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Synthesis, spectroscopic and thermal characterization of Fe(III)-mixed ligand complexes and spectrophotometric determination of Fe(III) in various samples

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ABSTRACT

The aim of the present study is to find a non time consuming, economical and reliable spectrophotometric procedures using commercially available spectrophotometric reagents for the determination of Fe(III) ions. The methods are based on the formation of colored ternary complexes using, 1,10-phenanthroline and eriochrome black T or tartrazine mixed reagents and improved using a cationic surfactant, cetyltrimethyl ammonium bromide. This surfactant interacts with the complex to build up true ternary complex. The most suitable conditions for determination of Fe(III) ions and the parameters affecting the reactions including pH, time, temperature, stoichiometric ratios and reagents concentrations are optimized. The effect of different interfering ions is studied together with the suitable masking agents. The developed methods are used for the determination of Fe(III) ions in the presence of cetyltrimethyl ammonium bromide in different types of water (polluted industrial waste, ground, river Nile and drinking water). The synthesis and spectroscopy studies of two Fe complexes were reported. Thermal analysis was carried out in order to give an idea about the thermal stability of the complexes.

1. Introduction

The importance of the determination of trace metal concentration in natural water samples was increased in contamination monitoring studies. Water percolating through soil and rock can dissolve minerals containing iron and hold it in solution. Occasionally, iron pipes also may be a source of iron in water. Iron does not clearly alter in pure water or in dry air, but when both water and oxygen are present (moist air), iron corrodes. 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. Several methods could be used for iron determination [1-7].

Moreover, iron is the metal, which appears together in very real samples, both natural and artificial. In most instances, the characterization of these samples includes the determination of metal ions present in them. Although, the determination of iron has been studied in different samples and by using different techniques, some of these methods required physical separation, preliminary treatment or non-universal instrumenttation [8]. Mixed organic reagents had been proposed for spectrophotometric multicomponent analysis of metal ions [9-20]. The limitations on the use of such systems usually raised from the necessity for finding a compromise condition with respect to the different metal complexes. In spite of this, the use of mixed reagent systems could be considered as an alternative means to extend the applicability of spectrophotometric multicomponent determination. Various organic solvents were reported for the spectrophotometric determination of iron, based on the formation of colored binary complexes in aqueous medium, extraction into organic solvents and enhancement of complex absorbance with surfactants or miceller media [21-24].

The recommended ASTM [25] spectrophotometric method for Fe(III) determination in water was based on reaction with 1,10-phenanthroline (ε (510 nm) = 1.10×10^4 L/mol.cm). However, some metal ions and anions interfered when present in considerable excess. Recently, the sensitivity of the spectrophotometric methods for Fe(III) determination had been markedly improved by using surfactants [26], or by forming ion-association complexes. However, some of these methods lacked selectivity or required close control of experimental conditions [27,28].

The present work reports extraction-spectrophotometric methods for iron(III) determination after its reduction to iron(II) with hydroxylamine hydrochloride using 1,10-phenanthroline (PHR) and eriochrome black T (EBT) or

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tartrazine (TZ) as mixed ligands in the presence of cetyltrimethyl ammonium bromide (CTAB) surfactant. The ternary complexes were extracted into 1,2-dichloroethane solvent and the absorbance was measured at the selected wavelength. Analytical characteristics and statistical analysis of the experimental results of the proposed methods were presented. The developed procedures are highly sensitive, fairly selective and have the advantage of being convenient for general laboratory use and applied to determine Fe(III) in industrial polluted, Nile water, ground and drinking water samples. The two Fe complexes were synthesized and characterized using different spectroscopic, molar conductance, magnetic moment, diffused reflectance and thermal analysis techniques.

2. Experimental

2.1. Materials and reagents

All chemicals and reagents used were of analytical grade and of analytical-reagent purity and double-distilled water was used throughout the whole work. Surfactants were used as received without further purification.

Iron chloride hexahydrate, 1,10-phenanthroline, hydroxyl amine hydrochloride, sodium acetate, hydrochloric and nitric acids were supplied from Aldrich. Absolute ethanol and sodium hydroxide were supplied from Adwic. Borax, sodium fluoride, eriochrome black T, sodium dihydrogen phosphate and sodium bromide were supplied from Merck. Potassium cyanide, sodium tartarate and oxalic acid were supplied from Egyptian Company for Chemicals. Tartrazine (E102) was supplied from BDH.

1,2-Dichloroethane, chloroform, 1,4-dioxane, acetone, methyl alcohol, ethyl alcohol, methylene chloride and dimethyl formamide were supplied from El-Nasr Company, Egypt.

Cationic surfactants of cetyltrimethyl ammonium bromide, cetylpyridinium chloride (CPC) and anionic surfactants of sodium laurylsulphate (SLS) and sodium alkyl-benzene sulphate (SABS) were supplied from Aldrich. Nonionic 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. Co-exiting ions like, sodium nitrate, chloride salts of potassium, strontium, barium, cadmium and iron, sulphate salts of manganese, aluminum and copper, calcium carbonate, ammonium thiocyanate, potassium hydrogen phthalate, EDTA, sodium thiosulphate and potassium cyanide were used as interfering materials and supplied from Egyptian Co. for chemicals.

2.2. Instrumentation

Absorbance measurements were carried out using UV-mini 1240 Shimadzu (UV-Visible spectrophotometer) in the wavelength range from 400-700 nm with 10 mm matched quartz cells. Adjustment of pH was done using Jenway pH meter, with automatic temperature compensation and combined electrode, which was more convenient to be used, where the glass electrode and a reference half-cell were arranged in the same equipment. A Perkin-Elmer Model 5000 atomic-absorption spectrometer utilizing an air-acetylene flame and equipped with iron hollow cathode lamp operating at 248.3 nm was used for the standard determination of these element under study.

