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Development of Extractive Spectrophotometric Determination of Manganese (II) Using [N - (O-Methoxy Benzaldehyde)-2-Aminophenol] (NOMBAP) as an Analytical Reagent

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Abstract: **Using analytical reagent N - (o - methoxy benzaldehyde) 2-aminophenol (NOMBAP) a feasible, sensitive and rapid spectrophotometric method has been developed for the determination of Mn (II). NOMBAP has been synthesized and characterized by elemental analysis. NOMBAP extracts Mn (II) quantitatively (99.45%) into n-Butyl alcohol from an aqueous solution of pH range 9.4 – 10.7. An intense peak at 480 nm (λ max) was observed in the extract of n-Butyl alcohol. Beer's law is obeyed over the concentration range 0.5 – 9.0 µg/mL for Mn (II). The molar absorptivity and Sandell's sensitivity for Mn - NOMBAP system is 62381.9 L mole^{-1}cm^{-1} and 0.0082µg cm^{-2} respectively. Job's Continuous Variation and Mole Ratio Method confirms that the extracted (Mn:NOMBAP) complex has composition 1:2. The average of 10 determination of 5 µg of Mn (II) in 10 cm^3 solutions was 4.999 µg, which is varied between 4.995 and 5.003 at 95% confidence limit and standard deviation is ±0.006. Interference by various ions has been studied. The proposed method is rapid, sensitive, reproducible and accurate and it has been satisfactory applied for determination of Manganese in Ore and Alloy samples)**

Index Terms: **Alloy sample, Extractive Spectrophotometry, Manganese (II), Ores, Solvent Extraction.**

I. INTRODUCTION

Manganese (Mn) is transition element with an atomic number 25. Mn does not exist in Free State in nature; often it is present along with Iron in minerals. Solvent extraction is important tool in separation technique. Due to its simplicity rapidity it is used in the separation of metal ions at trace level (Anovski et al., 1972; Monior –Williams, 1949). Solvent extraction coupled with spectrophotometrically plays significant role in pharmaceutical science. (De et al, 1970) Schiff bases play crucial role as chelating agents in complexes of transition metal (Hayashi et al., 2002; Temel & Hosgoren, 2002). Various reagents (Chang et al.,2019; Feig, 1949; Gili et al., 1997; Husaain et al.,2019; Holloway & Melnik ,1996; Nath et al., 1974; Scott, 1939;; Sayed et al., 2010; Shaheen et al., 2019; Vinusha et al.,2019) are available for the spectrophotometric determination of Manganese (II).

N - (o - methoxy benzaldehyde) 2-aminophenol (NOMBAP) acts as a tool for the extractive spectrophotometric methods for the determination of iron (Makhijani & Barhate, 2013) and Cu(II) (Makhijani & Barhate, 2013) and Nickel (II) (Makhijani et al., 2018). In the present communication, we describe the extractive spectrophotometric determination of Mn (II) with [N - (o - methoxy benzaldehyde) 2-aminophenol (NOMBAP).

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.

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A. General Procedure for Synthesis of N-(O-Methoxy Benzaldehyde) 2-Aminophenol (NOMBAP

o-methoxy benzaldehyde and & 2-aminophenol (made in ethanol) in ratio 1:1 was refluxed for 4 hours as shown in Fig.1. The reaction mixture was cooled to separate out sharp yellow crystal product NOMBAP (yield 78%, M.P.870-880C). The recrystallized for NOMBAP was done by using aqueous ethanol as per reported procedure recommended by Vogel (Vogel AI, 1989).

