the fact that the lead oxalate is not perfectly pure, the factor 1.669 will give a closer approximation. On this basis, for 0.5 gram of ore taken for assay, the solution should contain 1.5185 grams of potassium permanganate per liter, in order that 1 cc. may equal 1 per cent. lead. It is best to standardize on about 0.200 gram of pure lead dissolved in a little 1:2 nitric acid and put through the entire process.

Notes.—The lead oxalate formed in the above process is not pure white, but yellowish, and still contains about 1 per cent. of lead chromate. It appears to be sufficiently uniform in its nature to give accurate results.

Instead of dropping filter and precipitate into the flask for titration, as described above, a neater method of procedure is as follows: Place the flask under the funnel and pour through and over the filter about 75 cc. of hot dilute acid, containing 5 cc. of strong sulphuric acid, and then wash the filter and residue well with hot water, so that the final bulk of the filtrate will be about 125 cc. Titrate the hot liquid as before. This method takes a little longer and gives practically the same results as the simpler way, but it has the advantage of a permanent end-point, there being no organic matter present to slowly decolorize the pink tinge.

Calcium does not interfere with the method, nor does antimony. Bismuth in small amounts is without material influence. Ten per cent. of bismuth added to a mixture containing about 23 per cent. of lead raised the result 0.36 per cent., most of the bismuth being removed as sulphate and chromate.

DENVER, COLO.

[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 150.]

THE ELECTROLYTIC DETERMINATION OF BISMUTH.

BY F. J. METZGER AND H. T. BEANS.

Received January 29, 1908.

Much has been written about the determination of bismuth in the electrolytic way and many electrolytes have been proposed. Without attempting any detailed discussion of the numerous publications which have appeared on the subject, the difficulties with which one almost invariably has to contend may be briefly summed up as follows:

When a bismuth solution is electrolyzed there is deposited not only metallic bismuth on the cathode, but frequently there is a simultaneous deposition of peroxide on the anode and it has been suggested that both anode and cathode be weighed for each determination. Again, the deposited metal is nearly always black and spongy, and in cases where accurate results have been obtained it has been necessary to exercise the greatest care in washing and drying in order to prevent loss mechanically. A method which has been recommended especially for comparatively large quantities of bismuth is the amalgam method originally proposed by Vortman.[1] In this method a known quantity of mercury salt is added to the bath and the deposit of bismuth amalgam weighed. From this weight the bismuth is obtained by difference. The quantity of mercury recommended is four times that of the bismuth present.

The method described in this paper presents none of the difficulties encountered in previous methods; the metal is deposited in compact, adherent form and can be washed and dried without any possible chance of loss, nor is there ever any deposition of peroxide on the anode when the electrolysis is completed.

It has been found that by the addition of acetic acid to a bismuth nitrate solution precipitation by hydrolysis may be completely prevented, even though the solution be subsequently largely diluted. It is also possible to obtain this result by first eliminating all free nitric acid by the addition of sodium hydroxide to alkaline reaction and then redissolving the precipitated bismuth hydroxide by means of acetic acid, the whole operation being carried out in the cold. It has also been observed that the addition of boric acid to the bath has a decided effect on the character of the deposit and in addition it serves to bring about, readily, complete solution of bismuth hydroxide without the addition of very large quantities of acetic acid.

The apparatus employed is a slightly modified form of that originally proposed by Gooch and Medway,[2] using a rotating cathode. The platinum thimble employed as cathode was connected to the shaft by means of a rubber stopper wound with fine platinum wire for contact and had an available surface of forty square centimeters. In all cases it was driven at the rate of about seven hundred revolutions per minute.

As a basis for the experiments a bismuth solution was prepared by dissolving chemically pure bismuth nitrate in water containing 25 cc. conc. nitric acid per liter. The solution was then carefully standardized by gravimetric methods.

The method of procedure was in all cases as follows: To a known quantity of the standard solution phenolphthalein was added, then sodium hydroxide solution, drop by drop, to alkaline reaction. The precipitate formed was redissolved in acetic acid and then two grams of boric acid were introduced. The solution was diluted, heated to 70–80° and electrolyzed. The working conditions are shown in the following table:

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[1] Ber., 24, 2749.

[2] Am. J. Sci. [4], 15, 320.

