attention in this laboratory. Further, anodes other than silver are being employed to determine those best suited for the various anions.

In conclusion it may be noted.

1. As a rapid gravimetric method of analysis this procedure offers great advantages in time and in the fact of its allowing precipitation to take place without washing, filtration or ignition.

2. The simultaneous titration of the alkali makes it possible to determine two salts together, such as sodium chloride and sodium bromide. Or, by weighing the dry mixture beforehand, sodium and potassium chlorides can be determined and their respective amounts calculated with great accuracy and in less than an hour.[1] By weighing beforehand, titrating the alkali and weighing the halogen, sodium chloride, bromide and iodide could be determined in a mixture. The same principle would of course apply to compounds other than the halides.

3. The analysis of salts like sodium carbonate furnishes an interesting confirmation of the existence in solution of such an unstable group as CO_3 which can thus be made to attack metallic silver far more readily than nascent oxygen from the hydroxyl group.

4. Whereas the electro-analysis of salts for their metal ion has received great attention for many years, the hitherto neglected anion may now receive its share of investigation by this procedure, and a new field is opened up scarcely less extensive than that of metal determination.

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY.]

THE ELECTROLYTIC PRECIPITATION OF COPPER FROM AN ALKALINE CYANIDE ELECTROLYTE.[2]

BY ANNA L. FLANIGEN.

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The electrolyte generally used in the precipitation of copper, by the current is one containing nitric or sulphuric acid. It was the first electrolyte used with this metal and it serves well, not only when copper alone is under consideration, but it furnishes also an excellent medium in which to bring about separations of various metals. Further, an ammonium hydroxide electrolyte containing ammonium salts answers well. To these have been added the alkaline cyanide electrolyte. It recommends itself because from it the deposits of copper are most adherent and have beautiful lustre. There is never any tendency towards sponginess on the part of the metal deposit. Another point of interest is that as copper is often obtained in analysis in the form of sulphide, which is soluble in potassium or sodium cyanide, several steps in the analysis of copper minerals or ores

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[1] This has recently been done by Mr. McCutcheon in this laboratory.

[2] From the author's Ph. D. thesis, 1906.

can be omitted, and the time factor in this way be much reduced. However, the knowledge that potassium cyanide exerts a solvent effect upon platinum when under the influence of the current has disturbed the minds of analysts quite generally when the suggestion has been made to precipitate copper from a cyanide electrolyte, using at the time platinum anodes. The possibility that the latter may lose platinum which, in turn, would be co-deposited with the copper has tended to a disuse of the cyanide electrolyte in copper determinations. Indeed, Franz Spitzer[1], in an exhaustive study "Ueber das elektromotorische Verhalten von Kupfer und Zink gegenüber ihren cyankalischen Losungen," while granting that if consideration be given the solvency of platinum in alkaline cyanide, very good results for copper may be obtained, thinks that this electrolyte is superfluous for this metal, excepting in the matter of separations. By its use, however, some very important separations of copper have been executed. As it is in the Laboratory of the University of Pennsylvania that the cyanide electrolyte has met with most frequent application and has given such satisfactory results, it was but natural that an attempt should be made to learn the availability of this electrolyte, particularly in reference to its use with copper. Spitzer found that the solvent action of the cyanide on the platinum was most appreciable. He used quantities of potassium cyanide varying from 3.3 to 22 molecules for one molecule of copper sulphate. In all of his experiments he found a decrease from 0.2 to 1.8 mg. in weight on the part of the anode. He also introduced potassium carbonate or sodium carbonate with the cyanide solution, but discovered that they tended to restrain the deposition of metal. This was also observed on adding caustic potash. He finally used only the cyanide, remarking that the rapidity in the precipitation of the copper depended upon the rapidity with which the cyanide was oxidized at the anode.

In the present investigation the thought was first to ascertain the most satisfactory conditions for the deposition of the copper from the cyanide solution, to observe at the same time the rate of deposition, and to find under what condition platinum dissolved from the anode, and also the influence of time during which the cyanide might exert its solvent effect.

