid radical poured off in the liquid after the completion of the decomposition.

In the first paper published, relating to the use of a mercury cathode, it was shown that if in electrolyzing metallic halides, *e. g.*, sodium chloride, barium bromide, cobalt chloride, etc., use was made of a silver anode, the halogens could be determined simultaneously with the metals. Naturally, it was wished to know whether upon rotating the anode in halide solutions the halogens might be as easily determined. Accordingly, a flat platinum spiral and a disk of platinum, coated with metallic silver, were used as rotating anodes. The halogens of the electrolyzed halides promptly combined with the silver and for a while constituted an adherent deposit of silver halide, but as the layer thickened it began, because of the rapid rotation, to detach itself and become suspended in the solution. A silver disk was substituted for the silver-coated platinum anode with a like result. A large platinum dish, silver-coated and made a stationary anode, was used along with a smaller inner dish coated with mercury and made a rotating cathode with no better results. The silver halide formed upon the anode was disturbed by the agitation of the electrolyte, not equally readily it is true, and fell away from its electrode. Whether a scheme can be devised to make this perfectly adherent so that the metals may be quickly determined as in the case of sulphates and nitrates remains to be seen. Apparently, there is no reason why it should not be realized. Unwilling to exclude metallic halides from the field of experimentation, the problem was to eliminate the bad effects of the escaping halogens, for these did come off copiously in the electrolysis of any metallic halide upon employing the high current densities used with sulphates and nitrates. They also attacked the rotating platinum anode energetically. Could these undesirable behaviors be eliminated? Might not a layer of some organic liquid, superimposed on the aqueous halide, take up the halogens liberated in the electrolysis? A solution of cadmium bromide was made the electrolyte; upon it were placed 10 cc. of anhydrous ether. The anode was made to rotate quite rapidly and the current passed. The ether absorbed the bromine very fully and nicely. The heat of decomposition, however, caused a too rapid volatilization of the solvent so that toluene and xylene were substituted, in the later experiments, for the ether.

Both liquids proved most successful. The platinum anode was weighed before and after numerous experiments. Its decrease in weight for the entire series of experiments did not exceed 0.5 mg., a difference in weight that might easily be due to something other than solution of the anode.

COBALT CHLORIDE.

Five cubic centimeters of solution, containing 0.1250 gram of cobalt, were covered with 10 cc. of pure toluene and electrolyzed with a current of from 2 to 4 amperes and 5 volts. The liquid was colorless in five minutes and the metal completely precipitated in seven minutes. A second cobalt chloride solution (= 0.1050 gram of cobalt) gave 0.1050, 0.1049, 0.1052 and 0.1048 gram. On using xylene as the solvent, equally good results were obtained.

GOLD CHLORIDE.

The conditions prevailing were:

5 cc. gold chloride equal 0.1200 gram of gold.

Toluene, 10 cc.

Current, 2 to 3 amperes.

Volts, 10.

Time, five minutes.

Gold found, 0.1200, 0.1201 and 0.1198 gram.

Gold is precipitated very rapidly so that it is advisable that the current be not too strong. The perfectly satisfactory conditions were found to be those which have been mentioned at the opening of this paragraph. The gold chloride solution should not stand long in contact with the mercury cathode because metal soon begins to separate and is with difficulty absorbed by the mercury.

IRON CHLORIDE.

Here the conditions were:

5 cc. ferric chloride equal 0.1030 gram of iron.

Toluene, 10 cc.

Amperes, 2 to 4.

Volts, 9.

Time, twelve minutes.

Iron found: 0.1025, 0.1030, 0.1029 and 0.1031 gram respectively.

MERCURIC CHLORIDE.

This electrolyte also lent itself quite well to the method. Five cc. of the solution contained 0.2525 gram of mercury. On

placing the solution upon the mercury, a slight coating was produced. It proved a poor conductor for with a pressure of 10 volts a scarcely perceptible current was observed. Upon the liberation of acid the current rose to 1 ampere and then to 3 amperes, with the pressure falling to 7.5 volts. The mercury was completely precipitated in ten minutes. Conditions:

5 cc. solution equal 0.2525 gram of mercury.

