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Spectrophotometric determination of iron and copper ions in industrial wastewater, cooling water and scale of power station

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ABSTRACT

Sensitive and selective spectrophotometric procedures were proposed for the determination of Fe(III) and Cu(II) using simple chromogenic reagents. The procedure of iron determination was based on the formation of ternary complex between Fe(III) and 4,7-diphenyl-1,10-bathophenanthroline (DPBP)–eosin in acid medium. On the other hand, the procedure of copper (II) determination was based on the formation of ternary complex between Cu(II) and 4,7-diphenyl-1,10-bathophenanthroline (DPBP)–Eriochrome Black-T (EBT) in alkaline medium. The ternary complexes were extracted in the presence of cetyltrimethyl ammonium bromide with chloroform. The molar absorptivities of the Fe(III)–DPBP–eosin and Cu(II)–DPBP–EBT ternary complexes were $2.23 \cdot 10^5$ and $9.35 \cdot 10^4\,\mathrm{L\,mol^{-1}\,cm^{-1}}$ at 542 and 565 nm, respectively. Beer's law is valid over the concentration ranges from 0.280 to 7.814 and from 0.320 to 8.260 $\mu\mathrm{g\,mL^{-1}}$ for Fe(III) and Cu(II), respectively. Sandell sensitivity (0.0025 and 0.0679 $\mathrm{ng\,cm^{-2}}$), relative standard deviation (0.257–1.94 and 0.305–1.85), limits of detection (0.076 and 0.045 $\mu\mathrm{g\,mL^{-1}}$) and quantification (0.253 and 0.150 $\mu\mathrm{g\,mL^{-1}}$) for Fe(III) and Cu(II) ions, respectively, are calculated. The procedures are applied for the determination of Fe(III) and Cu(II) in different polluted water sources, drinking water, river water as well as cooling water and boiler scales. The results obtained are compared with those obtained using atomic absorption spectroscopy. The effects of different tolerances are studied in the presence of masking agents.

Keywords: Iron and copper determination; Spectrophotometry; Water analysis; Boilers

1. Introduction

The recommended ASTM (ASTM Standards, 1982) spectrophotometric method for iron determination in water was based on its reaction with 1,10-phenanthroline [ε (510 nm) = $1.1 \cdot 10^4\,\mathrm{L\,mol^{-1}\,cm^{-1}}$]. However, some metal ions and anions interfered when present in considerable excess. Moreover, bathophenanthroline reacted with Fe(II) to form a springy soluble complex extractive in ethanol–chloroform or isopentyl alcohol

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[1]. The selectivity of this method was similar to that of 1,10-phenanthrolene with twice the sensitivity [ε (530 nm) = $2.24 \cdot 10^4\,\mathrm{L\,mol^{-1}\,cm^{-1}}$]. Tetlow and Wilson [2] adapted the bathophenanthroline method to determine iron in water. Recently, the sensitivity of the spectrophotometric methods for iron determination had been markedly improved using surfactants and micellar systems [3–21], or by forming ion-association complexes. Copper also could be determined by spectrophotometric methods [22–33].

However, some of these methods lacked selectivity or required close control of experimental conditions [34,35]. The present work reports an extraction–spectrophotometric method for Fe(III) determination after its reduction to iron(II) with hydroxylamine hydrochloride using 4,7-diphenyl-1,10-bathophenanthroline as a primary ligand and eosin as the counterion in the presence of cetyltrimethyl ammonium bromide (CTAB) surfactant. The ternary complex is thermostated at 45˚C for 25 min and extracted into chloroform and the absorbance is measured at the selected wavelength. On the other hand, an extraction-spectrophotometric method for Cu(II) determination using 4,7-diphenyl-1,10-bathophenanthroline as a primary ligand (DPBP) and Eriochrome Black-T (EBT) as the secondary ligand in the presence of CTAB surfactant was suggested. The ternary complex is thermostated at 50˚C for 45 min and extracted into chloroform and the absorbance is measured at the selected wavelength. A highly sensitive method for the determination of copper (II) based on the formation of Cu(II)–DPBP–EBT ternary complex is established.

We suggested simple, rapid and reliable spectrophotometric methods for the determination of iron and copper ions in different types of water with friendly available reagents. The methods are based on ternary complexes formation of Fe(III) and Cu(II) with DPBP–eosin and DPBP–EBT in the presence of micellar medium of CTAB, respectively. The developed procedure is highly sensitive, fairly selective and has the advantage of being convenient for general laboratory use and applied to determine Fe(III) and Cu(II) in industrial polluted water, river water, boiler feed water and boiler scales water for electrical power stations, alloys and drinking water.

2. Experimental

2.1. Materials

Iron chloride hexahydrate, 4,7-diphenyl-1,10-bathophenanthroline (DPBP), eosin (sodium salt), hydroxylamine hydrochloride, disodium salt of ethylenediamine tetraacetic acid (EDTA), hydrochloric and nitric acids were supplied from Aldrich. Absolute ethanol and sodium hydroxide were supplied from Adwic. Copper(II) chloride dihydrate, EBT, borax, sodium fluoride, disodium hydrogen phosphate, sodium sulphate and sodium bromide were supplied from Merck. Potassium cyanide, potassium iodide, cerium sulphate, sodium oxalate, sodium citrate, ammonium chloride, potassium nitrate, nickel perchlorate, stronsium chloride, barium chloride, calcium chloride, sodium thiosulphate, sodium bromide, sodium chloride, hydrogen peroxide, sodium tartarate, chromium chloride hexahydrate, sodium dihydrogen phosphate and oxalic acid were supplied from Egyptian Co. for Chemicals. Chloride salts of cadmium, arsenic, manganese, cobalt, aluminium, nickel, zinc, iron and molybdenum were also used and supplied from Egyptian Co. for Chemicals. While n-propanol and acetonitrile (AR) were supplied from Aldrich. Carbon tetrachloride, chloroform, methanol, acetone, benzene, toluene, xylene, diethyl ether, cyclohexane, petroleum ether, 1,4-dioxane, n-butanol, methylene chloride, dimethyl formamide and acetic acid were supplied from El-Nasr company.

