Estimation of copper in copper salts at different pH conditions and buffer media by iodo-potentiometric technique

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ABSTRACT

Copper in cupric salt / brass is, generally, estimated by the well known iodometric method. Many modifications were made to the procedure to improve results. In the present investigation, for the first time, copper in copper solutions are estimated by using iodo-potentiometric technique of analysis. In the present paper, the results of both the redox potentiometric and titrimetric methods of analysis are correlated successfully to estimate the amount of copper in the samples of copper salts at different pH and buffer media conditions. The results of the present investigation clearly hints that copper can be estimated effectively at pH between 2.0 and 3.5 using NaOH and CH_3COOH; while the desired pH range, preferably, is 2.0 - 3.0 for ammonia and acetic acid as buffer reagents. The results obtained for copper salts using NaOH or NH_4OH, with citric acid as acidifying agent, is poor. This is due to the formation of a product of complexation with one of the reagents. However, it can be observed that the estimation of copper gives fairly good result with error, if the pH of the solution is maintained at pH = 2.0 by the addition of citric acid. Thus, redox iodo- potentiometric technique is also used as an excellent analytical tool for analysis; and the results obtained for copper estimation are comparable to any standard methods of analysis. © 2008 Trade Science Inc. - INDIA

INTRODUCTION

A comprehensive survey of literature pertaining to the estimation of copper revealed that, generally, iodometric[1-3] method is adopted. The iodometric method of determining copper consists essentially in treating a solution of the cupric salt with a soluble iodide which precipitates cuprous iodide and liberates iodine. The latter can be titrated with standard sodium thiosulphate. The method has, however, certain difficulties[2,3] which are familiar to those who have used the method, and which limit its accuracy. This is a rapid, quantitative reaction in acidic solutions, if there is a large excess of iodide ion present and if the copper is in the form of a simple ion rather than a complex one.

The reaction involving copper (II) ion and iodide takes place quantitatively since the copper (I) ion formed as result of the reduction is removed from the solution as a insoluble precipitate of copper (I) iodide. Copper (II) iodide is unstable since the iodide reduces Cu^{2+} to Cu^+.

The method is, however, widely used on account of its speed but hardly to be classed in accuracy with a number of other iodometric methods. A modification of this method was proposed by Bruhns[4] with the object of using less iodide than is necessary by the usual method. The modification consists in adding potassium thiocyanate along with the iodide, which precipitates the more

insoluble cuprous thiocyanate instead of cuprous io-dide. This modification has been shown repeatedly to give unreliable results and recently[5] the reasons for the failure of the method. Briefly, the modified method gives low results because both iodine and thiocyanogen are liberated simultaneously to a certain extent, and react on each other.

In principle, however, the Bruhns[4] method has one advantage, since cuprous Thiocyanate is more insoluble than cuprous iodide, thus tending to make the reaction more complete due to the more complete removal of cuprous ion. It was observed during their investigation, cuprous thiocyanate does not adsorb iodine at low concentrations of the latter, but becomes white as the free iodine is removed by titration, which makes the end-point exceedingly sharp in the presence of starch. It appeared probable that the undesirable side reactions occurring in the Bruhns[4] method could be eliminated by adding the soluble thiocyanate late in the course of the titration. In that case the method should have greater accuracy than the usual method. The qualitative effect of adding a thiocyanate can be shown very easily. If this salt is added, during a titration, just as the endpoint is reached by the usual method, the starch iodide color is markedly intensified.

Iodometric methods[1] depend on the following equilibrium: $I_2 + I^- \rightarrow I_3^-$.

Since the solubility of I_2 in water is quite low, the formation of the tri-iodide ion, I_3^-, allows us to obtain useful concentrations of I_2 in aqueous solutions. The equilibrium constant for this reaction is approximately 700. For this reason, iodometric methods are carried out in the presence of excess iodide ion.

A cursory survey of literature regarding the estimation of copper indicated that estimation based on the redox potentials of iodometry using potentiometric technique is not available for reference.

It is evident, sometimes, that certain difficulties[2,3] arise in the estimation of copper in salts; and also attribute the cause may be due to any of the following :
a. the formation of intermediate product of complexation during the reaction with the reagents and
b. also due to the variable pH conditions of the medium, for reasons.

As a result of the above facts, the reduction of Cu^{2+} to Cu^+ is not quantitative.

This has prompted us to investigate /estimate the amount of copper present in a sample through redox potential measurements through potentio-metric technique; and also corroborating the results simultaneously, using titrimetric method of analysis, maintaining different pH condition of the medium. We have carried out this investigation using different buffer reagents, too, to elicit out the effective range of pH for quantitative determination of copper; and the preferable acidifying reagents for both iodometric and potentiometric techniques. We have attempted to correlate, logically, both of these results successfully.

EXPERIMENTAL

(i) Cell set up for potentiometric investigation

Potentiometry is one of the versatile methods used for quantitative analysis in analytical chemistry. In this case, potential of an indicator electrode in equilibrium with redox ions to be determined is measured. Such redox titrations involve the transfer of electrons from the substance being oxidized to the substance being reduced.

Oxidized form + n electrons = reduced form

For such reaction, the potential (E) acquired by the indicator electrode at 25^0C is given by

$$E = E^0 + \frac{0.0591}{n} \log \frac{[ox]}{[red]} \tag{1}$$

The potential is controlled by the ratio of these concentrations terms. It is possible to titrate two substances by the same titrant provided the standard potentials of the substances being titrated, and their oxidation or reduction products, differ by about 0.2 V.

The electrochemical cell set up desired for the investigation is

Hg/Hg$_2$Cl$_2$/KCl (Satd) // Redox analyte/Pt
(reference electrode)   (Indicator electrode)

Therefore, $E_{Indi} = E_{cell} + 0.2422$ volts.
Where, E_{ref} is a saturated calomel electrode of constant potential, 0.2422 Volts at 25^0C. The potentials measured in this investigation are not under standard conditions but under laboratory conditions and concentrations of the reagents.

