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Comparative study of Copper (II) using 4-Hydroxy 3, 5 dimethoxy benzaldehyde 4-hydroxy benzoyl hydrazone and Cinnamaldehyde 4-hydroxy benzoylhydrazone in presence of micellar medium by Spectrophotometry

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ABSTRACT

Two simple, sensitive, rapid and selective spectrophotometric methods have been developed for the determination of Copper (II) by using newly synthesized reagents 4-Hydroxy 3, 5 dimethoxy benzaldehyde-4-hydroxybenzoylhydrazone (HDMBHBH) and Cinnamaldehyde 4-hydroxy benzoylhydrazone (CMHBH) in presence of neutral surfactant TritonX-100 (5%) (micellar medium). Copper (II) forms a yellow coloured water-soluble complex with HDMBHBH and CMHBH in the pH range 9.0-12.0. The Cu (II)-HDMBHBH complex shows maximum absorbance at λ_{\max} 383 nm in the pH range 8.0-9.0 and Cu (II)-CMHBH shows at λ_{\max} 375 nm in the pH range 8.0-9.0. At these wavelengths (λ_{\max}), the complex shows maximum absorbance while the reagent blanks shows negligible absorbance. Hence, analytical studies were carried out at λ_{\max} 383 nm at pH 9.0 for HDMBHBH and 375 nm at pH 9.0 for CMHBH against reagent blanks. Beer's law is obeyed in the range 0.063-0.635 $\mu\text{g ml}^{-1}$ and the optimum concentration range from ringbom plot is 0.127-0.571 $\mu\text{g/ml}$ for Cu (II)-HDMBHBH, and 0.158-1.588 $\mu\text{g ml}^{-1}$, 0.317-1.429 for Cu (II)-CMHBH. The molar absorptivity and Sandell's sensitivity for the coloured solution were found to be $3.41 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ and $0.0018 \text{ } \mu\text{g. cm}^{-2}$ for HDMBHBH, $2.77 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$, and $0.00229 \text{ } \mu\text{g. cm}^{-2}$ for CMHBH respectively. The interference effects of various diverse ions have been studied. Cu (II) forms 1:1 complex with HDMBHBH and CMHBH stoichiometry with stability constant 14.12×10^6 for HDMBHBH and 10.10×10^6 for CMHBH. The standard deviation in the determination of 0.317 $\mu\text{g ml}^{-1}$ of Copper (II) is 0.006 for HDMBHBH and 0.004 for CMHBH in the determination of 0.317 $\mu\text{g/ml}$ of Copper (II). The Relative standard deviation is 4.05% for HDMBHBH and 4.7 % for CMHBH. First and second order derivative spectroscopic methods was developed at λ_{\max} 405 nm and 433 nm for HDMBHBH and at 410 nm and 440 nm for CMHBH, for the determination of Copper (II) which is more sensitive than the zero order method. The developed method has been employed for the determination of Copper (II) in Beer, Wine, Biological materials and in alloy samples. The results are in good agreement with the certified values.

Keywords: Comparative study of Copper (II), Spectrophotometry, Beer, Wine, Biological materials, alloy samples, micellar medium, Triton x-100 (5%), HDMBHBH, CMHBH.

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INTRODUCTION

The potential analytical applications of hydrazones and its derivatives have been reviewed by Singh et al [1]. Hydrazones are important class of known analytical reagents. Due to analytical potentialities of hydrazones herein we report the synthesis, characterization and analytical properties of reagents 4-Hdroxy 3, 5 dimethoxybenzaldehyde -4-hydroxybenzoylhydrazone (HDMBHBH) and Cinnamaldehyde 4-hydroxy benzoylhydrazone (CMHBH). As the light of the above herein we report the direct and derivative spectrophotometric methods for determination of Copper (II) using HDMBHBH and CMHBH) in Beer, Wine, Biological materials and in alloy samples. Derivative spectrophotometry is a very useful approach for determining the concentration of single component in mixtures with overlapping spectra as it may eliminate interferences.

