THE RAPID DETERMINATION OF COPPER, SILVER, CADMIUM AND BISMUTH BY MEANS OF THE MERCURY CATHODE AND STATIONARY ANODE.

By R. C. Benner.

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In the search for rapid methods in electrochemical analysis, all desire for simplicity seems to have departed. Various means have been used to agitate the electrolyte. The rotation of the anode or cathode by mechanical means, the use of a solenoid, and the passing of a gas through it have all been tried, but not until recently has any one thought that the evolution of the gas by the electrolytic current might stir the electrolyte sufficiently to allow the metals to be deposited in an adherent and weighable form. This has been done by Stoddard,[1] Frary[2] and the author[3] with the gauze electrode, in case of copper. It has been shown qualitatively by Stoddard[4] with the mercury cathode and stationary anode, for copper, silver, etc.

In both cases the current densities are higher than ordinarily used with stationary electrodes. With the gauze electrode of the author's there was used a current density of 10 amperes for every 100 square centimeters, and in case of the mercury cathode made use of in this work, a normal density of 35 to 40 amperes. This proves that the rate of deposition in a weighable form must be due, at least in part, to the stirring of the electrolyte by means of the liberated gas.

Therefore, in order to determine whether the evolution of gas would stir the liquid sufficiently to allow complete deposition to take place rapidly and in a weighable form, higher current densities than had been used before for this purpose, were utilized in carrying out the determination of several metals by means of the mercury cathode and a stationary anode.

In order to avoid all danger of loss by the rapid evolution of gas by high currents, taller electrodes than used by Smith were constructed. When these contained 40 to 50 grams of mercury, they did not overload the balance. The mercury used in these determinations was distilled and purified by the method of Hillebrand each time before using. In each case, after the deposition in question was complete, the mercury was washed with distilled water until the current dropped to zero. The current was then broken, leaving the beaker full of water and the anode examined for small globules of mercury by means of a magnifying glass. Mercury was frequently carried to the anode, either by washing or by the rapid evolution of gas from the cathode but could usually be removed

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[1] This Journal, 31, 385 (1909).

[2] May meeting of the American Electrochemical Society.

[3] *J. Ind. Eng. Chem.*, 2, 348.

[4] *Loc. cit.*

by rinsing the anode up and down in the water contained in the beaker. After the anode had been freed from mercury, the water was either poured or siphoned off and the last part removed by means of a capillary tube. The cathode was then washed with absolute alcohol, the greater portion poured off, the last part being removed by the capillary tube. Finally it was washed with ether, the greater portion poured off and the remainder allowed to evaporate. The electrode was placed in a desiccator for one-half an hour. The removal of the last of the water by means of a siphon with a capillary end makes one washing with alcohol and one with ether sufficient.

Copper.—Copper, being one of the easiest metals to determine electrolytically, with accuracy, under the most varied conditions, was selected for the preliminary work. To carry out these experiments, two solutions of nitrate were prepared by dissolving weighed amounts of chemically pure copper foil in the smallest possible amount of nitric acid, diluting to a definite volume with water and checking the copper content by electrolysis with platinum electrodes. The two solutions contained respectively 0.3731 and 0.1912 gram of copper in ten cubic centimeters.

The solutions were electrolyzed with currents varying from three to four amperes in 20 cc. of solution, both sulphuric and nitric acid solutions being used.

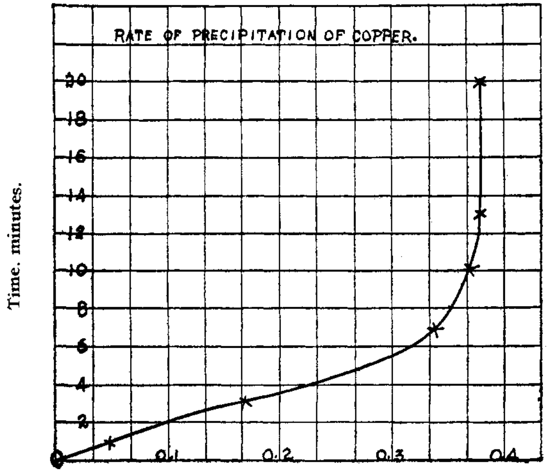
Amount of copper.						
Taken.	Found.	Error.	Amperes.	Volts.	Volume of the solution.	Acid, 4 drops.
0.3831	0.3835	0.0004	3–4	6–8	20 cc.	H_2SO_4
0.3831	0.3837	0.0006	3–4	6–8	20 cc.	no acid
0.3831	0.3832	0.0001	3–4	6–8	20 cc.	no acid
0.3831	0.3834	0.0003	3–4	6–8	20 cc.	4 drops nitric
0.3831	0.3831	0.0000	3–4	6–8	20 cc.	4 " "
0.1912	0.1919	0.0007	3–4	6–8	20 cc.	4 " "
0.1912	0.1911	0.0001	3–4	6–8	20 cc.	4 " H_2SO_4
0.1912	0.1913	0.0001	3–4	6–8	20 cc.	4 " "
0.1912	0.1906	0.0006	3–4	6–8	20 cc.	no acid
0.1912	0.1910	0.0002	3–4	6–8	20 cc.	no acid
0.1912	0.1912	0.0000	3–4	6–8	20 cc.	no acid