The molar conductance of solid complexes in DMF (10^{-3} mol/L) was measured using Jenway 4010 conductivity meter. Elemental microanalyses of the separated solid chelates for C, H, N and S were performed in the Microanalytical Centers at Cairo University, Egypt. The analyses were repeated twice to check the accuracy of the data. Infrared spectra were recorded on a Perkin-Elmer FT-IR type 1650 spectrophotometer in the region 4000-400 cm^{-1} as KBr disc. The diffused reflectance spectra were measured on a Shimadzu 3101 PC spectrophotometer. The molar magnetic susceptibility was measured on powdered samples using Faraday method. The diamagnetic corrections were made by Pascal's constant and $Hg[Co(SCN)_4]$ was used as a calibrant. The magnetic data for the background of the sample holder were corrected. The thermal analysis (TG) was carried out in dynamic nitrogen atmosphere (20 mL/min) with a heating rate of 10 °C/min using Shimadzu TG-60H thermal analyzer.

2.3. Procedure for the determination of Fe(III)

A stock solution of 5×10^{-4} mol/L $FeCl_3.6H_2O$ was prepared by accurately weighing 0.1351 g and dissolving in bi-distilled water to 100 mL in a volumetric flask. The solution was acidified to prevent the hydrolysis of the metal salt. 0.1% (*w*:*v*) of 1,10-phenanthroline solution was prepared by dissolving the accurate weighed amount of 100 mg in 100 mL absolute ethyl alcohol. 0.1% (*w*:*v*) of EBT and TZ were prepared by dissolving the accurate weighed amount of 100 mg in 100 mL bi-distilled water. 10% (*w*:*v*) solution of hydroxylamine hydrochloride was prepared by dissolving the accurate weighed amount of 10 g of the substance in 100 mL bi-distilled water. Solutions of CTAB, CPC, SLS and SABS (10^{-2} mol/L) were prepared by accurately weighing 3.644, 3.580, 2.884 and 3.060 g, respectively, the corresponding Triton X-100, Tween 60, and Tween 80 were prepared as 5% (*v*:*v*) solutions and dissolved in the appropriate solvent and completing to the required volume in a measuring flask. Series of universal buffer solutions covering the pH range from 2.0 to 12.0 were prepared as recommended by Britton and Robinson. 100 mL of the acid mixture (0.04 mol/L with respect to boric, acetic and phosphoric acids) was titrated with 0.2 mol/L sodium hydroxide to get the desired pH. Borax, acetate and phosphate buffers were prepared by dissolving the accurate weighed amount of 10 g in 100 mL bi-distilled water, respectively, according to the recommended method. Potassium hydrogen phosphate (0.2 mol/L), sodium fluoride (1.0 mol/L), sodium bromide (0.5 mol/L) and potassium iodide (0.1 mol/L), respectively, were prepared by dissolving the accurate weighed amount from each material in a definite volume of bi-distilled water to get the required concentration. Solutions of co-exiting ions (10^{-2} mol/L) were prepared by dissolving the accurate weighed amount in 100 mL bi-distilled water. Solution of HCl (1.0 mol/L) was prepared by accurate dilution with bi-distilled water from concentrated solution, while NaOH solution (1.0 mol/L) was prepared by dissolving the weighed amount in the desired volume using bi-distilled water. The water was always twice distilled from all glass equipments; re-distillation was carried out from alkaline permanganate solution. All solutions were protected by keeping them in a dark colored quickfit volumetric flask during the whole work.

2.4. Determination of Fe(III) in different water matrixes

Collection, storage and pretreatment of all samples were carried out as illustrated in 20th edition of the Standard Methods for the Examination of Water and Wastewater [29]. The glass sample containers cleaned with concentrated hydrochloric acid contained not more than 0.00005% of iron and then rinsed with distilled water free from iron before used to remove deposits of iron oxide. The samples were treated with acid at the time of collection to place the iron in the solution and prevent the deposition of iron on the walls of the sample containers. The samples stored at 4 °C for not more than 24 hours by avoiding exposure of samples to the light. 100 mL of water samples were collected and were acidified to pH = 2.0 with nitric acid to prevent the adsorption of iron ions on the surface of sample containers. The water samples were filtered through a Millipore 0.45 µm pore size membrane and analyzed within 6 hr of collection. Aliquot (0.5 mL) of water samples was pipetted into 25 mL quickfit dark bottle and 1.0 mL of 10% (*w*:*v*) hydroxylamine hydrochloride, 1.2 or 0.5 mL of 0.1% (*w*:*v*) 1,10-phenanthroline, 1.2 or 0.7 mL of 0.1% (*w*:*v*) EBT or TZ solutions and 5.0 mL of 10% (*w*:*v*) universal buffer (pH = 3.0, in case of 1,10-phenanthroline-EBT mixed reagent) or sodium acetate buffer (pH = 3.0, in case of 1,10-phenanthroline-tartrazine mixed reagent) were added. 0.4 or 1.0 mL of 10^{-2} mol/L CTAB were added. The mixture was thermostated in water bath at 25 °C for 30 or 20 min., respectively, and transferred to 25 mL separating funnel. Extraction was achieved by shaken with 5.0 mL (2.5 mL two times) (in case of 1,10-phenanthroline-EBT mixed reagent) or (3 mL + 2 mL) (in case of 1,10-phenanthroline-TZ mixed reagent) of 1,2-dichloroethane for 5 minutes and the absorbance of organic phases were measured at λ_{max} = 570 or 410 nm, respectively, against the reagent blank prepared similarly except Fe(III). The amount of Fe(III) was obtained either from the calibration graph or the regression equation. The amount of Fe(III) was also estimated by the reference method.

2.5. Determination of the stoichiometric ratio

The stoichiometry of the ternary complexes formed was examined by applying molar ratio and continuous variation methods [30,31].

