Development of Extractive Spectrophotometric Determination of Mn(II) with of 2- {4-(1h benzimidazole-2-yl) phenyl imino}-2-hydroxy-4-methoxy benzaldehyde as an Analytical Reagent

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Abstract : A spectrophotometric method has been developed for the determination of Mn (II) 2-{4-(1H benzoimidazole-2-yl) phenyl imino}-2-hydroxy-4-methoxy benzaldehyde as an extractive reagent. The reagent forms a colored complex, which has been quantitatively extracted into n- butanol at pH-9.8. The method obeys Beer's law over a range from 1 to 10 ppm. The Molar absorptivity and Sandell's sensitivity calculated were 0.1166×10^4 $LMol^{-1}cm^{-1}$ and 0.21019 µg cm^{-2} respectively. The proposed method is very sensitive and selective. The method has been successfully applied to synthetic and commercial samples.

Index Terms: **Manganese, Spectrophotometric determination, n-butanol,**

2- {4-(1H benzoimidazole-2-yl) phenyl imino}-2-hydroxy-4-methoxy benzaldehyde

1. INTRODUCTION

Manganese is the fifth most abundant element in the earth crust. It an essential for plant mineral nutrient, playing a key role in several physiological processes, particularly photosynthesis and also essential micronutrient for function of brain[1-3], bone growth[4]. It acts as a co-enzyme[5,6] to assist metabolic activities in the human body. Manganese benefits for the formation of connective tissue, absorption of calcium from the thyroid gland, regulates the blood sugar level. Too much Mn can be toxic. According to lenntech, symptoms can be forgetfulness, dullness, weakness headaches and Perkinson's disease schizophrenia[7-9]. It is used as an alloying element for many different applications include batteries as an additive in gasoline, a pigment in paint, for making low cost stainless steel[10]. As coloring in ceramics glass[11,12] and used for most beverage cans[13]. Therefore, the determination of Mn in biological and chemical sample is necessary.

In spectrophotometric determination of manganese allow number of reagents[14-19] such as dithiocarbamates[20], 8-hydroxyquinoline[21].however these methods suffer from some limitation such as equilibrium time [22-24], masking agent [25] for superior in sensitivity and selectivity in the literature is developed for the extractive photometric determination of Mn (II) with BPIHMB. The proposed method is free from limitation. The new extractive spectrophotometric determination method is simple, sensitive, precise and rapid. Therefore, it will be applied for the determination of Mn at trace level in real sample and synthetic mixture.

2. EXPERIMENTAL

The reagent 2- {4-(1H benzimidazole-2-yl) phenyl imino}-2-hydroxyl-4-methoxy benzaldehyde (BPIHMB) was prepared by the given procedure. The stock solution of Manganese (II) was prepared by dissolving a weight amount of its sulphate in double distilled water containing dilute sulphuric acid, which was diluted to the desired volume with double distilled water and standardized by formaldoxime. Absorbance and pH measurement were carried out on a Shimadzu UV- Visible 2100 spectrophotometer with 1cm quartz cells and digital pH meter with combined glass electrode respectively.

2.1 PROCEDURE FOR THE EXTRACTION

1.0 mL of aqueous solution containing 0.1 mg of manganese metal and 1 ml of reagent were mixed in 50 mL beaker. The pH of the solution adjusted to 9.8 with 0.1M borax and NaOH, keeping the volume 10 ml. The solution was transferred to 100 mL separatory funnel. The beaker was washed twice with n-butanol and transferred to the same funnel. The two phases were shaken for two minutes and allowed to separate. The organic phase was collected in 10 mL measuring flask and made up to the mark with organic solvent, if required. After separation of the two phases, the pH of the aqueous phase was measured and the Mn (II) in each phase was determined by formaldoxime method.

3. RESULTS AND DISCUSSION

The reagent BPIHMB forms greenish colored complex with Mn (II), which was extracted into organic phase. The extraction of Mn (II) forms aqueous phase by BPIHMB in n-butanol is studied over a wide range experimental condition. The results of various studies are discussed below.

3.1 Extraction as a function of P^H

The extraction of Manganese with 2- {4-(1H benzimidazole-2-yl) phenyl imino}-2-hydroxyl-4-methoxy benzaldehyde has been studied over the P^H range 1- 10 and was observed that percentage extraction of Mn (II) is maximum at P^H 9.8.

3.2 Absorption spectrum

The absorption spectrum of Mn (II):2- [{4-(1H benzoimidazole-2-yl) phenyl} imino]-2- hydroxy-4-methoxy benzaldehyde in n-butanol shows the maximum absorption at 415 nm. The absorption due to reagent at this wavelength is nearly negligible. Hence the absorption measurements were carried out at 415 nm.

