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Oxidative Coupling Methods for the Spectrophotometric Determination of Vanadium (V) in Diverse Sample Matrices

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Abstract— Vanadium(V) is a transition metal of growing analytical interest owing to its widespread presence in various environmental, biological, and industrial samples. Accurate and sensitive approaches are essential for the determination of vanadium (V) for environmental monitoring, metallurgical processes, and biomedical studies. This research article presents innovative oxidative coupling protocols for the determination of vanadium by the spectrophotometric method in diverse sample matrices. The proposed methods harness the power of oxidative coupling reactions, capitalizing on the unique chemical properties of vanadium(V) ions. All these methods have several advantages including simplicity, cost-effectiveness, and the ability to analyze vanadium(V) in complex sample matrices. The methodology involves the reaction of vanadium(V) ions with suitable chromogenic reagents, resulting in the formation of intensely colored complexes. The absorbance of these complexes is then measured spectrophotometrically at specific wavelengths, allowing for the quantification of vanadium(V) concentrations. Importantly, the oxidative coupling reactions employed in this study exhibit high specificity for vanadium(V) ions, minimizing interference from other species in the sample matrix. A comprehensive investigation of the analytical performance of these oxidative coupling methods was conducted. Calibration curves were constructed using standard vanadium(V) solutions, demonstrating excellent linearity over a wide concentration range, and highlighting their sensitivity. The precision and accuracy of the methods were assessed through replicate measurements and recovery studies, yielding satisfactory results. One of the key strengths of the proposed methods lies in their versatility. They were successfully applied to various sample types, including environmental water samples, soil, and plant extracts. The ability to adapt these methods to diverse matrices underscores their applicability in real-world scenarios.
Keywords: Vanadium, MBTH, Spectrophotometric, oxidative coupling, Water sample, soil sample, plant sample.

1. Introduction

In recent years, Vanadium, a versatile transition metal with significant industrial and environmental implications, has attracted substantial attention. Vanadium exhibits a wide range of oxidation states, from -1 to +5, making its chemistry notable for the presence of four adjacent oxidation states: +2 (lilac), +3 (green), +4 (blue), and +5 (yellow). Vanadium (II) compounds function as reducing agents, while vanadium(V) compounds act as oxidizing agents and are particularly stable in solution. Notably, vanadium (IV) compounds are often found in the form of vanadyl derivatives, which incorporate the VO2+ center.

Approximately 85% of vanadium produced is utilized as ferrovanadium as a steel additive [1]. Axles, bicycle frames, crankshafts, gears, surgical equipment and tools, and other vital components are all made from vanadium steel. Vanadium has a very restricted biological role. Some nitrogen-fixing microorganisms employ a nitrogenase containing vanadium. Vanadium is required for acidians and sea squirts to produce vanadium chromogen proteins. Vanadium is also required at very minute levels by rats and hens, and shortage results in lower development and reproduction. Vanadium is a contentious dietary supplement, partly because it increases insulin sensitivity [2]. Vanadyl sulphate may help persons with type 2 diabetes regulate their blood sugar levels [3]. In diabetic rats, anti-diabetic arylalkyl amine vanadium salts have also been tested [4]. Vanadium may be advantageous in the prevention of heart disease, according to laboratory and epidemiological evidence [5]. Vanadium is used in a variety of tablets and nutritional supplements to boost strength and avoid diabetes. Pentavalent vanadium ions in drinking water are thought to enhance sugar, nitrogen, and lipid metabolism, lowering blood glucose and cholesterol levels, preventing obesity, increasing insulin resistance, alleviating gout

symptoms, increasing motor functions, and/or speeding up sweating and urination [6]. Vanadium compounds are all considered hazardous. Vanadium's toxicity is determined by its oxidation state, with vanadium(V) being more poisonous than vanadium (IV) [7]. Tetravalent VOSO4 has been shown to be more hazardous than trivalent $V2O_3$ [8]. Vanadium is mostly ingested by humans through meals such as buckwheat, soybean, olive oil, sunflower oil, apple, and egg.