(i) The molar ratio method (mrm): 0.5 mL of 5×10^{-4} mol/L Fe(III) was putted in a 25 mL quickfit dark bottle and different volumes of 5×10^{-4} mol/L of 1,10-phenanthroline solution ranged from 0.2 to 2.0 mL and constant volume (0.5 mL) of 5×10^{-4} mol/L EBT or TZ and the procedure was completed as described above. The same procedure was carried out by adding different volumes ranged from 0.2 to 2.0 mL of 5×10^{-4} mol/L EBT or TZ solution in the presence of constant volume (0.5 mL) of 5×10^{-4} mol/L 1,10-phenanthroline solution. The procedure was completed as described above and the absorbance was plotted against ratio of reactants.

(ii) The continuous variation method: A series of solutions were prepared by mixing different volumes of Fe(III) solution (5×10^{-4} mol/L) with different volumes of (5×10^{-4} mol/L) 1,10-phenanthroline solution, in the presence of 0.5 mL of (5×10^{-4} mol/L) EBT or TZ or different volumes of (5×10^{-4} mol/L) EBT or TZ in the presence of constant volume (0.5 mL) of (5×10^{-4} mol/L) 1,10-phenanthroline, so that the total number of moles is kept constant. The procedure was followed as above and the absorbance data obtained were plotted against mole fraction of Fe(III) ions.

2.6. Sensitivity, precision and accuracy of the method

2.6.1. Procedure for standard addition method

In 25 mL quick fit dark bottle, water sample (0.5 mL) from ground water (El-Obour City, Egypt), Nile water or drinking water samples was spiked by adding different concentration of standard Fe(III) solution (1.397, 2.795 and 5.59 μg/mL) and the procedure was completed as detailed above.

2.7. Synthesis of Fe(III) complexes

The Fe(III) complexes with PHR and EBT or PHR and TZ reagents were prepared by the addition of hot solution (60 °C) of the Fe(III) chloride (1 mmol) in absolute ethanol (15 mL) to the hot solution (60 °C) of the PHR ligand (0.3 g, 1 mmol) and EBT ligand (0.462 g, 1 mmol) or TZ ligand (0.534 g, 1 mmol) in ethanol and DMF (15 mL). The resulting mixture was heated under reflux for 3h with stirring. The reaction mixture was left overnight to get precipitate. The precipitate was dried and weighed to calculate the yield.

3. Result and discussion

The determination of Fe(III) as Fe(III)-PHR-EBT or Fe(III)-PHR-TZ ternary complexes in the presence of CTAB was found to have a maximum absorbance at 510 nm (ε = 3.34×10^{4} L/mol.cm) or 535 nm (ε = 1.38×10^{4} L/mol.cm) while there was a great depression in the absorption spectrum of Fe-EBT and Fe-TZ complexes as shown in Figure 1 and 2.

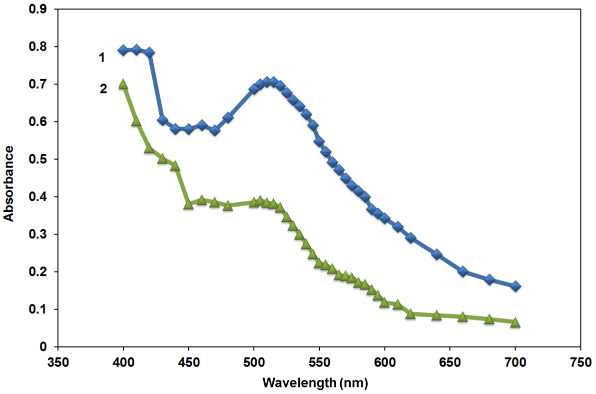

Figure 1. Absorption spectra of Fe(III)-PHR-EBT ternary complex in the presence of CTAB surfactant and 1,2-dichloroethane solvent. (1) Fe(III)-PHR-EBTand (2) Fe(III)-EBT at T = 30 °C and t = 5 min and sodium acetate buffer (pH = 5.5). [Fe(III)] = 5×10^{-4} mol/L, [PHR] = [EBT] = 0.1% (*w*:*v*).

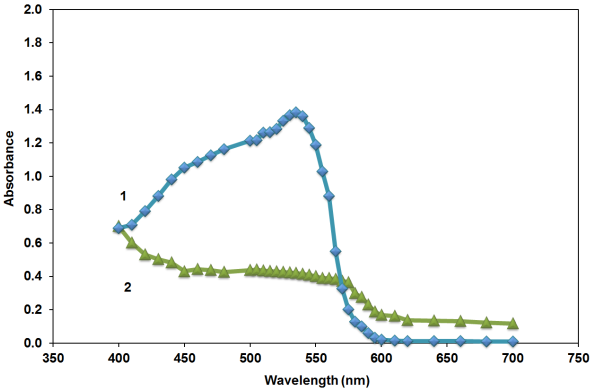

Figure 2. Absorption spectra of Fe(III)-PHR-TZ ternary complex in the presence of CTAB surfactant and 1,2-dichloroethane solvent. (1) Fe(III)-PHR-TZ and (2) Fe(III)-TZ at T = 30 °C and t = 5 min and sodium acetate buffer (pH = 4.5). [Fe(III)] = 5×10^{-4} mol/L, [PHR] = [TZ] = 0.1% (*w*:*v*).

3.1. Optimization of variables

The effect of pH on the formation of Fe(III)-PHR-EBT and Fe(III)-PHR-TZ ternary complexes in the presence of 10^{-2} mol/L CTAB and 10% (*w*:*v*) of hydroxylamine hydrochloride (as reducing agent) is investigated over the pH range from 2.0 to 5.0 using sodium acetate buffer. The absorbance values of the ternary complexes increased gradually and reached maximum value at pH = 3.0 (Figure 3). The absorbance values decreased with increasing pH more than 3.0. This can be attributed to the formation of hydroxo complex or hydrolysis of the metal ion. The effect of buffers type on the absorbance of the ternary complexes at the optimum pH was investigated using phosphate, borate and universal buffers (pH = 3.0). Universal or acetate buffers solution (pH = 3.0) is selected and the suitable pH is prepared and used instead of HCl and NaOH to adjust the pH at the optimum pH for the formation of Fe(III)-PHR-EBT and Fe(III)-PHR-TZ ternary complexes.

