into the circle of experimentation, but it is only now in the present—a period nearly forty years later—that interest is being taken in the determination of acidulous groups by the help of the current. To the writer, the possibilities that suggest themselves with other halides than those of the alkali and the alkaline earth metals seem great, and it is his hope that he may be permitted to continue studies in this direction for a little while longer.

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, NO. 71.]

METAL SEPARATIONS IN THE ELECTROLYTIC WAY.

BY EDGAR F. SMITH.

Received June 26, 1903.

THE purpose of this communication is to submit the results obtained in trying to effect the separation of silver, mercury and copper from selenium and tellurium. These gaps in electrochemical analysis existed with two exceptions, *viz.*, silver from selenium, and copper from tellurium, and as the separations were needed both for practical reasons and also to extend and complete the possible range of applicability of the current in analysis, they were tried with evident success, as shown in the sequel.

SILVER FROM SELENIUM.

(*a*) *In Alkaline Cyanide Solution.*—In the *Zeitschrift für anorganische Chemie*, 31, 393 and This Journal, 25, 225, appeared Meyer's account of a method of determining the atomic weight of selenium, which consisted in electrolyzing silver selenite in cyanide solution. The results were so very concordant that there can be little question as to the completeness of the separation of the two metals. Working conditions were not given by Meyer, hence it was thought advisable to give those which in this laboratory proved very satisfactory for this particular separation. They appear in the following lines:

Silver present	0.1341 gram.
Sodium selenate present	0.2500 gram.
Potassium cyanide	3 grams.
Total dilution	150 cc.
$N.D_{100}$	0.02 ampere.
Pressure	2.5 volts.
Temperature	60° C.
Time	6 hours.
Silver found	0.1333 gram.

In another trial, with conditions like those just described, the silver which was precipitated weighed 0.1334 gram. These slight differences from the required amount of metal seemed to show that perhaps the current might well be increased toward the end of the experiment. This was done in two instances, from 0.03 ampere and 2.5 volts to 0.05 ampere and 3.5 volts. In consequence, the precipitated silver weighed 0.1340 gram instead of 0.1341 gram; further, the period of precipitation was reduced to three hours. The deposit of silver was pure white in color. The washing and drying were performed as so frequently mentioned in former accounts of silver determinations, and the details need not be given here.

(*b*) *In Nitric Acid Solution.*—The separation proving to be most satisfactory in an alkaline cyanide solution, the next step was to ascertain what would result in conducting it in the presence of an acid. The following conditions prevailed:

Silver present	0.1341 gram.
Sodium selenate present	0.2500 gram.
Nitric acid (sp. gr. 1.43)	1 cc.
Total dilution	150 cc.
$N.D_{100}$	0.015 ampere.
Pressure	1.25 to 2 volts.
Temperature	60° C.
Time	3 hours.

The silver deposit weighed 0.1342 gram. It was perfectly adherent and crystalline in appearance.

SILVER FROM TELLURIUM.

(*a*) *In Alkaline Cyanide Solution.*—It was believed that no difficulty would be met in making this separation with conditions similar to those pursued with silver from selenium in the same electrolyte. They were therefore tried. The precipitation of the silver proceeded very satisfactorily for an hour or more, then the deposit commenced to grow dark in color, and very soon black flakes appeared as a scum on the surface of the liquid and on the deposit as well. This behavior was always noticed, so that the efforts in this direction were abandoned. The attempt to separate mercury and copper from tellurium in cyanide solutions also resulted negatively. As will be observed below, their separation from selenium was most successful. By analogy, it would be expected that if silver, mercury and copper could be separated from

selenium in an alkaline cyanide bath, their separation from tellurium probably ought to follow as well under similar conditions. Here it did not. It is only another instance of cases where experiment alone can give the true answer.

(*b*) *In Nitric Acid Solution.*—

Silver present	0.1341 gram.
Sodium tellurate present	0.1344 gram.
Nitric acid (sp. gr. 1.43)	1 cc.
Dilution	150 cc.
$N.D_{100}$	0.01 to 0.015 ampere.
Pressure	1.25 to 2.0 volts.
Temperature	60° C.
Time	3 ½ hours.

The white crystalline deposit weighed 0.1344 gram.

In a second trial with like conditions the precipitated silver weighed 0.1341 gram.

MERCURY FROM SELENIUM.

