

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF HOLY CROSS COLLEGE]

A STUDY OF THE ELECTROLYTIC DETERMINATION OF COPPER IN THE PRESENCE OF PLATINIC ION¹

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In the procedure for the electrolytic determination of copper, as outlined by Fales,² it is recommended that the cathode should not be weighed until the electrolysis is completed, after which the copper is dissolved off by means of 6 molar nitric acid and then the cathode itself is weighed, the difference in weight being that of deposited copper. Such a procedure is deemed necessary in view of the fact that during electrolysis the anode may dissolve to the extent of several tenths of a milligram with subsequent plating out on the cathode.³ Strange as it may seem this is the only reference to this phenomenon that may be found. According to Popoff,³ since the platinum is plated over the copper, both the platinum and copper deposited are removed by the nitric acid and consequently there is no need of Fales' precaution.

The object of the present investigation was to determine whether the deposited platinum remained on or was removed from the cathode upon dissolving the copper deposit.

Experimental Procedure

The copper sulfate used was Baker's c. p., which had been recrystallized several times. The electrolyte was made by dissolving this copper sulfate in distilled water and making up to the proper concentration by dilution. These solutions were standardized by electrolysis, using a rotating platinum wire anode and platinum gauze cathode as electrodes. A current of 1.5 amperes was used, this being increased to 2.0 amperes during the last ten minutes of the electrolysis. Electrolysis was carried out in a tall form 300-cc. beaker, covered with split watch glasses, which was placed within a wide-mouthed one-liter beaker.

Fifty cc. of standard copper sulfate is placed in the 300-cc. beaker and 2 cc. of 16 molar nitric acid and 2 cc. of 18 molar sulfuric acid are added and the whole diluted to 200 cc. The same current density was used as in the standardization. After electrolysis had proceeded for about thirty minutes and the cathode was well covered with deposited copper, 1 cc. of the electrolyte was pipetted off and 1 cc. of a standardized platinum chloride solution was added. In this way no fresh surface of the electrode was

¹ This paper is constructed from a thesis submitted by Joseph J. Molloy to the Faculty of Holy Cross College in partial fulfilment of the requirements for the degree of Master of Science.

² Fales, "Inorganic Quantitative Analysis," Century Book Co., New York, 1925, p. 386.

³ Although C. W. Easley, *THIS JOURNAL*, 32, 1123 (1910), has reported only a slight solvent effect of chlorine on a platinum anode, it is a well-known fact that fairly high concentrations of nitric and sulfuric acids do have an appreciable effect. This is reported by Popoff, *ibid.*, 51, 1304 (1929), and has also been experienced by us in this Laboratory.

exposed. In every instance it was observed that the platinum was plated over the copper, this being evident from the darkening of the cathode deposit.

The electrolysis was made to proceed until no positive test for copper was obtained with sodium diethyl dithiocarbamate. A discussion of the method employed in using the indicator and the effect of interfering elements will be found below. The time required for complete deposition varied with the concentration of the copper sulfate used, ranging from fifty minutes for a 64-mg. deposit to ninety minutes for a 315-mg. deposit.

When deposition was complete the cathode was removed in a manner which was partly the method of Beans and Stillman⁴ and partly the siphon method as described by Popoff.⁵ At the end of the electrolysis, distilled water was run into the electrolyte until the outside beaker was two-thirds full. Then the whole was gradually lowered, distilled water being played upon the cathode as the copper deposit was exposed, the current being shut off only when the electrodes were completely out of the electrolyte. The method resulted in practically no loss of cathode deposit, is efficient, requires but little time and obviates the use of a siphon.

