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Spectrophotometric determination of V(V) in environmental, biological, pharmaceutical and alloy samples by novel oxidative coupling reactions

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Abstract

A Novel, rapid, sensitive and selective reactions are developed for spectr[illegible]hotometric de[illegible]rmination of trace amounts of vanadium (V) in environmental, biological, pharmaceutical and alloy samples was studied. The[illegible]ethods were [illegible]sed on interactions of 4-bromophenyl hydrazine (4-BPH) with *N*-(1-naphthyl ethylenediamine dihydrochloride (NEDA) in the pr[illegible]ce of [illegible]adium in acidic medium (acetate buffer of pH 3.0) to give violet colored derivative or on the oxidation of 4-bromoph[illegible]yl[illegible]azine by vanadium in basic medium and coupling with chromotropic acid (CA) to yield red color derivative. The violet color derivative [illegible]ving ap[illegible]bance maximum at 570 nm which is stable for 7 days and the red derivative with λ_{max} 495 nm for 5 days. Beer's law was obeyed fo[illegible]an[illegible]ium in the concentration range of 0.5–6.0 μg ml^{-1} (violet derivative) and 0.6–7.0 μg ml^{-1} (red derivative), respectively. The[illegible]m reacti[illegible] conditions and other important analytical parameters were established to enhance the sensitivity of the proposed methods. [illegible]terferen[illegible] due to v[illegible]ious non-target ions was also investigated. The proposed methods were applied to the analysis of vanadium (V) in envi[illegible]mental, b[illegible]ogical, ph[illegible]maceutical and steel samples. The performance of proposed methods were evaluated in terms of Student's *t*-test an[illegible] Var[illegible]e r[illegible] *F*-test[illegible]ndicates the significance of proposed methods over reported method.

Keywords: Vanadium (V); 4-Bromophenyl[illegible]ydr[illegible]e (4-BPH); *N*-([illegible]aphthyl ethylenediamine dihydrochloride (NEDA); Chromotropic acid (CA); Spectrophotometry; Environmental; Biological; Pharma[illegible]utical an[illegible]teel samples

1. Introduction

Vanadium [illegible] compo[illegible]nds us[illegible] extensively in the steel and petroch[illegible]ical in[illegible]ustries. [illegible]dium species are most stable and [illegible]re toxic [illegible] an environment. Vanadium affects the numerous p[illegible]ic[illegible]gical pro[illegible]sses and biochemical reactions in living systems. [illegible]anadium remains a relatively unknown trace element, as its us[illegible] are still being targeted in various clinical applications worldwide. However, vanadium deficiency consistently impairs biological function is lacking. Vanadium content in food is directly dependant upon the concentrations present in the soil. Once consumed, vanadium is stored primarily in fatty tissues, and the remaining amounts stored in the kidney, liver, spleen, or bone. Vanadium is a trace element of highly critical role in biochemical processes and of significant importance in environmental, biological and industrial analysis due to its toxicity. Vanadium in trace amounts is an essential element for cell growth at μg l^{-1} levels, also has been shown to inhibit cholesterol synthesis and to increase the oxidation of fatty acids of higher concentrations. It is excreted through urine. The amount of vanadium in blood and urine depends upon intensity and duration of its exposure. Vanadium also regarded as beneficial element that helps in the carbohydrates metabolism, prevention of some heart diseases, and also essential for certain animals, plants and microorganism.

Vanadium acts as a growth-promoting factor and participates in fixation and accumulation of nitrogen in plants, whereas high concentration of vanadium reduces the productivity of the plants

