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Spectrophotometric determination of Cu (II) and Ni (II) using 4-hydroxybenzaldehyde thiosemicarbazone

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Abstract: The reagent 4-hydroxybenzaldehydethiosemicarbazone (**4-HBTS**) gives green coloration with Cu (II) as well as Ni (II) in acidic medium. This observation is used for the simultaneous determination of both the metal ions using second order derivative spectrophotometry. Optimum conditions were established for this determination. Job's and mole-ratio methods are used for the determination of composition of the metal complexes. Determination of the metal ions was carried out in BAS alloys, and NTP ballbearings.

Introduction

Thiosemicarbazones are known as good analytical reagents for the3determination of metalions[1-5].It is easy to synthesize thiosemicarbazones and they remain stable for a long time. Further they form stable complexes with many metalions[6-10]. Many reagents are not available for the simultaneous determination of Cu (II) and Ni (II) using derivative spectrophotometry. However, Survey of the literature revealed that diacetylmonoximethiosemicarbazone[11,12]. Diacetylmonoxime-4-phenyl-3-thiosemicarbazone[13,14] and1-phenyl-1,2-propanedione-2 oximethio-semicarba - zone are used for the determination of Cu (II) and Ni (II) using zero order spectrophotometry. Derivative spectrophotometry [15]is a very useful technique because it decreases the interference of foreign ions and may be advantageously used for the simultaneous determination of metalions having overlapping spectra. In this research article we describe our results on the simultaneous determination of Cu (II) and Ni (II) in acidic medium using second order derivative spectrophotometry.

Experimental

(i) Preparation of 4- HBTS

The reagent was prepared by simple condensation of 1 mole of 4-hydroxy-benzaldehyde with 1-mole of thiosemicarbazide in a clean 250ml round bottomed flask 4-hydroxybenzaldeyde was dissolved in 100ml of methanol and thiosemicarbazide was dissolved in hot water. The solutions were mixed and refluxed for two hours. On cooling brown colored product was formed which was collected by filtration. It was recrystalized using methanol and dried in vacuum. The yield was 70% by weight. and the M.P. 207-209^{0}C. The structure of the compound was established using **IR** spectra (Fig.1).

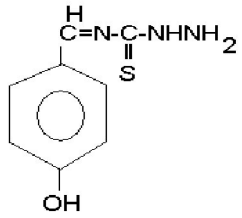

Fig. 1

(ii) Solutions preparation

Buffer solutions are prepared using HCl, CH_3COOH and NaOAC in acidic medium and NH_4OH, NH_4Cl in basic medium.

(iii) Preparation of metal solutions and reagent solution

The standard Cu (II) solution and Ni (II) solutions were prepared using analytical reagent grade samples. Appropriate quantity of 4-hydroxy - benzaldehydethiosemicarbazone is dissolved in DMF for making 0.1M reagent solution.

Zero order spectrums of copper and nickel

A Solution containing 1ml $1x10^{-3}$ M copper sulphate and 1ml of $1x10^{-3}$M nickel sulphate are taken in a 25ml volumetric flask. 10ml of a buffer solution of p^H 6 is added. The contents of the flask are made up to the mark with distilled water. The solution is shaken well for uniform concentration. A blank solution is prepared on the same lines but without containing the metal ions.

Simultaneous determination of Cu (II) and Ni (II) with second order derivative spectrophotometry

An aliquot of the solution containing $3x10^{-4}$M Cu (II) and $3x10^{-4}$M Ni (II) is taken in a 25ml volumetric flask. 10ml of buffer solution (P^H6) is added and 1ml $2x10^{-2}$M reagent is added. The contents of the flask are made up to the mark with distilled water. The solution is shaken well for homogeneity. A blank solution is prepared on similar lines without containing the metal ions.

Results and discussion

Studies carried out with various metal ions with the present reagent revealed that 4-HBTS gives a green colored solution with Cu (II) and pale green colored solution with Ni (II). The authors have carried out the effect of P^H on the color reaction in presence of Cu (II) as well as Ni (II). The color development is maximum in the P^H range5 – 6 with both the metal ions taken individually. In view of this a solution of P^H 6 is fixed for further investigations.

