

SHORT COMMUNICATION

Extractive spectrophotometric determination of copper(II) in water and alloy samples with 3-methoxy-4-hydroxy benzaldehyde-4-bromophenyl hydrazone (3,4-MHBBPH)

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Abstract: A facile, sensitive and selective extractive spectrophotometric method was developed for the determination of copper(II) in various water and alloy samples using a newly synthesized reagent, 3-methoxy-4-hydroxy benzaldehyde 4-bromophenyl hydrazone (3,4-MHBBPH). Copper(II) forms an orange colored complex with (3,4-MHBBPH) in acetate buffer medium (pH 4) which increases the sensitivity and the complex was extracted into chloroform. Under optimum conditions, the maximum absorption of the chloroform extract was measured at 462 nm. The Beer law was obeyed in the range of 0.20 to 4.0 $\mu\text{g ml}^{-1}$ of copper. The molar absorptivity and the Sandell's sensitivity of the complex were $2.0520 \times 10^4 \text{ mol}^{-1} \text{ cm}^{-1}$ and $0.2540 \mu\text{g cm}^{-2}$, respectively. The detection limit was found to be $0.0270 \mu\text{g mL}^{-1}$. A detailed study of various interfering ions made the method more sensitive. The method was successfully applied for the determination of Cu(II) in water and alloy samples. The performance of the present method was evaluated in terms of Student 't' test and Variance ratio 'f' test, which indicate the significance of the present method over reported methods.

Keywords: copper(II), 3-methoxy-4-hydroxy benzaldehyde 4-bromophenyl hydrazone (3,4-MHBBPH), spectrophotometry, water and alloy samples.

INTRODUCTION

Copper is available in nature in the free state in the form of sulphides, chlorides and carbonates. Copper is utilised in electrical industries and in industrially useful alloys. Biologically copper is essential in small amounts for the synthesis of haemoglobin. A deficiency of copper causes diseases such as anaemia, while an excess of it causes "Jaundice" and "Wilson disease". As a pollutant, copper is of particular concern because of its high degree of toxicity to aquatic organisms. In

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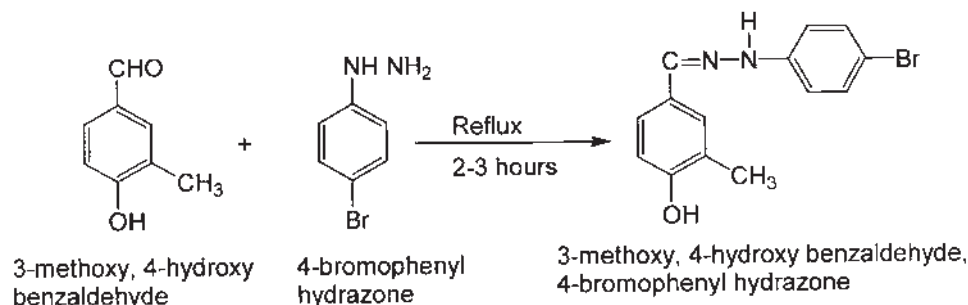
view of this, the separation and determination of copper from associated elements is indispensable. Several analytical techniques have been monitored for the determination of copper(II), they include atomic absorption spectrometry,¹⁻⁸ voltammetry,⁹⁻¹¹ spectrophotometry,¹²⁻¹⁴ inductive coupled plasma-atomic emission spectrometry¹⁵⁻¹⁷ and inductive coupled plasma-mass spectrometry.¹⁸ A few reagents¹⁹⁻³¹ are available for the spectrophotometric determination of copper(II), as shown in Table I. These reported reagent suffer from several disadvantages, such as poor sensitivity, selectivity and a few require special conditions for the formation of the complexes with the reagents and a few are commercial.

The aim of the present work was to provide a facile, sensitive and rapid extractive spectrophotometric method for the determination of trace amounts of copper(II) in water and alloy samples and other natural samples of significant importance. In this study, new analytical reagent 3-methoxy-4-hydroxybenzaldehyde-4-bromophenyl hyzdrazone (3,4-MHBBPH) for the determination of copper(II) in water and alloy samples was successfully sythesized.

