Section of Physics and Chemistry.

Quantitative Separation of Tin from Manganese, Iron and Chromium by Electrolysis.

BY M. N. PUSCHIN.

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W. J. Williams, F. I. C.

There has been given in one of the preceding memoirs* a process for the quantitative separation of tin from nickel and cobalt, based on the property of these latter of not separating from solutions acidified with oxalic acid.

À priori it seems probable that iron, as the third metal of the iron group, as well as manganese and chromium, very close in the system to the three preceding metals, would not separate from solutions acidified with oxalic acid, and would thus permit their quantitative isolation from tin.

These suppositions were completely realized as far as regards iron and manganese, and partially in regard to iron granting the property of the latter of forming oxalates of the protoxides as well as of the oxides.

SEPARATION OF TIN FROM COMBINATIONS OF THE PROTOXIDES OF IRON AND OF MANGANESE.

The oxalates of the protoxides of iron and of manganese are completely analogous to those of nickel and cobalt; they are difficultly soluble in solutions acidified with oxalic acid; they give precipitates of a bright yellow color for iron and whitish for manganese, if the solution is heated nearly to boiling. Like

*Journal de la Société Physico-Chimique Russe, XXXVII, 828.

nickel and cobalt, neither the iron nor the manganese will be separated by the current from a solution in equilibrium with these precipitates. This is shown by the following experiment: To 25 c.c. of a solution of iron sulphate or manganese sulphate, containing about 0.5 gram of iron or of manganese, are added 25 c.c. of an acid solution of ammonium oxalate (saturated at room temperature) and 100 c.c. of a similarly saturated solution of oxalic acid; on heating the liquid nearly to boiling, it gave a precipitate of oxalate of protoxide of iron or of manganese. After the solution has been allowed to stand a while, the liquid is submitted to electrolysis, at the room temperature. Here are the results tabulated:

TABLE I.

Experiment.	Weight of the Cathode before experiment.	Tension of the Electrodes.	Density of the Current per square decimeter.	Duration of the Experiment.	Weight of Cathode after experiment.
With manganese—					
	{ 13.1764	3.2 volts	2.5 amperes	2 hrs. 35 min.	13.1764
	{ 13.1764	4.2 "	4.0 "	1 " 25 "	13.1764
With iron—					
	{ 13.4234	3.2 "	4.5 "	2 " 50 "	13.4234
	{ 12.4234(?)	3.5 to 4.2 "	4.0 "	1 " 48 "	13.4234

It follows from the above table, that under the conditions therein indicated, the current will separate neither iron nor manganese from the solution. Since it is easy to separate tin quantitatively from acid solutions of binoxalate by ammonia binoxalate (Klassen's method), it is clear that it is also easy to separate tin quantitatively in this way from manganese and from iron where these exist in the solution as salts of protoxides.

However, it must be observed that in analyses iron is more frequently found in combinations of the oxide than of the protoxide; since the combinations of protoxide easily change to combinations of oxide, without introducing any new metal, such as bromine for example. That is why in studying the method of the electrolytic separation of tin from iron, the combinations (or salts) of iron oxide should be especially considered. The same is true in a certain degree for manganese. But it is much more difficult to separate tin from the salts of iron oxide.

The binoxalates of iron (or of manganese) and of ammonium, differing from the salts of the protoxides, dissolve in a solution of oxalic acid; on the other hand, the salt of ferric oxide, under the influence of the cathode current, easily decomposes into a salt of

the protoxide, which being insoluble in oxalic acid, precipitates in part at the bottom of the cell and in part envelopes the cathode, thus preventing the regular precipitation of the tin. The different attempts made to find a means of solving this difficulty have not hitherto given any satisfactory results; therefore the problem of the separation of tin from iron can be considered as only half solved, especially in respect to iron protoxide.

SEPARATION OF TIN FROM COMPOUNDS OF MANGANESE OXIDE.

The question of the separation of tin from compounds of manganese oxide presents a more favorable aspect. In the presence of a sufficient quantity of oxalic acid, if the tension does not exceed 3 volts, under the experimental conditions indicated above, and the density of the current is not too great, the manganese is not deposited on the cathode, neither as metal nor as an insoluble oxalate of the protoxide, so its complete separation from tin is possible. This follows from the following experiments:

TABLE II.

