

havior towards oxidizing agents, and its agency in the bleaching of ferric sulphocyanate.

4. Isopersulphocyanic acid, its occurrence in sulphocyanic acid, and a characteristic reaction.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY.]

THE DETERMINATION OF ANIONS IN THE ELECTROLYTIC WAY.¹

By JOEL H. HILDEBRAND.

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The negative groups in salts—the anions—have in the period of metal determination received scant attention from the electro-analyst. The few observations of Vortmann² and Specketer³ have attracted little attention, and only since Smith⁴ by the use of a mercury cathode and a silver anode made successful estimation simultaneously of both components in sodium chloride, barium chloride, strontium bromide, etc., has the idea of estimating anions electrolytically become a subject of serious thought. The experiments of Withrow (thesis 1905) were directed to this end. They, however, showed that ultimate and most complete success would probably come only by the use of the combined anode and mercury cathode. The present investigation was begun with this thought constantly in mind. The results clearly prove that it is now possible to determine not only halogens, but even anions such as CO₃, CNS, Fe(CN)₆ and others. Salts that are analyzed with difficulty by time honored methods are now electrolyzed most easily and with exceeding accuracy in exceedingly short periods of time. That separations of anions will also be made in the same manner appears certain, although the present study has been restricted to their determination alone, and to the perfection of the apparatus necessary for that purpose.

Results with Stationary Anode.

Apparatus.—The mercury cathode cell as described by Myers⁵ was used to contain the solution to be electrolyzed. Three platinum gauzes (5 by 10 cm.) attached to stiff platinum wires and rolled into cylinders with the shorter dimension as axis and of such diameter as to be suspended readily in the cell were the anodes. These gauzes were plated with silver, the coating being made as heavy as possible. After washing with water, alcohol and ether, the deposits were carefully brushed with a soft camel's hair brush to remove all loosely adherent silver and then weighed.

¹ From author's Ph. D. thesis, 1906.

² *Monatsh.* **15**, 280; **16**, 674. *Electrochem. Z.* (1894) **1**, 137. *Akad. d. Wissenschaft. Wein.*, **11** 7, 95.

³ *Z. Electrochem.*, **4**, 539.

⁴ *This Journal*, **25**, 890 (1902).

⁵ *This Journal*, **26**, 1124.

Method of Procedure.—The chief difficulty, as with previous workers, was that of determining the end of the decomposition. In spite of the greatest care in keeping the mercury and the interior of the cell absolutely clean in order to minimize the secondary decomposition of the amalgam, the formation of some alkali could never be entirely prevented, and after the salt was all decomposed the weight of the gauze could be further increased indefinitely by the formation of silver oxide from the electrolysis of the alkali. Various schemes were tried to determine the end of the decomposition, the one finally serving the purpose being as follows :

At the beginning of the operation the gauze was suspended within about 5 mm. of the surface of the mercury and the liquid diluted so as to cover only about one-third of the gauze. During the electrolysis the potential was kept constant. The strength of the current, falling as the action progressed, indicated the completeness of the decomposition. The current was only prevented from dropping to zero by the slight amount of alkali formed. When it reached a minimum—usually from 0.005 to 0.02 amperes—the level of the liquid was raised a few millimeters from time to time, and as soon as the fresh surface showed the formation of brown silver oxide—which could easily be distinguished from the bluish black chloride—the gauze was removed, immersed in alcohol then in ether, dried and weighed. By this method it was possible to obtain consecutive concordant results. In each case the amalgam was washed into a beaker and after it had decomposed the alkali was titrated with tenth normal sulphuric acid using methyl orange as an indicator.

Sodium Chloride

The following table gives the results obtained for sodium chloride. The current in amperes, at the beginning and end of each decomposition, is given in the third column.

