

Extra labor, one man at bullion melting to assist superintendent, laborers for clean-up and shipping residue, etc., mechanics for special work occasionally.

136,519.5 pounds sulphides contained 572,544.45 fine ounces of silver.

PRODUCT RETURNED.

	Fine ounces silver.	Per cent. total silver.
Fine bullion, free from gold.....	551,329.89	96.29
Residue.....	15,773.41	2.76
Cleanings.....	5,328.87	0.93
On hand.....	2,191.09	0.38
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Total.....	574,623.26	100.36
Plus clean-up.....	2,078.81	0.36

All weights of sulphides and products, excepting one covering less than 200 ounces, and all the assays are the originals made by the Daly Mining Company.

The advantages of this process are the phenomenal percentage of silver recovered, and that it is an entirely liquid one from beginning to end, so that there is no loss from handling dry products. There is no roasting to cause loss. A large percentage of the silver is recovered as very fine bars, ready to enter the market. It is so simple and so easily carried out, and the plant is so small and inexpensive that it can be installed at individual leaching works.

Finally, the cost of operating is small; in fact, the value of the bluestone recovered returns a large proportion of the operating expenses.

NOTES ON THE ELECTROLYTIC DETERMINATION OF IRON, NICKEL AND ZINC.

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THE experimental part of this work was undertaken in the spring of 1892. During the progress of the work various articles on the electrolytic department of these metals have been published. Some of these investigations are closely related to those carried out by us. As, however, they differ in some important particulars and as some observations have been made which, so far as we are aware, have not as yet been reported, it

seemed well to present the results obtained although some parts of the work are still incomplete.

In the method of manipulation, free use was made of the text-books of Classen and of Smith. A number of cells of the Grove-Tyndall form furnished the current. The current was controlled by means of a rheostat-box. The amperage was determined by means of a "Weston" volt-meter. The metals were deposited in platinum dishes of 300 cc. capacity.

In no case was any attempt made to separate metals by careful regulation of the voltage as the practical utility of such methods may be doubted till the literature of the subject is more copious.

I. THE ELECTROLYTIC DEPARTMENT OF IRON.

The method of Classen and V. Reiss¹ for the determination of the metals in their double oxalate solutions, a method which gives such admirable results in most determinations, cannot be applied with the same degree of convenience to iron, as a strong, current and a hot solution are necessary.

Smith and Muir² found that iron is very readily precipitated from ammonium tartrate solutions containing free ammonia. They found, however, that under such circumstances the iron contains carbon. Still tartrate solutions seemed to offer possibilities for quantitative determinations sufficient to warrant a fuller investigation of the subject.

Six grams of tartaric acid was dissolved in water and added to a solution of ferrous sulphate. The solution was then diluted to 150 cc. and rendered strongly alkaline with ammonia. The solution was then placed in a platinum dish, submitted to the action of a current of 0.115 ampere and four volts for six hours.

Taken 0.0477 gram iron. Weight found 0.0476 gram iron.

After weighing, the precipitate was dissolved in dilute sulphuric acid. A trace of the odor of hydrocarbons was present. The solution was then oxidized; precipitated with ammonia and determined in the usual gravimetric way. The weight of the iron oxide corresponded to 0.0465 gram of iron. The carbon present evidently compensated for the weight of the unprecipitated iron.

¹ *Ber. d. chem. Ges.*, 14, 1622.

² *J. Anal. Chem.*, 5, 488.

The following determinations were made in a similar manner :

No.	Current amperes.	Time. Hours.	Solution.	Iron taken. Gram.	Weight found. Gram.	Carbon by difference. Gram.
1	0.185	4	Strongly alkaline.	0.0620	0.0418
2	0.115	14	Strongly alkaline.	0.0476	0.0487	0.0011
3	0.115	6	Slightly alkaline.	0.0291	0.0294	0.0003
4	0.5	5	Strongly alkaline.	0.0476	0.0492	0.0018
5	0.5	5	Strongly alkaline.	0.0351	0.0364	0.0013

These figures show that strong currents and free ammonia are favorable to the precipitation of carbon. Hence attention was turned to the electrolysis of iron in neutral ammonium tartrate solutions.

To twenty-five cc. of an iron sulphate solution, sodium hydroxide was added till the greater part of the iron was precipitated. A dilute solution of tartaric acid was now added till the greater part of the precipitate was dissolved; five grams of ammonium tartrate were added and the whole diluted to 150 cc. The solution made up in this way was found to be exactly neutral to litmus. It was necessary to employ a stronger current than when free ammonia was present. The following determinations were made :

No.	Current. Amperes.	Time. Hours.	Iron taken. Grams.	Weight found. Grams.	Iron calculated from Fe_2O_3 . Grams.
1	0.4	6	0.0630	0.0634
2	0.4	6	0.0630	0.0635
3	0.5	4½	0.0630	0.0626	0.0620

In all cases carbon was detected in the precipitated iron.

Attention was next given to the determinations of iron in sodium tartrate solutions. In some cases free sodium hydroxide was present. The sodium salt conducts the current much better than the ammonium salt. The precipitation of iron proceeds satisfactorily for a time. After a little black spots appear. When a strong current is employed a white precipitate of ferrous carbonate forms on the deposited metal. Currents of two to four volts and of 0.05 to 0.1 amperes were employed to effect the separation of the iron from the solution. Towards the end of the precipitation carbon deposits rapidly. Vortmann,¹ by using

¹ *Chem. Centrbl.*, 1893, 1070.

currents of low voltage and precipitating the iron in fractions on weighed electrodes, seem to have avoided some of the unfavorable conditions above described. However the general deportment of iron in sodium tartrate solutions was so unpromising that the investigation was not carried further in this direction.

