

## **Extraction-Spectrophotometric Determination of Iron(III) with Thiocyanate and Cetyltrimethyl Ammonium Bromide in Scales**

Y. Z. Hussein, S. H. Etaiw\* and A. A. Abuel Ela

Chemistry Department, Faculty of Science, Al-Azhar University, Nasr City, Cairo, Egypt.

\* Chemistry Department, Faculty of Science, Tanta University, Tanta, Egypt

**Summary-** Iron (III) was extracted at pH 2.8 as ion associate with ammonium thiocyanate (SCN) and cetyltrimethylammonium bromide (CTAB) into toluene and was spectrophotometrically determined at 475 nm. The calibration curve was linear in the concentration range 0.11-2.9 ppm of iron (III) and the apparent molar absorptivity was  $2.9 \times 10^4$  l.mol<sup>-1</sup>.cm<sup>-1</sup>. The molar composition of the ion-associate iron(III)-SCN-CTAB was 1:3:3 by Job's method and molar ratio method. Common cations did not interfere and the method has been applied for the determination of trace amounts of iron(III) in scale samples.

### **Introduction**

Several organic solvents have been used for the extraction of iron complexes such as chloroform, n-butanol, diethyl ether, methyl isobutyl ketone, 1,2-dichloro ethane, toluene and xylene. Iron was extracted and determined spectrophotometrically using various complexing agents such as thiocyanate<sup>(1-2)</sup>, phenanthroline<sup>(3)</sup>, PAR<sup>(4)</sup>, ferron<sup>(5)</sup> and 3-hydroxy-2-(2-thienyl)-4-hydroxy chromen-4-one (HTC)<sup>(6)</sup>. Extraction-spectrophotometric methods based on the formation of ion-association formed by reaction of the anionic iron(III)-thiocyanate with organic bases<sup>(7-12)</sup> have been determined. Whereas, some cationic surfactants have been used as counter iron complex<sup>(13-17)</sup>. On the other hand, the composition of the extracted ion-associate formed between iron(III)-bathophenanthroline and eosin dye into chloroform was 1:2:3<sup>(18)</sup>.

In the present work, iron(III) reacts with ammonium thiocyanate ( $\text{NH}_4\text{SCN}$ ) in presence of cetyltrimethyl ammonium bromide (CTAB) to form 1:3:3 ion-associate. The system was extracted into toluene at pH 2.8. Optimal conditions have been incorporated into a proposed analytical procedure which was applied to determine iron(III) in scales.

## Experimental

### Apparatus

Measurements of absorbance were conducted using SHIMADZU UV-VIS-NIR scanning spectrophotometer. pH measurements were measured using ion analyzer model CRISON pH/mV meter digit 501 equipped with a combination glass-calomel electrode.

### Reagents

All chemicals used in the proposed method were of analytical reagent grade. Aqueous solutions were prepared with bi-distilled water. Ferrous ammonium sulphate ( $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ ), (A.R.),  $1 \times 10^{-2}$  M; Ammonium thiocyanate, (El-Nasr Chemical Co.) 0.2M; Cetyltrimethylammonium bromide (Aldrich),  $1 \times 10^{-2}$  M was prepared by dissolving 0.9111 g in warm water and diluted to 250 ml. ; Acetate buffer solution series in the pH range 1.5-4.5.

### General Procedure

Transfer an aliquot of the sample solution containing  $\leq 2.9 \mu\text{g}$  of iron(III) to 125 ml separating funnel. Add 2.0 ml of 0.2 M of ammonium thiocyanate, 0.5 ml of  $1 \times 10^{-2}$  M of CTAB, 5.0 ml of acetate buffer solution of pH 2.8 and 10.0 ml toluene for extraction iron(III) in organic solvent. Shake well the mixture for 5 minutes, then measure directly the absorbance of the organic layer at 475 nm against a reagent blank. For scale sample, weigh accurately 0.5 g of the dry scale sample in a beaker, add 10 ml aqua regia, boil gently and evaporate to dryness. The residue was dissolved in 1:1 hydrochloric acid and diluted to suitable volume. Then, follow the above steps to determine iron(III) in scales.

## **Results and Discussion**

### **Effect of pH**

The influence of pH of the aqueous phase on the absorbance of the extracted iron(III)-SCN-CTAB ion-associate in toluene was studied in the pH range 1.5-4.5. Maximum and constant absorbance of the extracted ion-associate was obtained by adjusting the pH of the aqueous phase with acetate buffer solution in the range 2.5-3.0. Hence, all the studies were carried out in acetate buffer solution of pH 2.8.

