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Development of an extractive spectrophotometric method for the determination of Fe (III) using 4-methyl 2, 3-pentanedione dioxime

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ABSTRACT

A new analytical reagent 4-methyl 2, 3-pentanedione dioxime (H_2MPDDO) is proposed for the extraction and spectrophotometric determination of Fe (III). The reagent H_2MPDDO reacts with iron to give yellow colored complex which can be quantitatively extracted into dichloromethane at pH 2.0. The organic extract shows maximum absorption at 235 nm where absorption due to similarly prepared reagent blank is negligible. The beer's law is followed in the concentration range 1-10µg/ml of Fe (III). The molar absorptivity and sandell's sensitivity of Fe (III) - H_2MPDDO complex are 3.03 x 10^3 l/mol/cm and 0.019 µg/ml/cm^2 respectively. The proposed method is rapid, sensitive, reproducible, accurate and has been satisfactory applied for determination and separation of iron (III) in synthetic mixtures. It also provides a relative inexpensive alternative to more expensive instrumental method like Atomic absorption spectrophotometer.

Key words : Iron (III), H_2MPDDO, Extraction, Recovery of iron from synthetic mixture

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INTRODUCTION

Iron is vital constitution of plant and animal life and is the key components of hemoglobin. Iron also occurs in configuration with molybdenum in enzymes that catalyze nitrogen fixation. Iron has a number of important functions in the overall metabolism of the plant. Lack of iron causes anemia in human being and at other side excess of iron in body causes haemachromatosis. Thus, the determination of trace amount of iron is important. There are certain reagents applied for determination of iron by solvent extraction method [1-3]. Flame and graphite furnace atomic absorption spectroscopy (AAS) [4-8] are the most commonly used techniques for iron determination. But these methods are disadvantageous in terms of cost and instruments used in routine analysis. AAS is often lacking in sensitivity and affected by matrix conditions of samples such as salinity. Extractive methods [9-12] are highly sensitive but generally lacks in simplicity. Spectrophotometry is essentially a trace analytical technique and is one of the most powerful tools in chemical analysis. A wide variety of reagents have been proposed for the spectrophotometric determination of iron(III) [13-23]. Amongs them, 1,10–phenanthroline is considered as most selective and sensitive reagent for the iron determination[24]. But this method suffers from interference of foreign ions, stability, simplicity and range of determination.

The extractive spectrophotometric analysis enables to separate desired metal ion, which is to be estimated in presence of other metal from samples. In the present method a novel analytical reagent 4-methyl 2, 3-pentanedione dioxime (H_2MPDDO), was used for the extractive spectrophotometric determination of Fe(III). Developed method can be employed for efficient determination of iron at µg level. The results of analysis obtained were compared with those obtained by known method with certified values of iron. The proposed method is sensitive, rapid and free from limitations.

MATERIALS AND METHODS

Instruments : A Simadzue 2450 UV-Visible spectrophotometer with 1.0 cm quartz cell was used for absorbance studies. An Elico LI-120 digital pH-meter was used for pH adjustment.

Synthesis of 4-methyl 2, 3-pentanedione dioxime (H_2MPDDO) : Isonitroso 4-methyl 2-pentanone (HIMP) prepared by procedure reported[25]. An alcoholic solution of 4-methyl 2-pentanone (3g) was taken in flask and mixed with aqueous solution of hydroxyl amine hydrochloride (5g). Then on refluxing for 1 hr on water bath, shiny crystals of 4-methyl 2, 3-pentanedione dioxime were separated and filtered off. Residue was washed with hot water and recrystallized in ethanol.

Stock solution of Fe (III) 5000µg/ml : The stock solution was prepared by dissolving calculated amount of ferric alum, $FeNH_4(SO_4)_2.12H_2O$ in double-distilled water containing 2 ml concentrated sulphuric acid. The solution was diluted to 250 ml with double distilled water. A working standard solution was prepared by an appropriate dilution of the standard solution as and when required.

