# Determination of Fe (III) with 1-nitroso-2-naphthol in Micellar Medium by Derivative Spectrophotometry

G. A. SHAR AND G. A. SOOMRO
*Department of Chemistry*
*Shah Abdul Latif University Khairpur, Sindh, Pakistan*

**Summary:** A spectrophotometeric and first derivative spectrophotometeric determination of iron(III) is carried out with 1-nitroso-2-naphthol as complexing reagent in aqueous phase using non-ionic surfactant Tween 40. The iron is determined in the range 1.7–120 ng mL$^{-1}$ with detection limit ($2\sigma$) of 1.7 ng mL$^{-1}$. The molar absorptivity and Sandell's sensitivity are $1.69 \times (10^4$ mol$^{-1}$ cm$^{-1})$ and 7.9 ngcm$^{-2}$ at 446 nm. The optimum pH of the complex is 1. The critical micelle concentration (cmc) of Tween 40 is 5 %. Absorption studies in the first derivative mode is carried out to determine the absorption maximum of the complex for higher sensitivity and to overcome interference due to the presence of certain metal ions. The present method is compared with that of AAS and no significant difference is noted between the two methods at 95 % confidence level. The method has been applied for the determination of Fe(III) in industrial waste water and steel samples.

## Introduction

Iron is the most important element of the human body, as it plays pivotal role in the erythro-poiesis and also in oxygen transport through haem. Deficiency of iron is associated with myocardial infarction and anemia. The excess intake can cause siderosis and damage to organs (hemochromatosis) [1]. In chemical analysis, metal chelation followed by solvent extraction and spectrophotometric detec-tion is the preferred mode of analysis for a number of metal ions [2-3] due to rapidity, simplicity and wide applications. Several spectrophotometric methods have been developed in which the solvent extraction step is conveniently replaced by the use of a surface-tant [4-5]. Due to the solubility of several compounds in micelles (aggregates of surfactants), many analyti-cal techniques for the determination of metal ions in aqueous system, have been developed and modified [6-15]. Micellar media is mainly used to enhance the absorption sensitivities, thus simplifying the system by replacing the toxic organic solvents. Determina-tion of iron and ruthenium as ternary complexes by extractive second derivative spectrophotometry has been reported [16]. Derivative spectrophotometric determination of copper(II) in non-ionic micellar medium has been reported [17]. Tween series surfactants are very soluble in aqueous systems than other non-ionic surfactants. 1-nitroso-2-naphthol forms coloured water-insoluble complexes with a large number of metal ions and the use of surface active reagent increase the solubility of 1-nitroso-2-naphthol has been reported [18]. Derivative mode spectrophotometry is recently shown to be more useful than classical spectrophotometry for solving several analytical problem [19]. The use of derivative mode spectrophotometry offers a useful means of enhancing the sensitivity and selectivity of the method besides convenient solution to well defined analytical problems such as resolution of multi component systems, overcoming interference due to sample turbidity, matrix back ground and enhance-ment of spectral details [20-21]. The scale of this increase depends on the shape of the normal absorption spectra of the analyte and the interfering substances, as well as on instrumental parameters and the measurement technique (e.g. peak -to-trough or zero-crossing), chosen by the analyst in a given analytical procedure.

In the present work, determination of Fe (III) as 1-nitroso-2-naphthol complex, in a non-ionic surfactant Tween 40 using first derivative mode spectrophotometric method is reported. The method was successfully applied for the determination of Fe (III) in industrial waste and steel samples.