Copper is essential for all plants and animals. It is an essential constituent of about thirty enzymes and glycoproteins and is required for the synthesis of hemoglobin and for some biological processes. It also promotes iron absorption from the gastrointestinal system, is involved in the transport of iron from tissues in to plasma, helps to maintain myelin in the nervous system, and is important in the formation of bone and brain tissues. A deficiency of copper causes diseases such as anaemia. Though Copper is an essential element it becomes hazardous when present in excess. Excess of copper causes jaundice and Wilson disease. Excess of copper in water is not only harmful to human beings, but also interferes with the self purification of bulk water and exerts an adverse effect on the microbiological treatment of waste water. Too much Copper in water has also been found to damage marine life.

For the determination of Copper (II), at microgram quantities, a number of hydrazone derivatives and several analytical techniques such as AAS, ICP-AES, ICP, X-Ray fluorescence spectroscopy and UV-visible spectrophotometry were employed. Among them, spectrophotometric methods are preferred because they are cheaper and easy to handle.

Hydrazones and its derivatives reacts with many metal ions forming colour complexes and act as chelating agents. In general the technique of solvent extraction is widely used in the spectrophotometric determination of metal ions. However, organic solvents such as benzene and chloroform are often carcinogenic, toxic and cause environmental pollution. It is significant to develop a method which does not involve solvent extraction. A micellar solution has the ability to enhance the stability of metal complex and has been utilized as a medium for the spectrophotometric determination of the metal chelate [2-5].

MATERIALS AND METHODS

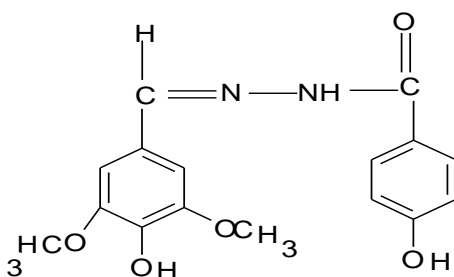
The absorbance and pH measurements were made on a Shimadzu UV-visible spectrophotometer (Model UV-160A) fitted with 1.0 cm Quartz cells and Elico digital pH meter (Model LI 120) respectively. Suitable settings for derivative were as follows. The spectral band length was 5 nm, the wavelength accuracy was 0.5 nm with automatic wavelength correction

and the recorder was a computer controlled thermal graphic printer with a cathode ray tube and one degree of freedom in the wavelength range 300 – 800 nm.

The reagents (HDMBHBH and CMHBH) were prepared by the Sah and Daniels [6] procedure

Preparation of HDMBHBH

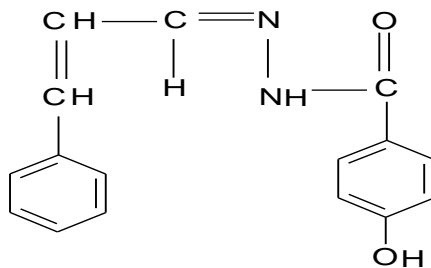
1.82 g of 4-hydroxy 3, 5 dimethoxy benzaldehyde (I) and 1.52 g of 4-Hydroxy benzhydrazide (II) were dissolved in sufficient volume of Carbinol and the mixture is refluxed for 4 hours. The contents were allowed to cool and the product was separated by filtration. A crude sample (yield 80%) is obtained ($C_{16}H_{16}N_2O_5$). The resultant product is recrystallised twice from hot methanol. Pure light greenish coloured crystals of 4-Hydroxy 3, 5 domethoxy benzaldehyde 4-hydroxy benzoylhydrazone (HDMBHBH) (III) (m.p. 292-294°C.) was obtained.



Structure of HDMBHBH

Preparation of CMHBH

1.32 ml of Cinnamaldehyde (I) and 1.52 g of 4-Hydroxy benzhydrazide (II) were dissolved in sufficient volume of methanol and the mixture is refluxed for 4 hours. The contents are allowed to cool and the product was separated by filtration. A crude sample (yield 80%) is obtained ($C_{16}H_{13}O_2N_2$). The resultant product is recrystallised twice from hot methanol. A pure light yellowish crystal of Cinnamaldehyde-4-hydroxy benzoylhydrazone (CMHBH) (III) (m.p. 242-244°C.) was obtained.



