THE ELECTRO-ANALYSIS OF MERCURY COMPOUNDS WITH A GOLD CATHODE.

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(A Paper read before the Faraday Society, Tuesday, March 30, 1909,
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Some years ago I carried out a long series of experiments upon the electro-analysis of mercury. In the first place a platinum basin sand-blasted on the interior was employed as cathode, but owing to the tendency for the mercury to form in drops and to run down to the centre of the basin there was a possibility of losing a portion of it in washing. There was also another objection—the mercury deposit could not be washed with alcohol and ether in order to dry it rapidly, because this made it still less adherent, and often covered the mercury with a thin greyish pellicle. Consequently it was

Electrolyte.	Current Density.	E.M.F.	Temperature.	Time in Hours.	Error Per Cent.
HNO ₃	0·2–0·6	1·5–3·2	60°	21·5	+0·8
„	0·1–1·0	1·5–3·6	50°	5·5	+0·23
„	0·2–0·8	1·5–3·3	60°	7·0	+2·0
„	0·2–1·0	1·6–3·0	40°	19·0	+1·2
H ₂ SO ₄	0·2–0·75	1·7–2·8	50°	6·0	+0·4
„	0·2–0·3	1·9–2·9	60°	5·25	+1·4
„	0·2–0·9	2·4–3·0	60°	6·0	+1·0
Na ₂ S	0·1–0·8	0·75–1·5	normal	23·0	+0·4
„	0·15–0·8	2·1–7·0	„	22·0	+1·2
KCN	0·1–0·5	3·2–5·0	„	17·0	+0·05
HCl	0·5	6·0	„	20	+0·556
„	0·1–0·3	—	„	15	+0·556
„	2·25	5·0	40°	2·25	+0·258

necessary to place the moist basin in a desiccator to dry, and this took some hours. I therefore thought that perhaps a gold cathode would get over these difficulties, because the mercury as it was deposited would amalgamate with it. Messrs. Johnson, Matthey & Co. made a gold flag electrode alloyed with 5 per cent. of platinum to harden it, as pure gold was found to be too soft. The electrode was in the form of the flag electrodes designed by me in 1903 (*Electrochemist and Metallurgist*, vol. iii, p. 22), and had a total surface of 0·5 square decimetre. It was found that the mercury amalgamated evenly all over the surface of the electrode, and at the end of a determination it was readily removed by cautious heating over the Bunsen burner. But the weight of the electrode increased slightly after being amalgamated and the amalgam was removed. After the first amalgamation, however, the weight was practically constant.

A very large number of determinations were made with specially purified mercuric chloride and also mercuric bromide and sulphate. The electrolytes employed were nitric acid, sulphuric acid, hydrochloric acid, potassium cyanide, and sodium sulphide. A remarkable fact soon became evident—the results were uniformly too high, varying from 0·5 to 2·5 per cent., and it made very little difference whether the electrolysis was completed quickly or whether it took a long time. On the previous page are a few of the results obtained.

These results were rather surprising, as the tendency in depositing mercury electrolytically, using a platinum cathode, is to obtain low results. Some experiments were therefore carried out, using solutions containing the same amount of mercury salt and the same quantity of electrolyte. Two such solutions were then electrolysed in series, employing a platinum cathode in one case and the gold electrode in the other. A few of the results obtained are appended.

It is thus seen that in the majority of cases the platinum electrode gave results which were within the limits of experimental error, but that again

Electrolyte.	Current.	Temperature.	Time in Hours.	Gold Electrode, Error Per Cent.	Platinum Electrode, Error Per Cent.
HNO ₃	0·2 -0·9	40°	6	+1·0	-0·7
"	0·1 -0·2	normal	22·5	+0·75	-0·4
"	0·1 -0·4	"	21	+1·0	-1·2
Na ₂ S	0·15-0·8	"	20	+1·1	-0·4
"	0·15-0·2	"	22	+1·2	-0·4
H ₂ SO ₄	0·2 -0·8	40°	6·5	+2·0	-0·2
"	0·2 -0·25	normal	22·5	+0·7	-0·4
KCN	0·5	40°	18·0	+0·05	-5·0

the gold electrode showed uniformly high results. It was thought that perhaps the cause of the high results with the gold electrode might be due to alloy formation with the potassium persulphate, which was at times added to prevent the formation of insoluble mercurous salts. Therefore, instead of using potassium or sodium persulphate as oxidising agent, pure hydrogen peroxide free from inorganic salts was employed. The results, however, were exactly the same, namely, still too high.

