SPECTROPHOTOMETRIC DETERMINATION OF IRON(III) IN ENVIRONMENTAL SAMPLES OF INDUSTRIAL AREA USING 2-FUROHYDROXAMIC ACID (2-FHA)

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Abstract

A new simple and selective spectrophotometric method for the determination of Fe(III) in various environmental samples like soil, biomass, particulates (SPM, RSPM) based on the formation of Fe(III)-2-FHA complex in aqueous medium has been established. A reddish brown complex show intense colour pH 5.0 - 5.5 at λ_{max} 480 nm. The tolerance limit of diverse ions examined is very high. The molar absorptivity and Sandell's senstivity of the method with 2-FHA are 3.58×10^3 liter/mol/cm and 0.109 µg/cm^2 respectively. The relative standard deviation of the method is 0.01419 for the determination of 5µg/25ml of Fe(III).

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Introduction

Iron is a toxic (in excess) as well as an essential trace element for all living beings. Several spectrophotometric methods (Manjula et al 2007, Vladescu et al 2009, Arifien et al 2004, Srilalitha et al 2011, Luca et al 1987, Satake et al 1980, Obradovic et al 2005, Achar et al 2005, Malik et al 1997, Prezeszlakowski et al 1982, Shkrollhi et al 2007, Malik 2000, Ivic et al 2003, Komy et al 2005, Zaijun et al 2004) for the determination of Iron have been reported. Spectrophotometric method is advantageous due to common availability, low cost of instrumentation, simplicity of the procedure, accuracy and selectivity of the technique.

Here a new heterocyclic hydroxamic acid (2-FHA), is used as a complexing agent for the spectrophotometric determination of Iron(III) in aqueous medium.

Hydroxamic acids have been widely used as reagents for solvent extraction of metals (Svehla et al 1978, De et al 1970, West et al 1941). The deep colour and preferential solubility in water of the metal chelates of hydroxamic acids have been widely employed for developing gravimetric, colorimetric and solvent extraction methods. Hydroxamic acid has therefore; found numerous analytical application (Agrawal 1980). There was however a growing tendency in the recent past to employ organic compounds, especially hydroxamic acid which are usually more sensitive as well as selective for analytical purpose. They give colour reactions with metals (Daridson 1940, Sandell 1964, Arya et al 1986, Sahu et al 1987) which are very rapid and detectable. Hydroxamic acids are also selective and give reproducible results for the spectrophotometric determination of V(V) Raghawan 2007).

Experimental; Materials and Methods

Apparatus

Systronics spectrophotometer model 106 and Systronics pH meter model 331 were used for determination of λ_{max} and pH measurement respectively.

Reagents

All chemicals used were of analytical regent grade. A stock solution of Iron(III) was prepared by dissolving 0.289 anhydrous Ferric Chloride in 100 ml of double distilled water. The metal content of the solution was standardized by EDTA method (Merck et al 1982). Working standards of lower concentration of Fe(III) were prepared daily by diluting aliquots of the stock solution to prevent the formation of Fe(III) hydrolyzed species in water. 2-Furohdroxamic acid ($C_5H_5NO_3$) was synthesized following the reported procedure (Rajput 1984) in brief 0.1 mole hydroxylamine hydrochloride, 50 ml diethyl ether and 0.2 mole of $NaHCO_3$ were taken to make slurry. To this 0.1 mole of Furoyl chloride was added dropwise with the constant stirring in duration of about 2 hours. The pinkish white precipitate was purified with hot ethyl acetate. A 0.629 M (8%w/v) solution of 2-FHA in distilled water was employed. 1M HCl/1M NH_4OH solution was used for experimental work.

Procedure

An aliquot of the solution containing 5µg of Fe(III) was taken in 25 ml volumetric flask. Adjust the pH of the solution to 5.2. Add 7 ml of reagent and make up the volume to 25 ml with double distilled water. Reddish brown colored complex is formed. The stability of the colored complex is achieved after 5 minutes.