Vanadium, at various oxidation levels, has been found to be harmful to animals. The kidney, spleen, reproductive, and development of treated animals were all impacted by large dosages of vanadium salts administered orally [2, 9, 10]. As far as long-term effects are concerned, inhalation of vanadium pentoxide (V^{5+}) particles resulted in increased incidence of tumors in the respiratory tract of rats and mice [11], which prompted the classification of vanadium pentoxide as “possibly carcinogenic for humans” (category 2B) by the International Agency for Research on Cancer [12]. When consumed in excess, vanadium can have several negative impacts on human health. Inhaling vanadium through the air might result in pneumonia and bronchitis. Vanadium's immediate side effects include inflammation of the lungs, throat, eyes, and nasal passages. The assessment of vanadium concentration in environmental samples has drawn a lot of interest because of the necessary and harmful effects it has on biological systems. As a result, it is extremely desired to determine the presence of vanadium in environmental and biological samples, and the relevant approaches have been examined [13]. It is noteworthy that, Efforts have been made to establish analytical methods for the detection of vanadium in environmental, biological, and geological samples.

Numerous techniques have been documented for quantifying vanadium concentrations, with the common approach involving spectrometric methods, notably atomic absorption spectrometry, for the assessment of vanadium content in environmental samples [14-16], Chromatography [17-19] inductively coupled plasma mass spectrometry [20], inductively coupled plasma optical emission spectroscopy [21], ultrasonic nebulization inductively coupled plasma optical emission spectrometry [22], Some of these techniques suffer from several disadvantages such as highly expensive instruments used for the regular analysis and matrix effects. Some of these methods necessitate specialized electrodes for vanadium determination, while others employ catalytic approaches known for their high sensitivity [23], but they generally lack simplicity. Hence, accurate determination of vanadium at trace levels using simple and rapid methods is of paramount importance. Spectrophotometry is widely employed for conventional laboratory analysis because of its low cost, speed, and easy automation. Hence numerous spectrophotometric methods have been proposed for the determination of vanadium in environmental and biological samples, using various chromogenic reagents. Numerous spectrophotometric methods developed for the determination of vanadium up to 1986 have been well discussed by Marczenko [24]. Recently, various chromogenic reagents proposed for the determination of vanadium spectrophotometrically between the years 1979 and 1992 have been reviewed by Taylor and Van-Staden [7], with particular emphasis on methods intended for the determination of V(V) and (IV) in each other’s presence.

Numerous spectrophotometric techniques for vanadium determination have been documented, centering around the reaction of vanadium with 3,5-dinitrosalicylic acid and rhodamine B under mildly acidic conditions. [25], 1,5-diphenylcarbohydrazide, in acetonic media [26]. Diantipyryl-(3-hydroxy)phenylmethane [27]. Oxidation of 2,2’-iminodibenzoic acid[28], benzidine-phosphoric acid [29] Erichrome cyanine R and benzyldodecyldimethyl ammonium bromide [30]. Some phenothiazine [31] and Perphenazine [32] derivatives have been recommended for the spectrophotometric determination of vanadium-based on the oxidation of these derivatives by vanadium under acidic conditions. Numerous kinetic and catalytic spectrophotometric techniques have been documented for the assessment of vanadium in diverse sample matrices, including methods employing indigo carmine [33] in combination with bromate and Diphenylamine (DPhA) [34]. Manual procedures for kinetic measurements are tedious and time-consuming. Moreover, it is difficult to control the timing of mixing of reagents and sample precisely and reproducibly, and subsequent measurement of the reaction product, which is essential to achieve good reproducibility.

The above-mentioned methods for spectrophotometric determination of vanadium have several disadvantages in terms of cost and the instrument used in routine analysis and also lack simplicity or sensitivity, and some methods use organic solvents for extraction. Hence, its accurate determination at trace levels using a simple, cost-effective, and rapid method is of paramount importance. Spectrophotometry is essentially a trace analysis technique and is one of the most powerful tools in routine chemical analysis.

Its presence in diverse sample matrices, ranging from environmental waters to metallurgical products and biological tissues, necessitates accurate and reliable analytical methods for its determination. Among the various oxidation states of vanadium, vanadium(V) holds particular significance due to its prevalence and importance in various applications. Spectrophotometric methods have long been employed in analytical chemistry for their simplicity, cost-effectiveness, and versatility. These methods harness the absorbance of light by chemical species to quantify their concentrations. In the case of vanadium(V), oxidative coupling reactions have emerged as powerful tools for spectrophotometric determination. In this work, the author has tried to develop a simple and cost-effective method via spectrophotometric methods for the determination of vanadium. The method is based on a diazo coupling reaction using a new reagent 3-Methyl-2-benzothiazolinone hydrazone hydrochloride hydrate (MBTH) as electrophilic coupling reagent and n-(1-naphthyl) ethylenediamine dihydrochloride (NEDA) as a coupling agent.

