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Extractive Spectrophotometric Method for Determination of Manganese (II) using [N - (O - Hydroxy benzylidene) Pyridine - 2 - Amine] (NOHBPA) as an Analytical Reagent

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Abstract: *Simple, economical, sensitive, feasible and rapid spectrophotometric method has been developed for the determination of Mn (II) by using schiff base N - (O-Hydroxy Benzylidene) Pyridine - 2-Amine (NOHBPA) NOHBPA has been synthesized conventionallyas well as microwave method and was characterized by elemental analysis. NOHBPA extracts Mn (II) quantitatively (99.65%) into n-amyl alcohol from an aqueous solution of pH range 9.2 – 10.4. An intense peak at 500 nm (λ max) was observed in the extract of n-amyl alcohol. Beer's law is obeyed over the concentration range 1 to 14 µg/ml for Mn (II). The molar absorptivity and Sandell's sensitivity for Mn - NOHBPA system is 37649.7 Lmole-1cm-1 and 0.0012µg cm-2 respectively. Job's Continuous Variation and Mole Ratio Method confirms that the extracted (Mn:NOHBPA) complex has composition 1:2. The proposed method is rapid, sensitive, reproducible and accurate and it has been satisfactory applied for determination of Manganese in Ore and Alloy samples.*

Keywords: Solvent Extraction, Extractive Spectrophotometry, Manganese (II), Ores, Alloy sample.

I. INTRODUCTION

'Mn' having an atomic number 25is a transition element. Mn does not exist in free state in nature, often it is present along with Iron in minerals. Manganese is a metal with important industrial metal alloy uses, particularly in stainless steels. Depending on their oxidation state, manganese ions have various colors and are used industrially as pigments. The permanganates of alkali and alkaline earth metals are powerful oxidizers. Solvent extraction is most promising tool used in separation technique. Due to its simplicity, rapidity it is used in the separation of metal ions at trace level.[1,2] Solvent extraction coupled with spectrophotometrically plays a significant role in pharmaceutical science.[3]. Schiff bases play crucial role as chelating agents in complexes of transition metal.[4-5] Various reagents[6-15]are available for the spectrophotometric determination of Manganese (II).

[N - (O-Hydroxy Benzylidene) Pyridine -2-Amine (NOHBPA) acts as a analytical reagent for the extractive spectrophotometric methods for the determination of iron[16] and Cu(II) [17] and Nickel (II).[18] In the present communication, we describe the extractive spectrophotometric determination of Mn (II) with [N - (O-Hydroxy Benzylidene) Pyridine -2-Amine (NOHBPA).

II. EXPERIMENTAL SECTION

ELICO - SL 159 spectrophotometer with optically matched quartz or glass cells of 1cm path length were used for absorbance measurement. An ELICO – LI 127 pH meter was employed for pH measurements.

2.1 General Procedure For Synthesis Of N - (O-Hydroxy BenzylidenePyridine -2-Amine (NOHBPA)

NOHBPA was prepared as shown in Figure-1 by refluxing an equimolarquantities of ethanolic solution of 2-aminopyridine and o-hydroxybenzaldehyde for 6 hrs. Yellow crystal was separated out after cooling of reaction

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mixture (yield 75%, m.p.60 -62^0 C). Aqueous ethanol was used for purification of NOHBPA by recrystallization as per reported method20. Spectral and elemental analysis was used for the characterization of the product. [19]

