Electrolytic Determination and Separation of Bismuth

Part III. The Determination and Separation from Copper in Alkaline Solution

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LASSIEUR[1] has described the separation of copper and bismuth by electrolytic methods as "a difficult problem, as yet only imperfectly solved." From the point of view of the present work a further difficulty lay in the fact that most of the methods described were concerned chiefly with the determination of the copper in mixtures of the two metals. This applies to the method of Lassieur,[1] in which the copper is deposited first from an ammoniacal solution, and to that of

Moldenhauer,[2] in which copper is deposited from an acid solution containing phosphoric acid. Hollard and Bertiaux[3] used an ordinary chemical separation, making use of electrolytic deposition as a final step only; Schoch and Brown[4] also fell back on a chemical method. A second method used by Hollard and Bertiaux[5] relied on the co-precipitation and subsequent separation of lead and bismuth as oxides; this method was applicable only to traces of bismuth.

Two methods were described by Sand.[6] In the first of these the two metals were contained in a tartaric acid solution from which the copper was deposited first; the deposition, however, had to be repeated, owing to the initial separation being incomplete. Another method, depending on the formation of a soluble bismuth tartrate, was suggested by Schleicher[7]; in this the copper was deposited first, as shown by the measurements of deposition potential carried out by Root.[8]

In the second method suggested by Sand[6] the copper was converted into a double cyanide, a compound requiring a very high potential for its decomposition, and bismuth was deposited first. This method, which appeared from the literature to be the most suitable for the determination of bismuth in presence of copper was based on a slow method of Smith.[9] The electrolysis was carried out in alkaline solution.

Smith determined bismuth in presence of a citrate at room temperature, the deposition taking nine hours. Sand, using a rotating anode, made the determination in about half-an-hour at about 80° C., sodium tartrate being used to keep the bismuth in solution. It was found necessary to add formaldehyde to prevent the formation of bismuth pentoxide on the anode. In the slow method this was unnecessary, apparently because of the lower anodic potential.

On repeating the separation by Sand's procedure difficulties arose through the use of formaldehyde, which causes a blackening of the solution, owing to the formation of colloidal bismuth. In this connection it may be noted that Gutbier[10] has used formaldehyde in the preparation of colloidal bismuth from alkaline bismuth nitrate and glycerol solutions.

Sand recommended the use of 10 ml. of formaldehyde in a total electrolyte of 80 to 100 ml. In the present work it was found that 2·5 ml. caused precipitation of the metal, while the addition of smaller amounts failed to prevent the formation of oxide, even when a low current density was used. It is possible that in the earlier work impure formaldehyde was used, and this may account for the different effect obtained.

Experiments were made on solutions containing bismuth alone with other reducing agents that have been used as depolarisers. Hydrazine salts and glucose caused blackening, while citrates and formates were ineffectual in preventing the formation of the pentoxide. With hydroquinone, although no oxide was observed on the anode, low results were obtained. Hydroxylamine salts alone were found to be suitable.

In experiments on solutions prepared from both nitrate and chloride solutions, equally good deposits were obtained with either. Objections have been brought against the use of cyanides, and their effect was therefore studied. It had been found that, in general, alkaline solutions containing cyanides tend to behave irregularly,[11] possibly owing to anodic polymerisation; in the present work it was found possible to obtain reproducible results by always using the method of controlled potential. A solution containing a cyanide also attacks the platinum of the electrodes[12,13]; by keeping the amount of added cyanide low good results could be obtained, but the cathode lost slightly in weight; this loss amounted to about 0·5 mg. when 2 g. of potassium cyanide were present in about 100 ml. of electrolyte. The loss appears to be due to the dissolving and re-depositing of platinum, which is afterwards lost in cleaning the cathode and has therefore no effect on the result of the analysis. The deposits obtained were of good appearance and adhered well to the electrode.

