[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, NO. 93.]

THE ELECTROLYTIC DETERMINATION OF MERCURY WITH THE USE OF A ROTATING ANODE.[1]

BY RALPH O. SMITH.

Received August 28, 1905.

ONE OF the very first electrolytes applied in the electrolytic determination of mercury was a solution of the nitrate or chloride of the metal acidulated with nitric acid. The time required for the deposition of the metal varied from twelve to sixteen hours, but by heating the electrolyte to 70° four hours were sufficient for the complete precipitation.

Exner,[2] by the use of a rotating anode and a high current density, was able to precipitate 0.5 gram of mercury in twelve minutes. He used a solution of mercurous nitrate acidulated with 1 cc. of concentrated nitric acid.

Fischer and Boddaert[3] were able to confirm Exner's work, but used a little longer period—about twenty minutes—for the precipitation.

The following experiments were made to determine the rate at which, with the help of a rotating anode, it was possible to precipitate mercury from a solution of mercurous nitrate. The electrolyte consisted of 25 cc. of mercurous nitrate solution (equal to 0.2560 gram of mercury) and 1 cc. of concentrated nitric acid (sp. gr. 1.17), with a total dilution of 115 cc.

TABLE I.

Experiment.	Time. Minutes.	Mercury found.	Volts.	$N.D._{100}$ amperes.
1	2	0.2040	6.5	7.4–7
2	4	0.2387	7.7–7.5	7.6–8
3	6	0.2477	7.9–8	7 –7.1
4	8	0.2559	7	7.2–6.9
5	10	0.2558	7 –7.4	7 –7.1
6	15	0.2561	7 –6.7	7.3–6.9
7	20	0.2558	7	7.4–7
8	20	0.2561	8.4–6.2	7.2

The residual liquid from Expts. 4, 5, 6, 7, and 8 gave no test for mercury. In experiment 8 the electrolyte was not previously

---

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

[2] This Journal, **25**, 896.

[3] *Z. Elektrochem.*, **10**, 950.

heated; the others had been heated. No difference was noted, hence there was evidently no loss of mercury in the other experiments.

To further confirm the preceding observations 50 cc. of mercurous nitrate solution, containing 1 cc. of concentrated nitric acid (sp. gr 1.17), were diluted to 115 cc. and electrolyzed. These conditions were repeated in each of the following experiments:

TABLE II.

Experiment.	Time. Minutes.	Mercury found.	Volts.	$N.D_{100}$ amperes.
9	2	0.3612	6 –7	7.1–7.2
10	4	0.4772	6.3–6.6	7.2
11	8	0.5077	6.7–6.6	7.3–7.1
12	10	0.5122	6.4–6.3	7.2–7.1
13	12	0.5121	7 –6.6	7.2–7
14	20	0.5119	6 –6.4	7.2–7

From the preceding results the time curves, as shown in Fig. 1, were drawn.

In speaking of this method of precipitating mercury Exner mentions that the dish used as a cathode lost 0.0006 gram in weight in three experiments. In the present study a greater loss in the weight of the platinum cathode was noted. A dark film of platinum black always remained when the mercury deposit was dissolved from off the dish with hot nitric acid. It was removed by polishing with sand. The loss in weight of the dish was on an average 1.5 mg.

The time required for the precipitation of 0.25 gram of mercury from this electrolyte was eight minutes, while ten minutes proved sufficient for the precipitation of 0.5 gram of the metal.

Another electrolyte which was found most satisfactory in the electrolytic determination of mercury was that of an alkaline sulphide.[1] It also proved to be most helpful because it could be applied directly to ores of mercury, for example, cinnabar. It remained, however, to determine the rate at which mercury might be completely precipitated from this electrolyte, using a rotating anode. Accordingly, a solution of mercuric chloride was prepared, 25 cc. of which contained 0.2603 gram of mercury. This is the quantity which was used in the experiments given below.

[1] Smith's "Electrochemical Analysis," p. 74 (1902).

TABLE III.