EXPERIMENTAL

Synthesis of 3-methoxy-4-hydroxy benzaldehyde-4-bromophenyl hydrazone

Equimolar solutions of 3-methoxy-4-hydroxy benzaldehyde and 4-bromophenyl hydrazine in aqueous medium were refluxed for 2-3 h, after which contents were cooled to room temperature, a solid product separated. The solid was filtered, washed with water, dried and recrystallized from hot aqueous methanol (m. p. 147 °C, 91 % yield as shown in Scheme 1).



Scheme 1. Synthesis of 3-methoxy-4-hydroxy benzaldehyde 4-bromophenyl hydrazone.

Reagents

All reagent used were of analytical reagent grade. Double distilled water was used throughout the experiments. A stock solution of Cu(II) (0.01 M) was prepared by dissolving 2.505 g of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (Merck, Germany) in double distilled water in a 1000 ml volumetric flask. Copper(II) working standard stock solutions were prepared freshly by appropriate dilution of the standard stock solution with double distilled water. A reagent solution (0.1 M) was prepared by dissolving 0.393 g of reagent in 100 ml of methanol. Acetate buffer was prepared by dissolving 8.2 g sodium acetate in 800 ml of water. It was adjusted to pH 4.0 with high purity glacial acetic acid and stored in a clean 1 l metal-free polyethylene bottle.

TABLE I. Comparison of analytical parameters of the present method with other spectrophotometric method for the determination of copper

Reagent	λ_{\max}/nm	Optimum pH range	Beer's law validity range/ppm	Molar absorptivity $\text{mol}^{-1} \text{cm}^{-1}$	M:L	Remarks	Ref.
8-Methoxy-2-chloroquinolin-3-carbaldehyde thiosemicarbazone	410	5.0	3.0	0.0026768	1:1	Interference no. of metal ions and poor sensitivity and selectivity	10
7-Methoxy-2-chloroquinoline-3-carbaldehyde thiosemicarbazone	400	4.0	5.0	343.4	–	Mo(V) interfere, very poor sensitivity	20
2,5-Dihydroxy acetophenone benzoin hydrazone	–	5.00	0.3–3.00	0.011	–	High reagent consuming and poor selectivity	21
Pyruvaldehyde (<i>N,N</i> -dibutyl)bis-thiosemicarbazone	488	5.12	–	10900	1:1	Less sensitivity	22
2-Carboxy benzaldehyde thiosemicarbazone	346	–	0.5–5.0	12000	1:1	Less sensitivity	23
2,4-Dihydroxy-5-bromoacetophenone thiosemicarbazone	400	6.00	12.7	1450	1:1	Very poor sensitivity and selectivity	24
2,2-Dipyridyl-2-pyridyl hydrozone	–	11.9–12.6	Up to 1.0	0.038	–	Interference of mutual ions and expensive reagent	25
Benzaldehyde-4-(2-hydroxy-5-sulfo-phenyl)-3-thiosemicarbazone	325	4.5	7.62	7.44	1:2	very poor sensitivity	26
4-Chlorosemimonso-acetophenone thiosemicarbazone	400	7.5–8.5	0.2–2.0	2518	1:2	Ag(I),Ni(II),Co(II),Pb(II),Cd(II) cyanide,tartrate and edta interfere,less sensitive	27
2,4-Dihydroxy benzophenone benzoin hydrazone	–	4.0	0.31–2.20	0.0155	–	Less sensitive and stable	28
2,4-Dihydroxy benzophenone isonicotinoyl hydrazone	–	2.0	0.063–2.550	0.0165	–	Less sensitive more reagent consumption	29
Benzildithiosemicarbazone	380	4.0	0.5–4.0	16347	1:1	Low detection limit and detection unit	30

TABLE I. Continued

Reagent	λ_{\max}/nm	Optimum pH range	Beer's law validity range/ppm	Molar absorptivity $\text{mol}^{-1} \text{cm}^{-1}$	M:L	Remarks	Ref.
2,5-dimercapto-1,3,4 thiadiazole	390	0.02–0.014	–	0.000565	1:2	High reagent consumption and highly commercial	31
3-Methoxy, 4-hydroxy benzaldehyde 4-bromophenyl hydrazone	462	2.0–4.0	–	–	1:1	Low reagent consumption, economical color forming reagent, less interference, highly stable.	Present method

Apparatus

A Hitachi U 2001 spectrophotometer with 1.0 cm matched quartz cells was used for all the absorbance measurements. An Elico Li-129 model pH meter with a combined glass electrode was used for all the pH measurements.