Rate of Precipitation.

In the determination of the rate of precipitation, 20 cubic centimeters of solution were electrolyzed, with a current of four amperes and six to seven volts, in the presence of four drops of concentrated nitric acid.

	Amount of copper.		
Time min.	Taken.	Found.	
1	0.3831	0.0535	
3	0.3831	0.1767	
7	0.3831	0.3485	
10	0.3831	0.3782	
15	0.3831	0.3827	
20	0.3831	0.3833	Copper all out.

Examination of the preceding determinations shows that the results were equally good under any of the conditions used, being as accurate as those obtained with the rotating anode and mercury cathode. The precipitation was not as rapid in this case as where the electrolyte was agitated by mechanical means. This was more than compensated for, however, by the simplicity of the apparatus and was not enough slower to be detrimental to the use of this method. It was possible, in 20 minutes, with a current of four amperes, to precipitate 0.3833 gram of copper from 20 cubic centimeters of solution containing four drops of concentrated nitric acid. It has been observed that a black deposit, which was taken to be the peroxide, formed on the anode but redissolved as the electrolysis neared completion. The copper amalgam was washed without delay as soon as the electrolysis was complete, as oxidation takes place readily.



Weights of copper deposited.

Silver.—Silver, as well as copper, is easily and accurately determined by all electrolytic methods. To carry out the experimental work on silver, a solution was prepared by dissolving a weighed amount of chemically pure silver foil in the smallest possible amount of nitric acid and diluting to a definite volume. Ten cubic centimeters of this solution

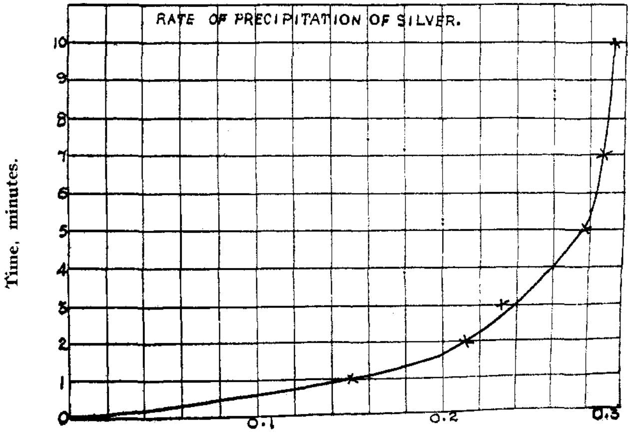
Silver present.	Silver found.	Error.	Acid.	Amperes.	Volts.
0.1428	0.1430	0.0002	None	4–5	7–8
0.2856	0.2862	0.0006	"	4–5	7–8
0.1428	0.1427	0.0001	5 drops H_2SO_4	4–5	7–8
0.1428	0.1425	0.0003	"	4–5	7–8
0.1428	0.1425	0.0003	4 drops HNO_3	4–5	7–8
0.2141	0.2147	0.0006	"	3–4	4–5
0.2141	0.2146	0.0005	4 drops H_2SO_4	3–4	4–5

contained 0.1428 gram of silver. The solution was then electrolyzed under the same conditions as copper with the additional trial of several organic acids.

Rate of Precipitation.—In order to determine the rate of precipitation 20 cc. of the solution were electrolyzed with a current of four amperes and six to seven volts in the presence of about one drop of nitric acid.

