cc. A blank determination should always be run and the corresponding correction made.

To prepare the calcium phosphate solution, suspend five grams of calcium carbonate in 50 cc. of distilled water and add 10 cc. of ortho-phosphoric acid (85 per cent.) slowly while stirring.

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RAPID ELECTRO-ANALYSIS WITH STATIONARY ELECTRODES.

BY JOHN T. STODDARD.

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In the interesting development, during the last few years, of methods for the rapid precipitation of metals by the electric current, the efficiency of cathodes of gauze, and of mercury with stationary anodes seems to have been largely overlooked. General attention was directed in 1903 to the fact that electro-analyses could be made in much less than the usual time by using stronger currents with rotating electrodes. Gooch and Medway[1] rotated the cathode, Exner,[2] the anode; and since that time much work has been published on the use of the rotating anode with dish, gauze, and mercury cathodes. The agitation of the solution, which is apparently the chief function of the rotating electrode, has also been accomplished by rotation of the solution while the electrodes are stationary—recently by Frary[3] through the clever use of a solenoid. Rotation has come to be regarded as the essential feature of rapid electro-analytical procedure.

The experiments described in this paper show that rotation is not essential; that similarly rapid results can be obtained with stationary electrodes and no agitation of the solution beyond that produced by the heating effects and gas-evolution caused by the strong currents employed.

I. The Gauze Cathode with Stationary Anode.

In July, 1899, Cl. Winkler[4] published a brief paper on "Die elektrolytische Metallfällung unter Anwendung von Elektroden aus Platindrahtgewebe" in which he stated that with a cathode of platinum gauze good deposits of a number of metals could be obtained when higher current densities than usual were employed; and that the time of precipitation was reduced to one-fourth of the usual time. The efficiency of the gauze was ascribed to the utilization of the entire surface and to the fact that the deposited metal closes on itself around each wire of the mesh, and thus adheres better than on a plane surface. Winkler records the use of a current of 0.5 ampere, and calculates the current density as

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[1] *Am. J. Sci.*, 4th Series, **15**, 320.

[2] THIS JOURNAL, **25**, 896.

[3] *Z. Elektrochemie*, **23**, 308 (1907).

[4] *Ber.*, **32**, 2192.

D_{100} = 5.1 amperes. From the data which are given, it is evident, however, that an error was made in the calculation of the gauze surface; and instead of being 9.8 sq. cm., it was about 66 sq. cm., so that the current density was only about 0.76 ampere. It may be that this fact is in part responsible for the slight interest which this suggestion for more rapid precipitation seems to have aroused.

Gauze cathodes were immediately tried in this laboratory, and it was soon evident that much more rapid precipitation than that reported by Winkler could be effected by the use of stronger currents; and, on the appearance of Gooch and Medway's paper,[1] a few experiments were made which showed that copper was deposited on gauze with a stationary anode in about the same times as those given for the rotating cathode. No careful study of the matter was, however, made until recently.

The cathodes employed are cylinders of platinum gauze, 3 cm. in diameter and 3 cm. long. The gauze is that described by the maker as "52 mesh" (to the inch), and the cathode is calculated to have a total surface of about 40 sq. cm.

The weight of the cathodes is about 12 grams each; they might, however, be considerably lighter, as the wire which serves as the frame of the cylinder and for connecting with the electrolytic stand is unnecessarily heavy (1.4 mm.). Half its weight could be saved by using wire of 1 mm. in diameter, and the weight of the cathode brought down to 7 or 8 grams.

The anodes are cylinders of platinum foil, about 0.8 cm. in diameter and 2.5 cm. long, and in the electrolysis are placed concentrically within the cathodes.

The precipitations are carried out in 80 cc. beakers with about 50 cc. of solution—a volume which, while covering the electrodes well, gives the advantage of concentration. The wires of both electrodes are bent at an angle of somewhat more than 90° so as to rest on the lip of the beaker and allow a watch-glass cover to be used conveniently. At the end of the experiment, without interrupting the current, the solution is drawn off for testing and the cathode washed with distilled water by the aid of a siphon whose end is slipped between the electrodes.

The following solutions were used:

1. Cadmium nitrate with just enough potassium cyanide to give a clear solution.

2. Copper sulphate with 7 or 8 drops of conc. nitric acid. The solution is heated to about 60°.

3. Nickel sulphate with 1.5 grams of ammonium sulphate and 12 to 15 cc. of conc. ammonia.

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[1] *Loc. cit.*

4. Silver nitrate with the least possible excess of potassium cyanide. The solution is heated nearly to boiling.

5. Zinc sulphate with an excess of sodium hydroxide; or with sodium hydroxide to partial solution of the precipitate and then just enough potassium cyanide to give a clear solution. The solution is heated.