Cationic surfactants of CTAB, cetylpyridinium-chloride (CPC) and anionic surfactants of sodium laurylsulphate (SLS) and sodium alkyl-benzene sulphate (SABS) were supplied from Aldrich. Non-ionic surfactants of polyoxyethylene-p-tert-octylphenol (Triton X-100), polyoxy-ethylene (20) sorbitan monostearate (Tween 60) and polyoxyethylene (20) sorbitan (Tween 80) were supplied also from Aldrich. Protective colloids like gelatin were supplied from Aldrich.

2.2. Reagents

All chemicals were of analytical reagent grade and bidistilled water was used throughout. Fe(III) standard solution, $1 \cdot 10^{-2}\,\mathrm{mol\,L^{-1}}$, is prepared by dissolving 1.2055 g of $FeCl_3{\cdot}6H_2O$ in 250 mL of $1.00\,\mathrm{mol\,L^{-1}}$ HNO_3. Cu(II) standard solution, $1 \cdot 10^{-2}\,\mathrm{mol\,L^{-1}}$, is prepared by dissolving 0.3951 g of $CuCl_2{\cdot}2H_2O$ in 250 mL of $1.00\,\mathrm{mol\,L^{-1}}$ nitric acid. Working solutions were prepared by appropriate dilutions.

About 0.1% (w/v) solution of 4,7-diphenyl 1,10-bathophenanthroline (DPBP) was prepared by dissolving 100 mg in 100 mL absolute ethyl alcohol. 0.1% (w/v) Solutions of eosin and EBT were prepared by dissolving the accurate weighed amount of 100 mg in 100 mL double-distilled water, and Ten percentage (w/v) solution of hydroxylamine hydrochloride was prepared by dissolving the accurate weight of 10 g of the substance in 100 mL double-distilled water. CTAB, $1 \cdot 10^{-2}\,\mathrm{mol\,L^{-1}}$, was prepared by dissolving 0.3642 g in 100 mL double-distilled water. Working solutions were prepared by appropriate dilutions. Acetate buffer was prepared by adjusting the pH of 0.40 mol L^{-1} of acetic acid with 1.00 mol L^{-1} sodium hydroxide to the desired value. Oxalate buffer was prepared by adjusting the pH of 0.20 mol L^{-1} of oxalic acid with 1.00 mol L^{-1} sodium hydroxide to the desired value.

2.3. Apparatus

A Perkin–Elmer Lambda 3B spectrophotometer fitted with Perkin–Elmer PECSS software, equipped with a 1 cm quartz cell and interfaced to a PC was used for absorption measurement. A Janco Electronic Ltd digital pH meter with combined glass/calomel electrode is used to measure the pH values.

A Perkin–Elmer Model 5000 atomic-absorption spectrometer utilizing an air-acetylene flame and equipped with iron and copper hollow-cathode lamps operating at 248.3 and 324.7 nm, respectively, was used for the standard determination of these elements under study.

2.4. Procedures

2.4.1. Stoichiometric ratio of the ion association complexes formed

The stoichiometry of the ternary complexes formed was examined by applying molar ratio and continuous variation methods [36,37].

2.4.1.1. The continuous variation method. A series of solutions were prepared by mixing different volumes (0.10–0.90 mL) of Fe(III) ($2 \cdot 10^{-5}$ mol L^{-1}) with 1.0–2.0 mL of (10% w/v) hydroxylamine hydrochloride, 0.50 mL of $2 \cdot 10^{-5}$ mol L^{-1} eosin and 5.00 mL of (10% w/v) sodium acetate buffer solution (pH 4.5) were added. After 10 min, 0.90–0.10 mL of $2 \cdot 10^{-5}$ mol L^{-1} DPBP solutions was added, so that the total number of moles is kept constant. The mixture was thermostated in water bath at 40˚C for 20 min. The same procedure was followed by keeping DPBP constant (0.50 mL) and varying the volume of eosin (0.90–0.10 mL). The absorbance data obtained were plotted against mole fraction of Fe(III) ions.

A series of solutions were prepared by mixing different volumes (0.10–0.90 mL) of Cu(II) ($2 \cdot 10^{-5}$ mol L^{-1}) with 0.50 mL of $2 \cdot 10^{-5}$ mol L^{-1} DPBP and 5.00 mL of (10% *w/v*) oxalate buffer solution (pH 10.2). After 10 min, 0.90–0.10 mL of $2 \cdot 10^{-5}$ mol L^{-1} EBT solution was added, so that the total number of moles was kept constant. The same procedure was followed with keeping EBT constant (0.50 mL) and varying the volume of DPBP (0.90–0.10 mL). The absorbance data obtained were plotted against mole fraction of Cu(II) ions.