Experiments.	Quantity taken for analyses.	Tension at the electrodes. Volts.	Density of current per sq. decimeter. Amperes.	Result.	Per cent
1 {	Tin (Sn).....0.4269 gr.	2.2 to 2.6	0.8 to 1.0	Sn 0.4260	98.79
	Manganese (Mn)...0.5 gr.				
2 {	Tin (Sn).....0.4634 gr.	2.2 to 2.9	0.8 to 1.0	Sn 0.4623	99.76
	Manganese (Mn)...0.5 gr.				
3 {	Tin (Sn).....0.5253 gr.	2.2 to 2.8	0.8 to 2.0	Sn 0.5244	99.83
	Manganese (Mn)...0.7630 gr.				
4 {	Tin (Sn).....1.0761 gr.	2.2 to 2.9	1.5 to 3.0	Sn 1.0760	99.99
	Manganese (Mn)...0.5 gr.				

From the above table it is evident that the method given for the electrolytic separation of tin from manganese gives perfectly satisfactory results. It must be particularly noticed that when half way through the electrolysis it is desirable to add 5 to 10 grams of oxalic acid, that the solution may remain sufficiently acid. Then, as has been said above, the tension of the electrodes must not be increased above 3 volts, or, under these conditions, traces of manganese may be deposited. The density of the current should not be too great; for example, it should not exceed 3 to 4 amperes to the square decimeter, for the too rapid disengagement of hydrogen at the cathode can cause (though only to a small extent) the reduction of the salt of manganese oxide to an insoluble salt of protoxide, which is assuredly not to be desired.

SEPARATION OF TIN FROM CHROMIUM.

The separation of these two metals is the easiest and the most complete of all. The chromium is not deposited by the current in a solution acidified with oxalic acid. Experiments prove it.

About 5 grams chromium were dissolved in a mixture of hydrochloric acid and bromine. As in the preceding experiments the solution was neutralized with ammonia, and 25 c.c. of a solution of ammonium oxalate, saturated at room temperature, and 100 c.c. of a similar solution of oxalic acid were added, after which the liquid was electrolyzed:

TABLE III.

Weight of Cathode before experiment.	Tension of electrodes.	Density of Current per square decimeter.	Duration of experiment.	Weight of Cathode after experiment.
13.6609 gm.	2.9 to 4 volts	4.8 to 5.6 amperes	1 hr. 20 min.	13.6609 gm.
13.6609 gm.	5 "	9.2 "	2 " 25 "	13.6606 gm.

These two experiments show clearly that the chromium does not separate from the solution under these conditions. Accordingly about 0.5 gm. tin and approximately as much chromium were dissolved in a mixture of hydrochloric acid and bromine; to the neutralized solution 25 c.c. of a solution of ammonium oxalate, saturated at room temperature, were added and 100 c.c. of a similarly saturated solution of oxalic acid, all the liquid diluted with about 200 or 250 c.c. of water was electrolyzed. The results are given in

TABLE IV.

	Quantities taken for analyses.	Tension of the electrodes.	Density of Current per sq. centimeter.	Result.	Per ct.
1.	{ Tin (Sn) 0.5518 gm. Chromium (Cr) . . 0.58 gm. }	2.5 volts	1.2 amperes	0.5505 gm.	99.77
2.	{ Tin (Sn) 0.5090 gm. Chromium (Cr) . . 0.5 gm. }	4.0 "	5 "	0.5089 gm.	99.98
3.	{ Tin (Sn) 0.5516 gm. Chromium (Cr) . . 0.53 gm. }	3.9 "	5 "	0.5514 gm.	99.96

This table shows clearly a very perfect separation of tin and chromium by the method described, and the results obtained for tin are very satisfactory.

ELECTROLYTIC DETERMINATIONS.

The following is a resumé of the work which forms part of the "Contributions of the John Harrison Laboratory of Chemistry."

They treat of the electrolytic charge and of the electrolytic separation of metals, using a rotary anode. This anode, introduced by Exner, permits of very rapid work.

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J. R. Withrow has studied the electrolytic precipitation of gold from gold chloride, in the presence of potassium cyanide and sodium sulphide; he used Ingham's* apparatus, and the precautions laid down by Exner† were followed in the experiments with cyanide.

The first trials confirmed Exner's observations, showing, nevertheless, a smaller minimum of time than he indicated. The deposits, washed without interrupting the current, were of a beautiful yellow color, and formed very adherent microscopic needles.

