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SIMULTANEOUS DETERMINATION OF Cd(II) AND Cu(II) AS (S)-5-METHOXY-2-[[(4-METHOXY-3, 5-DIMETHYL-2-PYRIDINYLE-METHYLE] SULFINYLE]-1H-BENZIMIDAZOLE USING DERIVATIVE SPECTROPHOTOMETRY

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ABSTRACT

The reagent (S)-5-methoxy-2-[[(4-methoxy-3, 5-dimethyl-2-pyridinyle-methyle] sulfinyle]-1H-benzimidazole gives yellow coloration with Cd (II) as well as Cu (II) in acidic medium. This observation is used for the simultaneous determination of both the metal ions using Zero and 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 ball bearings.

KEY WORDS: Copper, cadmium, ESMPZL, Derivative Spectrophotometry, BAS alloys, NTP ball bearings.

INTRODUCTION

The determination of heavy metals in environmental, biological and food samples has drawn significant attention due to the toxic and nutritional effects of these elements or their compounds. [1,2] Copper is widely distributed in nature and is an essential trace element for humans. [2,3] Copper functions as a cofactor and is required for structural and catalytic properties of a variety of important enzymes, including cytochrome oxidase, tyrosinase, p-hydroxyphenyl pyruvate hydrolase and dopamine β hydroxylase [4]. Nonetheless, Cu shows some toxicological effects. Food, beverages and drinking water are potential sources of excess exposure. Daily intake of Cu in adults varies between 0.9 and 2.2 mg. The amount of Cu ingested is relatively low and most humans are able to control excess amounts of Cu in the body by either decreased absorption or increased excretion [5]. Exposure to elevated concentrations of Cu primarily affects the liver and is typically manifested by the development of liver cirrhosis, episodes of hemolysis and damage to renal tubules, brain and other organs. [2, 6] Cadmium can be accumulated in biological systems, becoming a potential contaminant along the alimentary chain. This element has harmful effects on human health, affecting several organ systems, such as nervous, gastrointestinal, reproductive and skeletal and biochemical activities [2, 7, 8]. The need for regular monitoring of trace elements in materials has led to an increasing demand for suitably sensitive and selective analytical methods [9, 10]. Recently adsorptive stripping voltammetry has been employed as a powerful technique for determination of ultratrace levels of metals. This method is an extremely sensitive technique that offers low detection limits and is based on adsorptive accumulation of metal ions and suitable complexing agent on the electrode surface while potential is scanned in the negative direction [11, 12]. Several organic compounds such as 1-(2-pyridylazo)-2,7-dihydroxynaphthalene, [13] 8-quinolinol, [14] carbamoyl phosphonic acid, [15] xylenol orange [16] and thymolphthalexone[17] have been used as complexing agent for the simultaneous voltammetric determination of copper and cadmium. Mohammad Bagher Gholivand, Alireza Pourhossein, Mohsen Shahlaei et al [18] proposed a Simultaneous determination of Cd and Cu by using environmental water and tea samples by adsorptive stripping voltammetry to describe a sensitive AdCSV procedure by using dithiosalicylic acid as acomplexing agent [18]. This ligand forms a complex with both elements and can be used as an accumulating agent free from interference. This method makes use of a well-defined differential pulse voltammetric reduction peak resulting from stripping of the accumulated Cu and Cd-ligand complex on the mercury drop in the medium. The peak currents were proportional to concentration in mg mL^{-1} ranges.

Here in we report the simultaneous second order derivative spectrophotometric determination of cadmium (II) and copper (II) using (S)-5-methoxy-2-[[(4-methoxy-3, 5-dimethyl-2-pyridinyle-methyle] sulfinyle]-1H-benzimidazole [ESMPZL]. The proposed simultaneous method involves the use of peak-to-base line measurement technique.

Experimental

(i) Preparation of ESMPZL

Esomeprazole is 5-metoxy-2-[[(4-methoxy-3, 5-dimethyl-2-pyridinyl] methyl] sulfinyl]-1H-benzimidazole. It is white crystalline powder freely soluble in water and its molecular formula is $C_{17}H_{19}N_3O_3S$. (M.Wt:345.11). The structure of esomeprazole is given in Fig. 1.

