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Determination of Manganese in Albizia Plant Samples Using 4-Amino antipyrene-3, 5- Di amino benzoic acid (AAPDAB) By Spectrophotometric Method

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ABSTRACT

A new technique has been devised to find tiny quantities of manganese (II). For the spectrophotometric detection of manganese, the 4-Amino antipyrine -3, 5-diaminobenzoic acid (AAPDAB) has been proposed as a new analytical reagent. The color responses happen instantly, and for more than five hours, the greatest absorbance was found at 390 nm. The pH range from 3 to 5 is where complex formation is seen. Metal and ligand were obtained in a 1:1 (M: L) composition using the Molar ratio relationship and the Job's approach. The calibration graph had a limit of detection (LOD) of 0.15 g ml^{-1} and was linear in the range A_{390} = 0.27577 - 0.00765. In the Mn (II) concentration range of 0.126–2.628 g/ml, the system complies with Beer's law. The AAPDAB method was used to determine the presence of manganese in some plant samples since it is more sensitive. The AAPDAB was discovered to have a molar absorptivity of 6.35 X 10^3 L $mol^{-1}cm^{-1}$ and a Sandell's sensitivity of 0.00157 g/ml g cm^{-2} of Mn (II). Manganese (II) levels in environmental plant samples have been successfully determined using the approach, with satisfactory results.

Keywords: Spectrophotometry, Manganese determination, AAPDAB reagent, plant samples.

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INTRODUCTION

The majority of manganese is fixed and unavailable to plants as manganese oxides. The pH level and the degree of soil oxidation determine manganese availability. The plant species and genotypes within that species determine the manganese tolerance limit [1]. In most cases, the manganese shortage is less than 20 ppm. This inadequacy signifies the emergence of several brownish patches. Other crops that exhibit manganese deficiency include potatoes, sugar beets, legumes (such as common beans, peas, and soy beans), palm crops, and cereal cereals (such as wheat, barley, and oats). The soluble sugar content of various plant sections decreases as a result of manganese deficiency's impact on photosynthesis. Inadequate rates of fertilizer utility might also lead to deficiencies [2]. In actuality, manganese shortage is most commonly found in sandy soils, organic soils with a pH of greater than six, and tropical soils. Both pH and Redox conditions were primarily controlled by the bioavailability of manganese in the soil.

The legume family, which includes the Albizia plant, is native to tropical regions of the globe. The Siris tree is the popular name for this tree. In addition to being non-toxic, it has the ability to fix nitrogen. In India, Ayurveda medicine uses it to treat allergies brought on by respiratory conditions. It makes the blood pure. This plant can be found in humid, tropical regions including Bangladesh, China, Sri Lanka, and India. Diabetes has been treated with albiziaodoratissima in traditional medicine [3]. Many plants and substances produced from them have been used to treat diabetes, and therefore the plants offer a potential source of hypoglycemic medications. Albizia plant was collected in Kangundi forest, Kuppam, A.P. India.

Data on the usage of o-nitro benzolazo salicylic acid for ferrous, cobalt, nickel, and zinc detection may be found in the literature [4]. However, there is no information in the literature on the determination of manganese using o-nitro benzolazo salicylic acid [5]. In the literature, not much information was discovered on the measurement of manganese using 4-Amino antipyrine -3, 5-di amino benzoic acid (AAPDAB). Advanced analytical and atomic absorption spectrophotometric techniques are typically used to analyze manganese in biological and environmental samples. These instruments need high-tech lab environments. Therefore, utilizing a straight forward UV visible spectrophotometer and an inductively coupled plasma-optical emission spectrometer in accessible labs, a different approach is devised for the trace detection of manganese (II). The procedure is expanded to include Mn (II) detection and analysis for soil and water samples. The 4-Amino antipyrine -3, 5-diaminobenzoic acid (AAPDAB). It is a potentiality reagent as a novel spectrophotometric technique in the current investigation.

Comparing the spectrophotometric method to atomic absorption and emission methods, the former required more expensive equipment. When compared to other approaches, the spectrophotometric method yields higher sensitivity. In contrast to existing spectrophotometric techniques, the suggested approach is more selective and sensitive. Apart from its simplicity, it has additional benefits including fast color development and reduced interference, as well as reliability and reproducibility. We have compared the data from the ICP-OES with those from the UV-visible spectrophotometer. In this work, the novel reagent 4-Amino antipyrine -3, 5-diaminobenzoic acid (AAPDAB) is used to determine Mn and analytical characteristics. Due to the reagent's increased sensitivity, it can also detect Mn in a variety of soil, water, and medicinal plant samples.