With the exception of silver, the character of the deposited metal is scarcely affected by the strength of current used. With silver, if the current exceeds 1.5 amperes the deposit is yellowish, and with much stronger currents becomes voluminous and closes the mesh; with less than 1.5 amperes, the precipitated silver is white and fine.

The sodium hydroxide solutions of zinc give deposits which after a time fill the mesh, but which give quantitative results. A much finer deposit is obtained from the cyanide solution, but the precipitation is somewhat slower.

As the strong currents heat the solutions, often to boiling, the preliminary heating is perhaps not necessary. In some cases, notably with the nickel solutions, so much frothing sometimes occurs that it is necessary to reduce the current. This necessity may be avoided by the use of a deeper beaker.

The metals were completely precipitated in times which are given in the following table. The current density is not given; D_{100} is in all cases equal to the current noted divided by 0.4. The fall of potential between the electrodes is also omitted as it has little significance; it is only necessary to have at command sufficient voltage to deliver the required current through the electrolytic cell. In these experiments a storage battery of ten cells in series was employed:

TABLE I.

Metal.	Approx. weight. Grams.	Current. Amperes.	Colorless in minutes	Complete precipitation, minutes.
Cadmium	0.42	5	..	15
Copper	0.5	6	5	10
Copper	0.5	8	4.5	8
Nickel	0.34	6	5	8
Nickel	0.49	6	8	12
Nickel	0.6	6	10	16
Silver	0.25	1–1.5	..	10
Silver	0.5	1	..	17
Zinc (NaOH)	0.5	4	..	15
Zinc (NaOH)	0.4	8	..	10
Zinc (KCN)	0.5	6	..	30

Some determinations on both gauze and mercury cathodes are given at the end of this paper.

II. The Mercury Cathode with Stationary Anode.

When the use of the mercury cathode proposed by Wolcott Gibbs, in

1880, was taken up at the University of Pennsylvania,[1] stationary anodes were at first employed, with comparatively low currents and correspondingly long times for precipitation—over-night determinations; but in 1904–1905 Kollock and Smith[2] introduced the use of the rotating anode with the mercury cathode, and found that with strong currents the metals were precipitated in astonishingly short times.

While studying the efficiency of the gauze cathode, as described in the first part of this paper, the suggestion occurred that the heating and gas-evolution produced by strong currents should so effectually agitate the solution used with the mercury cathode as to make the rotation of the anode unnecessary for rapid precipitation in a cathode material in which the metal dissolves. Though it seemed very unlikely that the combination of mercury cathode, stationary anode and strong current had not been tried, and, if so, rejected for some good reason, the experiment was made; and it proved that, under these circumstances, cadmium, copper, nickel, silver, and zinc (and presumably other metals) were precipitated in times which are at least comparable with those reported for the rotating anode.

The procedure is essentially that described by E. F. Smith in the fourth edition of his *Electro-Analysis*.

A 45–50 cc. beaker is used with about 40 grams of mercury, and an anode consisting of a flat spiral of platinum wire placed 0.5 to 1 cm. from the surface of the mercury. The electrode wires are bent as in the case of the precipitations on gauze so that a watch-glass cover may be used. At the end of the precipitation, the solution is siphoned off for testing, and the mercury washed with distilled water by the aid of the siphon, without interrupting the current, until the latter drops to about zero. The mercury is again washed with water, then with alcohol, and finally with ether, and dried at a very gentle heat.

The solutions used in testing the efficiency of the method were the nitrates of cadmium and silver, and the sulphates of copper, nickel, and zinc. Five or six drops of sulphuric acid (1 : 4) were added in each case except that of silver, where the same amount of nitric acid was used. The silver solution becomes black as soon as the current is closed, from finely divided "peroxide," but clears again in three or four minutes. All the solutions are rapidly heated by the currents employed, and the only limit to the strength of current which can be used is that indicated by possible loss from too violent boiling.

The following table shows in what times complete precipitation takes place.

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[1] THIS JOURNAL, **25**, 884.

[2] *Ibid.*, **27**, 1255.

TABLE II.