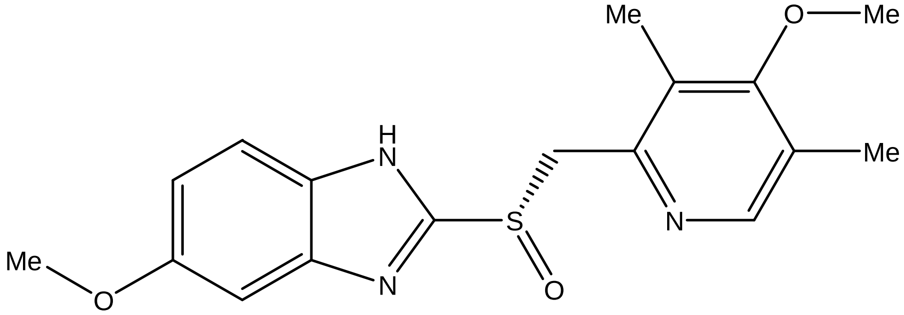
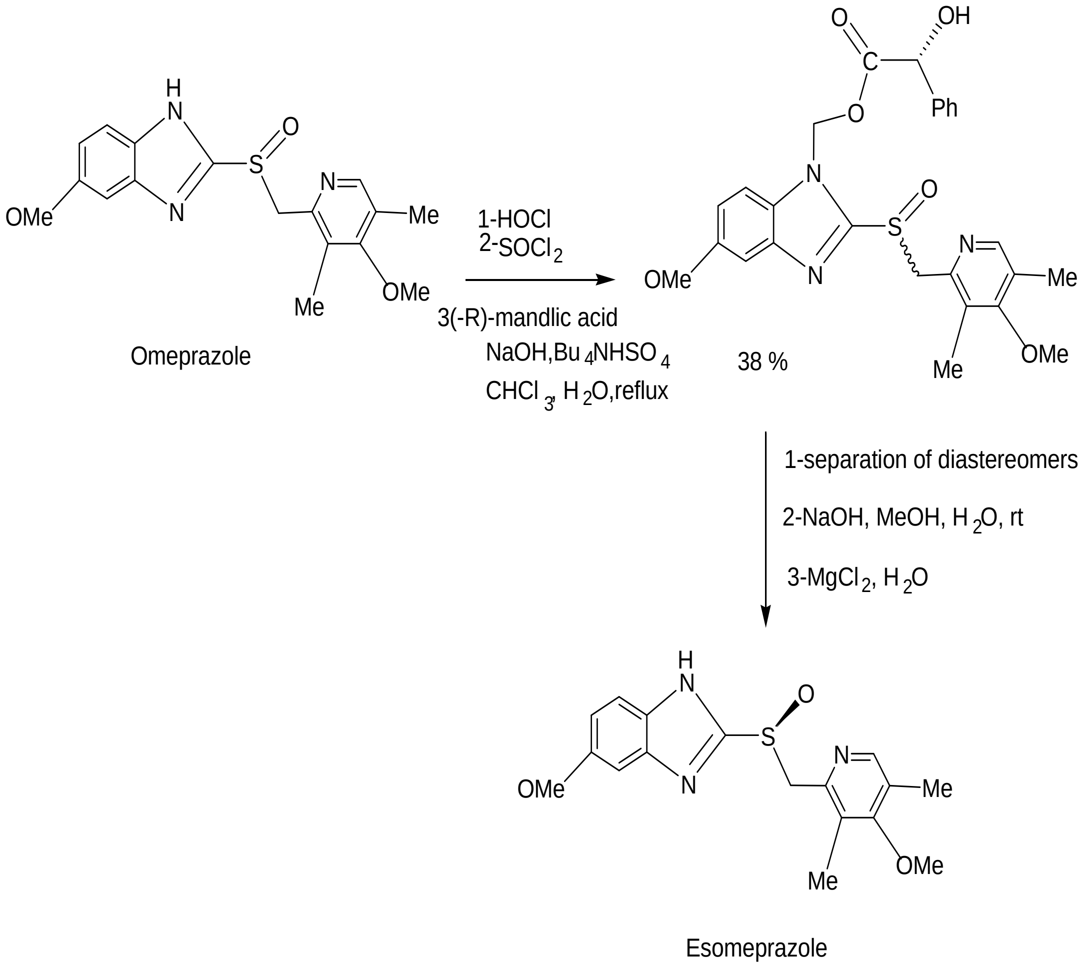


Fig. 1 (S)-5-methoxy-2-[[(4-methoxy-3, 5-dimethyl-2-pyridinyl)-methyl]sulfinyl]-1H benzimidazole (ESOMEPRAZOLE)

Synthesis and characterization of esomeprazole:

Conversion of omeprazole to esomeprazole:



Esomeprazole was characterized by IR, ^{1}H-NMR and Mass spectral data.