After the cathode was removed it was washed with distilled water, then 95% alcohol, dried and weighed. The copper was now dissolved in 6 molar nitric acid, the cathode washed in distilled water, then in 95% alcohol, dried and weighed. Thus any increase in weight of the cathode over the original weight would be due to the platinum which had plated out on it and had not been dissolved off during the solution of the copper. *In every case the cathode gained in weight.*

The electrolyses were run using various concentrations of the copper sulfate solution and adding 1 cc. of platinic chloride solution, which was also varied in concentration. In this manner we studied the effect of the weight of the copper deposit and also the

TABLE I
EXPERIMENTAL RESULTS

Expt.	Initial wt. of cathode, g.	Cu added to soln., g.	Pt added to soln., g.	Wt. of cathode and deposit, g.	Final wt. of cathode, g.	Gain in wt., g.
1	14.7263	0.0637	0.004	14.7931	14.7280	0.0017
2	14.7275	.0637	.002	14.7930	14.7293	.0018
3	14.7292	.0637	.001	14.7939	14.7300	.0008
4	14.7300	.0637	.001	14.7946	14.7309	.0009
5	14.7307	.1274	.002	14.8598	14.7321	.0014
6	14.7321	.1274	.002	14.8610	14.7337	.0016
7	14.7337	.1274	.001	14.8622	14.7346	.0009
8	14.7367	.3130	.001	15.0506	14.7373	.0006
9	14.6653	.0637	.004	14.7322	14.6683	.0030
10	14.6682	.0637	.002	14.7335	14.6696	.0014
11	14.6694	.0637	.001	14.7341	14.6703	.0009
12	14.6703	.0637	.001	14.7348	14.6711	.0008
13	14.6710	.1274	.002	14.8000	14.6723	.0013
14	14.6722	.1274	.002	14.8014	14.6740	.0018
15	14.6738	.1274	.001	14.8020	14.6748	.0010
16	14.6758	.3130	.002	14.9904	14.6773	.0015
17	14.6773	.3130	.002	14.9918	14.6784	.0011
18	14.6783	.3130	.001	14.9923	14.6792	.0009
19	14.6792	.3130	.001	14.9931	14.6801	.0009

⁴ J. W. Stillman, "New Direct Method for the Electrolytic Determination of Copper," Dissertation, Columbia University, 1920.

⁵ Ref. 3, p. 1303.

effect of the concentration of platinum on the increase in weight of the cathode. These results are given in Table I.

In order to show that the amount of platinum remaining on the cathode seems to be a function of the amount of platinum present in the electrolyte and not on the amount of copper deposited, the following tables are arranged. Table II shows the result of the experiments with one milligram of platinum present and Table III shows the result of the experiments with two milligrams of platinum added to the electrolyte.

TABLE II
RESULTS OF EXPERIMENTS

Expt.	Cu added to solution, g.	Pt added to solution, g.	Pt remaining on cathode, g.
3	0.0637	0.001	0.0008
4	.0637	.001	.0009
7	.1274	.001	.0009
8	.3130	.001	.0006
11	.0637	.001	.0009
12	.0637	.001	.0008
15	.1274	.001	.0010
18	.3130	.001	.0009
19	.3130	.001	.0009
			Mean 0.00085

TABLE III
EXPERIMENTAL DATA

Expt.	Cu added to solution, g.	Pt added to solution, g.	Pt remaining on cathode, g.
2	0.0637	0.002	0.0018
5	.1274	.002	.0014
6	.1274	.002	.0016
10	.0637	.002	.0014
13	.1274	.002	.0013
14	.1274	.002	.0018
16	.3130	.002	.0015
17	.3130	.002	.0011
			Mean 0.0015

These results show that even though there would not be any platinum in the electrolyte at the beginning of a copper determination, the platinum which might dissolve off the anode will deposit not only over the copper but also *through* it, because the platinum was not added in our experiments until a heavy deposit of copper was deposited on the cathode. Also it will be seen that all of the platinum which is deposited on the cathode is not removed by the solution of the copper deposit by the nitric acid. Therefore the procedure outlined by Fales, *viz.*, deposit the copper, weigh, dissolve off the deposit and then weigh the cathode, will take care of any additional weight which might be due to solution of the anode and subsequent deposition on the cathode.