General Procedure for determination of Iron (III) : To an aliquot of 50µg of Iron (III) solution, 1 ml of 0.2% alcoholic reagent solution followed by 1ml of pH at 2.0 buffer solution were added. The volume was made up to 10 ml with distilled water and extracted with 8 ml of dichloromethane for 1 min. The yellow colored organic phase was separated and diluted to 10 ml with dichloromethane. Anhydrous sodium sulphate was added to remove traces of water. The absorbance of organic phase was measured at 235 nm against the similarly prepared reagent blank. The amount of iron compared from the standard calibration curve.

RESULTS AND DISCUSSION

Selection of Wavelength and Optimum pH : The absorption spectrum of Iron (III) - H_2MPDDO complex extracted into dichloromethane was recorded against similarly prepared reagent blank. (Fig-1) showed an absorption maximum at 235 nm for complex where absorption due to reagent blank was negligible. Hence all absorption measurements were carried out at 235 nm against similarly prepare reagent blank.

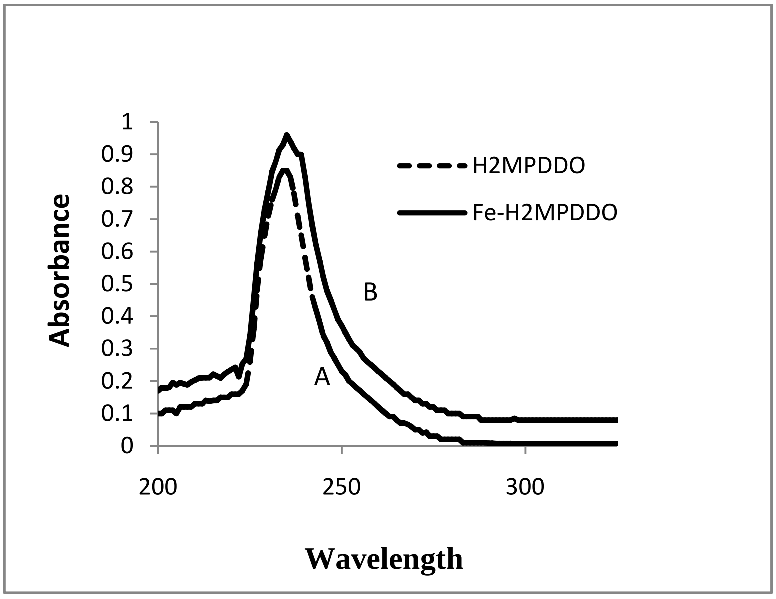

Fig.1 A- Absorption Spectrum of reagent blank against dichloromethane
B- Absorption spectrum of Fe(III) –H_2MPDDO complex against reagent blank

The complex could be quantitatively extracted at pH 1.0-3.0, where yield was maximum (>99.95%) Fig.2. A pH 2.0 was therefore employed in the subsequent studies.

Effect of Reagent Concentration : The effect of H_2MPDDO concentration was studied by carrying out extraction at fixed pH but at varying concentration of reagent. 1 ml of the 0.2% reagent in alcohol was found to be sufficient for the quantitative extraction of 50µg of Iron (III) into dichloromethane. Excess of reagent does not have any significant effect on the recovery of nickel. Therefore 0.2% reagent (1ml) was used for further studies. Iron (III) - H_2MPDDO complex was extracted with in various solvents. Among those solvents dichloromethane (99.95%) was selected as a solvent for further studies.

To a sample solution containing 50µg of Iron, 1 ml of 0.2% H_2MPDDO solution in alcohol and various amount of ammonium buffer solution (pH 2.0) were added and the extraction was carried out in dichloromethane by the developed method. The absorbance remains constant when 0.5-1.0 ml buffer solution was used for all the experiments. The colour development was instant; however, shaking period was (5-120 sec). The optimum period of shaking required to the complete transfer of coloured complex into organic phase was found to be 60 sec. The studies on the absorbance of the organic extract at different time interval revealed that the extracted Fe(III) - $(H_2MPDDO)_2$ was stable for 3 days.

Analytical Constants : The absorbance of the extracted species was a linear function of Fe(III) concentration in the range of up to 50.0µg/ml at 235 nm. The sandells sensitivity of method was found to be 0.0190 µg/ml/cm^2, while the molar absorptivity was 3.03 x 10^3 l/mol/cm. The precision accuracy of method was determined. The average of ten determinations with 50 µg Fe(III) was found to be 49.95 µg with the standard deviation of 0.169 and the deviation from mean at 95 percent confident limit was ± 0.121.