### **Spectral Characteristics**

The extraction of iron(III) with thiocyanate into toluene have been studied in the absence and presence of some cationic surfactants.

The absorption spectra of the extracted iron(III)-SCN-CTAB ion-associate has an absorption maximum at 475 nm, whereas in absence of CTAB shifted to shorter wavelength at 462.5 nm as shown in Fig.1. On the other hand, their reagents blank do not exhibit color. Ion-association complex is formed by the electrostatic combination of oppositely-charged ions which have low charge and high molecular weight including quaternary ammonium salt with thiocyanate<sup>(19)</sup>. High molecular weight (CTAB) is of particular importance in the extraction of ion-association into nonpolar solvent (toluene) .

### **Effect of SCN Concentration**

The influence of SCN concentration on the absorbance of the extracted system have been studied in the range  $2 \times 10^{-3}$  M–0.1 M of SCN. Maximum and constant absorbance of the extracted complex was obtained using  $3.5 \times 10^{-2}$  M and 0.1 M of SCN.

### **Effect of CTAB Concentration**

The influence of CTAB concentration on the absorbance of the formed ion-associate was carried out using CTAB concentration ranged between  $2 \times 10^{-2}$

$4 \times 10^{-4} \text{ M}$  and  $3 \times 10^{-2} \text{ M}$ . The study revealed an optimum CTAB concentration ranged between  $4 \times 10^{-4} \text{ M}$  and  $3 \times 10^{-3} \text{ M}$  for maximum color of the extracted system.

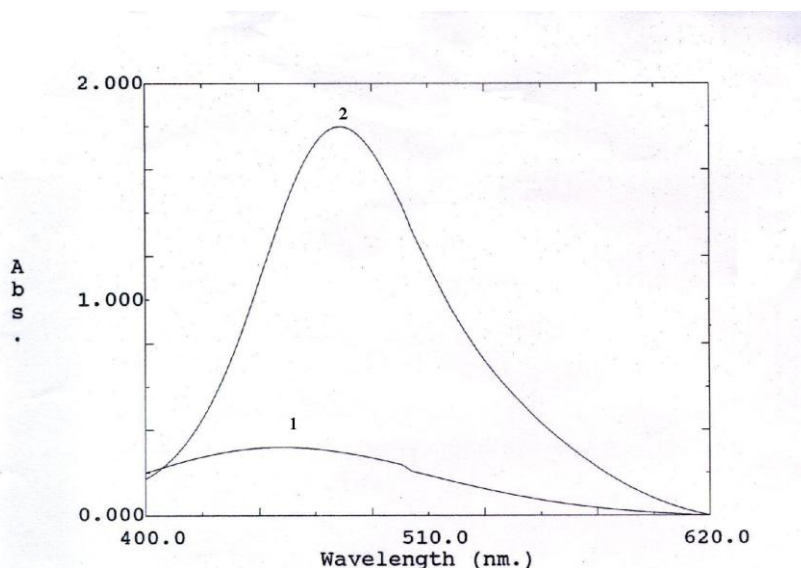


Fig.(1): Absorption spectra of iron(III)-SCN complex in the presence and absence of CTAB. Curve 1, Fe(III)-SCN complex; Curve 2, Fe(III)-SCN-CTAB ion-associate.

### Effect of Shaking Time

The effect of shaking time on the extraction of the ion associate iron(III)-SCN-CTAB in toluene was carried out in the interval time 1-10 minutes. The absorbance of the complex attained a maximum value by shaking, after 4 minutes and remained constant for more than three days. In the procedure, a shaking time of 5 minutes was to be used.

### Extraction Solvent and Extractability

Different organic solvents such as benzene, toluene, xylene, chloroform, carbon tetrachloride, n-butylacetate, petroleum ether, cyclohexanone and pentylacetate have been examined for extracting ion associate iron(III)-SCN-CTAB system as shown in Fig. 2. Variable intervals of shaking time have been employed for each set of experiments to ensure maximum extraction. Maximum extraction has been examined using toluene as suitable solvent which was used in procedure.

