597. *The Electrolytic Determination of Gallium.*

By (the late) H. TERREY and J. THABIT.

An electrolytic method for the determination of gallium in an alkaline sulphate solution is described. The platinum gauze electrodes are protected by prior deposition of copper.

THE only quantitative electrolytic work done on gallium is that by Reichel [1] who used a concentrated ammonium sulphate bath. It has been found by us to suffer numerous defects. For instance, with a standard gallium sulphate solution, the results varied by more than 1%, even when an empirical factor was used, as suggested by Reichel. The amount of platinum dissolved off the anode varied with current density and time. The solution became turbid as the electrolysis proceeded, and the deposit of gallium on the platinum gauze cathode was dull, which suggested inclusion in it of foreign matter. The platinum cathode was attacked on removal of the deposited gallium no matter what solvent was used, in that the cathode retained a black coating where the gallium had been deposited.

Reichel recommended heating the solution on a water-bath; however, the high current applied (5 amp.) generates sufficient heat to maintain a temperature of about 70°, so that no more than initial heating is required.

The work described below overcomes these difficulties.

EXPERIMENTAL

To avoid attack on the platinum cathode on removal of the deposited gallium, it was first plated with copper. Besides protection, such a plated cathode has the advantages of a higher hydrogen overvoltage and of providing a good visual background: completion of deposition can be tested by raising the level of the liquid and noting whether deposit formed on the newly wetted surface of the cathode.

However, copper deposited from an acid copper sulphate solution was attacked by the basic solution used later for electrodeposition of gallium. It was found more accurate to add to the gallium solution a known volume of copper solution, the copper content of which had been determined electrolytically from a similar basic solution.

A cathode–anode potential of about 2 v is enough to deposit copper. If the potential is raised before all the copper has been deposited, gallium will be co-deposited with copper as a dark layer which withstands temperatures in the range 110—120° without loss of gallium, although the latter in the pure state melts at 31°, and this heat-resistance is of an advantage when the cathode is finally dried.

When this procedure is followed the platinum cathode is attacked on dissolution of the deposited gallium and copper, and platinum black remains. Brightness is restored to the cathode by heating it to redness; it is important to leave the cathode in a hot dilute nitric acid for long enough to allow complete dissolution of the deposit, then to wash it thoroughly with water before the heating.

The bath solution had the following composition: to a known weight of pure gallium oxide was added water (*ca.* 200 ml.) and concentrated sulphuric acid (10 ml.). The mixture was heated to dissolve the oxide and then the total volume was made up to 1 l.

Co-deposition of Copper–Gallium.—A measured volume of gallium sulphate solution, mixed with 25 ml. of standard copper sulphate solution (containing about 0·002 g. of copper per ml.),

---

[1] Reichel, *Z. analyt. Chem.*, **1933**, **87**, 321.

was made basic by 10 ml. of 5N-sodium or -potassium hydroxide. The precipitated gallium hydroxide dissolves in the excess of alkali hydroxide. Then ammonium sulphate (3—5 g.) is added, the solution becoming dark blue. The total volume of solution should not exceed 100 ml.

By applying a potential of about 2 v copper is deposited first. If a bright gallium deposit is sought later on, all the copper has to be deposited first by this low potential before increasing the voltage to pass a current of 4—5 amp. If this higher potential is applied before all the copper has been deposited, simultaneous deposition of copper and gallium occurs and a dark deposit on the cathode results. Such a dark co-deposit gives as accurate results as bright gallium deposit.

After complete deposition the bath container is removed, and, without interruption of the current, the electrodes are washed with distilled water at least three times, then with absolute alcohol or acetone. The cathode is then dried for 10 min. in an oven at 110°, cooled, and weighed. The tabulated results were obtained with a gallium sulphate solution containing 2·2241 g. of gallium per l. (the oxide being assumed to be 99·9% pure) and a copper sulphate solution containing 1·48 g. of copper per l.

Cu and Ga found (g.)	Cu added (g.)	Ga found (g.)	Ga present (g.)	Cu and Ga found (g.)	Cu added (g.)	Ga found (g.)	Ga present (g.)
0·0371	0·0148	0·0223	0·0224	0·2035	0·0372	0·1663	0·1668
0·0370	0·0148	0·0222		0·2036	0·0372	0·1664	
0·0372	0·0148	0·0224		0·2032	0·0372	0·1660	
0·0926	0·0372	0·0554	0·0556	0·2587	0·0372	0·2215	0·2224
0·0925	0·0372	0·0553		0·2587	0·0372	0·2215	
0·0926	0·0372	0·0554		0·2585	0·0372	0·2213	
0·1480	0·0372	0·1108	0·1112				
0·1479	0·0372	0·1107					
0·1481	0·0372	0·1109					

Deposition in the Absence of Copper.—The same procedure was applied, *i.e.*, addition of 5N-sodium hydroxide (10 ml.) to the gallium sulphate solution, then ammonium sulphate (3—5 g.). A current of 4—5 amp. was passed to deposit gallium directly on to the platinum cathode. The solution does not require external heating because after a short time the temperature of the solution (about 75 ml.) rises to 60—70°.

In this procedure some practice is required to detect the end of the deposition (by exposing a new area of the cathode to the solution) because the bright silvery colour of the deposited gallium is rather similar to that of the platinum electrode. The difference however, can be detected with a little practice. Washing is effected as above.

The cathode should be dried at a lower temperature than that mentioned above. It is best suspended above the drying oven so that a current of warm air flows over it; in this way melting of the gallium deposit and the formation of droplets of the metal is avoided. This is satisfactory for small quantities of gallium (*e.g.*, 0·05 g.), but with larger quantities there is a tendency for the deposit to remain soft, and a danger that some of it may adhere to the pan of the balance. For this reason the co-deposition procedure is recommended for such larger amounts.

The following tabulated typical results refer to volumes similar to those detailed above.

Ga found (g.)	Ga present (g.)	Ga found (g.)	Ga present (g.)	Ga found (g.)	Ga present (g.)
0·0222	0·0224	0·1107	0·1112	0·2212	0·2224
0·0224		0·1109		0·2216	
0·0221		0·1106		0·2213	
0·0552	0·0556	0·1660	0·1668		
0·0555		0·1662			
0·0554		0·1660			

General Remarks.—Whichever method is used, the bath solution remains clear at the end of the electrolysis; no colloidal turbidity occurs. The weight of the platinum anode remains almost constant (±0·0002 g.). When larger quantities (*e.g.*, 10 g.) of ammonium sulphate were used the anode loss was more than 0·0005 g., and the bath solution became cloudy, as usually happens when Reichel's procedure is used.

The deposit of gallium obtained by either method can be dissolved in hot dilute nitric acid; if platinum black is formed, brightness can be restored by the method described above.

WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES,
UNIVERSITY COLLEGE, LONDON, W.1.
[Present address (J. T.): DEPARTMENT OF CHEMISTRY,
ROYAL COLLEGE OF ARTS AND SCIENCES,
BAGHDAD, IRAQ.]

[*Received, February 25th,* 1957.]