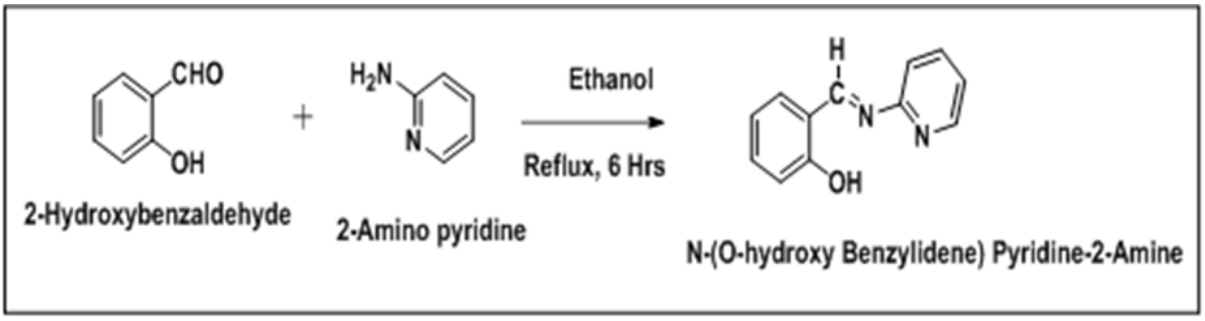

Figure 1: Synthesis of Ligand NOHBPA

2.2 Green Synthesis Of N - (O-Hydroxy Benzylidene) Pyridine -2-Amine (NOHBPA)

In a beaker, ingredients (0.005 moles of o- hrdoxy benzaldehyde & 0.005 moles of 2-amino pyridine) & few drops of pure alcohol were irradiated in the microwave oven at 180^0 for 3 minutes. The reaction was completed in a short time (1.4 min) with higher yields. Elemental analysis & physical data are shown in Table I

Table I: The Analytical and Physical data of ligand

Compound (Colour)	Molecular Weight	Reaction period & %yield Conventional methods	Reaction period & %yield microwave methods	Melting point	% C Found (Calculated)	% H Found (Calculated)	% N Found (Calculated)
NOHBPA (Yellow)	**198.14**	**(5-6 hours) 70-75 % yield**	**(1.4 min) 90-92% yield**	**62^{o}C**	**73.15 (72.73)**	**5.18 (5.05)**	**14.31 (14.14)**

2.3 Preparation of Stock Solution

A stock solution of Mn (II) was prepared by dissolving manganese sulfate in double distilled water containing dilute sulphuric acid & it was standardized by Potassium Periodate method.[20]Working solutions of Mn (II) were made by suitable dilution.

2.4 Extractive Spectrophotometric Determination of Mn (II)

Aqueous solution containing 1 to 14 µg of Mn (II), 2ml of 2% solution of NOHBPA (DMF) and 2 ml of Ammonium chloride and ammonia of Buffer solution pH 10.0 were mixed. This solution(10 ml) was digested on boiling water bath for 5 minutes. After cooling the solution was equilibrated for half minute with 10 ml ofn-amylalcohol and the phases were allowed to separate. The absorbance of n-amyl alcohol extract was measured at 500 nm against a reagent blank prepared under identical conditions. The Mn (II) content of the sample solution was found by calibration curve. To investigate The effect of other ions, the respective foreign ions were added to aqueous phase before the extraction and adjustment of pH.

2.5 Determination of Manganese in Pyrolusite Ore and Manganese Steel Sample

Sample weighing 0.1gm to 0.2 gm was dissolved in10 ml aquaregia. The resulting solution was evaporated to dryness and the residue was then dissolved in 10 ml of 1 M HCl. The final solution was diluted up to the mark in a 100 ml volumetric flask with doubly distilled water. Using an aliquot of this solution (1 ml) Manganese was analyzed by the procedure as described earlier.

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III. Results and Discussion

Manganese (II) could be extracted quantitatively (99.65%) by NOHBPA into n-amyl alcohol from an aqueous solution of pH range **9.2 – 10.4** using Ammonium chloride and ammonia buffer

Extraction of Ni(II) was done in organic solvents. The values of extraction coefficient were in the order n amyl alcohol > n-butanol > ethyl acetate> chloroform > carbon tetra chloride > chlorobenzene > bromobenzene >nitrobenxenxe>benzene as described in figure I1 Due to the highest extraction coefficient, n amyl alcohol was the choice of solvent for the entire extraction process..