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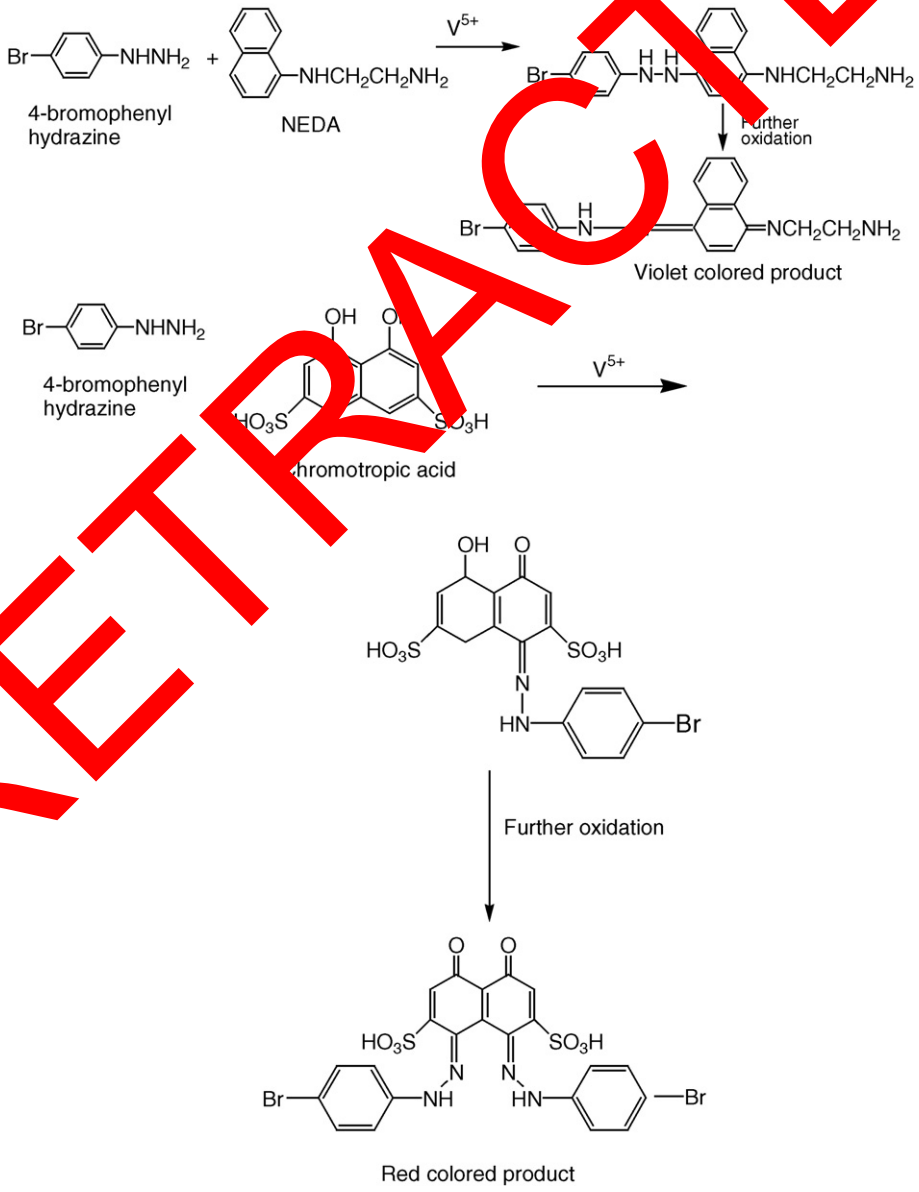
[1]. Therefore, the determination of vanadium in environmental and biological samples is highly desirable. In survey of literature reveals that several analytical techniques have been reported for the determination of vanadium such as high performance liquid chromatography [2,3], voltammetry [4], atomic absorption spectrometry [5,6], spectrofluorimetry [7], atomic emission spectrometry [8] and ion chromatography inductively coupled plasma-optical emission spectrometry [9]. These techniques have also some limitations in terms of high cost of instruments used in routine analysis and matrix effects. These techniques suffer from several disadvantages such as few techniques are expensive (AAS, ICP-AES and IC-ICP-OES), few other have poor sensitivity and few others are require specific electrodes for the determination of vanadium.

In scrutiny of literature reveals that several spectrophotometric methods have been reported for the determination of vanadium in environmental and biological samples. Recently, few authors introduced various reagents for spectrophotometric determination of vanadium in various samples such as 2-(2-quinolylazo)-5-diethylaminophenol [10], varamine blue [11], eriochrome cryamine R [12], 2-benzylacetate [13], pyrogallol [14], 2-hydroxyacetophenone oxime [15], 4-(2-pyridylazo) resorcinol [16], tannic acid [17], 2-(5-chloro-2-pyridylazo)-5-dimethylaminophenol [18] *N,N′*-bis(2-hydroxyl-3-sulfopropyl)-tolidine [19] and 2-(8-quinolylazo)-5-dimethylaminophenol [3]. The above reported reagents were suffers from poor selectivity, interference of large number of metal ions, require specific protonic solvent for the extraction of color species and few other are require activator for catalytic photometric determination of vanadium. These deficiencies have encouraged the authors to develop novel oxidative coupling reactions for facile, sensitive, accurate and reliable methods for the determination of trace amounts of vanadium in environmental and biological samples. The determination of vanadium (V) has



Scheme 1. Oxidative copuling reations of 4-BPH–NEDA and 4-BPH–CA with vanadium.

not been reported yet by oxidative coupling reaction in the literature till now.