Structure of CMHBH

Table: 1.Spectral data of Reagents (HDMBHBH and CMHBH)

Assignments	IR Spectral bands(cm^{-1}) of		Assignments	The ^1H NMR (300 MHz) spectrum of in DMSO solvent	
	HDMBHBH	CMHBH		HDMBHBH	CMHBH
ν NH stretching	3529	3452	NH	11.54 (S, 1H)	δ 11.57(S,1H)
ν OH stretching	3075	3218-3092	OH (phenolic)	10.13 (S, 1H)	10.74 (S, 1H)
$\nu > \text{C}=\text{O}$ stretching	1642	1620	N=C-H	8.1 (S, 1H)	8.19-8.22 (S, 1H)
ν C=N stretching	1609	1577	ArH (pyridine ring)	7.77 – 7.80 (D, 2H)	7.77 – 7.80 (D,2H)
			ArH (aldehydic)	6.84 –6.96 (M,4H)	7.60 – 7.62 (D,2H)
			-OCH ₃ (2 Methoxy)	6.63 (S, 6H)	

The mass spectrum of HDMBHBH and CMHBH shows that molecular ion peak at m/z 317.1 ($M+ 1$) and 267 ($M+ 1$) respectively.

The structures of HDMBHBH and CMHBH were confirmed based upon above IR, NMR and mass spectral data

A 0.01M solutions of HDMBHBH and CMHBH in Dimethyl formamide (DMF) were employed in the present studies. The reagent (HDMBHBH and CMHBH) solutions (0.01M) were prepared by dissolving suitable quantity (0.316 g for HDMBHBH and 0.264 for CMHBH) of the compound in 100 ml of dimethyl formamide. The reagent solution is stable for 6 hours in presence of micellar medium. The working solutions were prepared daily by diluting the stock solution to an appropriate volume. All other chemicals used were of analytical grade.

RESULTS AND DISCUSSION

The reagents 4-Hydroxy 3, 5-dimethoxy benzaldehyde 4-hydroxy benzoylhydrazone (HDMBHBH) and Cinnamaldehyde 4-hydroxy benzoylhydrazone (CMHBH) were easily synthesized as any other Schiff base reagent. In basic medium, the ligands presumably coordinates the metal ions as di-anion to give neutral complexes. The absorption spectra of reagents (HDMBHBH, CMHBH) and Copper (II) complex under the optimum conditions are shown in Figure1&2.

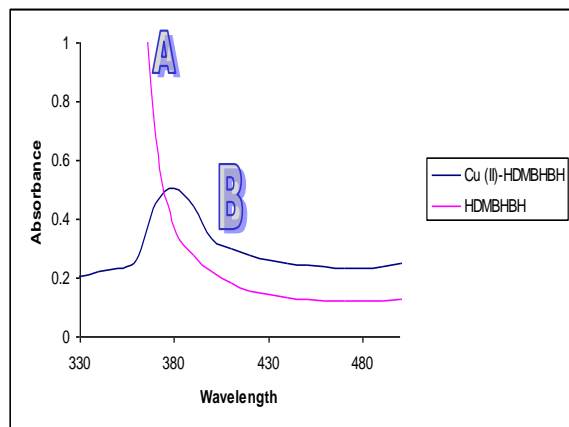


Fig-1 Absorption spectra of
 (a) HDMBHBH Vs Buffer blank
 (b) Cu (II)-HDMBHBH Vs Reagent blank
 HDMBHBH - 2×10^{-3} M (0.5 ml)
 Cu (II) - 2×10^{-4} M (0.5 ml)
 pH 9.0 (3.0 mL)
 Triton-X-100 (5%)-0.5 ml