The question now presented itself: "Is the precipitation of carbon with iron peculiar to tartrates or may we expect it when other organic compounds are present?"

To answer this question a number of qualitative tests were made by adding to the iron solution before passing the current, solutions of sugar, alcohol, glycerol or of salts of formic, acetic, lactic, citric, succinic or benzoic acids. The currents employed were of the lowest voltage and amperage sufficient to give a deposit of several milligrams in the course of an hour. As ammonium oxalate gives no precipitate of carbon under any circumstances, so far as we are aware, this reagent was used to hold the iron in solution when necessary. The iron was used in the form of ferrous sulphate.

When formates were present in the absence of other organic compounds, no trace of carbon could be detected in the precipitated iron. In all other cases the precipitated iron contained carbon. In the case of citric acid a quantitative determination was made.

A solution of ferrous sulphate containing five grams of citric acid in the form of sodium and potassium salts with a little free acid was submitted for fourteen hours to a current of 0.2 ampere.

Taken 0.0726 gram iron. Weight found 0.0740 grain iron.

The absence of carbon in the case of oxalates and formates is explained by the fact that these compounds break up under the influence of the current giving off all carbon in the form of its highest oxidation product, *i. e.*, carbon dioxide.

In all cases the amount of carbon deposited was increased by the employment of stronger currents, but in no case was it possible to obtain a precipitate free from carbon, except in the case of formates and oxalates, when organic matter was present.

DETERMINATION OF IRON IN SOLUTIONS CONTAINING AMMONIUM OXALATE AND SODIUM BORATE.

We found that a slight modification of Classen's method

greatly facilitated the precipitation of iron. The following gave satisfactory results:

Twenty-five cc. of a solution of ferrous sulphate were taken, five grams of ammonium oxalate were added and brought into solution by the aid of gentle heat. Five cc. of a saturated solution of borax were now added and the entire solution diluted to 150 cc. A current of 0.02 ampere was allowed to act on the cold solution for sixteen hours. Towards the end of the operation the anode became covered with a slight brown coating. A slight brown deposit also appeared on the dish above the iron deposit. The following method was used to dissolve these deposits. Water was added until the surface of the liquid was raised above the brown deposit in the dish. The positive electrode was then brought in contact for a moment with the side of the dish thus short-circuiting the battery and generating considerable heat in the electrodes. This had the effect of liberating and dissolving the brown deposit. The current was allowed to act for half an hour longer when the dish was removed from the circuit, washed, dried and weighed.

The precipitate was perfectly adherent and showed no tendency to oxidize when washed with alcohol and ether. The following is a tabular statement of the results obtained :

No.	Ammonium oxalate. Grams.	Saturated borax solution. cc.	Current. Ampere.	Time. Hours.	Iron taken. Gram.	Iron found. Gram.
1	5	5	0.02	16	0.0938	0.0933
2	5	10	0.02	17	0.0938	0.0935
3	6	10	0.06	4	0.0938	0.0938
4	5	5	0.072	2	0.0938	0.0939
5	6	5	0.125	2	0.0938	0.0938

It will be seen from the above that the presence of borax facilitates the precipitation of iron in ammonium oxalate solutions. The cause of the appearance of the slight brown deposit and the extent to which it might cause an error in results will be investigated later.

II. THE DETERMINATION OF NICKEL.

The determination of nickel presented no difficulties. The greater part of the experiments with iron were performed in an

analogous way with nickel: in no case was carbon deposited with the nickel. When iron and nickel are deposited together as an alloy in the presence of organic compounds the nickel does not prevent the contamination of the precipitate with carbon.

III. DETERMINATION OF ZINC.

Nearly all the published methods for the electrolytic determination of zinc give fairly satisfactory results. The tendency of the metal to be deposited in a spongy condition and the liability to oxidation are the principal difficulties usually encountered.

The tendency to oxidation may be prevented by the presence of formic acid in the solution, which by the liberation of hydrogen with the metal exercises a reducing action.

By the electrolysis of zinc formate in the presence of formic acid Warwick¹ did not succeed in obtaining a complete deposit. The deposit is greatly influenced by the presence of sodium formate in the solution.

To a solution of zinc sulphate three cc. of formic acid were added and the solution partially neutralized with one gram of sodium carbonate. The entire solution was diluted to 150 cc. and placed in a current of 0.02 ampere for three hours.

Taken 0.0611 gram zinc. Found 0.0603 gram zinc.

In a similar manner the following determinations were made :

No.	Formic acid. cc.	Sodium carbonate. Gram.	Current. Ampere.	Time. Hours.	Weight taken.	Weight found.
1	4	1.5	0.125	3	0.0611	0.0612
2	5	1.0	1.000	3	0.0611	0.0611
3	5	1.0	0.050	3	0.0611	0.0611

The deposit adhered well, was compact and evenly distributed on the surface of the dish, the color was light gray, in some cases almost metallic in luster. As will be seen from the figures, a considerable variation in the strength of the current is allowable. This method is not allowable in the presence of the metals of the hydrogen sulphide group, as well as in the presence of iron, nickel and cobalt.

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¹ *Ztschr. anorg. Chem.*, 1, 291.