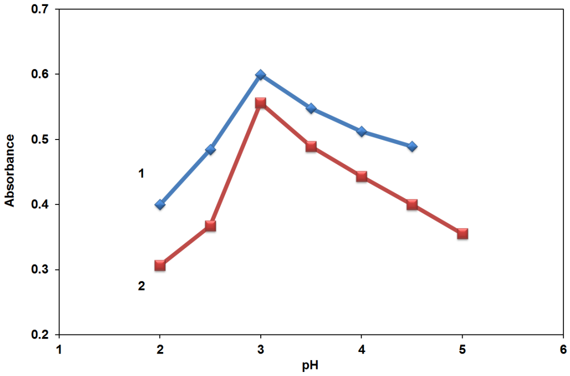

Figure 3. Effect of pH on the formation of the Fe(III)-PHR-EBT (curve 1) and Fe(III)-PHR-TZ (curve 2) ternary complexes in the presence of CTAB surfactant and 1,2-dichloroethane solvent at T = 30, 25 °C, t = 5 min and λ_{max} = 510, 535 nm. [Fe(III)] = 5×10^{-4} mol/L, [PHR] = [EBT] = [TZ] = 0.1% (*w*:*v*).

The influence of various surfactants and protective colloids and volumes of the suitable surfactant on the colour reactions showed that the absorbance of the ternary complexes decreased in the presence of nonionic surfactants. There are slight increases in the absorbance of the ternary complexes in the presence of anionic and cationic surfactants. Maximum enhancement of the absorbance of Fe(III)-PHR-EBT and Fe(III)-PHR-TZ ternary complexes were obtained in the presence of CTAB (Figure 4), where 0.4 and 1.0 mL of 10^{-2} mol/L CTAB, respectively, increased the absorbance of the ternary complexes.

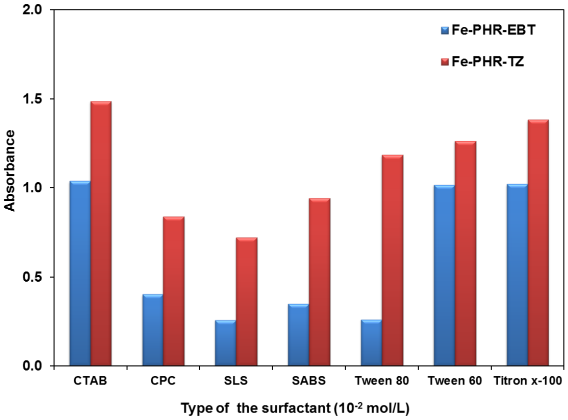

Figure 4. Effect of different types of surfactant (10^{-2} mol/L) on the formation of the Fe(III)-PHR-EBT and Fe(III)-PHR-TZ ternary complexes in the presence of universal or acetate buffer (pH = 3.0) and 1,2-dichloroethane solvent at T = 30, 25 °C, t = 5 min and λ_{max} = 510 , 535 nm. [Fe(III)] = 5×10^{-4} mol/L, [PHR] = [EBT] = [TZ] = 0.1% (*w*:*v*).

It is observed that from 5 to 30 or 20 minutes after the extraction, the absorbance increased horizontally with time. After 30 or 20 minutes, the absorbance values increased slightly for about 120 minutes. Therefore, 30 and 20 minutes were the most suitable time selected for the determination of Fe(III) as Fe(III)-PHR-EBT and Fe(III)-PHR-TZ ternary complexes, respectively. The absorbance is gradually increased with the increase in the temperature and attains maximum value at 25 °C. As the temperature increased above this, the absorbance of ternary complexes decreased (Figure 5).

The effect of organic solvents such as xylene, absolute ethanol, methanol, carbon tetrachloride, benzene, diethyl ether, 1,4-dioxane, 1,2-dichloroethane, dichloromethane, dimethyl formamide, petroleum ether, *n*-propanol, and chloroform was studied. The results indicate that xylene, 1,4-dioxane and petroleum ether form milky color and the other solvents found to be miscible with the aqueous layer. Therefore, quantitative extraction is achieved when chloroform, dichloromethane and 1,2-dichloroethane are used. 5 mL of 1,2-dichloroethane (2.5 mL × 2 times) or (3 mL + 2 mL) and 5 minutes shaking for both Fe(III)-PHR-EBT and Fe(III)-PHR-TZ ternary complexes, respectively, was found to be the most effective for ternary complexes extraction. Effect of reagents concentration was investigated using different volumes of hydroxylamine hydrochloride in the range from 0.1 to 3.0 mL, PHR and EBT or TZ reagents in the range from 0.1 to 2.0 mL. It is found that, maximum absorbance readings are obtained in the presence of 1.0 mL of 10% (*w*:*v*) hydroxylamine hydrochloride, 1.2 or 0.5 mL of 0.1% (*w*:*v*) of PHR and 1.2 or 0.7 mL of 0.1% (*w*:*v*) of EBT or TZ reagents for the formation of Fe(III)-PHR-EBT and Fe(III)-PHR-TZ ternary complexes, respectively.

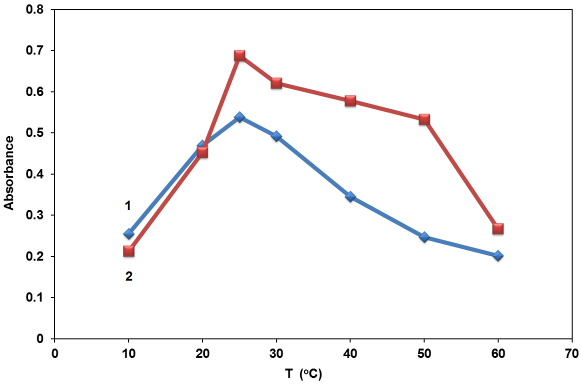

Figure 5. Effect of temperature on the formation of Fe(III)-PHR-EBT and Fe-PHR-TZ ternary complexes in the presence of CTAB surfactant, 1,2-dichloroethane solvent and universal or acetate buffer (pH = 3.0). [Fe(III)] = 5×10^{-4} mol/L, [PHR] = [EBT] = [TZ] = 0.1% (*w*:*v*) at t = 5 min and λ_{max} = 510 or 535 nm, respectively.