As stated above, the indicator used to determine when deposition was complete was sodium diethyl dithiocarbamate. This indicator was introduced by Callan and Henderson.⁶ It is used as follows: 1 cc. of the electrolyte is pipetted into a 100-cc. Nessler cylinder, diluted with distilled water, made ammoniacal, 10 cc. of a 0.1% solution of the indicator added and the whole diluted to 100 cc. and well mixed. If copper is present, a clear brownish-yellow color is obtained. This is then matched against a standard, in a Duboscq colorimeter, the standard containing 0.00001 g. of copper per cc. It was found that a decided test for copper could be obtained with a solution containing 0.001 mg. with this indicator. Callan and Henderson have investigated the effects of iron, lead and zinc on the use of this indicator. Since these are not the only elements which are encountered in copper determinations, we thought it would be well to determine the effects of others which are found in these analyses. They are as follows.

NICKEL.—If present, even to the extent of one milligram per 100 cc., nickel gives a decidedly light green precipitate which interferes with the copper reaction. No method of overcoming this difficulty was found.

CADMIUM.—Cadmium gives a cloudy white turbidity which interferes with the copper reaction. No method of overcoming this difficulty was found.

ARSENIC.—As arsenate ion, even when present in fairly large quantities, arsenic does not interfere; as arsenite, however, unless the solution be made strongly ammoniacal, it will yield a white turbidity if present in excess of one milligram per 100 cc.

BISMUTH.—This element presented many difficulties, chief among them being the fact that even after the ammoniacal solution was filtered the filtrate showed a higher concentration of copper than was added. If the solution is made ammoniacal, boiled and filtered and then treated with the indicator, this difficulty is obviated.

Manganese, aluminum and magnesium, which are now encountered in the new light weight alloys, will not interfere with the copper reaction if the ammoniacal solution is boiled and filtered before adding the indicator.

Summary

1. From a study of the electrodeposition of copper in the presence of platinic ion, it has been found that the platinum deposits not only over the copper but also through it, causing an increase in weight of the cathode. It is therefore recommended that the cathode be weighed after the copper is dissolved off, instead of weighing before the deposition, in order to obtain the true weight of the cathode.

2. It has also been shown that the weight of the copper deposited,

⁶ Callan and Henderson, *Analyst*, **54**, 650 (1929).

within limits, does not affect the amount of platinum remaining on the cathode after solution of the copper deposit.

3. The effects of certain elements on the use of diethyl dithiocarbamate as an indicator for copper have been shown.

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SOLUTIONS OF SALTS IN PURE ACETIC ACID. IV. CUPRIC ACETATE AND AMMONIUM CUPRIC ACETATE

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Introduction

In the first article of this series,¹ it was mentioned that cupric acetate is but slightly soluble in pure acetic acid, and that its solubility is markedly increased upon the addition of ammonium acetate; it was suggested that in this respect the cupric and ammonium acetates might be regarded as analogous to the corresponding hydroxides, whose interaction in aqueous solution is so familiar a phenomenon. No quantitative solubility data for cupric acetate in anhydrous acetic acid have been reported previously. Sandved,² however, determined the isotherm for the ternary system cupric acetate-acetic acid-water at 25°, and a short extrapolation from his data indicates the solubility in the pure acid to be about 0.24 mole per cent. of cupric acetate, the solid phase being the acid salt $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{HC}_2\text{H}_3\text{O}_2$. In the present investigation the solubility of cupric acetate over a range of temperatures has been measured, both in pure acetic acid and in the presence of ammonium acetate in varying concentration. The effect of potassium acetate, at one concentration, was determined also. Consideration of the results obtained has led to certain new ideas, which will be developed below, with respect to the analogy between these solvent effects and the corresponding phenomena in aqueous solution.

Method

Preparation of Materials.—The acetic acid, ammonium acetate and potassium acetate employed were all prepared as described in the second paper of this series.³ The anhydrous cupric acetate used was prepared by recrystallizing the hydrate from solution in dilute acetic acid, and dehydrating at 90° until analysis showed no water to be present. Samples of the product, which was dark bluish-green, were analyzed for copper by the electrolytic and by the iodimetric method, and gave closely concordant results, averaging 34.99% of copper (calcd. for $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$, 35.00%).

Binary System.—The solubility of cupric acetate in pure acetic acid was determined

¹ Davidson, *THIS JOURNAL*, 50, 1890 (1928).

² Sandved, *J. Chem. Soc.*, 2967 (1927).

³ Davidson and McAllister, *THIS JOURNAL*, 52, 507 (1930).