MATERIALS AND METHOD

Apparatus:

Shimadzu (Model- 1800) UV-VIS spectrophotometer and ELICO model LI-610 pH meter with combination electrodes were used for measurements of absorbance and pH, respectively. ICP-OES (Inductively Coupled Plasma-Optical Emission Spectrometry Model-7000) methods were used for the quantitative analysis of heavy metals in all samples. The heavy metals were analyzed by Inductively Coupled Plasma-Optical Emission Spectrometry.

Reagents and Solutions:

All of the chemicals utilized were obtained from Merck and were of the highest purity analytical-reagent grade. Glass containers were cleaned using double-distilled deionized water, acidified $K_2Cr_2O_7$ solutions, Con. HNO_3 washing, and multiple rinses with high purity deionized water. In a polypropylene bottle, standard solutions and environmental water samples were stored.

Synthesis of 4-AminoAntipyrene-3, 5-DiaminoBenzoic Acid (AAPDAB):

50 ml of methanol were used to dissolve a solution of 1 ml (0.0092 moles) of 4-amino antipyrine and 0.55 g (0.002 moles) of 3, 5-diaminobenzoic acid. To mix the ingredients, a 250ml round bottom flask was used. The mixed liquid was heated through reflux for 10 hours after which 10 ml of 1M sodium acetate was added to the mixture. On cooling the reaction, a brownish product separated. After filtering, the product was repeatedly washed with warm water, then with 50% methanol, and finally with n-hexane. This substance was created by recrystallizing methanol, and it underwent vacuum drying. The yield percentage was 93%, the melting point was 82^0C and schematic representation of the reagent was depicted in Figure 1.

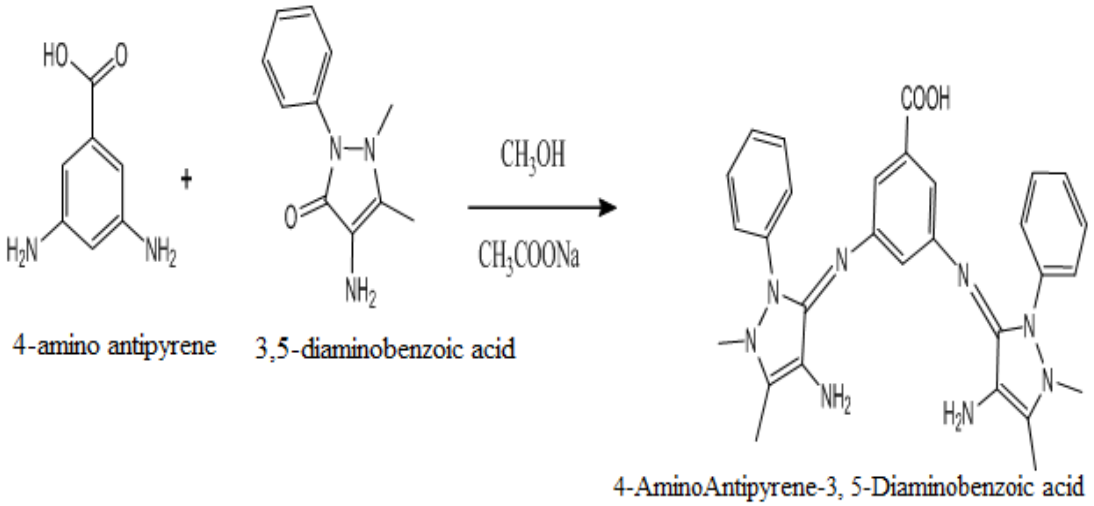

Figure 1: Preparation and Structure of AAPDAB reagent

Characterization of Reagent (AAPDAB):

The reagent has been synthesized and characterized by IR, ^{1}HNMR, UV Vis. Spectra and mass spectral data. Infrared spectrum of AAPDAB shows bands at 3432, 2957, 2926, 2110, 1726, 1638, 1491, 1269, and 744 respectively corresponding to υ (O-H) symmetric stretch, υ (N-H) stretch, υ (C-H) stretch, υ (C - N) (w) stretch, υ (C = O), υ (C = N), υ (C- C) stretch, υ (C- H) stretch and N-H(w). H^{1}NMR spectrum of AAPDAB (DMSO–d^{6}) showed signals at 7.0-6.8 (13), due to Aromatic protons, 2.45 (3H) due to -CH_3 group, 3.2 (3H) due to -N-CH_3 group, 5.4 (2H) due to-NH_2, and 8.8-8.6 (1H) due to –COOH group.

