Asian Journal of Chemistry Vol. 14. No. 1 (2002), 213–216

Extraction and Spectrophotometric Determination of Iron(III) with N-(*o*-methyl) Phenyl-N-Hydroxy-N′-(*o*-Methyl) Phenyl-Benzamidine Hydrochloride and Thiocyanate

ALOK MISHRA* and (Ms) HEMLATA MOHABEY†
Department of Chemistry
Government Digvijay Postgraduate College, Rajnandgaon , India

N-(*o*-methyl) phenyl-N-hydroxy-N^{I}-(*o*-methyl) phenyl-benzamidine hydrochloride is proposed as a new reagent for selective extraction and spectrophotometric determination of iron(III) in presence of thiocyanate. The orange-red mixed complex is formed which is extractable into benzene. The optimum acidity range for the extraction and spectrophotometric determination of the complex is 0.25 M to 0.6M. Molar absorptivity and Sandell's sensitivity of the complex at its λ_{max} (470nm) have been found to be 11480 L mole^{-1} cm^{-1} and 0.0047 cm^{-2} respectively. The system obeys Beer's law in the range 0.4 ppm to 4 ppm and interference due to the presence of a number of cations and anions have been studied and the method is successfully applied to determine iron content in a number of iron drugs, soil samples and iron ores.

Key words: Extraction, spectrophotometric, determination, iron(III)

INTRODUCTION

The biochemical, physiological and industrial importance of iron is well known. This needs development of methods for determining iron at various concentration levels in diverse matrices[1–3]. Spectrophotometric methods based on the use of thiocyanate[4] suffer from various concentration levels in various experimental limitations such as the amount of thiocyanate, the time of standing, non-linearity of Beer's law, reproducibility, etc. The method based on the formation of mixed ligand complexes of iron(III) with N-hydroxy ethylene diamine NN′N″ triacetate[5–7] and thiocyanate is fairly selective but less sensitive. Several new methods have been developed for the determination of Fe(III) in micro amount[8–12]. N′-Hydroxy-N,N-diaryl benzamidines, a new type of organic analytical reagents[13, 14], have been found to react with iron(III) producing pH dependent blue and red purple coloured complexes in alcohol which are useful for colorimetric determination of iron (III) but the method suffers from interferences from several other metal ions[13]. N-(*o*-methyl)-phenyl-N′-hydroxy-N-(*o*-methyl) phenyl-benzamidine hydrochloride a newly sythesised reagent with thiocyanate is proposed for extraction and spectrophotometric determination of iron(III) as a mixed complex. The method is successful applied to determine the iron content of iron formulations and soil samples.

†Govt. K.D.M. College, Rajnandgaon, India.

EXPERIMENTAL

A Carl-Zeiss spekol spectrophotometer was employed for absorbance measurements. The pH values were determined with a Systronics pH meter type 321. Stock solution of iron(III) was prepared by dissolving 0.56 g of pure iron wire (E. Merck) in 50 mL 1 : 3 nitric acid. It was boils to expel oxides of nitrogen and diluted to one litre. It was standardised gravimetrically with 8-hydroxy quinoline[15]. 2% Aqueous solution of potassium thiocyanate was prepared. All the chemicals used were of AnalaR grade.

Preparation of N-(*o*-methyl) phenyl-N-hydroxy-N^{I}-(*o*-methyl)-phenyl benzamidine hydrochloride

The reagent HTPMBH was prepared by condensation of equimolar quantities of N-(*o*-methyl)-phenyl hydroxylamine and N-(*o*-methyl)-phenyl benzamidoyl chloride in ether at low temperature 0–5°C. The hydroxymidine hydrochloride obtained was recrystallised from absolute alcohol. Yield 82%, m.p. 181°C. Calculated for $C_{21}H_{21}N_2OCl$: C = 74.13, H = 5.40, N = 7.20%; found: C = 74.23, H = 5.47, N = 7.12%

Procedure: An aliquot of iron(III) solution containing 50 μg of the metal was placed in a 125 mL separatory funnel. To this 5 mL of 2% potassium thiocyanate solution was added. The acidity was adjusted to the required value and diluted to 25 mL. The solution was equilibrated for 2 min with 25 mL of 0.1% benzene solution of HTPMBH. The benzene extract was then dried over anhydrous sodium sulphate. The absorbance of the coloured species was measured at the wavelength of maximum absorption against reagent blank.

RESULTS AND DISCUSSION

The absorbance of the ternary iron(III)-HTPMBH-SCN complex was maximum at 470 nm with molar absorptivity 11480L mole^{-1} cm^{-1} in benzene. The Sandell's sensitivity of thiocyanate mixed complex of iron(III) with HTPMBH was 0.0047 μg per cm^2. Beer's law is obeyed in the range of 0.4 ppm to 4.0 ppm at 470 nm and optimum concentration range on the basis of Ringbom plot[16] is 1.2 ppm to 4.0 ppm of metal. The standard deviation and relative standard deviation of the method were ± 0.0057 and ± 1.39 respectively with mean absorabance 0.41 unit for 10 measurements, each containing 50 μg iron(III)/ 25 mL.

Effect of variables: The optimum acidity range for iron-thiocyanate mixed ligand complexes of HTPMBH was found to be 0.25–0.60 M hydrochloric acid in which iron(III) was quantitatively extracted. Below 0.25 M and beyond 0.60 M hydrochloric acid concentration low absorbance values were obtained.