Procedure

To an aliquot of working standard solution containing 1–100 μl in a 50 ml separating funnel 5.0 ml of acetate buffer solution (pH 4.0), 2.0 ml of reagent solution and salting out agent (0.1 M magnesium sulphate) were added. The mixture was shaken with 5.0 ml portions of chloroform for 30 s and allowed to stand for few minutes. The organic phases are collected and made up to the mark in a 25 ml volumetric flask with chloroform and the absorbance was measured at 462 nm against the corresponding reagent blank. A calibration graph was constructed.

Procedure for the determination of Cu(II) in natural water samples

Different water samples (tap water, river water, spring water) were collected from various places in and around Tirupati, A. P., India. The sample (150 ml) were stored at 0–5 °C in metal-free polyethylene bottles. The water samples were filtered through a Whatman filter paper No. 41 and the clean solution was collected into a 250 ml beaker. The contents were diluted up to the mark with double distilled water. 15 ml of this solution was further diluted to obtain a working solution for the determination of Cu(II) as described in the above procedure and compared with the reported method²⁹ with statistical validation. The results are summarized in Table II.

Procedure for the determination of Cu(II) in sea water samples

100 ml of seawater was taken from the Bay of Bengal near Sullurpet, Nellore dist., A. P., India and spiked with known amounts of metal ion. The pH of the sample was adjusted to pH 4.0 with acetate buffer as reported in literature.³² The metal ion present in the sea water was analyzed by the previously described procedure. The analytical data are presented in Table II.

TABLE II. Determination of copper(II) in various water samples

Sample	Copper added $\mu\text{g ml}^{-1}$	Proposed method				Reported method ³³	
		Found ^a $\mu\text{g ml}^{-1}$	Recovery % ^a	<i>t</i> -Test	<i>f</i> -Test	Found ^a $\mu\text{g ml}^{-1}$	Recovery %
Synthetic mixture	0.4	0.39	97.5±0.16	4.95	0.62	0.37	92.55±0.09
	1.0	0.90	95.0±0.10	1.92	0.44	0.93	03.0±0.06
	1.6	1.55	96.8±0.09	1.19	0.02	1.52	95.0±0.47
Lake water ^b	–	0.38	–	–	–	0.36	–
	0.8	1.18	98.3±0.05	5.80	0.01	1.16	92.0±0.36
	1.2	1.58	97.5±0.06	4.12	0.79	1.56	97.5±0.05
River water ^b	–	0.39	–	–	–	0.37	–
	0.8	1.19	95.0±0.48	2.73	0.00	1.17	91.2±0.03
	1.2	1.59	91.1±0.09	1.00	1.00	1.57	90.9±0.09
Springer water ^b	–	0.19	–	–	–	0.18	–
	0.4	0.59	97.5±0.08	4.93	0.53	0.58	92.5±0.12
	0.6	0.79	98.3±0.12	5.13	0.11	0.78	93.0±0.04
Sea water ^c Upper level	–	0.59	–	–	–	0.57	–
	0.9	1.49	93.3±0.16	2.08	0.36	1.47	91.1±0.09
	1.2	1.79	95.0±0.18	4.47	0.07	1.77	90.3±0.05
Lower level	–	0.59	–	–	–	0.58	–

TABLE II. Continued

Sample	Copper added $\mu\text{g ml}^{-1}$	Proposed method				Reported method ³³	
		Found ^a $\mu\text{g ml}^{-1}$	Recovery % ^a	<i>t</i> -Test	<i>f</i> -Test	Found ^a $\mu\text{g ml}^{-1}$	Recovery %
Lower level	0.9	1.49	95.5±0.07	1.93	0.08	1.48	93.3±0.23
	1.2	1.79	95.8±0.09	0.68	0.62	1.78	95.0±0.06
Polluted water	–	0.38	–			0.37	–
	0.6	0.98	96.6±0.27	1.26	0.10	0.97	95.0±0.09
	0.8	1.18	97.5±0.07	1.07	0.16	1.17	96.25±0.18

^a*n* = 5, ^bCollected around Tirupati area, ^cCollected from Bay of Bengal, near Sullurpet, Nellore district, A. P., India

Procedure for the determination of Cu(II) in alloy samples

1 g of alloy sample was dissolved in a 10 ml of aqua regia and evaporated to the minimum volume, extracted with 10 ml of 2 M HNO₃ and then diluted with double distilled water to a suitable volume (10 ml). This serves as the stock solution. The experimental solution was prepared by pipetting out 10 ml of the stock solution into a 100 ml volumetric flask and the solution was made up to the mark with distilled water. A known volume of this solution is placed in a 10 ml volumetric flask and made up to the mark and analysed by the general procedure given previously.