(ii) Procedure

In order to ascertain best conditions needed for

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quantitative precipitation of copper as cuprous iodide, we have performed the experiments at different buffer media reagents and pH conditions. The following series of stock solutions of copper sulphate (0.1, 0.08, 0.06, 0.05, 0.04, 0.02 and 0.01Molar) are prepared from $CuSO_4.5H_2O$ (Assay:99.5 %). The potential (E) measurements of different copper solution during the investigations are made with following reagents:
(1). 4N NaOH; (2). 1:1 Ammonia solution; (3). 1:1 Acetic acid; (4). 4N citric acid ; (5). Standard $Na_2S_2O_3$ solution; (6). Freshly prepared starch; (7). 5% NH_4CNS solution

Specifically, we are interested in the following systems at different pH conditions for investigation.
(1). $CuSO_4$ + NaOH + CH_3COOH; (2). $CuSO_4$ + NH_4OH + CH_3COOH; (3). $CuSO_4$ + NaOH + Citric acid; (4). $CuSO_4$ + NH_4OH + Citric acid

The potentiometric and volumetric titrations of the above systems are carried out in two-in-one cell as shown (figure 1) maintaining different P^H conditions.
1. Pipette out 25 ml of copper sulphate solution into the cell.
2. Insert the Pt (indicator) and Calomel (reference) electrodes into the cell. Insert combined glass electrode to note the pH of the medium.
3. Use a magnetic bead stirrer to swirl the reacting solutions.
4. Record the steady potential(E) in millivolts and note the pH of the medium.
5. Add 4N NaOH/ 1:1Ammonia solution drop by drop till a pale blue precipitate (turbid) is formed. Note the potential and pH.
6. Add the weak acid (acetic /citric) drop by drop till a definite desired pH is maintained.
7. Add 5ml of 10% KI solution. Iodine is liberated. Record the steady potential after 10-15 minutes. This is the potential of the solution under the conditions of reaction as explained by equation (1) and marked as E_1.
8. Titrate with standard $Na_2S_2O_3$ solution till the entire solution turns pale straw yellow.
9. Add 2ml of 5% NH_4CNS followed by the addition of 1ml of freshly prepared starch. The solution turns bluish black.
10. Titrate with standard $Na_2S_2O_3$ solution till the sharp disappearance of blue color. Iodine is consumed

completely. Note the Volume standard $Na_2S_2O_3$ solution consumed.
11. Record the steady potential,(E_2) which accounts for as given in equation (2).
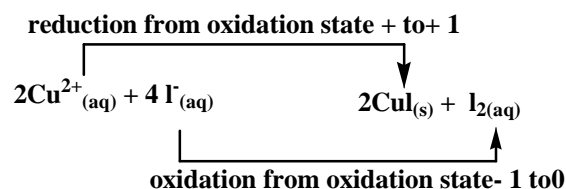
One minor problem[2,3] with this particular iodometric titration is that copper(I) iodide forms a weak complex with molecular iodine which slows down its reaction with thiosulfate. As a consequence of this, once the starch indicator has turned from blue to colorless, the blue color returns after a few seconds as I_2 is slowly released into the solution by the CuI-(I_2) complex. This "after-bluing" can be avoided by adding some ammonium thiocyanate, NH_4SCN, just before the end point is reached. The thiocyanate ion, SCN^-, replaces the complexed I_2 from CuI-(I_2), releasing the I_2 to solution where its reaction with thiosulfate is rapid.

$CuI-(I_2) + SCN^- (aq) \rightarrow CuI-(SCN^-) (aq) + I_2 (aq)$
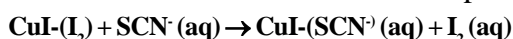
The data for the prepared series of copper sulphate solutions are recorded and are given in TABLES 1- 8. The steady potentials in millivolts are recorded after the addition of each reagent and the corresponding pH of solutions are also noted using a digital pH meter. Particularly, we are interested in the potential difference $[E_1 - E_2]$, which is related to the amount of iodine liberated from an equivalent amount of copper present in the sample. Copper in copper salt can also be estimated simultaneously in the same cell by iodometric titration method. The volume of standard $Na_2S_2O_3$ solution consumed is also recorded (TABLES 1-8).

RESULTS AND DISCUSSION

Copper(II) ions oxidise iodide ions to iodine, and in the process are themselves reduced to copper(I) iodide.

reduction from oxidation state + to+ 1

$$2Cu^{2+}_{(aq)} + 4 I^-_{(aq)} \longrightarrow 2CuI_{(s)} + I_{2(aq)}$$

oxidation from oxidation state- 1 to0

(a) The reaction of iodide ions with copper(II) ions

This is the reaction that liberates the iodine for titration: it is

$2Cu^{2+} + 2 e^- \rightarrow 2Cu^+$	$E^o = + 0.15V$
$I_2 + 2e^- \rightarrow 2 I^-$	$E^o = + 0.54V$
$2Cu^{2+} + 4I^- \rightarrow 2Cu^+I^- + I_2$	$E_1^o = - 0.39V$ (1)

The reaction is not spontaneous-but it does occur, and very quickly too.

The value of E^o can be used to give the equilibrium constant for the reaction, and it comes to around 10^{-7}. This is very small, and indicates little reaction. But this is under standard conditions. The factor that makes the reduction reaction possible is the fact that Cu^+ is not in solution at a concentration of 1 mol dm^{-3}.

Copper(I) iodide is an extremely insoluble solid. The equilibrium constant for the reaction

$$Cu^+ (aq) + I^- (aq) \rightarrow CuI (s)$$
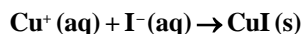
is around 10^{12}. Thus as soon as any Cu^+ appears it immediately precipitates, and this is sufficient to drive the reaction over to the right hand side. Indeed it is not hard to show that the equilibrium constant for the production of solid copper(I) iodide as distinct from copper(I) under standard conditions is of the order of 10^5. This reaction is complete by anyone's standards, and certainly is complete enough for the reaction to be used in quantitative analysis.

