CHAPTER 2

A COMPARATIVE ACCOUNT OF THE COPPER - IODIDE

AND COPPER - TRICYANATE REACTIONS.
Copper salts react with iodide to give a creamy white precipitate of copper(I) iodide and a triiodide ion. In this reaction simultaneous reduction of copper(II) to copper(I) and precipitation of copper(I), by iodide takes place. These two processes may be combined and represented in the following equation:

$$2Cu^{++} + 3I^- = 2CuI(s) + I_3^-$$

The reaction between copper(II) and iodide is a reversible one. Therefore only by proper control of conditions this reaction can be used for the iodometric determination of copper. Iodide concentration and the acidity, are the two important factors that control the rate of the reaction and the accuracy of the method. Presence of reasonable excess of iodide is always necessary. Iodide enhances the effective oxidizing strength of copper(II) by precipitating copper(I) as cuprous iodide and thus very much lowering its concentration relative to that of copper(II). Being one of the reactants in the system, excess of iodide also helps the reaction to go fast to completion.

Hydrogen ion, though not participating in the reaction either as reactant or appearing as product has a greater influence over the reaction. If the pH of the medium is above 4.5, hydrolysis of copper(II) takes place appreciably or even cupric hydroxide gets precipitated and the reaction will be
incomplete\(^2\). Under these conditions, in the iodometric determination of copper, a fleeting end-point will be obtained\(^3\). The starch - iodine blue colour reappears soon after the decolourization by thiocyanate due to shift in the equilibrium of the reaction towards right. In practice, however, it is necessary to maintain the pH of the sodium greater than 4 in order to suppress the occurrence of proton-transfer equilibrium of the following type:

\[
\begin{align*}
\left[\text{Cu(H}_2\text{O)}_4\right]^{++} + \text{H}_2\text{O} & \rightleftharpoons \text{Cu(H}_2\text{O)}_3\text{(OH)}\right]^+ + \text{H}_3\text{O}^+ \\
\left[\text{Cu(H}_2\text{O)}_3\text{(OH)}\right]^+ + \text{H}_2\text{O} & \rightleftharpoons \left[\text{Cu(H}_2\text{O)}_2\text{(OH)}\right]^{-} + \text{H}_3\text{O}^+
\end{align*}
\]

The species \(\left[\text{Cu(H}_2\text{O)}_3\text{(OH)}\right]^+\) and \(\left[\text{Cu(H}_2\text{O)}_2\text{(OH)}\right]^{-}\) are known to react slowly with iodide\(^4\). On the other hand, if the pH of the reaction mixture is less than 3.5 atmospheric oxidation of iodide will be induced by the copper(II) - iodide reaction\(^5\). Hence the accuracy of the iodometric method for copper will be decreased. Moreover in strongly acidic solutions, the elements such as arsenic and antimony which are common associates of copper in ores, interfere with the method\(^6\). The fact mentioned, therefore, demand that the iodometric titration for the determination of copper be performed at pH 3.5 - 4.5 only.

Yet another significant source of negative error in the iodometric method for copper arises from adsorption of triiodide by the copperous iodide precipitate\(^7\). This difficulty could be
over come by adding a small excess of alkali thiocyanate to the reaction mixture near the end-point. Alkali thiocyanate metathesizes copper(I) iodide to copper(I) thiocyanate.

\[ \text{Cu}_2\text{I}_2 + 2\text{SCN}^- \rightleftharpoons \text{Cu}_8(\text{SCN})_8 + 2\text{I}^- \]

Solid copper(I) thiocyanate has almost no tendency to absorb triiodide ions and therefore the titration with thiosulphate becomes stoichiometric. However the addition of thiocyanate helps to achieve satisfactory results only under specified conditions. Walthoff observed that the thiocyanate and iodide, if added to a neutral solution of a cupric salt, acid being added later leads to lower consumption of thiosulphate than required. Oxidation of thiocyanate by iodine to cyanide and sulphate was said to be the reason for the decrease in the thiosulphate titre. On the other hand if the acid was added first and then iodide and lastly thiocyanate, oxidation of thiocyanate by iodine was found to be eliminated. Even in this case if the mixture is allowed to stand for some time before titration, again the thiosulphate consumption was found decreased.