The following table gives a series of trials undertaken with the object of ascertaining the minimum of time necessary for a total precipitation:‡

Nos.	Weight of gold present in gms.	K C N in gms.	Dilution in c.c.	Current in amperes.	Volts.	Time in minutes.	Weight of gold collected in gms.
1	0.2754	2.5	80	5	} 8.0 to 7.0	10	0.2746
2	0.2754	2.5	80	5		5	0.2706
3	0.2754	2.5	80	5	7.6 to 6.7	6	0.2720
4	0.2754	2.5	80	5	7.5 to 6.7	8	0.2754
5	0.2754	2.5	80	7	9.5 to 9.0	7	0.2748
6	0.2754	2.5	80	10	} 11.5 to 13.0	2	0.2667
11	0.2754	2.5	80	15		4	0.2750
12	0.2754	2.5	80	12	19.0 to 12.0	3	0.2621
13	0.2754	2.0	55	12-10	21.0 to 18.0	3	0.2742

This shows that eight minutes are sufficient with a current of 5 amperes, seven with one of 7 amperes, and four minutes with a current of 15 amperes.

A second series shows that with the same experimental conditions, it is not necessary to exceed 10 amperes, as a stronger current causes ebullition of the electrolyte.

Withrow has made, under the conditions he found most favorable, two series of experiments with solutions containing 0.25

*Journal of Amer. Chem Soc'y, XXVI, 1269.

†Journal of the Amer. Chem. Soc'y, XXVI, 1256.

‡Experiments 7 to 10 were excluded, as the author considered them inexact. Further, in experiment 11 he said he experimented with a current of 15 amperes, while the table only stated 10. I have re-stated this figure.

gram and 0.5 gram of gold; the latter are grouped in the following table:

Nos.	Weight of gold present in gms.	K C N in gms.	Dilution in c.c.	Current in amperes.	Volts.	Speed per minute.	Time in minutes.	Wt. of gold found in gms.
1	0.522	5	60	10	10.0 to 8.0	800	10	0.5216
2	0.522	5	60	10.0 to 10.2	10.0 to 7.3	800	12	0.5226
3	0.522	2.5	55	10.0 to 10.8	14.5 to 9.6	800	10	0.5222
4	0.522	2.5	55	10.0 to 10.3	14.0 to 9.4	810	12	0.5234
5	0.5465	3.5	60	10.0 to 10.5	8.3 to 7.0	790	12	0.5461
6	0.5465	5	60	10.0 to 10.2	9.3 to 8.3	790	1	0.1891
7	0.5465	5	60	10.5 to 10.5	8.3 to 7.0	800	3	0.4341
8	0.5465	5	60	10.0 to 10.3	9.6 to 7.1	825	5	0.5286
9	0.5465	5	60	10.0	8.6 to 6.7	780	7	0.5437
10	0.5465	5	60	10.3 to 10.0	8.3 to 6.3	790	11	0.5468
11	0.5465	5	60	10.0	7.8 to 6.8	790	12	0.5467

Experiments 1 and 2 show the precipitation is complete in from 10 to 12 minutes; 3 was made to show the effect of decreasing the quantity K C N; in this case it formed a deposit on the anode like yellow pollen, soluble in concentrated hydrochloric acid. Withrow obtained this deposit in his control experiments with a fixed anode when the precipitation lasted more than two hours.

Withrow obtained very good results by replacing potassium cyanide by sodium sulphide; but to work with this mixture it is necessary to put the sulphide first in the electrolytic cell and not to add the chloride until the anode is in motion. The results of experiments with a solution containing 0.25 grams of gold were within a trifle the same whether using cyanide or sulphide. In the latter case 0.5 gram of gold was deposited in twelve minutes.

Exner was the first to use the rotatory anode for the determination of tin. L. Witmer* used this method in the case where the electrolyte was ammonium sulphide. The ammonium sulphide was run from a burette into the electrolytic cell, then the salt of tin was introduced, and then sufficient water to make up a total volume of 100 c.c. was added. The anode was then put in motion and the current sent through the apparatus. The deposits of tin were washed with water, then alcohol and then ether. The following table gives the results obtained with stannic chloride; the added water was raised to boiling; the deposited tin, weighing 0.5 gram, was gray and crystalline; the anode revolved at a speed of

*Journal of the Amer. Soc'y. 1907, XXIX, 473.

