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## Amperometric determination of copper (II) in alloy samples and synthetic mixtures using gallacetophenone phenylhydrazone

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### ABSTRACT

Gallacetophenone phenylhydrazone (GPPH) has been used as an analytical reagent for amperometric determination of copper. Copper(II) is quantitatively determined by GPPH at pH 4.0-6.0. After studying the polarographic behaviour of GPPH and copper(II) at dropping mercury electrode (DME), applied potential is fixed at -0.4V vs saturated calomel electrode (SCE). The method is applied for the determination of copper in brass, chalcopyrites and synthetic mixtures. The stoichiometry of the complex is found to be 3:2 (metal : ligand). This is also confirmed from the micro analytical data of the solid complex, thermo gravimetric and differential thermal analysis curves of the complex. © 2011 Trade Science Inc. - INDIA

### KEYWORDS

Copper(II);  
Gallacetophenone-  
phenylhydrazone (GPPH);  
Amperometry;  
Elemental analysis;  
Thermal analysis.

### INTRODUCTION

Various oximes, hydrazones and phenylhydrazones of phenolic aldehydes and ketones have been employed as analytical reagents for the determination of copper(II). However only a few of them have been introduced for the amperometric determination of copper. Neuberger<sup>[1]</sup> has employed salicylaldehyde oxime for copper in which the reaction between metal ion and reagent is slow at room temperature. Banerjea and chakrabarty<sup>[2]</sup> have used the same reagent for the amperometric determination of copper by a direct titration in sodium acetate (pH 4.2). Langer<sup>[3]</sup> has employed 2-benzoin oxime as a titrant for copper in alkaline medium. Reagents such as resacetophenone<sup>[4]</sup>, resacetophenone oxime<sup>[5]</sup>, peonoloxime<sup>[6]</sup>, mandelamidoxime<sup>[7]</sup> are also extensively employed for the amperometric determination of copper(II). Reddy<sup>[8]</sup>

has investigated gallacetophenone oxime for the amperometric determination of copper in acetate buffer (pH 4.5) at an applied potential of -0.6V vs SCE. The metal to ligand ratio of the complex is 3:2. Iron and aluminium interfere in the determination of Cu(II). Gallacetophenone chalcone<sup>[9]</sup> has also formed the similar type of complex with copper. The other useful reagents for the amperometric determination of copper(II) are 1-hydroxy-2-acetonaphthoneoxime<sup>[10]</sup> and resacetophenone phenylhydrazone<sup>[11]</sup>. Cha et al.<sup>[12]</sup> have studied the effects of competitive binding on the amperometric determination of copper with electrodes modified with chromo trope 2B. As only a few phenylhydrazones have been employed for the amperometric determination of copper, an attempt has also been made with gallacetophenone phenylhydrazone in the present study. The author in his attempt reveals that the reagent can not be strongly recommended for

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the gravimetric determination of copper but it can be successfully employed as an amperometric titrant.

### EXPERIMENTAL

All chemicals used were of analytical reagent grade, unless stated otherwise. Stock solution of copper(II) was prepared by dissolving in distilled water containing few drops of sulphuric acid and the solution was standardized by iodometry<sup>[13]</sup>. Lower concentrations of the solution were prepared by suitable dilution of the stock solution with distilled water. Solutions of other ions were prepared from their salts. Gallacetophenone phenylhydrazone was prepared as per the standard procedure given by Blatt<sup>[14]</sup> and Curniss et al.<sup>[15]</sup>. The molecular formula of the compound is  $C_{14}H_{14}N_2O_3$  and it melts at 146-147°C. An ethanolic solution of the reagent was employed and pH was adjusted using acetic acid and sodium acetate buffer. A 0.2% aqueous solution of gelatin was prepared freshly before use.

#### Apparatus

A Toshniwal manual Polarograph Model No. C L-02B with inbuilt digital microammeter, A digital pH meter L I-120 and Stanton Redcrafts DTA, TG and DTG simultaneous analyser model STA 780 were used.

#### Procedure

The polarographic behaviour of gallacetophenone phenylhydrazone and copper(II) at DME was studied to arrive at the suitable voltage to be fixed for the amperometric determination of copper. 25ml of the acetate buffer (pH 4.0), 5ml of 0.01M reagent, 1ml of 0.2% gelatin and 5ml of alcohol were taken in a titration cell and finally diluted to 50ml. Hydrogen gas was bubbled through the solution, then the drop time of the DME was adjusted to 2-3 seconds and polarogram of the reagent recorded. The polarograms of the supporting electrolyte, copper(II) and the reagent are shown in figure 1. The half wave potentials of copper(II) and reagent are found to be -0.05V vs SCE and -1.25V vs SCE respectively. The titration was carried out by fixing the applied voltage at -0.4V vs SCE.