Another point of study was to ascertain the influence of the addition of definite volumes of ammonia water or ammonium carbonate solutions. Finally, the rotating anode was used, and, as will be seen, with decidedly satisfactory results.

The conclusion arrived at from the study of the various results is evident. Cyanide solutions of copper salts can be employed in the determination and separation of the metal. Solution of the anode does not take place under the conditions given, and the cyanide electrolyte must be regarded as wholly reliable.

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[1] Z. Elektrochem. (1905), Nos. 23 and 25.

In the first experiment slightly more potassium cyanide was used than really necessary for the solution of the copper cyanide. The liquid had the room temperature. The current ran five hours. The copper deposit was exceedingly bright and adherent. On allowing the current to act for a period of eighteen hours, the copper showed the presence of platinum; further, the anode suffered a loss in weight.

$CuSO_4$ Cu in grams.	KCN in grams.	N. D.$_{100}$ Amp.	Volts.	Temp.	Time in hrs.	Cu found in grams.
0.2031	1.5	0.21	4	28 C.	6	0.2031
0.2031	1.5	0.23	4	28 C.	18½	0.2034

Upon repeating the experiment with the preceding conditions, excepting to increase the temperature the results were:

$CuSO_4$ Cu in grams.	KCN in grams.	N. D.$_{100}$ Amp.	Volts.	Temp.	Time in hrs.	Cu found in grams.
0.2031	1.5	0.28	4	65 C.	1¾	0.2033
0.2031	1.5	0.48	4	65 C.	1½	0.2033

The copper deposits were brilliant in appearance. They contained no platinum. The anode sustained no loss.

The quantity of alkaline cyanide was now doubled. The electrolysis took place at room temperature. At the expiration of five hours the copper was fully precipitated and contained no platinum. On continuing the decomposition through a longer period, platinum made its appearance in the copper.

$CuSO_4$ Cu in grams.	KCN in grams.	N. D.$_{100}$ Amp.	Volts.	Temp.	Time in hrs.	Cu found in grams.
0.2031	3	0.05	4	28 C.	18	0.2035
0.2031	3	0.05	4	28 C.	5	0.2030

The application of heat to a solution containing so much alkaline cyanide appeared to develop paracyanogen about the anode and it interfered, seemingly, with the copper precipitation.

$CuSO_4$ Cu in grams.	KCN in grams	N. D.$_{100}$ Amp.	Volts.	Temp.	Time in hrs.	Cu found in grams.
0.2031	3	0.6	4	65 C.	1¾	0.2024
0.2031	3	0.54	4	65 C.	2	0.2025
0.2031	3	0.52	4	65 C.	2	0.2028

Upon further increasing the amount of alkaline cyanide, platinum was precipitated even from hot solutions and the loss in weight of the anode was quite appreciable.

$CuSO_4$ Cu in grams.	KCN in grams.	N.D.$_{100}$ Amp.	Volts.	Temp.	Time in hrs.	Cu found in grams.	Loss in Wt. of Pt.-anode.
0.2031	5	0.76	4	28 C.	18	0.2032	0.0016
0.2031	5	0.84	4	65 C.	3	0.2032	0.0013
0.2031	5	1.5	4	65 C.	4½	0.2031	0.0016

This dissolved platinum was found afterwards in the copper and its weight deducted from the weight of the deposit of the latter metal. These trials show that from heated solutions of copper salts, containing but a slight excess of alkaline cyanide there is no doubt of the complete precipitation of the copper, and what is better, no platinum is deposited with it.

The addition of ammonium carbonate to the alkaline cyanide electrolyte did not prove beneficial in any way. Numerous trials demonstrated this point beyond question. With varying amounts of ammonium hydroxide, however, in the alkaline cyanide, the results were decidedly encouraging, especially upon the application of heat to this electrolyte.

