

A SIMPLE METHOD FOR SPECTROPHOTOMETRIC DETERMINATION OF TRACES OF COPPER

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ABSTRACT

The utility of Patton and Reeder's indicator, HHSNNA, for the trace spectrophotometric and visual colorimetric determination of Cu^{2+} is explored. A wine red complex of composition 1:1 is found to be formed between Cu^{2+} and HHSNNA. The complex has λ_{max} at 530 nm with $\epsilon = 25,558 \text{ L mole}^{-1}\text{cm}^{-1}$ and is stable for more than 2 hrs. Beer's law is obeyed between 0 to 1.5 ppm. The developed procedure, besides being based on aqueous phase, is highly selective and fairly sensitive. The utility of the method is brought to the lime light by analyzing some certified materials, and synthetic mixtures.

Key words: Copper, Patton and Reeder's indicator, Spectrophotometric method, Analysis of Certified and Synthetic Samples

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INTRODUCTION

Patton and Reeder's metal-ion indicator, 2-hydroxy-1-(2-hydroxy-4-sulpho-1-naphthylazo)-3-naphthoic acid (HHSNNA), is widely used for the direct volumetric determination of Ca^{2+} in the presence of Mg^{2+} by EDTA¹. But its potentiality as a chromogenic reagent for the trace spectrophotometric determination of heavy metal ions has not so far been explored. In the present work, a procedure is developed for the trace determination of Cu in aqueous phase. The developed method, besides having the adding advantage of being based on aqueous phase, is highly selective and in sensitivity, simplicity, precision and accuracy, it outshines the hitherto existing procedures based on aqueous phase²⁻¹⁷. Further the method can be used for the visual colorimetric determinations of Cu in poorly equipped labs.

EXPERIMENTAL

All the chemicals used were of A.R. or G.R. Grade. Stock solution of Cu^{2+} was prepared using $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and standardised¹. 0.1 M methnolic solution of HHSNNA was used. Spectrochem (AIMIL, New Delhi) with tube-cells of matched glass of path length of 0.5 inch (1.27 cm) were used for the O.D. measurements.

General Procedure

Spectrophotometric method

To an aliquot of Cu^{2+} (0 to 150 μg) in 100 ml volumetric flask, 2.0 ml of 0.1M HHSNNA solution and 50 ml of 1.0 N NaOH, were added and resulting solution was diluted to 100 ml using distilled water. Thus made-up solution was kept a side for 15 min. Blank solution was also prepared. Blue color in the sample and blank solutions, slowly vanished with the emergence of wine-red and pale yellow colors respectively. The complete disappearance of blue color in the blank solution was taken as the signal for the complete development of color in the sample solution. O.D. was measured against the blank at different wavelengths ranging from 350 nm to 700 nm. The absorbance Vs wavelength curve showed maximum absorbance at 530 nm. At 530 nm, whether this color complex of Cu obeys Beer's law or not, is assessed by measuring the absorbencies for increasingly known concentration solutions of Cu^{2+} . It is found that the linearity relationship between O.D. and Conc. of Cu^{2+} is obeyed in the region 0- 1.5 ppm of Cu. The quantitiveness of this method is tested with respect to some certified materials and synthetic mixtures

containing known concentrations of Cu. (vide Table 1). It is found the procedure is quite successful with errors of the order $\pm 0.4\%$.

Nessler's series visual colorimetric method

In poorly equipped labs where Standard Spectrophotometers are not available for conducting routine Cu analysis in samples, the present developed color has been tested with respect to its quantitiveness by adopting Nessler's Series visual colorimetric method. In this method, standard colors were prepared in series of Nessler's tubes of capacity 100 ml in the same lines of the above said method. Unknown colors were developed and compared with standard colors as described in the standard procedure¹. The method was found to be adoptable with an error of $\pm 0.8\%$.

RESULTS AND DISCUSSION

It is observed in this work that Cu^{2+} forms a highly stable wine-red complex with the reagent HHSNNA and the complex is stable even in 0.4 N to 0.8 N NaOH at which the reagent is losing its intensive blue color while the wine-red color of the Cu complex remains and this paved the way to affectively use the procedure for visual colorimetric determinations also; the difference in color intensities can be very easily viewed with naked eye.

The Cu-HHANA complex is found to have $\epsilon = 25,558 \text{ L mole}^{-1}\text{cm}^{-1}$ and Beer's law is obeyed between 0 to 1.5 μm .

Factors Effecting

The Complex formation is found to be dependent on pH, time of development of color, and temperature.

Dependence of pH

Whatever may be the initial hydrogen ion concentration, if the final solution has 0.4 to 0.8 N NaOH, the stable complex is found to be formed completely and the developed procedure is found to be successful. Above 0.8 N of NaOH, the O.D. of the complex was found to be decreasing which indicates the partial dissociation of the complex itself. In dealing with samples of un-known acidity, drops of dil. NaOH are to be added until a slight permanent precipitate of $\text{Cu}(\text{OH})_2$ is formed and thus formed precipitate is made to be just re-dissolved with dil. HCl. Then the development of color is done as described in the general procedure.

Effect of time

The optimum time needed for the formation of complex is found to be 15 minutes. In presence of large amount of foreign ions namely, NaCl, KBr, KI, NaNO_3 , or HgCl_2 , the developing time is found to be decreased from 15 min. to 5 to 10 min only. This may be attributed to de-aquation of Cu^{2+} by the salts, which facilitate the reagent, HHSNNA, to occupy the coordination sites of Cu^{2+} .

Effect of Temperature

Temperature is found to have profound say on the developing time. With the increase in temp., the developing time needed is found to be decreasing. It is found that the complete development of color occurs when the sample containing flask is kept in boiling water bath for about 2-3 minutes.

