

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY,
No. 66.]

OBSERVATIONS ON THE ELECTROLYTIC PRECIPITATION OF ZINC AND OF COPPER.

BY EDGAR F. SMITH.

Received July 3, 1902.

THE suggestions made for the electrolytic determination of zinc are numerous. During the last few months the writer has had occasion to have some of them tried with the view of fixing the most advantageous working conditions, and in the course of this inquiry has noted what appears to him to be a matter of some analytical interest, *viz.*, that by employing as electrolyte a zinc salt solution containing an alkaline acetate very satisfactory results are obtainable in a comparatively brief period. It was Riché who first proposed this electrolyte, but it has not met with general use, perhaps because the proper working conditions were lacking. These are given in this communication. They have been repeatedly employed by different persons in this laboratory and have proved to be trustworthy. It was thought advisable, in the determinations made, to use as cathodes platinum dishes, upon the inner surface of which there was deposited a silver coating instead of one of copper.

WORKING CONDITIONS.

Potassium zinc sulphate	0.2002 gr. Zn.
Sodium acetate	1 gram.
Acetic acid (99 per cent.)	0.3 cc.
Total dilution	150 cc.
Cathode surface	100 sq. cm.
N.D. ₁₀₀	0.36-0.70 ampere.
Voltage	4-5.
Temperature	65° C.
Time	2 hours.

A flat platinum spiral was used as anode. The solution was heated to the required temperature before the current was passed through it. At the beginning the pressure equaled four volts. This was maintained for an hour when it was increased to five volts, with the corresponding rise in amperage. On exposing a clean silver surface, if there was no further deposition of zinc and the liquid showed an acid reaction, a few drops of ammonia water were added to the point of neutralization and the action of the

current continued for about fifty minutes longer, after which a portion of the liquid was tested for zinc by the ferrocyanide method.

It will usually be noticed after an hour's action that the solution seems to be filled with bubbles. This is the proper time to introduce the ammonia water for neutralization. When the metal has been fully precipitated the liquid should be siphoned off, and the zinc deposit be washed with water, alcohol and ether. It may then be dried and weighed. By this procedure these results were obtained:

Zinc potassium sulphate. Grams.	Zinc found. Gram.	Zinc required. Gram.
1.3598	0.2006	0.2002
1.3580	0.1997	0.2000
1.2621	0.1806	0.1862
1.2742	0.1879	0.1883

The deposits of metal were all very adherent, free from sponginess and light gray in color.

Very often questions are asked regarding the availability of electrolytic methods in determining the quantities of metals in technical products. The idea seems to exist that these methods may be satisfactory enough and yield good results so long as pure salts or mixtures of the same are used, but that equal success will probably not be reached if natural products are used. Perhaps it would be well to try all proposed methods in this particular. The writer has no doubt in his own mind as to the outcome. It will be wholly satisfactory. Believing this he had several samples of zinc blende decomposed rapidly with acid, the solutions evaporated to dryness, the residues taken up in water and a drop or two of sulphuric acid, when the liquids were filtered and mixed with sodium acetate and a little free acetic acid, after which they were electrolyzed with conditions like those previously recorded. The results were as follows:

Zinc blende. Gram.	Zinc found. Gram.	Zinc. Per cent.
0.2523	0.1681	66.62
0.2497	0.1662	66.56

These values agree closely with those obtained by the ordinary gravimetric methods, but it need scarcely be mentioned that the

time-factor is very greatly reduced, so that this procedure will recommend itself. The point might be raised that blends frequently contain iron; will it not contaminate the zinc? Such was not observed to be the case in any of the many determinations conducted in this way. Probably, if the quantity of iron present should be large there might serious doubt arise, but in all instances of that kind as the acetate solution is heated before the current is allowed to act, the basic iron acetate would appear, could be filtered out, and the solution then be treated as previously directed. The method surely deserves a thorough trial at the hands of analysts.

In this connection it may not be out of place to call attention to copper determinations in chalcopyrite made in the electrolytic way. This again is a natural product and with those who have felt uncertain how the copper determination by means of the current would result, it has been customary, after decomposition of the mineral, to precipitate the copper as sulphide, then dissolve it in nitric acid or in potassium cyanide and electrolyze. This is not necessary. After the mineral is decomposed, paying no attention to the sulphur, evaporate to dryness, take up the residue with a little sulphuric acid and water, and then proceed with the electrolysis, using such conditions as these:

Total dilution	150 cc.
Concentrated sulphuric acid.....	10 cc.
Temperature	60°-70°.
N.D. ₁₀₀	0.8-1.0 ampere.
Volts ..	2-3.
Time	1 hour, 30 minutes.

RESULTS.

Chalcopyrite. Gram.	Copper found. Gram.	Copper. Per cent.
0.2900	0.0963	33.20
0.2900	0.0969	33.41
0.5800	0.1932	33.31
0.5800	0.1936	33.37
0.5800	0.1936	33.37

The liquid siphoned off from the deposit of copper may be nearly neutralized with ammonia water and, after the introduction of ammonium oxalate, be electrolyzed at a temperature of 40°-65°, with a current of N.D.₁₀₀ = 0.5-1.0 ampere and 2-3.5 volts.

RESULTS.		
Chalcopyrite. Gram.	Iron. Gram.	Iron. Per cent.
0.5800	0.1746	30.10
0.5800	0.1750	30.17

The question has been asked whether it is not possible, in a case like that of chalcopyrite, to render the original solution of the mineral ammoniacal and, not regarding the precipitated ferric hydrate, proceed with the electrolytic deposition of the copper. Many have felt that there was danger of iron entering into the deposit of copper, while others have declared that such a condition was not to be feared. During the past winter numerous tests of this question have been made in this laboratory, working with chalcopyrite. It has been found that if platinum dishes be employed as cathodes to receive the copper, the latter has invariably been contaminated with iron, but that if platinum cylinders, dipping into the ammoniacal solution contained in beaker-glasses, were used for cathodes the copper deposited upon them was free from iron.

The writer has had the assistance of Messrs. J. H. Graham and F. E. Walker in the experimental part of this study and would here acknowledge his indebtedness to them.

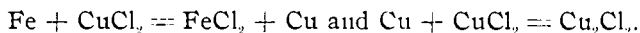
UNIVERSITY OF PENNSYLVANIA.

THE USE OF POTASSIUM-FERRIC CHLORIDE FOR THE SOLUTION OF STEEL IN MAKING THE DETERMINATION OF CARBON.

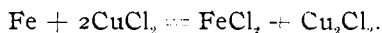
BY GEO. WM. SARGENT.

Received July 27, 1906.

THE reaction considered to take place when steel or iron drillings dissolve in potassium-cupric chloride is expressed thus:



This result expressed without indicating the intermediate reaction is written as follows:



The solution takes place more quickly and without any loss of carbon if hydrochloric acid (sp. gr. 1.2) is present in the ratio of 1 cc. to 13 cc. of the double chloride solution. The above equations do not contain the potassium chloride since the part enacted