Mass spectrum of AAPDAB shows a signal at 522 (M+1) corresponding to its molecular ion peak. The molecular formula of the reagent is C_{29} $H_{30}N_8O_2$ (M. Wt. 522). The UV Vis. Spectrum of the concentration 1X10^{-3}M solution of AAPDAB was recorded at unique pH values. At pH 4.0 the pk values are calculated pk^{1}=pk^{2} due to deprotonation of ligand the practical structure can be fashioned.

AAPDAB Solution (1 X 10^{-3}M):

AAPDB was weighed to create the stock solution for AAPDAB, which was then placed into a 25 ml volumetric flask. Dimethyl formamide was used to dissolve the reagent AAPDAB, which was then diluted with the appropriate amount of the solvent. In order to achieve the required concentration, the stock solution was diluted. A brand-new reagent solution was made ahead of each use.

Manganous (II) Solution:

By dissolving 0.272g of Manganese sulphate (AR grade) in Milli-Q water and Manganese stock solution with concentration (1 X 10^{-3} M) was prepared. To this solution, 2 or 3 drops of

concentrated hydrochloric acid were added. The metal ion solution was diluted up to the check mark in a 100 ml volumetric flask. The stock solution was standardized by using EDTA titration by utilizing xylenol orange as an indicator. By using the stock solution, the following dilutions were made individually.

Buffer Solution:

With the help of the literature and by following strategies preferred for the preparation of buffer solution. The following solutions were utilized for the preparation of buffers solution given below. 1M Sodium acetate + 0.1M hydrochloric acid (0.5 – 3.0), 0.2M Sodium acetate + 0.2M acetic acid (3.5 – 6.0) , 1M Sodium acetate + 0.2M acetic acid (6.5 – 7.5), 2M Ammonia + 2M ammonium chloride (8.0 – 12.0) buffer solutions are prepared in distilled water. Suitable portions of these solutions are mixed to get the desired pH.

Medicinal Leaf samples:

By using microwave digestion, the leaf samples were prepared for analysis. The PTFE jars were filled with roughly 1g (dry mass) of leaf sample materials, which were then immediately covered with 10 ml of strong nitric acid. The digesting regimen included a 10-minute ramp-up in time until the temperature reached 150^0C. 800 W was the power. After the program was finished, the vessels were cooled, vented, and opened. Two milliliters of 30% hydrogen peroxide was then added, and the solutions were filtered into 25 milliliter volumetric flasks and made up with double-distilled water. Similar digestive techniques were used to prepare the blanks, but without plant material [6].

RESULTS AND DISCUSSION:

Absorption spectra of Manganese complexes and AAPDAB complexes:

In comparison to the reagent blank, the absorption spectra of the Mn (II) and AAPDAB complex solution were recorded. Water was used as a blank to capture the absorption spectra of the reagent solution of AAPDAB. A graph is drawn between absorbance on Y- axis and wavelength (nm) on X-axis and was shown in Figure 2.

In keeping with the methods presented in the earlier reports [7], pH 4.0 was used for additional analysis [8, 9]. The study of manganese and AAPDAB complexes used a wavelength range of 250–600 nm [10]. The typical spectra were shown in Figure 2. Figure 2 depicts the Mn (II) complex solution and shows that the reagent has a significantly lower absorbance at 390 nm, where there is the greatest retention. The wavelength of 390 nm was then chosen for further analysis.