In thiocyanate system a 25 and 130 fold molar excess of HTPMBH and thiocyanate, respectively, were adequate for complete extraction. Addition of excess of reagent causes no adverse effect on the absorbance values of the mixed complexes.

A time of 2 min was sufficient for complete extraction. The complex was stable for at least 34 h at 27 ± 2°C. Variation in temperature from 20° to 40°C did not influence the absorbance values of these coloured systems.

Choice of Solvent: Benzene was found to be the best suitable extracting solvent. Carbon tetrachloride, chloroform, toluene, xylene can also be used as extracting solvent.

Composition: The formation of 1 : 1 : 2 (metal : reagent : thiocyanate) mixed complex in benzene was confirmed by curve fitting method[17].

Interferences: In the determination of iron(III) at 0.3 M hydrochloric acid the effects of diverse ions were studied as described in earlier procedure. Reasonable amounts of chloride, bromide, nitrate, sulphate, tartrate, urea, thiourea, alkaline earth metals did not interfere with the determination of iron.

The tolerance limits of other ions causing an error less than 2% are shown in parentheses (in ppm): phosphate (1200), arsenate (1600), fluoride (1400), Mn^{2+} (600), Fe^{2+}, Co^{2+}, Cr^{3+}, (800), Zr^{4+} (400), W^{6+} (200), V^{5+} (50), Cu^{2+} (10).

Application of the Method

The validity of the method has been tested by analysing various samples. The iron content of the samples was determined precisely and accurately and the results were compared with other standard methods (Table-1).

TABLE-1
DETERMINATION OF IRON IN STEEL SLAG ORE SOIL
BIOCHEMICAL AND BIOLOGICAL SAMPLES

Samples	Certified Fe %	Calculated iron content			
		Phenanthroline method	Error (%)	Hydroxiamidine method	Error (%)
1. *Steel BCS*					
(a) –64a	83.46	84.01	+0.55	84.03	+0.57
(b) –252	94.82	94.79	–0.03	94.78	–0.04
(c) –241/1	71.00	71.20	+0.2	71.20	+0.20
2. *Stainles Steel*					
(a) Slag	11.15	11.18	+0.03	11.16	+0.01
(b) Ore	46.83	46.80	–0.03	46.81	–0.02
(c) Soil	7.43*	7.41	–0.02	7.42	–0.01
3. *Biochemical Samples*					
(a) Ferronocum (Sandoz)	0.325 g	0.323 g	–0.6153	0.323 g	–0.6153
(b) Radicyte (Merck)	0.300 g	0.297 g	–1.0000	0.298 g	–0.6666
4. *Biological Samples*					
(a) *Solanum tuberosum*	0.007%	0.0066%	–0.0004%	0.0066%	–0.0004%
(b) *Spinach oleracea* (leaves)	0.0109%	0.0110%	+0.0001%	0.0111%	+0.0002%
(c) *Brassica oleracea* (leaves)	0.04%	0.0420%	+0.0020%	0.0410%	+0.0010%

* XRF method

ACKNOWLEDGEMENT

Authors are grateful to the principal, Government Digvijay Postgraduate College, Rajnandgaon for supporting this work.

REFERENCES

1. B.A. Sommer and D.W. Margerum, *Inorg. Chem.*, **9,** 2517 (1970).
2. H.N. Po and N. Sutin, *Inorg. Chem.*, **10,** 428 (1971).
3. D.L. Leussing and I.M. Kolthoff, *J. Am. Chem. Soc.*, **75,** 2476 (1953).
4. Colorimetric Determination of Traces of Metals, 3rd Edn., Interscience Publication, New York, p. 537 (1959).
5. J.T. Wood and M.G. Mellon, *Ind. Engg. Chem. Anal.*, **13,** 155 (1941).
6. I.M. Kolthoff and E.B. Sandell, Text Book of Quantitative Inorganic Analysis, The Macmillan Co., p. 636 (1952).
7. K. Yamamoto and K. Ohashi, *Anal. Chem. Acta*, **88,** 141,(1977).
8. Ashok Kumar Malik, *Chim. Acta Turc.*, **26,** 5 (1999).
9. V. Krishna Reddy, J. Thippaiah, C. Kesava Rao, P. Ravindra and T. Sreenivasulu, *J. Indian Chem. Soc.*, **76,** 275 (1999).
10. Zorana Grabaric, Ljerka Bokic Branaka Stefanovic, *J. Assoc. of Anal. Chem.,*. **82,** 682 (1999).
11. P. Dominik, *Talanta,* **51,** 701 (2000).
12. S.L. Sarma, G.N. Ramesh, C.J. Kumar and A.V. Reddy, *J. Indian Chem. Soc.*, **77,** 405 (2000).
13. K. Satyanarayana and R.K. Mishra, *Anal. Chem,.*, **46,** 1609 (1974).
14. K. Satyanarayana and R.K. Mishra, *J. Indian Chem. Soc.*, **53,** 469, 928 (1976).
15. A.I. Vogel, A Text Book of Quantitative Inorganic Analysis, Longmans Green & Co. Ltd., London, p. 524 (1964).
16. A. Ringbom, Z *Anal. Chem.*, 115, 332 (1939).
17. L.G. Sillen, *Acta Chem. Scand.*, **10,** 185 (1956).

(*Received:* 3 August 2001; *Accepted:* 3 October 2001) AJC-2479