Interferences

The recovery of 0.64 ppm of Cu^{2+} was found to be quantitative with an error of $\pm 0.4\%$ in the presence of the following foreign ions (vide Table No.1):

Cations

- 300 ppm of Zn(II), As(III or V), Pb(II) & Al(III) and 200 ppm of Hg(II) are found to be not interfering.
- Sn(II) (120 ppm) Ni(II) (25 ppm), Fe(III) (500 ppm) & Mn (50 ppm) are not interfering and in fact, they are precipitated out as their hydroxides at the high pH values of the method.
- Cd(II) (500 ppm), Bi(III) (200 ppm) and Ag(I) (100 ppm) can be kept in solution without affecting the O.D. of the complex with 5 ml of 0.1 N EDTA, 10 ml of 10% KI and 10 ml of 1.0N Hypo respectively in a total final sample volume of 100 ml.

- The interference of Ca(II) (200 ppm), Ba(II) (275ppm) or Ni(II) (70 ppm) can be avoided by masking with 10 ml of 0.1N EDTA in a final volume of 100 ml.
- The interference of two and half fold excess of Co(II) can be eliminated by adding to the sample solution, 500 ppm of Fe(III) and then following the general procedure. The ferric hydroxide formed scavenges Co(II)-HHSNNA without affecting O.D. of Cu-HHSNNA complex.

Anions

- 1000 ppm of SO_3^{2-} , Mo (VI), WO_4^{2-} , CrO_4^{2-} , V(V), TeO_4^{2-} , CO_3^{2-} , IO_3^- , oxalate, phosphate and tartarate and 500 ppm of F^- , SCN^- , $\text{S}_2\text{O}_3^{2-}$ and SO_4^{2-} , are found to be not interfering.
- 50 ml of 20% of NaCl, KBr, KI and NaNO_3 in a final volume of 100 ml are not interfering, It is interesting to note here that in the presence of excess of KI, Cu^{2+} is getting reduced to Cu^+ ion, which fact is supported by the appearance of blue color when starch is added to the solution. But no trace of the characteristic white precipitate of cuprous iodide is seen because the excess of KI solubilizes cuprous ion in solutions especially at such trace amounts of Cu. To this mixture, if the reagent, HHSNNA, is added and the alkali conditions are maintained as described in the general procedure, wine-red color is developed and O.D. maintains intact. This indicates that the aerial oxidation of cuprous iodide to cupric iodide and subsequent Cu-HHSNNA complex formation, are quantitative.

Table-1: Determination of Copper in Various Samples Using the Spectrophotometric Method Developed in this Work

S. No	Composition	Copper Content		Relative Mean Deviation
		Certified/fed	Found*	
1	Brass	60.99%	60.45%	0.06%
2	Gun Metal	84.95%	85.05%	0.10%
3	Steel	0.47%	0.46%	0.08%
4.	Synthetic Mixtures: a. Cu:Fe (0.5:99.5) b. Cu:Zn:Sn:Pb:Fe (60:35:2:2:1)	0.50% 60.00%	0.49% 60.20%	0.11% 0.18%
	c. Binary and ternary mixtures of ions having Cu^{2+} (at 0.64 ppm) as one component, were prepared as noted under the INTERFERENCES and analyzed for Cu^{2+} . The recovery of Cu^{2+} was found to be quantitative with an error of $\pm 0.4\%$			
5	Seawater: a. Collected at Bapatla, A.P., on the east costal line of India in the Bay of Bengal b. Typical Synthetic Sea Water having Composition(in grams per Liter): Na:K:Ca:Mg:Cl: SO_4^{2-} , CO_3^{2-} (10.7:0.39:0.42:1.34:19.3:2.69:0.073)	10.00 ppm 15.00 ppm 20.00 ppm 10.00 ppm 15.00 ppm 20.00 ppm	9.95 ppm 14.96 ppm 19.74 ppm 9.72 ppm 15.04 ppm 20.32 ppm	0.22% 0.18% 0.12% 0.72% 0.68% 0.51%

* Average value of seven determinations

Composition of the Complex

The Job's continuous variation and mole-ratio methods indicate 1:1 stoichiometry for Cu -HHSNNA complex.

Applications

1. Determination of Cu in Brass and Steel

Brass or Steel of certified composition was brought into solution as described in the standard procedure by using Conc. HNO_3 and Conc. HCl^1 . Solutions were analyzed for Cu^{2+} as described in the general

procedure. To impart more general nature to the developed procedure in this work, synthetic mixtures of Cu:Zn:Sn:Pb:Fe and Fe:Cu were prepared to simulate Brass and Steel and analyzed for Cu.

Recovery experiments were also done in the presence of some foreign ions having the similar chemical nature of Cu. Results are present in the Table No. 1. The recovery was found to be quantitative.

2. Sea Water

Suitable amounts of Cu^{2+} were fed to the sea water samples collected at Bapatla on the East Coastal line of India in the Bay of Bengal. The recovery of Cu^{2+} was made as described in the general procedure except that 10 ml of 0.1 N EDTA was to be added to make innocuous the interfering foreign ions.

A synthetic typical mixture of ions was also prepared to simulate the general sea water and recovery experiments for Cu^{2+} were conducted. The results are presented in Table No. 1. The recovery was found to be quantitative.

CONCLUSIONS

A simple spectrophotometric method has been developed for the trace determination of copper in aqueous phase exploring the complex formation between Cu^{2+} and Patton and Reeder' indicator. The procedure is highly selective and fairly sensitive. The adoptability of the procedure has been tested with some certified materials and synthetic mixtures.

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