Ultra Violet Spectrophotometric Determination of Iron(III) with SHAM

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Summary- The colour reaction of iron (III) with SHAM was investigated spectrophotometrically in the UV-region. A 1:2 iron(III)-SHAM brown complex was formed in pH 5.5 using acetate buffer solution. Beer's law was followed up in the concentration range 0.09-5.36 □ g/ml of iron. The apparent molar absorptivity of the complex was 1.3 x 10^4 $l.mol^{-1}.cm^{-1}$ at 257 nm. The interference of large number of foreign ions were studied. Sodium fluoride and thiourea were used as masking agents. The method was successfully applied for the determination of iron(III) in boiler feed water, ground water, industrial waste water and glycol samples.

Introduction

Several methods have been described for the spectrophotometric determination of iron (III) in aqueous medium. Some organic reagents such as thiocyanate[1], o-phenanthroline[2], 9,10-phenanthrene quinone[3], anthraquinone[4], semicarbazone[5], tetracycline[6], tetrakis[7], thiosalicylic acid[8], azo dyes[9-14] andtriphenylmethane and xanthene dyes[15-17] were used to react with iron at various pH values.

The aim of this study is to develop a reliable, rapid and simple spectrophotometric method for determining iron (III) in boiler feed water, ground water, industrial wastewater and glycol samples. The present method involves the reaction of iron (III) with salicylhydroxamic acid (SHAM) in the UV-region at maximum wavelength 257 nm. The influence of pH, solvent, ligand concentration, time, composition of the complex and foreign ions have been studied. SHAM was used as a therapeutic agent to serve as a potent inhibitor of the bacteria enzyme urease[18].

Experimental

Apparatus

Measurements of absorbance were conducted on SHIMADZU UV-VIS-NIR scanning spectrophotometer using 1 cm matched quartz-cells. pH was measured using ion analyzer model CRISON pH/mV meter digit 501.

Reagents

All chemicals used were of analytical reagent grade. Aqueous solutions were prepared with either bi-distilled water or deionized water.

Iron (III) stock solution of 1×10^{-2} M, was prepared by dissolving 1.9607 g of ferrous ammonium sulphate $Fe(NH_4)_2(SO_4)_2.6H_2O$ in water containing 10.0 ml of concentrated sulphuric acid. The solution was diluted to 500 ml with water in a volumetric flask.

SHAM (C_6H_4-CO-$NH(OH)_2$), solution of 1×10^{-2} M, was prepared by dissolving 0.3825 g of SHAM in warm water and diluting to 250 ml in a volumetric flask with the same solvent.

Acetate buffer of pH 5.5, was prepared by adjusting the pH of 0.1 M acetic acid solution with 0.05 M sodium acetate solution to the desired value.

General Procedure

Transfer an aliquot solution containing < 5.4 μg ml^{-1} of iron (III) into a 25 ml volumetric flask. Add 2.5 ml SHAM solution of 1 x 10^{-2} M and completed with acetate buffer of pH 5.5. Leave to 15 minutes, then measure the absorbance of the coloured solution at 257 nm against a reagent blank.

Results and Discussion

Iron (III) reacts with SHAM at pH 5.5 to form stable brown complex in aqueous medium. Some surfactants and protective colloids were tested for binary complex and there is no measurable change in absorbance.

Effect of pH

The pH of the reaction mixture was varied from 2.5 to 7.0. A constant maximum absorbance was observed in the pH range 5.3-5.8 as shown in Fig.1.

Hence, all the subsequent studies were carried out in acetate buffer solution of pH 5.5.