An aliquot of standard copper(II) solution was transferred into the titration cell and the above contents were added keeping the volume at 50ml. The solution

was titrated with the reagent at -0.4V vs SCE. The current readings noted were corrected for volume changes and plotted against the volume of the reagent added. An 'L' shaped curve was obtained and the end point was evaluated graphically by the extrapolation method. The procedure was repeated with known but different aliquots. The results of the some of the determinations are given in TABLE 1.

#### Precision and accuracy

For a set of five determinations of 4.04 mg of copper(II), the average value found was 4.06 mg. The standard deviation was 0.01 mg and the relative standard deviation was 0.42%.

### RESULTS AND DISCUSSION

#### Composition of the complex

The composition of the complex was arrived from the micro analytical data of the solid complex, thermo gravimetric and differential thermal analysis curves in addition to the above amperometric method.

#### Elemental analysis

The elemental analysis for carbon, hydrogen and nitrogen of the copper(II) – GPPH complex from Australian Micro analytical service are presented in TABLE 2.

#### TG and DTA studies of Cu-GPPH complex

In order to arrive at the stability and composition of the metal chelate, thermo gravimetric (TG) and differential thermal analysis (DTA) of the solid complex was done. The TG, DTA curves of the complex are shown in figure 2.

The thermo gravimetric curve of Cu-GPPH complex shows that the decomposition of the complex starts even at 105°C itself and there is no stable region before it is converted to cupric oxide. Hence the complex has to be ignited to oxide to recommend the method for gravimetric determination. The DTA curve shows exothermic peak with a shoulder. This corresponds nearly to the loss of one mole of reagent. Hence, a meta stable complex with one mole of reagent only is formed at 280°C. Hence the reagent can not be strongly recommended for its gravimetric determination. However this reagent has been successfully employed for the

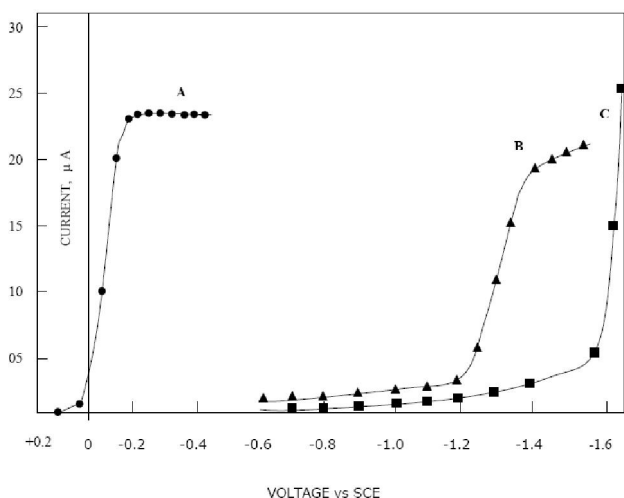


Figure 1 : Polarograms of (A) Copper (II), (B) GPPH, (C) Supporting electrolyte (pH=4.0, acetate buffer)

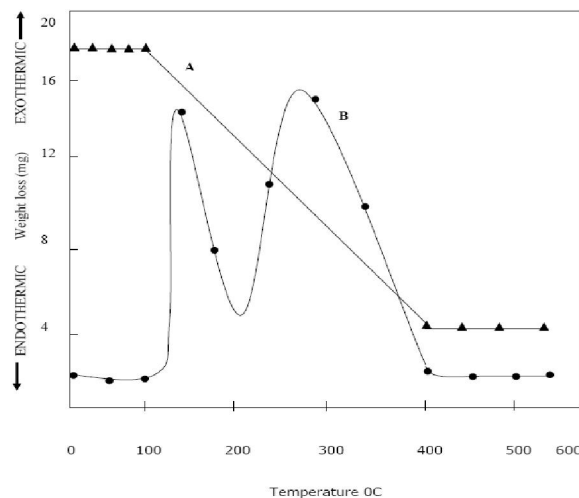


Figure 2 : TG and DTA curves of Copper-GPPH complex, (A) Thermo gravimetric curve, (B) Differential thermal analysis curve

TABLE 1 : Amperometric determination of Copper(II)

Copper taken(mg)	Copper found(mg)	Error (mg)
1.01	1.02	0.01
2.02	2.01	0.01
3.03	3.04	0.01
4.04	4.06	0.02
5.05	5.04	0.01
6.06	6.08	0.02
7.07	7.08	0.01
8.08	8.06	0.02

TABLE 2 : Elemental analysis of Cu-GPPH complex

Element	Carbon	Hydrogen	Nitrogen	Copper
Calculated %	47.86	3.16	7.99	27.19
Found %	47.79	3.24	7.88	27.24

The results reveal that Cu(II) reacts with GPPH in 3:2 ratio amperometric determination of copper.

**Determination of copper in presence of foreign ions**

Cadmium (II), nickel (II), zinc (II), manganese (II), palladium (II), aluminium (III), selenium, tellurium, arsenic, antimony, tin and iron are commonly associated with copper in its ores, alloys, slags and slimes. The determination of copper in presence of these ions is therefore of analytical interest.