The developed methods have been successfully applied for the determination of vanadium in various environmental and biological samples. The advantages of the proposed methods are that the reagents used are inexpensive, non-carcinogenic, water-soluble, and offer simple, reproducible methods. The chromogenic products absorb at longer wavelengths, with reagent blanks being highly colorless.

2. Experimental Methods

A. Chemicals and Instrumentation:

Instruments utilized in this study included a Systronics UV-Vis spectrophotometer -610 equipped with 1.0 cm matched cells for absorbance measurements. All chemicals employed were of analytical grade, and distilled water served as the solvent throughout the experiment. Fresh solutions of Methyl-2-benzothiazolinonehydrazone hydrochloride (MBTH), N-(1-Naphthyl) ethylenediamine dihydrochloride (NEDA), and Ammonium metavanadate were prepared daily.

B. Standard procedure for quantifying vanadium(V) concentrations.

i. Calibration graph

In a final 3 ml of the reaction mixture, comprising 14.3 µM MBTH, 6.33 µM NEDA, and 0.016 M acetic acid-sodium acetate at pH 3.5, various concentrations of vanadium were introduced. The alteration in absorbance of the colored solutions was measured at 570 nm relative to a control that included all reagents except vanadium. The resulting product exhibited remarkable stability at room temperature, and the analysis demonstrated adherence to Beer's law within the range of 0.49 mM to 10.3 mM of vanadium, displaying excellent linearity. A calibration graph depicting this relationship is presented in **Figure 1.**

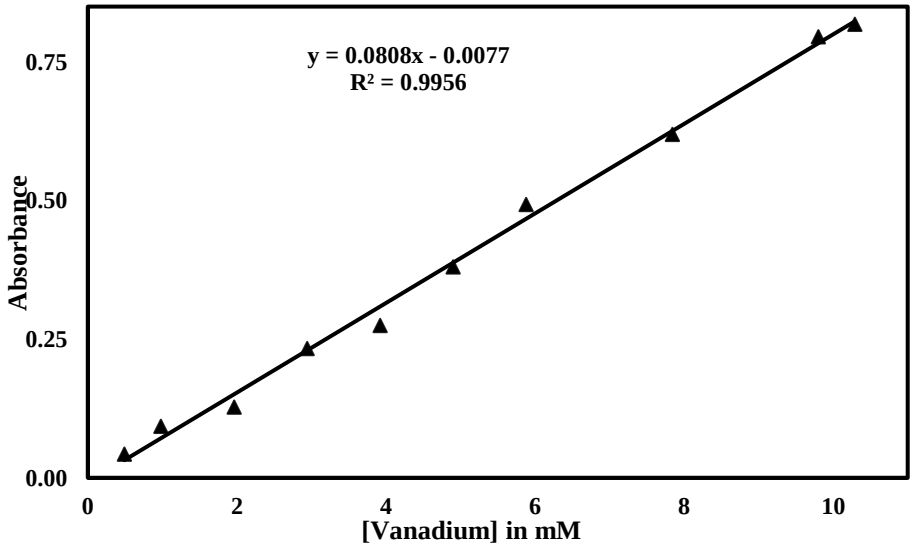


Fig 1: Beer's law graph for vanadium.

ii. Determination of vanadium in soil and water sample

For soil samples representing the uppermost layer, a 5g portion was weighed, followed by drying and grinding. Subsequently, distilled water was added and thoroughly mixed. After allowing the contents to settle overnight, they were filtered through Whatman no. 1 filter paper. The resulting precipitates were washed repeatedly with distilled water, and the sample solutions were adjusted to a final volume of 25.0 ml with distilled water. This prepared solution was then subjected to analysis using the proposed method.

iii. Determination of vanadium in plant samples

To prepare the plant (grass) sample for analysis, it was initially washed with distilled water to remove any adhering soil, followed by careful drying with filter paper to determine its weight accurately. Subsequently, a 25ml solution of 0.1M Na_2CO_3 was added to a precisely weighed portion of the plant sample (0.25 g) contained in a 50 ml glass beaker. The mixture was boiled for 15 minutes and then filtered through Whatman no. 1 filter paper. The resulting precipitates underwent multiple washes, first with 0.1M Na_2CO_3 and then with distilled water. The sample solutions were eventually adjusted to a final volume of 25.0 ml with distilled water, and this prepared solution was subjected to analysis using the proposed method.

iv. Determination of vanadium in water samples

100 ml water samples from the environment were filtered and analyzed for vanadium using the same method, yielding negative results for vanadium(V). To confirm the accuracy of the method, known amounts of vanadium(V) were intentionally added (spiked) to these samples and subsequently analyzed using the proposed method.