3.3 Influence of diluents

The suitability of diluents was investigated using organic solvents such as chloroform, ethyl acetate, ethyl/methyl ketone, toluene, n-butanol, carbon tetra chloride. The extraction of Mn (II) was quantitative with BPIHMB in n-butanol. Hence, n-butanol was used for further extraction studies as it gave better and quicker phase separation.

3.4 Effect of salting out agent

The presence of 0.1M salts of various alkali and alkaline metals does not show any effect over the absorbance value of Mn (II):2-{4-[1H-benzoimidazole-2-yl] phenyl imino]-2-hydroxy-4-methoxy benzaldehyde complex extract. Therefore, no salting out agent was required during the extraction.

3.5 Effect of reagent concentration

Various volumes of 0.1% reagent solution were added to the sample solution containing 100µg of Manganese at respective P^H values. The absorbance remained nearly constant when the volume of the reagent solution used was 1 ml. Therefore, 1 mL of 0.1 % reagent was chosen for the quantitative determination of the metal.

3.6 Effect of equilibrium time and stability of the complex

The study of change in absorbance with variation in equilibrium time (Figure 1) extraction of the complex into organic solvent shows that equilibrium time of 60 sec. are sufficient for the quantitative extraction of manganese. The study of stability of color of the Mn (II): BPIHMB complex with respect to time shows that the absorbance due to extracted species is stable up to 72 hours, after which slight decrease in absorbance is observed. Throughout the experimental work, for practical convenience, the measurements have been carried out within one hour of extraction of manganese.

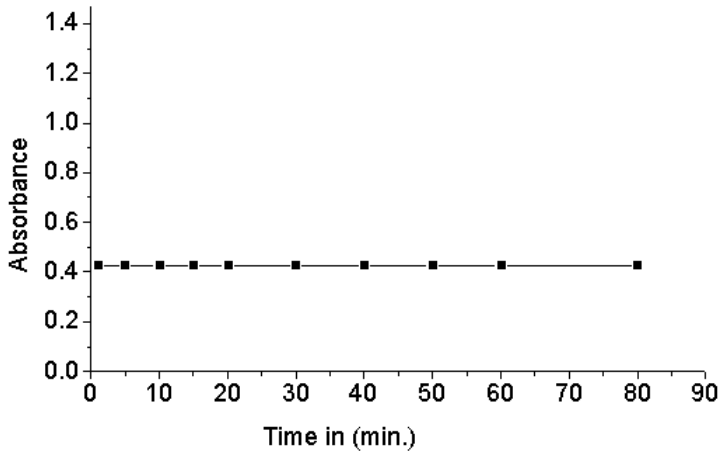

Fig. 1 Equilibrium time

3.7 Calibration plot

A calibration plot of absorbance against varying manganese concentration and fixed BPIHMB concentration gives linear and reproducible graph in the concentration range 1 to 10 ppm of manganese (Figure 2). This shows that the Beer's law is obeyed in this range. The Molar absorptivity and Sandell sensitivity were calculated to be is 0.1166×10^4 L mol^{-1} cm^{-1} and 0.2101 µg $/cm^{-2}$ respectively.

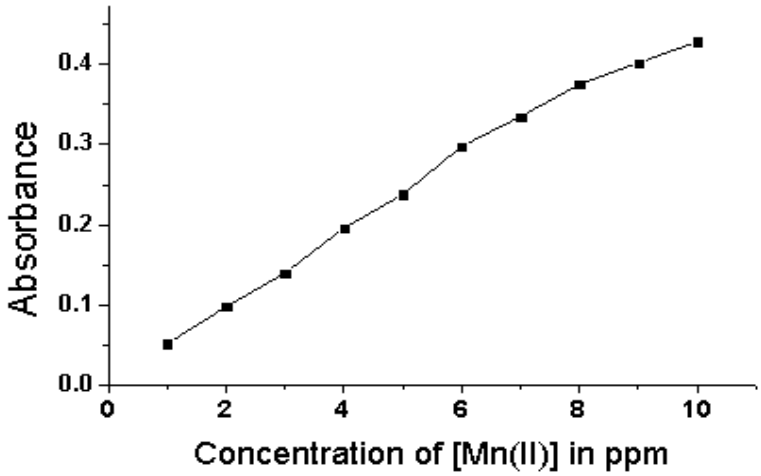

Fig. 2 Calibration plot of Mn (II) with BPIHMB

3.8 Nature of extracted species

The composition of extracted species has been determined by Job's continuous variation method (Fig.3), Slope ratio method (Fig. 4) and Mole ratio method. It shows that the composition of Mn (II): BPIHMB complex is 1:2. (Fig. 5)

