sodium ion, which is washed away. It is the loss of the sodium ion that reduces the ratio of Na to U in $Na_2U_2O_7$ below 1 : 1.

The extent to which the reversibility of the reaction proceeds will depend upon two factors. In the first place, if the solubility products of the uranyl compounds formed are near that of sodium uranate, the formation of the former can not proceed very far before equilibrium is established. Besides this, the more the sodium uranate is washed, the more will it tend to pass over into the insoluble uranyl compounds up to a certain point where equilibrium is again reached.

In the light of this, then, the various formulas deduced are readily explained. The sodium uranate used for the preparation of Patera's precipitate was not thoroughly washed free of alkali until in a different physical form (*i. e.*, after ignition); hence the ratio of sodium to uranium in Patera's precipitate would naturally be different from the corresponding ratio found for the pure sodium uranate, from which all but an unweighable trace of alkali had been removed. The ratio 3 : 4 obtained in the case of No. 14 is also explained, as in this case the sodium uranate was washed longer, that is, until absolutely no alkali was left.

To sum up, then, it has been found that, while sodium uranate may actually be precipitated as $Na_2U_2O_7$, on completely removing the excess of alkali by washing with water, the precipitate undergoes a partial hydrolysis or reversal of the reaction by which it was formed, the extent of this reversal depending upon the amount of washing and upon certain physical constants not yet determined.

There is still a necessity for more work in this field to determine definitely what compounds are formed by the reversal of the reaction, the limit to which the reversal can proceed, and the solubility products of the compounds formed. It would also be of interest to determine whether the uranates of the other metals act in a manner analogous to sodium uranate.

QUANTITATIVE LABORATORY, June, 1909.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY.]

THE DETERMINATION OF THALLIUM IN THE ELECTROLYTIC WAY.

BY GILBERT W. MORDEN.

Received July 3, 1909.

The analytical behavior of thallium salts toward the electric current has been the subject of investigation by Schucht,[1] Heiberg[2] and Neumann.[3] The former used a nitric acid solution but the separation

---

[1] *Berg. und Hüttenzeitung*, **39**, 122 (1880).

[2] *Z. anorg. Chem.*, **35**, 346

[3] *Ber.*, **21**, 356.

was not quantitative. Heiberg's method of determining the thallium as an anodic oxide was accurate but consumed far too much time. Neumann proposed to precipitate the thallium as metal from the double cyanide or double oxalate electrolyte and then to dissolve the deposit in hydrochloric acid, measure the volume of hydrogen obtained and from this volume to calculate the weight of thallium present. This procedure was, however, not purely electrolytic.

The purpose of the present investigation was, therefore, to develop a rapid electrolytic method for the determination of thallium that should in point of accuracy compare favorably with the analytical procedures now followed.

Since there is no difficulty in separating the metal by the electric current, the problem to be solved was the prevention of oxidation of the deposited metal. This was attempted in two ways: (1) By covering the separated thallium with a non-oxidizable metal. (2) By the formation of an amalgam not sensitive to oxygen.

The Rapid Determination of Thallium by Depositing on It a Protective Metallic Coating.—Silver, copper and nickel are generally used in order to protect other metals from oxidation. In the case of thallium these cannot be used because they are higher than thallium in the potential series of metals; that is, if a solution of any of these metals were brought in contact with a deposit of thallium in order to form a protective coating for the thallium, the latter metal would go into solution, and an equivalent quantity of the more electro-positive element would be deposited. On reference to the potential series of metals it will be seen that zinc is more electro-negative than thallium and is hence fitted to act as a protective metal for the latter.

The Rapid Determination from a Solution of the Double Cyanide by Means of a Rotating Anode and Platinum Dish Cathode.—The apparatus for these determinations is described in Smith's "Electro Analysis," 4th ed., p. 44. Ten cc. of a solution of Tl_2SO_4 containing about 0.1 g. thallium were decomposed in the platinum dish with potassium cyanide and the resulting precipitate dissolved in excess of that salt. The platinum spiral anode was placed in position and the solution electrolyzed with a current of $N. D._{100} = 1$ A and 3–4 volts. The anode rotated about 400 times per minute. Potassium iodide was used as external indicator for the completeness of the deposition of the thallium.

When the solution gave no test for thallium the electrolyte was siphoned out with the simultaneous introduction of pure water into the dish, until the zero reading of the ammeter indicated that all the original solution had been removed. A definite volume of zinc sulphate solution in sodium acetate was then added. (The zinc content of this solution had previously been determined electrolytically.) With a voltage of

6–7 and a current of N. $D._{100} = 3$ A the zinc was deposited on the thallium. Usual precautions in manipulating the zinc deposit must be taken.