This is a rapid, quantitative reaction in acidic solutions, if there is a large excess of iodide ion present and if the copper is in the form of a simple ion rather than a complex one.
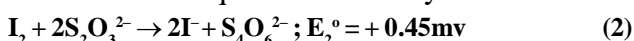
The iodine that is liberated can be titrated in the usual manner with standard thiosulphate solution. The reaction involving copper (II) ion and iodide takes place quantitatively since the copper (I) ion formed as result of the reduction is removed from the solution as a insoluble precipitate of copper (I) iodide.

(b) The reaction of sodium thiosulphate with iodine

The redox potential of the titration part of the reaction of sodium thiosulphate with iodine is as follows

$$I_2 + 2e^- \rightarrow 2I^- ; \qquad E^o = + 0.54 \text{ mv}$$
$$S_4O_6^{2-} + 2e^- \rightarrow 2S_2O_3^{2-} ; \ E^o = + 0.09 \text{ mv}$$
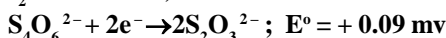
The overall equation reaction by convention is:

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-} ; E_2^o = + 0.45 \text{mv} \qquad (2)$$
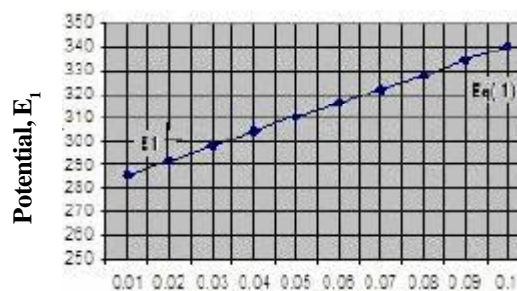
The reaction is feasible under standard conditions.

The weak acid (acetic or citric) is added to the solutions of copper drop by drop till a definite p^H is

**Figure 1: A two-in-one cell set up for potentiometric analysis with magnetic bead stirrer**

Molar concentration of copper colution

Figure 2: A plot of steady potentials of copper solutions Vs Molar concentration of copper for equation (1)

**TABLE 1: Potential and titrimetric data for $CuSO_4$ solutions with reagents ($NaOH + CH_3COOH$)**

|	Reagents	Potential in millivolts	0.1M $CuSO_4$ + NaOH + CH_3COOH P^H	0.08M $CuSO_4$ + NaOH + CH_3COOH Potential in millivolts	P^H	0.06M $CuSO_4$ + NaOH + CH_3COOH Potentia in millivolts	P^H	Potential in millivolts	0.05M $CuSO_4$ + NaOH + CH_3COOH P^H	0.04M $CuSO_4$ + NaOH + CH_3COOH Potential in millivolts	P^H	0.02M $CuSO_4$ + NaOH + CH_3COOH Potential in millivolts	P^H	Potential in millivolts	0.01M $CuSO_4$ + NaOH + CH_3COOH P^H
1	$CuSO_4$	168	3.98	194	4.16	254	4.3	219	4.26	231	4.26	142	4.71	112	5.03
2	4N NaOH	131	4.7	175	-	175	5.15	205	4.94	195	5.13	137	5.93	172	10.8
3	1:1CH_3COOH	139	3.96	177	3.85	218	4.0	215	4.01	220	4.05	-	4.0	45	3.9
4	10% KI (E_1)	340	4.35	328	4.20	316	4.1	310	4.38	304	4.41	292	4.18	286	4.1
5	Addition of $Na_2S_2O_3$ till the disappearance of blue color (E_2)	205	5.12	185	4.26	166	4.4	156	4.6	146	4.25	128	4.25	120	4.3
6	E_1 - E_2	135	-	143	-	150	-	154	-	158	-	164	-	166	-
7		Iodometric titration	Vol $_{Na2S2O3}$ = 10.8 ml	Vol $_{Na2S2O3}$ = 8.6 ml		Vol $_{Na2S2O3}$ = 6.4 ml		Vol $_{Na2S2O3}$ = 5.3 ml		Vol $_{Na2S2O3}$ = 4.2 ml		Vol $_{Na2S2O3}$ = 2.1 ml		Vol$_{Na2S2O3}$ = 1.0 ml	

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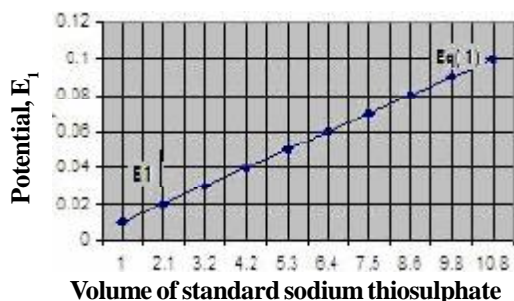
Figure 3: A plot of steady potentials of copper in solutions Vs Volume of standard sodium thiosulphate consumed at the end point (Equation 2)
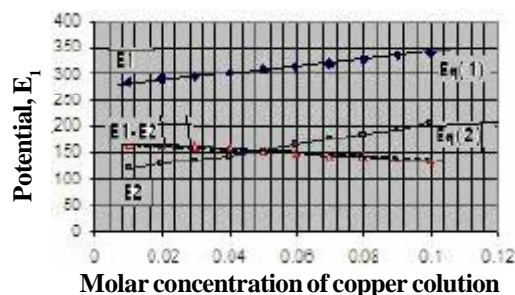
Figure 4: A plot of potentials, E_1, E_2 and [[E_1 - E_2] Vs Molar concentration of copper solution in the presence of NaOH and acetic acid reagents at pH =4.0
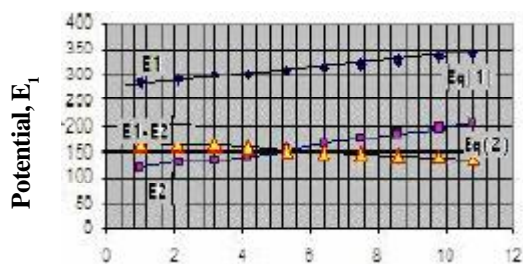
Figure 5: A calibration plot of potentials, E_1, E_2 and [E_1-E_2] Vs volume of standard $Na_2S_2O_3$ consumed at the equivalence point of titration

maintained in a cell set up as shown in figure 1.