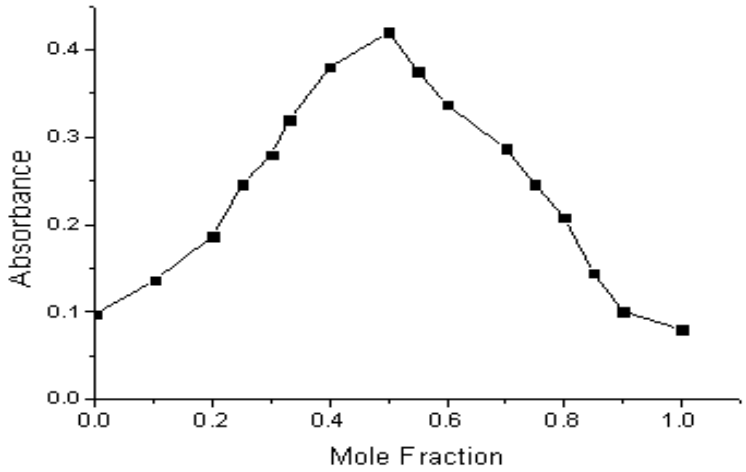

Fig. 3. Job's continuous variation method

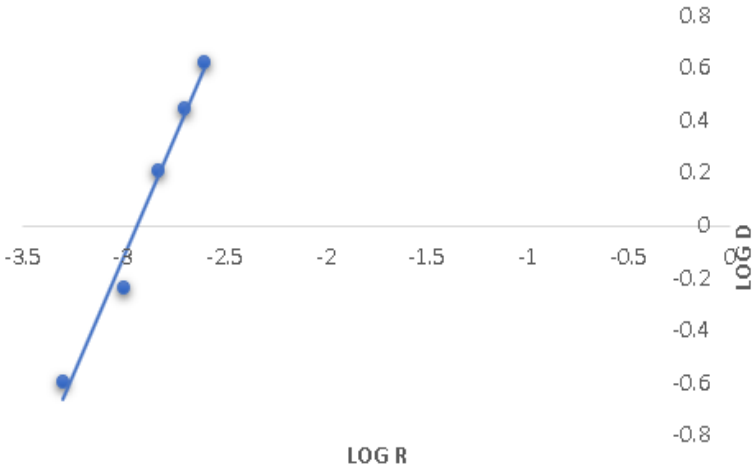

Fig. 4 Slope ratio of Mn (II): BPIHMB

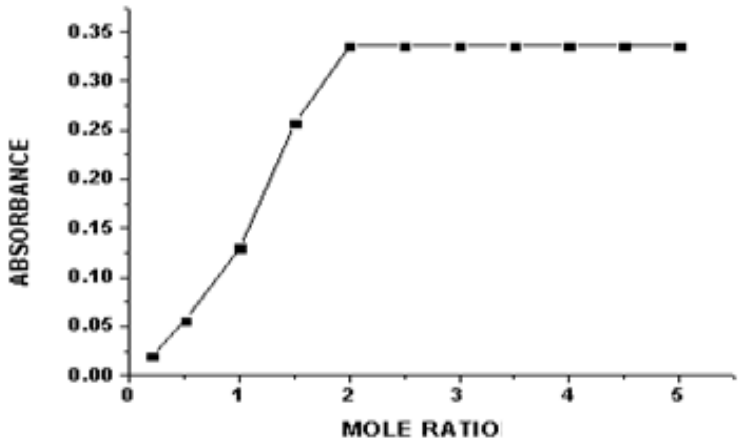

Fig. 5 Mole ratio of Mn(II) : BPIHMB

3.9 Effect of divalent ions and foreign ions

The effect of other ions presents in various amount indicated no interference in the spectrophotometric determination of 50 µg of manganese. The ions which show interference in the spectrophotometric determination of manganese were overcome by using appropriate masking agents (Table 1).

Table 1: Effect of divalent ions and foreign ions

Sr.No.	Ions	Amount of add. In (mg)	Absorbance
1	-		0.238
2	Ba^{+2}	10	0.238
3	Co^{+2}	12	0.238
4	Ni^{+2}	11	0.238
5	Cu^{+2}	14	0.238
6	Pb^{+2}	20	0.238
7	K^{+2}	15	0.238
8	Mg^{+2}	12	0.238
9	Ca^{+2}	16	0.238
10	Na^{+2}	14	0.238
11	Mo^{+2}	17	0.238
12	Mn^{+2}	16	0.238
13	Zn^{+2}	15	0.238
14	So_4^{-}	18	0.238

3.10 Precision and Accuracy

The precision and accuracy of the developed spectrophotometric method has been studied by analyzing five solutions each containing 70 µg of manganese in the aqueous phase. The average of five determinations was 70.084 and variation from mean at 99% confidence limit was ±0.15575.

