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Spectrophotometric determination of copper in alloys using naphthazarin

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Abstract

Naphthazarin (5,8-dihydroxy-1,4-naphthoquinone; Naph) is proposed as a chromogenic reagent for the spectrophotometric determination of copper(II). The polynuclear complex has a mole ratio of Cu:Naph = 4:6 in a 50% v/v ethanol/water medium containing 0.1 M ammonium acetate and 1.5% (w/v) sodium dodecyl sulfate. The copper–naphthazarin complex shows an absorption maximum at 330 nm with a molar absorptivity of $1.84 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$. Beer's law is obeyed up to 4.5 ppm of copper(II). The method was applied for copper determination in alloy samples with satisfactory results. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Naphthazarin; Copper determination; Alloy; Spectrophotometry

1. Introduction

Several methods are available for trace determination of copper including spectrophotometry. Naphthazarin (5,8-dihydroxy-1,4-naphthoquinone; Naph) was first introduced as a chromogenic reagent for the spectrophotometric determination of beryllium in manitol buffer pH 5 and 1,4-dioxane solvent by Underwood et al. [1–3]. Its capability of forming chelate polymers with some divalent metal ions including copper

ion has been studied [4–6] Agnihotri et al. [7,8] used this reagent for the determination of beryllium, aluminium, thorium and uranium in a micellar medium containing Triton X-100 and ammonium acetate. Acid–base characteristics of naphthazarin in 50% v/v ethanol/water medium have been studied by Idriss and Saleh [9]. They also used this reagent for the determination of yttrium. The successful separation of naphthazarin derivatives from plant pigments of the Boraginaceae family as copper complexes [10–13] raised the interest of the authors to use naphthazarin as a reagent for copper determination in a micellar medium. In our work, naphthazarin was used in a 50% v/v ethanol/water medium containing ammonium acetate pH 7 and sodium dodecyl sulfate

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(SDS) surfactant. In such a medium, selective determination of copper in alloy samples was developed. The solvent extraction step was ex-

cluded. The problems of poor water solubility of naphthazarin and precipitation of the complex were minimized.

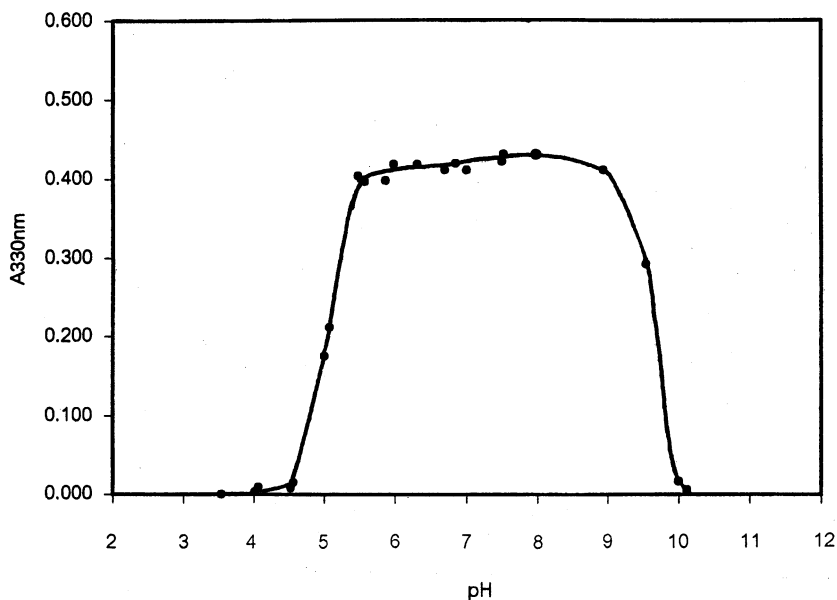


Fig. 1. Effect of pH on the absorbance at 330 nm of the Cu–Naph complex (2.0×10^{-5} Cu^{2+} + 1.0×10^{-4} M Naph) in 50% EtOH containing 0.1 M NH_4OAc and 1.5% SDS.