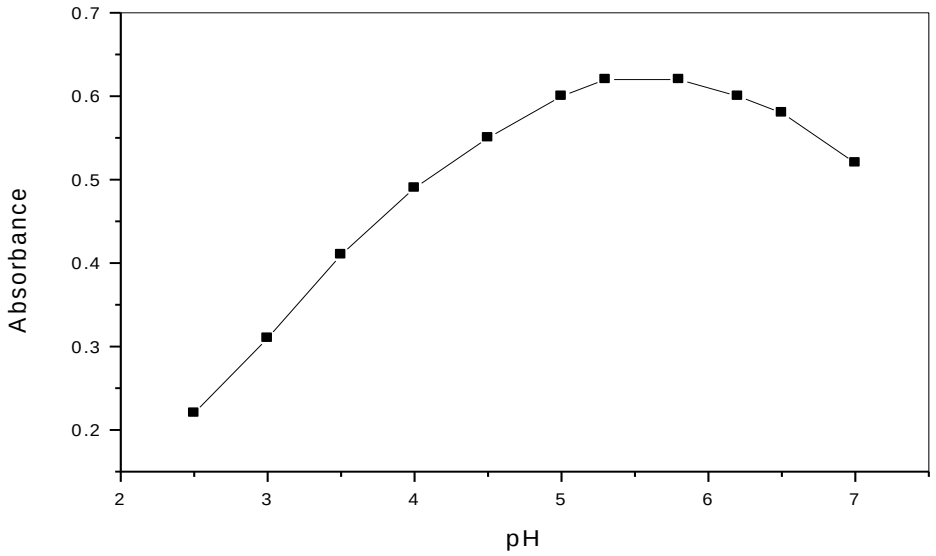

Fig.(1): Effect of pH on the absorbance of iron-SHAM binary complex.

Spectral characteristics

The absorption spectra of the ligand SHAM and of its complex with iron(III) showed that the maximum absorption of the ligand is at 243 nm while that of the complex is at 295 nm as shown in Fig.2 (curves 1 & 2), respectively.

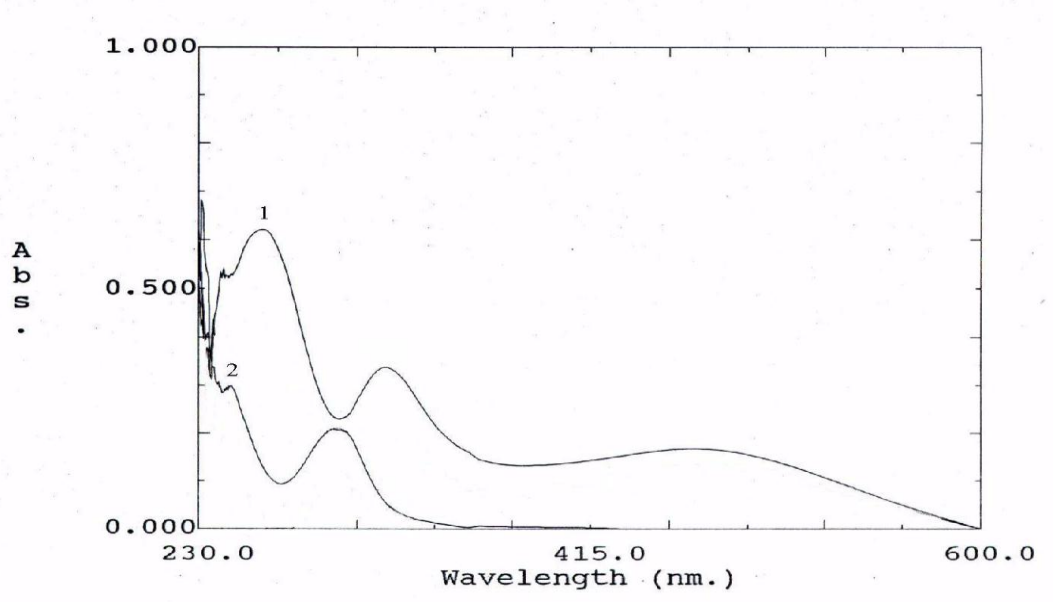

Fig.(2): Absorption spectra of iron(III)-SHAM complex. curve 1, the binary complex; curve 2, its reagent blank.

Effect of Reagent Concentration

It was found that, water is considered as the best solvent for dissolving the reagent SHAM. The reagent concentration was varied between 4 x 10^{-5} M and 1.6 x 10^{-3} M throughout the study. Maximum colour was developed using a reagent concentration ranging between 8 x 10^{-4} M and 2 x 10^{-3} M as shown in Fig.3. Therefore, 2.5 ml of 1 x 10^{-2} M SHAM was used in the recommended procedure.