IR (KBr) ν_{max}: 3346, 3168, 2961, 2928, 2683, 1657, 1597, 1449, 1255, 1218,1092, 876, 710 cm^{-1}

^{1}H NMR (DMSO-d_6, 500 MHz) :δ 2.20 (s, 3H, CH_3), 2.22 (s, 3H, CH_3), 3.73 (s, 3H, OCH_3), 3.88 (s, 3H, OCH_3), 4.60 (d, 1H), 4.77(d, 1H), 6.97, 6.99 (m, 2H, Ar-H), 7.65 (m, 1H, Ar-H), 8.25 (s, 1H, Pyridine ring), 9.57 (s, 1H, NH) ppm.

MS m/z: found 345.11 [M^+]; calcd. 345. Anal $C_{17}H_{19}N_3O_3S$.

(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 reagentsolution

The standard Cd (II) and Cu (II) solutions were prepared using analytical reagent grade samples. Appropriate quantity of (S)-5-methoxy-2-[[(4-methoxy-3, 5-dimethyl-2-pyridinyle-methyle] sulfinyle]-1H-benzimidazole dissolved in DMF for making 0.1M reagent solution.

Zero order spectra of cadmium and copper

A Solution containing 1ml $1x10^{-3}$ M cadmium sulphate and 1ml of $1x10^{-3}$ M copper sulphate are taken in a 25ml volumetric flask. 10ml of a buffer solution of pH 6.5 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 Cd (II) and Cu(II) with second order derivative Spectrophotometry.

An aliquot of the solution containing $3x10^{-4}$M Cd (II) and $3x10^{-4}$M Cu (II) is taken in a 25ml Volumetric flask. 10ml of buffer solution (pH 6.5) 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 ESMPZL gives a yellow colored solution with Cd (II) and yellow colored solution with Cu (II). The authors have carried out the effect of pH on the color reaction in presence of Cd (II) as well as Cu (II). The color development is maximum in the pH range 5 – 6 with both the metal ions taken individually. In view of this a solution of pH 6.5 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 5.89x 10^{10} and 2.74x10^{11} for cadmium and copper respectively.

As mentioned above, series of solutions are prepared containing varying concentrations of the two metal ions. Blank solutions are also prepared on the same lines, but without containing metal ions. For each of the solution, the second order derivative spectrum is recorded. These are shown in figures 5. Graphs are plotted between the concentration of Cd (II) and peak amplitude as well as valley amplitude. Similar linear plots are obtained even in the case of copper when graphs are plotted between concentration and peak or valley amplitude.

It may be mentioned here that straight line plots are obtained even with the sum of peak and valley amplitudes. These linear plots are shown in figs. 6 and 7 for Cd (II) and Cu (II) separately.

Thus the second order derivative spectrophotometric method is very useful to make simultaneous determination of Cd(II) and Cu(II) in microgram quantities. Greater sensitivities can be achieved by using the sum of the amplitudes of peak and valley for drawing calibration plots. Cd(II) can be determined in the range 2.130 –12.769 µg/ml and Cu(II) can be determined in the range 1.269 - 7.629 µg/ml using this method. No prior separation of the two metals is required in this determination. This method can be used for the analysis of alloys or simulated mixtures containing both the metal ions.

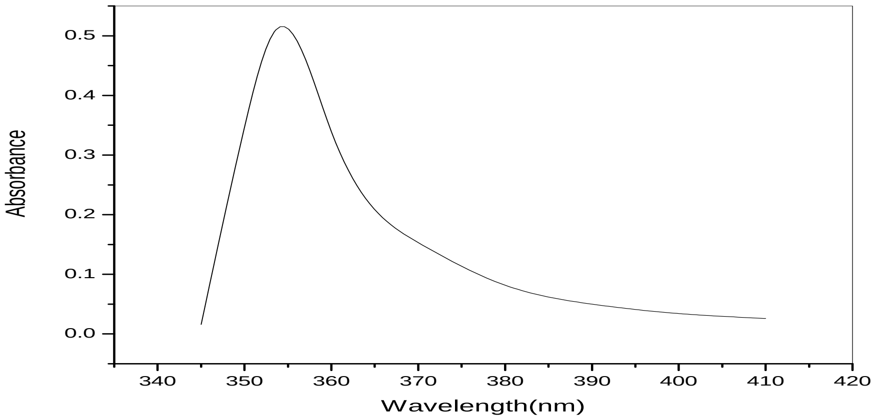


Fig: 2. Zero order spectrum of Cd(II) in presence of ESMPZL

[Cd(II)] = 4 x 10^{-5}M;