It appeared possible that the gold might absorb cathodic hydrogen, and therefore the electrode was carefully weighed, made the cathode in dilute sulphuric acid, and the current passed for 4·5 hours. It was then carefully dried in exactly the same manner as when it was coated with mercury—that is, washed in distilled water, then in absolute alcohol and absolute ether, and hung in a desiccator over sulphuric acid for an hour. The weights were—

Before electrolysis	...	...	...	...	18·6119.
After electrolysis	...	...	...	...	18·6120.

The weight was therefore not altered.

There was the possibility that the cathode might absorb hydrogen when coated with mercury, but not otherwise. Consequently mercury was deposited on it, after which it was carefully dried and weighed. It was then boiled in water and in alcohol, dried, and again weighed. There was no noticeable alteration in weight. The coated electrode was then boiled in

hydrogen peroxide solution without alteration in weight. Finally it was made the cathode in dilute sulphuric acid, and the current passed for 12 hours. No increase in weight took place, therefore no hydrogen had been absorbed.

From the first table it is seen that the time of deposit was usually rather long, from $5\frac{1}{2}$ to 24 hours. The apparatus was therefore placed in a powerful magnetic field in such a manner that the electric current lines were cut by the magnetic lines of force and a current of from 3 to 5 amperes was passed. This caused a violent agitation of the electrolyte, the solution passing down the one side of the cathode and up over the other side. The time of deposit was now from 45 to 60 minutes. The results, however, were still too high, but under these conditions they rarely exceeded 1 per cent.

Experiments were also tried with a silver cathode in one series of experiments; the cathode was made of a close spiral of silver wire 1.5 mm. in diameter. This was rotated within an anode of platinum gauze. It was not, however, possible to rotate very rapidly or to deposit more than about 0.1 grm. of mercury upon the electrode. With rapid rotation there was a tendency for the mercury to collect at the bottom of the spiral and be thrown off; this was also the case when considerable quantities of mercury were deposited out.

In another series of experiments a spiral platinum anode was rotated within a wide coil of silver wire of 1.5 mm. diameter. In both series of experiments the results obtained were high, but the metal did not deposit out so well or amalgamate so freely as with gold.

Edgar Smith has shown that mercury can be very rapidly and successfully deposited upon a mercury cathode when a rapidly rotating anode is employed. I have also carried out a series of experiments which show this to be the case. There is, indeed, no doubt that for the electrolytic determination of mercury a cathode of the same metal gives the most satisfactory results. The only objection to a mercury cathode is in the manipulation.

I had two vessels of quartz made by Messrs. Johnson, Matthey & Co., which are illustrated in Figs. 1 and 2.

In vessel Fig. 1 the platinum wire to make electrical connection with the mercury was passed down a capillary tube fused against the inside of the vessel. The reason for doing this was the fact that platinum has a lower fusing point than quartz, consequently it is by no means a simple matter to make a liquid-tight seal. The objection, however, to having the wire passing down the inside in this manner was the necessity of making the vessel rather wide, in order that the anode when rotated should be central. Another difficulty was siphoning off of the liquid, so as to wash and dry the mercury at the end of the operation. Consequently the vessel illustrated in Fig. 2 was designed. There was sealed in at one side just above the level of the mercury a quartz siphon. The platinum wire connection is sealed in at the bottom through a narrow quartz tube. The inner portion of the connecting wire which comes in contact with the mercury is made of iridium, and is welded to the platinum which passes outside. The reason for doing this is that platinum, when used as cathode, more or less amalgamates with the mercury. The beaker holds about 85 cm., and when in use is filled with solution up to the dotted line.

When the electrolysis is finished the rotation of the anode is stopped. A piece of rubber tubing is fastened on to the narrow limb of the siphon tube, and water poured in until the siphon commences to operate. The outflowing solution is collected in a beaker. As soon as the solution has fallen to the bottom of the anode more water is added, and this is continued until the

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ammeter needle falls to zero. The water is then allowed to drain out as completely as possible. The last portions are removed with spills of filter-paper. Purified methylated spirit is then run in and allowed to siphon over,

FIG. 1.

FIG. 2.

then one washing of absolute alcohol, and finally one washing of dry ether, methyl alcohol, or dry pure acetone. Dry air is then blown over the mercury for 10 minutes, or aspirated over it by closing the mouth of the beaker with a bored cork, through which a glass tube is passed. The whole apparatus is then placed in a desiccator for 10 minutes, and afterwards weighed.