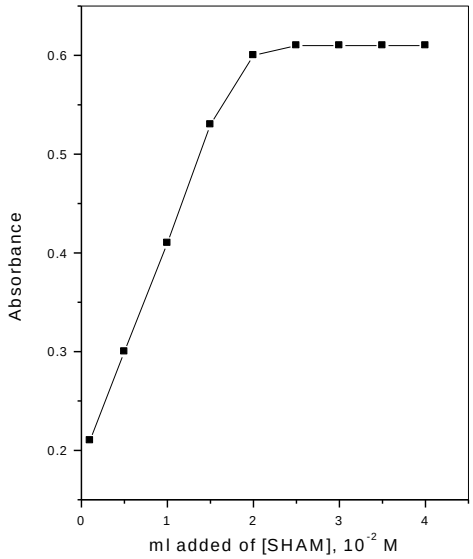

Fig.(3): Effect of SHAM concentration on the absorbance of the binary complex.

Effect of Time

The formation and stability of the iron (III)-SHAM binary complex with respect to time has been examined by preparing a solution of the coloured complex under the normal conditions of the determination. The study revealed that, the complex absorbance reached maximum value within 13 minutes from mixing and remained constant for more than five days. Consequently, a standing time of 15 minutes was recommended for the determination of iron (III) in the binary complex.

Calibration Graph and Statistical Analysis of Results

The iron (III)-SHAM complex obeyed Beer's law up to 5.36 □ g/ml of iron(III) as shown in Fig.4. The molar absorptivity of the binary complex as

determined by least squares method is 1.3 x 10^4 l.mol^{-1}.cm^{-1} at 257 nm and the calculated value of Sandell's sensitivity index of the complex is 4.3 ng.cm^{-2}.

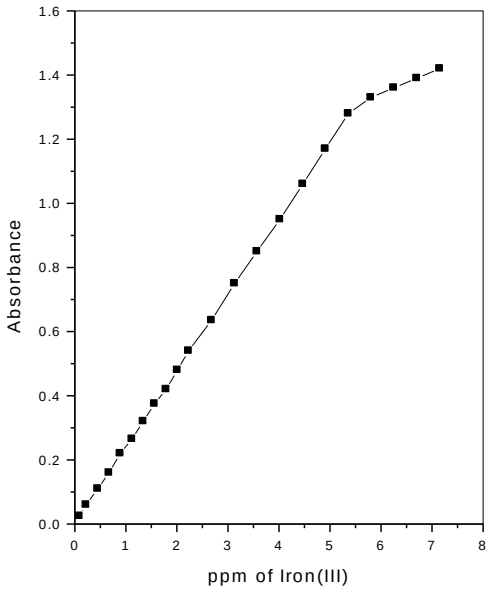

Fig.(4): Calibration graph for the determination of iron(III) with SHAM as binary complex.

The precision of the developed method was evaluated using twelve samples each containing 2.68 □ g/ml of iron (III) per 25 ml of solution. The mean value of absorbance was 0.63 with a standard deviation of 0.007. The equation of calibration graph as calculated by a least squares fit relation for eighteen readings is A = 0.02 + 1.3 x 10^4 C where: A, the absorbance of the complex; C, the concentration of iron (III) and the term 0.02, the intercept. The statistical analysis of data obtained are summarized in Table 1.

Table 1: Statistical analysis of iron (III)-SHAM binary complex.

The complex	**Iron(III)-SHAM**
□ nm	257
Least square equation	A = 0.02 + 1.3 × 10^4 C
Linear range "□ g ml^1"	0.09-5.36
R	0.99994
□^{2}	8.8193
$S_{y/x}$	4.1 x 10^{-3}
S_b	5.28 x 10^{-3}
S_a	2.9697
DL "□ g/ml"	0.09

Where:

A, absorbance value; C, concentration of iron (III) □ g/ml; □ nm, maximum wavelength of iron (III)-SHAM complex; r, correlation coefficient; $\square^2$, the variance value; $S_{y/x}$, standard deviation of residuals; S_b, standard deviation of slope of regression equation; S_a, standard deviation of 2.68 □ g ml^1 of iron (III)

(number of replicates, n = 12); DL, detection limit.