2.4.1.2. Molar ratio method (MRM). About 2.00 mL of $2 \cdot 10^{-5}$ mol L^{-1} Fe(III) solution was put in a 25.00 mL calibrated measuring flask with 1.00–2.00 mL of (10% *w/v*) hydroxylamine hydrochloride, 1.00 mL of $2 \cdot 10^{-5}$ mol L^{-1} eosin and 5 mL of (10% *w/v*) sodium acetate buffer solution (pH 4.5). Different volumes of $2 \cdot 10^{-5}$ mol L^{-1} of DPBP solution ranged from 0.25 to 2.00 mL and the procedure was completed as described above. The same procedure was carried out by adding different volumes that ranged from 0.15 to 1.00 mL of $2 \cdot 10^{-5}$ mol L^{-1} Fe(III) solution with 1.00–2.00 mL of (10% *w/v*) hydroxylamine hydrochloride, 1.00 mL of $2 \cdot 10^{-5}$ mol L^{-1} DPBP and 5.00 mL of (10% *w/v*) sodium acetate buffer solution (pH 4.5). After 10 min, different volumes of $2 \cdot 10^{-5}$ mol L^{-1} eosin ranged from 0.25 to 2.00 mL was added. The procedure was completed as described above and the absorbance was plotted against the ratio of reactants.

About 2.00 mL Of $2 \cdot 10^{-5}$ mol L^{-1} Cu(II) solution was put in a 25.00 mL separating funnel and 5.00 mL of (10% *w/v*) oxalate buffer solution (pH 10.2) and 1.00 mL of DPBP ($2 \cdot 10^{-5}$ mol L^{-1}) were added. After 10 min, different volumes (0.25–2.00 mL) of $2 \cdot 10^{-5}$ mol L^{-1} of DPBP were added and the procedure was completed as described above. The same procedure was carried out by mixing 2.00 mL of $2 \cdot 10^{-5}$ mol L^{-1} Cu(II) solution with 1.00 mL of $2 \cdot 10^{-5}$ mol L^{-1} EBT and 5.00 mL of (10% *w/v*) oxalate buffer solution (pH 10.2). After 10 min, different volumes (0.25–2.00 mL) of $2 \cdot 10^{-5}$ mol L^{-1} DPBP were added and the procedure was completed as described above. The absorbance was plotted against the ratio of reactants.

2.4.2. Determination of Fe(III) with DPBP and eosin

An aliquot of the sample solution containing 0.28 μg Fe(III) was treated with 1.0 mL of (10% *w/v*) hydroxyl amine hydrochloride solution as reducing agent and 5.00 mL of (10% *w/v*) sodium acetate buffer solution (pH 3.6–5.2). After 10 min, 1.00 mL of (0.1% *w/v*) DPBP solution, 1.00 mL (0.1% *w/v*) eosin and 2.00 mL of $1 \cdot 10^{-2}$ mol L^{-1} CTAB were added. The mixture was thermostated at 40˚C for 20 min and then transferred to 25.00 mL separatory funnel. Extraction was achieved by shaking vigorously with 5.00 mL of chloroform for 2–3 min. The organic layer was separated and centrifuged at 3,000 rpm for 2 min and dried over Na_2SO_4, then its absorbance was measured at 542 nm against a reagent blank prepared in the same way but without adding Fe(III).

2.4.3. Determination of Cu(II) with DPBP and EBT

Transfer an aliquot sample solution containing 0.32 µg Cu(II) into flask. About 1.0 mL of (0.1% *w*/*v*) DPBP solution and 5.0 mL of (10% *w*/*v*) oxalate buffer solution (pH 9.5–11.2) were added. After 5 min, 0.80 mL of (0.1% *w*/*v*) of EBT solution was added followed by 2.00 mL of $1 \cdot 10^{-2}$ mol L^{-1} CTAB. The mixture was thermostated at 50˚C for 45 min and transferred to a 25 mL separatory funnel. Extraction was achieved by shaking vigorously with 5.00 mL of chloroform for 2–3 min. The organic layer was separated and centrifuged at 3,000 rpm for 2 min and dried over Na_2SO_4, and then its absorbance was measured at 565 nm against a reagent blank prepared in the same way.

2.4.4. Spectrophotometric determination of Fe(III) and Cu(II) in water and polluted water samples

The analysed water samples were obtained from different locations in Egypt. The ASTM [38] procedure for water sampling was followed. The samples were collected in acid-rinsed bottles and the samples were preserved by acidification with concentrated nitric acid. The samples were then stored in refrigerator at approximately 4˚C. The preserved samples were digested in the digestion vessel using the microwave unit in order to convert metal associated with particulate to the form of free metal ions. Aliquots of the solutions were analysed by the developed procedure for Fe(III) and Cu(II) determination using DPBP and eosin or DPBP and EBT. In case of Fe(III) ion determination, 0.20 mL of $1{\cdot}10^{-2}$ mol L^{-1} EDTA was added for masking of Cd(II), Mn(II), Co(II), Al(III), Cu(II), Ni(II), Zn(II) and Mo(VI) ions. While in case of Cu(II) ion determination, 0.20 mL of 0.10 mol L^{-1} sodium fluoride (masking of Fe(III), Al(III)), 0.20 mL of 0.50 mol L^{-1} sodium bromide, 0.20 mL of 0.10 mol L^{-1} potassium iodide and 0.50 mL of 0.20 mol L^{-1} potassium hydrogen phosphate as masking agents were added to prevent interference action of the diverse ions.

