CHAPTER I

DETERMINATION OF COPPER
Copper is one of the oldest metals known to man and one of the earliest metals tackled by analytical chemistry in the form of green colour imparted by copper salt to a flame and blue colour given to its solution by volatile alkali. There are probably more methods available for the determination of copper than for any other single element. The metal has been estimated by almost all the analytical routes such as gravimetry, titrimetry, polarography and spectrophotometry etc. in a number of ways. However, certain techniques have been found to be eminently suited for the estimation of this element and have attained wide acceptance. Thus, electrodeposition onto a platinum electrode is an excellent method and has been adopted as the standard procedure for the determination of copper in macro as well as micro amounts. Another method that has attained wide use is the volumetric iodide method, wherein the free iodine liberated by the reaction between copper(II) and iodide ions is titrated with thiosulphate. The accuracy afforded by this method and the limited number of interferences make the procedure suitable for a large number of metallurgical and geochemical applications. The electronegativity of copper is such that it permits the convenient simultaneous polarographic determination of small amounts of copper and various other metals. Of the numerous organic reagents that can be employed for the photometric estimation of copper, dithiozone, sodium diethylidithiocarbamate, 2,2'-biquinoline and
salicylaldoxime\textsuperscript{19,20} are among the more widely used.

Like other approaches, for the gravimetric estimation of copper also a large number of reagents have been employed. Hydrogen sulfide or thioacetamide\textsuperscript{21}, thiocyanates\textsuperscript{22,23}, α-benzoinoxime\textsuperscript{2}, salicylaldoxime\textsuperscript{24}, salicylimine\textsuperscript{25}, cupferron\textsuperscript{26}, 8-hydroxyquinoline\textsuperscript{2}, quinaldic acid\textsuperscript{27}, α-nitroso p-naphthol\textsuperscript{2}, resacetophenone\textsuperscript{28}, diphenylhydantoin\textsuperscript{29}, 1,2,3 benzotriazole\textsuperscript{30}, benzylacetone\textsuperscript{31}, and 2 (0-hydroxyphenyl) benzoxazole\textsuperscript{32,33} are the few eminent earlier reagents for copper. These and the various other reagents evolved for the gravimetric determination of copper up to early sixties have been dealt in details by Elwell and Scholes\textsuperscript{34} and Kodama\textsuperscript{35}. Later reagents for the estimation of copper include various substituted derivatives of some of the above reagents in addition to many new compounds. Various workers\textsuperscript{36-51} have separately explored compounds falling in the category of oximes for the determination of copper. Sen Sarma\textsuperscript{52} employed thiomalic acid whereas Sandzhaiya\textsuperscript{53} estimated copper using dihydroxymaleic acid. Cherkesov et al\textsuperscript{54} used fumaric acid in pyridine medium for the precipitation of copper. Papafil and co-workers in addition to certain oximes have also used tetraphenyloxalamidine\textsuperscript{55} and p-aminoazobenzene\textsuperscript{56} as reagents for copper. Matei and Cacea\textsuperscript{57} estimated copper using the condensation product of benzoin and p-aminophenol. Precipitation of copper with α-β dioxoimino acetoacet-o-chloroanilide in the pH range 2.1 to 8.9 was effected by Dave and Talati\textsuperscript{58}. Raut\textsuperscript{59} introduced thiohydantoins and Majumdar et al\textsuperscript{60} suggested bismuthidol as reagents for the metal ion. Studies on the preparation and analytical application of hydroxytriazenes were
carried out by Sogani and coworkers\textsuperscript{61,62}. They also introduced
N,N'-phenylhydroxylamine (1-hydroxy-3-methyl) 1-phenyl-2-thiourea\textsuperscript{63}
as gravimetric reagent for copper. Dutt et al\textsuperscript{64,65} suggested
monalzine and dalzine as precipitants for copper. Ray and Ray\textsuperscript{66}
separated copper from a large number of metal ions using
3-hydroxyiminomethyl-salicylic acid. Salicylaldehyde derivatives
were also used for similar separation by Kiyoharu Isagi\textsuperscript{67}. During
their studies on complex compounds of isoniazid, Crecu et al\textsuperscript{68-70}
separately developed conditions for the precipitation of copper
thiocyanate, benzoate and fumarate of isoniazid. Pirtea\textsuperscript{71}
suggested a simple gravimetric method for the micro determination
of copper using thiocyanate and hydrochloride of 1,10-phenanthroline
or 2,2'-bipyridyl. Perimidine\textsuperscript{72}, purpurogallin\textsuperscript{73} and related
compounds have also been recommended for the gravimetry of copper.
Doadrio et al\textsuperscript{74} precipitated copper with Reinecke's salt in
ammonical medium, whereas Ackermann and Kaden\textsuperscript{75} achieved
quantitative precipitation with the same reagent in 2 molar
hydrochloric acid medium. Hydrazones\textsuperscript{76-78} have also been applied
gravimetrically for the estimation of copper. Poonia and
associates\textsuperscript{79} estimated copper with mercaptoacetamidophenol. Reddy
etal\textsuperscript{80} reinvestigated ammonium thiocyanate procedure for the
determination of copper. Benzohydrazide\textsuperscript{81}, diphenylcarbazide\textsuperscript{82}
thiosemicarbazide\textsuperscript{83} and their derivatives have also found
applications in the estimation of copper. Tandon and Gupta\textsuperscript{84}
determined the metal using N-1-naphthoxamic acid. Substituted
phenylhydroxylamines\textsuperscript{85,86} and butylamines\textsuperscript{87} have also been
reported as gravimetric reagents for copper and so also are
quinoxaline-2-carboxylic acid and benzimidazole-2-carboxylic acids and their derivatives. Erdey et al. used 4-aminohepxic acid, Manku and Sarpal employed dehydroacetic acid, while Narayana and co-worker have used thiosalicylic acid for the precipitation of copper. Bera and Chakravorty precipitated copper with 2-mercapto methylbenzimidazole in presence of cyanides at pH 4-5. Copper has also been precipitated as tetrathiocyanatomercurate(II) and thiocyanato chromate(III) complexes. Mehta et al. employed substituted anthranilic acids as reagents for copper. The other reagents reported for copper are mono thioureaphthalic acid, 2-mercapto benzoxazole, 2-mercapto pyridine 1-oxide, thiosalylamide, 8-acetyl-7-hydroxy-4-methyl coumarin and N-hydroxy N'-diphenylformamidine. Hydrazinium thiocyanate reported very recently by Vittal and associates appears to be an attractive reagent and is likely to enjoy a promising analytical future.