[ESMPZL] = 8 x 10^{-4}M;

pH = 6.5

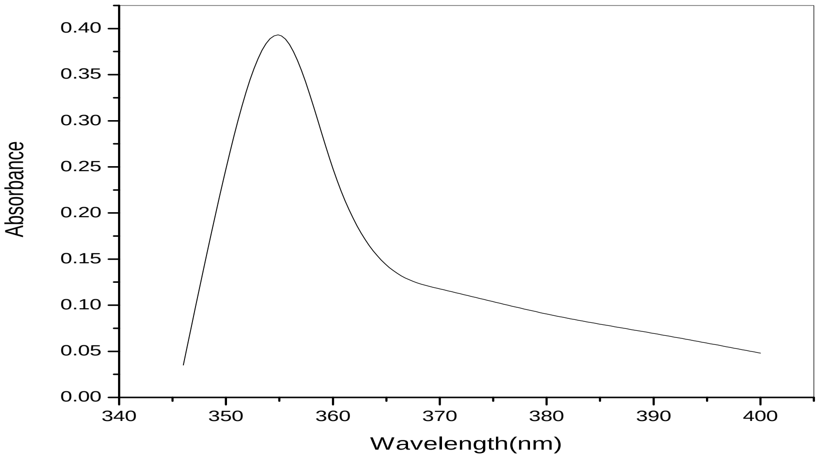


Fig: 3 Zero order spectrum of Cu(II) in presence of ESMPZL

[Cu(II)] = 4 x 10^{-5}M;

[ESMPZL] = 8 x 10^{-4}M ;

pH = 6.5

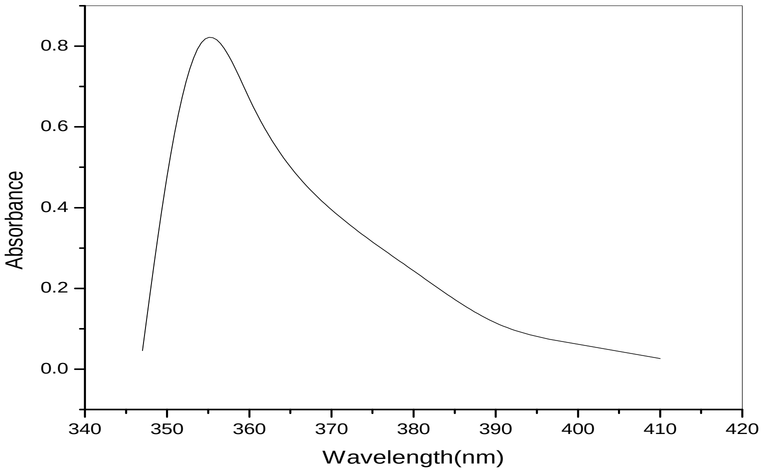


Fig: 4 Zero order spectrum of Cd(II) + Cu(II) in the presence of ESMPZL

[Cd(II)] = 4×10^{-5} M, [Cu(II)] = 4×10^{-5}M;

[ESMPZL] = 8×10^{-4}M;