Cd(II) is not electro active at or before -0.5V and it does not give any precipitate with GPPH in acetate buffer. Zn(II) and Ni(II) give neither a reduction wave at -0.4V vs SCE nor a precipitate with the reagent

TABLE 3 : Determination of copper in presence of foreign ions

Amount of copper taken = 4.04 mg

Foreign metal ion added mg	Copper found mg	Difference mg
20 Cd(II)	4.06	0.02
20 Ni (II)	4.06	0.02
20 Mn(II)	4.04	0.00
20 Zn(II)	4.02	0.02
20 Fe(III)*	4.04	0.00
20 Al(III)*	4.06	0.02
20 As(III)	4.06	0.02
20 As(V)	4.02	0.02
20 Sb(III)**	4.04	0.00
20 Sb(V)**	4.05	0.01
10 Se(IV)	4.06	0.02
10 Te(IV)	4.82	0.78
10 Te(VI)	4.04	0.00
20 Pb(II)**	4.04	0.00

\* in presence of sodium fluoride

\*\* in presence of ammonium tartrate

under the experimental conditions. Iron interferes polarographically in the titration and it gives a blue coloured precipitate under these conditions. The interference of iron can be masked by using sodium fluoride as masking agent. Al(III) gives no reduction wave under experimental conditions but forms yellow coloured complex with the reagent and its reaction is masked by sodium fluoride. Te(IV) and Se(IV) do not interfere in the amperometric determination of copper(II) as they do not form precipitates with the

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TABLE 4 : Determination of copper in brass and chalcopyrites

Name of the sample	Reported composition %	Copper found %	SD	RSD (%)
Brass	Cu (67.4), Zn (28.6), Sn (1.09), Pb (2.23), Fe (0.30) & Ni (0.33)	67.56**	0.098	0.15
Chalcopyrites	32.88*	32.72**	0.096	0.29

\* by the iodometric method

\*\* for a set of 5 determinations

TABLE 5 : Determination of Copper in synthetic mixture

	Copper(II) ion added $\mu$ $\text{ml}^{-1}$	Copper(II) found*	SD	RSD (%)
Synthetic mixture	0.5	0.48	0.0086	1.74
	1.0	0.98	0.007	0.71
	1.5	1.48	0.01	0.67

\* for a set of 5 determinations

reagent and also do not give diffusion waves at -0.4V. Copper is determined in presence of tellurate, arsenite and arsenate. It is also determined in presence of antimonite, antimonate and lead by using the ammonium tartrate as masking agent. The interference of tin in the amperometric method is unlikely as Sn(II) can be precipitated as meta stannic acid. The results are presented in the TABLE 3.

It is seen from the above that the determination of copper can be carried out in presence of its commonly associate species.

### Analysis of brass for copper

Copper has also been accurately determined in brass (Cu 67.4%, Zn 28.6%, Sn 1.09%, Pb 2.23%, Fe 0.30%, Ni 0.33%) at the above pH value and percentage copper obtained agree with the reported values within the experimental error.

For the determination of copper in brass which was obtained from Bureau of Analyzed Samples (London) was brought into solution by the standard procedure. A 5ml portion was transferred into the titration cell, dilute sodium carbonate solution added to neutralize the mineral acid and then acidified slightly with acetic acid. And the determination of copper was carried out by the procedure described earlier. Results are given in TABLE 4.

### Analysis of chalcopyrites for copper

Chalcopyrites sample supplied by A.P. Mining Corporation, Mylaram was treated according to the

standard procedure. About 1g of the powdered and dried sample was accurately weighed and dissolved in 25ml of concentrated HCl and 5ml of concentrated  $\text{HNO}_3$  by gentle heating. 20ml concentrated  $\text{H}_2\text{SO}_4$  were added and the solution was evaporated to white fumes when the precipitated sulphur was dissolved. The contents were cooled, diluted with distilled water and heated to dissolve ferric sulphate and other soluble salts. The solution was filtered and diluted to 500ml. A 50ml portion was standardized iodometrically using sodium fluoride to mask iron(III). A 5ml portion was transferred into the titration cell and dilute sodium carbonate solution was added to neutralize the acid. The determination of copper was carried out by the procedure described earlier and the results are given in TABLE 4.

### Analysis of Cu(II) in synthetic mixtures

The present method was successfully applied for the determination copper(II) in synthetic mixtures. The results are given in TABLE 5.

## CONCLUSIONS

Gallacetophenone phenylhydrazone reacts with copper in the ratio of 2:3 and this reagent has been successfully employed for the amperometric determination of copper. A number of metal ions which are associated in many of its ores do not interfere in the determination. The determination of copper(II) in the presence of considerable amount of zinc and iron makes it suitable for the analysis of it in brass, chalcopyrites and synthetic mixtures.

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