The reagents listed in the preceding paragraphs precipitate copper in the weighable compound form. As compared to these, the reagents which reduce divalent copper to the metal as a prelude to gravimetry are really meager in number. In other words very few reagents have been used as metal precipitant for copper. Aluminium and zinc metals, being more electropositive, have been employed either in the form of strips or as powders for the reduction of copper(II). Hydrazine has also drawn the attention of many researchers for the reduction of copper salts. Reduction of a copper(II) sulphate solution with hydrazine in presence of sodium chloride
is said to result in the precipitation of insoluble copper(I) chloride\textsuperscript{106}, whereas in presence of sodium hydroxide, precipitation of copper(I) oxide is achieved\textsuperscript{107}. Addition of a hot hydrazine sulphate solution to a sodium hydroxide suspension of copper(II) hydroxide is reported to cause complete precipitation of metallic copper\textsuperscript{108,109}. Hypovanadous salts by Mittal and Mehrotra\textsuperscript{110} and sodium tetrahydroborate by Hohnstedt et al\textsuperscript{111} are probably the only metal precipitants suggested for copper subsequently.

Ascorbic acid has been used extensively for the reductometric estimations\textsuperscript{112,113} of several metal ions including copper(II)\textsuperscript{114}. In these methods, divalent copper is reduced to cuprous ion which gets complexed simultaneously by some auxiliary reagent like chloride, bromide or thiocyanate. The catalytic effect of copper(II) on the aerobic oxidation of ascorbic acid and the related kinetics has also been studied by several workers\textsuperscript{115-118}.

Ascorbic acid has also been employed in the redox-gravimetry of selenium\textsuperscript{119}, silver\textsuperscript{120}, mercury\textsuperscript{121}, gold\textsuperscript{122} and palladium\textsuperscript{123}. However, identical work on copper finds little mention in the existing literature. Under a time bound programme intended mainly towards developing a quick and accurate method for analysing the constituent elements in copper tellurides, the author has earlier used ascorbic acid both in alkaline and acid medium for reducing respectively copper(II) and Tellurium(IV) to the metals\textsuperscript{124}. However, limitation of time then did not permit a systematic and detailed investigation of the various factors such as stoichiometry of the redox-reaction, influence of alkali, effects of other metal ions and the nature of precipitate etc.
These were studied subsequently and the results are presented in this chapter. While reinvestigating the copper(II) ascorbic acid system, the reduction of copper(II) has been followed from neutral to strongly alkaline medium and optimum conditions for the reduction have been worked out. Based on the experimental results arrived at in ascertaining the minimal quantity of ascorbic acid required for a quantitative reduction, the stoichiometric aspects of the redox system have been reported and discussed. Effects of a large number of foreign metal ions have been studied and possible applications of the method have been suggested.