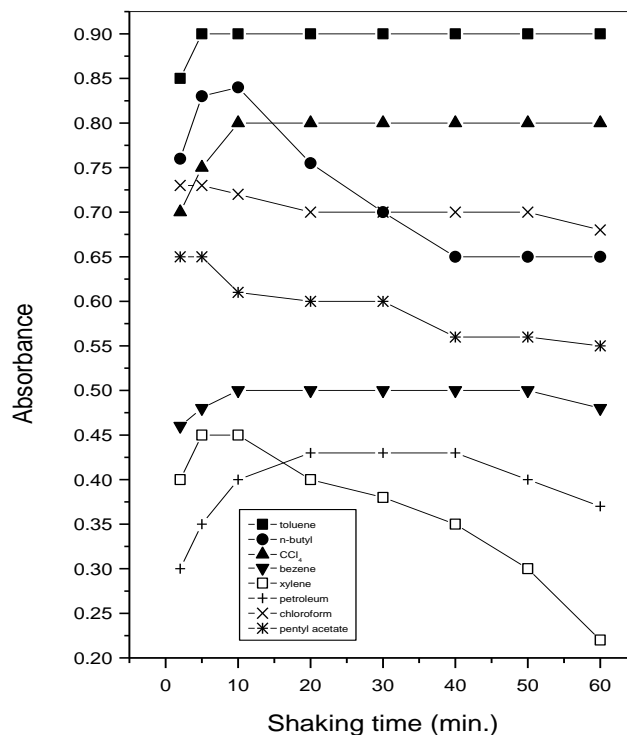


Fig.(2): Effect of solvents and shaking time on the absorbance of iron(III)- SCN-CTAB ion-associate.

The extractability of the complex in toluene has been tested by a repeated extraction of a sample containing  $5 \times 10^{-5} \text{M}$  of iron(III) with two portions of toluene. The results obtained confirm 99.5% extraction of the complex in one run.

### Calibration Graph, Sensitivity and Precision of the Method

The calibration curve of the extracted iron(III)-SCN-CTAB ion associated complex was obeyed Beer's law over the concentration range 0.11-2.9  $\mu\text{g/ml}$  of iron(III) in the organic phase. The molar absorptivity of the extracted species was  $2.9 \times 10^4 \text{ l.mol}^{-1}.\text{cm}^{-1}$  at 475 nm. The calculated value of Sandell's sensitivity index of the extracted species was  $1.9 \text{ ng.cm}^{-2}$ . The precision of the method has been evaluated by measuring the absorbance of ten samples each containing 0.33 ppm of iron(III) and the mean value of absorbance was 0.60 with a standard deviation of 0.003.

## Composition of Complex

The composition of the extracted iron(III)-SCN-CTAB ion-associate established by both molar ratio and continuous variation method was found to be 1:3:3. The continuous variation method was used to determine stability constant ( $\beta$ ) and its value  $2.2 \times 10^6$ .

## Effect of Interfering Ions

The extent of interferences of various anions and cations have been studied by measuring the absorbance of the extracted complex containing 1.5  $\mu\text{g}$  of iron(III) and different amounts of a foreign ions. The tolerance limit was taken as the amount that cause  $\pm 2\%$  error in the absorbance value. The tolerance limits of various ions were summarized in Table 1. The ion-associate complex iron(III)-SCN-CTAB was exhibited good selectivity for most common cations and anions. On the other hand, silver, arsenate, fluoride, tartrate and phosphate were seriously interfered.

Table 1: Effect of interfering ions on the determination of iron(III) with SCN and CTAB

Diverse Ion	Tolerance Limit
$\text{Na}^+$ , $\text{K}^+$ , $\text{NH}_4^+$ , $\text{Cl}^-$ , $\text{CO}_3^{2-}$ , $\text{ClO}_4^-$ , $\text{S}_2\text{O}_3^{2-}$ , formate, succinate, sulphate, malonate and citrate.	> 10.000
$\text{Ca}^{2+}$ , $\text{Mg}^{2+}$ , $\text{Ba}^{2+}$ , $\text{Ni}^{2+}$ , $\text{Cd}^{2+}$ , $\text{Zn}^{2+}$ , $\text{Co}^{2+}$ , $\text{B}^{3+}$ , $\text{NO}_2^-$ , $\text{NO}_3^-$ , thiourea, acetylacetone, ethanolamine, DEA and TEA.	> 5000
$\text{Pb}^{2+}$ , $\text{Be}^{2+}$ , $\text{Sr}^{3+}$ , $\text{Al}^{3+}$ , $\text{Sc}^{3+}$ , Cr(III), Cr(VI), Mo(VI), W(VI), Ti(IV), Zr(IV), V(v), EDTA and $\text{Br}^-$ .	> 1000
$\text{Fe}^{2+}$ , $\text{Mn}^{2+}$ , $\text{Cu}^{2+}$ , $\text{Hg}^{2+}$ and $\text{I}^-$ .	> 500

Determination of iron(III) in scales

The method has been used to determine iron(III) in scales which exist in boiler drums of some thermal power stations and also, in pipe lines of furnaces

in Cairo oil refinery company. Iron(III) was determined in aliquot of scale solutions by the developed method. The results obtained summarized in Table 2 and were in good agreement with those obtained by atomic absorption spectrometry (AAS).