350 to 400 revolutions per second. It was noticed that there was a very rapid precipitation of tin during the first ten minutes, then a sudden fall lasting during the deposition of the last traces of the metal:

Quan. of sulphide		Time in		Tin col- lected in		Quan. of sulphide		Time in		Tin col- lected in	
Nos.	in c.c.	Amp's.	Volts.	minutes.	gms.	Nos.	in c.c.	Amp's.	Volts.	min's.	gms.
1	25	5	7.5	30	0.5069	9	20	5	9	2	0.1275
2	25	5	8.0	30	0.5067	10	20	5	9	3	0.1922
3	20	5	9.0	30	0.5070	11	20	5	9	4	0.2475
4	20	5	9.0	20	0.5067	12	20	5	9	5	0.2927
5	20	5	9.0	20	0.5064	13	20	5	9	10	0.4796
6	20	5	9.0	20	0.5070	14	20	5	9	15	0.7917
7	15	5	10.0	25	0.5067	15	20	5	9	20	0.5070
8	20	5	9.0	1	0.0704						

When the weight of tin collected is one gram or over, the results are very high. This does not appear to be due to occluded water. Witmer has electrolyzed solutions of variable richness in tin and found that there was nothing occluded so long as the deposit did not exceed 0.8 gram, but above this weight the quantities of tin deposited were too high. He concluded that when using a rotating anode, and ammonium sulphide as the electrolyte, tin could be determined rapidly; that the deposit of tin was produced more rapidly by heating the electrolyte, but the presence of polysulphides must be avoided, as they exercise a retarding influence.

Julia Langness* used a different anode from Exner, whose, as is known, was of a spiral form. The new anode consists of a platinum cap (or cover) seven centimeters in diameter and three centimeters deep, pierced with ten apertures each 1.8 c.m. long and 0.5 c.m. wide; the base is also pierced with a hole 1.3 c.m. in diameter; thus the free circulation of the liquid is assured. It should be equidistant from the walls of the cathode. The dilution should be weaker than with the spiral anode, for during the rotation of the anode, the liquid is forced into the space bounded by the cathode and the exterior wall of the anode. The volume of the electrolyte should not exceed 65 c.c. Julia Langness has studied the determination of different metals and has examined different electrolytic separations with the help of this anode.

In the case of copper the two anodes, spiral and cap, have been used in comparison with each other; among the numerous experiments that have been made we quote the following: 25 c.c. of cop-

*Journal of Amer. Chem. Soc'y, XXIX, 459.

per sulphate, to which were added 1.2 grams ammonium nitrate and 25 c.c. of ammonia, were diluted to 125 c.c., raised to boiling and electrolyzed; with a spiral anode (current of 9 amperes under 8 volts) the precipitation was completed in fifteen minutes; with the new anode (current of 17 amperes under 6 volts) 0.4824 grams of copper were deposited in six minutes. The solution contained 0.4967 gram of copper.

Silver has given good results; silver was precipitated from a solution of nitrate and redissolved in potassium cyanide and two grams of cyanide were added in each case, the electrolyte was then diluted, raised nearly to boiling and electrolyzed. The following results were obtained with Exner's anode (shown in the first table) and with the new anode (second table):

Nos.	Volts.	Amp's.	Time in minutes.	Wt. of sil- ver found in gms.	Nos.	Volts.	Amp's.	Time in minutes.	Wt. of sil- ver found in gms.
1	5	2.8	1	0.2046	5	5	2.8	5	0.5225
2	5	2.8	2	0.3391	6	5	2.8	7	0.5270
3	5	2.8	3	0.4858	7	5	2.8	10	0.5301
4	5	2.8	4	0.5043					

The precipitation was completed in ten minutes. Here are the results with the new anode, the differences of the current are largely due to the variation in the distance of the electrodes:

Nos.	Volts.	Amp's.	Time in minutes.	Wt. of sil- ver found in gms.	Nos.	Volts.	Amp's.	Time in minutes.	Wt. of sil- ver found in gms.
1	5	10	4	0.5304	4	5	9	2	0.5304
2	5	6	4	0.5306	5	5	9	1	0.5116
3	5	8	3	0.5306					

Some trials made with nickel showed that it was possible to precipitate 0.5 grams of metal from a solution containing ammonium sulphate in five minutes.

In the case of zinc, Julia Langness precipitated 0.25 gm. of metal in three minutes with a current of 13 amperes under 6 volts, the solution containing 4 grams of NaOH.

Platinum is deposited very well electrolytically, but it requires considerable time; this factor is considerably reduced by the new method, the metal is entirely precipitated from 25 c.c. of solution of potassium chloroplatinate with a current of 16 amperes under 10 volts.