2.4.5. Spectrophotometric determination of Fe(III), Cu (II) in boiler scale and Cu(II) in different alloy samples

The proposed procedure was also utilized to determine Fe(III) and Cu(II) ions in boiler scale and Cu(II) in different alloy samples. The sample was treated with aquaregia, boiled gently and then evaporated to dryness. The residue was dissolved in 50.00 mL of hydrochloric acid (1:1 *v*/*v*), filtered if necessary and diluted to 500 mL. Fe(III) and Cu(II) were determined in aliquots of this solution by the developed procedure in the presence of 0.2 mL of $1 \cdot 10^{-2}$ mol L^{-1} EDTA or 0.20 mL of 0.10 mol L^{-1} sodium fluoride, 0.20 mL of 0.50 mol L^{-1} sodium bromide, 0.20 mL of 0.10 mol L^{-1} potassium iodide and 0.50 mL of 0.20 mol L^{-1} potassium hydrogen phosphate, respectively, as masking solutions to prevent interference of the diverse ions.

3. Results and discussion

3.1. Absorption spectra

The absorption spectra of the extracted Fe(III)-DPBP–eosin and Cu(II)–DPBP–EBT ternary complexes in the presence and absence of surface active material (CTAB), along with that of its reagent blank are shown in Figs. 1 and 2, respectively. Curve 1 in Figs. 1 and 2 shows an absorption maxima of Fe(III)–DPBP–eosin and Cu(II)–DPBP–EBT at 542 and 565 nm, in the presence of CTAB, respectively. Whereas curve three in Figs. 1 and 2 shows an absorption maxima of Fe (III)–DPBP–eosin and Cu(II)–DPBP–EBT ternary complexes at 542 and 520 nm, in the absence of CTAB, respectively. Consequently, absorbance measurements in the absence of CTAB are referred to the reagent blank.

3.2. Influence of experimental conditions

The optimum experimental conditions for the determination of Fe(III) and Cu(II) are illustrated in Table 1.

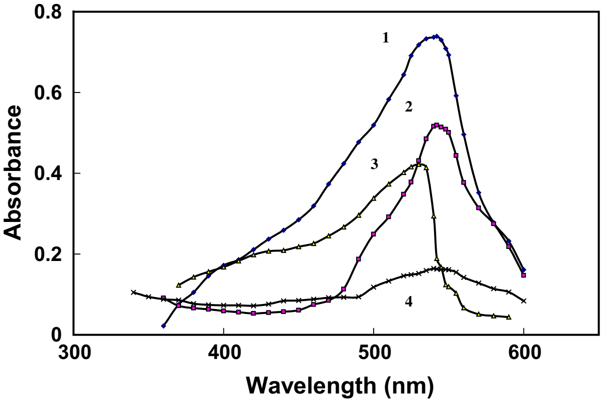

Fig. 1. Absorption spectra of Fe(III)–DPBP–eosin in the presence and absence of CTAB.
Notes: (1) Fe(III)–DPBP–eosin complex in the presence of CTAB, (2) DPBP–eosin reagent blank in the presence of CTAB, (3) Fe(III)–DPBP–eosin complex in the absence of CTAB, (4) DPBP–eosin reagent blank in the absence of CTAB.

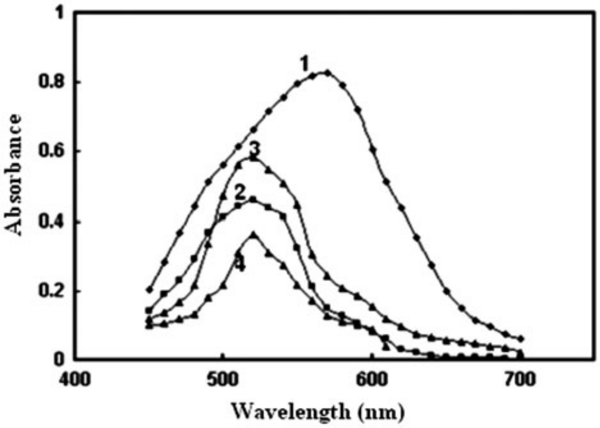

Fig. 2. Absorption spectra of Cu(II)–DPBP–EBT in the presence and absence of CTAB.

Notes: (1) Cu(II)–DPBP–EBT complex in the presence of CTAB, (2) DPBP–EBT blank in the presence of CTAB, (3) Cu(II)–DPBP–EBT complex in the absence of CTAB, (4) DPBP–EBT blank in the absence of CTAB.

Table 1

Optimum conditions procedure for the determination of Fe (III) and Cu(II)

Fe(III) DPBP–eosin			Cu(II) DPBP–EBT		
pH	Reagents conc. (*w*/*v*)%		pH	Reagents conc. (*w*/*v*)%	
	DPBP	Eosin		DPBP	EBT
3.6–5.2	0.1	0.1	9.5–11.2	0.1	0.1

3.2.1. Effect of pH, temperature and time

The optimum pH ranges for the formation of Fe (III)–DPBP–eosin and Cu(II)–DPBP–EBT ternary complexes were 3.60–5.20 and 9.50–11.20, respectively. In recommended procedures for the determination of Fe (III) with DPBP–eosin and Cu(II) with DPBP–EBT, pH 4.50 and 10.20 adjusted with acetate and oxalate buffer were selected, respectively. It is found that the absorbance values of the extracted ternary complexes increases till pH 4.50 (in case of Cu(II)) and 10.20 (in case of Fe(III)) and then decreases with further increase in the pH. Thus in the recommended procedures, acetate and oxalate buffer solutions were recommended for the subsequent studies. Before extraction, the pH was rechecked again and adjusted with NaOH solution.

It is found that, the absorbance of the extracted ternary complexes in chloroform increases by increasing the temperature from 5 to 40˚C and from 10 to 50˚C for Fe(III)–DPBP–eosin and Cu(II)–DPBP–EBT, respectively. Above this temperature, lightening in colour of the ternary complexes is observed and the absorbance is slowly decreased.