Studies relating to the effect of metal ion concentration, reagent concentration, time, organic solvent are carried out to establish the optimum conditions for maximum color development. The order of addition of various components of the reaction system has no influence on the color reaction. It is also observed that a minimum of 10 times excess of the reagent is essential for the complete formation of color either with individual metal ion (or) an admixture. The color is quite stable for one hour; hence the absorbance measurements can be made from various solutions even after one hour.

Job's continuous variation method and mole ratio method are performed to determine the composition and stability constants of the complexes. Both the metal ions form 1:2 (M:L) complexes with the reagent. The stability constants are $5.93x\ 10^{10}$ and $2.76x10^{11}$ for copper and nickel respectively.

Zero order spectrums

The zero order spectra of Cu (II) (Curve a, Fig 2) and Ni (II) with the reagent (Curve b, Fig 2) against the reagent blank are recorded in the wavelength range 300 to 700 nm and are shown in Fig. 2. the spectrum of the reagent is also recorded under the same conditions using buffer blank (curve c, Fig.2) An analysis of the figure reveals that the reagent shows λ_{max} at 314nm and Cu and Ni complexes showed maximum absorbance at 355 and 362 nm respectively. An attempt to make simultaneous determination of Cu (II) and Ni (II) did not produce fruitful results. It is because of the small difference in the λmax values (7 nm only). The zero order spectrum of the mixture of Cu(II) and Ni(II) is recorded against the reagent blank and is shown in fig.2 (curve d).The resolution of Cu (II) and Ni(II) is not possible and the resolution becomes more difficult as the concentration of metal ions are increased.

Second order derivative spectrophotometry

The spectrum for a solution consisting of Cu (II) and Ni (II) as well as the reagent in acidic medium of P^H 6 is recorded against the reagent blank and shown in Fig.2 (curve e). An examination of the figure suggests that there are two peaks corresponding to the two metal ions at 408 and 434 nm respectively. Individual second order derivative spectra are recorded for both the metal ions under the same conditions. The results revealed that the peak and valley at 408 and 420nm correspond to Ni and 434 (peak), 446 (valley) correspond to Cu (II).

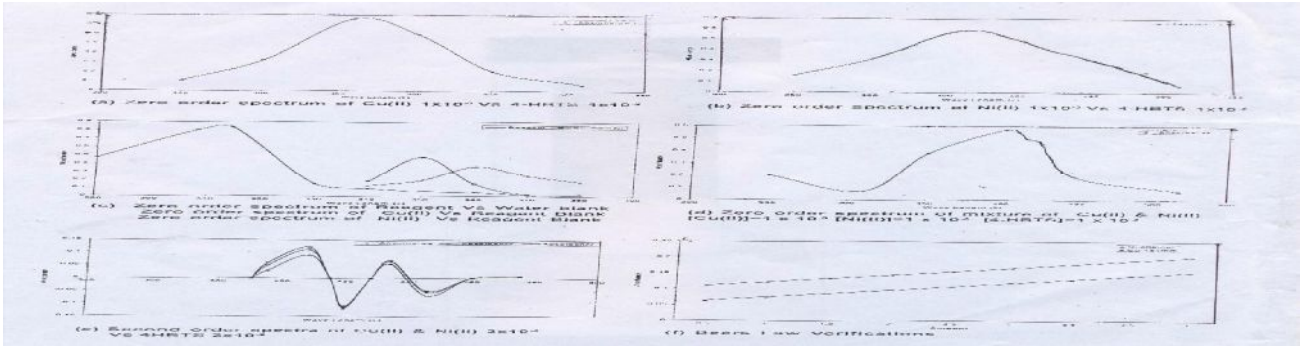

Fig. 2.

Experiments pertaining to the effect of copper concentration and nickel concentration on respective peak and valley amplitudes are carried out. The simultaneous determination of the metal ions was carried out using zero crossing measurement method[16,17]. Salinas and coworkers adopted the same method for simultaneous determination of tetracyclines[18]. Linear plots were obtained in both the cases indicating the suitability of second order derivative spectrophotometry for simultaneous determination of Cu(II) and Ni(II) in acid medium (Fig.2, Curve f). Graphs are also plotted taking the sum of peak and valley amplitudes for both the metal ions individually. Straight line plots are obtained even in this case.