But the best results are certainly obtained from palladium; the electrolyte was a solution of palladium ammonium chloride in

ammonia, 10 c.c. containing 0.268 gram of palladium. The following table gives a resumé of the experiments made, 20 c.c. of solution, to which 20 c.c. of boiling ammonia were added, and the whole then diluted to 60 c.c. with boiling water:

Nos.	Volts.	Amp's.	Time in minutes.	Wt. of pal- ladium found in gms.	No.	Volts.	Amp's.	Time in minutes.	Wt. of pal- ladium found in gms.
1	15	14	3	0.5358	3	17	11-20	1	0.4966
2	17	14-20	2	0.5357					

Rhodium deposits best from a solution of the double rhodium sodium chloride, $\text{Na}_2 \text{Rh Cl}_6$, to which a few drops of sulphuric acid are added. Julia Langness gives the figures grouped in this table:

Nos.	Volts.	Amp's.	Time in minutes.	Wt. of rho- dium found in gms.	Nos.	Volts.	Amp's.	Time in minutes.	Wt. of rho- dium found in gms.
1	7	8	15	0.0577	5	8	15	4	0.0573
2	7.5	8	10	0.0580	6	6.5	11	4	0.0563
3	8	9	10	0.0575	7	7	11	4	0.0567
4	8	9	7	0.0576					

The spiral anode was used in experiment 1. In the second part of the work Julia Langness studied the separation of different metals; 1st, gold from platinum and palladium; 2d, copper from platinum; 3d, silver from platinum, from copper, from nickel, from zinc, from a mixture of copper and platinum, and from copper in the alloy for coins.

Smith & MacCutcheon* have used the rotatory anode in a most interesting manner. It was found that in electrolyzing a solution of an alkaline chloride, as neutral as possible, with a rotatory silver anode and a mercury cathode, a colloidal solution of the hydroxide could be produced. If, for example, a solution of cerium chloride is placed in Hildebrand's apparatus, and is electrolyzed by a current of 0.8 to 0.02 amperes under 8 or 10 volts, a cerium amalgam is formed. This amalgam decomposes when all the chlorine has gone to the silver electrode, and the liquid in the interior compartment of the apparatus assumes a red color by transmitted light, it now contains a colloidal compound of cerium. This compound gives the following re-actions:

With ammonia—red-brown precipitate.

With sodium chloride—red-brown precipitate.

*Journal of the Amer. Chem. Soc'y, 1907, XXIX, 1455.

With Potassium hydrate—after the addition of a dilute solution; the false solution assumes a pale brown tint, no precipitate; after treatment with permanganate and ammonia, a brown precipitate forms resembling cerium hydroxide.

Potassium chromate—red-brown precipitate.

Potassium iodide—red-brown precipitate.

Stannous chloride—red-brown precipitate.

Hydrogen peroxide—red-brown precipitate.

Hydrogen peroxide and ammonia—yellow precipitate, resembling hydrated cerium dioxide.

This red-brown precipitate which is formed when a salt is added to the mock solution is a mixture of oxides.

If the electrolysis is made with a rotary anode, no colloid is formed but a white precipitate of ferrous hydroxide appears. The colloid forms best with a difference of potential of 8 volts. With a smaller voltage (from 3 to 5 volts) nothing is produced; with a greater, there is a rapid precipitation.

False solutions of hydroxides can also be produced by the electrolysis of the chlorides of lanthanum, neodymium, praseodymium and yttrium; also of ferric chloride.

The electrolysis of a solution of aluminum chloride gives, almost at once, a white, gelatinous precipitate; the filtrate is opalescent and remains so several weeks. Sodium chloride gives a precipitate soluble in sodium hydrate. Chromium chloride, using a current of 0.9 amperes under 5 volts, seems to form a colloid, sodium chloride precipitating chromium hydroxide.

These are the only chlorides with which Smith & MacCutcheon obtained good results. It appears that colloids can only be obtained from the sesqui-chlorides.

ABRASIVE GARNET PRODUCTION IN 1906.

The production of abrasive garnet in the United States in 1906 amounted to 4650 short tons, valued at \$157,000. This falls short by 400 tons in quantity but exceeds by \$8,905 in value the production in 1905, which was 5050 short tons, valued at \$148,095. The average price per ton was \$33.75, which is the highest since 1902, and a large increase over the average in 1905—\$29.32. The production came chiefly from New York, a part coming from Pennsylvania.

No production of garnet was reported from North Carolina in 1905, but reports published in the mid-summer of 1907 indicate that the output for this year will be large, as the mine in Madison County is being operated with an estimated production of 125 tons of garnet a month. The product of this mine is used chiefly for abrasive purposes, though several very fine, clear gem stones are said to have been found.