Toluene, 10 cc.

Current, 1 to 3 amperes.

Volts, 10 to 7.5.

Time, ten minutes.

Mercury found: 0.2524, 0.2525, 0.2524 gram.

TIN CHLORIDE.

Stannous chloride was dissolved in just enough hydrochloric acid to prevent the formation of any oxychloride. When the solution was too concentrated the tin was deposited so rapidly that it was not immediately incorporated with the mercury, and particles of it floated around in the electrolyte and in the layer of toluene. For this reason the electrolyte was diluted. The conditions giving satisfactory results were:

I.

5 cc. stannous chloride equal 0.0800 gram of tin.

Toluene, 10 cc.

Amperes, 2 to 3.

Volts, 7 to 6.

Time, 10 minutes.

Tin found, 0.0798, 0.0806 and 0.0802 gram

II.

10 cc. stannous chloride equal 0.1600 gram of tin.

Toluene, 10 cc.

Amperes, 2 to 3.

Volts, 7 to 6.

Time, 15 minutes.

Tin found, 0.1595 and 0.1600 gram.

CADMIUM BROMIDE.

This solution was so prepared that 5 cc. of it contained 0.2212 gram of metal. After the addition of 10 cc. of toluene, the liquid was electrolyzed with a current of 2 amperes and 5 volts. The

toluene became red in color but later changed to yellow. The odor of bromine was not detected. In ten minutes 0.2215 gram of metal was precipitated. The aqueous solution gave no test for it.

These examples will suffice to show that by using toluene, metallic chlorides can be electrolyzed with the mercury cathode and rotating anode, applying high currents and high pressure. It was not thought necessary to include other halides. Just what the action of the halogen was could only be determined by fractional distillation of the several portions of toluene which had been used in the various decompositions. This was done. There remained, after expelling the unattacked toluene, a portion which boiled at about 162–164° C., corresponding in this particular to a chlorotoluene. Before we could, however, ascertain which one of the possible chlorinated products it really was there appeared in the *Journal of the Chemical Society* (London), **87**, 1034, a contribution upon "Studies in Chlorination," in which hydrochloric acid was electrolyzed under a layer of boiling toluene. The products were shown to be *o*- and *p*-chlorotoluene, which were subsequently oxidized to *o*- and *p*-chlorbenzoic acids. The chlorinated body obtained by us was presumably a mixture of *o*- and *p*-chlorotoluene. The purpose of the study being rather the electrolysis of metallic chlorides and not the action of electrolytic chlorine, further work in this direction was discontinued. Our study seems, however, to be a confirmation of the observation to which reference has just been made. Whether metallic chlorides would be preferable to hydrochloric acid for chlorinations of this description must be decided by others, as it is not our intention to develop this line of research.

At various times in this laboratory, since the introduction of the mercury cathode, separations have been made of iron from uranium, aluminium, thorium, lanthanum, praseodymium, neodymium, cerium and zirconium. They were most satisfactory. It remained to ascertain whether they would prove to be as good if they were conducted with the high currents and high voltage possible with the rotating anode. The nitrate or sulphate of each of the metals was tried first alone to discover whether it was at all affected. As this proved that not one of the metals mentioned in the preceding paragraphs was precipitated, the separations were begun and conducted as shown in the following sections:

IRON FROM URANIUM.

Uranyl sulphate. Gram.	Iron present. Gram.	Volume of solution. cc.	Sulphuric acid in drops (30 = 1 cc.).	Current. Amperes.	Volts.	Time. Minutes.	Iron found. Gram.	Error. Gram.
0.2	0.1777	7	2	3-5	7-5	15	0.1777
0.1	0.1777	6	2	2-5	7-5	15	0.1772	-0.0005
0.2	0.1777	7	3	2.5-5	7-5	15	0.1769	-0.0008
0.2	0.1777	7	2	2.5-3.5	7-5	15	0.1775	-0.0002

IRON FROM ALUMINIUM.