**EXPERIMENTAL**

**REAGENTS AND EQUIPMENTS**

**Copper(II) sulphate solution** was prepared by dissolving 2.00 g of electrolytic copper metal in minimum volume of 1.2 sp. gr. nitric acid, fuming it to white dense fumes with 10 ml of concentrated sulphuric acid, cooling and making it up to 1 litre. This solution was standardised iodometrically.

**1M Sodium hydroxide solution** was prepared from AR(BDH) pellets.

**Ascorbic acid** (E. Merck) was used as 2% aqueous solution and as solid.

**Wash solution** was prepared by dissolving 10 g of sodium hydroxide in 1 litre water.

**0.05N Sodium thiosulphate** was prepared by dissolving 12.413 g of AR(BDH) salt in distilled water and making it up to
1 litre. This was standardised against electrolytic copper iodometrically using 1% starch solution as indicator.

Solutions of various metal ions having a concentration of 2mg/ml were prepared from respective An reagents of Zn(II), Pb(II), Al(III), Sn(IV), Se(IV), Te(IV), Nb(V), Mo(VI) and W(VI), and standardised.

All other chemicals used were of analytical reagent grade.

Metrohm Herisau, pH meter with combined glass electrode was used for pH measurements.

Debye-Scherrer camera (11.48 cm dia.) with Phillips x-ray generator was used for obtaining diffraction patterns of the precipitates.

**OPTIMUM pH AND NaOH POLARITY**

In order to determine the optimum alkalinity for reduction, solutions equivalent to 51 mg copper were transferred in different 250 ml beakers and the pH were adjusted to 8, 9, 10, 11 and 12 respectively with dilute NaOH solution, maintaining the volumes at around 60-70 ml. Ascorbic acid solutions containing around 200 mg of the reagent with pH preadjusted with dilute NaOH, to the respective copper solutions, were introduced. The solutions were heated to boiling and were allowed to boil for 15-20 minutes and the estimations accomplished according to the procedure given later. In another set similar aliquots of copper solutions were transferred in different beakers and diluted to 70 to 80 ml. 10M NaOH solutions were added so as to achieve the overall molarities ranging from 0.1M to 5M in volumes of 100 ml.
Approximately 200 mg ascorbic acid was added and after boiling, the estimation of copper was completed. These results are recorded in table 1.

**MINIMUM QUANTITY OF ASCORBIC ACID**

In different 250 ml beakers, solutions containing 60 mg copper were taken and made 1M in NaOH in volumes of 100 ml using 10M NaOH solution. To these, varying amounts of ascorbic acid were added. The solutions were boiled for 15 to 20 minutes and cooled. The precipitates were filtered, washed and the metal evaluated as given in the procedure. Results of these experiments are compiled in table 2.

**OPTIMUM BOILING TIME**

Solutions containing 51 mg of copper were transferred in different 250 ml beakers. In all the cases, the solutions were made 1M in NaOH maintaining the volumes at 100 ml. To each of them 100 mg of solid ascorbic acid was added. The solutions were boiled for varying periods ranging from 5 to 30 minutes and the metal in each case was estimated gravimetrically as in earlier experiments. These results are presented in table 3.