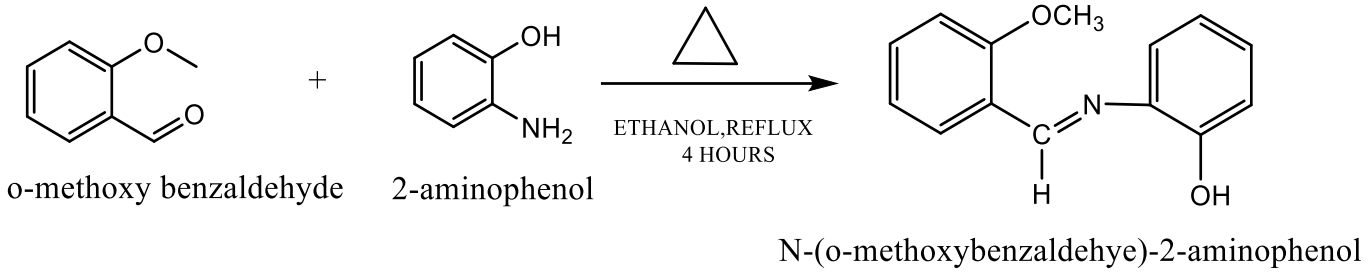

Fig. 1. Synthesis of Ligand NOMBAP

B. Green Synthesis of N-(o-Methoxy Benzaldehyde) 2-Aminophenol (NOMBAP)

In a beaker ingredients (0.005 moles of o-methoxy benzaldehyde & 0.005 moles of 2-aminophenol) & few drops of pure alcohol were irradiated in the microwave oven at 180° for 2 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)
Ligand NOMBAP	**227.28**	**5 hours 78%**	**1.4 minutes 92%**	**88^{0}C**	**73.12 (73.91)**	**5.14 (5.71)**	**6.41 (6.159)**

C. 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 (Vogel A.I, 1978). Working solutions of Mn (II) were made by suitable dilution.

D. Extractive Spectrophotometric Determination of Mn(II)

Aqueous solution containing 0.5-9.0 µg of Mn (II), 1ml of 0.5% solution of NOMBAP (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 of n-Butyl alcohol and the phases were allowed to separate. The absorbance of n-Butyl alcohol extract was measured at 480 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.

E. 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.

III. Results and Discussion

Manganese (II) could be extracted quantitatively (99.45%) by NOMBAP into n-Butyl alcohol from an aqueous solution of pH range 9.4 -10.7.

Organic solvents used for extraction of Mn (II) can be arranged on the basis of their extraction coefficient values as n-Butyl alcohol > n-amyl alcohol > benzyl alcohol > ethyl acetate > chloroform > carbon tetrachloride > bromobenzene > chlorobenzene > xylene > nitro benzene (Fig. 2). n-Butyl alcohol being the best extracting solvent; hence, was used for extraction throughout the work.

The n-Butyl alcohol extract of Mn- NOMBAP complex showed an intense peak at 480 nm. The absorbance due to the reagent is negligible at this wavelength, so the absorption measurements were taken at this wavelength (Fig. 3).

The color of the n-Butyl alcohol extract was found to be stable at least 48 hrs at room temperature.