Aluminium sulphate. Gram.	Iron present. Gram.	Volume of solution. cc.	Sulphuric acid in drops (30 = 1 cc.).	Current. Amperes.	Volts.	Time. Minutes.	Iron found. Gram.	Error. Gram.
0.2	0.1777	7	2	2-5	9-7	15	0.1777
0.2	0.1777	7	0	2-4	9-7	15	0.1782	+0.0005
0.2	0.1777	7	2	2-5	9-7	15	0.1781	+0.0004
0.3	0.1777	8	2	2-4.5	7-6	15	0.1782	+0.0005

IRON FROM THORIUM.

Thorium nitrate. Gram.	Iron present. Gram.	Volume. cc.	Sulphuric acid in drops (30 = 1 cc.).	Current. Amperes.	Volts.	Time. Minutes.	Iron found. Gram.	Error. Gram.
0.2	0.1777	7	2	2-4	7-6	15	0.1777
0.2	0.1777	7	2	3-5	6-5	15	0.1777
0.3	0.1777	8	2	3-4	7-5	15	0.1777
0.2	0.1777	7	2	3-4	7-5	15	0.1776	-0.0001

IRON FROM LANTHANUM.

Lanthanum sulphate. Gram.	Iron present. Gram.	Volume. cc.	Sulphuric acid in drops (30 = 1 cc.).	Current. Amperes.	Volts.	Time. Minutes.	Iron found. Gram.	Error. Gram.
0.2	0.1220	10	2	2-4	8-6	15	0.1221	+0.0001
0.15	0.1220	10	2	2-4	8-6	15	0.1226	+0.0006
0.25	0.1220	10	2	2-4	8-6	15	0.1226	+0.0006

IRON FROM PRASEODYMIUM.

Praseodymium sulphate. Gram.	Iron present. Gram.	Volume. cc.	Sulphuric acid in drops (30 = 1 cc.).	Current. Amperes.	Volts.	Time. Minutes.	Iron found. Gram.	Error. Gram.
0.25	0.1235	7	2	2.4	8.5	20	0.1240	+0.0005
0.3	0.1235	8	2	3.5	9.6	20	0.1234	-0.0001
0.3	0.1235	8	2	2.4	8.5	20	0.1229	-0.0006
0.25	0.1235	7	2	2.4	8.5	20	0.1230	-0.0005

IRON FROM NEODYMIUM.

Neodymium sulphate. Gram.	Iron present. Gram.	Volume. cc.	Sulphuric acid in drops (30 = 1 cc.).	Current. Amperes.	Volts.	Time. Minutes.	Iron found. Gram.	Error. Gram.
0.16	0.1235	7	2	3.4	7.5	20	0.1242	+0.0007
0.24	0.1235	8	2	3.5	9.5	20	0.1236	+0.0001
0.24	0.1235	8	2	3.5	9.7	20	0.1237	+0.0002
0.16	0.1235	7	2	3.5	9.5	20	0.1237	+0.0002

IRON FROM CERIUM.

Cerium sulphate. Gram.	Iron present. Gram.	Volume. cc.	Sulphuric acid in drops (30 = 1 cc.).	Current. Amperes.	Volts.	Time. Minutes.	Iron found. Gram.	Error. Gram.
0.12	0.1235	8	2	2.4	9.6	20	0.1237	+0.0002
0.24	0.1235	9	2	2.4	9.6	20	0.1236	+0.0001
0.36	0.1235	10	0	2.5	10.7	25	0.1230	-0.0005

IRON FROM ZIRCONIUM.

Zirconium sulphate. Gram.	Iron present. Gram.	Volume. cc.	Sulphuric acid in drops (30 = 1 cc.).	Current. Amperes.	Volts.	Time. Minutes.	Iron found. Gram.	Error. Gram.
0.2	0.1235	7	0	2.4	7.5	20	0.1238	+0.0003
0.3	0.1235	8	1	2.4	7.5	20	0.1230	-0.0005
0.5	0.1235	10	2	2.5	6.5	25	0.1238	+0.0003