Time Minutes	Volts	Amperes	Sodium in grams		Chlorine in grams	
			Present	Found	Present	Found
135	3.5	0.08-0.01	0.0460	0.0461	0.0708	0.0713
210	3.5	0.09-0.003	0.0460	0.0456	0.0708	0.0706
150	3.5	0.20-0.005	0.0460	0.0460	0.0708	0.0706
220	3.5	0.24-0.005	0.0460	0.0458	0.0708	0.0705
200	3.5	0.21-0.005	0.0460	0.0462	0.0708	0.0709
120	3.5	0.16-0.01	0.0460	0.0459	0.0708	0.0712
130	3.5	0.20-0.02	0.0460	0.0461	0.0708	0.0705
70	3.5	0.15-0.04	0.0460	0.0459	0.0708	0.0707
	3.5	0.14-0.03	0.0460	0.0463	0.0708	0.0711
	3.5	0.13-0.02	0.0460	0.0463	0.0708	0.0710

The deposits were always perfectly adherent in character, unless the silver coating was too thin. No attempt was made to protect them from

the light, so that both here and with other substances, they were always very dark colored.

Sodium Bromide

The procedure adopted with the chloride was immediately successful in this case.

Time Minutes	Volts	Amperes	Sodium in grams		Iodine in grams	
			Present	Found	Present	Found
60	4.0-3.5	0.13-0.02	0.0232	0.0235	0.0804	0.0794
45	4.0-3.5	0.15-0.05	0.0232	0.0237	0.0804	0.0806
50	3.5	0.12-0.03	0.0232	0.0231	0.0804	0.0806
100	3.5	0.13-0.01	0.0232	0.0237	0.0804	0.0812
60	3.5	0.12-0.05	0.0232	0.0238	0.0804	0.0804
	3.5	0.09-	0.0232	0.0230	0.0804	0.0805

Sodium Iodide

Equally satisfactory results were obtained with this salt.

Time Minutes	Volts	Amperes	Sodium in grams		Iodine in grams	
			Present	Found	Present	Found
70	4. -3.5	0.10-0.02	0.0154	0.0156	0.0850	0.0850
70	3.5	0.05-0.01	0.0154	0.0156	0.0850	0.0857
45	3.5-3.	0.10-0.02	0.0154	0.0154	0.0850	0.0845
75	3.	0.07-0.01	0.0154	0.0157	0.0850	0.0846
60	4. -3.5	0.08-0.02	0.0154	0.0156	0.0850	0.0855
60	3.5	0.08-0.02	0.0154	0.0156	0.0850	0.0852

Potassium Sulphocyanide.

This salt proved more troublesome because the potassium amalgam usually started to decompose quite rapidly near the end of the electrolysis.

Time Minutes	Volts	Amperes	Potassium in grams		CNS in grams	
			Present	Found	Present	Found
45	3.5	0.10-0.06	0.0375	0.0371	0.0558	0.0558
120	3.5	0.07-0.04	0.0375	0.0379	0.0558	0.0560
105	4-3.5	0.10-0.01	0.0375	0.0379	0.0558	0.0560
135	3.5	0.06-0.01	0.0375	0.0375	0.0558	0.0566
65	4-3.5	0.09-0.01	0.0375	0.0373	0.0558	0.0553

It was soon found that silver ferro- and ferri-cyanides could be formed, and, what seemed still more remarkable, silver carbonate. In the last instance the decomposition was complete, there being no trace of carbon dioxide liberated at the anode. The deposit, afterwards immersed in dilute sulphuric acid, liberated carbon dioxide with effervescence. However, it was impossible to make these depositions quantitative, as the silver salts formed were not coherent and at the edge of the gauze near the mercury—where the deposit was thick—part of it always became detached. Believing that perhaps this difficulty could be removed by using an anode in which the gauze was horizontal, thus presenting a uniform surface over which the deposit might be distributed, and at the

same time decreasing the resistance so that the decomposition might be more rapid, the following plan was adopted :