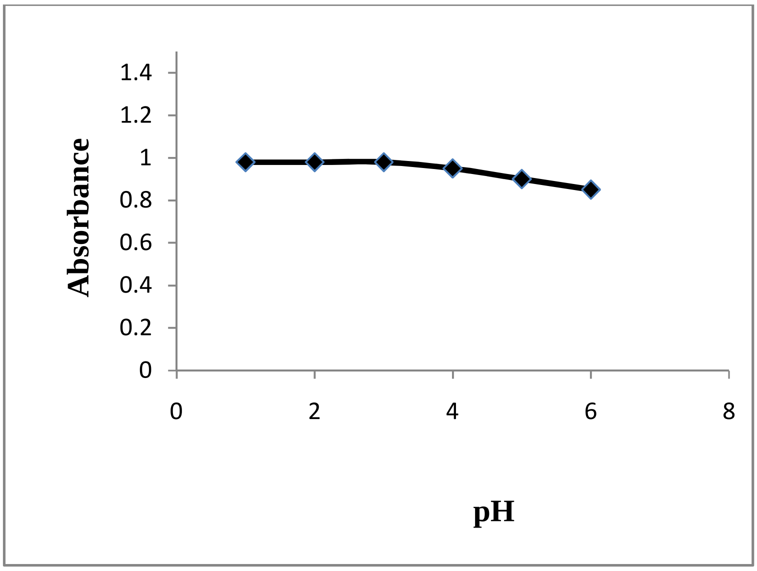

Fig. 2 Effect of pH on Extraction

Effect of Diverse ions : Iron (III) could be extracted in presence of large number of foreign ions. Under optimum conditions, the effect of diverse ions on extraction of 50µg Iron (III) was investigated. The solutions for diverse ions, required for interference studies, were prepared by dissolving their commonly available chemically pure salts in double distilled water to give cations (10 mg/cm^3) and anions (20 mg/cm^3). The tolerance level for diverse ions investigated were as follows.

Upto 20 mg : Acetate
Upto10 mg : Cl^- Br^- I^- $S_2O_3^{2-}$ BrO_3^- ClO_3^{--} NO_2^- SCN- Oxalate Urea Tartrate F^- NO_3^- SO_3^{2-}
Upto 5 mg : CO_3^{2-} S^{2-} Hg^{+2} Pb^{+2} Zn^{+2} Mn^{+2} Cr^{+6}
Upto 3 mg : Cd^{+2}
Upto 2.5 mg : V^{+6} Sn^{+2} Sr+^{2}
Upto 2 mg : Mo^{+6} W^{+6}
Upto 1 mg : Pt^{+2} Au^{+3} Al^{+3} Bi^{+3} Sb^{+3}

Fe(II), Ni(II), Cu(II), Co(II), Pd(II) interference seriously. The tolerance amount was set as the amount of foreign ion that causes an error of not more than ± 2 percent in the recovery of metal ion.

Determination of Iron (III) in synthetic mixture : The developed method was applied for the determination of iron (III) The amount of iron (III) in the synthetic mixture was determined by using general procedure. The results obtained are summarized in Table–1.

Table -1 Determination of Iron (III) in Synthetic mixtures

Name of Sample	**Fe found by present Method***	**Standard Deviation**
Synthetic Mixture#		
Fe^{+2}(50 µg)+ Zn^{+2}(1000 µg) + Cd^{+2}(1000 µg)	49.99	0.007
Fe^{+2}(50 µg)+ Mn^{+2}(1000 µg) + Cr^{+3}(1000 µg)	49.99	0.007
Fe^{+2}(50 µg)+ Hg^{+2}(1000 µg) + As^{+2}(1000 µg)	49.98	0.014
Fe^{+2}(50 µg)+ Sn^{+2}(1000 µg) + Pb^{+2}(1000 µg)	49.97	0.021

*#Value in µg *Mean of three determinations ®Value in percentage*

CONCLUSION

The proposed method can be used for determination of Iron at trace levels. A method has advantages of reliability, reproducibility, and good sensitivity, simple, instant colour development, and minimum interference. The method has been successfully applied for the separation of Iron at trace level in synthetic mixtures.

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