Stoichiometry of the Complex

The molar composition of iron (III) to SHAM was determined under the experimental conditions for maximum absorption following the methods of molar ratio and continuous variations, Both methods showed that the composition of the complex was 1:2 (iron(III)-SHAM).

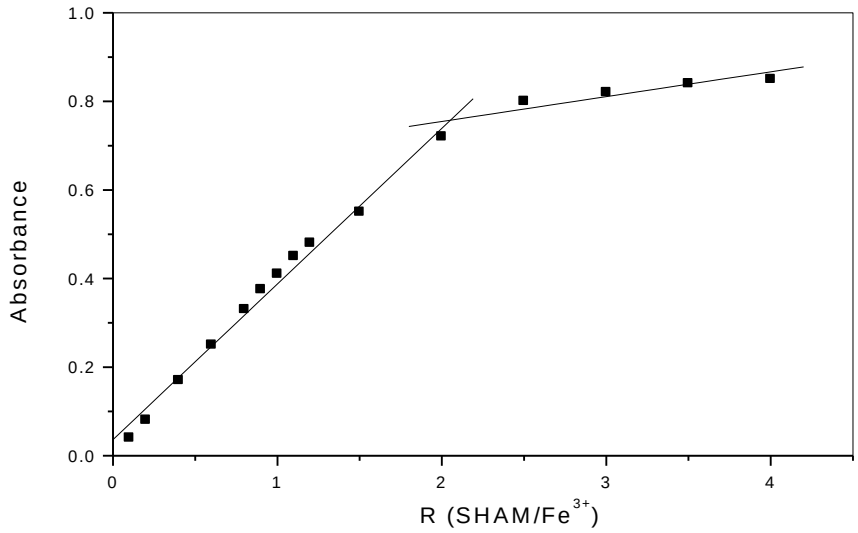

Fig.(5): Determination of iron(III)-SHAM ratio in the binary complex using the molar ratio method

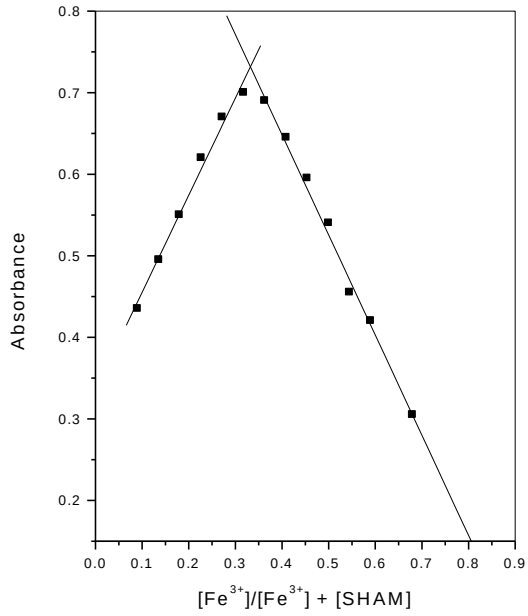

Fig.(6): Determination of iron-SHAM ratio in the binary complex using the continuous variation method.

Interference Study

The effect of various anions and cations was studied by setting the tolerance limit at an amount to cause an error in the absorbance of ± 2% in the determination of iron (III). The effect of foreign ions is given in Table 2. However, metal ions such as Al(III), Cu(II) and Fe(II) interfered and some masking agents were used to improve the selectivity of the method. On the other hand, EDTA and ascorbic acid seriously interfered.

Table 2: Effect of diverse ions on the determination of iron(III)-SHAM complex.