## Results and Discussion

Fig. 1 shows absorption spectra in first derivative mode spectroscopy of Fe (III)-1-nitroso-2-naphthol complex at 430 nm (i.e. a shift from 446 nm). It can be seen in the Fig. 1 the height of the peak at (PH) 430 nm and the depth of the trough (TD) at 400 nm were linearly related to the metal ion concentration. It can be seen by comparing Fig. 1 that
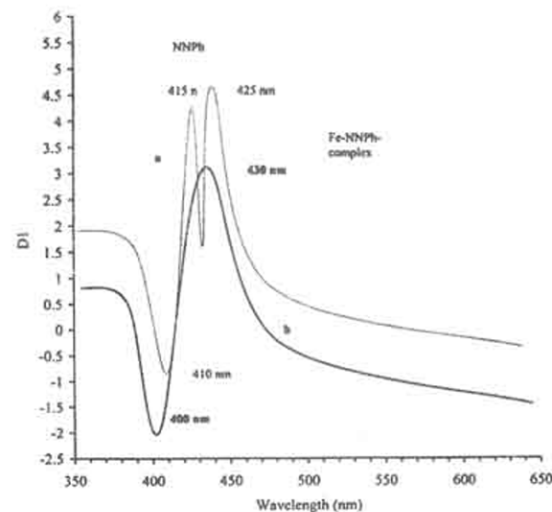
Fig. 1:   First derivative spectra of (a) 1-nitroso-2-naphthol (b) iron (III)-1-nitroso-2-naphthol complex in 5% Tween 40 at pH 1.

the first derivative spectra are more resolved than those obtained for the normal mode. It can be seen that the first derivative spectra are more resolved than those obtained for the normal mode. However, even higher derivative orders yield sensitive but irreproducible signal, so this possibility was discarded. As derivative spectroscopy provides additional possibilities because it enhances the detectability of minor spectral features, this technique was adapted. The first order derivative spectrum is of great significance as it exhibits the $\lambda_{max}$ of the complex which is other wise difficult to ascertain due to several absorbing species and only a shoulder appears in the normal absorption spectrum due to the desired component. Weak and broad peaks give higher sharpest peak; other close peaks were changed from normal mode wavelength to new ones length showing no close ness to other neighbour peaks. The micelle of non-ionic surfactant with polyoxyethylene group comprises two parts. One is the hydrocarbon tail directed to the interior core of micelle and the other is the hydrated polyoxyethylene group located at outer sphere. Organic compounds and metal chelates having large affinity towards polyoxyethylene group may be incorporated. 1-nitroso-2-naphthol could be dissolved by this phenomenon, because this species has a hydroxyl group, which interacts with the ether oxygen of polyoxyethylene group, by hydrogen bonding. It seems that micelle in solution was formed because 5 % Tween 40 solution was above (0.0013 %, w/v) concentration [22].

Composition of the complex formed under experimental conditions was investigated by job's method of continuous variations. Composition of the complex formed under experimental conditions was investigated by Job's method of continuous variations. From Fig. 2 it can be inferred that metal: ligand ratio is 1:3.
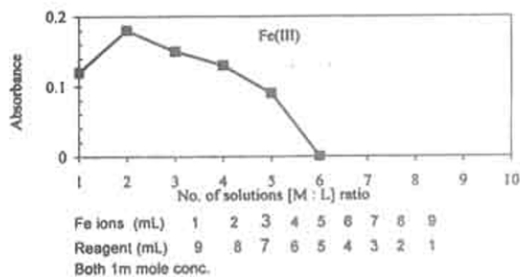


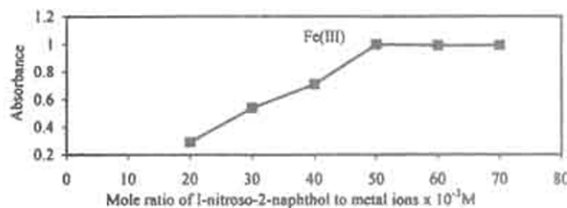Fig. 2:   Job's plot of metal: ligand ratio.



Fig. 3:   Effect of amounts of 1-nitroso-2-naphthol on the absorbance of Fe (III).