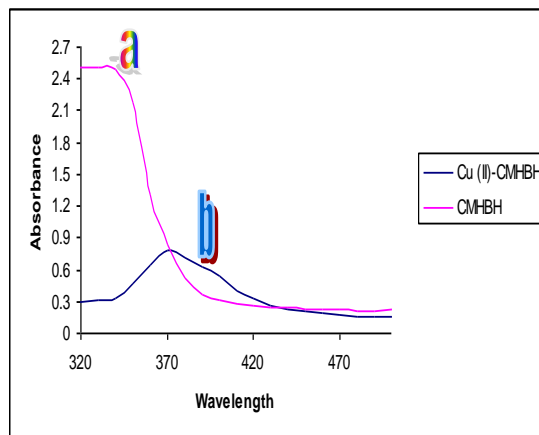


Fig-2 Absorption spectra of
 (a) CMHBH Vs Buffer blank
 (b) Cu (II)-CMHBH Vs Reagent blank
 CMHBH - 5×10^{-3}
 Cu (II) - 5×10^{-4} M (0.5 ml)
 pH 9.0 (3.0 mL)
 Triton-X-100 (5%)-1.0 ml

Effect of reagent (HDMBHBH and CMHBH) concentration

A 10-fold molar excess of reagent (HDMBHBH and CMHBH) was necessary for complex and constant colour development. Excess of the reagent has no effect on the absorbance of the complex. The absorbance of the complex solution was found independent of the order of the addition of the reagents.

Effect of time

Time stability of the coloured solution

The absorbance of the solution was measured at different time intervals to ascertain the time stability of the colour of the complex. The colour reaction between Copper (II) with HDMBHBH and CMHBH was found to be instantaneous at room temperature. A slow decrease in absorbance was observed for the coloured species after 10 min. The stability of the complex was increased by adding neutral surfactant Triton X-100 (5%) and the colour remained stable for more than 6 hours.

The effect of surfactants

The effect of various surfactants such as Triton X-100, Sodium dodecyl benzene sulphonate (SDBS) and Cetyltrimethyl ammonium bromide (CTAB) on the absorption profiles of the system has been investigated and presented in Table 2. In presence of Triton X-100 (5%) both complex were more stable and exhibited maximum absorbance, hence Triton X-100 (5%) has been selected for further studies.

Table: 2. Influence of different surfactants

Surfactant	Absorbance of Cu (II)-HDMBHBH complex at λ_{\max} 383 nm	Absorbance of Cu (II)-CMHBH complex at λ_{\max} 375 nm
None	0.305	0.428
Triton X-100 (5%)	0.525	0.776
CTAB (5%) (Cationic)	0.483	0.623
SDBS (5%) (Anionic)	0.443	0.556

Optical characteristics, precision and accuracy data.

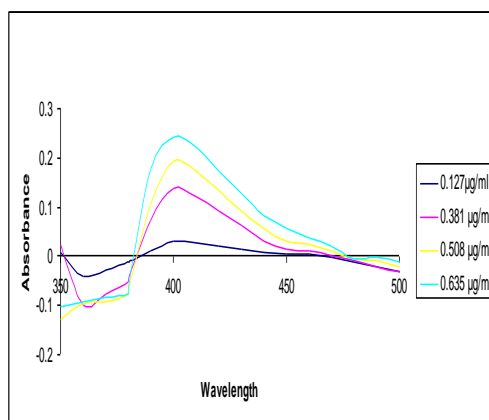
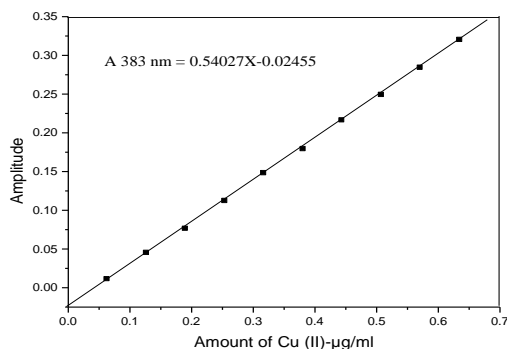
Beer's law limits, molar absorptivity and Sandell's sensitivity values, regression equation and correlation coefficients for Copper (II)-HDMBHBH and Copper (II)-CMHBH complex were compared and presented in Table 3. From this it was noticed that in derivative spectra the peak position shift towards higher wavelengths and Beer's law range was also improved compared to zero order method.