**PROCEDURE**

**Determination of copper(II) in pure solution**: An aliquot containing 20 to 200 mg of copper was taken in a 250 ml beaker. 10M NaOH solution was introduced till the pale-blue gelatinous precipitate of cupric hydroxide was formed. The contents were
diluted to 60-70 ml and an adequate volume of the alkali was
further added to maintain its overall molarity at or above 1M.
Ascorbic acid (a minimum of 3-4 times the weight of copper present
in aliquot) was then added, when a colloidal reddish yellow
precipitate appeared almost immediately. The solution was heated
to boiling and was allowed to boil further for about 10-15 minutes.
The reddish yellow precipitate was reduced gradually to metallic
copper which settled down leaving behind a clear colourless
supernatant liquid. The contents were cooled and the copper
filtered under suction through a weighed sintered glass crucible.
It was washed 3 to 4 times with hot wash solution, then with hot
water till free from alkali and finally with a small quantity of
absolute alcohol. The precipitate was sucked dry, heated at
110°C to constant weight and weighed. Alternatively the precipitate
was filtered through pulp, washed, dissolved in minimum volume
of 1.2 sp. gr. HNO₃, diluted to about 80 ml and titrated
iodometrically¹²⁵ or complexometrically¹²⁹. These results are
presented in table 4.

**Determination of copper(II) in the presence of foreign
metal ions**: To an aliquot containing 30 mg copper, in a 250 ml
beaker, were added standardized solutions containing different
amounts of foreign ions. Solution was made 2 to 3M in NaOH in a
volume of 100 ml. Approximately 100 mg of ascorbic acid was
added and copper was estimated as per the procedure described
above. The results of these investigations are given in table 5.
ANALYSIS OF SYNTHETIC TELLURIDES AND SELENIDES OF COPPER

Synthetic solutions of copper tellurides and copper selenides were prepared by weighing electrolytic copper and high purity tellurium or selenium in weight ratios as are found in common selenides and tellurides (table 6), in a 250 ml beaker and dissolving in a minimum volume of 1.2 sp. gr. HNO₃ by slow heating. Excess HNO₃ was removed by fuming with concentrated H₂SO₄. The residue, when cool, was taken up with HCl and made up to 250 ml in a standard volumetric flask such that overall normality of HCl in the solution was maintained at about 2.5N. In a 25 ml aliquot, copper was first determined by ascorbic acid in alkaline medium as described under procedure. The alkaline filtrate was transferred to a 500 ml beaker and evaporated to 100 ml. In case of tellurides¹₂⁴, the solution was made 2.5 to 4N in HCl, solid ascorbic acid (4 to 5 folds of the tellurium present) was added, the solution was boiled for 10 minutes and cooled. The metallic tellurium was filtered through sintered glass crucible and washed several times with hot water till free from chloride ions. It was further washed a few times with absolute alcohol, heated at 105° to constant weight and weighed. During the analysis of selenides¹¹⁹, the filtrate from copper estimation was concentrated and neutralised with HCl and after adding ascorbic acid the solution was adjusted to pH 1-2. It was boiled for 10 minutes and the metal evaluated as in case of tellurium.
DISTILLATION OF COPPER II ALLOYS

0.2 g of an alloy sample was dissolved in minimum quantities of HNO₃ and HCl and heated with 5 ml concentrated H₂SO₄ to dense white fumes, salts were dissolved in water, solution filtered if necessary, and made 2 to 3M in NaOH keeping the total volume at 100 ml. Ascorbic acid, approximately 3-4 times that of copper present, was added and copper estimated gravimetrically according to the procedure for pure solution. Results, which are also verified by electrogravimetry or by a selective complexometric method, are given in table 7.

X-RAY DIFFRACTION INVESTIGATION OF THE PRECIPITATES

Samples for x-ray diffraction were made by coating the powered precipitates on glass fibres using quick fix adhesive. The specimen diameters were 0.05 cm. The samples were rotated during 4 to 5 hours exposure employing iron radiation with manganese filter. The 'd' values measured from the patterns at figures 1, 2 and 3 are compared with ASTM card values for copper and cuprous oxide, in table 8.

RESULTS AND DISCUSSION

A series of experiments were carried out to study the effect of variation in overall alkali concentration on the reduction of copper(II) by ascorbic acid. While higher values of copper were obtained in weakly alkaline medium, the values were found to diminish gradually with increasing alkali
Figure 1: X-ray diffraction powder photograph of the precipitate obtained at pH 9.

Figure 2: X-ray diffraction powder photograph of the precipitate at pH 13.

Figure 3: X-ray diffraction powder photograph of the precipitate from 1M NaOH medium.
concentration until they become quantitative in sodium hydroxide medium at 1M or above. This may be attributed presumably to the precipitation first of cuprous oxide alone, followed by a mixture of cuprous oxide and the metal and finally metallic copper only as the alkali concentration attained a value of 1M or above. This assumption gets further substantiated by x-ray diffraction studies of the precipitates taken at different alkali concentrations and following the diffraction patterns as given in figures 1, 2 and 3 and the corresponding 'd' values as shown in table 8. They reveal that at pH 9 the precipitate consisted predominantly of cuprous oxide, that at pH 13 of a mixture of the oxide and the metal and the one in 1M sodium hydroxide medium, of the metal alone. From the above observations and the results presented in table 1, it can be concluded that a sodium hydroxide medium of 1M and above was suited ideally for the reduction of copper(II) to the metal.