Result and Discussion

Absorption spectra

The absorption spectra of Fe(III)-2-FHA complex and its reagent blank in aqueous solution are shown in Fig. 1; The 2-FHA complex examined in this investigation exhibit the absorption maximum at 480 nm. At the same wave length the reagent blank of 2-FHA also show some absorbance.

Effect of pH

pH was adjusted to 5.2 to 7 ml of reagent was added and volume up to made up 25 ml volumetric flask with double distilled water. Reddish brown colour complex was formed after 5 minute. The intensity of the colored complex was studied in the range 1.5 to 6.0 pH. Two absorption maximum were established at pH 2 and at pH range 5.0 to 5.5. The latter showed the maximum intensity of the colored complex. Hence further experiments were carried out at pH 5.2.

Effect of other variables

Full color development of the complex in the aqueous solution was observed after 5 minutes. The colored complex was stable up to 30 minutes. At least 0.163 M 2-FHA was necessary for full color development of the complex and further addition of more 2-FHA after 0.201 M makes colored complex hazy. The complex was stable for at least 30 minutes at the temperature ($25\pm2^{o}C$). The stability of the colored complex decreases with the increase in temperature.

The molar absorptivity and Sandell's sensitivity of the complex is $3.58x10^{3}$ liter/mol/cm and 0.109 $\mu g/cm^{2}$ respectively. A linear relationship between the absorption and Iron(III) concentration over 2 to 16 μgml^{-1} of Fe(III) was obtained with a relative standard deviation 0.01419 at a level of 5µg Fe(III)/25ml for 7 replicate measurements. Spectral data and statistical analysis of the colored complex is shown in Table 1 and Table 2 respectively.

Composition of complex

The composition of the coloured complex was evaluated by Curve Fitting method[32] by plotting log D {(Aequ/Amax-Aequ.)} Vs log 2-FHA. The result indicate that the 1:1 complex is predominant at lower pH and the three chelated species (Fe_2L_3), predominates in the pH range of 5.0 - 5.5 (Farkas et al 1999).

Comparison of the method

The analytical characteristics of various spectrophotometric methods reported for determination of Fe(III) was compared in Table 3. The present method is highly selective and can be used in different complex material for the determination of

Iron(III). Fe(III) easily form complex with 2-FHA at pH 5.2 in aqueous medium which makes the method simple and selective. The effect of ions co-existing with 5 µg of Fe(III) was examined as described in the procedure and the tolerance limit of diverse ions is listed in Table 4.

Application

Iron(III) content in a variety of complex materials such as soil, biomass, particulates (SPM, RSPM) were determined by the present method. The reproducible results were obtained with wide range of Iron content. The samples were digested by appropriate method. The metal Fe(III) was determined by present method and compared by Atomic Absorption Spectrophotometer FS 240 shown in Table 5.

Conclusion

The results obtained indicates that the 2-FHA can be effectively used for determination of Fe(III) in aqueous medium. The method is simple, rapid and selective. The important feature of this method is that the reagent is water soluble and does not require any organic extraction and is thus eco-friendly. The complex is stable for 30 minutes. The method has a detectable range from 2-16 µg/ml for Iron(III). The results show very good agreement with standard method. The method is found to be very precise. This method has been successfully used for determining Fe(III) directly in environmental samples, biomass, and soils.