Table: 3. Optical characteristics, precision and accuracy data.

Characteristics	Results	
	HDMBHBH	CMHBH
λ_{\max}	383 nm	375 nm
pH range	8.0-10.0	8.0-10.0
Optimum pH range	8.0-9.0	8.0-9.0
Mole of reagent required per mole of metal ion for full colour development	10 (folds)	10 (folds)
Molar absorptivity ($L \cdot mol^{-1} \cdot cm^{-1}$)	3.41×10^4	2.77×10^4
Sandal's sensitivity ($\mu g/cm^2$)	0.0018	0.00229
Beer's law validity range ($\mu g/ml$)	0.063-0.635	0.158-1.588
Optimum concentration range ($\mu g/ml$)	0.127-0.571	0.317-1.429
Composition of complex (M: L) obtained in Job's and molar ratio method	1:1	1:1
Stability constant of the complex	14.12×10^6	10.10×10^6
Standard deviation in the determination of 0.317 $\mu g/ml$ (HDMBHBH) and (CMHBH) of Copper (II) - for ten determinations.	0.006	0.004
Relative standard deviation (%)	4.05	4.7

Regression coefficient	0.99991	0.99978
Detection limit (µg/ml)	0.018	0.012
Determination limit (µg/ml)	0.054	0.036

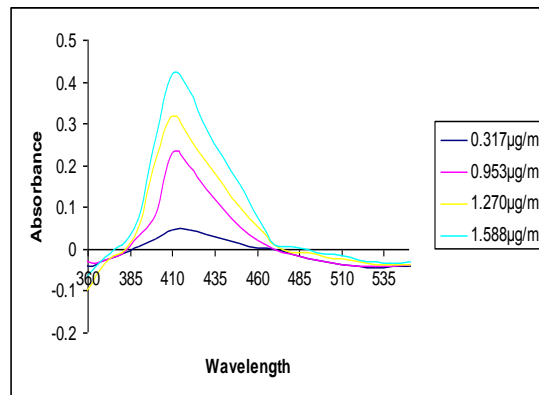
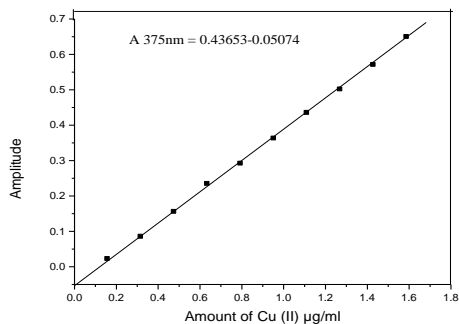
The calibration graph follows the straight-line equation $Y = aX + b$; where c is the concentration of the solution, Y is measured absorbance or peak height and a and b are constants. By substituting the Cu (II)- HDMBHBH complex experimental data in the above equation, the calibration equations were calculated as $\lambda_{max} 383 \text{ nm} = 0.54027X - 0.02455$ for zero order data and $\lambda_{max} 405 \text{ nm} = 0.42385X - 0.02152$ For first derivative data and $\lambda_{max} 433 \text{ nm} = 0.67462X - 0.02784$ For second order derivative data which gives the straight lines.



Cu (II)-HDMBHBH - Beer's law
 Zero order
 HDMBHBH- 2×10^{-3} M (0.5 ml)
 Cu (II) - 2×10^{-5} M (0.5 ml)
 pH --9.0 (3.0 ml)
 Triton-X-100 (5%)-0.5 ml
 λ_{max} -----383 nm

Cu (II)-HDMBHBH - Beer's law
 first order derivative spectra
 HDMBHBH- 2×10^{-3} M (0.5 ml)
 Cu (II) - 2×10^{-5} M (0.5 ml)
 pH --9.0 (3.0 ml)
 Triton-X-100 (5%)-0.5 ml
 λ_{max} -----405 nm

By substituting the Cu (II)-CMHBH complex experimental data in the above equation, the calibration equations were calculated as $\lambda_{max} 375 \text{ nm} = 0.43653 - 0.05074$ for zero order data and $\lambda_{max} 410 \text{ nm} = 0.29136 - 0.04629$ for first derivative data, $\lambda_{max} 442 \text{ nm} = 0.4101 - 0.05355$ for second derivative data which gives the straight lines.