In order to ascertain the minimum boiling time some experiments were done and from the results given in table 3, it can be seen that a 10 to 15 minutes boiling time was adequate enough to get a quantitative precipitate with metallic lusture.

As in any other gravimetric approach, use of excess reagent has been recommended in the present procedure. However, an investigation involving a large number of experiments was undertaken to evaluate mainly the minimum quantity of ascorbic acid required for a quantitative reduction of the metal ion and also to study the probable course of the redox reaction. Reductions of a given quantity of copper(II) at 1M sodium hydroxide concentration were carried out with varying amounts of ascorbic acid and the
Experimental results are compiled in Table 2. It is seen that 85 mg of ascorbic acid was adequate enough to effect a quantitative precipitation of 60 mg of copper. This would not have been possible if the two hydrogen atoms as are available in the reaction:

\[ C_6H_8O_6 \rightarrow C_6H_6O_6 + 2H^+ + 2e^- \]

only were taking part in the reduction and unless the dehydroascorbic acid undergoes further oxidation making available 2 more hydrogen atoms.

According to Gopal Rao\textsuperscript{126} and others\textsuperscript{127,128}, ascorbic acid with structure I, given below, enolises, in aqueous solutions, into a compound with structure II which easily undergoes reversible oxidation into dehydroascorbic acid having structure III. The dehydroascorbic acid changes into 2,3 diketo gluconic acid IV, with the opening of the original lactone ring. On oxidation with alkaline hypoiodite, the compound IV yields quantitatively a mixture of L-threonic acid and oxalic acid.

\[
\begin{align*}
\text{I} & \quad \text{II} & \quad \text{III} & \quad \text{IV} \\
\text{C} = \text{O} & \quad \text{C} = \text{O} & \quad \text{C} = \text{O} & \quad \text{COOH} \\
\text{H} - \text{C} - \text{OH} & \quad \text{C} - \text{OH} & \quad \text{C} = \text{O} & \quad \text{C} = \text{O} \\
\text{C} = \text{O} & \quad \text{C} - \text{OH} & \quad \text{H} - \text{C} - \text{OH} & \quad \text{H} - \text{C} - \text{OH} \\
\text{H} - \text{C} - \text{H} & \quad \text{CH} - \text{C} - \text{H} & \quad \text{HO} - \text{C} - \text{H} & \quad \text{HO} - \text{C} - \text{H} \\
\text{CH}_2\text{CH} & \quad \text{CH}_2\text{OH} & \quad \text{CH}_2\text{OH} & \quad \text{CH}_2\text{OH}
\end{align*}
\]

A reduction mechanism involving a four electron transfer as suggested above looked probable in the present work and could
be substantiated if the existence of oxalic acid in the final product was confirmed. For achieving this the filtrate obtained after the reduction was just acidified with hydrochloric acid to which calcium chloride solution and adequate quantities of ammonium chloride and ammonium hydroxide were added. The white precipitate so obtained was coagulated by heating, filtered, washed, and dissolved in 1:1 sulphuric acid. In one portion of the solution, calcium was checked on atomic absorption spectrophotometer, while in the other oxalic acid was detected by the disappearance of permanganate colour. These two tests confirmed the presence of oxalic acid in the oxidised solution and agree with the scheme given earlier that in the ultimate analysis ascorbic acid is oxidised to oxalic acid and threonic acid and that both ascorbic acid and dehydroascorbic acid do participate in the reduction of copper(II) to the metal.