The stoichiometric ratio, determined from both molar ratio and continuous variation methods [30,31], show that two linear portions intersected at the suitable metal:reagent ratio. Therefore, 1:1:1 [Fe]:[PHR]:[EBT or TZ] is suggested for the complex formation.

3.2. Validation

The influences of the diverse ions on the determination of Fe(III) as Fe(III)-PHR-EBT or Fe(III)-PHR-TZ ternary complexes are given in Table 1. The cations used as interfering ions are added as their chloride, nitrate or sulphate salts and the anions are those of ammonium, potassium or sodium salts. The tolerance limit is taken as the amount that causes ±2% error in the absorbance value. It is found that, Co(II), Ni(II), Cu(II), Cd(II), Zn(II), Mn(II), Pb(II), Cr(III) and Al(III) ions interfere seriously, while the other ions have little effect on the determination. To minimize the interfering action of metal ions, the influence of some masking agents on the color reaction of Fe(III) with PHR and EBT or TZ was studied. The tolerance limits of masking agents were increased or decreased by the addition of masking agents after development of the color reaction. Addition of 0.4 mL of 1.0 mol/L sodium fluoride (masking agent for Al(III), Cd(II), Co(II), Cu(II), Ni(II) and Cr(III)), 0.3 mL of 0.5 mol/L sodium bromide (masking agent for Mn(II) and Zn(II)) and 0.2 mL of 0.1 mol/L potassium iodide (masking agent for Pb(II)) were efficient in decreasing the interference effect of these metal ions.

The absorbance-concentration relation is linear and Beer's law is obeyed in the concentration range from 0.279 to 6.60 and 1.40 to 19.56 µg/mL with molar absorptivity of 3.34×10^{4} and 1.38×10^{4} L/mol.cm, respectively, Sandell's sensitivities [32] was found to be 0.081 and 0.030 µg/cm², percent recovery

Table 1. Effect of foreign ions on the determination of Fe(III) as Fe(III)-PHR-EBT and Fe(III)-PHR-TZ.

Ion added	**PHR-EBT**	**PHR-TZ**
	Tolerance limit [Ion/Fe(III)]	**Tolerance limit [Ion/Fe(III)]**
F^-	2500	2500
Oxalate, tartrate, citrate, NH_4^+	2000	2000
Na(I), K(I), NO_3^-, PO_4^{3-}	1000	1000
Ce(III), ClO_4^-, Sr(II), Mo(VI)	600	600
Mg(II), As(V), Ba(II), Ca(II)	500	500
$S_2O_3^{2-}$, I^-, Br^-, Cl^-	200	200
Cd(II), Mn(II), Co(II), Cr(III), Pb(II)	100	100
Al(III), Cu(II), Ni(II), Zn(II)	100	100

Table 2. Analytical parameters for the determination of Fe(III) ion via its reaction with PHR-EBT and PHR-TZ mixed reagents.

Parameters	**PHR-EBT**	**PHR-TZ**
Maximum wavelength (λ_{max}, nm)	510	535
Molar absorptivity (L/mol.cm)	3.34×10^4	1.38×10^4
pH	3.0	3.0
T (°C)	25	25
t (min)	20	20
Beers law limit (µg/mL)	0.279-6.60	1.40-19.56
Percentage recovery (%)	99.11-100.8	98.78-101.6
Sandell's sensitivity (µg/cm²)	0.081	0.030
$y = mx+z$		
Slope	0.072	0.040
Intercept	0.31	0.17
Correlation coefficient (r)	0.996	0.998
SD *	0.04-0.01	0.07 0.02
RSD % *	0.33-3.57	0.15-1.45
% Error	(-0.36)-(0.89)	(1.21)-(-1.61)
Detection limit, LOD, (µg/mL)	0.20	1.39
Quantitation limit, LOQ (µg/mL)	0.66	5.71

* Number of replicates n = 4.

Table 3. Determination of Fe(III) in industrial waste water, ground water, Nile water and drinking water samples.

Sample	**Fe(III), µg/mL**			**Fe(III), µg/mL**			**Fe(III), µg/mL**			***t*-test** [d]	
	PHR-EBT reagent (Method A)			**PHR-TZ reagent (Method B)**			**Reference method**				
	Found	**SD** [a]	**RSD (%)**	**Found**	**SD** [a]	**RSD (%)**	**Found**	**SD** [a]	**RSD (%)**	**A**	**B**
Industrial waste water (Helwan City)	5.58	0.01	0.18	5.59	0.03	0.54	5.57 [c]	0.03	0.54	2.00	1.33
Industrial waste water (Helwan City)	4.39	0.03	0.68	4.38	0.02	0.46	4.37 [c]	0.04	0.92	1.33	1.00
Ground water (El-Obour City-well (1))	0.17 [b]	0.01	1.88	0.163 [b]	0.02	1.76	0.16	0.02	2.50	2.00	2.00
Ground water (El-Obour City-well (2))	0.72	0.04	1.31	0.710 [b]	0.01	1.42	0.70	0.05	3.14	1.00	2.00
River-Nile water	0.35	0.03	0.48	0.335 [b]	0.02	2.86	0.33	0.03	2.64	1.33	2.00
Drinking water	0.072 [b]	0.01	1.33	0.073 [b]	0.01	2.32	0.07	0.02	2.67	1.00	1.00

[a] Number of replicates = 4.
[b] Using standard addition method.
[c] After dilution.
[d] Tabulated t-value at 95% confidence interval is 3.18.

values for four repeated times was 99.11-100.80 and 98.78-101.60% and RSD = 0.33-3.57 and 0.15-1.45%, respectively, for the determination of Fe(III) using PHR-EBT and PHR-TZ mixed reagents. The LOD and LOQ values are found to be 0.2 and 0.5 µg/mL (in case of PHR-EBT reagent) and 0.66 and 1.65 µg/mL (in case of PHR-TZ reagent) (Table 2). The high values of correlation coefficient (0.996 and 0.998) indicate the good linearity of all calibration graphs. From the above parameters, the methods were suitable for direct determination of Fe(III) ion in different types of water (polluted industrial waste, ground, river Nile and drinking water) and the results are in good agreement with those obtained by the atomic absorption technique by using t-values at 95% confidence level. The calculated t-values were found to be less than the tabulated t-values (3.18 at n = 4) at 95 % confidence level, thus confirming no significant difference between the performance of the proposed method and the reference method (Table 3).

