gangue filtered off, the filtrate was received in a No. 5 porcelain dish and exactly 5 grams of dry sodium carbonate added. The dish was then covered to prevent loss by spattering, and 4 cc. of formic acid (sp. gr. 1.22) were run in. The solution was boiled and filtered hot into the weighed and silvered platinum dish. The unwashed precipitate was then rinsed back into the porcelain dish by 6 cc. of 1:10 formic acid and the paper washed; 5 grams of sodium carbonate were then added and the solution boiled, filtered into the platinum dish and the paper well washed. Two basic formate precipitations were found to be sufficient. To the contents of the dish were then added 2 cc. of the 1:10 formic acid and it was then heated nearly to boiling and electrolyzed. The deposits were excellent.

Blende taken. Gram.	Na_2CO_3. Gram.	HCOOH (sp. gr. 1.22). cc.	Amperes.	Volts.	Time. Minutes.	Zinc found.	
						Gram.	Per cent.
0.5000	5.5	4.8	5	9	25	0.3284	65.68
0.5000	5.5	4.8	5	9	25	0.3281	65.62
0.5000	5.5	4.8	5	9	25	0.3298	65.96
0.5000	5.5	4.8	5	9	25	0.3289	65.78
0.5000	5.5	4.8	5	9	25	0.3295	65.90

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, No. 87.]

ELECTROLYTIC SEPARATIONS POSSIBLE WITH A ROTATING ANODE.[1]

BY DONALD S. ASHBROOK.

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A YEAR ago, Exner,[2] working in this laboratory, demonstrated that by using a high current density and great pressure with a rotating anode it was possible to determine fourteen metals in the electrolytic manner much more rapidly than had ever been done previously. The deposits were, in all instances, most satisfactory. These results constituted an important advance in electrochemical analysis. The objection once put forward, that too much time was necessary in such work, was completely removed. Indeed, Exner's investigation has wholly revolutionized electro-analysis. However, there remained the question as to how far this procedure

[1] From the author's thesis for the Ph.D. degree.

[2] This Journal, **25**, 896.

would lend itself to the separations of the several metals. This point became the guiding thought in the investigation here presented.

The apparatus and method of procedure have been fully described and amply developed by Exner, so that they need not be again entered upon, but the separations which were successful and have value will now be described in such detail as to enable others to repeat them with certainty of success.

COPPER.

I. From Aluminum.

(*a*) *In Sulphuric Acid Solution.*—Dilution, 125 cc.; 0.1 cc. of sulphuric acid (sp. gr. 1.83); $N.D_{100} = 4$ to 5 amperes and 1 to 4.8 volts; time, ten minutes. Copper present, 0.2696 gram; aluminum, 0.2500 gram; copper found, 0.2696, 0.2696 and 0.2695 gram. On increasing the amount of sulphuric acid to 1 cc., the deposit was much smoother and more uniform.

(*b*) *In Nitric Acid Solution.*—Dilution, 125 cc.; 1 cc. of nitric acid (sp. gr. 1.43); $N.D_{100} = 3$ amperes and 4 to 5 volts; time, twenty minutes. Copper present, 0.2874 gram; aluminum, 0.2500 gram; copper found, 0.2873, 0.2874 and 0.2874 gram. The conditions given here were most satisfactory for copper in this electrolyte. The speed may range from 300 to 400 revolutions per minute.

(*c*) *In Phosphoric Acid Solution.*—Dilution, 125 cc.; 10 cc. of phosphoric acid (sp. gr. 1.085); 50 cc. of 10 per cent. solution of Na_2HPO_4; $N.D_{100} = 5$ amperes and 6 volts; time, ten minutes. Copper present, 0.2742 gram; aluminum, 0.2500 gram; copper found, 0.2741, 0.2742 and 0.2741 gram. These conditions gave the best deposits. They were spongy in appearance, but perfectly adherent and were washed with ease. On dissolving them in nitric acid and testing with an ammonium molybdate solution, a slight precipitate of ammonium phosphomolybdate was obtained in every case. The amount of phosphorus was so slight, however, that it would not affect the weight of the deposit materially.

II. From Antimony.

(*a*) *In Tartrate Solution.*—Dilution, 125 cc.; 8 grams of tartaric acid; 25 cc. of ammonia; $N.D_{100} = 5$ amperes and 5 volts;

time, ten minutes. Copper present, 0.2742 gram; antimony, 0.2500 gram. Nearly all of the antimony was precipitated with the copper.