$CuSO_4$ Cu in grams.	K CN in grams.	NH_4OH in c.c.	N. D.$_{100}$ amp.	Volts.	Temp.	Time in hrs.	Cu found in grams
0.2015	1.5	10	1	5	65 C.	1	0.2014
0.2015	1.5	10	0.66	5	65 C.	1	0.2015
0.2015	1.5	10	0.98	5	65 C.	1	0.2015
0.2015	1.5	10	0.66	5	65 C.	1	0.2015

The ammonium hydroxide had the specific gravity 0.93 at 24°. The appearance of the copper deposits was all that could be desired. An increase in the volume of the ammonium hydroxide extended the length of the precipitation period; furthermore, the copper deposits tended to sponginess. The conditions recorded above never failed to yield satisfactory results. There was no loss in weight of the platinum anode, consequently no platinum in the deposit of copper.

A solution of copper sulphate was saturated with hydrogen sulphide. The copper sulphide was dissolved in just sufficient cyanide, ten cubic centimeters of ammonium hydroxide were added and the electrolysis conducted as previously outlined. The deposits of copper had a bright metallic lustre.

$CuSO_4$ Cu in grams.	K CN in grams.	NH_4OH in c.c.	N. D.$_{100}$ amp.	Volts.	Temp.	Time in hrs.	Cu found in grams
0.2013	1.5	10	0.98	5	65 C.	1½	0.2011
0.2013	1.5	10	0.92	5	65 C.	1½	0.2010

The ammonium-alkali cyanide, having proved successful with a stationary anode, trials were made when the latter was rotated. At first cyanide alone was used, but later ammonia was present.

$CuSO_4$ Cu in grams.	K CN in grams.	NH_4OH in c.c.	N. D.$_{100}$ amp.	Volts.	Temp.	Time in mins.	Cu found in grams
0.2030	1.5	..	7.4	10	65 C.	10	0.2024
0.2030	1.5	..	8.2	10	65 C.	10	0.2028
0.2030	1.5	..	7.2	10	65 C.	10	0.2026
0.2030	1.5	10	7.1	10	65 C.	10	0.2027
0.2030	1.5	10	10.	10	65 C.	10	0.2027
0.2030	1.5	10	7.6	10	65 C.	10	0.2027
0.2030	1.5	15	8.	10	65 C.	10	0.2027

The results were just as good when working with as much as 0.5 gram of copper. Even in such cases 10 cc. of ammonium hydroxide were sufficient.

Chalcopyrite was also decomposed,its copper precipitated as sulphide, this dissolved in alkali cyanide and the solution, in the presence of ammonia, electrolyzed with concordant percentage results. Platinum was constantly sought for but not found. The anodes were regularly weighed before and after their use, but showed no loss. Copper was successfully separated from iron—the quantity of the former being twice that of the latter. The same occurred when the quantity of iron greatly exceeded that of the copper.

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY.]

ELECTROLYTIC DETERMINATIONS AND SEPARATIONS WITH THE USE OF A ROTATING ANODE[1].

BY JULIA LANGNESS.

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The following paragraphs contain data obtained by the use of a rotating *dish* anode in the electrolysis of several metallic salt solutions. Curves accompany the various experiments to show more clearly the progressive deposition of metal.

The remarkably short period in which copper, silver, nickel and zinc are precipitated by the use of the *dish* anode leaves no doubt as to the superiority and advantage of electrolytic methods over ordinary gravimetric procedures.

The separations of metals, using the rotating anode, make the rapid methods even more useful. There seems little doubt but that in a short time many of the electrolytic separations now quite satisfactory with stationary electrodes will be further improved by the addition of conditions under which they can be executed with rotating anodes, using increased current and pressure, thereby decreasing the time factor to a minimum.

The spiral anode used and described by Exner has been employed in nearly all the work done in this laboratory on the rapid precipitation of metals in the electrolytic way.

It was with a view of still further reducing the time element that a new form of anode was devised, following a brief description of which, will be recorded a series of experiments illustrating its advantage over the older forms.

The new anode is a platinum dish of the same general form as the cathode (see Figure 1). It is about 7 cm. in diameter and 3 cm. deep. Its sides are provided with ten slits perpendicular to the edge, each slit about 1.8 cm. long, and 0.5 cm. wide. These openings, together with a circular opening 1.3 cm. in diameter in the bottom of the dish, insure free circulation of the liquid.

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[1] From the author's Ph. D. thesis, 1906.