3. Results And Discussion

At room temperature, vanadium(V) induces the oxidation of MBTH, forming a diazonium cation. This cation rapidly couples with NEDA in an acidic environment, giving rise to the formation of a highly vibrant, blue-coloured species.

A. Absorption spectra

The formation of highly intense, blue-coloured species is integral. To determine the wavelength at which this coloured species exhibits maximum absorbance, a scan of the sample was conducted across the visible range of 400 – 750 nm. This analysis was performed in a 3 ml solution comprising 14.3 µM MBTH, 6.33 µM NEDA, 0.016 N acetic acid-sodium acetate with a pH of 3.5, and varying concentrations of vanadium(V). The optimal wavelength for maximum absorbance was identified at 570 nm, a point at which the reagent blank displayed minimal or negligible absorbance, as illustrated in **Figure 2.**

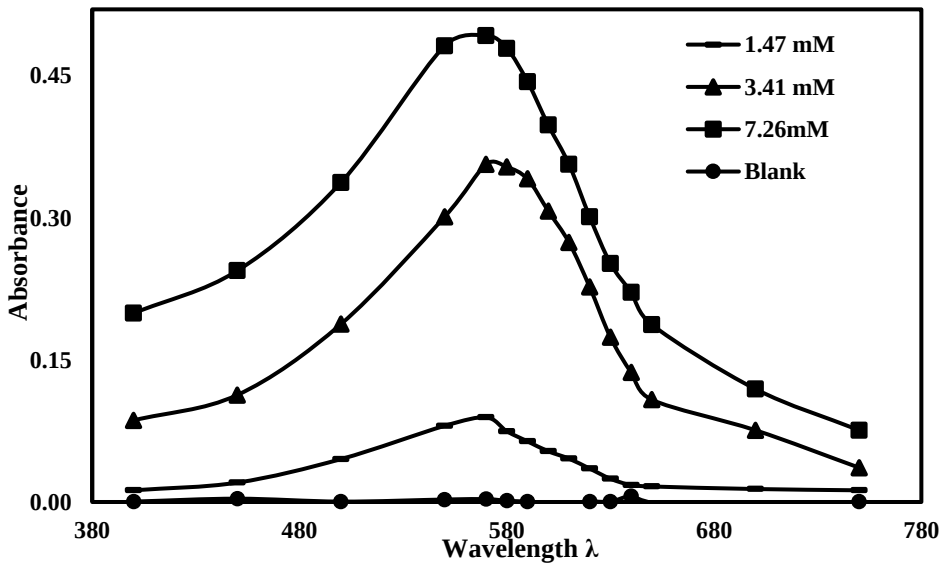


Fig 2: Absorption spectra Blank and three different concentrations of vanadium with 14.3 µM MBTH, 6.33 µM NEDA and 0.016 N Acetic acid sodium acetate of pH 3.5 in 3 ml of solution

B. Optimization of reaction conditions

The effectiveness of the proposed method for vanadium measurement has been enhanced through a comprehensive investigation into the influence of reagent concentrations and various other factors.

i. Effect of the temperature

The effect of temperature on the reaction product was investigated using a 3 ml reaction mixture consisting of 14.3 µM MBTH, 6.33 µM NEDA, 0.016 M acetic acid-sodium acetate at pH 3.5, and 6.82 mM of vanadium, within a temperature range of 10 to 60°C. The results demonstrated that the coloured product remained stable at 25°C, with reproducible results. Further temperature increases did not alter the absorbance values, while lower temperatures decreased the reaction completion time. Consequently, all analyses were conducted at room temperature, which was identified as the optimal condition. The temperature's impact on the reaction product is depicted in **Figure 3.**