Table 2: Determination of iron(III) in boiler drums and pipelines scales using SCN and CTAB.

Location	Fe(III), ppm		S.D
	AAS	*Found	
North Cairo power station, unit no. 4	5.24	5.25	0.033
North Cairo power station, unit no. 6	3.34	3.34	0.034
West Cairo power station, unit no. 1	17.38	17.39	0.036
West Cairo power station, unit no. 2	11.70	11.68	0.027
Shoubra El-Kheima power station, unit no. 1	7.44	7.44	0.042
Shoubra El-Kheima power station, unit no. 2	6.85	6.85	0.034
Shoubra El-Kheima power station, unit no. 3	5.60	5.60	0.029
South Cairo power station, unit no. 2	14.52	14.52	0.035
South Cairo power station, unit no. 3	18.90	18.91	0.042
Tepeen, unit no. 5	5.25	5.25	0.02
Talkha , unit no. 1	21.70	21.70	0.032
Talkha, unit no. 2	17.90	17.90	0.039
Damanhour, unit no. 2	24.68	24.67	0.028
Cyoof, unit no. 2	12.32	12.31	0.033
Assuit, unit no. 2	13.36	13.37	0.044
Cairo Oil Refinery Company (Furnace Pipelines no. 1)	6.30	6.30	0.025
Cairo Oil Refinery Company (Furnace Pipelines no. 2)	5.40	5.40	0.023
Cairo Oil Refinery Company (Furnace Pipelines no. 3)	4.80	4.79	0.023

\* mean value of five replicates

## References

1. Specker, H.; Jackwerth, E.; Hovermann, G., *Z. Anal. Chem.*, **177**, 10 (1960).
2. Luke, C. L., *Anal. Chim. Acta.*, **36**, 122 (1966).
3. Rustamov, N. Kh., *Azerb Khim. Zh.*, **3**, 38-42 (1999)
4. Das, S.; Das, H. K., *J. Indian Chem. Soc.*, **74**(9), 740-741 (1997)
5. Arya, Satya, Prakash; Mahajan, Meenakshi., *Ann. Chim (Rome)*, **87**(7-8), 529-34 (1997)
6. Arya, Satya, Prakash; Mahajan, Meenakshi; Jain Preeti., *Indian J. Chem.*, **39** A (5), 552-53 (2000).
7. Jha, A. R.; Mishra, R. K., *Analyst*, **106**, 1150 (1981).
8. Siepak, Jerzy., *Z. Chem.*, **29**(5), 183 (1989).
9. Ramappa, P. G.; Manjappa, S., *Curr. Sci.*, **58**(14), 797-8 (1989).
10. Chowdhury, R.P.; Pal, B.K.; Mitra, B.K., *Mikrochim. Acta*, II, 515 (1980).
11. Mendenz, H.J.; Mateos, A.A.; Mateos, E.J.M., *Microchem. J.*, **30**, 154 (1984).
12. Patel, K.S.; Shukla, A.; Goswami, A.; Chandavanshi, S.K.; Hoffman, P., *Fresenius J. Anal. Chem.*, **369** (6), 530-34 (2001)
13. Bayan, K.G.; Das, H.K., *Talanta*, **35**, 57 (1988).
14. Shijo, Y., *Bull. Chem. Soc. Jpn.*, 50, 1013 (1977).
15. Zaki, M.T.M.; Mahmoud, W.H.; El-Sayed, A.Y., *Talanta*, **35**, 253 (1988).
16. Shijo, Y., *Bull. Chem. Soc. Jpn.*, **84**, 2793 (1975).
17. Kamara, T., Matsumae, S.; Hasebe, K., *Bunseki Kagaku*, **19**, 462 (1970).
18. Zaki, M.T.M.; El-Zawawy, F.M.; Ghorab, A.A.; Esmail, M.A., *Anal. Sci.*, **8**(2), 229-32 (1992).
19. Shevchuk, I. A., "Extraction with Organic Bases" Vysshaya Shkola, Kieve (1978).