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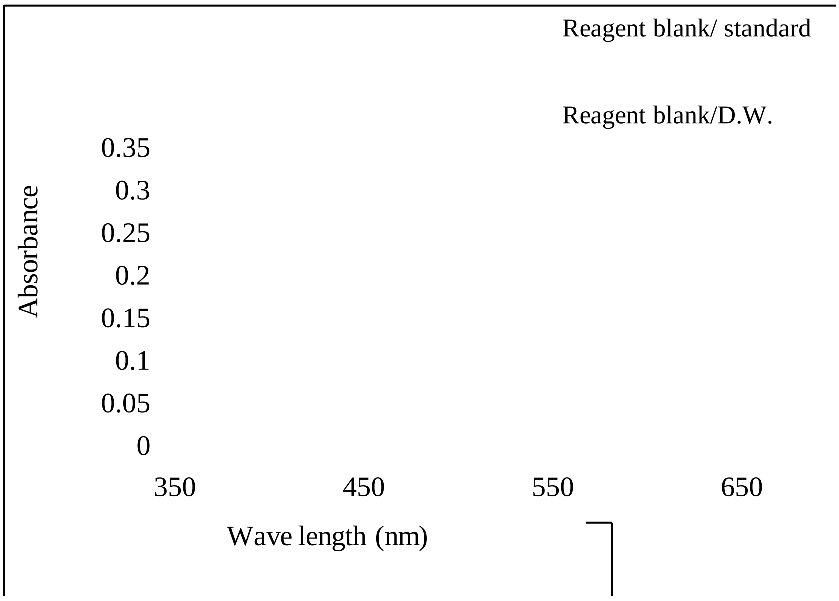

Fig. 1---Absorption spectra of Fe(III)-2-FHA complex in aqueous medium.

$C_{Fe} = 8.92 \times 10^{-5}$M; $C_{2\text{-FHA}} = 0.176$ M.

Table 1 – {Spectral data for the determination of Iron(III)-2-FHA complex by the Proposed method [Y* = bc+a;]}

Parameters	Results
Colour	Reddish brown
λ_{max}	480 nm
Beer's law (μg/ml)	2-16
Molar absorptivity (liter/mol/cm)	3.58×10^3
Sandell's sensitivity (μg/cm^2)	0.109
Regression equation (Y*)	
Slope (b)	0.037
Intercept (a)	0.083
Standard error of estimation	0.00536
Correlation coefficient	0.969117

Table 2 - Statistical analysis of precision of Fe(III)-2FHA complex (n = 7).

Mean	0.3227
Standard Error	0.00536
Median	0.32
Mode	0.33
Standard deviation	0.01419
Sample variance	0.00020
Kurtosis	0.62260
Skewness	-0.04222
Range	0.045
Minimum	0.3
Maximum	0.345
Sum	2.259
Count	7

Table 3 - Comparision of differnet paramerts of spectrophotometric methods for determination of Iron(III)

Reagent used	Optimum pH/acidity range	λmax (nm)	Molar absorptivity (l/mol/cm) Sandell's Sensitivity- µg/cm^{2}	Beer's law (µg/ml)	Remark	Ref.
4-Aminoantipyrine	Acidic	620	(0.872X10^{4}) 0.0058	0.2 - 4.8 µg/ml	The sequence of addition of reactant is important	Manjula et al 2007
Solochrome Yellow 2GS	2.8 - 3	490	(3.75X10^{3})	0.3 -5.0 µg/ml	applicable only in drinking water but limit is very low	Vladescu et al 2009
Thiourea monophosphate	7.77	325	(4.22X10^{3}) 0.019	2.1 -7.8 µg/ml	Solvent water ethenol medium is used	Arifien et al 2004,
Salicyladehyde acetoacetic acid hydrazone	3	525	(61.2X10^{3}) 0.9126X10^{-3}	0.027 – 0.27 µg/ml	Used for determination of less amount of Fe(III) only alloy	Srilalitha et al