Fig. 3 indicates the effect of mole ratio of 1-nitroso-2-naphthol for Fe (III) in the complex formation and is observed that different metals have different mole ratios. For iron it is 50 to 70 m. moles of the reagent. There fore, 50 m. mole of the reagent require 1m.mole of the metal ion. Fig. 4 shows the optimum pH 1.0 for Fe (III) 1-nitroso-2-naphthol complex formation. Fig. 5 shows the calibration graph of Fe (III)-1-nitroso-2-naphthol complex in the range of 1.7-120 ng mL$^{-1}$ at 430 nm in first derivative mode spectrophotometery. The detection limit is lowered significantly  from 3.3 to 1.7 ng mL$^{-1}$. All other experimental conditions are same as in normal mode spectroscopy. Molar absorptivity is $1.69 \times (10^4$ mol$^{-1}$cm$^{-1}$), Sandell's sensitivity (7.9 ngcm$^{-2}$). Beer's law linear range in normal mode is 0.5-4.0 μg mL$^{-1}$.

Comparison of detection limit of the present method with other sensitive methods is given in Table-1.

*Study of interference's by foreign ions*

In the Fe (III) determination with 1-nitroso-2-naphthol in presence of 5 % Tween 40 were studied

Table-1: Comparison of sensitivities of various methods

| Present method | Fluorimetric method [Ref. 24] | Spectroscopic method [25] | AAS method [26] | Electrothermal atomization-AAS method [27] | FAAS method [28] | (ICP-AES) method [29-31] |
|---|---|---|---|---|---|---|
| 1.7 ng mL$^{-1}$ | 7 ng mL$^{-1}$ | 100-800 ng mL$^{-1}$ | 2 ng mL$^{-1}$ | 2-20 ng mL$^{-1}$ | 4 ng mL$^{-1}$ | 0.2 ng mL$^{-1}$ 0.1-80 μg mL$^{-1}$ |

AAS   Atomic absorption spectroscopy
FAAS  Flame atomic absorption spectroscopy
ICP   Inductive couple plasma
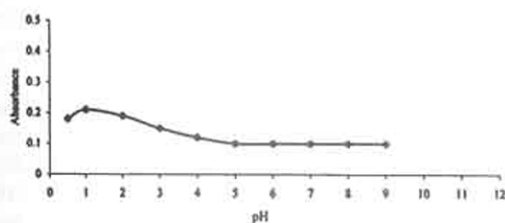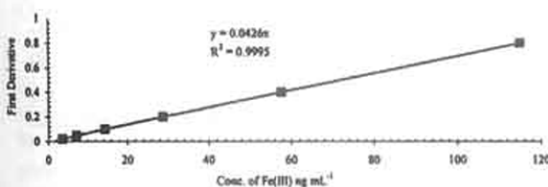AES   Atomic emission spectroscopy



Fig. 4:  Effect of pH on the absorbance of metal-1-nitroso-2-naphthol complex.



Fig. 5:  Calibration graph of Fe (III)-1-nitroso-2-naphthol complex in 5% Tween 40 at pH 1 at ($\lambda_{max}$ 430 nm and 400 nm) in first derivative mode spectroscopy.

results are shown in the Table-2, these interference's can be avoided in general by the addition of complexing agent like EDTA which forms stable complexes with many metal ions so that in this medium Fe (III) reaction with 1-nitroso-2-naphthol is highly selective with at pH 1. Cd (II), Ni (II), Cu (II), Co (II) and Pb (II) interfere at low trace level as given in Table-2. The interference due to absorption by Cu (II), Co (II) and Ni (II)-1-nitroso-2-naphthol com-plex in normal mode spectroscopy is thus removed by the use of first derivative mode spectroscopy.

### Validation of method

Proposed method was verified by % recovery test by standard addition method, results were compared with AAS, which are in good agreement with (AAS) given in Table-3.