Moreover, the influence of time on the formation of ternary complexes is studied. The absorbance is measured at regular intervals of time. The absorbance of the ternary complex increases with increasing time till 20 and 45 min for Fe(III)–DPBP–eosin and Cu(II)-DPBP–EBT, respectively, and then decreases with increasing time.

3.2.2. Effect of reagents concentration

Fe(III) reacts with DPBP and eosin to form ternary complex and their effect on the Fe(III)–DPBP–eosin complex formation has been studied. It is found that the absorbance of the ternary complex is maximum in the presence of 1.0 mL of DPBP (0.10%), and eosin (0.10%) and hence recommended for the next studies.

The influence of DPBP and EBT concentrations on the formation of their Cu(II) ternary complex is studied. The absorbance of the ternary complex has maximum reading in the presence of 1.0 mL of DPBP and EBT, and hence recommended for the next studies.

3.2.3. Effect of surfactants

Studies on the influence of a cationic, anionic and non-ionic surfactants as well as protective colloids on the spectral characteristic of the associated complexes of Fe(III) and Cu(II) were investigated (Table 2). Sensitivity of the colour reactions were increased by addition of cationic surfactants. Maximum enhancement of the absorbance of Fe(III)–DPBP–eosin and Cu(II)–DPBP–EBT ternary complexes were obtained in the presence of the CTAB cationic surfactant (Table 2). Moreover, the influences of CTAB concentration ($1 \cdot 10^{-2}$ to $1 \cdot 10^{-6}$ mol L^{-1}) on the absorbance of the coloured Fe(III) and Cu(II) complexes were studied and the data obtained revealed that the maximum absorbance was obtained in the presence of $1 \cdot 10^{-2}$ mol L^{-1} CTAB in this current study. Also the effect of adding different volumes of $1 \cdot 10^{-2}$ mol L^{-1} CTAB solution is studied in order to select the suitable volume capable of solublizing the ternary complex (Fig. 3). The data obtained show that 8% of $1 \cdot 10^{-2}$ mol L^{-1} CTAB relative to the total volume is sufficient for complete solublizing the ternary complexes. For the procedures based on the formation Fe(III)–DPBP–eosin and Cu(II)–DPBP–EBT in the presence of CTAB, complete colour development was obtained after thermostated for 20 min at 40˚C and 45 min at 50˚C on the formation of ternary complexes of Fe (III)–DPBP–eosin and Cu(II)-DPBP-EBT, respectively. The sensitized complexes have an increase in the

Table 2
Influence of surfactants and protective colloids on the absorbance of Fe(III)–DPBP—eosin and Cu(II)–DPBP–EBT complexes

		Fe(III) DPBP –eosin		Cu(II) DPBP-EBT	
Surfactant or protective colloid	Type	Absorbance	ε (L mol^{-1} cm^{-1})	Absorbance	ε (L mol^{-1} cm^{-1})
CTAB	Cationic	0.891	$2.23 \cdot 10^5$	0.935	$9.35 \cdot 10^4$
CPC	Cationic	0.414	$5.17 \cdot 10^4$	0.621	$6.21 \cdot 10^4$
SLS	Anionic	0.269	$3.36 \cdot 10^4$	0.334	$3.34 \cdot 10^4$
SABS	Anionic	0.191	$2.38 \cdot 10^4$	0.221	$2.21 \cdot 10^4$
Triton X-100	Nonionic	0.411	$5.14 \cdot 10^4$	0.366	$3.66 \cdot 10^4$
Tween 80	Nonionic	0.289	$3.61 \cdot 10^4$	0.278	$2.78 \cdot 10^4$
Tween 60	Nonionic	0.306	$3.82 \cdot 10^4$	0.338	$3.38 \cdot 10^4$
Gelatin	Protective colloid	0.080	$1.00 \cdot 10^4$	0.107	$1.07 \cdot 10^4$

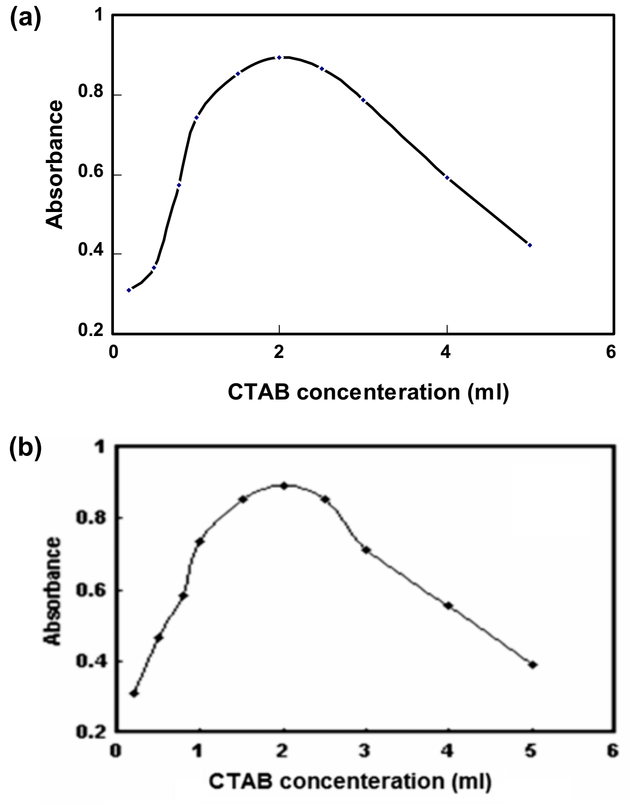

Fig. 3. Effect of CTAB ($1 \cdot 10^{-2}$ mol L^{-1}) concentration by (volume) on the formation of (a) Fe(III)–DPBP–eosin and (b) Cu(II)–DPBP–EBT ternary complexes.

absorbance value at maximum wavelength of 542 and 565 nm for Fe(III) and Cu(II) procedures.