4. APPLICATION

The proposed method was successfully applied for the determination of manganese from various alloys and synthetic mixtures. The results found to be in good agreement with those obtained by the standard known method.

5. CONCLUSION

The proposed method is highly sensitive and selective than the other reported methods for extractive spectrophotometric determination of microgram amounts of manganese. It offers advantages like reliability and reproducibility in addition to its simplicity, instant color development and suffers from less interference. It has been successfully applied to the determination of manganese at trace level in synthetic mixtures and alloys.

REFERENCES.

[1] Kazi, T.G, Afridi, H.I; Kazi, N., Jamali, M.K; Arain, M.B.; Jalbani, Kandhro.2008. G.A. Bio Trace Elem Res,1(122).
[2] Underwood.1977. E.J. Trane Elements in Human and Animal Nutrition, Academic Press: New York, P (170).
[3] Critchfield, J.W.; Carl, E.F.; Keen. 1993. C.L. Epil. Res, 3(15).
[4] K, schwarz. 1977. Clinical chemistry and chemical Technology of metals", ed. S.S. Brown, pp. 3-22, Elsevier, Amsterdam

[5] Leach, R.M. 1977. Trace Elements in Human Health and Disease, vol.2.
[6] Prassad, A. S. (1961): Trace elements in human health and disease Vol. 1. Zinc and copper, Zn. In Prasad, A.S. and obserleas D. ed. N. Y. Academic Press. 470. pp
[7] Soko, L; chimuka, L.; Cukrowska, E; Pole. 2003. S. Anal Chin Acta, 25(485).
[8] Silva Avila, Daiana; Luiz Puntel, Robson; Aschner. Michael (2013). Manganese in Health and Disease In Astrid sigel; Helmut Sigel; Roland K.O. Sigel (eds). Interrelations between Essential Metal Ions and Human Diseases. Metal Ion in Life Science. Springer, 13: (199-227).
[9] Emsley, John. 2001. Manganese Nature's Building Blocks. An A-Z Guide to the Elements. Oxford, U.K: Oxford University Press, PP. (249-253).
[10] Corathers, Lisa A. June 2008. Minerals Yearbook: Manganese (PDF). Washington, D.C. 2009. United States Geological survey, Retrieved 30.
[11] Dastur, Y.N.; Leslie, W.C. (1981). Mechanism of work hardening in Hadfield Manganese steel. Metallurgical Transactions A, 12(5): 749.
[12] Shepard, Anna Osier. 1956. Manganese and Iron -Manganese paints". Ceramics for Archaeologist. Carnegie Institution of Washington, PP. 40-42.
[13] Kaufman, John Gilbert 2000. Application for Aluminum Alloys and Tempers. Introduction to aluminum alloys and tempers. ASM International, pp. 93-94.
[14] Chikuma M. Nakaya Y, Yokoyama A, Maitani T and Tanaka H.1980. Fresenius's Anal Chem, 300(5): 414.
[15] Samya Mairaj and Fazlur Rehman. 2011. orient. J. Chem., 27(1): 221-225.
[16] RB Pawar, SB Padgaonkar and AD Sawant. 2001. Indian.J.Chem. Technology, Vol.8, pp. 200-203.
[17] Hoshi S and Inoue S. Bunseki Kagaku. 1983. 32(4): 287.
[18] J.A. Dave and S.S. Shah. 2008. Asian J. Chem., 20: 4141.
[19] NKB patel, KK Desai. 2004. Asian J.Chem, 16(2) : 1076-80.
[20] Y.Nakabayashi, K. Nagaoka, Y.Masuda and R.Shinke, Buriseki Kagaku.1991. 40, 301.
[21] N.M. Kuzmin, G.I. Zhuratev, I.A. Kuzovlev, A.N. Galaktionova and T.I. Zukarova, zh. Analit. Khim.1969. 24-89.
[22] D.F.C. Morris, E. L. Short and D. Slater. 1964. J. Inorg. Nucl. Chem., 26, 627.
[23] A.K. De and U.D. Ray. 1971. Sep. Sci, 6(25).
[24] A. Chatterjee and S. Basu, Fresenius. 1991. J. Anal. Chem, (61)340.
[25] Anant P. Areker and Ashok K. Shetty. 1997. Analytical Science, 13.