E_1 represents the steady redox potential for equation (1) under experimental conditions (pH = 4.0), which is due to the reaction of cupric ions with iodide liberating iodine (figure 2). Standard sodium thiosulphate is used as a titrant; and the freshly prepared starch is added when the colour of the iodine containing solution is pale straw yellow. When the blue color of the solution disappeared at the equivalence point of titration, the steady potential is recorded as E_2(equation 2), in figure 3. Simultaneously, the volume of standard $Na_2S_2O_3$ run down at the equivalence point of titration is also recorded. The experimental data are collected for 1.0, 0.8, 0.06, 0.05, 0.04, 0.02 and 0.01 molar copper sulphate solution series (Figures 4,5 and 6).

The equation (3) clearly shows the decrease of potential, E_1, with the decrease of molar concentration of copper ions for redox Cu^{2+} / Cu^+ couple.

$$E1 = E^0{}_{Cu^{2+}/Cu^+} + \frac{2.303RT}{2F} \ log \ \frac{[Cu^+]}{[Cu^{2+}]} \qquad (3)$$

Similarly, it is observed that the steady potential, E_2, decreases with the decrease of I_2 content in solutions for the above series. The equation (4) illustrates the behaviour of change of potential with iodine content.

$$E1 = E^0{}_{I2/I^-} + \frac{2.303RT}{2F} \ log \ \frac{[I^-]}{[I_2]} \qquad (4)$$

It is reasonable to understand that the difference of the two steady potentials E_1 and E_2, that is; [E_1 - E_2] for a particular concentration of copper ions under investigation is related to the amount of I_2 liberated. The

TABLE 2: Potential and titrimetric data for $CuSO_4$ solutions with reagents (NH_4OH + CH_3COOH) at P^H = 4.0

| Reagents	0.1M $CuSO_4$ + NH_4OH + CH_3COOH		0.08M $CuSO_4$ + NH_4OH + CH_3COOH		0.06M $CuSO_4$ + NH_4OH + CH_3COOH		0.05M $CuSO_4$ + NH_4OH + CH_3COOH		0.04M $CuSO_4$ + NH_4OH + CH_3COOH		0.02M $CuSO_4$ + NH_4OH + CH_3COOH		0.01M $CuSO_4$ + NH_4OH + CH_3COOH	
	Potential in millivolts	P^H	Potential in millivolts	P^H	Potential in millivolts	P^H	Potential in millivolts	P^H	Potential in millivolts	P^H	Potential in millivolts	P^H	Potential in millivolts	P^H
1 $CuSO_4$	181	3.93	184	4.03	207	4.05	201	4.31	195	4.14	191	4.58	126	4.90
2 1:1 NH_4OH	175	4.61	78	3.71	200	4.74	192	4.95	1881	4.89	177	5.3	121	7.78
3 1:1 CH_3COOH	178	3.87	79	3.9	201	3.97	198	3.97	190	3.97	181	3.97	136	4.02
4 10% KI (E_1)	343	4.19	333	4.3	322	4.37	317	4.33	311	4.46	300	4.25	294	4.5
5 Addition of $Na_2S_2O_3$ till the dis – appearance of blue color (E_2)	237	4.65	215	4.67	192	5.17	181	4.52	169	4.6	146	4.5	134	4.9
6 E_1 - E_2	106	-	118		130		136		142		154		160	
7 Iodometric titration	Vol $_{Na2S2O3}$ =10.6ml		Vol $_{Na2S2O3}$ =8.1 ml		Vol $_{Na2S2O3}$ =6.2 ml		Vol $_{Na2S2O3}$ =5.2 ml		Vol $_{Na2S2O3}$ =4.2 ml		Vol $_{Na2S2O3}$ =2.0 ml		Vol $_{Na2S2O3}$ =1.0 ml	
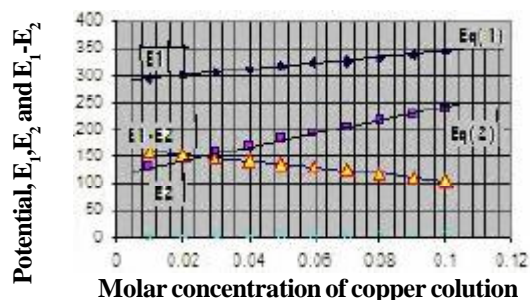
Figure 6: A calibration plot of potentials, E_1, E_2 and $[[E_1 - E_2]$ Vs molar concentration of copper solution in the presence of Ammonia and acetic acid reagents
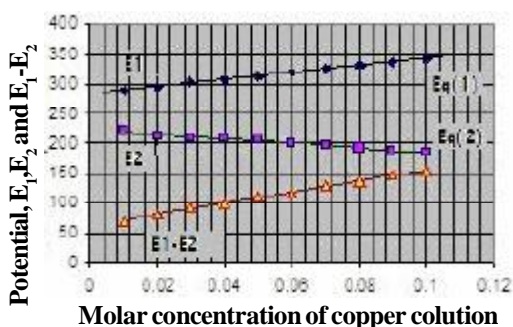

Figure 7: A plot of potentials E_1, E_2 and $[E_1 - E_2]$ of copper solutions Vs molar concentrations of copper solutions

stochiometry involved in the iodometric reaction is

2 mols of Cu^{2+} ions $\equiv$ 2 moles of $Na_2S_2O_3 \equiv$ 1 mole of I_2

The above stochiometric relationship is depicted in figures 2 and 3.

For the estimation of Cu^{2+} ions using NaOH and CH_3COOH reagents, the figure 4 denotes linear change of potentials, E_1 (Equations 1) with molar concentration of copper ions at a definite pH= 4.0. Similarly, variation of potentials, E_2 (equation 2), and $[E_1 - E_2]$ with

molar concentration of copper solutions and the volumes of standard sodium thiosulphate consumed, are shown in the figures 4 and 5.