Kruger and Fachir have explained the phenomenon in the following way:

\[ 2\text{Cu}^{2+} + 4\text{I}^- \rightleftharpoons \text{Cu}_2\text{I}_2 + \text{I}_2 \]

\[ \text{Cu}_2\text{I}_2 + 2\text{SCN}^- \rightleftharpoons \text{Cu}_8(\text{SCN})_8 + 2\text{I}^- \]

\[ 2\text{Cu}^{2+} + 4\text{SCN}^- \rightleftharpoons \text{Cu}_8(\text{SCN})_8 + (\text{SCN})_8 \]

In the third reaction thiocyanate is bringing about reduction
of copper(II) to copper(I) without liberation of iodine
and hence leads to a decrease in the thiosulphate consumption.
The action of thiocyanate over copper(II) is similar
to that of iodide - copper(II) reaction.

In mineral acids such as sulphuric or hydrochloric
acids thiocyanate reacts with copper(II) initially to give
a black precipitate of cupric thiocyanate. The precipitate
passes slowly into white cuprous thiocyanate. It is
insoluble in water and dilute mineral acids.

In aqueous sodium copper(II) exists as aquo-complexes,
some of which are known to react slowly with iodide. Thiocyanate is less active compared to iodide in reacting with
copper(II). It must be therefore much more slow in its
action with the copper(II) aquo-complexes. However, in acetic
acid medium the oxidising strength of copper(II) is more
pronounced than in neutral or mineral acid media. This is
illustrated in the reaction between reducing sugars and
copper(II). A well known method for the determination of sugars
is based on the reduction of copper(II) to copper(I) and
its precipitation as cuprous oxide. In alkaline medium sugars
can reduce copper(II) easily. Fehling's solution consisting
of cupric sulphate and sodium hydroxide and Benedict's reagent consisting cupric sulphate and sodium carbonate are employed
as reagents for the detection and determination of reducing
sugar. The same reducing sugars fail to reduce copper(II) either in neutral or in mineral acids. However, sucrose acetate in glacial acetic acid medium\(^{13}\) (Pasteur's reagent) can be reduced readily by reducing sugars. These reactions point to the fact that some how the reduction of copper(II) to copper(I) is facilitated in acetic acid medium rather than in neutral or in mineral acid media. Presence of high concentration of acetate ion provides suitable environment for the formation of acetate complexes and prevents formation and the proton-transfer equilibrium between the aquo-complexes which are less reactive. Further, copper(II) in association with acetate ligand becomes a more powerful oxidant compared to copper(II) in combination with any other group or ion.

The similarity in the action of iodide and thiocyanate with copper(II) suggested to the author that this slow reaction between thiocyanate and copper(II) could be made to proceed fast enough, for a quantitative precipitation of copper(II) directly as cuprous thiocyanate by changing the conditions in the reaction theatre. Since the presence of acetic acid enhances the effective oxidising power of copper(II), the reaction between thiocyanate and copper(II) was studied in the medium of organic acids such as acetic and propionic acids.
SUMMARY

The action of iodide and thiocyanate with copper(II) was critically reviewed. The extent of the reductibility of copper(II) to copper(I) in acid, neutral and alkaline media is pointed out. The possibility of enhancing the reductibility of copper(II) with thiocyanate by way of using organic acids such as acetic and propionic, as reaction media in envisaged and exploring the same for a simpler gravimetric procedure for the metal is indicated.
REFERENCES


6. Ibid., P.494.


12. Ibid., 3.457.

13. Ibid., 3.454.