RESULTS AND DISCUSSION

Copper(II) reacts with 3,4-MHBBPH to form a 1:1 orange colored complex in buffer of pH 4.0, and the complex was extracted into chloroform. The organic extract showed a maximum absorption at 462 nm. The formation of the complex and its extraction into chloroform are instantaneous. The complex is stable for more than 12 h.

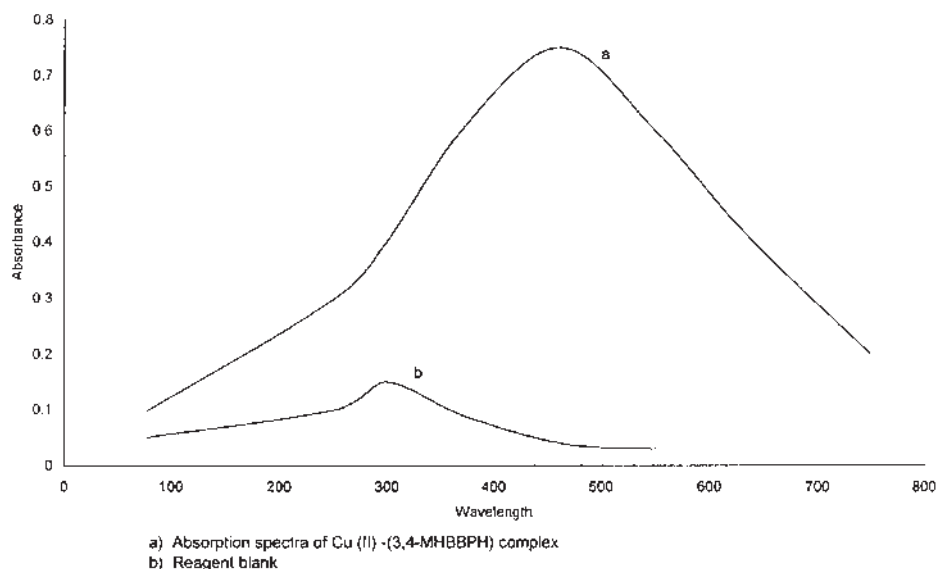


Fig. 1. Absorption spectra of Cu(II)–3,4-MHBBPH complex system.

Under the experimental condition, the absorption spectra of 3,4-MHBBPH and the (Cu(II)–3,4-MHBBPH) complex were scanned. Whereas 3,4-MHBBPH exhibited an absorption maximum at 390 nm, the [Cu–3,4-MHBBPH]²⁺ complex gave an absorption peak at 462 nm. The difference between the two peaks is 72 nm and could obviously be distinguished. Thus, the absorption peak at 462 nm was chosen as the maximum wavelength for Cu(II)–3,4-MHBBPH, as shown in Fig. 1.

The Beer law was obeyed in the concentration range 0.20 to 4.0 $\mu\text{g } \mu\text{l}^{-1}$ of Cu(II).

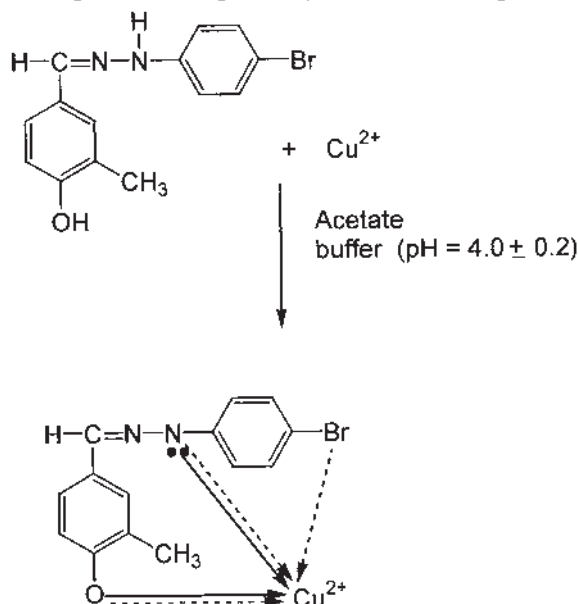
The molar absorptivity and Sandell's sensitivity of the complex at pH 4.0 was calculated as $2.0520 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ and $0.2540 \mu\text{g cm}^{-2}$, respectively. The correlation coefficient (*r*) for the experimental data was 0.9998.