Metal.	Volume of solution. cc.	Approx. weight. Gram.	Current. Amperes.	Colorless in minutes.	Complete precip., minutes.
Cadmium	30	0.25	7–5	..	10
Cadmium	25	0.21	5	..	10
Copper	15	0.3	3–4	5	10
Copper	20	0.4	4	6	8
Nickel	15	0.36	5.5	6	10
Nickel	25	0.5	7	10	15
Silver	20	0.4	8–7.3	..	6
Silver	25	0.5	4.8	..	8
Silver	25	0.5	5.8–6.5	..	7
Zinc	20	0.2	8–7	..	10
Zinc	25	0.5	6	..	15

In Table III some determinations are given with gauze and mercury athodes from the same solutions of the salts, and, for the sake of ready omparison of the results, there is added the weight of metal in one cubic entimeter of the solution, calculated from the weight found.

TABLE III.—DETERMINATIONS OF METALS MADE WITH STATIONARY ANODE.

Solution taken. cc.	Volume of electrolyte. cc.	Cathode used.	Current. Amperes.	Time. Minutes.	Metal found. Gram.	Metal in 1 cc. solution. Milligrams.	
$Cd(NO_3)_2$.							
25	50	Gauze	5–4.5	15	0.2132	8.528	
25	25	Mercury	5–6	10	0.2124	8.496	
$CuSO_4$.							
25	50	Gauze	4	20	0.4944	19.776	
25	50	Gauze	6	13	0.4943	19.772	
20	50	Gauze	6	8	0.3955	19.775	
15	15	Mercury	3–4	10	0.2963	19.753	
20	20	Mercury	4	8	0.3954	19.770	
$NiSO_4$.							
25	50	Gauze	6	12	0.4897	19.588	A
15	15	Mercury	5–5	10	0.2936	19.573	
25	50	Gauze	6	18	0.5986	23.944	B
15	15	Mercury	5.5	10	0.3593	23.953	
$AgNO_3$.							
25	50	Gauze	1	20	0.4958	19.832	
25	50	Gauze	1	17	0.4957	19.828	
20	20	Mercury	8–7.3	6	0.3970	19.850	
$ZnSO_4(KCN)$.							
25	50	Gauze	6	30	0.4991	19.964	
25	25	Mercury	6	15	0.4988	19.952	
25	25	Mercury	6	15	0.4989	19.956	

Summary.

It is shown in this paper that cadmium, copper, nickel, silver, and zinc (and probably other metals) can be precipitated from their solutions, completely and in weighable condition, by strong currents with the use of stationary electrodes, in substantially the same times as those required when rotating electrodes are employed.

The advantages of this are obvious: it means a return to the simplicity of apparatus and manipulation of the older and slower methods, while retaining the speed of the new. It should lead to the introduction of rapid methods of electro-analysis by those who have hesitated to employ them on account of the initial extra expense and the use of the machinery necessary for rotation.

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A METHOD FOR PREPARING STANDARD HYDROCHLORIC ACID SOLUTIONS.

BY G. A. HULETT AND W. D. BONNER.

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We find that the "constant boiling" hydrochloric acid has a very definite percentage composition, is easily obtained and from it a standard solution of hydrochloric acid may be made directly and with ease and accuracy. In some of the older text-books on quantitative analysis it is recommended that a constant boiling hydrochloric acid be used to make approximate solutions and then standardized but we have found no notice of its being used as a basis for volumetric work.

It has long been known that hydrochloric acid, when distilled, will approach a point where it distils over unchanged in composition whether we start with a strong or weak acid in the still, and when this point is reached the residue in the still has the same composition as the distillate. We are concerned with the definiteness of the composition of the constant boiling acid and its variation with the pressure. The last point will be considered first, as the work of Roscoe and Dittmar[1] gave sufficient data on this point. These investigators determined the composition of the constant boiling hydrochloric acid obtained when distilling under pressures varying from 65 mm. to 2510 mm., and on plotting these results on a large scale it was found that a satisfactory curve could be drawn and it appeared that for the region with which we are concerned (660 to 860 mm.) that a change of 10 mm. in pressure produced a change of only 0.024 per cent. in the composition of the acid. For this region the acid obtained is about 20 per cent. hydrochloric acid and a change of 10 mm. in the barometric pressure caused a change of only one part in 4000, so it would seem that only for the most exact work need the baro-

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[1] *J. Chem. Soc.*, **1860**, 128, and Roscoe, *Ann.*, **116**, 343.