pH = 6.5

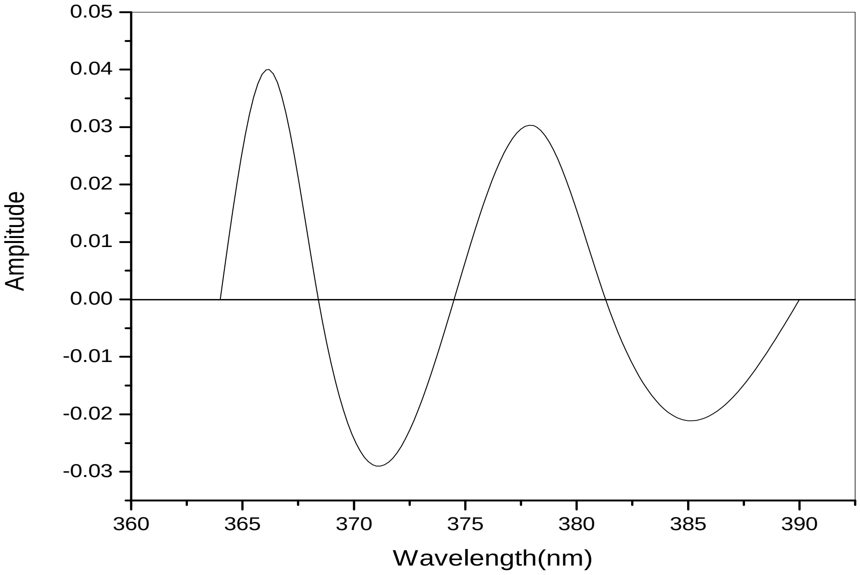


Fig: 5 Typical second order spectrum of Cd(II) + Cu(II) in the presence of ESMPZI

[Cd(II)] = 4×10^{-5} M, [Cu (II)] = 4×10^{-5}M;

[ESMPZL] = 8×10^{-4}M; pH = 6.5

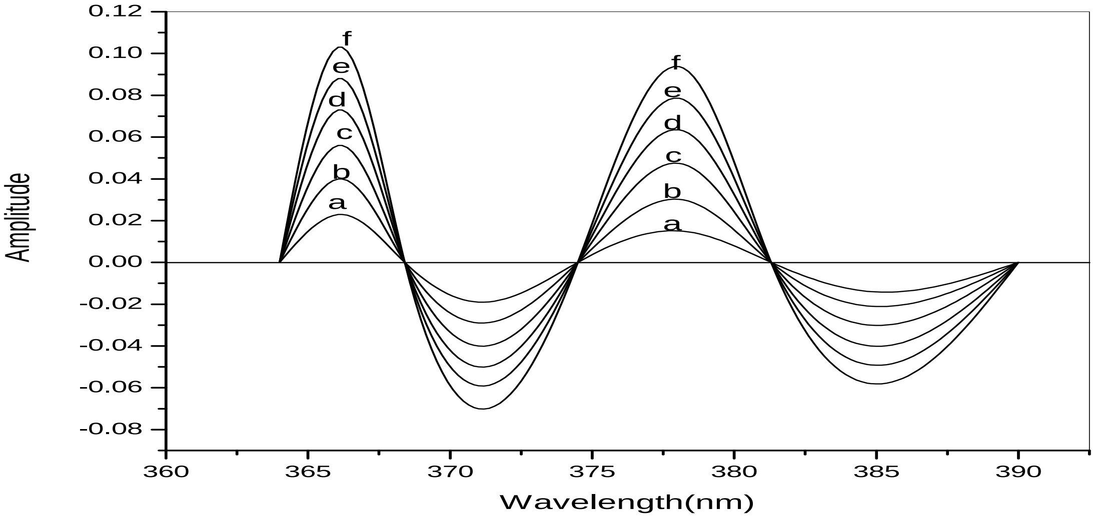


Fig: 6 Second order spectrum of Cd(II) + Cu(II) in the presence

of ESMPZL

[Cd(II)] = 4×10^{-5} M, [Cu(II)] = 4×10^{-5}M;