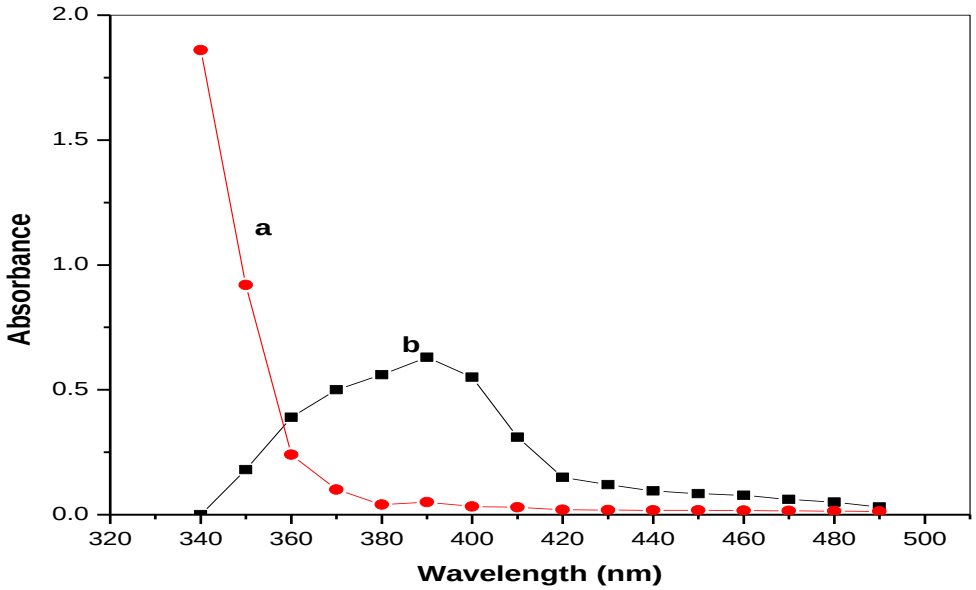

Figure 2: Absorption Spectra of a) AAPDAB Vs water blank b). Mn (II)- AAPDAB Complex Vs AAPDAB solution

Effect of pH on Experimental solution Absorbance:

The influence of pH on the color intensity of Mn (II) ($1X10^{-3}$) solution and AAPDAB reagent solution ($1X10^{-3}$) was investigated. The ideal pH scale 4 was established by using the method described as earlier. Figure 3 shows the graph that was made between the absorbance of the metal complexes and the reagent at various pH levels. The graph indicates that absorbance is constant in the pH range of 3-5 and that the complex exhibits maximum absorbance at constant pH. As a result, 4.0 pH was decided upon for further research.

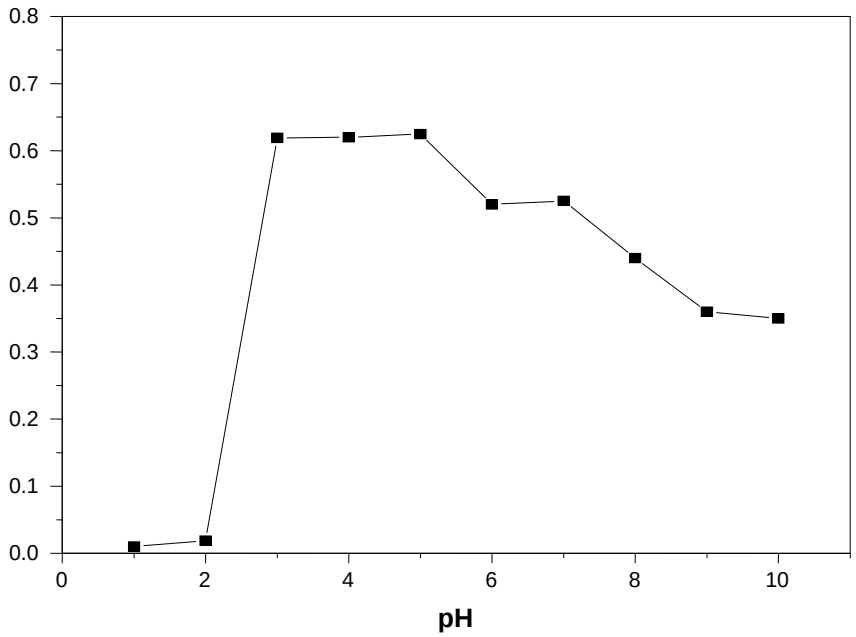

Figure 3: Effect of pH on Absorbance of Mn (II) complex

Figure 2 Absorption spectra are graphs between absorbance and wavelength that were created. In such case, the black line denotes the (II) - AAPDAB complex Vs AAPDAB solution, while the red line denotes the AAPDAB Vs water blank. It was recognized that the graph for AAPDAB Vs water blank has highest absorbance between 340 and 380 nm and remains constant as wavelength increases. Similar to this, for Mn (II)-AAPDAB complex vs AAPDAB solution, a rise in absorbance was seen at 350–400 nm wavelengths and a decrease with an increase in wavelength.