Table-2: Tolerance limits for interference's of metal ions and salts with 1-nitroso-2-naphthol in Tween 40 in normal mode spectroscopy Tolerance limits μg mL$^{-1}$

| Ion / salt | Fe(III) |
|---|---|
| KSCN | 1000 |
| NaF | 600 |
| Na$_2$C$_2$O$_4$ | 50 |
| KClO$_3$ | 1000 |
| Na$_2$tartarate | 1000 |
| Na$_2$citrate | 100 |
| KCN | 30 |
| Mg(II) | 800 |
| Al(III) | 100 |
| Cd(II) | 2 |
| Co (II) | 100 |
| Cr (III) | 50 |
| Cr (VI) | 8 |
| Fe (III) | - |
| Mn(II) | 500 |
| Ni(II) | 50 |
| Pb (II) | 3 |
| Zn (II) | 200 |
| Cu (II) | 100 |

At 95%, n=6
The conc. of metal ions is 2μg mL$^{-1}$

Table-3: Percent recovery of known amount added to tap water.

| Metal ions | Amount added | Amount found | Recovery (%) |
|---|---|---|---|
| Fe(III) | 1.70 ng mL$^{-1}$ | 1.69 ng mL$^{-1}$ | 99 ± 1 |
|  | 0.50 (μg mL$^{-1}$) | 0.49 (μg mL$^{-1}$) | 99 ± 1 |

At 95%, n=6

### Application

The proposed spectrophotometric method was applied to the determination of Fe (III) in industrial waste water samples. Results are shown in Table-4.

### Experimental

A UV/Vis spectrophotometer Perkin Elmer model Lambda 2 was used for recording normal as well as derivative spectra. Atomic absorption spectro-photometer, model Spectra AA. 20 Varian was used for metal ion determination. The Pye Model 292 pH meter was used.

Table-4: Determination of Fe (III) ions in industrial waste and steel samples

| Sample | Amount of Fe (III) determined ($\mu g\ mL^{-1}$) | | |
|---|---|---|---|
| | Present method | AAS method | C.V. % |
| *Industrial waste | | | |
| | 0.45 | 0.47 | 2.57 |
| Steel sample | 0.96 g | 0.95 g | 2.0 |

At 95%, n=6, *Kotri SITE area

### Reagents

All chemicals used were analytical grade reagents (Merck and Fluka A.G) unless otherwise stated. Standard Fe (III) stock solution of (100 $\mu g$ $mL^{-1}$) was prepared dissolving their nitrate salt. Other metal ions solutions were prepared from their nitrate or chloride salts. 5% Tween 40 solution was prepared by dissolving that in a 100 mL volumetric flask, and was diluting to the mark with double distilled water. Buffer solution of pH 1 was prepared by taking 0.2 M potassium chloride (25 mL) and 0.2M hydrochloric acid (67 mL) mixtures and adjusting the volume to 100 mL according to Perrin and Dempsey [23].

### Procedure

Absorption spectra (normal and derivative) of the following solutions were recorded, taking reagent blank as reference, in order to determine photometric characteristics of the 1-nitroso-2-naphthol-Fe (III) complex.

Two sets of solutions, one containing fixed metal ion and other without it, and each containing fixed amount of the reagent (185 $\mu g\ mL^{-1}$) and Tween 40 (5 %) in the pH range 0.5 -9.0 were prepared to determine the optimum pH range of the complexation reaction.

To study the impact of varying surfactant concentration on the absorbance of the 1-nitroso-2-naphthol-Fe (III) complex, a set of solutions containing increasing amounts of Tween 40 (2 %-10 %), fixed Fe (III) ions and 185$\mu g\ mL^{-1}$ 1-nitroso-2-naphthol, at the pH of the maximum complex formation, was prepared.

Effect of varying ligand concentration on the absorbance of the system was investigated by preparing a set of solutions containing $50 \times 10^{-3}$ to $70 \times 10^{-3}$ M of the reagent at the optimum pH.

Linear range was set by varying amount of the metal ions in the first derivative mode (1.0-120 ng

$mL^{-1}$ and  in the normal mode was  0.06 to 5.0 $\mu g$ $mL^{-1}$), 185 $\mu g\ mL^{-1}$ 1-nitroso-2-naphthol, and 5 % Tween 40 at pH 1 condition of maximum complex formation.