Diverse Ions	Tolerance limit [Ion]/[Fe(III)]
Li^{+}, Na^{+}, K^{+}, Ca^{2+}, Mg^{2+}, Ba^{2+}, Sr^{2+}, NH_4^{+}, Cl^{-}, F^{-}, H_2O_2, CO_3^{2-}, SO_4^{2-}, $S_2O_3^{2-}$	> 10.000
Ag^{+}, Ca^{2+}, SCN^{-}, Br^{-}, I^{-}, NO_2^{-}, NO_3^{-}, ClO_4^{-}, ethanol amine, acetyl acetone, DEA, TEA	> 5000
Cd^{2+}, Zn^{2+}, citrate, tartrate, malonate, thiourea, $NH_2OH.HCl$, oxalate, formate, borate	> 1000
Co^{2+}, Ni^{2+}, Mn^{2+}, Fe^{2+a}, Cu^{2+b}, Hg^{2+}, Pb^{2+}, Zn^{2+}, Sn^{2+}, Sn^{4+}, Al^{3+a}, phosphate, succinate	> 500
As^{3+}, Bi^{3+}, V^{5+}, Cr^{3+}, Cr^{6+}, Ti^{4+}, Zr^{4+}, Mo^{6+}, U^{6+}, W^{6+}	> 100

Masking agents:

a. 1 ml of 1×10^{-2} M sodium fluoride
b. 0.5 ml of 5×10^{-3} M thiourea.

Determination of Iron (III) in Water and Glycol Samples

The proposed method has been used to determine iron (III) in water and glycol samples. The analyzed water samples were boiler feed water in some thermal power stations, industrial wastewater in different plants, ground water of Shagar field in Ras Gharib, whereas glycol samples were obtained from Abu Sennan gas plant in western desert. Tables 3, 4 & 5 illustrate the concentration of iron (III) in the analyzed samples by the proposed method and the results obtained were in good accordance with atomic absorption spectrometric method.

Table 3: Determination of iron (III) in boiler feed water in thermal power stations using SHAM as reagent

Source of samples		Iron (III), "□ g/ml"		
Location	**Unit no.**	**AAS**	***Found "□ g/ml"**	**Standard deviation**
North Cairo power station	4	10.2	10.27	0.074
North Cairo power station	8	6.9	6.95	0.031
West Cairo power station	3	4.5	4.58	0.033
West Cairo power station	4	2.2	2.16	0.038
Shoubra El-Kheima power station	1	3.95	3.94	0.048
Shoubra El-Kheima power station	2	4.28	4.27	0.037
South Cairo power station	3	4.12	4.10	0.035
Abu-Soltan power station	2	8.65	8.64	0.04
Abu-Soltan power station	3	8.7	8.65	0.032
Talkha	6	3.4	3.44	0.05

* Average five determinations

Table 4: Determination of iron (III) in industrial waste water and ground water using SHAM as reagent

Samples	Iron (III), "□ g/ml"		
	AAS	*Found "□ g/ml"	Standard deviation
a- In wastewater			
Helwan Iron and Steel Factory	0.83	0.82	0.033
Helwan Coke Factory	1.68	1.64	0.027
Maadi Electroplating Plant	0.82	0.85	0.029
Madboly Tanning Company in Mistr El-Kadima	2.36	2.39	0.044
b- In ground water			
Shagar well no.3 in Ras Gharib	0.86	0.84	0.16
Shagar well no.7 in Ras Gharib	0.44	0.45	0.025
Shagar well no.8 in Ras Gharib	0.62	0.59	0.016
Shagar well no.9 in Ras Gharib	1.2	1.25	0.02
Gharib field associated water with crude oil in GPC	0.8	0.83	0.029
Gharib field associated water with crude oil in GPC	0.43	0.42	0.039

GPC : General Petroleum Company
* average of five determinations

Table 5: Determination of iron (III) in glycol samples using SHAM as reagent

Samples	Iron (III), "□ g/ml"		
	AAS	*Found "□ g/ml"	Standard deviation
Diethylene glycol (DEG)	0.5	0.53	0.22
Triethylene glycol (TEG)	17.4	17.34	0.029

* average of five determinations

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