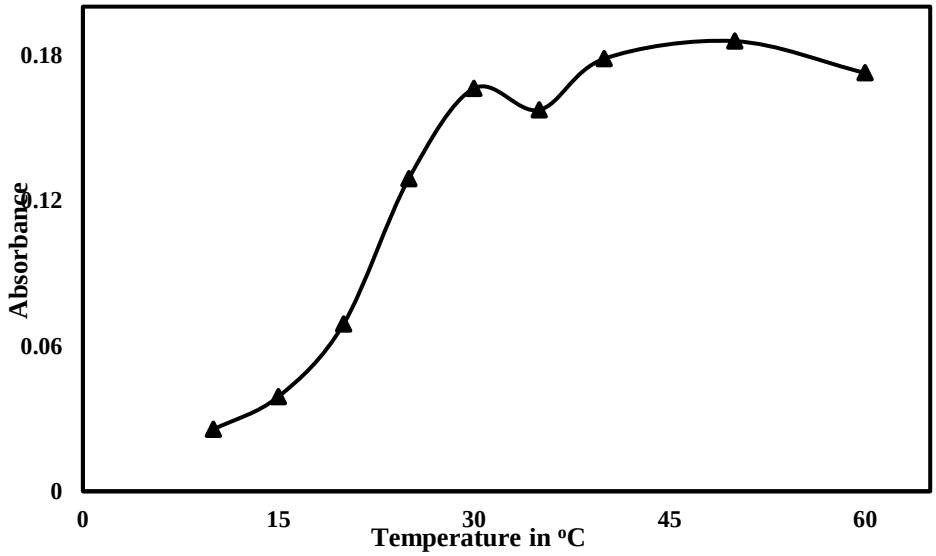


Fig 3: Effect of temperature on the reaction

ii. pH for maximum absorbance

A range of buffers, spanning from 0.1 to 100 mM, were employed in the reaction, including citric acid/potassium citrate at pH 3.6 - 5.6, acetate/acetic acid at pH 3.5 - 5.5, potassium dihydrogen phosphate/sodium hydroxide at pH 6.0 - 8.0, and potassium dihydrogen orthophosphate/dipotassium hydrogen orthophosphate at pH 6.0 - 7.8. The most significant colour development during the reaction was observed when using acetate/acetic acid at pH 3.5. Consequently, all subsequent investigations utilized 0.1 ml of a 0.5 M buffer solution with a pH of 3.5.

iii. Effect of the Sequence of Reactant Addition

The influence of the order in which reactants were added was investigated by testing various sequences while keeping the optimal quantities of reactants constant in the proposed method. The results demonstrated that the order of reactant addition did not have an impact on the absorbance values, as outlined in Table 1. Nonetheless, for the sake of consistency and uniformity, a specific order of reactant addition, listed in Table 1 under Serial No.1, was adopted for all vanadium(V) determinations.

Table 1: Effect of order of addition of the reactants

Serial No.	Order of addition[(a)]	Absorbance for 128 µM
1	A + B + C + D	0.368
2	C + A + B + D	0.369
3	B + C + A + D	0.364
4	C + B + A + D	0.375

[(a)] A = MBTH, B = NEDA, C = vanadium (V), D = Buffer

iv. Effect of time and temperature on the colour

Under optimal conditions, while the colour development process was initially slow, the reaction mixture was fine-tuned to achieve maximum and consistent absorbance. The colour development exhibited a gradual increase within the first 10 minutes, with no substantial changes observed thereafter over an extended

period. The resulting-coloured product displayed stability for up to 24 hours. Therefore, for routine analysis, it suffices to allow the reaction mixture to stand for 10 minutes at room temperature to achieve the desired results, as illustrated in **Figure 4.**