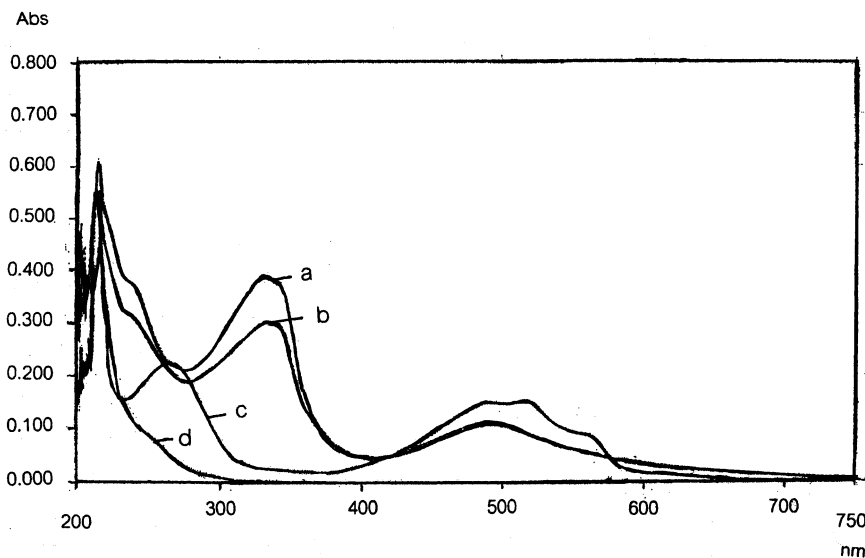


Fig. 2. Absorption spectra of solutions, (a) 6.0×10^{-5} Cu^{2+} + 6.0×10^{-5} M Naph, (b) 4×10^{-5} Cu^{2+} + 6.0×10^{-4} M Naph, (c) 6.0×10^{-5} M Naph, and (d) 6.0×10^{-5} M Cu^{2+} vs. the medium blank (50% EtOH containing 0.1 M NH_4OAc and 1.50% SDS).

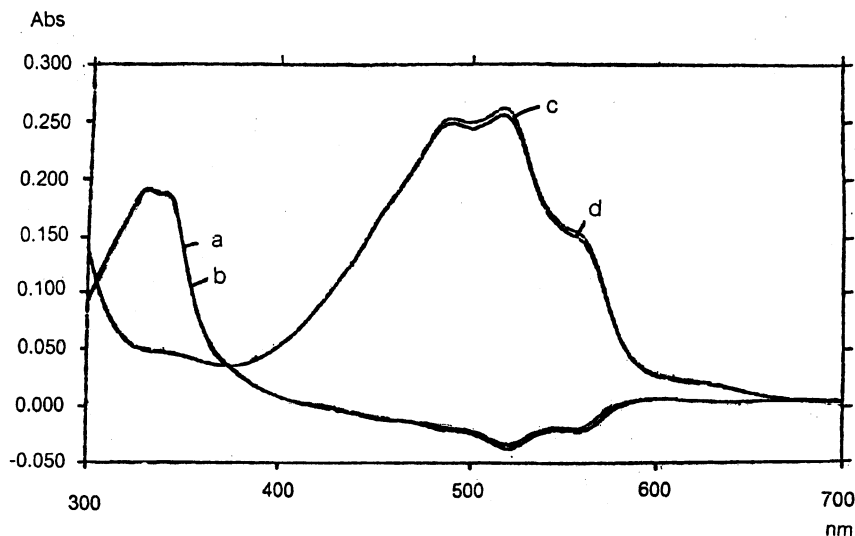


Fig. 3. Absorption spectra of (a) and (b) 2.0×10^{-5} Cu^{2+} – 1.0×10^{-4} M Naph in 50% EtOH containing 0.1 M NH_4OAc with and without 1.5% SDS, respectively; (c) and (d) 1.0×10^{-4} M Naph in the same media of (a) and (b), respectively. The solutions (c) and (d) were reagent blanks for (a) and (b) while their media were the blanks of their own spectra.

2. Experimental

2.1. Instruments

Absorption measurements were made on a Hitachi UV-3300 spectrophotometer using 1-cm quartz cells and 2-nm bandwidth with the reagent blank as a reference. The pH of the solutions was measured with a Mettler Toledo 320 pH meter and a combined glass electrode.

2.2. Reagents

All chemicals were of analytical grade unless otherwise specified. Deionized water and redistilled ethanol were used for preparation of the solutions. A stock naphthazarin solution (2.0×10^{-3} M) was prepared by dissolving an accurate amount of the reagent (98% purity, MERCK) in ethanol, and 2.0×10^{-4} M naphthazarin in ethanol was freshly prepared before use. A stock copper solution (1.0×10^{-2} M) was prepared from $\text{Cu}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$ in deionized water. More dilute solutions were obtained by dilution with appropriate concentrations of ammonium acetate and SDS solution to result in 0.1 M ammonium

acetate and 1.5% (w/v) SDS in the final measuring solution.