3.2.4. Effect of organic solvents

Several organic solvents (benzene, toluene, xylene, carbon tetrachloride, diethyl ether, 1,4-dioxane, cyclohexane, petroleum ether and n-propanol) were found to be of no use for the extraction of the ternary complexes of Fe(III)–DPBP–eosin and Cu(II)–DPBP–EBT, which either formed at the interface between the aqueous and organic layers or is incompletely extracted. Extraction was quantitative in chloroform as a solvent. Shaking for 2–8 min gives the same absorbance; shaking for 3 min was selected as the recommended procedures for the determination of Fe(III) and Cu(II). A repeated extraction of an aqueous solution of the Fe (III) and Cu(II) complexes shows that 99.2 and 98.4% formed with 2.8 and 3.2 μg of Fe(III) and Cu(II), respectively, were removed in one extraction step with 2 mL of $1 \cdot 10^{-2}$ mol L^{-1} CTAB and 5 mL chloroform.

3.3. Stoichiometry

The selection of most suitable ratio from Fe(III) interacted with DPBP and eosin is examined at pH 4.5 and 40°C for 20 min using molar ratio and continuous variation methods. Both molar ratio and continuous variation methods exhibit two linear portions intersected at 1:1:1 [Fe(III):DPBP:eosin] ratio.

The selection of most suitable ratio from Cu(II) interacted with DPBP and EBT mixed reagent is examined at pH 10.2 and 50°C for 45 min. The results obtained applying both molar ratio and continuous variation methods exhibit two linear portions intersected at 1:1:1 [Cu(II):DPBP:EBT] ratio.

3.4. Calibration graphs and statistical treatment of the experimental data

In Table 3 the analytical parameters and the most characteristic statistical data obtained from the different calibration curves are summarized. The molar absorptivity of Fe(III)–DPBP–eosin and Cu(II)–DPBP–EBT in a micellar medium of CTAB, as calculated

Table 3
Performance characteristics of the developed analytical method for the determination of Fe(III) and Cu(II) ions

Parameters Reagent	Fe(III) DPBP–eosin	Cu(II) DPBP–EBT
Beers law limit (μg mL^{-1})	0.28–7.81	0.32–8.26
Maximum wavelength ($\lambda_{\max}$)	542	565
Molar absorptivity ($\mathrm{L\,mol^{-1}\,cm^{-1}}$)	$2.23 \cdot 10^5$	$9.35 \cdot 10^4$
Sandell's sensitivity ($\mathrm{ng\,cm^{-2}}$)	0.0025	0.0679
Correlation coefficient (r^2)	0.924	0.915
Intercept (a)*	0.11	0.12
Slope (b)	0.885	0.93
SD (n = 10)	0.0015–0.0045	0.002–0.005
RSD (%)	0.257–1.94	0.305–1.85
Detection limit, D_L (μg mL^{-1})$^\#$	0.076	0.045
Quantitation limit, Q_L (μg mL^{-1})$^\#$	0.253	0.150

$^*Y = bx + a$ where x is the concentration μg mL^{-1}.

$^\#D_L$; 3.3 σ/S = lower detection limit, Q_L; 10 σ/S = Quantitation limit, σ SD of the blank, S slope of the regression equation.

SD = standard deviation of 0.28 μg mL^{-1} Fe(III) and 0.32 μg mL^{-1} Cu(II) (number of replicates; n = 10).

from the slopes of regression equation were $2.23 \cdot 10^5$ and $9.35 \cdot 10^4\,\mathrm{L\,mol^{-1}\,cm^{-1}}$ at 542 and 565 nm, respectively. The linear dynamic range for the determination of Fe(III) with DPBP–eosin was 0.280–7.814 μg mL^{-1}. The corresponding range for determination of Cu(II) with DPBP–EBT was 0.320–8.260 μg mL^{-1}. The Sandells sensitivity [39] of Fe(III)–DPBP–eosin and Cu(II)–DPBP–EBT ternary complexes were 0.00251 and 0.0679 μg cm^{-2}, respectively.

The precision of the methods for Fe(III) and Cu(II) determinations with DPBP–eosin and DPBP–EBT reagents were calculated using ten identical samples containing 0.28 and 0.32 μg mL^{-1} of Fe(III) and Cu(II), respectively. Determination of 0.280 μg mL^{-1} Fe(III) using a procedure DPBP–eosin reagent, the standard deviation (SD) and the detection limit values are found to be 0.0015–0.0045 and 0.076 μg mL^{-1}, respectively. In addition, the SD and detection limits values are found to be 0.002–0.005 and 0.045 μg mL^{-1}, respectively, for the determination of 0.32 μg mL^{-1} of Cu(II).

3.5. Effect of foreign ions

The selectivity of the proposed methods has been investigated. Table 4 shows the tested ions and their tolerance limits. The tolerance limit was taken as the amount that caused ±2% error in the absorbance (Table 4). Some masking agents have been used to improve the selectivity of the method. In the determinations of Fe(III) with DPBP–eosin and Cu(II) with DPBP–EBT, addition of 0.2 mL of $1 \cdot 10^{2-}\,\mathrm{mol\,L^{-1}}$ EDTA and 0.2 mL of 1.0 $\mathrm{mol\,L^{-1}}$ sodium fluoride in case of Fe(III) and 0.2 mL of 0.5 $\mathrm{mol\,L^{-1}}$ sodium bromide, 0.2 mL of 0.1 $\mathrm{mol\,L^{-1}}$ potassium iodide and 0.5 mL of 0.2 $\mathrm{mol\,L^{-1}}$ sodium dihydrogen phosphate in case of Cu(II) were used as masking solutions to improve the selectivity of the proposed methods.