Determination of Fe(III) using PHR-EBT mixed ligand reagent in ground water (El-Obour City (well 1)) and drinking water by using standard addition method with percent recovery of 100.6 and 102.9%, respectively. The SD = 0.01, RSD = 1.88 and 1.33 %, respectively, as shown in Table 3. The concentration of the unknown was found to be 0.17 and 0.072 µg/mL, respectively. The determination of Fe(III) using PHR-TZ mixed ligand reagent in drinking water, ground water (El-Obour City (well 1)), River Nile water and ground water (El-Obour City (well 2)) by standard addition method with percent recovery of 101.9, 101.4, 101.5 and 104.3%, respectively. The SD was ranging between 0.01 and 0.02, RSD = 1.76, 1.41, 2.86 and 2.32%, respectively, as shown in Table 4. The concentration of the unknown were found to be 0.163, 0.71 0.335 and 0.073 µg/mL for drinking water, ground water (El Obour City (well 1)), River Nile water and ground water (El Obour City (well 2)), respectively.

Results of the standard addition method were found in a good agreement with the reference method (Table 4), the values given in Table 3 and 4 reflect the high precision and accuracy of the proposed methods in the micro determination of Fe(III) under selected optimum conditions.

Table 4. Determination of Fe(III) ion in spiked drinking water, river-Nile and ground water sample (El-Obour city) using standard addition method.

Sample	**[Fe(III)] µg/mL Taken**	**Standard added**	**Fe(III), g/mL**			**Liner regression parameters**			
			PHR-EBT reagent [b]						
			Found	**SD [a]**	**RSD [a] (%)**	**Slope**	**Intercept**	***r***	**% Recovery [a]**
Ground water (El-Obour City (well (1))	0.16	0.000, 0.280, 0.559 and 1.397	0.17	0.01	1.88	0.395	0.058	0.997	100.6
Drinking water	0.070		0.072	0.01	1.33	0.327	0.017	0.995	102.9
Sample	**[Fe(III)] µg/mL Taken**	**Standard added**	**Fe(III), g/mL**			**Liner regression parameters**			
			PHR-TZ reagent [b]						
			Found	**SD [a]**	**RSD [a] (%)**	**Slope**	**Intercept**	***r***	**% Recovery [a]**
Ground water (El-Obour City (well (1))	0.16	0.000, 1.397, 2.795 and 5.590	0.163	0.02	1.76	0.097	0.025	0.999	101.9
Ground water (El-Obour City (well (2))	0.70		0.710	0.01	1.41	0.078	0.011	0.999	101.4
River-Nile water	0.33		0.335	0.01	2.86	0.097	0.025	0.999	101.5
Drinking water	0.07		0.073	0.01	2.32	0.101	0.068	0.999	104.3

[a] Number of replicates = 4.

[b] Tabulated *t*-value at 95% confidence interval is 3.18.

Table 5. Comparison of sensitivity and selectivity of some spectrophotometric methods used for Fe(III) determination.

Reagent	**Conditions**	**λ_{max}**	**ε, L/mol.cm**	**pH**	**Linear range, µg/mL**	**Ref.**
Thoicyanate	Ethyl acetate	474	3.2×10^4	-	0.01-6	[23]
Bathophenanthroline-neocuproine	NaClO$_4$-Methanol	533	9.4×10^3	-	3-100	[24]
Eriochrome cyanine R	Acetate	560	5.36×10^4	5.2	0.1-40	[25]
2-Carboethoxy-1,3-indandione	Methyl isobutyl ketone	500	1.2×10^4	1.5-3.5	0.06-1.8	[26]
N-4-(5-Sulfo-8-hydroxyquinolyl-7-azo)benzylidene	Aqueous	542	7.9×10^4	2.7	0.1-0.8	[27]
N-hydroxy-*N*,*N*-diphenylbenzamidine thiocyanate	Toluene	465	1.0×10^4	-	0.1-6.4	[28]
2-Pyrrolaldehyde-4-phenyl-3-thiosemicarbazone	Methanol-Acetonitrile	254	8.85×10^3	-	27-250	[29]
Ferrozine	Methanol	562	28.1×10^3	-	0.01-0.6	[30]
PHR-EBT-CTAB	1,2-Dichloroethane	510	3.34×10^4	3.0	0.279-6.60	[Present work]
PHR-TZ-CTAB	1,2-Dichloroethane	535	1.38×10^4	3.0	1.40-19.56	[Present work]

Table 6. Analytical and physical data of Fe(III) mixed ligand complexes.

Compound	**Color**	**Yield, %**	**Melting point (°C)**	**% Found (calcd.)**					**μ_{eff} (B.M.)**	**Λ_m (Ω^{-1}mol^{-1}cm^2)**
				C	**H**	**N**	**Cl**	**M**		
[Fe(EBT)(PHR)]Cl $C_{32}H_{18}ClNaN_5O_7SFe$	Reddish brown	87	195	52.42 (52.54)	2.96 (2.46)	9.79 (9.58)	4.58 (4.86)	7.92 (7.66)	5.67	67.80
[Fe(PHR)(TZ)]Cl$_2$ $C_{28}H_{16}Cl_2Na_3N_6O_9S_2Fe$	Yellowish brown	83	>300	39.73 (40.00)	1.78 (1.90)	9.92 (10.00)	8.03 (8.45)	6.41 (6.67)	5.82	115.6

In comparison with other methods for iron determination, the suggested method based on extracting Fe(III)-PHR-EBT or Fe(III)-PHR-TZ ternary complexes at pH = 3 and 25 °C for 30 minutes and for 20 minutes, respectively into 1,2-dichloro ethane, has the advantage of being simple, rapid, reproducible, fairly selective and highly sensitive. The method compares favorably with most sensitive spectrophotometric methods for iron determination by formation of ternary complex extractable into organic solvents. Table 5 summarizes the analytical characteristics of the proposed method along with similar spectrophotometric methods. Moreover, the developed procedure has been successfully used to determine iron in samples of different matrix composition.