III. From Arsenic.

(*a*) *In Ammoniacal Solution.*—Dilution, 125 cc.; 25 cc. of ammonia; 2.5 grams of ammonium nitrate; $N.D_{100} = 5$ amperes and 7 volts; time, fifteen minutes. Copper present, 0.2742 gram; arsenic, 0.2500 gram; copper found, 0.2740, 0.2741 and 0.2741 gram. The deposit was dark in color, smooth and adherent.

(*b*) *In Nitric Acid Solution.*—The conditions were the same as were used in the separation of copper from aluminum. Copper present, 0.2742 gram; arsenic, 0.2500 gram; copper found, 0.2741, 0.2742 and 0.2742 gram.

IV. From Cadmium.

(*a*) *In Nitric Acid Solution.*—The same conditions were used as in the separation of copper from aluminum. Copper present, 0.2742 gram; cadmium, 0.2500 gram; copper found, 0.2742, 0.2742 and 0.2742 gram.

V. From Chromium.

(*a*) *In Sulphuric Acid Solution.*—The same conditions were used as in the separation of copper from aluminum. Copper present, 0.2890 gram; chromium, 0.2500 gram; copper found, 0.2890, 0.2891 and 0.2890 gram. Better deposits were obtained by starting with a current of 3 amperes, increasing gradually to 5 amperes.

(*b*) *In Nitric Acid Solution.*—The same conditions were used as in the separation of copper from aluminum. Copper present, 0.2874 gram; chromium, 0.2500 gram; copper found, 0.2874, 0.2875 and 0.2874 gram. If the current was allowed to run above 3 amperes, the deposit weighed too high. A blank was run with chromium alone under the same conditions. It gave 0.0022 gram of a metal showing all the tests for chromium.

(*c*) *In Phosphoric Acid Solution.*—The same conditions were used as in the separation of copper from aluminum. Copper present, 0.2742 gram; chromium, 0.2500 gram; copper found, 0.2742, 0.2740 and 0.2742 gram. Slight traces of phosphorus were detected in the deposits.

VI. From Cobalt.

(*a*) *In Nitric Acid Solution.*—The same conditions were observed as in the separation of copper from aluminum. Copper present, 0.2874 gram; cobalt, 0.2500 gram; copper found, 0.2875, 0.2874 and 0.2874 gram. Cobalt was partially precipitated in the sulphuric acid and phosphoric acid electrolytes.

VII. From Iron.

(*a*) *In Sulphuric Acid Solution.*—The same conditions were used as in the separation of copper from aluminum. Copper present, 0.2696 gram; iron, 0.2500 gram; copper found, 0.2694, 0.2695, 0.2696, 0.2696 and 0.2695 gram.

(*b*) *In Nitric Acid Solution.*—The same conditions were observed as in the separation of copper from aluminum. Copper present, 0.2874 gram; iron, 0.2500 gram; copper found, 0.2873, 0.2875 and 0.2874 gram.

(*c*) *In Phosphoric Acid Solution.*—The same conditions were used as in the separation of copper from aluminum. Copper present, 0.2742 gram; iron, 0.2500 gram; copper found, 0.2743 0.2741 and 0.2742 gram; with 8 amperes in five minutes, Cu = 0.2741 gram. Slight traces of phosphorus were found in the deposits of copper.

VIII. From Lead.

(*a*) *In Nitric Acid Solution.*—The results were low, as lead seems to hold back the last traces of copper.

IX. From Magnesium.

(*a*) *In Sulphuric Acid Solution.*—The same conditions were used as in the separation of copper from aluminum. Copper present, 0.2696 gram; magnesium, 0.2500 gram; copper found, 0.2696 0.2696 and 0.2695 gram.

(*b*) *In Nitric Acid Solution.*—The same conditions were used as in the separation of copper from aluminum. Copper present, 0.2874 gram; magnesium, 0.2500 gram; copper found, 0.2874 0.2874 and 0.2875 gram. If the current was too high, a white deposit was obtained which dissolved in sulphuric acid without effervescence. A neutral solution of magnesium nitrate, acidified with 1 drop of nitric acid and electrolyzed with a current of 2 to amperes and 15 volts for twenty minutes, gave a white coating weighing 0.0334 gram.