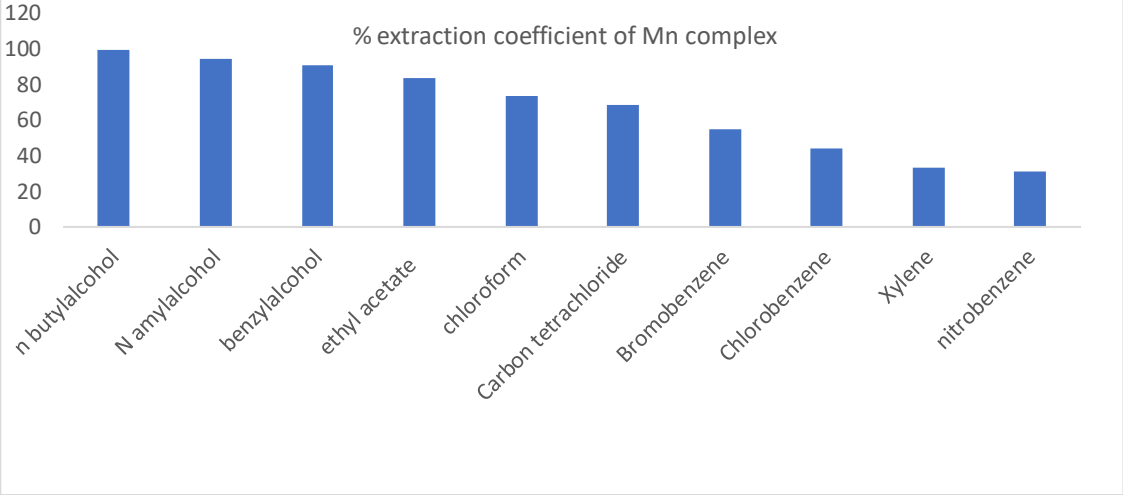

Fig. 2. % extraction of Mn into various solvents

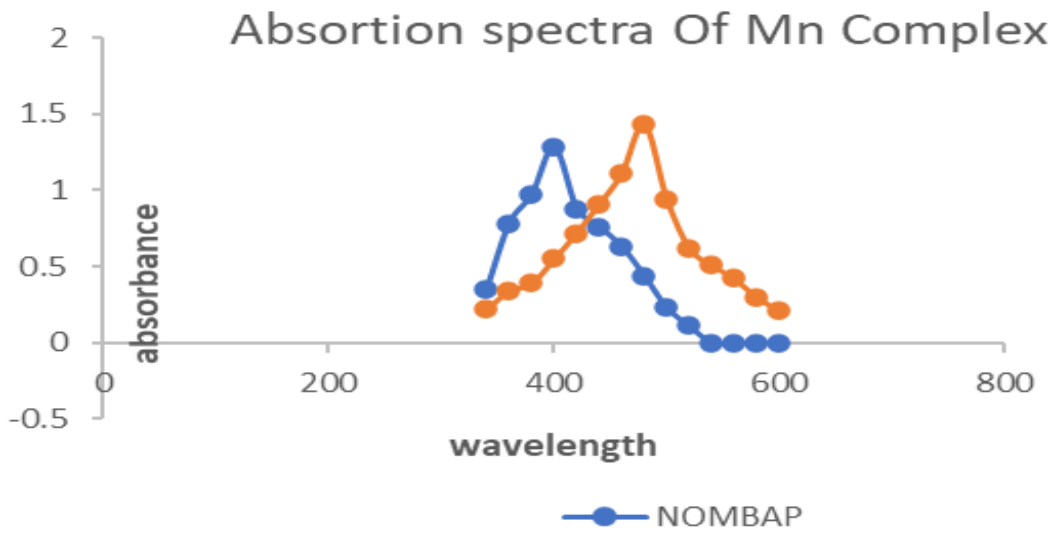

Fig. 3. Absorption spectra of Mn: NOMBAP Complex

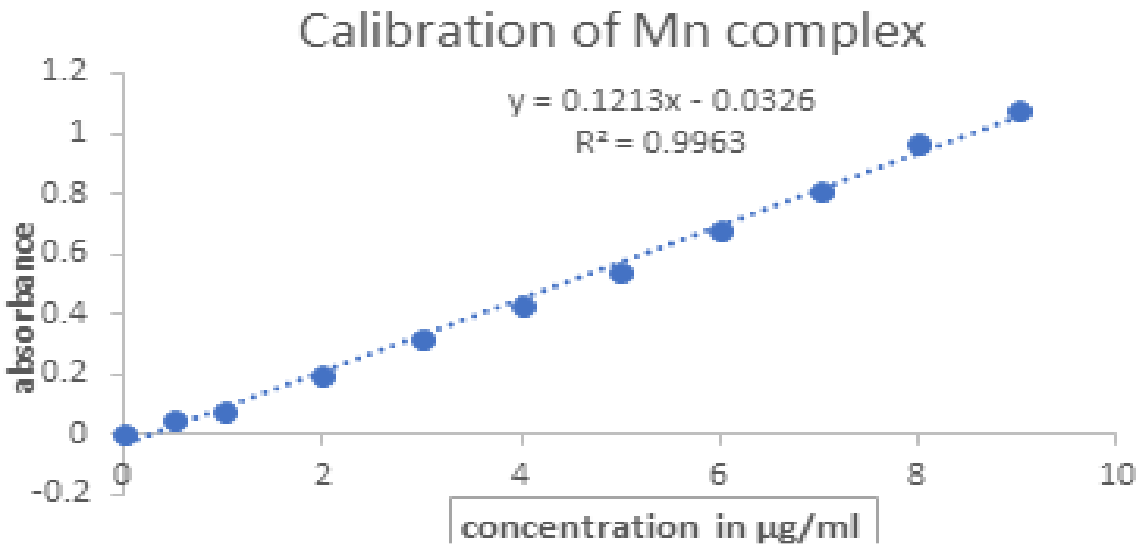

Fig. 4. Calibration curve of Mn: NOMBAP Complex

The system confirms Beer's law at this wavelength over a Mn (II) concentration range 0.5 – 9.0 µg/mL (Fig. 4). The molar absorptivity and Sandell's sensitivity of the extracted species on the basis of Mn (II) content were calculated to be 62381.9 L $mole^{-1}cm^{-1}$ and 0.0082 µ g cm^{-2} respectively.