(*a*) *In Alkaline Cyanide Solution.*—The example which follows demonstrated the applicability of the method:

Mercury present	0.1272 gram.
Sodium selenate present	0.2500 gram.
Potassium cyanide	1 gram.
Dilution	150 cc.
$N.D_{100}$	0.03 ampere.
Pressure	3 volts.
Temperature	60° C.
Time	5 to 6 hours.
Mercury found	0.1276 gram.

(*b*) *In Nitric Acid Solution.*—The conditions observed in the separation of silver from selenium will give most satisfactory results here.

MERCURY FROM TELLURIUM.

As previously observed, this electrolytic separation is not possible in an alkaline cyanide solution. It only remained, therefore, to ascertain whether it could be performed in a nitric acid solution. The trials were successful. One example will suffice to illustrate the most favorable conditions:

Mercury present	0.1272 gram.
Sodium tellurate present	0.2500 gram.
Nitric acid (sp. gr. 1.43)	3 cc.
Dilution	150 cc.

$N.D_{100}$	0.04 to 0.05 ampere.
Pressure	2 to 2.25 volts.
Temperature	60° C.
Time	5 hours.
Mercury found	0.1276 gram.

COPPER FROM SELENIUM.

(*a*) *In Alkaline Cyanide Solution.*—Two trials were made with conditions as follows:

Copper present	0.0745 gram.
Sodium selenate present	0.2500 gram.
Potassium cyanide	1 gram.
Dilution	150 cc.
$N.D_{100}$	0.2 ampere.
Pressure	3.5 to 4 volts.
Temperature	60° C.
Time	5 hours.
Copper found	(*a*) 0.0745 gram. (*b*) 0.0742 gram.

(*b*) *In Nitric Acid Solution.*—Just as in previous cases, all the results will not be given here. The conditions which proved most satisfactory were these:

Copper present	0.0745 gram.
Sodium selenate present	0.2500 gram.
Nitric acid (sp. gr. 1.43)	1 cc.
Dilution	150 cc.
$N.D_{100}$	0.05 to 0.08 ampere.
Pressure	2 to 2.5 volts.
Temperature	65° C.
Time	4 hours.
Copper found	(*a*) 0.0747 gram. (*b*) 0.0738 gram.

(*c*) *In Sulphuric Acid Solution.*—The quantities of copper and selenium present were the same as in the preceding separations. One cc. of concentrated sulphuric acid was added and the solution was electrolyzed with $N.D_{100} = 0.05$ to 0.10 ampere and 2 to 2.25 volts at a temperature of 65° C. The precipitated copper weighed 0.0743 gram instead of 0.0745 gram. The precipitation was finished in less than six hours.

COPPER FROM TELLURIUM.

The separation of these metals in cyanide solution, as already observed, failed. In nitric acid solution, they have been separated with perfect satisfaction.[1] It remained, therefore, to give the condi-

[1] Smith's "Electrochemical Analysis," 3rd edition, p. 134.

tions under which the two were separated with ease in the presence of sulphuric acid.

Copper present	0.0745 gram.
Sodium tellurate present	0.2000 gram.
Concentrated sulphuric acid	1 cc.
Dilution	150 cc.
$N.D_{100}$	0.05 to 0.1 ampere.
Pressure	2 to 2.25 volts.
Temperature	65° C.
Time	6 hours.
Copper found	(*a*) 0.0747 gram. (*b*) 0.0748 gram.

The writer has had the assistance of Mr. S. H. Ross in working out the details of these experiments, for which he would here acknowledge his indebtedness.

UNIVERSITY OF PENNSYLVANIA.

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THE RAPID PRECIPITATION OF METALS IN THE ELECTROLYTIC WAY.[1]

BY FRANZ F. EXNER.

Received July 5, 1903.

SEVERAL years ago experiments were made in this laboratory looking to the electrolytic separation of molybdenum from tungsten. The anode was made to rotate by means of a small electric motor,[2] the idea being to use high currents with a high speed of rotation of the anode, thus hastening the deposition and, by agitation of the electrolyte, overcoming certain disturbances which had arisen. In the particular case referred to, the results were not entirely satisfactory. The idea, however, was shortly after tried upon other metals with success and led to the present investigation. Klobukow[3] called attention to the agitation of the electrolyte, but never published any results. Gooch and Medway[4] recently described successful experiments made with copper, nickel and silver solutions by *rotating the cathode.*

The purpose of the present investigation was to note the results

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

[2] Smith's "Electrochemical Analysis," p. 77, third edition, 1902.

[3] *J. prakt. Chem.*, **33**, 475; **40**, 121.

[4] *Am. J. Sci.* [4], **15**, 320.