3.3. Stoichiometries of the novel Fe(III) complexes

The stoichiometries of the complexes have been deduced from their elemental analysis (Table 6), which indicates that the metal complexes fall into 1:1:1 (Fe:PHR:EBT or TZ) ratio which confirmed with the solution study applying molar ratio and continuous variation method. All the products were partially soluble in common organic solvents. Microanalytical data are in good agreement with stoichiometry proposed for complexes (Table 6). The elemental analysis corresponds to the formula [Fe(PHR)(EBT)]Cl and [Fe(PHR)(TZ)]Cl$_2$. The EBT ligand undergoes di deprotonation to form L^{2-} in Fe(III) complex and acts as a tetradentate ligand thus occupying four positions. While TZ ligand undergoes mono deprotonation to form L^{1-} in Fe(III) complex and acts as bidentate ligand thus occupying two positions. Meanwhile, PHR behaves as a neutral bidentate ligand and occupying two positions.

3.4. Molar conductance of the complexes

The molar conductance of 10^{-3} M solutions of the complexes in DMSO is measured at 25±2 °C. It is concluded from the results that Fe(III) chelates with PHR, EBT and TZ ligands under investigation were found to have molar conductance values of 67.8 and 115.6 Ω^{-1}mol^{-1}cm^2 for [Fe(PHR)(EBT)]Cl and [Fe(PHR)(TZ)]Cl$_2$, respectively, indicating their electrolytic nature.

3.5. Infrared spectra and nature of coordination

By comparing the infrared spectra of the free ligands (Table 7) to that of the prepared complexes the following points are observed. The ν(N=N) stretching band in the free EBT and TZ ligands is observed at 1642 and 1639 cm^{-1}, respectively [33-38]. This band is disappeared in case of [Fe(PHR)(EBT)]Cl complex and shifted to lower frequency value of 1645 cm^{-1} in case of [Fe(PHR)(TZ)]Cl$_2$ complex, upon complexation suggesting coordination via the azo group (M → N).

If the diazo nitrogen bonded to the phenol is coordinated to the metal ion, two 5-membered chelate rings are formed which, energetically, should be more favored [33-35,38].

The ν(C=N) vibration of PHR ligand appearing at 1642 cm^{-1} suffers a downward shift of 1611 and 1640 cm^{-1} for [Fe(PHR)(EBT)]Cl and [Fe(PHR)(TZ)]Cl$_2$ complexes, respect-

Table 7. IR spectral data of Fe(III) mixed ligand complexes *.

Band assignment	**PHR**	**EBT**	**TZ**	**[Fe(EBT)(PHR)]Cl**	**[Fe(PHR)(TZ)]Cl$_2$**
C=N	1642 s	-	-	1611 s	1640 s
O-H	-	3438 br	3440 br	3428 br	3435 br
N=N	-	1642 br	1639 s	Disappear	1645 s
C-N	1087 s	-	-	1144 br	1130 s
C-O	-	1203 m	1187 m	Disappear	1196 s
C=N out of plane	695 m	-	-	642 s	646 s
COO asymmetric	-	-	1561 br	-	1599 br
COO symmetric	-	-	1477 s	-	1482 s
M-O	-	-	-	528 br	530 w
M-N	-	-	-	450 w	419 s

* S = strong, br = broad, w = weak.

Table 8. Thermoanalytical results (TG and DTG) of ternary metal complexes.

Complex	**TG range (°C)**	**DTG$_{max}$ (°C)**	**n***	**Mass loss found (Calcd.) %**	**Assignment**	**Residues**
[Fe(PHR)(EBT)]Cl	50-450	69	1	28.28 (27.70)	Loss of HCl and $C_{11}H_4NO$	½Fe_2O_3
	450-750	191	1	31.90 (31.74)	Loss of $C_9H_9N_2O_2SNa$	
	750-1000	520	1	28.70 (29.55)	Loss of $C_{12}H_4N_2O_{2.5}$	
[Fe(PHR)(TZ)]Cl$_2$	30-300	56	1	8.69 (9.59)	Loss of 2HCl	½Fe_2O_3
	300-500	198	1	18.45 (18.87)	Loss of $C_6H_7N_2SO$	
	500-1000	467, 607	3	62.50 (63.89)	Loss of C_2H_2Na, $C_5H_5N_3Na$ and $C_{15}H_2N_2SO_{6.5}$	

* n = number of decomposition steps.

tively, thereby supporting the assumption that the Fe(III) ions are coordinated to the pyridyl nitrogen atoms. This is also evidenced from the shift of the out of plane bending of the pyridyl nitrogen; δ(C=N), from 695 cm^{-1} in PHR ligand to 642 and 646 cm^{-1} in the [Fe(PHR)(EBT)]Cl and [Fe(PHR)(TZ)]Cl$_2$ complexes, respectively [33-35,39].

The IR spectra of the complexes (Table 7) clearly demonstrated that the carboxylate COO stretching vibration is altered compared to ligand due to conformational changes. The fact that the C–O–O absorption of the complexes is shifted to lower wave numbers in the complexes compared to that of the ligand (1028 cm^{-1}) also confirms the complex formation [33-38].