TABLE I.

Expt. No.	50 per cent. acetic acid. cc.	Boric acid. Grams.	Volume. cc.	ND$_{40}$[2].	Voltage.	Temperature.	Time. Hrs.	Bi taken.	Bi found.	Error.
1	20	2	250	0.2–0.15	2.1 –2.8	74°–79°	¾	0.03956	0.0391	—0.00046
2	20	2	250	0.2–0.175	1.9 –2.75	75°–79°	1¼	0.0989	0.0990	+0.0001
3	20	2	250	0.2–0.15	1.9 –2.8	72°–75°	1½	0.0989	0.0990	+0.0001
4	20	2	250	0.2–0.17	1.9 –2.75	63°–77°	1¼	0.0989	0.0989	±0.0000
5	20	none	250	0.2–0.15	1.9 –2.7	74°–78°	1¼	0.0989	0.0989	±0.0000
6	20	2	250	0.2–0.15	1.9 –2.65	74°–83°	1¼	0.0989	0.0987	—0.0002
7	20	2	250	0.2–0.15	1.85–2.74	72°–77°	1¼	0.0989	0.0989	±0.0000
8	20	none	250	0.2–0.125	1.8 –2.6	77°–79°	1¼	0.0989	0.0986	—0.0003
9	20	2	250	0.2–0.2[1]	1.9 –2.8	75°–78°	1¼	0.0989	0.0984	—0.0005
10	20	2	250	0.2–0.17	1.85–2.75	76°–78°	1¼	0.0989	0.0992	+0.0003
11	20	2	250	0.2–0.17	1.8 –2.72	76°–79°	1¼	0.0989	0.0992	+0.0003
12	20	2	250	0.2–0.17	1.8 –2.64	77°–88°	1¼	0.0989	0.0991	+0.0002
13	20	none	250	0.2–0.175	1.8 –2.4	75°–78°	1¼	0.0989	0.0990	+0.0001
14	20	2	250	0.2–0.175	1.8 –2.7	73°–77°	1¼	0.1978	0.1981	+0.0003
15	20	2	250	0.2–0.16	1.8 –2.6	76°–77°	1¼	0.1978	0.1979	+0.0001
16	20	2	250	0.2–0.16	1.8 –2.55	73°–78°	1¼	0.1978	0.1978	±0.0000
17	20	2	250	0.2–0.17	1.77–2.55	70°–80°	1¼	0.1978	0.1980	+0.0002
18	20	none	250	0.2–0.175	1.75–2.37	75°–81°	1⅓	0.1978	0.1984	+0.0006
19	30	none	250	0.2–0.16	1.8 –2.45	70°–78°	2¼	0.3956	0.3962	+0.0006
20	30	2	250	0.2–0.175	1.75–2.5	70°–78°	2¼	0.3956	0.3953	—0.0003
21	30	none	250	0.2–0.15	1.7 –2.42	73°–79°	3¼	0.3956	0.3955	—0.0001
22	30	2	250	0.2–0.16	1.75–2.55	74°–77°	2¼	0.3956	0.3956	±0.0000
23	30	2	250	0.2–0.175	1.72–2.45	74°–79°	2¼	0.3956	0.3957	+0.0001
24	30	2	250	0.2–0.175	1.75–2.50	78°–79°	2½	0.3969	0.3968	—0.0001
25	30	none	250	0.2–0.175	1.76–2.55	75°–80°	3½	0.3969	0.3969	±0.0000

In Experiments 19–25 inclusive, the amount of acetic acid given does not completely redissolve the precipitate, but after the addition of the boric acid the solution becomes perfectly clear. In Experiments 19, 21 and 25, in which no boric acid was used, the slightly opalescent solution was electrolyzed, the solution, however, becoming perfectly clear during the period of the electrolysis.

The change in voltage during the electrolysis serves as an excellent indicator in the determination. The voltage remains constant until all but the last trace of bismuth has been deposited, when it begins to rise rapidly to a maximum at which it again remains constant. The electrolysis should be continued five or ten minutes beyond this maximum point. In the table given above the voltages recorded show the initial and final values. Table II being a record of Experiment 16 above, makes this a little more clear.

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[1] In this experiment the current was maintained constant.