(*c*) *In Phosphoric Acid Solution.*—The same conditions were used as in the separation of copper from aluminum. Copper present, 0.2742 gram; magnesium, 0.2500 gram; copper found, 0.2742, 0.2740 and 0.2742 gram.

X. From Manganese.

(*a*) *In Sulphuric Acid Solution.*—The same conditions were used as in the separation of copper from aluminum. Copper present, 0.2890 gram; manganese, 0.2500 gram; copper found, 0.2890, 0.2891 and 0.2890 gram.

(*b*) *In Nitric Acid Solution.*—The same conditions were observed as in the separation of copper from aluminum. Copper present, 0.2874 gram; manganese, 0.2500 gram. Copper found, 0.2872, 0.2874 and 0.2874 gram. Only a part of the manganese was deposited as peroxide on the anode, but floating particles were not observed in the liquid.

XI. From Nickel.

(*a*) *In Sulphuric Acid Solution.*—No satisfactory deposits were obtained. All conditions were tried. The nickel seemed to hold the copper back when they were present in equal amounts. When the copper was greatly in excess, it carried the nickel down with it.

(*b*) *In Nitric Acid Solution.*—See the thesis of Exner.

(*c*) *In Phosphoric Acid Solution.*—Nickel was partially deposited in this electrolyte.

XII. From Uranium.

(*a*) *In Sulphuric Acid Solution.*—The same conditions were used as in the separation of copper from aluminum. Copper present, 0.2890 gram; uranium, 0.2500 gram; copper found, 0.2889, 0.2890 and 0.2890 gram.

(*b*) *In Nitric Acid Solution.*—The same conditions were observed as in the separation of copper from aluminum. Copper present, 0.2742 gram; uranium, 0.2500 gram; copper found, 0.2742, 0.2741 and 0.2742 gram.

XIII. From Zinc.

(*a*) *In Sulphuric Acid Solution.*—Dilution, 125 cc.; 1 cc. of sulphuric acid (sp. gr. 1.83); $N.D_{100} = 3$ to 5 amperes and 5 volts; time, ten minutes. Copper present, 0.2890 gram; zinc, 0.2500 gram; copper found, 0.2890 gram, 0.2889, 0.2889, 0.2890 and 0.2888 gram. The current was increased gradually. The deposits were excellent.

(*b*) *In Nitric Acid Solution.*—See the thesis of Exner.

(*c*) *In Phosphoric Acid Solution.*—The same conditions were observed as in the separation of copper from aluminum. Copper present, 0.2635 gram; zinc, 0.2500 gram; copper found, 0.2635, 0.2633 and 0.2634 gram. Slight traces of phosphorus were found in the deposits of copper.

CADMIUM.

I. From Aluminum.

(*a*) *In Sulphuric Acid Solution.*—Dilution, 125 cc.; 1 cc. of sulphuric acid (sp. gr. 1.83): $N.D_{100} = 5$ amperes and 5 volts; time, ten minutes. Cadmium present, 0.2727 gram; aluminum, 0.2500 gram; cadmium found, 0.2728, 0.2727 and 0.2727 gram. The deposits were excellent, although slightly spongy, but perfectly adherent.

(*b*) *In Phosphoric Acid Solution.*—Dilution, 125 cc.; 10 cc. of phosphoric acid (sp. gr. 1.083); 50 cc. of a 10 per cent. solution of disodium hydrogen phosphate; $N.D_{100} = 5$ amperes and 7 volts; time, ten minutes. Cadmium present, 0.3032 gram; aluminum, 0.2500 gram; cadmium found, 0.3031, 0.3032 and 0.3032 gram. These deposits all showed slight traces of phosphorus.

II. From Chromium.

(*a*) *In Sulphuric Acid Solution.*—A beautiful silver white crystalline deposit of cadmium was obtained, which always weighed low.

(*b*) *In Phosphoric Acid Solution.*—The same conditions were observed as in the separation of cadmium from aluminum. Cadmium present, 0.3600 gram; chromium, 0.2500 gram; cadmium found, 0.3603, 0.3600 and 0.3600 gram.

III. From Cobalt.

(*a*) *In Sulphuric Acid Solution.*—Cobalt was partially precipitated in this electrolyte, and also in a phosphoric acid solution.