Cu (II)-CMHBH beer's law
 Zero order
 CMHBH -5×10^{-3} M (0.5 ml)
 Cu (II) -5×10^{-5} M (0.5 ml)
 pH -9.0 (3.0 mL)
 Triton-X-100 (5%)-1.0 ml
 λ_{max} -----375 nm

Cu (II)-CMHBH beer's law
 first order derivative spectra
 CMHBH -5×10^{-3}
 Cu (II) -5×10^{-5} M (0.5 ml)
 pH 9.0 (3.0 mL)
 Triton-X-100 (5%)-1.0 ml
 λ_{max} -----410 nm

Zero order method

The developed spectrophotometric methods proposed in the present studies were applied for the determination of Copper (II) in Beer, Wine, Biological materials and in alloy samples. The results are in good agreement with the certified values.

(a) Determination of Copper (II) in Beer and Wine samples

50 ml of beer or wine sample was taken in separate 250 ml beakers and digested in 5 ml of 5M HNO₃ and evaporated to dryness. The residue thus obtained was dissolved and diluted up to the mark in 100-ml volumetric flask with distilled water. The suitable aliquots of sample were analyzed and the results obtained are presented in Table-4.

Table: 4. Determination of Copper (II) in Beer and Wine samples

Sample	Amount taken	Amount of Cu (II) found (µg/ml)											
		HDMHBH						CMHBH					
		Zero order	Error (%)	D1	Error (%)	D2	Error (%)	Zero order	Error (%)	D1	Error (%)	D2	Error (%)
Beer	5.32	5.30	-0.37	5.31	-0.18	5.31	-0.18	5.28	-0.75	5.3	-0.37	5.3	-0.37
Wine	7.45	7.43	-0.26	7.44	-0.13	7.44	-0.13	7.41	-0.53	7.4	-0.26	7.4	-0.26

*Average of best three determinations among five determinations

A suitable aliquot of the sample solution was taken in a 10 ml standard flask containing 3.0 ml buffer solution, and 0.5 ml of reagent (HDMBHBH and CMHBH) solution. The contents were diluted to 10 ml with distilled water and its absorbance was measured at λ_{\max} against the reagent blank. The absorbance values were referred to the pre-determined calibration plot to compute the amount of Ruthenium present. The results are presented in table 4.

(b) Preparation of alloy sample solution

Alloy material (0.25 g) was dissolved in concentrated HCl (15 ml) by warming. A little concentrated nitric acid (1 ml) was added and slowly evaporated to dryness. The residue was dissolved in 10 ml of 1M HCl and the resulting solution was concentrated to ca. 5 ml, diluted to ca. 50 ml with distilled water, filtered and made up to 100 ml. Suitable aliquots of the sample were analyzed for the determination of copper (II) by following the recommended procedure.

A suitable aliquot of the sample solution was taken in a 10 ml standard flask containing 3 ml of buffer of pH 9.0 and 0.5 ml of reagent, and the contents were diluted to 10 ml with distilled water and its absorbance was measured at λ_{\max} against the reagent blank. The absorbance values were referred to the pre-determined calibration plot to compute the amount of Copper (II) present. The results are presented in table 5

Table 5. Determination of Copper (II) in Alloy samples

Alloy Sample	Certified value	Amount of Copper (II) %											
		HDMBHBH						CMHBH					
		Zero order	Error (%)	D1	Error (%)	D2	Error (%)	Zero order	Error (%)	D1	Error (%)	D2	Error (%)
BCS 179/3a	58.50	58.46	-0.06	58.47	-0.05	58.47	-0.05	58.23	-0.46	58.32	-0.3	58.4	-0.10
BCS 180/2b	68.12	68.10	-0.029	68.11	-0.014	68.11	-0.014	67.54	-0.85	68.01	-0.16	68.11	-0.01
Tin base white metallic	4.58	4.55	-0.65	4.57	-0.21	4.57	-0.21	4.38	-4.56	4.45	-2.96	4.53	-1.14