2.3. General procedure

An aliquot of standard or sample solution after acid digestion containing up to 90 mg of copper ion was added to the appropriate amount of ammonium acetate and SDS solutions to result in 0.2 M and 3.0% (w/v), respectively, in 10 ml. Then this solution was mixed with 10 ml of 2.0×10^{-4} M naphthazarin in ethanol before the absorbance was measured at 330 nm against the reagent blank prepared in the same way but without copper. In the presence of aluminium and/or iron interference, 2 ml of 4% (w/v) sodium fluoride was also added as a masking agent in the final solution.

2.4. Sample preparation for alloy samples

An accurate weight of 0.2 g of each alloy sample was treated with acid digestion as follows. Lead Bronze, 8 ml of 6 M HCl + 2 ml of 8 M HNO_3 was added to the sample and the mixture was boiled till the solution was clear. The volume was then adjusted to 50 ml before a further 100-

Table 1

Comparison of reagents for the spectrophotometric determination of copper(II)

Reagent ^a	Molar absorptivity, (l mol ⁻¹ .cm ⁻¹ , λ_{anal})	Extractant	Linear range (ppm)	Sample	Reference
DDTC	1.49×10^4 (436 nm)	CCl ₄	0.6–5.1	Cu alloy, industrial waste water	[10]
DDTC In SDS	1.37×10^4 (440 nm)	–			
DDTC In ADS	1.25×10^4 (434 nm)	–			
DDTC+ β -CD	1.3×10^4 (436 nm)	–	0–6	Al alloy, soil, millet, herbs, flour, vegetables	[17]
4-Me-BTAMB	3.1×10^4 (650 nm)	–	0.04–2	Al alloy	[18]
MBTAMB	7.0×10^4 (660 nm)	–	0–0.72	Al alloy	[19]
Cuprotest + Cl ₂ FICOOH	1.25×10^4 (530 nm)	–	0.3–9.5	Cu alloy	[20]
Bathophen + Cl ₂ FICOOH	5.03×10^5 (528 nm)	–	0.03–3.0	Limestone	[20]
NENA-BPO	1.72×10^5 (533 nm)	–	0–0.24	Flour	[21]
PA-FPQ	4.1×10^4 (590 nm)	–	0–1.0	Al alloy, bovine liver	[22]
H ₂ (enAA ₂)	1.3×10^3 (343 nm)	CHCl ₃	0–20	Cu alloy, pig feed	[23]
PAN In Triton X-100	5.21×10^4 (555 nm)	–	0.08–4.00	Alc. beverage, biological and alloy samples	[24]
Naph In SDS	1.84×10^4 (330 nm)	–	0.9–4.5	Cu alloy Zinc alloy	This Work

^a DDTC, diethyldithiocarbamate; SDS, sodium dodecylsulfate; ADS, ammonium dodecyl sulfate; β -CD, β -cyclodextrin; 4-Me-BTAMB, 2-[2-(4-methylbenzothiazolyl)azo]-5-dimethyl-aminobenzoic acid; MBTAMB, 2-[2'-(6-methyl-benzothiazolyl)azo]-4-dimethylaminobenzoic acid; Cuprotest, 2,3,8,9-dibenzo-4,7-diphenyl-5,6-dihydro-1,10-phenanthroline; Cl₂FICOOH, 2,7'-dichlorofluorescein; Bathophen, 4,7-diphenyl-1,10-phenanthroline; NENA-BPO, *N*-ethyl-2-naphthylamine-bezoylperoxide; PA-FPQ, poly[allylamine-co-*N*-4-(8-aminonquinolyl-5-azo)benzylideneallylamine]; H₂(enAA₂), bis(acetylacetone)ethylenediimine; PAN, 1-(2-pyridylazo)-2-naphthol; Naph, 5,8-dihydroxy-1,4-naphthoquinone.

fold dilution by the solution of 0.2 M ammonium acetate containing 3.0% (w/v) SDS. For Ni–Cu alloy, 10 ml of 8 M HNO₃ was added to the sample and the mixture was boiled till clear before the volume was adjusted to 50 ml, then a further 10-fold dilution was made by the solution of 0.2 M ammonium acetate containing 3.0% (w/v) SDS. For zinc base alloy, the weighed sample was first treated with 5 ml of 6 M HCl and gentle heating before 5 ml of 30% H₂O₂ was added. The solution was all clear before the volume was adjusted to 100 ml with the solution of 0.2 M ammonium acetate containing 3.0% (w/v) SDS. Each prepared sample (1 ml) solution was transferred into 9 ml of 0.2 M ammonium acetate containing 3.0% (w/v) SDS in a 20 ml volumetric flask before mixing with 10 ml of the naphthazarin reagent solution, and the absorbance measurement of the mixture was performed.

