## IODOMETRIC COPPER TITRATIONS.

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### Introduction.

In studying a large number of copper salts of amino acids,[1] we obtained the copper as a hydroxide or oxide by precipitating with alkali under suitable conditions. After washing the precipitate on the filter paper and the flask thoroughly, we transferred the paper with precipitate back into the flask and dissolved with 20–25 cc. of 10% acetic acid. The resulting copper acetate was then titrated with potassium iodide and sodium thiosulfate solution in the usual manner, using starch solution, finally, as an indicator. It was noticed that these solutions *did not show a return* of the usual *blue color* of *starch* produced in these reactions, or, in other words, showed a *stable end point*; while those titrations made in the presence of nitrates gave too high results and showed an *unstable end point*.

Recently Kendall[2] described a technic designed to remove the nitrites, based on the use of phenol under certain conditions. According to Kendall, his method is quick and when suitably controlled gives satisfactory and accurate values. In a later article Kendall[3] points out a source of error. We hope to show that the precipitation with alkali and solution with acetic acid will accomplish the same end, is simple, and accurate, removing all unnecessary and interfering substances from the copper solution.

### Experimental.

As a standard solution, we employed a 0.04 $M$ copper nitrate solution, made from cupric oxide,[4] standardized many times by the electrolytic method.

The standardized 0.04 $M$ copper nitrate solution is made by dissolving 3.184 g. of copper oxide in dilute nitric acid. After evaporating almost to dryness, to remove the excess of nitric acid, the copper nitrate solution was diluted and made up to one liter. To standardize this solution, we took 50 cc.[5] of 0.04 $M$ copper nitrate solution at 18°, in a platinum dish,[6] added 2 cc. of concentrated nitric acid, 3 cc. of 95% alcohol and brought the volume with water within $1/4$ inch of the edge of the platinum dish. Electric current of 0.8–1.2 amperes was then passed through the solution for about 6 hours. The end of electrolysis was shown by testing a small portion of the solution with hydrogen sulphide. When the electrolysis was finished the dish was inclined and

[1] Kober (Preliminary Communication), *J. Biol. Chem.*, **10**, 9 (1911).

[2] Kendall, THIS JOURNAL, **33**, 1947.

[3] Kendall, *Ibid.*, **34**, 317.

[4] Eimer and Amend's tested purity product.

[5] Carefully standardized flasks, pipets, burets and weights were used in this investigation.

[6] The platinum dish weighed about 50 g.

the nitric acid diluted and displaced by a stream of cold water from a wash bottle. The electrodes were removed and the dish was washed once more with water and the water finally removed from the platinum dish with 95% alcohol. The dish was then dried in an oven at a temperature of $70°-90°$ for 5 min. and in a vacuum desiccator for about two hours, after which it was weighed.

A few examples will suffice:

| Solution[1] No. | 0.04 $M$ Cu(NO$_3$)$_2$ taken. cc. | Copper found by electrolysis. | Equivalent in CuO. | Theoretical amt. of CuO for 0.04 $M$, Cu(NO$_3$)$_2$. | Factor. |
|---|---|---|---|---|---|
| 1 | 50 | 0.1263 | 0.1581 | 0.1592 | 0.993 |
| 1 | 50 | 0.1263 | 0.1581 | 0.1592 | 0.993 |
| 1 | 50 | 0.1264 | 0.1582 | 0.1592 | 0.994 |
| Average, | 50 | 0.1263 | 0.1581 | 0.1592 | 0.9933 |
| 2 | 50 | 0.1261 | 0.1578 | 0.1592 | 0.991 |
| 2 | 50 | 0.1260 | 0.1577 | 0.1592 | 0.990 |
| 2 | 50 | 0.1261 | 0.1578 | 0.1592 | 0.991 |
| Average, | 50 | 0.1261 | 0.1578 | 0.1592 | 0.9906 |

These results show that the cupric oxide is somewhat impure. In order to actually prove this we electrolyzed, dried and weighed portions of cupric oxide, which gave the following results:

| Sample No. | CuO taken. Grams. | Cu found by electrolysis. Grams. | Equivalent in CuO. Grams. | CuO found. Per cent. | Impurity Per cent. |
|---|---|---|---|---|---|
| 1 | 0.2539 | 0.2000 | 0.2503 | 98.58 | 1.42 |
| 2 | 1.6095 | 1.2672 | 1.5859 | 98.53 | 1.47 |
| 3 | 1.6095 | 1.2671 | 1.5858 | 98.53 | 1.47 |
| 4 | 1.6095 | 1.2670 | 1.5857 | 98.52 | 1.48 |

To determin the factor of the 0.04 $N$ sodium thiosulfate 50 cc. of standard copper nitrate solution were diluted to 100–150 cc. After adding 2–3 drops of 1% phenolphthalein indicator, 33% alkali was added drop by drop until a slight precipitate of copper hydroxide remained undissolved. The solution was then titrated with 0.2 $N$ carbonate-free sodium hydroxide[2] (containing Ba(OH)$_2$) until a change of color was observed. The solution, after settling, was filtered through good Swedish filter paper, and the precipitate and precipitating flask washed three or four times with a little water. The precipitate with filter paper was then transferred back into the flask and the copper hydroxide dissolved in 20–25 cc. of 10%

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[1] The determinations recorded in this paper were made during the course of a year, along with other work. Therefore, many different solutions were used, and obviously, the solutions have not always the same factor.

[2] An excess of alkali containing carbonate will of course keep some of the copper in solution as a carbonate complex, but under the conditions given above this is impossible.

acetic acid (warming the solution, if necessary). After adding 2–4 g.
of potassium iodide to the cooled solution, sodium thiosulfate was added
slowly until most of the iodine had disappeared. Then a little fresh starch
solution and more thiosulfate solution were added until the blue starch
color was discharged. The end point under these conditions was sharp
and stable. As many controls showed, the filter paper had no influence
on the results.

A few examples of titration[1] follow:

| 0.04 $M$ Cu(NO$_3$)$_2$ taken. cc. | Weight of copper found after electrolysis. Gram. | Dissolved in HNO$_3$, precipitated with NaOH, etc., titrated with 0.04 $N$ Na$_2$S$_2$O$_3$. cc. | Titrated directly, without electrolysis (precipitation method). cc. |
|---|---|---|---|
| 50 | 0.1261 | 48.93 | ... |
| 50 | 0.1260 | 48.88 | ... |
| 50 | 0.1261 | 49.03 | ... |
| 50 | ..... | ... | 48.99 |
| 50 | ..... | ... | 49.00 |
| 50 | ..... | ... | 49.00 |
| 50 | ..... | ... | 48.98 |
| 50 | ..... | ... | 48.90 |
| Average, 50 | 0.12607 | 48.95 | 48.97 |

The thiosulfate solution was kept in a dark bottle, provided with a soda lime and
calcium chloride tube. In a shaded place, and at room temperatures the solution
changed its strength, but slowly, as the following table shows:

| Dates, March | 11 | 12 | 13 | 14 | 15 | 16 | 17 |
|---|---|---|---|---|---|---|---|
| Factor....... | 0.9972 | 0.9969 | 0.9965 | 0.9959 | 0.9953 | 0.9943 | 0.9925 |

Even large amounts of nitric acid, or of any other mineral acid present
in copper solutions, do not interfere with the iodometric titrations if
the acid is neutralized with alkali and the copper hydroxide is filtered
off and redissolved with acetic acid as described above. This is shown
below:

| Solution No. | 0.04 $M$ Cu(NO$_3$)$_2$ taken. cc. | Added HNO$_3$ (conc.). cc. | Titrated by 0.04 $N$ Na$_2$S$_2$O$_3$. cc. |
|---|---|---|---|
| 1 | 25 | 0.0 | 25.00 |
| 1 | 25 | 0.5 | 25.00 |
| 1 | 25 | 1.0 | 25.00 |
| 1 | 25 | 2.0 | 24.99 |
| 1 | 25 | 3.0 | 24.97 |
| 1 | 25 | 4.0 | 25.02 |
| 1 | 25 | 5.0 | 25.00 |
| Average, 25 | | | 24.997 |

[1] Blank tests on the reagents were made from time to time, and corrections applied
when necessary.

| Solution No. | 0.04 $M$ Cu(NO$_3$)$_2$ taken. Factor 0.991. cc. | Acid added. | Titrated by 0.04 $N$ Na$_2$S$_2$O$_3$ F. = 1.008. cc. |
|---|---|---|---|
| 2 | 25 | none | 24.58 |
| 2 | 25 | none | 24.58 |
| 2 | 25 | 10 cc. HNO$_3$ | 24.56 |
| 2 | 25 | 10 cc. HNO$_3$ | 24.58 |
| 2 | 25 | 10 cc. HCl | 24.57 |
| 2 | 25 | 10 cc. HCl | 24.58 |

Average, 25 cc. = 24.77, 0.04 $M$                24.578 = 24.77, 0.04 $N$

The results show clearly that the amount and nature of the acid had no influence on the determination, when the copper was carefully removed as a hydroxide. That the flocculent hydrate or hydrogel may absorb a small amount of nitrate is very probable; but that the error of such an amount is small, and entirely negligible, is apparent from the results just given. The stability[1] of the end-point indicates the same conclusion.

In order to see if copper in the form of copper sulfide could be treated in the same manner and with the same accuracy, the following experiments were made:

To 25 cc. of 0.04 $M$ copper nitrate solution neutralized with alkali in a 250 cc. beaker, 2 cc. concentrated nitric acid were added and diluted to 50–100 cc. with water. After heating to 90°–95° hydrogen sulfide was passed slowly through the solution until the precipitation was complete. The solution was then filtered through a Gooch crucible, using a very fine asbestos mat.[2] To insure complete precipitation the filtrate was again treated with hydrogen sulfide, and filtered if necessary. After washing the precipitate and beaker several times with a little water, the Gooch crucible[3] with the copper sulfide was placed back in the same beaker and dissolved with strong nitric acid or aqua regia. This was accomplished by placing the beaker on the steam bath for 2–3 hours. After filtering off the sulfur and asbestos carefully the copper was precipitated as described above and titrated:

| 0.04 $M$ Cu(NO$_3$)$_2$ taken. cc. | Titration from CuS with 0.04 $N$ Na$_2$S$_2$O$_3$. cc. | Titration from controls. cc. |
|---|---|---|
| 25 | 24.98 | 25.03 |
| 25 | 24.97 | 25.00 |
| 25 | 25.04 | 25.06 |
| 25 | 25.07 | 25.05 |
| 25 | 24.84 | 24.83 |
| 25 | 24.85 | 24.83 |

Average, 24.96                24.97

[1] The end point, if dust from the air is excluded, will remain constant for hours.
[2] Kober, *Am. Chem. J.*, 41, 430 (1909).
[3] Filter paper cannot be used, instead of asbestos, as its hydrolytic products with mineral acids prevent the precipitation of copper hydroxide on neutralization.

Considering the number of manipulations and the error of buret reading, etc., the results can be considered satisfactory.

## Addendum.

Just before sending this paper for publication we read the article by Peters, in the April number of THIS JOURNAL, on the same subject. The difficulties caused by varying amounts of salts, of acids, of water, of nitrates and nitrites, etc., are removed by this precipitation method. We, therefore, expect that this method will, in all copper determinations, reduce the thiosulfate titrations to a uniform basis. The study of the influence of acids, salts, volume, etc., such as is made by previous investigators, is in our scheme superfluous.

March 30, 1912.

## NOTES.

*On the Detection of Potassium as Cobaltonitrite.*—In the last October number of THIS JOURNAL, **33,** 1566, Leon T. Bowser gives a new investigation of the potassium-sodium cobaltinitrite as an excellent means for the detection of very small amounts of potassium. Though the exactness of the author's statements hardly needs any confirmation, I will state, notwithstanding, that from my own many years' laboratory practice the precipitation of potassium by the de Koninck reagent is an excellent one and by far preferable to any other method. Only in one point I cannot agree with the author. The author says: "This salt .... has been known for fully half a century, but it is only in the last four years that its possibilities for determination of potassium have been revealed to the analytical chemist. For qualitative purposes it had enjoyed some degree of usefulness, but that it possessed some unusually valuable characteristics seemed to have previously escaped attention."

In fact L. L. de Koninck[1] employed the reaction in mention for detection of potassium in the year 1881 and since this time I myself have introduced this method in the laboratory under my management and in the guides I have written for laboratory use. In other laboratories, indeed, the reagent of de Koninck seems not to be employed in such a degree as it deserves.                                                 H. SALKOWSKI.

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*Note on the Qualitative Detection of Alkali Bicarbonates.*—In preparing sodium carbonate from sodium bicarbonate for the standardization of acids, it is desirable to have a means of ascertaining whether the bicarbonate is completely decomposed or not. As there appears to be no satisfactory test for bicarbonates in the presence of large quantities of normal carbonates given in the literature, the following was devised:

[1] *Z. anal. Chem.,* **20,** 390 (1881).