Time.	Amount of copper taken.	Copper precipitated.	
1	0.2856	0.1534	
2	0.2856	0.2167	
3	0.2856	0.2300	
5	0.2856	0.2790	
7	0.2856	0.2841	
10	0.2856	0.2862	Silver all out.

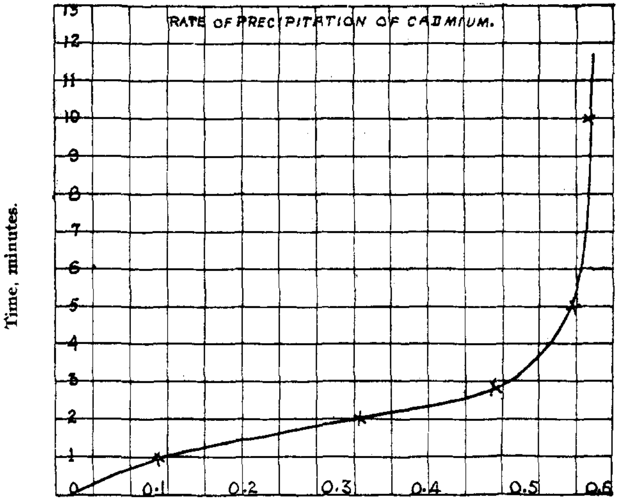
Examination of these results shows them to be comparable in every way with those obtained by means of the rotating anode and mercury cathode. It was possible to deposit 0.2862 gram of silver in ten minutes.



Weights of silver deposited.

Large amounts of mineral acids retard the rate of precipitation and give irregular results. All but about one in every ten are low. Citric, tartaric, oxalic and acetic acids were used with results similar to those obtained with large amounts of mineral acids.

Cadmium.—While cadmium has been accurately determined by means of the rotating anode and mercury cathode, it may also be determined by the method used for copper and silver with equally good results. A standard solution was made by dissolving chemically pure cadmium sulphate in water. The cadmium content was found, by the ordinary electrolytic method, to be 0.4828 gram of the metal in 10 cc. This solution was electrolyzed in the usual manner, both hot and cold, with equal success, as will be seen by consulting the following results. It was possible to precipitate 0.5743 gram of the metal in the short period of ten minutes.



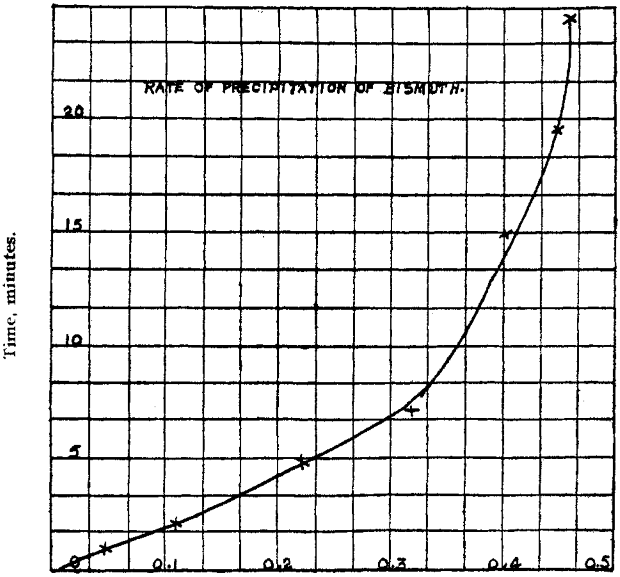
Weights of cadmium deposited.

Amount of cadmium.							Volume.	
Taken.	Found.	Error.	Amperes.	Volts.	Time.	Acid.	Temp.	Soln.
0.4828	0.4821	0.0007	3-4	7-8	15	4 drops HNO_3	hot	20 cc
0.4828	0.4819	0.0009	3-4	7-8	15	"	cold	20 cc.
0.4826	0.4834	0.0006	3-4	7-8	20	no acid	hot	20 cc.
0.9656	0.9649	0.0007	3-4	7-8	20	4 drops HNO_3	"	20 cc.
0.4828	0.4832	0.0004	3-4	7-8	15	"	cold	20 cc.
0.9656	0.9660	0.0004	3-4	7-8	20	"	"	20 cc.
0.4828	0.4836	0.0008	3-4	7-8	20	"	"	20 cc.
0.9656	0.9651	0.0005	3-4	7-8	20	4 drops H_2SO_4	"	20 cc.
0.4828	0.9635	0.0003	3-4	7-8	20	"	"	20 cc.