Table 2

Tolerance limits of the diverse ions in the determination of 2.0×10^{-5} M (1.3 ppm) Cu with naphthazarin that gave relative deviation of the results within $\pm 2\%$

Cation C	Mole ratio Cu ²⁺ :C	Anion A	Mole ratio Cu ²⁺ :A
Al ³⁺	1:50 ^a	Br [–]	1:3000
Be ²⁺	1:0.5	Cl [–]	1:7500
Ca ²⁺	1:70	F [–]	1:4800
Cd ²⁺	1:200	I [–]	1:3000
Co ²⁺	1:10	CN [–]	1:0.07
Cr ³⁺	1:0.01	SCN [–]	1:100
Fe ³⁺	1:50 ^a	PO ₄ ^{3–}	1:150
Mg ²⁺	1:200	Cr ₂ O ₇ ^{2–}	1:0.1
Mn ²⁺	1:50	EDTA	1:0.05
Ni ²⁺	1:3	Citrate	1:1
Pb ²⁺	1:100	Oxalate	1:1
Zn ²⁺	1:400	Tartrate	1:50

^a In the presence of 80 mg NaF.

Table 3
Determination of copper in reference alloy samples

Sample	Certified value of Cu (%)	Cu found (%), $\bar{X} \pm S$ ^a	Other components (%)
BCS number 364	80.6	83.0 \pm 2.2 ^b	Sn 9.35, Pb 9.25, Ni 0.28, Zn 0.13, Sb 0.18, P 0.056
Leaded bronze		79.7 \pm 1.6 ^c	
NBS number 882	31.02	31.37 \pm 0.74 ^b	Ni 65.25, Al 2.85, Ti 0.57, Fe 0.009, C 0.006, Si 0.006, S 0.0014, Mn 0.0007
Ni–Cu alloy		31.52 \pm 0.68 ^c	
NIST number 94c	1.01	1.01 \pm 0.01 ^b	Al 4.07, Mg 0.042, Fe 0.018, Mn 0.014, Pb 0.006, Ni 0.006, Sn 0.006, Cd 0.002, remainder is Zn
Zinc base alloy		1.03 \pm 0.03 ^c	

^a Results from five replications.

^b Results from five replications obtained by calibration graph.

^c Results from five replications obtained by standard addition technique.

3. Results and discussion

3.1. Effect of pH

The pH of the 50% v/v ethanol/water was varied by using acids, bases or buffers as the aqueous part before mixing with ethanol. Naphthazarin exhibits a red color with an absorption maximum at 515 nm in acidic media. The absorption maximum shifts to a longer wavelength at 600 nm in basic media. The Cu–Naph complex shows an intense absorption peak at 330 nm in the media of pH 5–7. The position of the absorption maximum of the Cu–Naph complex showed little difference between each medium of the same pH, but the sensitivity was different. In the above pH range, the forms of naphthazarin (LH₂) should be LH₂ and LH[−] according to the reported dissociation constants of pK₁ = 8.25 and pK₂ = 11.35 in the 50% v/v ethanol/water medium [9]. Among the media studied (HCl, HNO₃, H₂SO₄, HClO₄, HOAc, NaOH, NH₄OH, NaClO₄, NaOAc and NH₄OAc) at the same pH values, the Cu–Naph complex gave a higher absorbance in the medium containing ammonium acetate of pH 7, so this salt was used for further experiments. Using the solution of Cu–Naph with 1:5 mole ratio mixing, the concentration of ammonium acetate was varied. The absorbance of the complex at 330 nm increased with the concentration

of ammonium acetate and reached the maximum and remained constant in the wide range of 0.0005–0.4 M. The concentration of 0.1 M ammonium acetate in the measurement solution was chosen. In the presence of 1.5% (w/v) SDS, the effect of pH was studied by varying the pH of the ammonium acetate between 3.5–10.1 with acetic acid and ammonium hydroxide. The absorbance of the Cu–Naph complex in these media was maximum and constant in the pH range of 5.5–8.0 as in Fig. 1.

