IJRCE

ISSN 2248-9649

International Journal of

Research in Chemistry and Environment

Available online at: www.ijrce.org

Research Paper

Development of an Extractive Spectrophotometric Method for Determination of Mn (II) using 2, 4-dimethyl -3H- 1, 5 benzodiazepine

Sonali S. Patil

[*1]Department of Chemistry, J.S.M. College, Alibag, Raigad, Maharashtra, INDIA

(Received 27th February 2016, Accepted 13th April 2016)

Abstract: *A new analytical reagent 2, 4-dimethyl -3H- 1, 5 benzodiazepine (DBA) is proposed for the extraction and spectrophotometric determination of Mn (II). The Reagent was synthesized and characterized by IR, NMR, elemental analysis as well as Mass spectrometry. DBA reacts with Manganese to gives reddish yellow colored complex which can be quantitatively extracted into n-butanol at pH 7.2. The organic extract shows maximum absorption at 525nm where absorption due to similarly prepared reagent blank is negligible. The beer's law is followed in the concentration range 1-10 µg/ml of Mn (II). The molar absorptivity and sandell's sensitivity of Mn(II) -DBA complex is 3180 Lit mol^{-1}cm^{-1} and 0.03144 mg/cm^2 respectively. The proposed method is rapid, sensitive, reproducible, and accurate and has been satisfactory applied for determination and separation of Manganese (II) in commercial mixtures, pharmaceutical samples and alloys*.

Keywords: Manganese (II), Spectrophotometric determination, DBA reagent.

Introduction

The symbol of Manganese is Mn and atomic number 25 is hard and brittle metal. It is chemically reactive and decomposes cold water slowly. Manganese is present in large quantity at the floor of Oceans. It is important trace metal. It is important component of steel. Manganese is micronutrient and has a very important biological significance .It is essential element in both plants as well as animals; In plants Manganese appears to catalyse the formation of chlorophyll molecule although it is not a component of it. Due to deficiency of Manganese, leaves turns yellow leaving the veins green. In animal it is also an essential micronutrient necessary for bone growth and development, reproduction and lipid metabolism. Industrially it is also of great importance especially in steel industry used as a hardening agent and as an additive and to counter act the effects of sulphur in steel. Manufacture of dry cell and Alloys also consume significant amount of Manganese. Number of reagents had been reported[1-12] for spectrophotometric determination of Manganese. However these methods suffer from limitations such as longer extraction time[3,7], lower sensitivity and molar absortivity[1,2,4,6,7,10-12] requires longer standing time etc. In recent years with increasing use of Manganese in great variety of materials such as production of steel and Iron, manufacture of batteries, manufacture of alloys, welding rods and fluxes. Exposure to manganese in the atmosphere has been statistically associated with several types of respiratory diseases, heart diseases and cancers, inhaling manganese oxide cause chronic manganese poisoning. Chronic manganese poisoning is a diseases affecting central nervous system, resulting in total or partial disability if corrective action is not taken.

A spectrophotometric determination of Manganese (II) is based on the reaction of Manganese (II) ions with 2, 4 dimethyl-3H-1, 5 benzodiazepine, to give a red – colored product showing a maximum absorbance at 525 nm, with molar absorptivities is 3180 L mol^{-1} cm^{-1} for Manganese (II) and Sandell's sensitivity of 0.03144 mg/ cm^2. The present paper describes the preparation of 2,4 dimethyl -3H-1,5 benzodiazepine, is a sensitive and selective reagent for the spectrophotometric

determination of micrograms quantities of Manganese (II) without need for a preliminary steps.

Material and Methods

Instruments

A Shimadzu 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 Reagent

The reagent was synthesized by mixing 1 mole of O phenylenediamine and 2 moles of Acetyl acetone in Ethanol. The above mixture is refluxed for 2 Hours in round bottom flask. The solution thus obtained is poured in ice. Solid is formed, which is purified with ethanol. It is then characterized and used for extractive spectrophotometric determination of Mn (II). A stock solution of reagent with concentration 0.05% was prepared in methanol. The scheme of reaction is as shown in (Figure 1).

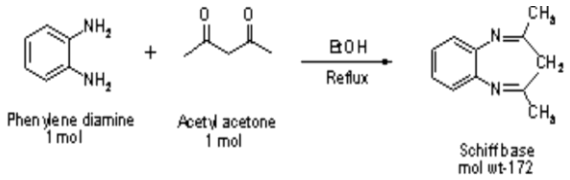

Figure 1: Synthesis of Reagent 2, 4-DIMETHYL - 3H- 1, 5 BENZODIAZEPINE (DBA)

Preparation of Stock Solution

A weighed quantity of $MnCl_2$ was dissolved in double distilled water Containing dilute Hydrochloric acid and then diluted to desired volume by double distilled water.