Experiment.	Time. Minutes.	Mercury found.	Sodium sulphide (sp. gr. 1.17). cc.	Volts.	N.D$_{100}$ amperes.
1	10	0.1959	..	10.5–10	5 –6.3
2	10	0.2582	10	7 –6.8	6 –6.2
3	10	0.2576	10	10 –7.7	10.1–9.6
4	10	0.2554	20	5.3–5.7	6 –5.8
5	12	0.2596	10	7.5–7	6 –6.2
6	13	0.2601	10	6.7–6.6	6
7	15	0.2602	10	7 –6.6	6 –5.9
8	15	0.2571	10	9.3–7.1	6 –6.2
9	20	0.2604	10	7 –6.5	6
10	25	0.2605	10	6.9–6.4	6 –5.9
11	8	0.2538	10	6.8–6.7	6 –6.2
12	5	0.2198	10	7	6.1–6.2
13	2	0.1371	10	6 –6.6	6 –6.2

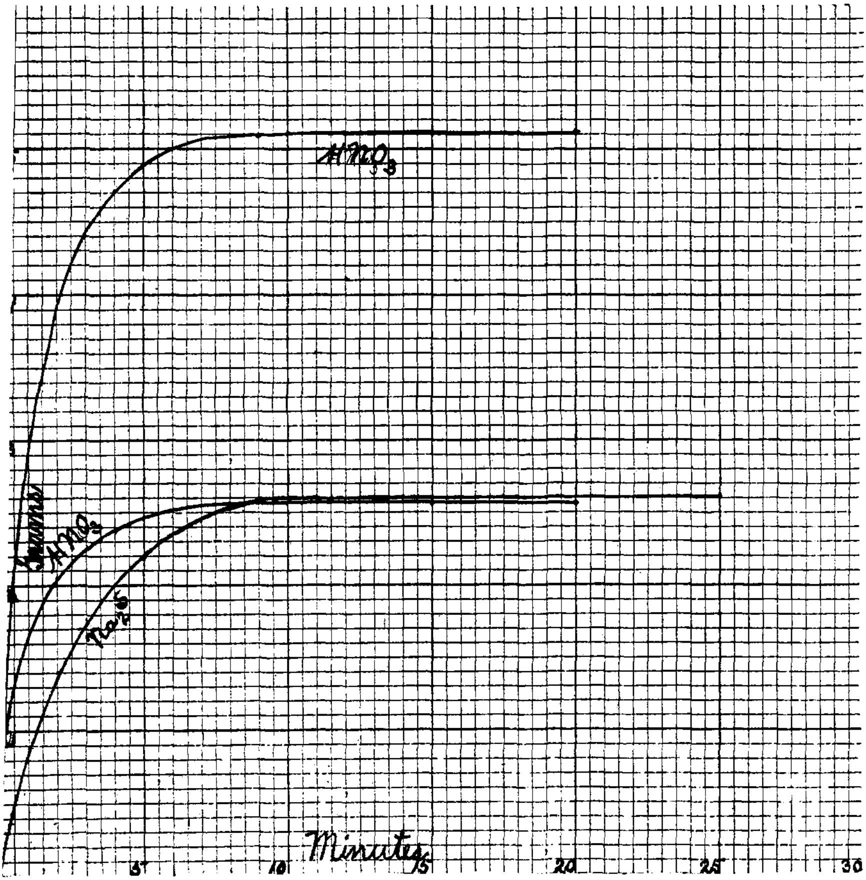
In Expt. 1 mercury sulphide had separated upon the surface and the sides of the liquid before electrolysis took place. As this material did not dissolve, the result is naturally low. The separation may be prevented by adding a sodium sulphide solution to that of the mercury salt before dilution.

In Expt. 3 the effect of a higher current density was tried without any apparent advantage. No beneficial result was observed in Expt. 4 by the use of a larger amount of sodium sulphide.

The residual liquid from Expts. 2, 3, 4, 5 and 8, when digested with an ammonium nitrate solution, showed the presence of mercury, but it could not be detected in the liquid from Expts. 6, 7, 9 and 10. The fact that more time was required for the precipitation of the mercury in Expt. 8 is due to the use of a cold electrolyte.

Expts. 11, 12 and 13 were conducted to learn how much metal was precipitated in two, five and eight minutes respectively, so that the data for the time curve, page 1273, might be complete.

In performing these experiments the alkaline liquid was in each instance siphoned off without interrupting the current, fresh water being added as it was removed until the ammeter stood at zero. The current was then interrupted and the deposit of metal washed with absolute alcohol and ether, the dish being warmed between the hands to remove the last traces of ether. After wiping the outside of the dish with a clean, soft cloth, it was allowed to stand in a desiccator for twenty minutes before weighing. It was found that the precipitated metal weighed the same



Rate of deposition of mercury.

after standing twenty minutes as after standing twenty-four hours.