Effect of the reagent concentration

To a series of 25 ml separating funnels, each containing 1.0 ml of Cu²⁺ solution (0.01 M) and 5.0 ml of buffer solution (pH 4.0) were added different volumes of the reagent solution and extracted with chloroform to obtain the maximum color formation. The absorbance of each solution was measured at 462 nm against the reagent blank. From the experimental observation, it was found that beyond a ten-fold excess of the reagent, the absorbance remained almost constant. Hence, for further studies, 2.0 ml of the reagent was recommended for complete color development.

Stoichiometry of the complex

On the basis of the Job's method of continuous variation as modified by Vosburg and Cooper for two phase systems, the composition of the extracted species was



Scheme 1a.

found to be Cu^{2+} : 3,4-MHBBPH = 1:1. The mole ratio of the method further confirmed the stoichiometry (Scheme 1a) of the complex as shown in Figs. 2 and 3.

Effect of solvent

The extraction of the Cu(II)–3,4-MHBBPH complex was tested in various organic solvents, such as toluene, benzene, xylene, *n*-butanol, 1-pentanol, dimethyl formaldehyde, CCl_4 , chlorobenzene, cyclohexane and chloroform. Among the various solvent studied chloroform was selected as the most suitable for the extraction of the Cu(II)–3,4-MHBBPH complex, because of its maximum absorbance and greater extraction ability, due to its polarity.

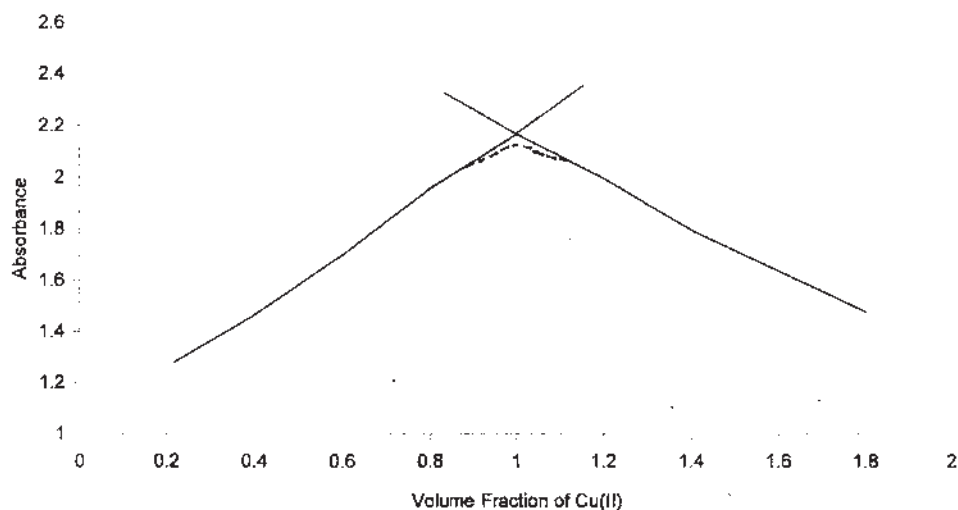


Fig. 2. Job's Continuous variation method for the Cu(II)–(3,4-MHBBPH) complex.

Ringbom plot for the (Cu(II)–3,4-MHBBPH) complex

The Ringbom plot is the established standard adopted to determine the optimum range of concentration for a system that obeys the Beer's law. The plot is drawn between $\log c$ of Cu(II) and $(1-T)$ (where T is the transmittance). The plot has a sigmoid shape with a linear segment intermediate absorbance values (0.60 to 2.20) and concentration values (0.8 to $2.80 \mu\text{g ml}^{-1}$). The slope of the Ringbom plot from Fig. 4 is 0.4562. Hence, the ratio between the relative error in the concentration and photometric error 0.60 for concentration of 0.80 for 0.75 % photometric error.