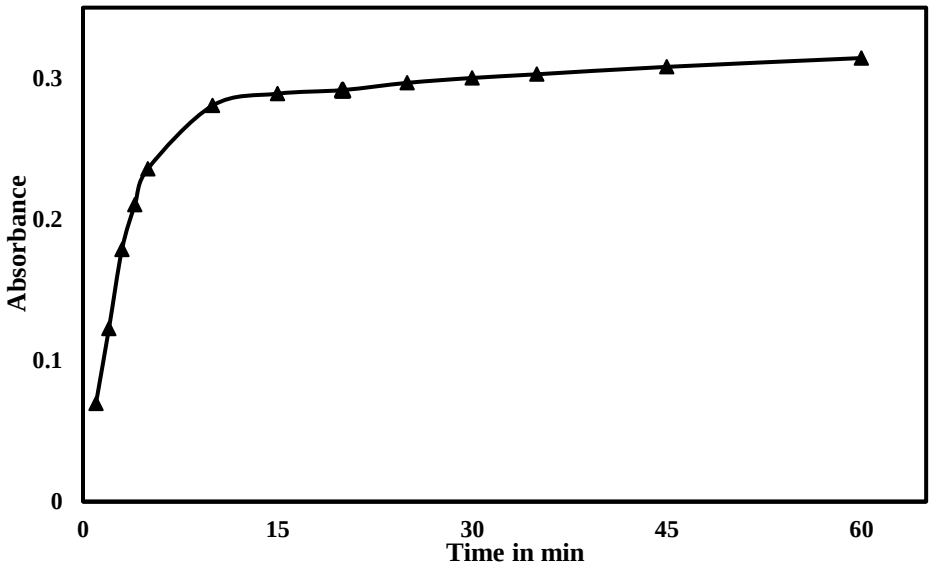


Fig 4: Effect of temperature on reaction.

v. Analytical characteristics

Under the optimized conditions, the calibration graph for vanadium determination spanning from 0.47 to 10.3 mM exhibited a coefficient of regression of 0.9956 **(Figure 2)**. Calculations yielded a molar absorptivity of 77.6 x 10^4 l mol-1 cm-1 and a Sandell's sensitivity of 0.0039 µg cm-1. Furthermore, the method's detection limit and quantification limit were determined to be 0.246 mg ml-1 and 0.737 mg ml-1, respectively. A series of ten replicate determinations for 4.9 mM of vanadium(V) resulted in a calculated relative standard deviation of 1.1%. Additionally, the analytical parameters of the oxidation coupling mixture can be found in **Table 2.** The precision and accuracy of the method were assessed by analyzing reaction mixtures containing known quantities of the reagents within the limits of Beer's law. The consistently low values for relative standard deviation and error attest to the high accuracy of the proposed method.

Table 2. Analytical parameters in the determination of Vanadium.

Parameters	**Characteristic**
Colour	Intense Blue
λ_{max} (nm)	570
Colour stability (hr)	24
Beer's law range (mM)	0.47 – 10.3
Reaction time (min)	10
Molar absorptivity (l mol^{-1} cm^{-1})	77.6 x 10^4
Sandell's sensitivity (mg cm^{-2})	0.0039
LOD, LOQ (mg ml^{-1})	0.246, 0.737
Correlation coefficient (R^2)	0.9956
Slope	0.0077
Intercept	0.0808
Relative standard deviation (%)	1.1

vi. Effect of foreign ions

The effect of different foreign ions on the determination of vanadium(V) was thoroughly examined. Solutions containing 2.94 mM of vanadium(V) alongside varying concentrations of foreign ions or potential interfering species were subjected to the proposed procedure. The tolerance limit, defined as the quantity

causing a ±3% absorbance error in the determination of 171 µM of vanadium(V), was determined. Notably, no interference was observed for a range of ions. However, certain strong oxidizing or reducing species were found to disrupt the proposed method. Specifically, Cr (VI), Ce (IV), Cu (II), and Fe(3+ & 2+) exhibited noticeable interference, with the interference caused by Fe(3+ & 2+) being successfully mitigated through the use of sulphamic acid, as indicated in Table 3.