The IR spectra of the EBT and TZ ligands show broad bands at 3438 and 3440 cm^{-1}, which can be attributed to the phenolic OH group. These bands are found at 3428 and 3435 cm^{-1} for [Fe(PHR)(EBT)]Cl and [Fe(PHR)(TZ)]Cl$_2$ complexes, respecttively, indicating coordination through the phenolic OH group [33-35,36]. Phenolic C-O stretching band is observed at 1203 and 1187 cm^{-1} in the free EBT and TZ ligands, respectively. In all complexes, this band disappeared in [Fe(PHR)(EBT)]Cl complex and appears at wavenumber in 1196 cm^{-1} region for [Fe(PHR)(TZ)]Cl$_2$ complex (Table 6), respectively, confirming the involvement of the phenolic group in complex formation [36].

New bands are found in the spectra of complexes in the regions 528-530 and 419-450 cm^{-1} which are assigned to ν(M-O) and ν(M-N) stretching vibrations [40], respectively. Therefore, from the IR spectra it is concluded that PHR coordinated to the Fe(III) ions in a bidentate neutral manner via the two pyridyl N atoms, while EBT coordinated via the azo N and two protonated phenolic O atoms. In addition, TZ binds to Fe(III) ion via azo N and deprotonated phenolic O atom.

3.6. Spectral and magnetic moment studies of Fe(III) complexes

The magnetic moments (μ_{eff}) of [Fe(PHR)(EBT)]Cl and [Fe(PHR)(TZ)]Cl$_2$ complexes are 5.67 and 5.82 B.M, respecttively, which are normal and suggest octahedral geometry for them [41-44].

From the diffused reflectance spectrum and according to previously published data [36,45-48], it has been observed that, the [Fe(PHR)(EBT)]Cl chelate exhibits bands at 16,245, 17,196 and 21,763 cm^{-1}. These bands can be assigned to the $^6A_{1g} \rightarrow T_{2g}(G)$, $^6A_{1g} \rightarrow {}^5T_1g$ and $^6T_{1g} \rightarrow {}^5T_1g$ (D) transitions in octahedral geometry of the complex. The spectrum shows also band at 28,645 cm^{-1} which may be attributed to ligand to metal charge transfer.

3.7. Thermal analysis

Thermal gravimetric analysis (TG) was used as a probe to proof the associated water or solvent molecules to be in the coordination sphere or in the crystalline form. The stages of decomposition, temperature ranges, decomposition product loss as well as the found and calculated weight loss percentages of the complexes are given in Table 8. The thermal decomposition process of the [Fe(PHR)(EBT)]Cl complex involves three decomposition steps. Decomposition of the complex started at 50 °C and finished at 1000 °C with three stages. The first stage of decomposition involves the removal of HCl and $C_{11}H_4NO$ molecules in the 50-450 °C temperature range, and is accompanied by a weight loss of 28.28% (calcd. 27.70%). The second stage of decomposition occurs in the 450-750 °C temperature range, corresponding to the loss of $C_9H_9N_2O_2SNa$, and is accompanied by a weight loss of 31.90% (calcd. 31.74%). While the third stage involves the removal of $C_{12}H_4N_2O_{2.5}$ molecule and in the 750-1000 °C temperature range, and is accompanied by a weight loss of 28.70% (calcd. 29.55%). The total weight loss amounts to 88.88% (calcd. 88.99%) leaving ½Fe_2O_3 as a residue of decomposition.

TG curve of the [Fe(PHR)(TZ)]Cl$_2$ complex shows five steps of decomposition. The first stage of decomposition occurs in the 30-300 °C temperature range, corresponding to the loss of 2HCl molecules, and is accompanied by a weight loss of 8.69% (calcd. 9.59%). The second stage of decomposition involves the removal of $C_6H_7N_2SO$ molecule in the 300-500 °C temperature range, and is accompanied by a weight loss of 18.45% (calcd. 18.87). While the remaining three stages involve the removal of C_2H_2Na, $C_5H_5N_3Na$ and $C_{15}H_2N_2SO_{6.5}$ molecules in the 500-1000 °C temperature range, and they are accompanied by weight loss of 62.50% (calcd. 63.89%). The total weight loss amounts to 91.23% (89.64%) and ½Fe_2O_3 was the residue of decomposition.

Based on all the previous spectroscopic, thermal and elemental analysis data, the structure of the complexes is given as shown in Figure 6.

4. Conclusion

The proposed methods for the determination of Fe(III) as Fe(III)-PHR-EBT and Fe(III)-PHR-TZ ternary complexes were

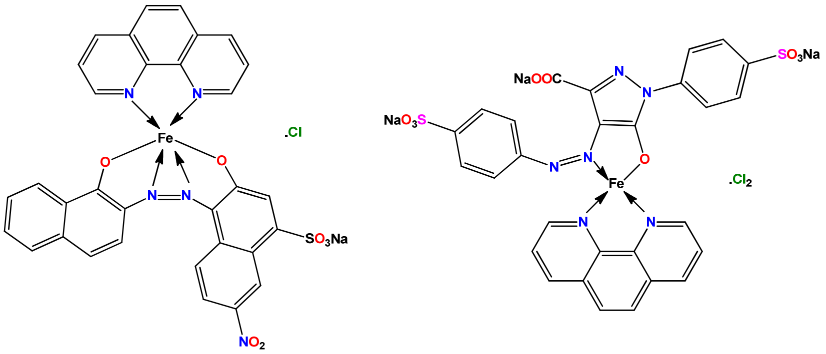

Figure 6. Structure of Fe(III) complexes.

proved to be simple, rapid and reproducible with an advantage of using a commonly available solvents i.e. 1,2-dichloroethane. The suggested methods with other frequently used spectrophotometric methods for Fe(III) determination as ternary complexes are listed in Table 6. Moreover, the proposed methods have been successfully used to determine Fe(III) in industrial waste, ground, River Nile and drinking water samples. Also the proposed methods are found to have high ε values and high linear range of concentrations. The complexes were synthesized and characterized using different spectroscopic techniques. The thermal decomposition of the complexes was also studied. The results obtained confirm the solution study with respect to stoichiometric ratio.

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