Precision and accuracy

The precision and accuracy of the proposed method was evaluated by the good results which were obtained by a reported method. The results are shown in Tables II and III. The good correlation between the two methods indicate that the present method is more sensitive than the methods reported in the literature.^{29,33}

Detection limit

Under the optimum conditions, the detection limits for determination of Cu(II) in various environmental samples was found $0.0270 \mu\text{g ml}^{-1}$ for a 200 ml volume of Cu(II) solution.

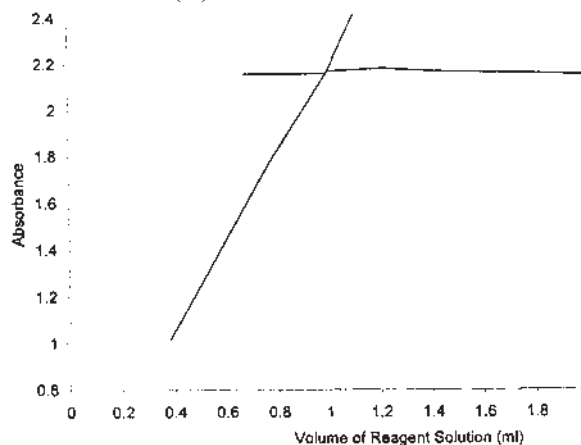


Fig. 3. Mole ratio method for the Cu(II)-(3,4-MHBBPH) complex.

Effect of salting out agents

Various salting out agents, such as lithium nitrate, thorium sulphate, magnesium sulphate, lithium chloride, ammonium chloride and ammonium sulphate were used for the enhancement of the extraction of the metal complex into the organic phase in a single step. It was observed that the presence of 1.0 ml of 0.1 M magnesium sulphate solution ensures the complete extraction. The aqueous phases

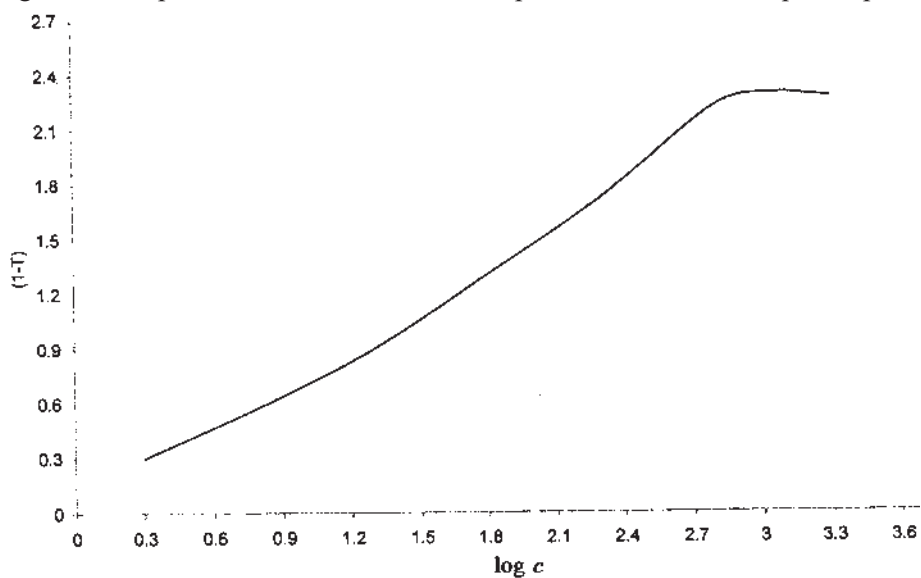


Fig. 4. Ringbom plot of Cu(II)-(3,4-MHBBPH) complex.

was tested for the complete extraction of no copper(II) using chloroform, and no copper(II) was found in the aqueous phase. It was established that 1.0 ml of 0.1 M magnesium sulphate as salting out agent and a ten-fold molar excess of the reagent quantitatively extracts copper(II) into to the organic phase.