The anode consisted of two circular disks of platinum gauze 5 cm. in diameter and having 300 meshes per sq. cm. The circumference was slightly fused in the blowpipe. These disks were mounted 5 mm. apart on a stout platinum wire, 1 mm. in diameter and 10 cm. long, which passed through the centers of the disks perpendicular to them. Each disk was attached to the axial wire by means of two smaller wires fitting tightly into two adjacent holes drilled at right angles to each other through the large wire. The disks weighed about 16 grams apiece. The total surface of each pair of disks is about 100 sq. cm. which is at least doubled when coated with several grams of silver. Since it requires about 30 cc. of liquid to cover the disks as against 150 cc. for a platinum dish of equal surface, it will be interesting to determine how it will compare with the usual platinum dish as a cathode for rapid deposition of metals, as well as an anode for lead and manganese peroxide. This will shortly be done in this laboratory. This form of electrode has the further advantage over the dish in the ease with which it may be washed and in its light weight. These anodes were always supported when not in use by fastening the axis in a clamp so that the disks might not come in contact with anything which might bend them. In order to suspend them from the balance beam in weighing, a loop of fine platinum wire was soldered to each axial wire about 2 cm. from the top.

Silver plating the anodes.—In plating the anodes with silver the rotator was always used, as a coating of from 3 to 4 grams of silver could thus be deposited. A number of determinations could then be made without replating the disks, the deposited silver salt being merely dissolved off by immersing for a few moments in potassium cyanide, thus exposing a fresh surface of silver.

The cell.—The anode, just described, was first tried with sodium chloride, the cell being a beaker of diameter slightly greater than that of the anode. Since it is difficult to fuse a platinum wire into a vessel of this size, connection was made with the mercury by means of a platinum wire fused through the closed end of a glass tube. Into this tube was put a little solder which was heated and then while molten, a stout copper wire was thrust into it. This tube was clamped so that it lay close to the side of the beaker, the platinum wire at the tip projecting into the mercury.

With this arrangement it was found that while the electrolysis was more rapid, the greater surface of mercury exposed to the liquid favored the deposition of the amalgam to an extent inconsistent with good results. Hence, a method was sought to dispose of the amalgam and prevent the presence of alkali about the anode. After much experimenting a cell was devised which answers the purpose admirably. In principle it re-