The estimation of copper is carried out using ammonia and acetic as reagents by maintaining a definite pH = 4.0 for all the prepared molar concentrations of copper solutions as given in TABLE 2. Both potentiometric analysis and the titrimetric data were collected in TABLE 2. The steady potentials, E_1 (equation 1), E_2 (equation 2) and $[E_1 - E_2]$ were also plotted. Figure 6 depicts the variation of potentials for equation (1),(2) and $[E_1 - E_2]$. TABLE 2 provides the information regarding the iodometric titration of the prepared solutions in the same cell set up under the identical conditions of investigation. One of the notable features is that titrimetric volumes of standard $Na_2S_2O_3$ obtained for this series is slightly lower than observed when NaOH and CH_3COOH are reagents.

The variations of the potentials (E_1), (E_2) and the trend of changes of $[E_1 - E_2]$ for the series of copper solutions are depicted in the figure 6.

Potentiometric analysis and the iodometric titrations were also carried out for copper solutions as prepared above and the results obtained are tabulated in TABLE 3 and 4 using NaOH and NH_4OH reagents; and finally, acidified with adequate amount of citric acid drop by drop to get the desired p^H of copper solutions. Though, E_1, E_2 and $[E_1 - E_2]$ of these solutions (TABLE 3) change linearly for a very small pH range(2.0 to 2.5) with change in molar concentration, the potential difference $[E_1 - E_2]$ and the titrimetric volumes observed are

TABLE 3: Potential and titrimetric data for $CuSO_4$ solutions with reagents (NaOH + citric acid) at $P^H = 4.0$

Reagents	0.1M CuSO₄ + NaOH + citric acid		0.08M CuSO₄ + NaOH + Citric acid		0.06M CuSO₄ + NaOH + citric acid		0.05M CuSO₄ + NaOH + citric acid		0.04M CuSO₄ + NaOH + citric acid		0.02M CuSO₄ + NaOH + citric acid		0.01M CuSO₄ + NaOH + citric acid	
	Potential in millivolts	pH	Potential in millivolts	pH	Potential in millivolts	pH	Potential in millivolts	pH	Potential in millivolts	pH	Potential in millivolts	pH	Potential in millivolts	pH
1 CuSO₄	188	3.78	221	3.83	223	3.97	213	4.07	224	4.06	217	4.36	145	4.9
2 4NaOH	186	4.50	219	4.57	218	4.66	209	4.68	221	4.68	211	4.99	130	5.4
3 4Ncitric acid	185	2.00	215	1.98	216	2.04	208	2.05	219	2.09	207	2.04	140	2.05
4 10% KI (E₁) Addition of Na₂S₂O₃	340	3.31	330	2.3	320	2.38	314	2.41	308	2.4	296	2.38	290	2.36
5 till the disappearance of blue color(E₂)	185	3.2	193	3.16	201	3.18	205	3.31	207	3.13	214	3.18	220	2.79
6 E₁ - E₂	155		137		119		109		101		82		70	
7 Iodometric titration	Vol Na2S2O3 = 9.8 ml		Vol Na2S2O3 = 8.0ml		Vol Na2S2O3 = 6.0 ml		Vol Na2S2O3 = 5.0 ml		Vol Na2S2O3 = 4.0 ml		Vol Na2S2O3 = 1.9 ml		Vol Na2S2O3 = 0.9ml	

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TABLE 4: Potential and titrimetric data for CuSO$_4$ solutions with reagents (NH$_4$OH + citric acid)

Reagents	0.1M CuSO$_4$ + NH$_4$OH + Citric acid		0.08M CuSO$_4$ + NH$_4$OH + Citric acid		0.06M CuSO$_4$ + NH$_4$OH + Citric acid		0.05M CuSO$_4$ + NH$_4$OH + Citric acid		0.04M CuSO$_4$ + NH$_4$OH + Citric acid		0.02M CuSO$_4$ + NH$_4$OH + Citric acid		0.01M CuSO$_4$ + NH$_4$OH + Citric acid	
	Potential in millivolts	pH	Potential in millivolts	pH	Potential in millivolts	pH	Potential in millivolts	pH	Potential in millivolts	pH	Potential in millivolts	pH	Potential in millivolts	pH
CuSO$_4$	188	3.78	221	3.83	223	3.97	213	4.07	224	4.06	217	4.36	145	4.9
1:1 NH$_4$OH	186	4.50	219	4.57	218	4.66	209	4.68	221	4.68	211	4.99	130	5.4
4N citric acid	185	2.00	215	1.98	216	2.04	208	2.05	219	2.09	207	2.04	140	2.05
10% KI (E$_1$)	339	3.31	330	2.3	319	2.38	315	2.41	310	2.4	301	2.38	295	2.36
Addition of Na$_2$S$_2$O$_3$ till the dis-appearance of blue color (E$_2$)	221	3.2	218	3.16	212	3.18	210	3.31	208	3.13	203	3.18	200	2.79
E$_1$ - E$_2$	118		112		107		105		102		98		95	
Iodometric titration	Vol $_{Na2S2O3}$ = 10.6 ml		Vol $_{Na2S2O3}$ = 8.4ml		Vol $_{Na2S2O3}$ = 6.3 ml		Vol $_{Na2S2O3}$ = 5.3 ml		Vol $_{Na2S2O3}$ = 4.3 ml		Vol $_{Na2S2O3}$ = 2.1 ml		Vol $_{Na2S2O3}$ = 1.0ml	
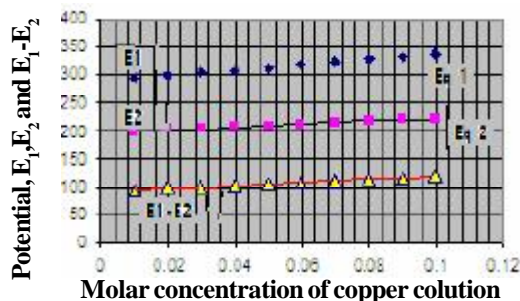
Figure 8: A plot of potentials E$_1$, E$_2$ and [E$_1$ - E$_2$] of copper solutions vs Molar concentrations of copper solution
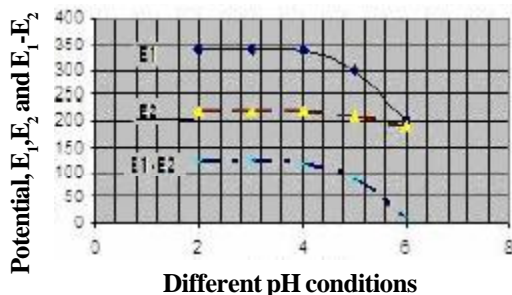
Figure 9: A plot of potentials E$_1$, E$_2$ and [E$_1$ - E$_2$] of copper solutions vs different pH media conditions