The rate of precipitation was determined with a current of four amperes and seven to eight volts, in the presence of five drops of concentrated sulphuric acid in 20 cc. of solution.

Time.	Amount of cadmium taken.	Amount of cadmium found.	
1	0.5743	0.1131	
2	0.5743	0.3339	
3	0.5743	0.4783	
5	0.5743	0.5566	
10	0.5743	0.5743	Cadmium all out.

Most methods for the determination of bismuth are far from satisfactory. This is true of most electrolytic, as well as of the common analytical methods. In the electrolytic methods the range of conditions for quantitative deposition of the metal in a weighable form is, as a rule, small, and must be strictly observed to obtain the best results. The best and most consistent results are obtained by the use of the mercury cathode, and rapid deposition may also be obtained by combining this with the rotating anode. In order that the rapid determination of this metal might be tried with the stationary anode and mercury cathode, a standard solution of bismuth was made by dissolving some chemically pure bismuth trioxide in the smallest amount of nitric acid which will hold the bismuth in solution when diluted to one liter with water. The amount of bismuth contained in 10 cc. of the solution was determined by precipitating with ammonium carbonate, igniting and weighing as the oxide. The electrolytic determinations were made under the usual conditions in the presence of varying amounts of acid, both nitric and sulphuric acids being used with equally good results, as will be seen by reference to the following table.



Weights of bismuth deposited.

Bismuth present.	Bismuth found.	Error.	Amperes.	Volts.	Time.	Acid added.
0.4650	0.4647	0.0003	3-4	6-7	20-30	none
0.4650	0.4649	0.0001	3-4	6-7	20-30	“
0.2325	0.2326	0.0001	3-4	6-7	20-30	1 cc. of HNO_3
0.2325	0.2325	0.0000	3-4	6-7	20-30	“
0.2325	0.2331	0.0006	3-4	6-7	20-30	½ cc. of H_2SO_4
0.2325	0.2327	0.0002	3-4	6-7	20-30	½ cc. of H_2SO_4
0.4650	0.4655	0.0005	3-4	6-7	20-30	none
0.4650	0.4658	0.0008	3-4	6-7	20-30	“

The original solution contained 0.85 cc. of concentrated nitric acid to every 10 cc. of solution.

The rate at which bismuth was precipitated was determined with 20 cc. of the solution containing 0.4650 gram of bismuth in the presence of 1.20 cc. of concentrated nitric acid.

Time.		Bismuth taken.	Bismuth found.
1		0.4650	0.0510
3		0.4650	0.1100
5		0.4650	0.2263
7		0.4650	0.3244
10		0.4650	0.3622
15		0.4650	0.4027
20		0.4650	0.4528
25	Bismuth all out.	0.4650	0.4645

During the electrolysis, what was taken to be the peroxide always collected on the anode, but, as in other cases, it always dissolved without any trouble before the determination was complete. The smaller the amount of acid present the more likely this was to form. In one or two cases small amounts of the oxide did not dissolve from the anode where it was rough but the amount was not weighable. A black precipitate of bismuth frequently collected under the anode on the mercury but as the electrolysis proceeded this amalgamated without difficulty. It was possible to precipitate, by means of this method, 0.4659 gram of bismuth in 25 minutes. Taking it all in all, this is as good a method as we have for the determination of bismuth.

Summary.

(1) The apparatus is as simple as any electrolytic apparatus made.

(2) The deposition by this method is nearly as rapid as by the rotating anode and mercury cathode.

(3) The results are as accurate as those obtained by other methods where mercury is used as the cathode.

UNIVERSITY OF ARIZONA, TUCSON.

THE ESTIMATION OF SMALL QUANTITIES OF NITROGEN BY PELOUZE'S REACTION.

BY A. T. DAVENPORT.

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During some recent work, in which the writer was engaged, it became necessary to estimate very small quantities of nitrogen occurring in the form of nitrates. Various methods for the determination were tried, but none of those which are ordinarily satisfactory, quite supplied the needs in this particular case. Among all the methods tried, that which most nearly fulfilled all the conditions imposed was one in which the following reaction, originally employed by Pelouze, was used: