A Sensitive Reaction of Cuprous Ion

By

Otozo Funakoshi

(Received April 11, 1929)

A short time ago F. Feigl[1] reported that p-dimethylaminobenzylidene rhodanine may serve as an extremely sensitive reagent for silver, with which the reagent forms a reddish violet precipitate. Just at that time as I was engaged in a work which necessitated my finding some means to precipitate cuprous copper from a solution as completely as possible, I naturally thought of the applicability of Feigl's reagent for this purpose, and tried to find out with what sensibility cuprous copper may thus be precipitated.

For reduction of copper, a saturated sodium bisulphite solution prepared by passing sulphur dioxide into a sodium carbonate solution till the solution gave a neutral reaction to litmus paper, was used. About 1.2 c.c. of such a solution was found to be quite sufficient completely to reduce 5 c.c. of 1% copper sulphate solution instantaneously.

As the reagent for silver precipitation, Feigl dissolved 0.03 gram of the rhodanine in 100 c.c. of acetone. In my case, however, it was inconvenient to use acetone solution, as this solvent forms with sodium bisulphite an insoluble addition-product so as to make the precipitation of the copper compound ambiguous. So an alcoholic solution containing 0.03 gram of the rhodanine in every 100 c.c. was taken, and this was added to the copper solution slightly in excess. Care must always be taken not to use the reagent in a large excess, otherwise the rhodanine separates out from the solution and contaminates the precipitate of copper. Whenever such contamination is suspected the solution in which copper rhodanine is suspended must be shaken with ether in order to dissolve the co-precipitated free rhodanine.

---

1. Zs. anal. Chem., **74**, 380 (1928)

To 5 c. c. of a copper solution containing 0.00127 gram of copper in the cuprous state, 18 c. c. of the alcoholic rhodanine solution above stated were added and the progress of the precipitation in a neutral solution was compared with that in a solution faintly acidified with sulphuric acid.

Neutral solution.	Acid solution.
A reddish violet precipitate was formed instantly and the solution became clear after an hour.	A reddish violet precipitate was formed instantly, but the solution did not become clear even after 2 hours.

Cupric ion also combines with the rhodanine and forms a brown precipitate in a neutral solution and yellowish green needle crystals in an acid solution. They are both soluble in water.

Neutral solution.	Acid solution.
The solution gradually became turbid and precipitated a brown substance. The solution coloured red, did not become clear unless left to stand for a long time.	The yellowish green crystals separated out. The solution was yellowish brown.

The precipitate of the cuprous compound is of reddish violet colour and resembles the corresponding silver compound very much. It is exceedingly insoluble in water, but as copper slowly undergoes oxidation to the cupric state it can not be washed with water repeatedly. When exposed in air for a few days the copper compound gradually decomposes and becomes dark brown.

In order to learn with what degree of accuracy the reaction may be employed for qualitative detection of copper, the sensibility of the reaction was examined by gradually increasing the dilution of the copper solution from which the metal was to be precipitated. The alcoholic solution of the precipitant was always used slightly in excess. The results are shown in the table given below.

The sensibility of the reaction by which copper in the cuprous state can be precipitated from a neutral solution with p-dimethylaminobenzylidene rhodanine is thus calculated to be 1 : 4,000,000. This is nearly of the same degree as the sensibility of silver precipitation, which was determined by Feigl[1] to be 1 : 5,000,000.

1. loc. cit.

Copper sulphate solution		Copper gm.	Sod. sulphite solution	Precipitant c.c.	Remarks
%	c.c.				
0.1	1	0.000254	3 drops	3.7	Immediate pption
0.01	1	0.0000254	2 „	1.0	„ „
0.0004	2	0.000002032	2 „	1.0	Pption after 10 minutes
0.0002	2	0.000001016	2 „	1.0	„ „ 30 „
0.00013	2	0.000000677	2 „	1.0	„ „ „ „
0.000125	2	0.000000635	2 „	1.0	„ „ 12 hours
0.0001	2	0.000000508	2 „	0.8	Ppte faintly observable after 12 hours

The writer takes this opportunity warmly to thank Professor Motooki Matsui under whose encouragement the work was carried out.