TABLE 5: Iodo-potentiometric data at different pH conditions for 0.1M copper sulphate-NaOH-Acetic acid

Reagents	Redox potentials. (mv) at pH = 2	Redox potentials. (mv) at pH = 3	Redox potentials. (mv) at pH = 4	Redox potentials. (mv) at pH = 5	Redox potentials. (mv) at pH = 6
CuSO$_4$	213	210	168	230	231
1:1 NH$_4$OH	39	207	131	219	217
1:1 acetic acid	47	204	139	72	37
10% KI (E$_1$)	340	340	338	299	200
Addition of Na$_2$S$_2$O$_3$ till the dis appearance of blue color (E$_2$)	220	220	219	211	190
E$_1$ - E$_2$	120	120	118	88	10
Iodometric titration	Vol $_{Na2S2O3}$ 10.8ml	Vol $_{Na2S2O3}$ 10.8ml	Vol $_{Na2S2O3}$ 10.7ml	Vol $_{Na2S2O3}$ 7.0ml	Vol $_{Na2S2O3}$ 0.30ml

quite low indicating that quantitative estimation copper are not possible for pH<2.5. In the investigation, experimental determination of copper is confined to pH = 2.0 for all copper solutions(TABLES 3 and 4) and data collected are not good for estimation, but still lower than observed for other previous conditions. Figures 7 and 8 are little unique in behaviour as regards the changes of potential [E$_1$-E$_2$] with different molar solutions of copper salt and is different from figures 5 and 6.

It is noticeable that the potential difference [E$_1$- E$_2$] in these cases decreases with the decease of copper concentrations with addition of NaOH or ammonia reagents acidified with citric acid ; evidently, perhaps due

to the formation of quite stable and unionized cupric citrate at pH < 2.5 conditions.

The effect of pH for the estimation of copper is also studied by varying the different buffer mixtures and estimation is performed at pH =2.0, 3.0, 4.0, 5.0 and 6.0 for one particular concentration, that is, 0.10 molar copper sulphate solution. The volume of sodium thiosulphate consumed for the titrations at different pH conditions are also recorded. These results are tabulated in TABLES 5-8. It is clear that the potentials E$_1$, E$_2$ and [E$_1$ - E$_2$] for the copper sulphate solutions do remain constant for a particular range of pH values and then,decreases gradually at higher values of pH. Figures 9 -10 illustrates the variation potential at different pH conditions for potentiometric studies.
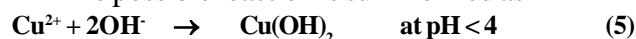
Figure 9 indicates clearly that all the three E$_1$, E$_2$ and [E$_1$ - E$_2$]) potential data are constant and the lines

are horizontal between pH conditions between 2.0 and 4.0 and thereafter, higher side of pH conditions, the potential values are found to decrease gradually to a lower value, for reasons.
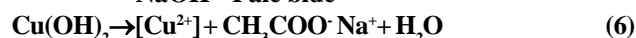
This behaviour is true even in the case of iodometric titre volumes of Standard $Na_2S_2O_3$ consumed for iodine liberated which remain the constant (TABLE 5) between the same pH range of investigation for the series and then, drops to a lesser values.

A point of remark that throws light on the fact is that free copper ions(Cu^{2+}) are available in solution and quantitative reduction of these ions to Cu^+ ions are possible with addition of 10% KI solution.

The possible reaction is summerized as

$$Cu^{2+} + 2OH^- \rightarrow Cu(OH)_2 \quad \text{at pH} < 4 \quad (5)$$
$$\text{NaOH} \quad \text{Pale blue}$$
$$Cu(OH)_2 \rightarrow [Cu^{2+}] + CH_3COO^- Na^+ + H_2O \quad (6)$$
$$\text{Free ions}$$

at pH between 2.0 and 3.5.

Hence, quantitative estimation of copper in solution is possible, if the pH is rigidly fixed between 2 and 3.5.

If, for reasons, the pH < 4.0 for the copper solutions, evidently, there is the possibility of the formation of a quite stable $Cu(OH)_2$ compound at these conditions; and thus, the availability of free copper ions may be less in solution resulting in lower estimated data for copper.

The results of the estimation of copper under different pH conditions with ammonia as reagent are given in TABLE 6.

Figure 10 illustrates that all the three E_1, E_2 and [E_1 - E_2] potential data are constant and the lines are horizontal between pH condition between 2.0 and 3.0 when ammonia and acetic acid is used as reagents; and thereafter, it is found to decrease gradually to a lower value, for reasons. It can be pointed out that all the cupric ions are available for estimation in solution for reduction as Cu^+ ions liberating proportionate amount of iodine, which is then titrated with standard Sodium thiosulphate solution (TABLE 6).