3.6. Determination of iron and copper ions

Mining of copper ore affects the environment, in many negative ways. Firstly, it uses land, so animals and plants are usually moved or plowed over. This usually means that there are less trees, as most copper reserves are in dense rainforests; resulting in an increase in the amount of carbon dioxide in the air, and a lower composition of oxygen. Also, there is a higher chance that animals and plants indigenous to these areas will become endangered or extinct. Furthermore, refining copper uses a lot of energy, usually coming from the burning of fossil fuels, meaning that a lot of carbon dioxide will be given off, as well as other dangerous pollutants. These chemicals can often cause acid rain; damaging crops, animals (including livestock) and humans. Iron is the most general, commonplace and conspicuous metal in our home life. The need for iron analysis in environmental, polluted water and material has been increased after reports on the different roles of Fe(III) and Fe(II) species in water, plants, animals and humans were evaluated.

The addition of different masking agents helps in improving the selectivity of the method where the per cent recovery values increased valuably.

It is found that maximum absorbance reading is obtained in the presence of 1.0 mL of 10% (w/v) hydroxylamine hydrochloride. Therefore, it is added

Table 4
Effect of co-existing ions on the determination of 0.28 μg mL^{-1} Fe(III) and 0.32 μg mL^{-1} Cu(II)

Ions added	Tolerance limit [Ion]/[Fe(III)]	[Ion]/[Cu(II)]
F$^-$	2,500	>3,500
Oxalate, Tartrate, CN$^-$	2000	2,500
Citrate, NH_4^+, Na$^+$, K$^+$, NO_3^-, PO_4^{3-}	1,000	2000
Ce^{3+}, ClO_4^-, Sr^{2+}	600	1,500
Ba^{2+}, Ca^{2+}, As^{5+}	500	1,000
$S_2O_3^2-$, I$^-$, Br$^-$, Cl$^-$	300	800
H_2O_2	100	150
Cd^{2+}, Mn^{2+}, Co^{2+}, Al^{3+}, Cu^{2+}, Ni^{2+}, Zn^{2+} Fe^{3+}, Mo^{6+}	100[a]	100[b]

[a] 0.2 mL of 0.01 M EDTA as masking solution is added.

[b] 0.2 mL of 1.0 M sodium fluoride + 0.2 mL of 0.5 M sodium bromide + 0.2 mL of 0.2 M potassium iodide + 0.5 g of 0.2 M potassium hydrogen phosphate as masking solution is added.

to the water samples before determination of Fe(III) in order to reduce Fe(III) to Fe(II), and hence determination of total iron. Thus an optimum condition of 1.0 mL of 10% (*w*/*v*) hydroxylamine hydrochloride is recommended for the next studies. Total iron has been successfully determined with DPBP–eosin reagent in cooling water, boiler scale of power stations, industrial wastewater, drinking water and Nile River water samples. The results obtained for total iron determination in cooling water for power stations; industrial wastewater, drinking water and river water by the suggested procedures along with standard atomic absorption spectrometric method [38] are given in Table 5. Moreover, the developed procedure for Cu(II)

Table 5
Determination of iron and copper in different types of industrial polluted water, boiler feed water, boiler scale of electrical power station, river nile water, drinking water and determination of copper in different alloys samples

	Fe(III), μg mL^{-1} DPBP–eosin			Cu(II), μg mL^{-1} DPBP–EBT			AAS, μg mL^{-1}	
Sample	Found	SD	RSD %	Found	SD	RSD %	Fe(III)	Cu(II)
Industrial waste water (October city)	0.988	0.002	0.197	0.780	0.020	2.146	0.981	0.730
Industrial waste water (10th Ramadan city)	1.232	0.029	2.340	0.690	0.005	0.676	1.228	0.720
Industrial waste water (Alexandria city Z2)	1.655	0.022	1.465	0.580	0.003	0.438	1.599	0.550
Industrial waste water (Alexandria city Z4)	0.994	0.025	2.526	0.920	0.005	0.581	0.999	0.890
Industrial waste water (Bader city)	1.477	0.023	1.562	0.880	0.006	0.732	1.467	0.860
Boiler feed cooling water U2 (Damanhoor power station)	0.611	0.013	2.105	0.051	0.006	9.725	0.601	0.054
Boiler feed cooling water U2 (Cyoof power station)	0.244	0.009	3.861	0.066	0.003	3.708	0.240	0.064
Boiler feed cooling water U1 (Abusultan power station)	0.673	0.019	2.961	0.073	0.003	3.893	0.668	0.077
Boiler feed cooling water U2 (Assuit power station)	0.348	0.002	0.615	0.044	0.004	8.794	0.342	0.047
Boiler feed cooling water U2 (Cairo west power station)	0.168	0.003	2.137	0.082	0.005	5.784	0.160	0.079
Boiler scale U2 (Damanhoor power station)	0.645	0.005	1.543	0.410	0.004	0.992	0.649	0.430
Boiler scale U2 (Cyoof power station)	0.456	0.003	0.811	0.560	0.007	1.305	0.501	0.530
Boiler scale U2 (Abu sultan power station)	0.711	0.004	0.589	0.580	0.004	0.793	0.718	0.600
Boiler scale U2 (Cairo west power station)	0.557	0.003	0.514	0.380	0.004	0.998	0.561	0.350
River–Nile water	0.751	0.025	3.268	0.860	0.004	0.511	0.747	0.820
Drinking water	0.246	0.015	5.689	0.060	0.004	0.729	0.241	0.063
Alloy steel (233)	–	–	–	5.040	0.094	1.090	–	5.000
Alloy steel (266)	–	–	–	3.300	0.046	1.430	–	3.280
Aluminum alloy (216/1)	–	–	–	4.380	0.063	1.470	–	4.310