Reagent Concentration's impact:

The full-color improvement necessary for the chemical reagent and the metal particle was set up by making suitable methods. The findings are shown in Table 1. According to Table 1, full-color development requires a 5-fold molar sufficient reagent solution [11]. As a result; additional research was carried out using the reagent's 5-fold molar abundance to Mn (II). Results were found with acceptable agreement to other parameters.

Table 1: Effect of AAPDAB concentration and the Absorbance of Mn (II) complex

[Mn (II)] =1 X 10^{-3} M, [AAPDAB] = 1 X 10^{-3} M & Wavelength = 390 nm.]

Mn (II): AAPDAB	Absorbance
1:05	0.568
1:10	0.635
1:15	0.667
1:20	0.680
1:25	0.657
1:30	0.662

Optimum Time required for Absorbance of Mn (II) complexes:

Based on the procedure, prescribed method was used to estimate the absorbance of the Mn (II) and AAPDAB complex at different time intervals in order to determine the time stability of the complexes [12]. The absorbance of the Mn (II) complex was determined at 390 nm. The concentrations of the [AAPDAB] solution and [Mn (II)] solution were each made at 1 $X10^{-3}$ M. The color developed instantly and stayed that way for five hours.

Order of Addition of constituents to Reaction mixture:

Mn (II) and AAPDAB (complex) have no negative effects on the absorbance of the order in which constituent solutions such as buffer solution, metal ion solution, and reagent solution are added to the reaction mixture.

System's adherence to Beer's law:

The approach described as per protocol and was used to investigate the relevance of Beer's law to the current system. The absorbance and manganese content were shown on a graph. The relationship between the absorbance and the amount of Mn (II) was shown in Figure 4. The straight line meets the requirement A_{390} = 0.27577 - 0.00765 for compliance. Additionally, the graph's standardization suggests that the system adhere to the Beer's law limit of 0.126 – 2.628 g/ml of Mn (II) [13, 14]. The system has a molar absorptivity property of 6.35 X 10^3L $mol^{-1}cm^{-1}$, and its Mn (II) sensitivities are 0.00157 g/cm^2 [15,16]. The determined Specific absorptivity of the system was 0.00882 ml $g^{-1}cm^{-1}$ [Figure 4]. For a set of ten measurements, the concentration of Mn (II) was determined to be 0.0114 g/ml, or 2.14 g/ml. The system's relative standard deviation was calculated to be 2.7436%. The system's mean absorbance was calculated to be 0.412 ± 0.01 respectively.

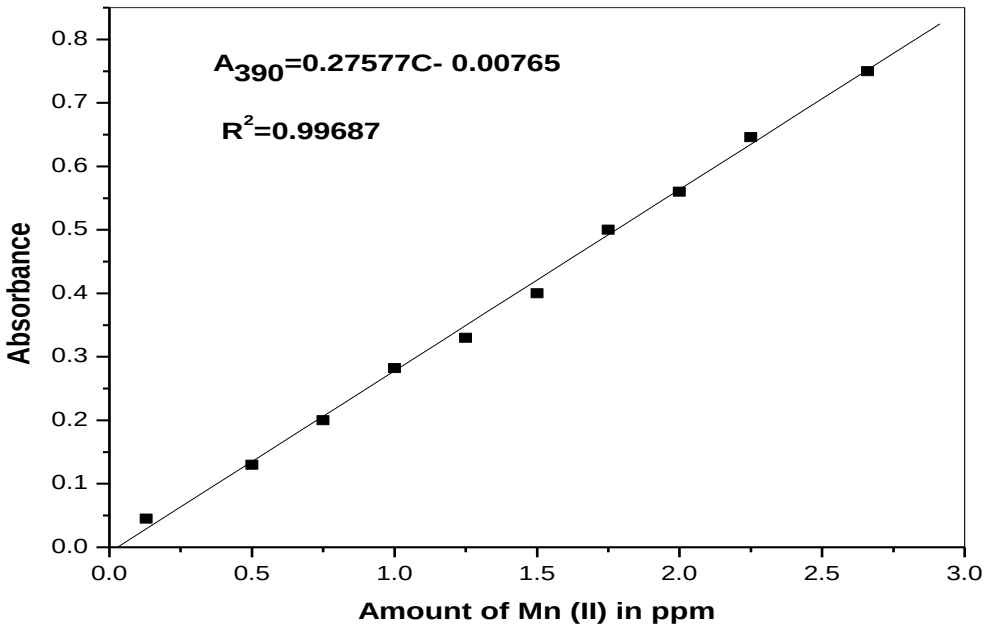

Figure 4: Calibration plot for Mn (II)

[pH = 4.0 [AAPDAB] 1X 10^{-3} M & Wavelength = 390 nm.]