At conditions, pH < 3.0, for these solutions, it can be observed that Cu^{2+} ions interact to form favorably the complex ion, $Cu(NH_3)_4^{2-}$. The non-availability of free Cu^{2+} ions result in lower potential data / volume of standard $Na_2S_2O_3$, which is lower than the expected

TABLE 6: Iodo- potentiometric data at different pH conditions for 0.1M copper sulphate-NH_4OH-acetic acid

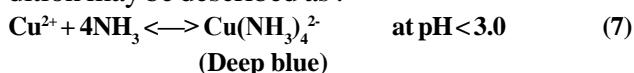| Reagents	Redox potentials. (mv) at pH = 2	Redox potentials. (mv) at pH = 3	Redox potentials. (mv) at pH = 4	Redox potentials. (mv) at pH = 5	Redox potentials. (mv) at pH = 6
CuSO4	183	194	181	187	183
1:1 NH4OH	181	188	175	190	183
1:1N acetic acid	188	187	178	191	136
10% KI (E1)	340	340	335	300	251
Addition of Na2S2O3 till the dis appearance of blue color (E2)	220	220	215	211	190
E1 - E2	126	125	118	89	61
Iodometric titration	Vol Na2S2O3 10.6ml	Vol Na2S2O3 10.6ml	Vol Na2S2O3 10.4ml	Vol Na2S2O3 3.5 ml	Vol Na2S2O3 1.0 ml
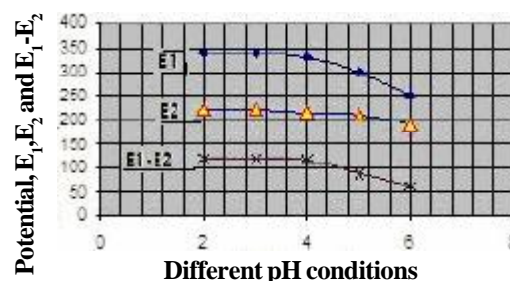
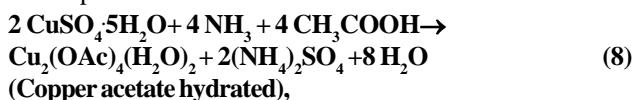Figure 10: A plot of potentials E_1, E_2 and [E_1 - E_2] of copper solutions vs different pH media conditions

values (TABLE 6).

The complexation reaction product under the condition may be described as :

$$Cu^{2+} + 4NH_3 <\longrightarrow Cu(NH_3)_4^{2-} \quad \text{at pH} < 3.0 \quad (7)$$
$$\text{(Deep blue)}$$

$$K_f = \frac{[Cu(NH_3)_3^{2-}]}{[Cu^{2+}](NH_3)^2}$$

where K_f has higher value. Or the formation of copper acetate is less probable.

$$2\,CuSO_4 \cdot 5H_2O + 4\,NH_3 + 4\,CH_3COOH \rightarrow$$
$$Cu_2(OAc)_4(H_2O)_2 + 2(NH_4)_2SO_4 + 8\,H_2O \quad (8)$$
$$\text{(Copper acetate hydrated),}$$
$$\text{Blue}$$

TABLE 8 gives potentiometric data for copper salt treated with NaOH and acidified with Citric acid. It is observed that the potential, E_1 and E_2 of the copper solution do not have constant pH range option and is only confined to pH = 2.0. At pH < 2.0, it can be observed that the potentials decrease considerably indicating that the involvement of free copper ions in solution is not there at all. This fact is clear that during the investigation

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TABLE 7: Iodo- potentiometric data at different pH conditions for 0.1M copper sulpate- NaOH- citric acid

Reagents	Redox potentials. (mv) at pH = 2	Redox potentials. (mv) at pH = 3	Redox potentials. (mv) at pH = 4	Redox potentials. (mv) at pH = 5	Redox potentials. (mv) at pH = 6
$CuSO_4$	180	180	190	197	-
1:1 NaOH	143	167	176	121	-
4N citric acid	150	170	171	135	-
10% KI (E_1)	339	333	329	274	-
Addition of $Na_2S_2O_3$ till the disapperance of blue color (E_2)	214	212	211	200	-
E_1 - E_2	125	121	118	74	-
Iodometric titration	Vol $_{Na2S2O3}$ 9.6 ml	Vol $_{Na2S2O3}$ 9.4 ml	Vol $_{Na2S2O3}$ 8,2 ml	Vol $_{Na2S2O3}$ 1.8ml	-

TABLE 8: Iodo-potentiometric data at different pH conditions for 0.1M copper sulphate-NH_4OH-citric acid

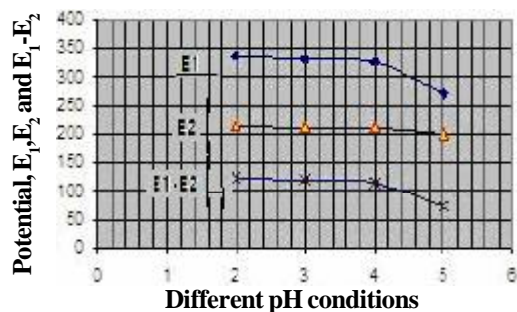| Reagents	Redox potentials. (mv) at pH = 2	Redox potentials. (mv) at pH = 3	Redox potentials. (mv) at pH = 4	Redox potentials. (mv) at pH = 5	Redox potentials. (mv) at pH = 6
$CuSO_4$	188	183	212	177	227
1:1 NH_4OH	186	194	209	152	220
4N citric acid	185	192	205	149	221
10% KI (E_1)	340	336	315	272	217
Addition of $Na_2S_2O_3$ till the disapperaence of blue color (E_2)	210	210	205	198	185
E_1 - E_2	130	126	110	74	32
Iodometric titration	Vol $_{Na2S2O3}$ 9.8 ml	Vol $_{Na2S2O3}$ 9.5 ml	Vol $_{Na2S2O3}$ 8.6 ml	Vol $_{Na2S2O3}$ 3.4 ml	Vol $_{Na2S2O3}$ 0.3ml