[2] The figures in the second column represent the point to which the current drops at the end of the experiment.

TABLE II.

Time. P. M.	ND_{40}.	Voltage.	Temperature.
2:50	0.2	1.8	73°
3:05	0.2	1.8	75°
3:20	0.2	1.8	76°
3:35	0.2	1.8	78°
3:43	0.19	2.0	78°
3:45	0.18	2.1	78°
3:50	0.175	2.4	78°
3:55	0.175	2.5	78°
4:00	0.160	2.55	78°
4:05	0.160	2.55	78°

The action of acetic acid on the deposited metal was found to be so slow that it is not necessary to siphon off the liquid at the end of the experiment. All that is required is to quickly substitute a beaker of water without interrupting either the current or rotator. The thimble is then detached, washed with alcohol and ether, allowed to dry and weighed after standing on the balance for ten minutes. To avoid any errors which might arise from changes in atmospheric conditions, the weight of the thimble was taken after dissolving off the deposited metal by immersing in nitric acid, washing and drying, etc., the same as above.

In all of the experiments given in Table I, the available cathode surface was forty square centimeters, and it was naturally supposed that a stronger current could be employed with a larger electrode, and in this way the time factor might be reduced. A large electrode having an available surface of one hundred square centimeters of the same form as the one previously used was procured with which we obtained the following result:

Expt. No.	50 per cent. acetic acid. cc.	Boric acid. Grams.	Volume. cc.	ND_{100}.	Voltage.	Temperature.	Time. Hrs.	Bi taken.	Bi found.	Error.
26	30	2	350	0.5–0.17	1.9–2.5	78°–80°	1½	0.3969	0.3972	+0.0003

In working with this larger electrode the current should be reduced to 0.2 ampere at the time when the voltage begins to rise.

As seen in the table the results are accurate without the use of boric acid. The metal is deposited in bright, compact form up to the time when the voltage begins to rise, *i. e.*, when only very small quantities remain in solution. From this point, if there be no boric acid present, the last traces of metal deposit over the surface of the bright coating in the form of a granular layer less firmly adherent and somewhat darker. With boric acid present the deposition is uniform to the very end of the experiment, giving a smooth, compact, adherent deposit having the characteristic color of the metal.

In not a single experiment was there any evidence of peroxide formation on the anode at the close of the determination. Occasionally there was a slight tinge of yellow on the anode at the very beginning of the electrolysis, but this, however, soon disappeared. The solution after each determination was examined for bismuth and none could be found.

The effect of boric acid on the deposition of other metals is being studied.

ANALYTICAL LABORATORIES,
January, 1908.

A SEPARATION OF IRON FROM MANGANESE.

BY RICHARD B. MOORE AND IVY MILLER.

Received December 30, 1907.

If to a solution of ferric chloride containing free hydrochloric acid, pyridine, in slight excess, be added, the iron is completely precipitated as hydroxide. Aluminium, chromium, and zinc, under such conditions, are not completely precipitated, while manganese, nickel, and cobalt remain in solution. This method can therefore be used to separate iron from the last three metals. The present paper deals only with the separation of manganese from iron by means of pyridine.

When pyridine is added to a neutral solution of a manganous salt no precipitate is obtained. On warming, the solution slowly oxidizes and the manganese begins to come down. The rate at which oxidation takes place, however, is about one-third as fast as the rate at which a manganous solution oxidizes when treated with ammonium chloride and ammonium hydroxide under similar conditions. If the manganous solution is made acid with a little hydrochloric acid before addition of the pyridine to slight excess, the solution may then be heated for ten minutes without oxidation. Consequently, pyridine possesses considerable advantages over ammonium hydroxide in the separation under question, especially when a large amount of manganese is present. Practically, its only disadvantage is its cost. A very fair separation can be made with one precipitation.

On washing ferric hydroxide precipitated by pyridine, no iron at first appears in the filtrate. As the excess of pyridine is washed out of the precipitate, however, colloidal iron passes through the filter. On washing the precipitate with pyridine water (1:500) the iron is completely retained by the filter.

In the following experiments Merck's pyridine, "Medicinal grade," was used. It was redistilled before using.

Pure iron wire was dissolved in 10 cc. of 4 *N* hydrochloric acid. A few drops of concentrated nitric acid were added and the solution