Foreign Ion effect:

The quantity of foreign ions was employed to investigate the effect of foreign ions on the applicability of the present approach. The manganese at a concentration of 2.14 g/ml was investigated with the interference of various ions. According to our tolerance limit value, the amount of foreign particle required to produce a 2% error was taken into account when calculating the absorbance of Mn (II) - AAPDAB complex [17, 18]. The tolerance limit values for foreign ions are shown as follows in Table 2. The table below shows that greater tolerance limit values were found for tungsten ions and citrate ions. The lower tolerance limit values work similarly.

Table 2: Tolerance Limit of Foreign ions in the Determination of 2.12µg/ml of Manganese

Ion Added	Tolerance Limit µg/ml	Ion Added	Tolerance Limit µg/ml
Citrate	384	W(v)	368
Tartarate	296	Mn (II)	22
Urea	288	Pb (II)	0.82
Iodated	254	Cr (VI)	1.0
Bicarbonate	244	Zn (II)	0.13[a]
Thio Cyanate	232	Cd (II)	0.22
Sulphate	192	Hg(II)	0.40
Oxalate	176	Ni (II)	0.23
Thiourea	152	Fe (II)	0.22
Nitrate	124	Au (III)	0.40
Acetate	118	Pt (IV)	0.39
Phosphate	20	Tl (III)	0.25

Bromide	16	Ag (I)	0.22
Chloride	7.1	V (V)	0.20
Fluoride	4.0	Cu (II)	1.2

Applications:

By using the developed method, manganese concentrations in Albizia medicinal plants were estimated. The outcomes were displayed in Table 3. Samples of the Albizia plant were gathered in the Kuppam kangundi forest. The amount of Mn for the Albizia plant by ICP-OES was clearly seen as suggested [19].

Table 3: Determination of Manganese in Albizia plant samples

Name of the Samples	Amount of manganese [a] found µg/ml	
	ICP-OES	Proposed Method
Albizia plant samples	1.722	**1.713**

Determination of Stability constants of Metal complexes:

The Molar ratio technique and Jobs continuous variation techniques were used to ascertain the composition of complexes [20, 21]. The stability constants of the complex were calculated using the data from Job's figure.

Jobs Methods:

As per the methods for determining the stability of complexes by using the Job's continuous variation method is as follows. A graph was made between the absorbance and the mole fraction of the reagent. The Job's plan is depicted in Figure 5. The graph showed that each mole of reagent and metal particle in the reaction mixture is represented by one mole [22, 23]. The composition of the reagent and the metal particles is then 1:1. Utilizing the data from the Job's curve experiment, the stability constants of the complexes are calculated. The stability constant of the complexes was determined using the following equation.

$$\beta = (1-\alpha)/\alpha 2C$$

Where α = Degree of dissociation (0.098), and C = Concentration corresponding to the point of intersection.