Figure 11: A plot of potentials E_1, E_2 and [E_1 - E_2] of copper solutions vs differnt pH media conditions
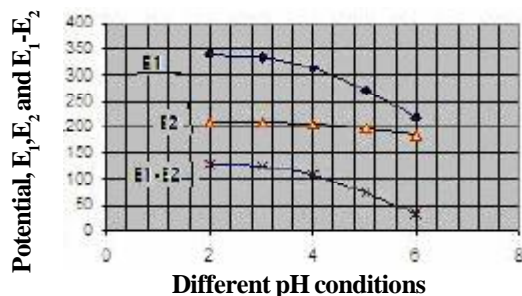

Figure 12: A plot of potentials E_1, E_2 and [E_1 - E_2] of copper solutions vs differnt pH media conditions

prior to the measurements,the solution is observed to be turbid, opaque and pale bluish even after acidification to give free copper ions. Titrimetric results corroborate the above fact and found that the volume of standard standard $Na_2S_2O_3$ solution required at equivalence point is low. Figure 11 illustrates the potential change behavior of copper solution with the addition of NaOH and citric acid at different pH conditions.

The potential change data for copper sulphate with buffer media NH_4OH and Citric acid is given in TABLE 8 and figure 12 illustrates graphically the similar trend indicating that only at pH =2.0 reasonable estimation of copper is possible with error. Therefore, it is observed that it not advisable to determine copper at higher pH conditions because copper ions exist as a citrate complex.

The error in the estimation of copper when treated with $NaOH/NH_4OH$ and citric acid buffer is evidently due to the formation of the unionisable complex, Cupric citrate. At pH< 4.0, the reactions may be

$$Cu^{2+} + 2OH^- \dashrightarrow Cu(OH)_2$$
$$Cu^{2+} + 4NH_3 \longleftrightarrow [Cu(NH_3)_4]^{2-} \tag{9}$$

After acidification with citric acid, fewer number of Cu^{2+} ions are available in solution and the remaining copper ions are involved in the formation citrate complex as stated below

$$Cu^{2+} + Citric\ acid, (CA) \rightarrow Cu(CA)\ at\ P^H < 2.0 \tag{10}$$
$$\textbf{Cupric citrate}$$
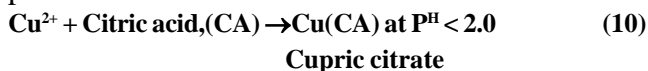
Possible points of error copper in iodometry:

(i) Addition of excess potassium iodide,

$$2Cu^{2+} + 4I^- \rightarrow Cu_2I_2 + I_2, \text{ and}$$

(ii) Titration of iodine with thiosulfate,

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$
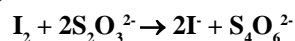
Precautions must be taken to avoid side reactions. For instance, iodine will slowly oxidize tetrathionate to sulfate, especially at high pH values. At low pH sulfurous acid may be formed by thiosulfate. Another source of error in strong acid solution is air oxidation of iodide:

$$O_2 + 4H^+ + 4I^- \rightarrow 2I_2 + 2H_2O$$

TABLE 9 : Data for copper in copper salts: Potentials, E_1 (mV) and volume (ml) of 0.232M $Na_2S_2O_3$ solution

Molar concentration of copper sulphate taken for the investigation	Potentials, E_1 equation (1)	Volume of 0.232M 0.232M $Na_2S_2O_3$ solution, ml	Molar concentrations of copper in the present investigation
0.1	340	10.8	0.1000
0.09	334	9.8	0.0900
0.08	328	8.6	0.0798
0.07	322	7.5	0.0696
0.06	316	6.4	0.0594
0.05	310	5.3	0.0492
0.04	304	4.2	0.0390
0.03	298	3.2	0.0297
0.02	292	2.1	0.0195
0.01	286	1.0	0.0093

1mV change of potential = 0.00166Molar of copper sulphate solution or; 1mV change of potential = 0.183 ml of 0.232M $Na_2S_2O_3$
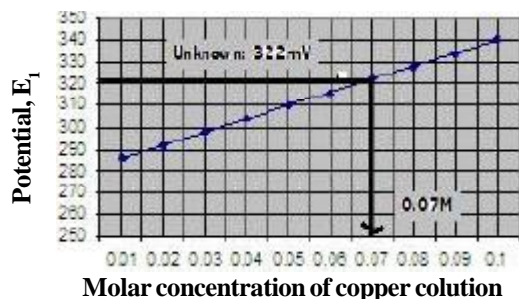

Figure 13: A calibration plot of potential, E1, and the molar concentarion of copper solution
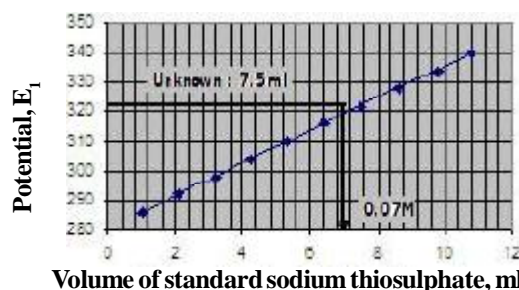

Figure 14: A calibration plot of the volume of standard sodium thiosulphate consumed and the molar concentration of copper solutions

This is called oxygen error.

In the present investigation of copper solutions, we have not faced any problem regarding the above aspects at the pH ranges referred to, in each case study. These side reactions are avoided by carrying out the copper estimation reactions preferably between pH range 2.0 - 3.5.

Determination of copper concentration from the present investigation:

The data collected for copper estimation through potentiometry and iodometric titration using NaOH and CH_3COOH as reagents are given in the TABLE 9 for reference and comparisonAfter recording the potential values E_1 and E_2 and or $[E_1 - E_2]$ for the unknown copper concentration solution, it is possible to find out concentration of copper from calibration plot, figure 13, for copper concentration series at pH = 4.0. Even, potentials E_2 and $[E_1 - E_2]$ of copper solutions can be similarly used to get the known concentration of copper in solutions.

From figure 14 ,it is clear that the molar concentration of the unknown can be determined , if you know the volume of sodium thiosulphate consumed in iodometric titration.

ACKNOWLEDGMENTS

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