IV. From Iron.

(*a*) *In Sulphuric Acid Solution.*—The same conditions were used as in the separation of cadmium from aluminum. Cadmium present, 0.3032 gram; iron, 0.2500 gram; cadmium found, 0.3031, 0.3032 and 0.3032 gram.

(*b*) *In Phosphoric Acid Solution.*—The same conditions were used as in the separation of cadmium from aluminum. Cadmium present, 0.3032 gram; iron, 0.2500 gram; cadmium found, 0.3032, 0.3031 and 0.3032 gram.

V. From Magnesium.

(*a*) *In Sulphuric Acid Solution.*—The same conditions were observed as in the separation of cadmium from aluminum. Cadmium present, 0.2727 gram; magnesium, 0.2500 gram; cadmium found, 0.2727, 0.2728 and 0.2727 gram.

(*b*) *In Phosphoric Acid Solution.*—The same conditions were used as in the separation of cadmium from aluminum. Cadmium present, 0.2727 gram; magnesium, 0.2500 gram; cadmium found, 0.2725, 0.2727 and 0.2727 gram.

VI. From Manganese.

(*a*) *In Sulphuric Acid Solution.*—The same conditions were used as in the separation of cadmium from aluminum. Cadmium present, 0.3600 gram; manganese, 0.2500 gram; cadmium found, 0.3600, 0.3599 and 0.3600 gram.

(*b*) *In Phosphoric Acid Solution.*—The same conditions were used as in the separation of cadmium from aluminum. Cadmium present, 0.3600 gram; manganese, 0.2500 gram; cadmium found, 0.3600, 0.3601 and 0.3600 gram.

VII. From Nickel.

(*a*) *In Sulphuric Acid Solution.*—The same conditions were used as in the separation of cadmium from aluminum. Cadmium present, 0.2727 gram; nickel, 0.2500 gram; cadmium found, 0.2727, 0.2727 and 0.2726 gram.

(*b*) *In Phosphoric Acid Solution.*—The nickel was partially precipitated in this electrolyte.

VIII. From Zinc.

(*a*) Zinc always came down with the cadmium in sulphuric acid solution and also in the phosphoric acid solution.

SILVER.

From Aluminum.

(*a*) *In Nitric Acid Solution.*—Dilution, 125 cc.; 1 cc. of nitric acid (sp. gr. 1.43); $N.D_{100}$ = 3 amperes and 3.5 volts; time, fifteen minutes. Silver present, 0.2600 gram; aluminum, 0.2500 gram; silver found, 0.2600, 0.2599 and 0.2600 gram. The deposits obtained in this electrolyte were very poor. The addition of ammonium nitrate helped matters but little. Great care was necessary in washing not to lose some of the deposit.

With the conditions given for the separation of silver from aluminum, the former was quantitatively separated from cadmium, chromium, cobalt, iron, lead, magnesium, manganese, nickel and zinc.

It was also tried to effect the separation of silver from a number of other metals in a potassium cyanide electrolyte. No success was attained. The successful separations with mercury were those with aluminum and magnesium. Failures resulted in the case of iron, nickel, cobalt, zinc, manganese and cadmium. The electrolytes tried were sulphuric acid and nitric acid. Other separations are in progress.

ON THE STRUCTURE OF ALLOYS. PART I. ALUMINIUM ALLOYS.[1]

By William Campbell.

Received June 30, 1904.

THE ALLOYS OF COPPER AND ALUMINIUM.

Previous Investigations.—Richards[2] describes the color of these alloys and gives the melting-points as determined by Le Verrier. He states that the natural compounds of aluminium and copper are those with the formulas $AlCu_3$ and Al_2Cu_3, and goes on to describe them. He says that the sharp fall in the melting-point at 37.5 per cent. aluminium indicates the alloy Al_3Cu_2, and remarks that it is a singular fact that the addition of copper to aluminium, in amounts up to 10 per cent., *lowers* the melting-point of the latter about 4° for every per cent. of copper present.

If the figures given by Le Verrier be plotted, we have a curve showing a drop to a minimum from pure copper to the 7.5 per cent. aluminium alloy, followed by a rise to a summit at the 10 per cent. alloy, then a sudden drop (with two slight halts) from this point at

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[1] Read before the New York Section of the American Chemical Society, January 8, 1904.

[2] "Aluminum," p. 535, et seq (1896 ed.).