It was of interest at this stage to examine whether dehydroascorbic acid was independently capable of reducing copper(II) quantitatively. Known amount of ascorbic acid was therefore oxidised in acid medium (pH 3-4) with excess of silver(I) solution and the excess silver was precipitated as chloride. The metal and the chloride were filtered and the filtrate containing only dehydroascorbic acid was used for the reduction of copper(II) in 1M sodium hydroxide medium. The amount of copper reduced was in conformity with the one calculated on the basis of two hydrogen atoms as are available in the oxidation of dehydroascorbic acid to oxalic acid and threonic acid, as seen from table 2. This is also supported by an earlier study on the reducing property of dehydroascorbic acid.
towards several dyes

In conclusion, it can be said that the reduction of copper(II) with ascorbic acid in alkaline medium involves a four electron change, two each from the steps given below:

\[
\text{Cu(OH)}_2 + \text{C}_6\text{H}_6\text{O}_6 \rightarrow \text{Cu}^0 + \text{C}_6\text{H}_6\text{O}_6 + 2\text{H}_2\text{O} \quad - - - (1)
\]

\[
\text{Cu(OH)}_2 + \text{C}_6\text{H}_6\text{O}_6 + \text{H}_2\text{O} \rightarrow \text{Cu}^0 + \text{C}_2\text{H}_2\text{O}_4 + \text{C}_4\text{H}_8\text{O}_5 \quad - - - (2)
\]

The second reaction however, goes through an intermediate step, wherein dehydroascorbic acid is changed into 2,3 diketogluconic acid which in turn reduces copper(II) and yields oxalic and threonic acid. As mentioned before the loss of the reagent due to atmospheric oxidation was minimised, in all probability due to the competitive reaction of the reagent with the metal ion, as compared to that with air.

Since copper(II) is first precipitated as hydroxide and then reduced, the removal of divalent copper ions from the solution is mainly done during hydroxide precipitation. Under such a situation atomic absorption spectrophotometric examination of the filtrate would not give a conclusive idea about the completeness of the reduction and hence is not carried out.

As seen from table 4, 20 to 200 mg of copper could be estimated by the present method with an error not exceeding 0.50%. The maximum error in the presence of foreign metal ions is 0.83%.

Since the reduction is carried out in sufficiently alkaline medium the metal ions forming insoluble hydroxides such as Ni(II),
Cd(II), Co(II), Mn(II), Fe(III) etc could not be tolerated. However, those yielding soluble hydroxides like Pb(II), Zn(II), Al(III), Sn(IV), Te(IV), V(V), W(VI) and Mo(VI) do not interfere (table 5). As described during experimental (cf. page 36), a most interesting feature of the analysis of selenides and tellurides (table 6) is that after reducing copper(II), the associated metal can be precipitated with the same reagent by simply making the solution acidic. The proposed method is rapid, simple and matches favourably in accuracy with the existing procedures for copper.
**TABLE 1**

Study of optimum pH and NaOH molarity for the reduction of copper(II).

<table>
<thead>
<tr>
<th>Copper(II) taken</th>
<th>51.00 mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ascorbic acid added</td>
<td>200 mg</td>
</tr>
<tr>
<td>Total volume</td>
<td>100 ml</td>
</tr>
<tr>
<td>Boiling time</td>
<td>15 - 20 min.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>pH</th>
<th>NaOH molarity</th>
<th>Copper found, mg</th>
<th>Gravimetrically</th>
<th>Volumetrically&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>57.00</td>
<td>50.95</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>56.65</td>
<td>50.95</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>56.40</td>
<td>51.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>56.15</td>
<td>50.95</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>55.95</td>
<td>51.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1</td>
<td>54.30</td>
<td>50.95</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>51.60</td>
<td>51.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>51.05</td>
<td>50.95</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.5</td>
<td>51.00</td>
<td>51.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>51.00</td>
<td>51.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.0</td>
<td>50.95</td>
<td>50.95</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.0</td>
<td>51.05</td>
<td>50.95</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup>: Precipitate dissolved in acid and copper estimated iodometrically using N/20 thiosulphate solution.
**TABLE - 2**

Evaluation of minimum quantity of ascorbic acid for the reduction of copper(II).

<table>
<thead>
<tr>
<th>Ascorbic acid added, mg</th>
<th>Cu found, mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>59.98&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>300</td>
<td>60.05&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>200</td>
<td>59.95&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>170</td>
<td>60.00&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>100</td>
<td>60.05&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>90</td>
<td>60.00&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>85</td>
<td>59.98&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>85</td>
<td>60.05&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>80</td>
<td>57.20&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>50</td>
<td>Incomplete reduction&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>180&lt;sup&gt;d&lt;/sup&gt;</td>
<td>59.95</td>
</tr>
<tr>
<td>170&lt;sup&gt;d&lt;/sup&gt;</td>
<td>59.90</td>
</tr>
</tbody>
</table>