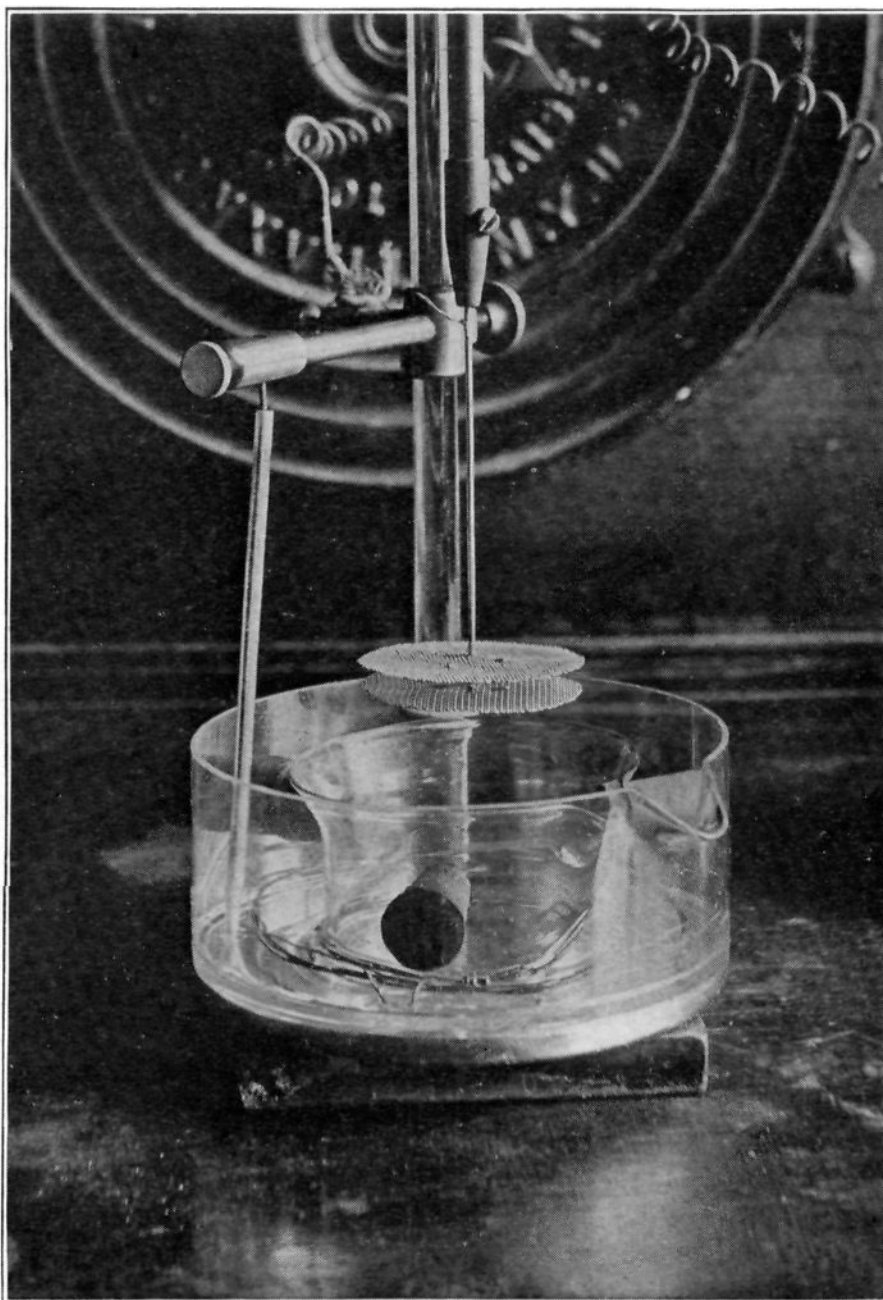


Fig. 1

sembles the Castner-Kellner process for caustic soda, the amalgam being formed in one compartment and decomposed in another. The outer cell is a crystallizing dish 11 cm. in diameter and 5 cm. deep. Inside of this is a beaker, 6 cm. in diameter, with the bottom cut off and the edge rounded so that a ring is formed 4.5 cm. high. This rests on a large Y of thin glass rod on the bottom of the crystallizing dish and is kept in position by three rubber stoppers fitting radially between it and the inside of the dish. In the outer compartment thus formed there is a ring of about six turns of nickel wire provided with three legs which are fastened to the ends of the glass Y and serve to support the ring about 1 cm. above the surface of the mercury when sufficient of the latter is poured in to seal off the two compartments. The cell and anode are shown in Fig. 1.

In using this cell, which must be kept scrupulously clean; pure, clean mercury is poured in so that its level is about three mm. above the lower edge of the bottomless beaker. The solution to be electrolyzed is then put into the inner compartment; while in the outer, is placed enough distilled water to cover the nickel wire, and to this are added a few cubic centimeters of a saturated solution of common salt. The amalgam formed in the inner compartment is by this arrangement immediately decomposed in the outer compartment, which acts as a cell whose elements are amalgam-sodium chloride-nickel wire. The sodium chloride serves merely to make the liquid a conductor so that the action may proceed more rapidly at the beginning. Without this device the amalgam is not entirely decomposed in the outer compartment as pure water does not attack it rapidly enough to prevent a partial decomposition in the inside cell. The mercury is connected with the negative pole of the battery by means of the glass tube, bearing the copper and platinum wires described above, which dips into the outer compartment. After the electrolysis is complete, the entire contents of the cell are poured into a beaker, the cell rinsed and the alkali titrated. After titration the mercury should be washed, the water decanted, and the metal poured into a large separatory funnel from which it can be drawn off clean and dry.

Sodium Chloride.