TABLE III. Determination of copper(II) in alloy samples

Samples	Standard Reference Sample	Amount of copper(II) found				
		Certified Value	Present method	Reported method ²⁹	<i>t</i> -test	<i>f</i> -test
1.	Tin base white metal	3.50	3.55±0.09	3.47±0.12	0.02	0.59
2.	Devard's alloy	47.90	47.90±0.07	47.88±0.07	0.58	1.00
3.	BCs 180/2	67.12	67.18±0.12	67.10±0.09	0.17	0.58
4.	BAs 106	4.08	4.14±0.07	4.01±0.18	0.09	0.16
5.	BCs 179/3	57.35	57.42±0.03	57.39±0.16	0.67	0.03
6.	Gun metal	0.78	0.33±0.09	0.23±0.05	0.01	0.42

^a*n* = 5

Effect of interfering species

Several anions and cations were studied in detail. Table IV summarizes the tolerance limits of interfering ions in the determination of 50 µg l⁻¹ Cu(II). The tolerance limit was taken as the amount causing an error of ± 2 % at the peak height.

TABLE IV. Tolerance limits of interfering ions on the determination of 50 µg l⁻¹ Cu(II) ion

Tolerance limit/µg l ⁻¹	Interfering ions
>50000	K(I),Na(II),Ca(II),Mg(II),Cl ⁻ ,Br ⁻ ,PO ₃ ³⁻ ,CO ₃ ³⁻ ,SO ₄ ²⁻ ,Al(III),Cr(III)
>10000	NO ₃ ,Zn(II),Hg(II)
>5000	Pb(II),Cd(II)
>800	Fe(II),Fe(III),Mn(II) Co(II),Ni(II)

^aCan be masked up to 10000 µg l⁻¹ by the addition of 2 ml⁻¹ of EDTA, thiosulfate, cyanide. ^bCan be masked up to 5000 µg l⁻¹ by the addition of 2 ml of 2 % citrate solution. ^cCan be masked up to 800 µg l⁻¹ by the addition of 1 % thiocyanate

Applications of the extractive spectrophotometric method for the determination of copper(II) by the present method

The results of the proposed extractive spectrophotometric method for the determination of Cu(II) in water and alloy samples are presented in Tables II and III. The obtained results were compared with reported methods^{29,33} in terms of Student's '*t*' test and Variance ratio '*f*'-test. The analytical data summarised in Tables II and III suggest that the percentage recovery of Cu(II) from water and alloy samples range from 92.5 to 97.2 %, which is more reliable and sensitive than the reported methods.^{29,33}

CONCLUSION

The proposed extractive spectrophotometric method is simple, highly sensitive and selective for the determination of Cu(II) in water and alloy samples. The limit of detection of the proposed method is superior when compared to reported method.^{29,33} The method has additional advantages over the reported methods due to easy preparation of complexation agent, high sensitivity of the very stable complex, low consumption of the reagent and minimal interferences.

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ИЗВОД

СПЕКТРОФОТОМЕТРИЈСКО ОДРЕЂИВАЊЕ Cu(II) У ВОДИ И УЗОРЦИМА ЛЕГУРА СА 3-МЕТОКСИ-4-ХИДРОКСИ-БЕНЗАЛДЕХИД-4-БРОМО-ФЕНИЛ ХИДРАЗОНОМ (3,4-МНВВРН)

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У раду је описана једноставна, селективна и осетљива спектрофотометријска метода за одређивање Cu(II) у узорцима вода и легурама. Одређивање је засновано на грађењу комплекса са новосинтетисаним 3-метокси-4-хидрокси-бензалдехид-4-бромо-фенил хидразоном (3,4-МНВВРН). Комплекс се формира у ацетном пуферу (pH 4), а потом екстрахује хлороформом. На $\lambda_{\max} = 462 \text{ nm}$, зависност апсорпције од концентрације следи Веег-ов закон у опсегу од 0,20 – 4,0 $\mu\text{g/ml}$ бакра. Моларна апсорптивност комплекса износи $2,052 \cdot 10^4 \text{ l } \mu\text{g}^{-1} \text{ cm}^{-1}$, а Sandell-ов индекс 0,2540 $\mu\text{g cm}^{-2}$. Граница детекције износи 0,0270 $\mu\text{g/mL}$ бакра. Испитан је утицај интерферирајућих јона у циљу повећања осетљивости одређивања бакра у узорцима вода и легурама.

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