EXPERIMENTAL

DEPOSITION OF BISMUTH.—Stock solutions were made up from pure bismuth, and known volumes were taken for each experiment; each amount contained 3 ml. of conc. nitric acid or 5 ml. of conc. hydrochloric acid. Excess of sodium hydroxide was added, and the precipitated bismuth hydroxide was redissolved by adding 2 to 3 g. of sodium hydrogen tartrate. Potassium cyanide, if used, was added as solid. The solution was diluted to about 100 ml., and 1·0 g. of hydroxylamine sulphate was added. The electrolysis was carried out at 75° C., the platinum gauze electrodes, the auxiliary electrode and voltmeter described by Lindsey and Sand[14] being used.

A saturated potassium chloride auxiliary electrode with a 50 per cent. sodium nitrate connection was used, the initial potential being 0·76 v. When the current fell to zero the auxiliary potential was raised in three steps to 0·90 v., and the electrolysis ended when the current fell to zero at this auxiliary potential. The deposited metal was washed and dried in the usual manner. Results are given in Table I.

TABLE I

Expt. No.	Wt. of KCN g.	Bismuth taken g.	Bismuth found g.	Time, minutes
1	2·0	0·2293	0·2293	15
2	2·0	0·2293	0·2292	25
3	7·5	0·2293	0·2297	15
4	3·0	0·2000	0·2000	20
5	—	0·2500	0·2499	25
6	—	0·2500	0·2498	25
7	—	0·2096	0·2097	20
8	—	0·2370	0·2368	15
9	—	0·2370	0·2369	25
10	—	0·2500	0·2502	25
11	—	0·1000	0·1003	20

In Expts. 7 and 8 the bismuth was originally present in chloride solution.

SEPARATION FROM COPPER.—The separations were all made in solutions obtained by dissolving the metals in nitric acid. Measured volumes of stock solutions were taken, each containing 3 ml. of conc. nitric acid and made alkaline by adding 3 g. of sodium hydroxide; the precipitated bismuth hydroxide was re-dissolved by adding 2 g. of sodium hydrogen tartrate. The basic copper precipitate was converted into the double cyanide by adding solid potassium cyanide to the cold solution until it became colourless; 2 to 3 g. were required. The solution was then treated exactly as described above for the deposition of bismuth.

Typical results are given in Table II.

TABLE II

Expt. No.	Bismuth taken g.	Bismuth found g.	Copper present g.	Time, minutes
1	0·2293	0·2292	0·25	25
2	0·2293	0·2297	0·25	15
3	0·2293	0·2292	0·50	15
4	0·0917	0·0915	0·25	12
5	0·1834	0·1837	0·25	10

SUMMARY.—Rapid and accurate determinations of bismuth may be made in alkaline tartrate solution by the use of hydroxylamine sulphate as a depolariser, and the method may be used for determining bismuth in presence of copper.

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REFERENCES

1. A. Lassieur, "*Electroanalyse Rapide*," Paris, 1927, pp. 97–99.
2. W. Moldenhauer, *Z. angew. Chem.*, 1926, **39**, 454.
3. A. Hollard and L. Bertiaux, *Chem.-Zgt.*, **28**, 782.
4. E. P. Schoch and D. J. Brown, *J. Amer. Chem. Soc.*, 1916, **38**, 1660.
5. A. Hollard and L. Bertiaux, "*Analyse des Metaux par Electrolyse*" (1906), p. 90.
6. H. J. S. Sand, *J. Chem. Soc.*, 1907, **91**, 373.
7. A. Fischer (*Ed.* A. Schleicher), "*Elektroanalytische Schnellmethoden*," Stuttgart, 1926, p. 171.
8. J. E. Root, *J. Phys. Chem.*, 1903, **7**, 428–465.
9. E. F. Smith, *Amer. Chem. J.*, 1890, **12**, 428.
10. A. Gutbier, *Z. anorg. Chem.*, 1926, **151**, 153–156.
11. H. J. S. Sand, *loc. cit.*, p. 401.
12. F. Spitzer, *Z. Elektrochem.*, 1905, **11**, 407.
13. A. L. Flanigen, *J. Amer. Chem. Soc.*, 1907, **29**, 455.
14. A. J. Lindsey and H. J. S. Sand, ANALYST, 1934, **59**, 328, 335.

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