*Average of five determinations. (a.) 58.5%Cu; 0.70%Sn; 0.35%Pb; 0.56%Ni; 0.86%Mn; 1.02%Fe; 2.22%Al; 0.044%Si; 35.8%Zn (b).68.12%Cu; 0.68%Fe; 30.15%Ni; 0.75%Mn; 0.05%C; 0.006%S; 0.005%Co; 0.0003%Pb (c). 82.2% Sn; 4.58% Cu; 0.17% Ni; 0.11% Bi; 0.024% Fe; 9.45% Sb; 3.18% Pb; 0.14% Cd; 0.040% Zn.

(c) Extraction of Copper from biological materials

50 grams of the biological materials was heated in 500 ml conical flasks with 40 ml of concentrated Nitric acid on a steam bath and shaken vigorously until a fine emulsion was formed. The heating was continued with the gradual addition of 6% H₂O₂ (40 ml). The aqueous phase was transferred to the beaker. The extraction was repeated twice with further addition of 20ml concentrated HNO₃ and 20 ml of 6% H₂O₂. The combined extract was evaporated to

dryness. The residue was dissolved in a minimum amount of dilute HCl and transferred into a 50 ml standard flask quantitatively. The contents were diluted to the mark with distilled water.

Table: 6. Determination of Copper (II) in Alloy samples

Biological Sample	AAS method	Amount of Copper (II) %											
		HDMBHBH						CMHBH					
		Zero order	Error (%)	D1	Error (%)	D2	Error (%)	Zero order	Error (%)	D1	Error (%)	D2	Error (%)
Ground nut oil	1.098	1.095	-0.27	1.097	-0.09	1.097	-0.09	1.088	-0.91	0.092	-0.54	0.095	-0.27
Mustard oil	2.251	2.247	-0.177	2.248	-0.13	2.249	-0.08	2.243	-0.35	2.245	-0.26	2.249	-0.08

Precision and accuracy

The precision and accuracy of the proposed methods were studied by analyzing (10 replicates) 0.317 µg/ml of Copper (II) and the RSD values were found to be less than 4.7 %.

Effect of diverse ions

In order to assess the analytical potential of the proposed methods, the effects of some diverse ions which often accompany Copper (II) were examined by carrying out the determination of 0.317 µg/ml (HDMBHBH) and 0.794 µg/ml (CMHBH) Copper (II) in the presence of foreign ions. An ion was considered to interfere in the determination if the absorbance observed differed by more than ± 2% from that for Copper (II) alone. The results presented in Table 6 indicate that many metal ions and anions do not interfere in the determination of Copper (II). However, Fe (III) interferes seriously as they readily form coloured species with HDMBHBH and CMHBH. The tolerance limit of Fe (III) was enhanced by using masking agents of fluoride, phosphate presented in Table 7. [7-26]

Table: 6 Tolerance limits of diverse ions in the determination of 0.317 and 0.794 µg/ml Copper (II).