This new form of apparatus was first tried on sodium chloride, the anode being stationary, with the following results :

Time Minutes	Volts	Sodium in grams			Chloride in grams	
		Amperes	Present	Found	Present	Found
30	4.0-2.5	0.50-0.02	0.0461	0.0459	0.0708	0.0704
45	3.5-2.5	0.34-0.01	0.0461	0.0708	0.0706
40	3.5-3.0	0.50-0.01	0.0461	0.0708	0.0704
45	4.0-3.5	0.65-0.01	0.0461	0.0708	0.0716
30	4.0-2.5	0.76-0.02	0.0461	0.0708	0.0713
55	3.0	0.26-0.02	0.0461	0.0708	0.0709

They were given merely for the sake of completeness as sodium chloride was not tried again. The use of the rotator would certainly have improved them.

Results with Rotating Anode

When it was found that silver bromide did not adhere completely to the stationary anode, the latter was rotated with the double advantage of making the deposit perfectly adherent and stirring the amalgam so that it was completely decomposed in the outer compartment. When the electrolysis was complete, therefore, nothing but pure water remained so that the current falling to 0.01 ampere or less indicated the end, and no harm could be done by running too long as further increase in weight was not possible.

In using the motor the weighed gauze anode is clamped in the shaft which is then lowered into the cell till the lower disk is about 5 mm. from the surface of the mercury. The motor and belt having been adjusted, the motor is started, and the electrolyzing current turned on. About 300 revolutions per minute is the best speed for the anode. Fig. 2 shows the entire apparatus.

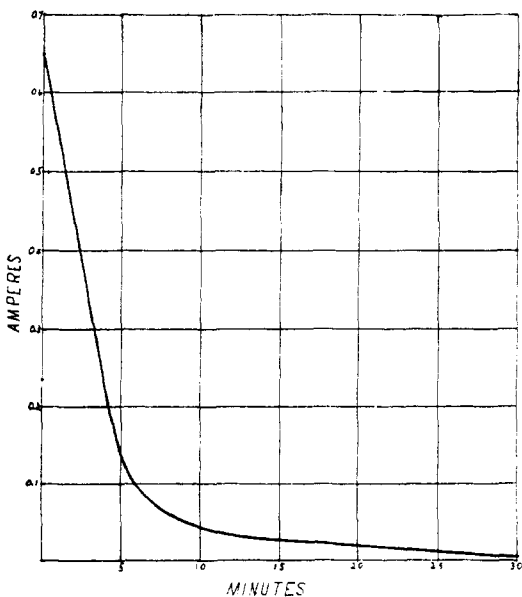


Fig. 3

The variation in current, as the electrolysis proceeds, is shown in the curve in Fig. 3 and the rate of decomposition calculated from it in Fig. 4.