[ESMPZL] = 8×10^{-4}M; pH = 6.5

a) 0.5 ml of Cd(II) and Cu(II) each

b) 1.0 ml ,,

c) 1.5 ml ,,

d) 2.0 ml ,,

e) 2.5 ml ,,

f) 3.0 ml ,,

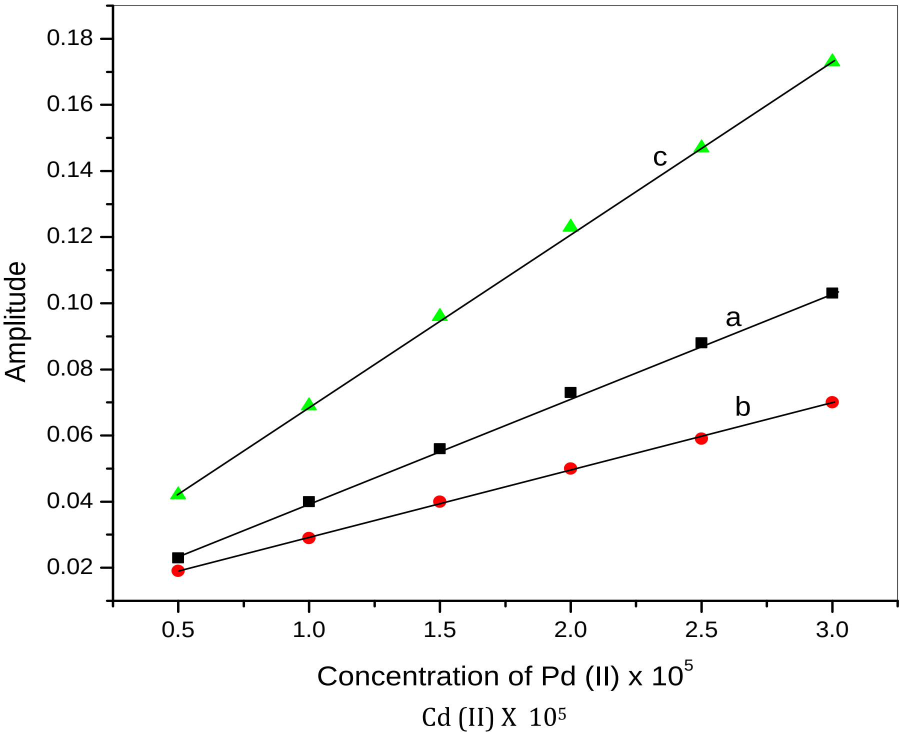


Fig: 7 Second derivative amplitude Vs Concentration of Cd(II)
pH = 6.5, a = Peak ; b = Valley ; c = Peak + Valley

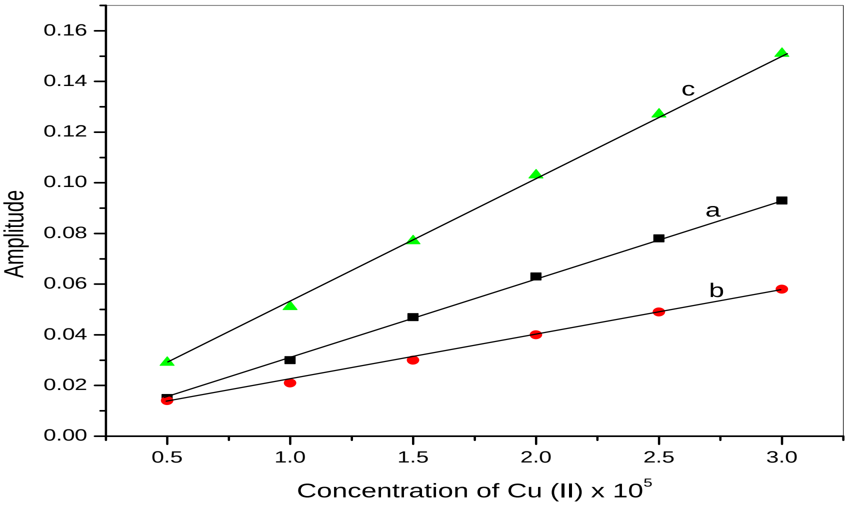


Fig: 8 Second derivative amplitude Vs Concentration of Cu(II)
pH = 6.5 , a = Peak ; b = Valley ; c = Peak + Valley

INTERFERENCE

Interference of various metal ions usually associated with cadmium and copper and various anions is investigated. The relevant data is shown in Table 1. It is seen from the table that Co (II) and Ni (II) seriously interfere while the other metals can be tolerated at least to certain extent. Most of the anion does 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)	
	Cadmium	Copper		Cadmium	Copper
Iodate	760	561	Co (II)	12	8
Tartarate	1103	884	V (V)	131	106
Bromide	639	621	Mo (VI)	25	60
Chloride	425	420	Al (III)	38	28
Thiocyanate	696	466	Cr (V)	46	32
Nitrate	445	401	Ni (II)	12	28

Table 2: Analysis of alloys using the present method

Alloys	Cerified Value%		Amount Found		Standard Deviation	
	Cd	Cu	Cd	Cu	Cd	Cu
BAS106	42	1.92	424	1.91	-3.3	-2
NTP ball bearing Material	46	10	457	10.03	-1.1	0.5

***Average of five determination**

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