Table 1: Condition and corresponding results

Condition	Results
Absorption Maxima	525nm
Solvent	n- butanol
pH range	7.2
Equilibration time	1.0 min
Stability of Manganese-reagent	70 hours
Beer's range	1 to 10 mg/cm^3
Molar absortivity	3180 Lit mol^{-1}cm^{-1}
Sandell's sensitivity	0.03144 mg/ cm^2
Mole ratio of Mn :reagent	1:1

Recommended Procedure

Mix 1 cm^3 aqueous solution containing 1-100mg of Manganese and 1cm^3 of 0.05% methanolic solution of reagent in 25 cm^3 beaker. Adjust the pH of the solution to required value with buffer solution Make the final volume 10 cm^3. Transfer the solution into 125 cm^3 separating funnel and equilibrate for 1min with 10 cm^3 n-butanol. Allow the two phases to separate and measure the absorbance of organic phase containing the complex at 525 nm against reagent blank.

Preparation of Calibration Plot

The calibration curve was prepared by taking known amount of Manganese which was treated as described in the procedure. A graph of absorbance against concentration was prepared (Figure 2). The concentration of the unknown Manganese solutions is determined from the calibration plot.

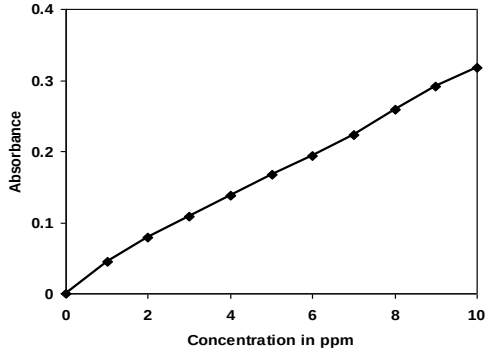

Figure 2: Calibration Plot of Mn (II) in mg/ml against Absorbance

Extraction as Function of pH

The extraction of Manganese was carried out at various pH conditions ranging from the pH1 to pH11 using various buffer solutions. The ratio of the organic phase to aqueous phase was kept 1:1. The present extraction was observed to be quantitative at pH 7.2. Therefore the pH was selected for the further studies. Figure 3 gives the effect of pH on the percentage extraction Mn(II): DBA.

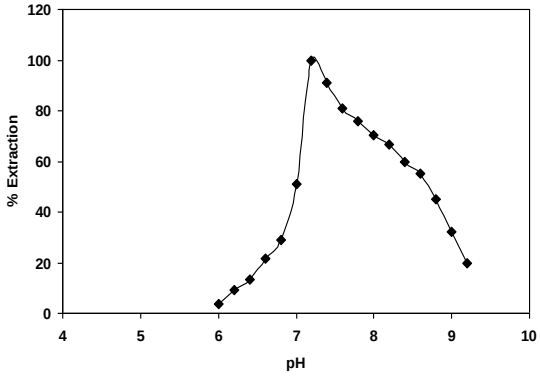

Figure 3: Effect of pH on the % extraction Mn(II): DBA

Influence of the Different Organic Solvents

The suitability of many organic solvents was studied using various organic solvents such as n-butanol,

toluene, cyclohexanone, cyclohexanol, chloroform, ethyl acetate, carbon tetrachloride and hexane. The extraction of Manganese was observed to be quantitave in n-butanol as organic solvent. Figure 4 shows the effect of solvent on Mn(II):DBA.

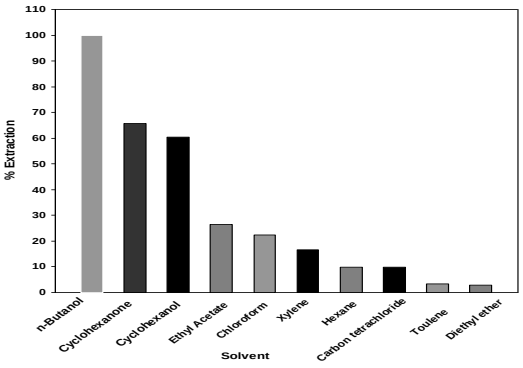

Figure 4: Effect of solvent on Mn(II):DBA

Composition of the extracted species

The composition of the extracted species was determined by using the Job's continuous variation method and verified by mole ratio method and slope ratio method. These methods show that the composition of Mn (II): DBA regent is 1: 1 (Figure 5).

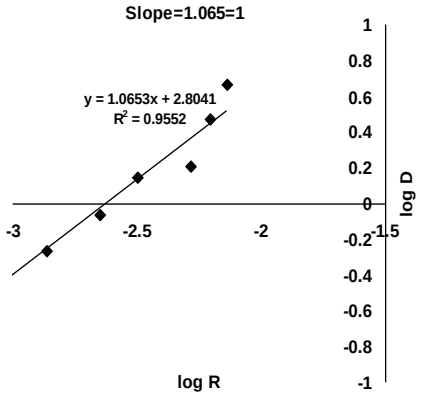

Figure 5: Slope Ratio method

Effect of foreign ions

The effect of diverse ions on the Manganese (II) determination was studied, in presence of a definite amount of a foreign ion. Various cations and anions were investigated in order to find the tolerance limit of these foreign ions in the extraction of Manganese (II) (Table 2).