The following table gives the results of a series of experiments:

					Current.				Time.	Weight.	
				Thallium.		Zinc.					
	$ZnSO_4$, cc.	Tl_2SO_4, cc.	NaAc, gm.	Acetic acid, cc.	Amp.	Volt.	Amp.	Volt.	Thallium and zinc, min.	Zinc, gm.	Thallium, gm.
1..	10	10	2.5	2	1.0	3.5	3.0	6.0	20	0.1686	0.0916
2..	10	10	2.5	2	1.0	4.0	3.0	6.0	20	0.1686	0.0911
3..	10	10	2.5	2	1.5	4.0	3.0	6.0	20	0.1686	0.0909
4..	10	10	2.5	2	1.0	4.0	3.0	6.0	20	0.1686	0.0915

Thallium can also be deposited from an acetic acid solution with the addition of sodium acetate. The advantage of this method is that it is not necessary to siphon the first liquid in order to cover the thallium with zinc but instead the solution of the zinc is added as soon as all the thallium has been precipitated.

RESULTS.

			Current.				Time.		Weight.	
			Thallium.		Zinc.					
	Tl_2SO_4, cc.	$ZnSO_4$, cc.	Amp.	Volt.	Amp.	Volt.	Thallium, min.	Zinc, min.	Zinc, gm.	Thallium, gm.
1...	10	10	1.0	3.0	3.0	6.0	25	20	0.1686	0.1114
2...	10	10	1.0	3.5	3.5	6.5	25	20	0.1686	0.1124
3...	10	10	1.0	3.3	3.5	6.5	20	20	0.1686	0.1117
4...	10	10	1.0	4.0	3.0	6.5	25	20	0.1686	0.1119
5...	10	10	1.5	3.5	3.0	7.0	20	20	0.1686	0.1112

The disadvantage of the protective covering method is the difficulty and uncertainty of obtaining a good non-porous coating of zinc on the thallium. For this reason an attempt was made to utilize the mercury cathode which had given such good results for so many other metals.

The form of mercury cup used was of the kind previously described in communications from this laboratory,[1] and the usual method of procedure with the mercury cathode was also followed.

It was found possible to obtain a good thallium amalgam even from an acid electrolyte but the difficulty lay in the washing of the amalgam without oxidation. On attempting to remove the last traces of water a thin, gray skin spread over the surface of the mercury. This coating dissolved in water and the solution gave a yellow precipitate with potassium iodide. It was found impossible to remove traces of water with alcohol or ether because these liquids dissolved the thallium from the amalgam. The use of hydrogen or carbon dioxide to exclude air in the drying process did not furnish better results.

Since the thallium amalgam proved to be unstable an attempt was made to find a non-oxidizable alloy of thallium. References to the liter-

---

[1] Myers, THIS JOURNAL, 26, 1124.

ature told of a stable zinc-thallium alloy. The very first attempt to use a zinc-thallium amalgam was successful. The amalgam was repeatedly washed and the water gave no precipitate with potassium iodide. Several other metals were tried as substitutes for zinc. These were Ni, Ag, Mg, Ba, Ca, Cr, and Cd, but the results were not satisfactory except with cadmium. The thallium amalgams with zinc and cadmium are not only stable towards water but it is possible to wash them with alcohol and ether without solution of the thallium, so that the usual rapid method of drying the electrolytic amalgam may be followed.

The procedure adopted in the determination of thallium by means of the mercury cathode, therefore, resolved itself into (1) the formation of a dilute zinc amalgam by electrolysis of a zinc sulphate solution in the ordinary mercury cup, and (2) the use of the zinc amalgam thus obtained as the cathode for the deposition of thallium.

The following table gives results obtained by this method:

	Tl_2SO_4, cc.	H_2SO_4. cc.	Time. min.	Current. Amp.	Volt.	Weight, gm.
1	10	10	7	5	11	0.1124
2	10	7	7	5	11	0.1120
3	10	7	7	5	11	0.1124
4	10	7	7	5	11	0.1125
5	10	7	10	5	11	0.2254
6	10	7	10	5	11	0.2252
7	10	7	10	5	11	0.2250

Similar results were obtained with a cadmium-thallium amalgam.

From a series of experiments made to ascertain the minimum quantity of zinc necessary to prevent oxidation of the thallium it was found that with so small a quantity as 0.0007 g. of zinc present the wash water was free from thallium when the amalgam contained 0.1142 g. of the latter metal.

From the foregoing it will be seen that the electrolytic determination of thallium can be quickly accomplished by the use of a mercury cathode and rotating anode.

UNIVERSITY OF PENNSYLVANIA.

AN APPLICATION OF GRADED POTENTIALS TO ORE ANALYSIS.

BY D. F. CALHANE AND J. C. WOODBURY.

Received July 5, 1909.

An ore was sent in recently to this laboratory for analysis, its content in lead, silver and copper being desired.

A qualitative analysis showed large amounts of lead, less of silver and copper, together with iron, magnesium, aluminum and calcium. The mineral was a carbonate.

The ore was evidently high in lead and low in the other constituents.