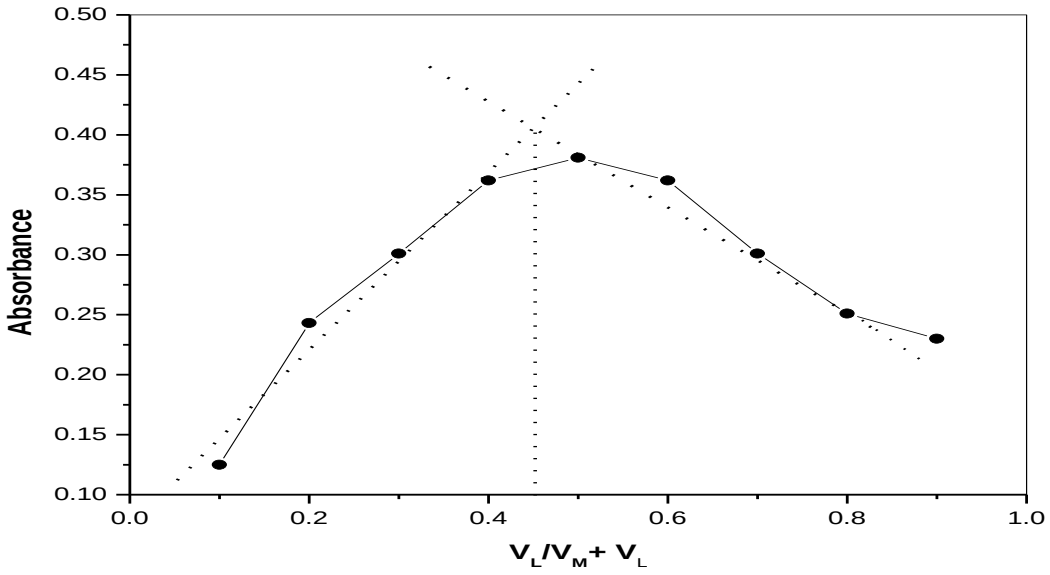

Figure 5: The plot of Job's curve [Mn (II) = 1 X $10^{-3,}$ Wavelength = 390 nm & pH = 4.0.]

The stability constant of the complex was determined using Job's approach by utilizing the numbers (0.098) and c (1 X 10^{-3}). By including those numbers in the aforementioned calculation, the stability constant of 1.39 X 10^{6} was determined. Stability constant/composition with 390 nm wavelength and 4.0 of pH.

Mole Ratio method:

The Mole ratio plot was shown in Figure 6, and this graph indicates that the complexes' composition is 1:1 (Mn: AAPDAB). Thus, the Mole ratio method is supported by the composition of the complex derived using Job's method. Based on the composition of the complex, the following structure is probably permissible for the [Mn: AAPDAB] complex. By using molar proportion methods, the spectrophotometric mole ratio of the metal to the ligands was taken into account [24]. The information produced by using various pH scale values was typically ensured by the spectrophotometric approach [25].

We may investigate the complexes with low stability by using a spectrophotometer, and by applying a specific approach, we can ascertain the ratio of the complexes. These solutions' maximum absorptions were measured using a spectrophotometer. The complexes of absorbance vs ligand and metal [L] / [M] were plotted on a graph. It was shown in the graph (Figure 6) that with the half of c and computed.

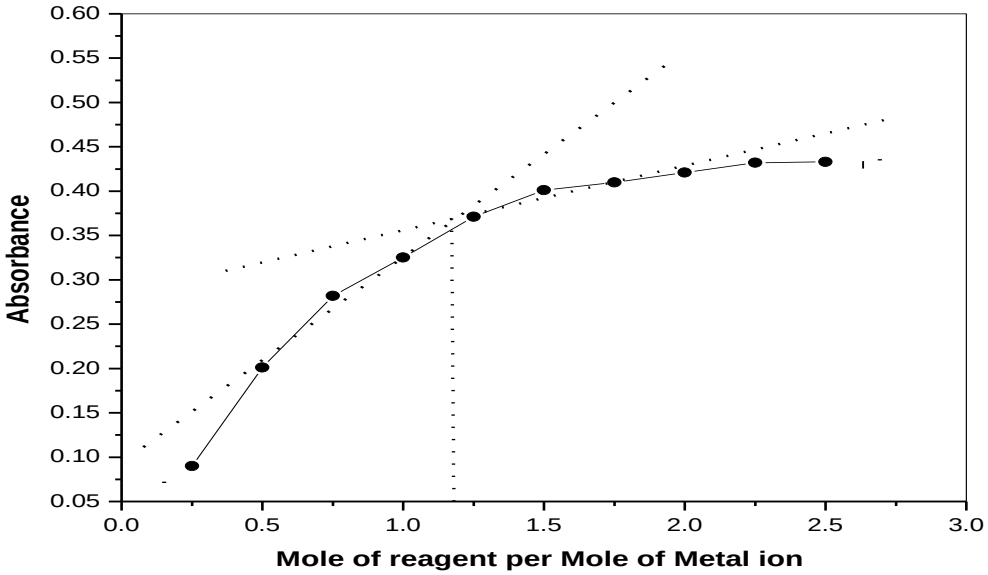

Figure 6: Molar Ratio plot [Mn (II) = 1 X 10^{-3}, Wavelength = 390 nm & pH = 4.0]

Structure of Mn - AAPDAB complex:

The Mn-AAPDAB complex was given the following structure, as illustrated in Figure 7, based on the analysis and experimentation mentioned above.