Ion Added	HDMBHBH Tolerance Limit (µg/ml)			CMHBH Tolerance Limit (µg/ml)		
	Zero order	D1	D2	Zero order	D1	D2
Iodide	1765	2269	2395	1649	1903	1903
Urea	780	840	960	420	540	600
Thiocyanide	349	349	349	581	697	697
Bromide	1038	1198	1198	719	860	860
Thiourea	990	1141	1141	685	761	761
Nitrate	806	930	930	620	744	744
Tetra borate	1524	1524	1524	1474	1524	1524
Acetate	472	531	590	590	697	697
Phosphate	1424	1614	1614	664	664	664
Chloride	532	603	674	355	426	426
Tartarate	1500	1625	1875	1000	1125	1250
Citrate	2459	2838	2395	1892	2081	2081
Flourude	360	360	360	284	322	341
Thiosulphate	1121	1121	1121	897	920	920
Na ⁺	690	736	736	460	575	575
Sn ⁺²	178	201	201	59.35	94.96	118.71
Al ⁺³	27	30	30	8.09	13.49	16.18
Ba ⁺²	274	315	343	137.33	164.79	205.99
Mo ⁺⁶	105	124	124	47.97	55.56	67.15
Hg ⁺²	44	46	50	20.09	40.11	60.17
La ⁺³	305	347	347	166.68	208	208
W ⁺⁶	330	367	386	183.84	220	220
Sr ⁺²	105	131	131	43.81	52.57	70.09
Se ⁺⁴	86	95	110	39.48	55.27	63.16
Bi ⁺³	417	438	480	104	146.28	188.08
Li ⁺²	1.0	5.0	6.0	5.0	6.0	6.0
Ce ⁺⁴	14	21	21	42.03	56.04	70.06
Fe ⁺³ *	1.11	1.11	1.11	1.67	2.72	3.35
Zr ⁺⁴	73	73	73	9.12	18.24	18.24
Pd ⁺²	4.2	5.3	5.3	3.19	5.32	5.32

Table: 7. masking agents for interfering ions of HDMBHBH and CMHBH

HDMBHBH	CMHBH
** Masked by fluoride 360 µg/ml	*Masked by phosphate 664 µg/ml

Table 8. Comparison of spectrophotometric methods for the determination of Copper (II)

Name of the Chromogenic Reagent	λ_{\max} (nm)	pH	Molar absorptivity $L \cdot mol^{-1} \cdot cm^{-1}$	Beer's law Range ($\mu g/ml$)	Reference
8-Methoxy-2-chloroquinoline-3-carbaldehyde thiosemicarbazone	410	5.0	2.67×10^3	Up to 3 ppm	7
N-(2,5-Dimethylphenyl)-p-toluimidoyl phenyl hydrazine	410	7.0-10.5	4×10^4	Upto 20 mg/ml	8
2,4-Dihydroxybenzaldehyde isonicotinoylhydrazone	430	2.0	1.65×10^4	0.063-2.55 $\mu g/ml$	9
2-Acetyl-4-phenyl-3-thiosemicarbazone	385	3-6	2.92×10^3	0.10-0.51	10
1-Phenyl-1,2-propanedione-2-oxime thiosemicarbazone	465	5.0	5.56×10^3	0.38-7.63	11
N-(2,5-Dimethylphenyl)-p-toluimidoyl phenyl hydrazine	370,	9.25	1.2×10^4	Upto 20 mg/ml	12
Cetyltrimethyl ammoniumbromide in presence of iodide	650	0.5-3.5	1.064×10^4	Upto 10 ppm	13
Cupron in the presence of Brij 35	445	8.0	6.6×10^4	Up to 7 ppm	14
2-Hydroxy-4-n-butoxyacetophenone oxime	370	8.5	1.77×10^4	0-8 mg	15
2-(2'-(6'-Methyl-benzothiazolyl)azo)-5-dimethyl amino benzoic acid	660	2.0-5.0	7×10^4	Up to 0.72 $\mu g/ml$	16
2-(2-(4-Methylbenzo thiazolyl)azo)-5-dimethylamino benzoic acid (4-Me-BTAMB)	650	2.0-5.0	3.1×10^4	0.04-2 μg	17
4-Hydroxy-3,5-dimethoxy benzaldehyde-4-hydroxy benzoylhydrazone (HDMBHBH)	383	8.0-9.0	3.41×10^4	0.063-0.635	Present method
Cinnamaldehyde 4-hydroxybenzoylhydrazone (CMHBH)	375	9.0	2.77×10^4	0.158-1.588	

CONCLUSION

The proposed methods are simple, accurate and have advantages over the reported methods which suffer from interference by large number of ions or require either heating or extraction or are less sensitive.

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