The deposit of mercury was dissolved from off the dish with hot nitric acid (1 : 1). The insoluble film of platinum black invariably remained upon the dish, indicating that the mercury had penetrated the platinum and formed an amalgam with it. In each experiment the dish lost in weight about 0.0025 gram.

The preceding results show that this electrolyte answers admirably for the rapid determination of mercury.

A sample of California cinnabar was distilled with lime, and showed the presence of 46.26 per cent. of mercury. Weighed portions of this same ore were heated to boiling with 20 cc. of sodium sulphide (sp. gr. 1.06) in a small beaker. The insoluble portion was allowed to subside and the supernatant liquid poured through a filter into a weighed platinum dish. The gangue was treated with a second portion of 10 cc. of sodium sulphide, and the solution filtered as before. This operation was repeated a third time and the gangue finally washed with hot water by decantation, and then thrown upon the filter, where it was washed until the filtrate was neutral to litmus.

The solutions obtained in this way were electrolyzed. A little longer period was required for the precipitation, as will be observed below, because the electrolyte was not heated at the beginning. The results follows:

TABLE IV.

Experiment.	Time. Minutes.	Sodium sulphide (sp. gr. 1.06). cc.	Ore.	Mercury found.	Per cent.	Volts.	N.D $_{100}$ amperes.
1	15	40	0.3007	0.1380	45.88	6.2–6.1	6 –6.2
2	20	40	0.3002	0.1393	46.40	6.3–5.7	6
3	25	40	0.3002	0.1395	46.46	6.9–5.7	6 –6.2
4	30	40	0.3004	0.1394	46.40	6.6–5.5	6.2–6.4
5	20	60	0.5003	0.2322	46.41	6 –5.1	6
6	25	60	0.5002	0.2321	46.40	5.6–4.9	6.2–6
7	30	60	0.5003	0.2325	46.46	5.8–5	6 –6.2

They show conclusively that the precipitation may be made in twenty minutes, no mercury having been detected in the residual liquid.

The time necessary for each of the above analyses did not exceed an hour and thirty minutes from the weighing out of the ore until the weight of the deposit had been obtained.

The gangue in each experiment was dried and ignited with lime. No mercury was found. In those cases where one-half gram of ore was used the quantity of sodium sulphide applied to its solution amounted to 60 cc.

It goes without saying, after an inspection of the above results, that the electrolytic procedure for the determination of mercury in its ordinary salts and in its most common and important ore is vastly superior to the time-honored method of distillation with lime, and indeed to any other method which has been applied for its estimation.

The deposits of mercury were always adherent and very satisfactory, so that we feel that this course may be recommended without hesitation to analysts.

UNIVERSITY OF PENNSYLVANIA.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, NO. 92.]

THE ELECTROLYTIC DETERMINATION OF CADMIUM WITH THE USE OF A ROTATING ANODE.[1]

BY ALICE L. DAVISON.

Received August 28, 1905.

INTRODUCTION.

IN VIEW of the work recently done in the rapid determination of metals electrolytically by the use of a rotating anode[2] it has seemed desirable to investigate each metal separately, studying the conditions under which it may be precipitated from different electrolytes. In this way, zinc, nickel and cobalt have been studied,[3] and data accumulated relating to the rapid precipitation of these metals. The purpose of the present work was to make a similar study of cadmium.

This metal may be determined easily and accurately by the electric current from a number of electrolytes, and its deposition by the aid of a rotating anode was shown by Exner[3] to be accomplished completely in a very short time. The apparatus used in the present investigation was the same as that employed by Exner, Ingham and Ashbrook[3] working in this laboratory, and the same general method of procedure was followed. The dilution of the electrolyte was from 90–125 cc., giving an average cathode surface of 100 sq. cm., and the average distance between the electrodes was 1 cm. With the motor used, six speeds of rotation were practicable for the anode, *viz.*, 430, 580, 630, 700, 810 and 840 revolutions, respectively, per minute. These are designated in the tabulated conditions by the numerals I to VI.

In each electrolyte special attention was given to the determination of the rate of precipitation, and the results were plotted graphically. In every case the solution, before electrolyzing, was heated until bubbles appeared on the bottom of the dish.

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

[2] This Journal, **25**, 896; **26**, 1251, 1269, 1283, 1595.

[3] *Loc. cit.*