<sup>a</sup> : Iodometric values.
<sup>b</sup> : Gravimetric result.
<sup>c</sup> : The supernatant solution had blue colour.
<sup>d</sup> : Ascorbic acid converted to dehydroascorbic acid with silver(I) in acid medium and then added.
<table>
<thead>
<tr>
<th>Boiling time in minutes</th>
<th>Cu found, mg</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Instantaneous</td>
<td>-</td>
<td>Reddish yellow precipitate was colloidal in nature</td>
</tr>
<tr>
<td>5</td>
<td>51.70</td>
<td>Precipitate slowly turned reddish brown.</td>
</tr>
<tr>
<td>10</td>
<td>50.95</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>51.05</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>50.95</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>51.00</td>
<td></td>
</tr>
</tbody>
</table>


**TABLE - 4**

Estimation of varying amounts of copper in pure solutions

<table>
<thead>
<tr>
<th>NaOH molarity</th>
<th>= 1M</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ascorbic acid added</td>
<td>= 3 - 4 times of copper present</td>
</tr>
<tr>
<td>Total volume</td>
<td>= 100 ml</td>
</tr>
<tr>
<td>Boiling time</td>
<td>= 10 - 15 min.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Cu taken, mg</th>
<th>Cu found, mg</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Gravimetrically</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>20.00</td>
<td>19.90</td>
</tr>
<tr>
<td>40.00</td>
<td>40.20</td>
</tr>
<tr>
<td>80.00</td>
<td>79.80</td>
</tr>
<tr>
<td>112.50</td>
<td>112.75</td>
</tr>
<tr>
<td>158.20</td>
<td>158.00</td>
</tr>
<tr>
<td>202.10</td>
<td>201.65</td>
</tr>
</tbody>
</table>
**TABLE - 5**

**Determination of copper(II) in presence of foreign metal ions**

<table>
<thead>
<tr>
<th>Copper(II) taken</th>
<th>= 30.00 mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ascorbic acid added</td>
<td>= 100 mg</td>
</tr>
<tr>
<td>FeCH molarity</td>
<td>= 2 - 3M</td>
</tr>
<tr>
<td>Total volume</td>
<td>= 100 ml</td>
</tr>
<tr>
<td>Boiling time</td>
<td>= 10 - 15 min.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Foreign ion, mg</th>
<th>Cu found, mg</th>
<th>% Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn(II) 25.00</td>
<td>29.94&lt;sup&gt;a&lt;/sup&gt;</td>
<td>-0.20</td>
</tr>
<tr>
<td>Pb(II) 20.00</td>
<td>30.12&lt;sup&gt;a&lt;/sup&gt;</td>
<td>+0.40</td>
</tr>
<tr>
<td>Al(III) 50.00</td>
<td>30.03&lt;sup&gt;a&lt;/sup&gt;</td>
<td>+0.10</td>
</tr>
<tr>
<td>Se(IV) 20.00</td>
<td>29.90</td>
<td>-0.33</td>
</tr>
<tr>
<td>Te(IV) 20.00</td>
<td>30.05</td>
<td>+0.17</td>
</tr>
<tr>
<td>Sn(IV) 20.00</td>
<td>29.90&lt;sup&gt;a&lt;/sup&gt;</td>
<td>-0.33</td>
</tr>
<tr>
<td>Nb(V) 15.00</td>
<td>30.25</td>
<td>+0.83</td>
</tr>
<tr>
<td>Ho(VI) 40.00</td>
<td>29.95</td>
<td>-0.17</td>
</tr>
<tr>
<td>W(VI) 42.00</td>
<td>29.80</td>
<td>-0.66</td>
</tr>
</tbody>
</table>

<sup>a</sup> Estimated complexometrically, rest all are gravimetric results.
TABLE - 6

Analysis of synthetic copper-tellurides and copper-selenides

| NaOH molarity | = 2 -3M |
| Ascorbic acid added | = 100 mg |
| Total volume | = 100 ml |
| Boiling time | = 10 - 15 min |

