

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF TEXAS.]

THE ELECTROANALYSIS OF SILVER WITH SOLUTIONS OF SILVER CHLORIDE IN AMMONIA.

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Received May 6, 1916.

A method for the quantitative electrodeposition of silver out of solutions of silver chloride in ammonia has not been published so far, but the use of this electrolyte appears to be very desirable, because it is likely to yield pure deposits while the cyanide electrolyte—the only other solvent for silver chloride heretofore employed in electroanalysis—produces impure deposits.

We have found that approximately 99.6% of the silver in an ammoniacal solution of silver chloride can be deposited by electrolysis in good form. It is merely necessary to increase the conductivity of the solution by adding enough of an ammonium salt (ammonium chloride) to the solution, and to electrolyze with a small current density at the ordinary temperature.

In order to deposit the small remnant of silver left in the electrolyte, the ammonia is neutralized with a slight excess of hydrochloric acid, and a weak reducing agent (oxalic acid) is added: from this electrolyte the remainder of the silver may be deposited completely and in good form. The presence of nitrates (or of nitric acid in the original mixture) does not affect the result.

Care must be taken to clean the platinum cathode thoroughly, to keep the current density small in order to avoid "burning" the deposit, and to wash and handle the electrode with the deposit *gently* to avoid knocking off the deposit. With a little care on these points, the determination is easily carried out and gives satisfactory results, as is shown below.

The following determinations were made with the electrolytic apparatus described in the foregoing paper by E. P. Schoch and D. J. Brown: Samples of pure sheet silver were dissolved in concentrated nitric acid and the silver was precipitated with a slight excess of hydrochloric acid. With several of the samples, the silver chloride was filtered, washed and dissolved in a slight excess of concentrated ammonia; and with others the original mixture (containing the excess of nitric acid) was treated with ammonia. About 20 g. of ammonium chloride and enough water were added to each mixture to bring the volume to approximately 150 cc. (enough to cover the electrodes), and the solutions were electrolyzed at room temperature with an initial amperage of 0.35 amp. (which with our apparatus required 1.1 volts between the electrodes). This voltage was kept constant until the current had dropped to zero: care had to be taken to reduce the current promptly while the metal was being deposited because the maximum allowable current density (which

cannot be exceeded without obtaining a dark and loosely adherent deposit) rapidly becomes less as the silver content of the solution becomes less. When the amperage had become practically zero, the voltage was allowed to rise gradually to 1.3-1.4 volts and electrolysis continued until a total of 25-30 minutes had elapsed. This period must necessarily be larger if the quantity of silver to be deposited is greater than that which we used.

Then, without disturbing the apparatus, about 3 g. of oxalic acid crystals were added to the solution, and enough concentrated hydrochloric acid to make the solution faintly acid to litmus paper. Without increasing the applied voltage, electrolysis was continued for about 20 minutes. Then the experiment was terminated, and the electrodes were washed and dried in the manner described in the preceding paper. The following results were obtained:

TABLE I.—DEPOSITION OF SILVER.

Silver present. G.	Found. G.	Error.	
		G.	%.
0.1595	0.1591	-0.0004	-0.25
0.5887	0.5886	-0.0001	-0.02
0.3704	0.3699	0.0005	-0.14
0.2958	0.2956	0.0002	-0.07
0.4030	0.4027	0.0003	-0.07
0.5139	0.5139	0.0000	0.0
0.2551	0.2551	0.0000	0.0

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[CONTRIBUTION FROM THE DEPARTMENT OF SOIL BIOLOGY OF THE OHIO AGRICULTURAL EXPERIMENT STATION.]

TITRAMETRIC DETERMINATION OF NITRITES.

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Received May 10, 1916.

The frequent necessity of determining nitrites in the investigation of the physiology of the process of nitrification, reveals the need of a satisfactory titrametric method for such determination.

Nitrite determinations are usually made by colorimetric methods. It would be more desirable to make nitrite determinations titrametrically and avoid the errors which are so often introduced in colorimetric methods, namely, errors of dilution, eye fatigue, color comparison and the individual error of the worker.

Historical.

The reaction of nitrous acid with hydriodic acid is well known: $2\text{HI} + 2\text{HNO}_2 \longrightarrow 2\text{H}_2\text{O} + 2\text{NO} + \text{I}_2$. Since this reaction proceeds quantitatively, titration of the liberated iodine with standard thiosulfate has been used as a titrametric method for determining nitrous nitrogen. The