Copper and nickel are bivalent transition metal ions and show similar chemical behavior. As a result, the simultaneous determination poses problems. Prior separation before determination is usually carried out in many cases .In the present method no prior separation is required. The method is simple, rapid, selective and applicable over a wide range of concentrations.

Interference

Interference of various metal ions usually associated with copper and nickel and various anions is investigated. The relevant data is shown in Table 1. It is seen from the table that Mn (II) and Sn (II) seriously interfere while the other metals can be tolerated at least to certain extent. Most of the anions do not show much influence.

Table 1 : Interference of foreign ions in the determination of 1.27µg/ml of Cu (II) and 1.17µg/ml of Ni (II).

Ion added	Tolerance limit (µg/ml)		Ion added	Tolerance limit (µg/ml)	
	Copper	Nickel		Copper	Nickel
Iodate	**761**	**560**	Mn (II)	**12**	**8**
Tartarate	**1104**	**883**	Cd (II)	**130**	**107**
Bromide	**640**	**620**	Al (II)	**25**	**60**
Chloride	**425**	**420**	Mo (VI)	**38**	**28**
Thiocyanate	**695**	**465**	V (V)	**46**	**32**
Nitrate	**446**	**400**	Sn (II)	**12**	**28**

Table 2 : Analysis of alloys using the present method

Alloys	Cerified Value%		Amount Found		Standard Deviation	
	Cu	Ni	Cu	Ni	Cu	Ni
BAS 106	41	1.93	425	1.89	-3.4	-2
NTP ball bearing material	45	10	456	10.04	-1.1	0.5

***Average of five determination**

Conclusions

Simultaneous determination of Cu (II) and Ni (II) in acidic medium using second order derivative spectrophotometry with 4-HBTS as a reagent is carried out. Both metal ions can be determined in the ranges – Cu 0.381 to 2.48µg / ml and Ni 0.35 to 2.8µg /ml using this method. The compositions and stability constants of the complexes are 1:2 (for both) $5.93x10^{10}$ (Cu) and $2.76x10^{11}$ (Ni). The method has been applied for the determination of copper and nickel in alloys.

References

1. K.P.Satheesh, V.SuryanarayanaRao, K.B. Chandrasekhar, J. Indian Coun.Chemists, 21(1), 51 (2004).
2. Smitha Nigam, Patel, M.H. and Arabinda Ray, Synth. React. Inorg. Met-Org. Chem., 28(7), 1187 (1998).
3. K.H.Reddy, P.Sambasivareddy and P.Ravindra Babu,J. Inorg. Biochem., 77,169 (1999).
4. N.C. Kasuga, K.Sekino, C.Koumo, N.S.Motoki and K.Nomiya, J. Inorg. Biochem., 84, 55 (2001).
5. J. Garcia-Tojal, J. Luis Pizarro, A.G.Roci, Maria Ugalde, A.Antonia, Jaun Luis serra, MariIsbel, Journal of Inorganic Biochemistry, 86, 627 (2001).
6. El Mostapha Jouad, Amedeerio, Magali Allain, M.A.Khan and G.M. Bouet, Polyhedron, 20, 67 (2001).
7. M.Rmesh,K.B.Chandrasekhar and K.H.Reddy, Indian J.Chem.Soc., 39, 1337 (2000).
8. M.Jayaramudu and K.H.Reddy.J. Chem. Soc., 38, 1173 (1999) .
9. K.B.Chandrasekhar and K.H.Reddy, Indian J. Chem., 40 A ,727 (2000).
10. K.B.Chandrasekhar and K.H.Reddy, J.Indian chem.. Soc, 78 , 340 (2001).
11. D.Mallikarjuna Rao , K.Hussain Reddy , D. Venkat Reddy , Talanta 38,1047(1991).
12. C.S.Devaragudi , K.Hussain Reddy , Talanta 44,1973 (1997).
13. K.Hussain Reddy , N.B.L.Prasad , T.S.Reddy , Talanta 59,425 (2003).
14. J.M Canopavon , A.Garcia de Torres , F. Pino , Ann. Quim . 74, 1047 (1978).
15. K.B.Chandrasekhar, K. H.Reddy and T.S.Reddy, J. Indian Chem.Soc.,80, 1176 (2003).

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