					and synthetic mixture	2011,
Aqueous Tetrahydrofuron	Aqueous	400	$(1.52x10^4)$	0.6 – 3.2	Organic solvent is related with its sensitivity and stability of the measurement	Luca et al 1987,
2-thenoyltri-fluoroacetone	2.4 -5.2	480 - 500	(3.9×10^3) 1.43×10^{-2}	0.4 – 2.4	Adsorption process is also used as a step for Fe determination	Satake et al 1980,
Disulphonated hydroquinone	2.6	600	----	0.65 – 6.45	Al^{3+},$Cr_2O_7^{2-}$,Ba^{2+} interfere	Obradovic et al 2005,
Thiocyanate	aqueous acidic medium	480	$(2.9565x10^4)$ 0.002	0.1-4.0ppm	Nitric acid containing 60% acetone is used	Achar et al 2005,
Microcrystaline napthalene in presence of tetraphenylborate)	aqueous	515	$(1.2X10^4)$	22.4 -372.9 µg	adsorption of the complex onto naphthalene is necessary,which is quite tedious andtakes ore time	Malik et al 1997,
Aliquat 336 and ferron in chloroform	aqueous	465	$(6.86X10^3)$	0.1 - 10	Extraction from organic phase chloroform is must	Prezeszlakowski et al 1982,
Ferron in the presence of N,N-Dodecytrimethyl ammonium bromide (DTAB)	3.5	-	(3.8×10^3)	0.05-2.6 g	Shows Lower range for beer’s law	Shkrollhi et al 2007,
diphenyl 1,10-phe nanthroline	4.5	534	$(2.26x10^4)$ 0.0189	0.5 - 20	Interference of Pb(II),Cu(II),Bi(II), Fe(II) removed by extraction with Chloroform	Malik 2000,

Cetyltrimethylammonium chloride	acidic	473	$(3.55X10^4)$	$1x10^{-6}$- 4X 10^{-5}mol dm^{-3}	Interference of Zn(II),Co(II),Hg(II), Cr(II),acetate must be removed before iron determination	Ivic et al 2003,
2,6-diacytilpyidine Dioxime and 2-acytil pyridine Monooxime	2.5& 7.5	428	$(8.48X10^3)$	0.7-5 µg/ml	Applicable in herbs, spices and beans with 2,6,-diacetylprydine dioxime and 2-acetylprydine monoxime	Komy et al 2005,
dimethyldithiocarbamate (ferbam) using 9-(4-carboxyphenyl)-2,3,7-trihydroxyl-6-fluorone	6.5	640	(1.06x ^{5}) 3.9 ng cm^{-2}	0-75 µg/ml	----	Zaijun et al 2004)
2-Furohdroxamic acid	5-5.5	480	$(3.58x10^3)$ 0.109	2-16 µg/ml	More simple selective and rapid	Present work

Table - 4 Tolerance limit of diverse ions, concentration of iron(III) = 5µg/25ml

Ions	Added as	Tolerable Amount mg/25ml
Cu^{2+}	$CuSO_45H_2O$	40
Pb^{2+}	$Pb(CH_3COO)_2$	78
Ni^{2+}	$NiSO_46H_2O$	38
Cr^{3+}	K_2CrO_4	25
Mn^{7+}	$KMnO_4$	60
Mo^{6+}	$(NH_4)_6Mo_7\ O_{24}.4H_2O$	30
Al^{3+}	$Al(NO_3)_3.9H_2O$	20
Ba^{2+}	$Ba(NO_3)_2$	12
Bi^{3+}	$Bi(NO_3)_2.5H_2O$	12
Cd^{2+}	$3CdSO4.5H_2O$	25
Co^{2+}	$CoSO_{4.}7H_2O$	50
$SO_4{}^{2-}$	$Na_2\ SO_4$	25
NO_3^-	$NaNO_3$	25
$PO_4{}^{3-}$	$(NaPO_3)_6$	15

Table 5 - The results of the analysis are compared with AAS method

Samples	Fe^{3+} (μ gm/ml) by proposed method	Fe^{3+} (μ gm/ml) by AAS method
Environmental sample (RSPM)	0.235	0.241
Environmental sample (SPM)	0.223	0.234
Soil sample	18750	18000
Biomass sample	2812.2	2875
Calotropis	50450	50,000