N amyl alcohol extract of Mn: NOHBPA complex shows an intense peak at 500 nm as shown in Figure-3 The absorbance due to the reagent is negligible at this wavelength,(wavelength for reagent = 400) Hence the entire experiment was done at wavelength 500 nm.

Calibration curve was plotted as shown in Figure-4 between absorbance values and concentration of Ni -complex. Calibration curve is linear over concentration range of 1.0 to 14.0 µg/ml. The molar absorptivity observed to be 37649.7 L mol^{-1} cm^{-1}.

2.0% DMF solution (2 ml) of NOHBPA was sufficient to extract Ni (II). It was found that color of the n amyl alcohol extract stable for at least 24 hrs at room temperature.

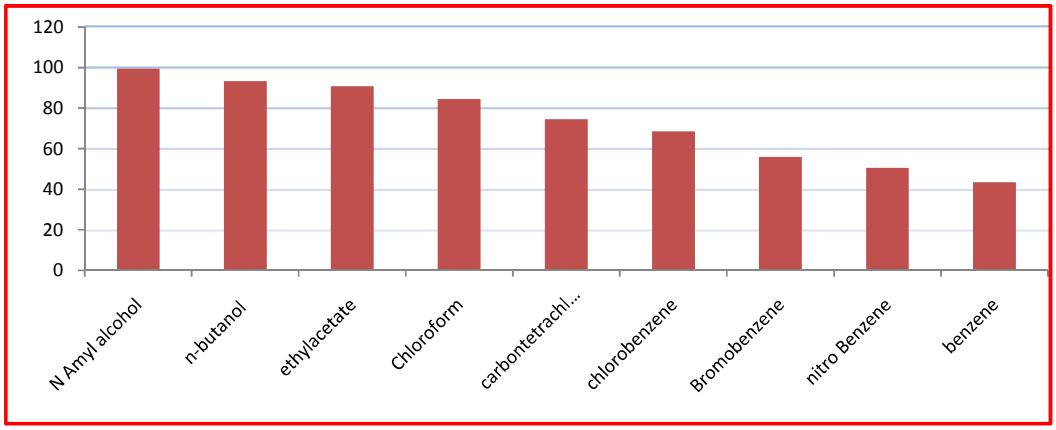

Figure 2: % extraction of Mn into various solvents

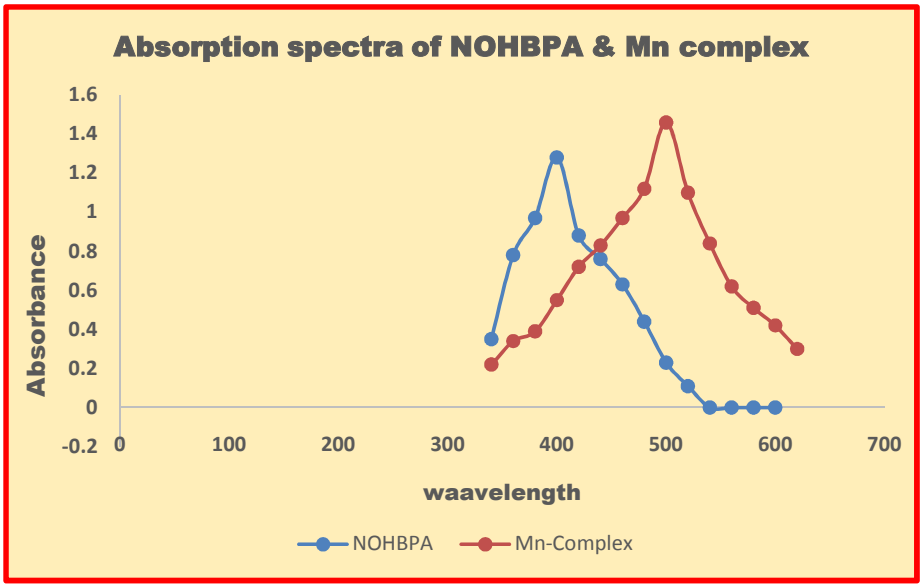

Figure 3: Absorption spectra of NOHBPA and Mn Complex

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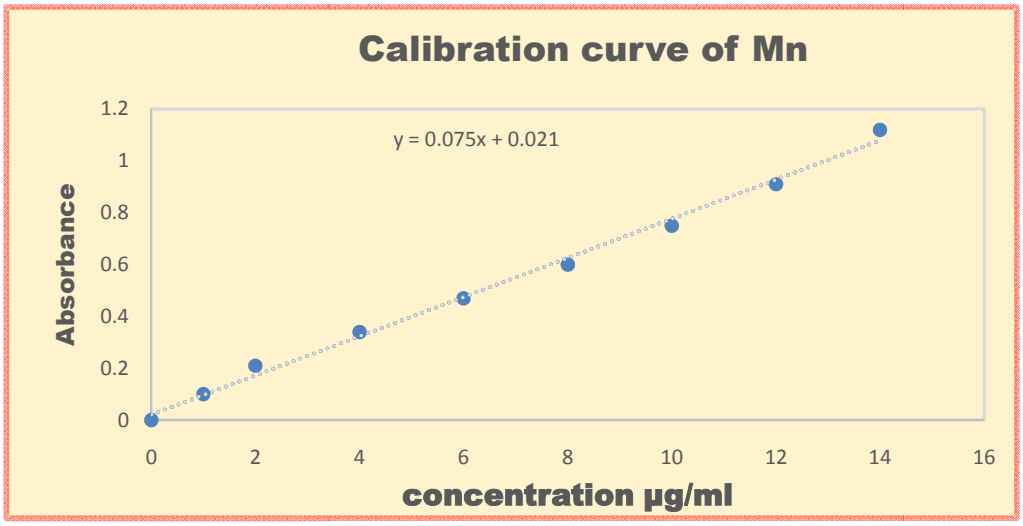

Figure 4: Calibration curve of Mn: NOHBPA Complex

IV. Effect of Other Ions

Mn (II) (100 µg) was determined in the presence of various ions. The following ions, did not interfere.

- 10 mg of each of, Li (I), Be (II), Ba (II), Ca (II), Sr (II), Al (III), Ti (III), V (V), Mo (VI), U (VI)
- 0.1mg each of Ag(I) & Pt (IV) and 20 mg each of chloride, bromide, iodide, phosphates, tartrate, acetate, citrate and thiosulphate, thiocyanide, tri ethanol amine, ascorbic acid.

Interference by various ions was removed by using appropriate masking agent.

- 10 mg of Cu (II) was masked by I ml of 2M EDTA or Sodium dihydrogen phosphate
- 10 mg of Ni(II) was masked by I ml of 2M 5-sulphosalicylic acid
- 10 mg of Fe(II) & Fe(III)was masked by I ml of 2MTri ethanol amine
- 10 mg of Co(II) was masked by I ml of 2M Ascorbic acid
- 10 mg ofCr(III was masked by I ml 2 M sodium fluoride

V. Composition of the Extracted Complex

The composition of the extracted complex was found to be 1:2 (Mn: NOHBPA) by Job's continuous variation and Mole ratio methods (Fig. 5 & Fig. 6).