It was found that 1 ml of 0.5 % solution of NOMBAP prepared in DMF was sufficient to extract 90 µg of Mn (II).

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

- 10 mg of Ni(II) was masked by I ml of 2M 5-sulphosalicylic acid
- 10 mg of Cu (II) was masked by I ml of 2M EDTA or Sodium dihydrogen phosphate
- 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

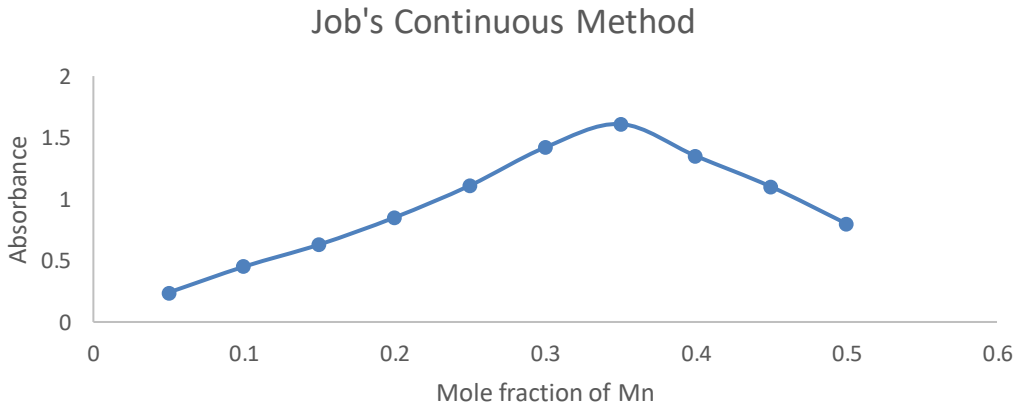

Fig. 5. Composition of Complex by Job's Method

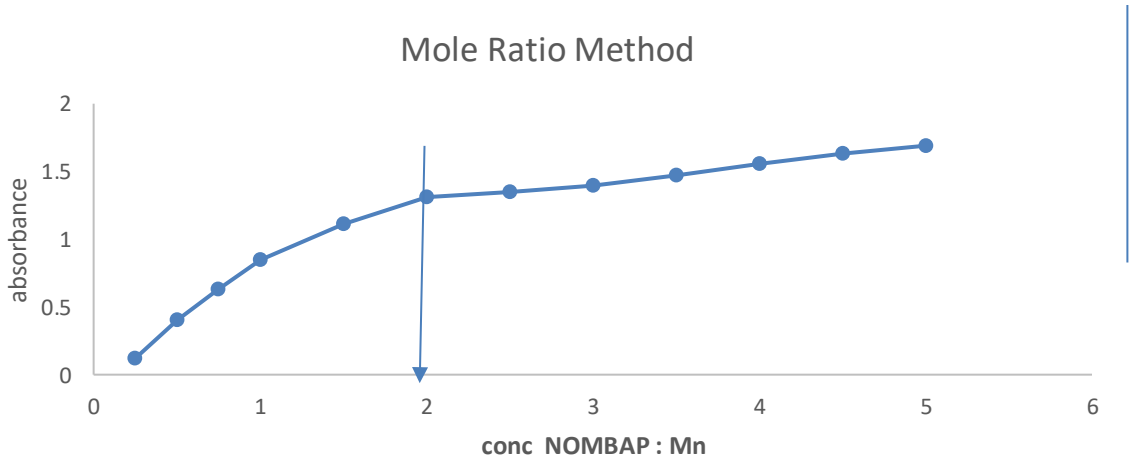

Fig. 6. Composition of Complex by Mole ratio Method

A. 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.

B. Composition of the Extracted Complex

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

C. Accuracy, Precision, Sensitivity and Applications of Method

The average of 10 determination of 5 µg of Mn (II) in 10 cm3 solutions was 4.999 µg, which is varied between 4.995 and 5.003 at 95% confidence limit and standard deviation is ±0.006.. The results of the analysis of the samples were comparable with the Potassium Periodate method (Vogel A.I., 1978) for Mn (II) as shown in Table 2.

Table II. 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%	35.00%
Potassium Periodate method	35.00%	1.60%

CONCLUSION

From the above experiments, it is found that Schiff base, [NOMBAP] 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.

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