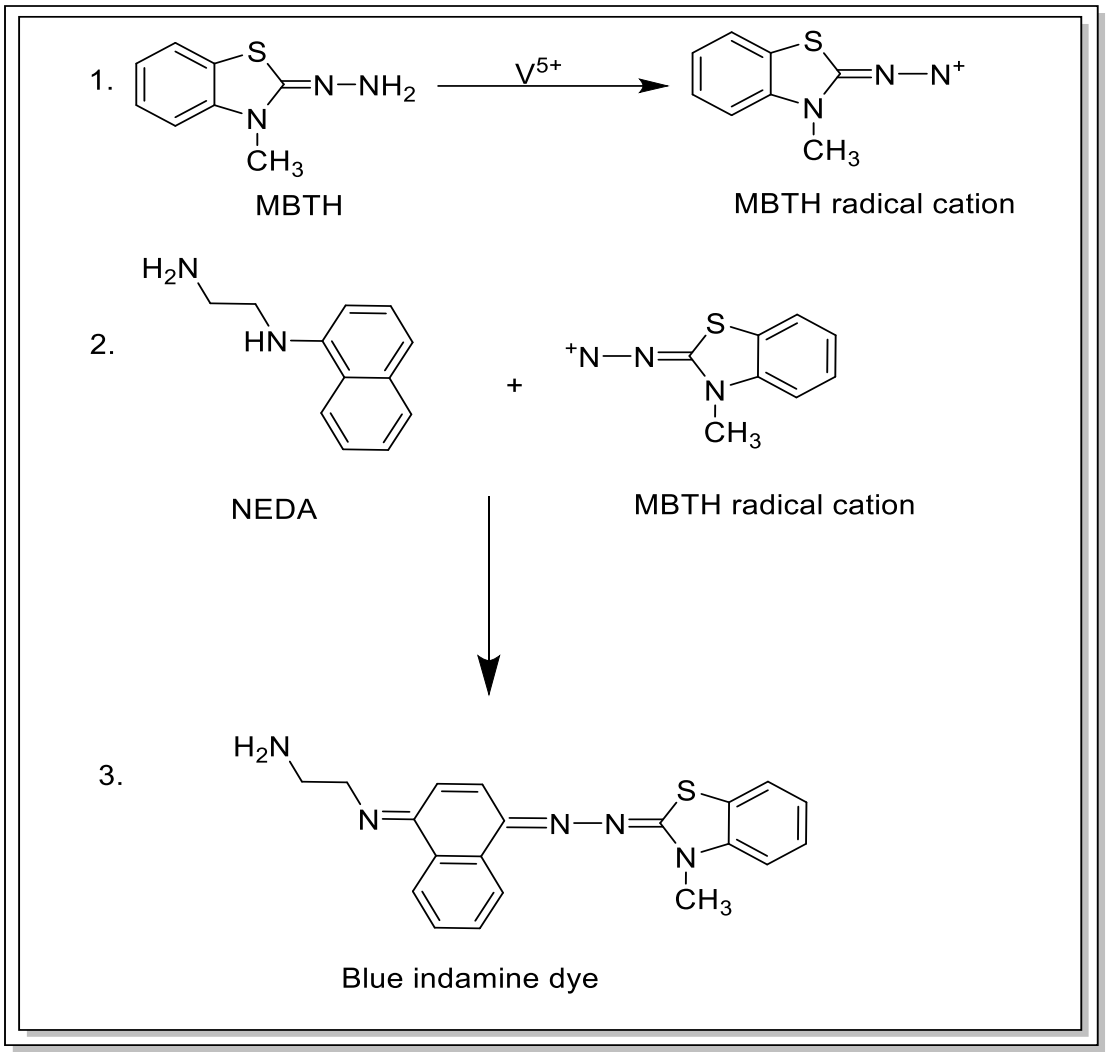
Table 3: Effect of foreign ions in the determination of vanadium (2.9mM).

Foreign ions	**Tolerance limit (µg ml^{-1})**	**Foreign ions**	**Tolerance limit (µg ml^{-1})**
Sulphamic acid	20000	Citrate, NO^{2-}	600
Cl^-, Br^-, NO_3^-	10000	Zr^{4+}, Ba^{2+}	250
Na^+, K^+	8000	Tartarate, WO_4^-	100
Zn^{2+}, SO_4^{2-}, Co^{2+},	7000	Cr^{3+}, Cu^{2+}	135
Mn^{2+}, Al^{3+}	5000	Ascorbic acid	15
Oxalate, EDTA,	2500	Ce^{4+}, Fe^{3+} [(a)]	10
HCO_3^-, CO_3^{2-}	1800	Fe^{2+}	8
Acetate	1000		

[(a)] Masking by the addition of 2 ml of 10% Sulphamic acid.

C. Reaction mechanism

The probable reaction mechanism involved is based on the intermolecular coupling of MBTH-NEDA in the presence of a strong oxidizing agent Vanadium to give an intense, blue-coloured product having maximum absorbance at λ_{max} = 570 nm. The reaction mentioned is analogous to HRP-catalyzed synthesis of polyaniline as suggested by Caramyshev et al [35]. Under the assay conditions, MBTH loses 2 electrons and one proton on oxidation with vanadium in the acidic medium of pH 3.5 forming the π-cation radical which acts as active coupling species. These intermediates react with amines like NEDA by the electrophilic attack on the most nucleophilic site on the aromatic ring of amines (i.e., ortho or para positions, if para positions to amine is substituted). The resulting intermediate is spontaneously oxidized in the presence of an oxidant to form an intense, blue-coloured product. The vanadium-catalyzed reaction of MBTH-NEDA is as shown in **Scheme 1**.