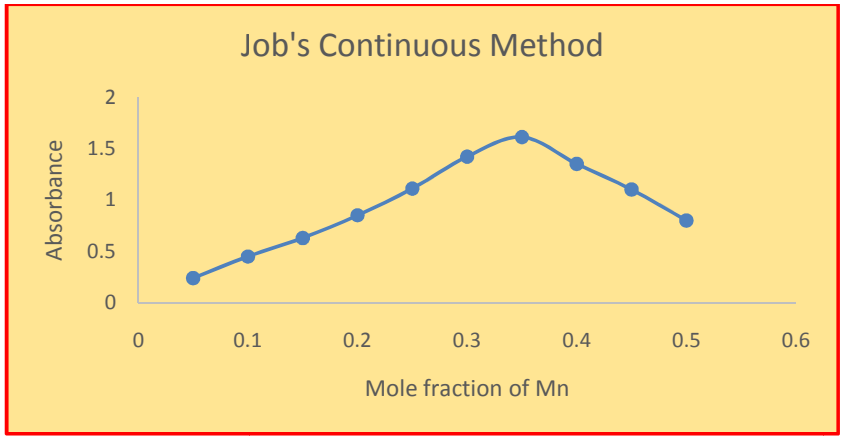

Figure 5: Composition of Complex by Job's Method

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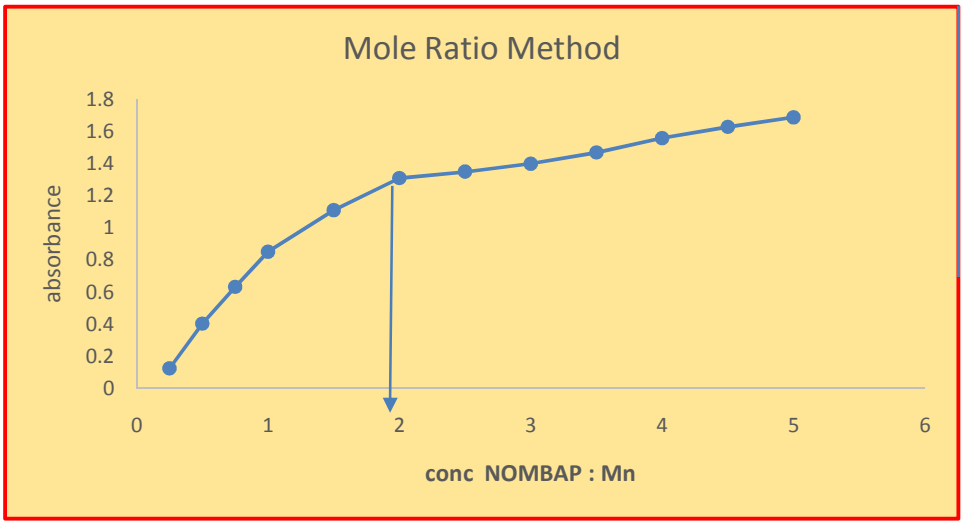

Figure 6: Composition of Complex by Mole ratio Method

VI. Accuracy, Precision, Sensitivity and Applications of Method

In order to determine the accuracy and precision of the proposed method, the experiment was repeated ten times. 40 µg of Mn (II) in 10 cm^3 solutions was taken. The average of 10 determination of 40 µg of Mn (II) in 10 cm3 solutions was 39.80 µg, which is varied between 40.25 and 39.35 at 95% confidence limit. Standard deviation and Sandell's sensitivity of the extracted species is found to be ±0.633 and 0.0012 µgcm-2 respectively. The results of the analysis of the samples were comparable with the Potassium Periodate method (Vogel AI 1978) for Mn (II) as shown in Table 2

Table 2: Determination of Manganese in Manganese steel sample and Synthetic Mixture.

SAMPLES	Pyrolusite ore	Mo-Mn steel
Present method (Based on the mean of three determinations)	34.80%	1.54%
Potassium Periodate method method	35.00%	1.60%

VII. Conclusion

From the above experiments, it is found that Schiff base, [NOHBPA] is a good sensitive reagent for development of rapid and sensitive extractive spectrophotometric method for the determination of Mn (II) and it has been competently applied for determination of Mn (II) in Manganese steel sample & Pyrolusite ore.

VIII. Acknowledgement

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