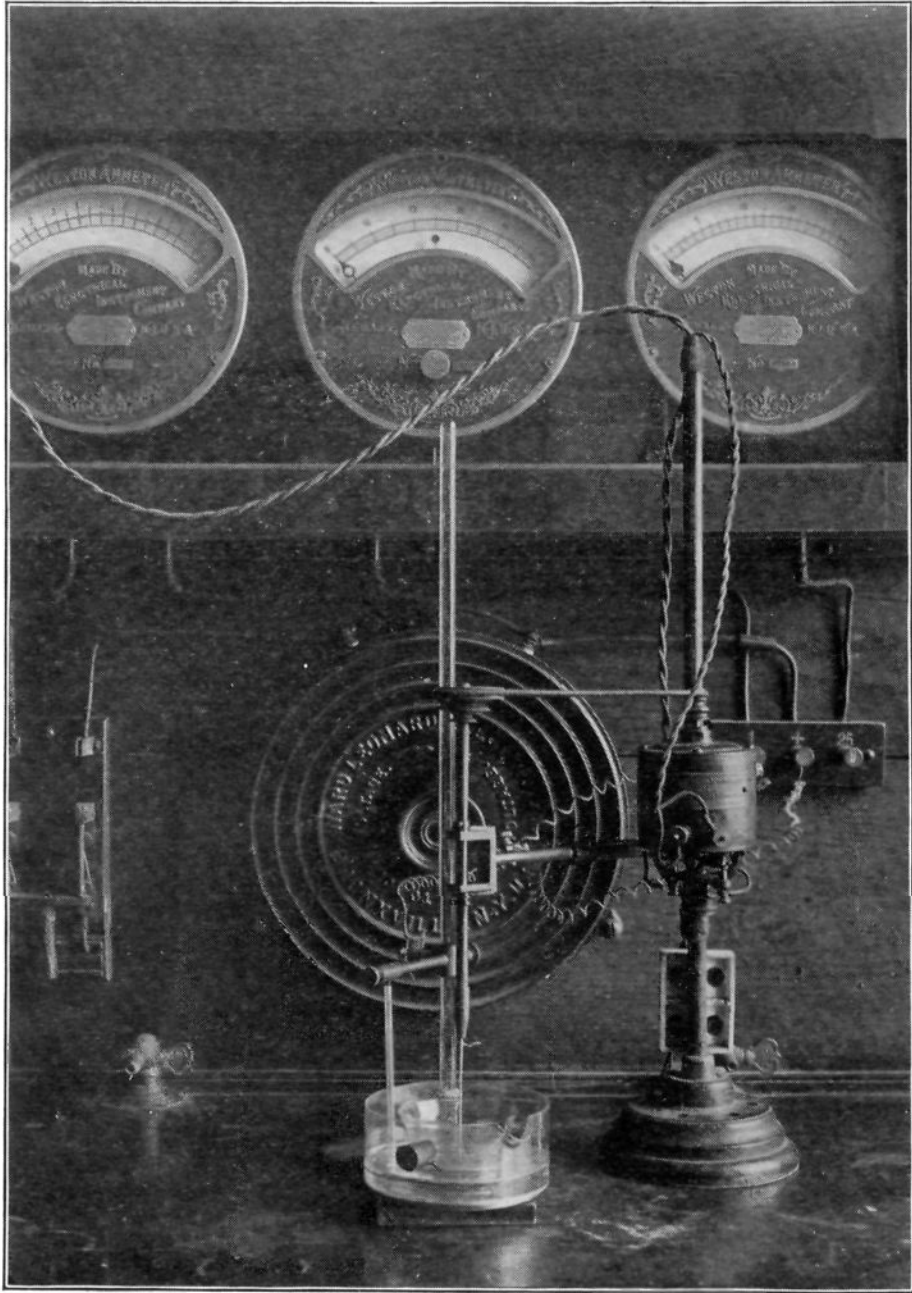


Fig. 2

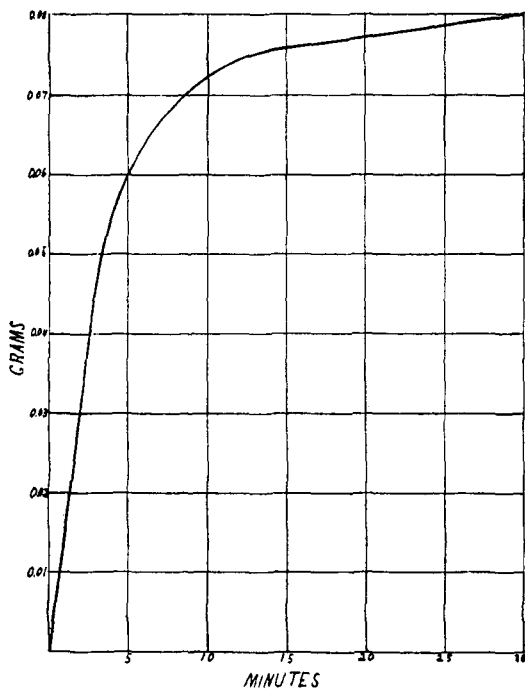


Fig. 4

It is not necessary to wash the anode after the salt is deposited as the water remaining is pure. This avoids any possibility of loss by the usual washing with water, alcohol and ether, although the latter two may be used where it is desired to still further reduce the time.