### Spectrophotometric metal ion determination in micellar solution

Appropriate volumes of stock solutions of metal ions, 1-nitroso-2-naphthol, and surfactant Tween 40 were added and made up to 25 mL volume with distilled water having metal ions concentration of 1.0-120 ng $mL^{-1}$ and 0.06-5.0 $\mu g\ mL^{-1}$, 1-nitroso-2-naphthol 185 $\mu g\ mL^{-1}$ and 5% Tween 40. Absorption spectra were recorded against reagent as reference to generate analytical calibration curves in normal mode ($\lambda_{max}$ 446 nm) or in first derivative mode (peak height at 430 nm) or (trough depth (TD) at 400 nm). Iron content of the standard and the sample was determined using AAS. The pH and wavelength used are listed in Table-5.

Table-5: Analytical characteristics of Fe (III)-1-nitroso-2-naphthol in presence of Tween 40 in normal mode spectroscopy

| Characteristics | Fe(III) |
|---|---|
| Beer's law range ($\mu g\ mL^{-1}$) | 0.5 –4.0 |
| Absorption maxima ($\lambda_{max}$, nm): (a) micellar | 446 |
| (b) $CCl_4$ | 446 |
| Molar absorptivity ($10^4\ mol^{-1}cm^{-1}$) | 1.69 |
| Sandell's sensitivity $ngcm^{-2}$ | 7.9 |
| Detection limit ( ng $mL^{-1}$) | 3.3 |
| pH range | 1 |
| Conc. of Tween 40 | 5% |
| Conc. of 1-nitroso-2 naphthol ($\mu g\ mL^{-1}$) | 185 |
| RSD ± | 11.23 |

At 95% cofidence limit, n=6

### The determination of Fe (III) in industrial waste and steel samples.

#### (a) Industrial waste

Industrial waste water sample, 1l obtained from industrial effluent collected from Kotri site area was filtered using Whatman filter paper. Concentrated nitric acid 4 mL and 30 % hydrogen peroxide 2 mL were added to the filterate. The resulting solution was preconcentrated in an oven at 110 $^0$C to a final volume of 25 mL. Appropriate amounts of Tween 40 and 1-nitroso-2-naphthol was added to a 25 mL calibrated flask to obtain final concentration of 5 % in Tween 40 and 185 $\mu g\ mL^{-1}$ in 1-nitroso-2-naphthol. Then 5 mL of the sample was added and

the absor-bance was measured against reagent blank. The same sample, 5 mL was diluted to 25 mL with double distilled water for AAS analysis.

### (b) The steel sample

The steel sample was washed with acetone and distilled water and was dried. The steel sample weighing 1.0053 and 0.5008 g were taken to 250 mL beakers. The 50 mL of 6 M HCl and 15 mL of 6 M $HNO_3$ were added, and the mixture was heated mildly. This steel solution was completely transferred to a 1000-mL volumetric flask, and was filled to mark. Two milliliters of this diluted solution was trans-ferred to another 1000-mL volumetric flask. Then, 5 mL of this diluted steel soluton was taken to five 10-mL volumetric flasks, and 0.0, 0.5, 1.0, 1.5, and 2.0 mL of 20 µg mL$^{-1}$ standard Fe (III) soluton was added to each flask, respectively. And, the other procedures follow brass sample procedure.

### Conclusions

Determination of trace amount of Fe (III) up to 1.7 ng mL$^{-1}$ can be carried out directly using 1-nitroso-2-naphthol, in non-ionic micellar media of 5 % Tween 40 in aqueous solutions. The method is simple and rapid with greater sensitivity, better selectivity, and improved precision and replaces extraction with toxic organic solvents. Fe (III) content samples determined by the present method is in agreement with the values obtained by atomic absorption spectroscopy.