<p>| Taken, mg | Found, mg |</p>
<table>
<thead>
<tr>
<th>Cu</th>
<th>Te</th>
<th>Se</th>
<th>Cu</th>
<th>Te</th>
<th>Se</th>
</tr>
</thead>
<tbody>
<tr>
<td>50.00</td>
<td>52.00</td>
<td>-</td>
<td>49.90</td>
<td>51.80</td>
<td>-</td>
</tr>
<tr>
<td>35.00</td>
<td>72.00</td>
<td>-</td>
<td>35.05</td>
<td>71.80</td>
<td>-</td>
</tr>
<tr>
<td>30.00</td>
<td>90.00</td>
<td>-</td>
<td>29.85</td>
<td>89.70</td>
<td>-</td>
</tr>
<tr>
<td>30.00</td>
<td>40.00</td>
<td>-</td>
<td>30.05</td>
<td>39.95</td>
<td>-</td>
</tr>
<tr>
<td>45.00</td>
<td>-</td>
<td>28.00</td>
<td>44.80</td>
<td>-</td>
<td>28.15</td>
</tr>
<tr>
<td>48.00</td>
<td>-</td>
<td>59.70</td>
<td>47.90</td>
<td>-</td>
<td>59.60</td>
</tr>
<tr>
<td>60.00</td>
<td>-</td>
<td>89.00</td>
<td>59.95</td>
<td>-</td>
<td>88.90</td>
</tr>
<tr>
<td>60.00</td>
<td>-</td>
<td>49.80</td>
<td>60.20</td>
<td>-</td>
<td>49.65</td>
</tr>
</tbody>
</table>

a: Gravimetrically.

Weight ratios correspond to Cu₂Te, Cu₂Se, Cu₂Te₃, Cu₃Te₂,
Cu₂Se, CuSe, Cu₂Se₃ and Cu₃Se₂ respectively.
### TABLE - 7

**Estimation of copper(II) in alloys**

<table>
<thead>
<tr>
<th>NaOH molarity = 2 - 3 M</th>
<th>Ascorbic acid added = 500 mg</th>
<th>Total volume = 100 ml</th>
<th>Boiling time = 10 - 15 min.</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Alloy composition</th>
<th>Cu present, mg</th>
<th>Cu found, mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>35% Zn, 65% Cu(^a)</td>
<td>130.00</td>
<td>129.50</td>
</tr>
<tr>
<td>40% Zn, 1.2% Sn, 58.8% Cu(^b)</td>
<td>117.60</td>
<td>117.00</td>
</tr>
<tr>
<td>10% Al, 90% Cu(^a)</td>
<td>180.00</td>
<td>179.65</td>
</tr>
<tr>
<td>10.2% Zn, 2.3% Pb, 87.5% Cu(^a)</td>
<td>175.00</td>
<td>175.25</td>
</tr>
<tr>
<td>7% Sn, 7% Pb, 3% Zn, 83% Cu(^b)</td>
<td>166.00</td>
<td>165.60</td>
</tr>
<tr>
<td>10% Sn, 1% Pb, 0.5% Zn, 88.5% Cu(^b)</td>
<td>177.00</td>
<td>177.45</td>
</tr>
</tbody>
</table>

\(^a\): Established electrogravimetrically.

\(^b\): Ascertained complexometrically.130.
TABLE - 8
X-ray diffraction data for the precipitates.

<table>
<thead>
<tr>
<th>ASTM</th>
<th>Observed values for precipitates at</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu₂O</td>
<td>pH 9</td>
</tr>
<tr>
<td>Cu</td>
<td></td>
</tr>
<tr>
<td>Card : 5-667 Card : 4-836</td>
<td>d</td>
</tr>
<tr>
<td></td>
<td>d</td>
</tr>
<tr>
<td>3.02</td>
<td>2.995</td>
</tr>
<tr>
<td></td>
<td>2.700</td>
</tr>
<tr>
<td>2.465</td>
<td>2.442</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>2.135</td>
<td>2.117</td>
</tr>
<tr>
<td></td>
<td>2.088</td>
</tr>
<tr>
<td></td>
<td>1.982</td>
</tr>
<tr>
<td>1.808</td>
<td>1.795</td>
</tr>
<tr>
<td>1.743</td>
<td>1.731</td>
</tr>
<tr>
<td>1.510</td>
<td>1.503</td>
</tr>
<tr>
<td>1.287</td>
<td>1.284</td>
</tr>
<tr>
<td></td>
<td>1.280</td>
</tr>
<tr>
<td>1.233</td>
<td>1.229</td>
</tr>
<tr>
<td>1.0674</td>
<td>1.0665</td>
</tr>
<tr>
<td>0.9795</td>
<td>0.9792</td>
</tr>
</tbody>
</table>
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