In this paper, the developed novel reactions for rapid, facile, sensitive, and selective spectrophotometric methods for the determination of traces of vanadium (V). It implied that the reactions are oxidative coupling in the presence of V^{5+} of 4-bromophenyl hydrazine(4-BPH) with *N*-(1-naphthyl)ethylenediamine dihydrochloride (NEDA) and 4-bromophenyl hydrazine(4-BPH) with chromotropic acid (CA), yielded the highly stable violet and red color derivatives and it was shown in Scheme 1. Based on this, the highly sensitive, selective and rapid methods were applied for the determination of vanadium (V) in environmental, biological, pharmaceutical and steel samples.

2. Experimental

2.1. Instrumentation

A HITACHI U 2001 spectrophotometer with 1 cm matched quartz cells were used for all absorbance measurements. A pH meter, Elico Li-129 Model glass-calomel combined electrode was employed for measuring pH values.

2.2. Chemicals and reagents

All chemicals and solvents used were of analytical reagent grade, and doubly-distilled water was used to prepare all solutions in the experiments. Standard stock solution containing 100 mg l^{-1} of vanadium (V) was prepared by dissolving 0.2393 g of ammonium vanadate (Merck chemicals, Mumbai, India) in 1000 ml volumetric flask and diluted up to mark with 0.01 M hydrochloric acid. Working solutions were prepared by appropriate dilution of the standard solution.

An aqueous solution of 1.5% (w/v) 4-BPH/NEDA reagent solution was prepared by dissolving 1 g of NEDA (from Sigma, USA), 0.5 g of 4-BPH (SD fine Chemicals, India), and a few drops of concentrated HCl, diluted up to the mark with doubly-distilled water and the solutions were refrigerated. 0.5% (w/v) 4-BPH/CA reagent solution was prepared by dissolving 0.5 g of 4-bromophenyl hydrazine (first dissolved in 5 ml of concentrated HCl) and 0.5 g of CA (both from S. Fine Chemicals, India) in 100 ml of doubly-distilled water. Finally, sodium hydroxide and sulfuric acid (both from S. Fine Chemicals, India) were used for the experiments. Acetate buffer solution was prepared by dissolving 13.6 g of sodium acetate trihydrate in 80 ml of water and adjusting the pH to 3 with hydrochloric acid, and the mixture was diluted to 100 ml with doubly-distilled water.

2.3. General procedure

2.3.1. 4-BPH–NEDA method

Stock solutions containing (0.5–6.0 μg ml^{-1}) of vanadium (V) (the volume of the test solution was restricted to 1 ml) were transferred into 25 ml calibrated flasks; 3 ml of 1.5% 4-BPH–NEDA reagent solution and 3 ml of acetate buffer were added to each flask, the violet color is formed instantaneously and diluted up to the mark. After dilution of 25 ml with doubly-distilled water, the absorbance at 570 nm was measured against the corresponding reagent blank and the calibration graph was constructed.

2.3.2. 4-BPH–CA method

An aliquot of sample solutions containing (0.6–7.0 μg ml^{-1}) of vanadium (V) were transferred to 25 ml standard flask; to each flask, 4 ml of 2 M NaOH and 4 ml of 0.5% 4-BPH–CA were added. Each mixture was allowed to stand for 2 min with occasional shaking to complete the reaction. After dilution to 25 ml with water, the absorbance at 495 nm was measured against the corresponding reagent blank and the calibration graph was constructed and shown in Fig. 1.

2.3.3. Procedure for determination of vanadium in soil sample

An air-dried homogenized soil sample (1 g) was weighed accurately and transferred in a 100 ml Kjeldahl flask. The sample was digested in presence of an oxidizing agent following the method recommended by [15]. The content of flask was filtered through a Whatman No. 42 filter paper, into a 25 ml calibrated flask and neutralized with dilute ammonia in the presence of 1–2 ml of 0.01% (w/v) tartrate solution. It was then diluted to the mark with doubly distilled water. Appropriate aliquots of 2 ml of the solution was transferred into a 25 ml calibrated flask and analyzed for vanadium content according to the general procedure after adding 1–2 ml of 0.01% (w/v) thiocyanate or fluoride solution as masking agent and shown in Table 2.