### Acknowledgment

### References

1.  J. E. Huheey, Inorganic chemistry in biological systems" *Inorganic chemistry*"3$^{rd}$ edn., 909 (1983).
2.  W. J. Simmons, *Anal. Chem.*, **45**, 1947 (1973).
3.  G.A. Olah, *Chem. Eng. News*, **54** (6), 6 (1976).
4.  G.A. Olah, *Chem. Eng. News* **54** (6), 7 (1976).
5.  M. P. San Andres, M. L. Marina and S. Vera, *Talanta*, **41**, 179 (1994).
6.  M. A Sanz. M. F. Fernandez, *Anal. Chem.* **58**, 2161 (1986).
7.  H. C. Gin. L. Hong. P. J. Mai, *Talanta, 41*, 1357 (1994).
8.  A. Lopez Garcia, E. Blanco Gonzalez, J. L. Garcia Alonso, A. Sanz Medel, *Anal. Chim. Acta.*, **264**, 241 (1992).
9.  T. Okada, *Anal. Chem.* **64**, 2138 (1992).
10. E. Paramauro, A. Bianco Prevot, E. Pelizzetti, *Anal. Chim. Acta.*, **264**, 303 (1992).
11. L. J. Cline Love, J. G. Habarta, J. G. Dorsey, *Anal. Chem.*, **56**, 1133 (1984).
12. X. Jin, M. Zhu, E. D. Conte, *Anal. Chem.*, **71**, 514 (1999).
13. G. A. Shar, G. A. Soomro and M. I. Bhanger, *J. Chem. Soc. Pak.*, **26**(2), 143 (2004).
14. A. K. Malik, K. N. Kaul, B. S. Lark, W. Faubel and A. L. J. Rao, *Turk. J. Chem.*, **25**, 99 (2001).
15. Afkhami A and Bhram M *Spectrochim Acta A Mol Biomol Spectrosc*, **60** (1-2), 181(2004).
16. M. I. Toral, P. Richter, A. E. Tapia, J. Hernandez, *Talanta*, **50**, 183 (1999).
17. N. K. Agnihotri, V. K. Singh and H.B. Singh, *Talanta*, **45**, 331 (1997).
18. J. Yun, H. Choi, *Talanta*, **52**, 893 (2000).
19. R. L. Sharma and H. B. Singh, *Talanta*, **36**(4), 457 (1989).
20. A. Ringbom, *J.Chem. Educ.*, **35**, 282 (1958).
21. L. G. Sillen, A. E. Martell, Stablity Constants of Metal Complexes, vol.1 and vol. 2 hemical Society, London, 1964 (1971).
22. P. Beeher, in M. J. Schiek (Ed.) *Surfactant Science Series*, vol. 1, Mareel Dekker, New York, p, 481 (1966).
23. D. D Perrin, B. Dempsey, *Buffers for pH and Metal Ion Control*, Chapman and Hall, ondon (1974).
24. A. Peditier, S. Rubio, A. Gomez-Hens and M. Valeareel, *Talanta*, **32**, 104 1985).
25. M. A. Bello Lopez, M. Callejon Mochon, J. L. Gomez Ariza and A. Guiraum Perez, *Analyst*, **111**, 1293 (1986).
26. L. C. Robles, C. Garcia-Olalla. Alemany and A.J. Aller, *Analyst*, **116**, 735 (1991).
27. N. GOYAL, P. J. Purohit, A.G. Page and M.D. Sastry, *Talanta*, **39**, 775 (1992).
28. J. R. Castillo, M. A. Belarra, M. Domingurez and J. Aznarez, *Talanta*, **29**, 485 (1982).
29. F. Buhl, W. Galas, Fresenius Z. *Anal. Chem.*, **332**, 366 (1988).
30. L. Halicz, I. B. Brenner, O.J. YOFFE, *J. Anal. At. Spectrom.*, **8**, 475 (1993).
31. H. Van Veen Eric, T.C. De Loos-Vollebregt Margaretha, P. Wassink Alex, H. Kalter, *Anal. Chem.*, **64**, 1643 (1962).