3.2. Effect of surfactant and stability of the complex

The stability of the Cu–Naph complex in the 0.1 M ammonium acetate, 50% v/v ethanol solvent depends on the mole ratio of naphthazarin/copper. When this ratio is below five, the absorbance decreased more than 2% after 10 min. Anionic micellar media of docetyl sulfate salts were used to eliminate the solvent extraction step in the determination of copper with the classical diethyldithiocarbamate reagent by San Andres, et al. [14]. In our work, addition of a surfactant was found to prolong the stability of the complex. SDS or Triton X-100 gave the same results. No significant increase of sensitivity or displacement of the maximum absorption wavelength was found in the presence of both surfactants and

SDS was selected for further study. The absorption spectra of Cu–Naph systems are shown in Figs. 2 and 3. However, for the ratio of naphthazarin/copper over ten times, without any surfactant, the absorbance of the complex remained constant over 2 h. Ten replicate measurements of the mixture (2.0×10^{-5} M Cu^{2+} and 1.0×10^{-4} M Naph; the mole ratio 1:5) in the presence of 1.5% SDS gave an average absorbance of 0.415 with a relative standard deviation of 0.82%. The presence of 1–2% of a surfactant keeps the absorbance constant for at least 15 min (absorbance deviation less than 2% within 15 min). Hence, all measuring solutions were adjusted to contain 1.5% of SDS

3.3. Effect of naphthazarin concentration

The absorbance at 330 nm of the solution containing various concentrations of naphthazarin (4.0×10^{-5} – 5.0×10^{-4} M) and a fixed amount of copper ion (2.0×10^{-5} M) in 0.1 M ammonium acetate and 50% v/v ethanol solvent gradually increased to a maximum and remained constant when the ratio of Cu:Naph reached 1:5 to 1:25. At higher concentrations of naphthazarin, the solution resulted in a dark red color and uncertainty due to the blank correction. Job's method indicated the ratio of Cu–Naph as being 4:6 in our medium. This could be because naphthazarin has been known as a potential binucleating ligand capable of forming stable polynuclear or binuclear chelates with bivalent ions and naphthazarin can act as a bridging unit between two metal-centers [15]. However, the ratio of Cu:Naph of the precipitated complex prepared in 50% EtOH was reported differently as being 3:4 by Bottei and Gerace [4]. It could be possible that polymerization of the complex would decrease in our medium. In subsequent experiments, at least five times of excess naphthazarin over the copper concentration was used wherever possible.

3.4. Analytical characteristics

Using the optimized conditions, a linear calibration graph was obtained up to 4.5 ppm ($7 \times$

10^{-5} M). The linear regression was $Y = 0.289X + 0.016$, $r = 0.998$. The apparent molar absorptivity of the complex was found to be $1.84 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ at 330 nm. The Sandell sensitivity was $0.004 \mu\text{g cm}^{-2}$. The detection limit and determination limit were statistically estimated [16] to be 0.3 and 0.9 ppm, respectively. Table 1 summarizes its characteristics in comparison with other reagents.

3.5. Interference

The effect of various cations and anions on the determination of 2.0×10^{-5} M copper ion was examined. The tolerance limits of various ions within relative errors of $\pm 2\%$ are shown in Table 2. Most of the cations examined with naphthazarin gave maximum absorption at about 610 nm. Only the Fe–Naph complex gave maximum absorption at the same position as Cu–Naph, but we found that interference from Fe^{3+} and Al^{3+} could be limited by adding NaF in the measuring solution. However, chromium ion was found to seriously interfere, so the determination of copper in chromium alloys was not feasible.

3.6. Application

The proposed method was applied to the determination of copper in reference alloy samples. The results obtained by using the calibration graph and standard addition techniques agreed well with the certified values as presented in Table 3.

4. Conclusion

In conclusion, we have developed a simple extraction-free method for the determination of copper in alloys and the sensitivity of which is comparable with other reagents as shown in Table 1. With a 1×10^{-4} M naphthazarin concentration in the measuring solution, the working range of copper determination is found to be 0.9–4.5 ppm of copper in 50% ethanol/water medium containing 0.1 M ammonium acetate and 1.5% (w/v) SDS.

Acknowledgements

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