Table 2: Effect of foreign ions

S. No.	Interfering ions	Tolerance limit
1	Acetate, Oxlate, CN^-, I^-, Br^-, NO3-, BrO^{-3}, ClO^{-3}, IO^{-3}, NO2-, SO4-,SO3	20
2	Tartarate	12
3	phosphate	14
4	Mg(II), Zn(II), Mo(VI), Ce(IV), Bi(III), Ca(II), As(III), Pb(II), Al(III),	12
5	V((V), Cd(II)	10
6	Na+, Ag+	8
7	Fe(II), Ni(II), Mn(II), Zr(II), Co(II), Fe(II),Cu(II), EDTA	Interfere strongly

Table-3: Masking agents

Interfering Ion	Masking agent added	Interfering Ion	Masking agent added
Pd (II)	Thiourea	EDTA	Boiled with concentrated HNO_3
Fe (II)	Sodium flouride	CN-	Boiled with concentrated HNO_3
Ce (IV)	Sodium flouride	Ni (II)	Thiourea
Cr (III)	Ammonium acetate	Zr (IV)	Sodium flouride
Citrate	Sodium molybdate	Tartate	Sodium molybdate
Ag (I)	Potassium Iodide	V (V)	Thiourea

The tolerance limit of the foreign ion was taken as the amount required causing an error of not more than 2% in recovery of Manganese (II). The ions which interfere in the spectrophotometric determination of Manganese were masked by using appropriate masking agents (Table 3).

Comparison between reagents

Various reagents were investigated by the earlier researchers for removal of Manganese (II). The proposed reagent 2, 4-dimethyl -3H- 1, 5 benzodiazepine (DBA) is found more superior as that of reported regents and are presented in (Table 4).

Table 4: Comparison between regents

Name of the Reagent	Limitations
Thenoyltrifluoro acetone	Cr(III), Fe(II), Hf(IV), Ni(II) Interferes.
Dithizone and 1,10 phenanthroline	Coexisting ions are removed by extraction with dithioone
Quinoline-8-ol	Unstable complex
4Ethoxy -2-hydroxy acetophenone oxime	Complex was extracted after 2 to 3 hours
3-Bromo benzoyl hydroxamic acid	Ag(I), V(V) , Co(II) Interferes.

Applications

The present method was applied for determination of amount of Manganese (II) in various samples of alloys, commercial mixtures; water samples etc. are in well agreement with standard methods, Table 5.

Every result is average of independent determinations.

Table 5: Applications

S. No.	Sample	% of Mn(II) in standard method	% of Mn(II) in present method
1	13% Mn-Steel	12.44	12.40
2	pyrolusite	63.50	63.41
3	Mn(II)(5) + Mg(II)(5)	4.97 ppm	4.96 ppm
4	Mn(II)(5) + Cr(II)(5)	4.98 ppm	4.98 ppm
5	Manganese ore	37.20	37.09

Conclusion

The results obtained show that the newly developed method in which the reagent 2, 4-dimethyl -3H- 1, 5 benzodiazepine (DBA) was synthesized, can be used for quantitative estimation of Mn (II). The proposed novel reagent is found to be more effective over reported reagent from earlier investigators. The proposed method is simple, rapid and requires less volume of organic solvent. The method is also precise, less time consuming and easily employed anywhere as does not require sophisticated instruments.

Acknowledgement

This work has been conducted by Dr Sonali suhas patil for her PhD research work at J.S.M. college alibag. I am very much thankful to the management for providing me an opprtunity to carray out this research work.

References

1. Deb K.K. and Mishra R.K., *J. Indian Chem. Soc.*, **55 (3):** 289**(1978)**.
2. Chikuma M., Nakaya Y., Yokohama A., Maitani T. and Tanaka H., Fresenius Z., *Anal Chem.*, **300(5)**: 414 **(1980)**.
3. Hoshi and Inoue S., Bimseki K., **32(4):** 287**(1983)**
4. Salinas F., Jimenez-Arraal M. and Mahedero M. C., Anal Lett., **16 (A17-A18) (1983)** 1449.
5. Salinas F., Jimenez-Arraal M., Microchem J., **31(1):** 113 **(1985)**
6. Menon S.K., Agrawal Y.K., and Desai M.N., Talanta, **36(6):** 675 **(1985)**
7. Izquierdo A., Dolors P.M., Garriga N. and Alegria J. M., Analyst, **111(3):** 309 **(1986)**
8. Laila A.A.R., *Anal. Chim. Acta*, **204(1-2)** 355**(1988)**
9. Batt A.B. and Desai K.K., *J. Inst. Chem.*, **63(5):** 191 **(1991)**
10. Burns D.T., Harriott M. and Barakal S.A., Fresenius, *J. Anal. Chem*., **343(6)**: 488 **(1992)**
11. Capitan-valleey L.F. Molina-Diaz A. and Pascual Reguera M., Fresenius J., *J. Anal. Chem.*, **344(1-2) (1992)**
12. Kamburoa M, Chem Anal, **40(1):** 93 **(1995)**.