Sodium Bromide

This salt gave the following results with the rotating anode :

Time Minutes	Volts	Amperes	Sodium in grams		Bromine in grams	
			Present	Found	Present	Found
30	5.0	0.65-0.01	0.0231	0.0233	0.0800	0.0798
30	5.0	0.65-0.01	0.0231	0.0233	0.0800	0.0802

In this case a dilution of about 25 cc. was used, it being necessary to cover only the lower disk, as this gave sufficient surface for the quantity of sodium bromide used.

Sodium Carbonate

Sodium carbonate required a little more care, it being found advantageous to deposit the carbonic acid a little slower, and also to use a slightly roughened silver surface—obtained by stopping the rotator several minutes before taking the disk from the silver plating bath. Furthermore, towards the end of the analysis, the liquid was diluted so as to expose the fresh silver surface of the second disk.

Time Minutes	Volts	Amperes	Sodium in grams		CO ₂ in grams	
			Present	Found	Present	Found
60	3.5-5.0	0.15-0.01	0.0323	0.0325	0.0420	0.0416
90	4.0-5.0	0.15-0.01	0.0323	0.0324	0.0420	0.0419
50	5.0	0.65-0.01	0.0346	0.0349	0.0450	0.0448
70	3.5-5.0	0.15-0.01	0.0346		0.0450	0.0447

In this instance the easiest way to clean the gauze is to ignite it gently instead of the usual washing with potassium cyanide, water and then drying.

Potassium Ferrocyanide.

This salt was analyzed very easily and quickly.

Time Minutes	Volts	Amperes	Potassium in grams		Fe(CN) ₆ in grams	
			Present	Found	Present	Found
30	4.0-4.5	0.15-0.01	0.0391	0.0384	0.0531	0.0531
30	3.0-5.0	0.15-0.01	0.0391	0.0389	0.0531	0.0532
30	4.0-5.0	0.20-0.01	0.0391	0.0387	0.0531	0.0527

Potassium Ferricyanide.

The behavior in this instance was equally satisfactory.

Time Minutes	Volts	Amperes	Sodium in grams		Fe(CN) ₆ in grams	
			Present	Found	Present	Found
35	2. -5	0.20-0.01	0.0392	0.	0.0710	0.0714
30	4. -5	0.40-0.01	0.0392	0.0389	0.0710	0.0712
40	4.5-5	0.30-0.01	0.0392	0.0389	0.0710	0.0713

Trisodium Phosphate.

Trisodium phosphate gave a deposit which was satisfactory at 4 volts but not completely adherent at 5 volts. The lower pressure and the smaller conductivity extended the time necessary to get out the last traces. To avoid this, in the last two determinations, a second anode was used near the end to receive these traces.

Time Minutes	Volts	Amperes	Sodium in grams		PO ₄ in grams	
			Present	Found	Present	Found
75	5-4	0.50	0.0343	0.0343	0.0472	0.0473
120	4	0.30	0.0343	0.0343	0.0472	0.0468
60	4	0.30	0.0343	0.0340	0.0472	0.0470
70	4	0.40	0.0343	0.0472	0.0478

The method was found unsuitable for such salts as sodium arsenate, potassium chromate and sodium oxalate. The silver deposit was formed, but a part of the salt was reduced by contact with the amalgam. Silver sulphite, silver sulphide and silver succinate were non-adherent. The oxide was produced by the electrolysis of caustic soda, but it was not complete, a part of the oxygen going off in gas. Owing to the partial solubility of silver borate—although it forms an adherent coating from a borax solution—the silver was slowly carried over to the mercury.

No attempt has been made to find the maximum amounts which could be deposited or the minimum time. These problems are now receiving

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_2 , 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

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

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