Scheme 1: Probable reaction pathway for the formation of coloured product by 2,4-DNPH and IPH

D. Within-day and between-day precision study

To assess the robustness of the method, we conducted five replicate determinations at varying concentration levels of vanadium(V). The results revealed that the within-day Coefficient of Variation (CV) values ranged from 0.0204% to 0.064%. Similarly, the between-day CV values, derived from the average of five determinations carried out over a five-day period, were in the range of 0.021% to 0.052%. These outcomes underscore the excellent reproducibility of the proposed method, both within a single day and across different days, as detailed in **Table 4.**

Table 4: Within-day and between-day precision study for the determination of vanadium(V).

Vanadium Added (mM)	Within-day		Between-day	
	Found [(a)] mM	RSD%	Found [(b)] mM	RSD%
0.98	0.99	0.064	1.00	0.052
4.90	4.78	0.0253	4.80	0.026
7.84	7.98	0.0204	8.03	0.021

[(a)] Mean value of ten determinations carried out in one day with 1 hr time interval.

[(b)] Mean value of five determinations carried out over five days.

E. Application and Recovery studies of the different samples.

Recovery studies were conducted by introducing a known quantity of standard vanadium solution into both the soil filtrate and leaf extract, followed by the calculation of recovery percentages using the formula [(final concentration – initial concentration)/added concentration]. These recovery studies demonstrated minimal interference and showcased the assay procedure's strong reproducibility, as depicted in **Table 5.** Similarly, recovery studies were carried out in water samples by spiking them with a known quantity of standard vanadium solution, and the results were interpreted using the same formula, confirming minimal interference and good reproducibility of the assay procedure. These results are presented in **Table 5.**

Table 5: Application of the proposed method for determination of vanadium(V) in various samples.

Sample number	Sample	Added µM	Found µM	Recovered µM	*Recovery %
1	Soil	0.98	0.87	0.84	85.4
2		4.9	4.34	4.31	87.9
3		7.84	8.20	8.17	104
4	Azadirachta indica	0.98	1.13	1.12	114.6
5		4.9	4.74	4.73	96.6
6		7.84	7.92	7.92	100.9
7	Pungemia	0.98	0.88	0.86	87.8
8		4.9	4.66	4.64	94.7
9		7.84	8.0	7.98	101.8
10	Tap water	0.98	1.07	1.02	103.6
11		4.9	4.83	4.78	97.6
12		7.84	7.87	7.82	99.8
13	Lake water	0.98	1.13	1.03	105.5
14		4.9	4.81	4.71	96.2
15		7.84	7.88	7.78	98.3
16	Borewell water	0.98	1.08	1.06	107.8
17		4.9	4.73	4.71	96.1
18		7.84	7.93	7.91	100.9

*= (Recovered vanadium / Added vanadium) X 100

4. Conclusion

The use of oxidative coupling methods for the spectrophotometric determination of Vanadium(V) in diverse sample matrices offers a versatile and effective approach for analytical purposes. Through the utilization of appropriate reagents and reaction conditions, this method can provide accurate and sensitive quantification of Vanadium(V) across a wide range of sample types, including environmental samples, biological specimens, and industrial materials. The method proposed, which entails the coupling of MBTH with NEDA as reagents for Vanadium(V) determination, offers a range of benefits, including simplicity, selectivity, stability, and sensitivity. Moreover, its capacity to tolerate common interfering species associated with Vanadium(V) adds to its attractiveness. Additionally, the absence of toxic organic solvents in the extraction of coloured species simplifies its applicability for routine analysis, aligning with safety and environmental considerations in analytical practices. The flexibility of oxidative coupling methods, combined with the advantages of spectrophotometric analysis, makes it a valuable tool for researchers and analysts seeking to assess the presence and concentration of Vanadium(V) in various applications. However, it is essential to carefully optimize the method for specific sample matrices and ensure the reliability of the results through proper calibration and validation procedures. Overall, the continued exploration and refinement of oxidative coupling techniques hold promise for advancing our understanding and monitoring of Vanadium(V) in diverse fields of study.

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