Table 6
Comparison of the sensitivities of the spectrophotometric methods for the determination of Fe(III)

Reagent, Conditions	Conditions	λ_{max} (nm)	ε (L mol^{-1} cm^{-1})	Linear range (µg mL^{-1})	Remarks	Ref.
Thoicyanate	Ethyl acetate	474	$3.20 \cdot 10^4$	0.01–6.0		[16]
Bathophenanthroline-neocuproine	$NaClO_4$−methanol	533	$9.40 \cdot 10^3$	3.00–100.0	Less sensitive	[30]
2-Carboethoxy-1,3-indandione	Methyl isobutyl ketone	500	$1.20 \cdot 10^4$	0.06–1.80		[13]
N-4-(5sulfo-8-hydroxyquinolyl-7-azo)benzylidene	Aqueous pH 2.7	542	$7.90 \cdot 10^4$	0.10–0.80		[14]
N-hydroxy-NN-diphenylbenzamidine thiocyanate	Toluene	465	$1.00 \cdot 10^4$	0.10–6.40	Less sensitive	[15]
2-Pyrrolaldehyde-4-phenyl-3-thiosemicarbazone	Methanol-acetonitrile	254	$8.85 \cdot 10^3$	27.00–250.0	Less sensitive	[33]
Chlorotetracycline	Phosphate nitric acid	435	–	0.50–20.00		[12]
3-Hydroxy-4-pyridinone (3,4-HPO)	$NaHCO_3$ and HNO_3	460		0.10–2.0		[19]
Bathophenanthroline-eosin-CTAB	Chloroform, pH 4.5, T = 45°C, t = 20 min	542	$2.23 \cdot 10^5$	0.280–7.814	Sensitive	The present work

Table 7
Comparison of the spectrophotometric methods utilized for the determination of Cu(II)

Reagent, Conditions	Conditions	λ_{max} (nm)	ε (L mol^{-1} cm^{-1})	Linear range (µg mL^{-1})	Remarks	Ref.
N-ethyl-3-carbazolecarboxaldehyde-3-thiosemicarbazone	n-Butanol	380	$2.20 \cdot 10^4$	0.40–3.60	Less sensitive	[32]
4-Benzylpiperidine-dithiocarbamate	TritonX-114	435	$2.75 \cdot 10^4$	5.00–200.0	Less sensitive	[28]
Thiomichlersketone	Polyethylene octyl Phenyl ether	500	$5.70 \cdot 10^4$	0.00–15.00		[22]
Pyridoxal-4-phenyl-3-thiosemicarbazone	Aqueous pH 3.0–5.5	440	$2.16 \cdot 10^4$	0.20–5.00	Less sensitive	[27]
Isonitrosoprophenonethiosemicarbazone	Aqueous pH 10.0	390	$0.584 \cdot 10^4$	0.50–6.00	Less sensitive	[31]
2,5-Dihydroxyacetophenone benzoic hydrazone	Acidic medium	400	$1.10 \cdot 10^4$	0.30–6.00	Less sensitive	[24]
Benzilidithiosemi carbazone	Chloroform	380	$1.63 \cdot 10^4$	0.50–4.00	Less sensitive	[25]
Diethyldithiocarbamate (DDTC)	$CHCl_3/CCl_4$	435	$2.86 \cdot 10^5$	0.2–12		[40]
Bathophenanthroline-EBT	Chloroform	565	$9.35 \cdot 10^4$	0.320–8.260	Sensitive	The present work

determination with DPBP–EBT is successfully utilized to determine Cu(II) in industrial wastewater, cooling water, boiler scale for power stations, drinking water, river water and different alloy samples. The results obtained in Table 4 are compared with the reference method [38].

4. Method validation

4.1. Linearity

The absorbance vs. concentration plots were found to be linear over the concentration ranges stated in Table 3 under the optimum experimental conditions

(Table 1). The linearity of the calibration graphs was demonstrated by the high values of the correlation coefficient (*r*) and the small values of the intercepts of the regression equations. The molar absorptivity and Sandell sensitivity are also shown in Table 3.

4.2. Accuracy and precision

In order to determine the precision of the proposed method, the results of the assay of the studied metal ions in different sources were compared with the reference AAS method. The low values of the relative standard deviation (%RSD) indicate the high precision and the good accuracy of the proposed methods.

4.3. Limits of detection and quantitation

Sensitivity of the method can be determined, through the limit of detection (LOD) and limit of quantification. The LOD and quantification were calculated and recorded in Table 3.

5. Conclusion

In comparison with the main spectrophotometric methods for iron and copper determination, the proposed method has the advantage of being simple, fairly selective, reproducible and highly sensitive (Tables 6 and 7) as indicated by the low values of SD and RSD. The standard validation protocol was applied to satisfy the requirements for the proposed method to determine Cu(II) and Fe(III) ions in pure and different samples. The proposed method has been successfully used in direct determination of iron and copper in cooling water, boiler scale for power stations, industrial wastewater, drinking water, Nile River water and different types of alloy samples. Moreover, the proposed spectrophotometric method is simple, inexpensive and insensitive to reaction conditions in comparison with atomic absorption and atomic emission methods. The method can be applied for routine analysis for the determination of Fe(III) and Cu(II) ions.

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