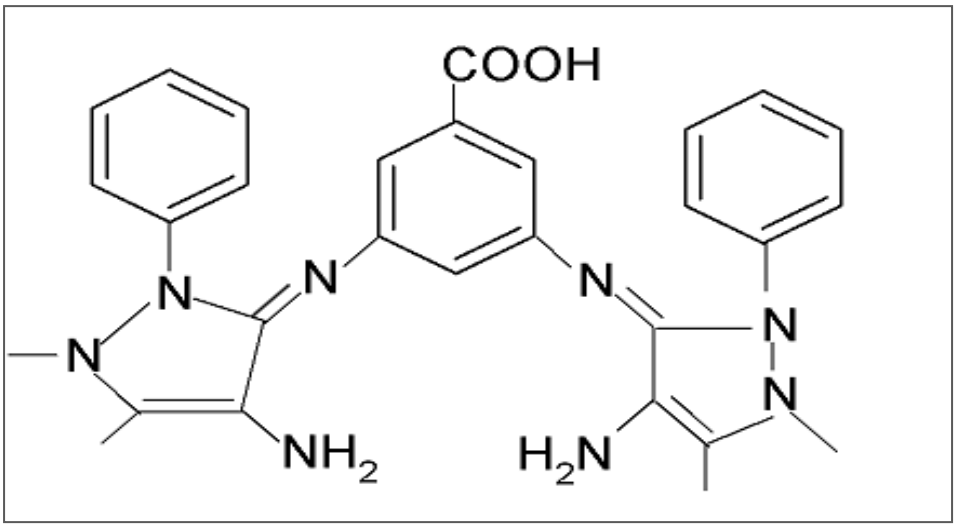

Figure 7: Structure of AAPDAB complex

Table 4: Physico-chemical and Analytical characteristics of Mn (II)–AAPDAB complex

S. No.	Characteristics	Results
1.	λ_{max} (nm)	390
2.	pH range (optimum)	3.0 – 5.0
3.	Mean absorbance	0.412 ± 0.01
4.	A mole of reagent required per mole of the metal ion for full color developed	5 Fold
5.	Time stability of the complex (in Hrs)	5

6.	Beer's law validity range (µg/ml)	0.126 - 2.628
7.	Molar absorptivity (L mol^{-1} cm^{-1})	6.35 X 10^3
8.	Specific absorptivity (ml g^{-1} cm^{-1})	0.00882
9.	Sandell's sensitivity (µg/ml)	0.00157
10.	The composition of the complex as obtained in Jobs and molar ratio methods (M:L)	1: 1
11.	Stability constant of the complex	1.39 X 10^6
12.	The standard deviation in the determination of 2.12 µg/ml of Mn (II) for ten determinations	0.0114
13.	Relative standard deviation (RSD)%	2.7436
14.	Y-intercept	-0.00765
15.	Angular coefficient (m)	0.27577
16.	Correlation coefficient (v)	0.99687
17.	Detection limit (µg ml^{-1})	0.05
18.	Determination limit (µg ml^{-1})	0.15

CONCLUSIONS:

When Mn (II) in an acidic medium was combined with 4-Amino antipyrine-3, 5-diaminobenzoic acid (AAPDAB), a yellow solution resulted. Table 4 provides a summary of the physicochemical parameters and analytical features of the Mn (II) and AAPDAB complex. Maximum estimation of the reagent solution was at 390 nm. The current system has a pH range of 3.0-5.0. 6.35 X 10^3 L $mol^{-1}cm^{-1}$ was the molar absorption factor. Sandell's system had a specific absorption factor of 0.00882 ml $g^{-1}cm^{-1}$ and a sensitivity of 0.00157 g/cm. The computed result for the applicability of Beer's law ranges from 0.126 to 2.628 g/ml. Using the Molar Ratio Relationship and the Job's technique, the composition metal and ligand were obtained in a 1:1 (M: L) ratio. The system's complicated stability constant was calculated to be 1.39 X 10^6. In a set of 10 replicate measurements, a concentration of Mn (II) of 2.14 g/ml required a tenfold molar excess of chemical reagent to improve full color, and the standard deviation was measured as 0.0114 g/ml. The relative standard deviation's computed value was 2.7436 percent. It was discovered that the mean absorbance was 0.412 ± 0.01.

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