2.3.4. Procedure for determination of vanadium in water sample

Each filtered water sample (100 ml) was analyzed for vanadium and gave negative results. To these samples known amounts of vanadium (V) were added and analyzed by the afore said procedure for vanadium.

2.3.5. Procedure for determination of vanadium in urine sample

Fifty milliliters of the urine sample was concentrated to 5 ml, by evaporation, spiked a known amount of vanadium was mixed with 5 ml of concentrated HNO_3 and 5 g of potassium sulfate,

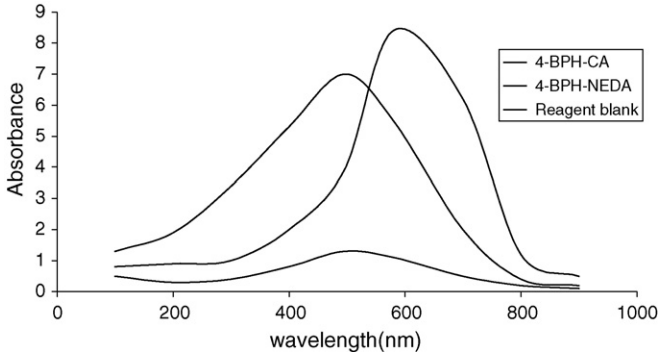


Fig. 1. Absorption spectra of oxidative coupling reaction of 4-BPH–CA and 4-BPH–NEDA system with vanadium.

and heated to dryness. The process was repeated 2–3 times. Then HNO_3 (1:3, 25 ml) was added to residue and digested on a water bath for 30 min. The contents were again evaporated to dryness, cooled, and the residue was dissolved in 20 ml water, filtered, and neutralized with 2–3 ml of 2% ammonia. The mixture was diluted to a known volume with doubly-distilled water. Appropriate aliquots of this solution were taken for the determination of vanadium by procedure discussed above.

2.3.6. Procedure for determination of vanadium in biological samples

The samples of plants and animal tissues were washed with distilled water to get them free from adhering soil or blood and were carefully wiped with filter paper before taking their wet weight. The samples were then dried, ashed and converted into solution by acid treatment as per standard procedures [20] and neutralized with dilute NH_4OH and then diluted to a known volume with water. An appropriate aliquot of this solution was finally analyzed according to the general procedure for vanadium. Since the vanadium content in samples used was negligible, synthetic samples were prepared by the addition of known amounts of vanadium to each sample prior to digestion.

2.3.7. Procedure for determination of vanadium in pharmaceutical samples

A volume of 15 ml of elixir sample was treated with 10 ml of concentrated HNO_3; the mixture was then evaporated to dryness. The residue was leached with 5 ml of 0.5 M H_2SO_4. The solution was diluted to a known volume with doubly-distilled water, and after neutralizing with 1–2 ml of 2% ammonia. An aliquot of the made up solution was analyzed for vanadium according to the general procedure for vanadium determination.

2.3.8. Procedure for determination of vanadium in alloy samples

A 0.1 g amount of an alloy steel (Cr, W) sample containing 0.13% of vanadium was weighed accurately and placed in a 50 ml beaker. To it, was added 10 ml of 20% (v/v) sulfuric acid and carefully covered with a watch glass until the brisk reaction subsided. The solution was heated and simmered gently after addition of 5 ml of concentrated HNO_3 until all carbides were decomposed. Then, 2 ml of a 1:1 (w/v) H_2SO_4 solution was added and the mixture was evaporated carefully on water bath until the dense white fumes dried off the oxides of nitrogen, and the cooled to room temperature. After appropriate dilution with doubly-distilled water, the contents of the beaker were warmed to dissolve the soluble salts. The solution was then cooled and neutralized with a dilute NH_4OH solution in the presence of 1–2 ml of 0.01% (w/v) tartrate. The resulting solution was filtered, if necessary, through a Whatman No. 40 filter paper into a calibrated flask of known volume. The residue (silica) was washed with a small volume of hot 1% H_2SO_4 followed by doubly-distilled water and the volume was made up to the mark with water.

A suitable aliquot of the above solution was taken into a 25 ml calibrated flask and the vanadium content was determined by the general procedure using 1–2 ml of saturated thiocyanate or fluoride solution as masking agent. Iron (III) can be effectively removed from the solution by precipitating with saturated fluoride solution. The precipitates were filtered off before the addition of 4-BPH–NEDA and 4-BPH–CA. Higher concentrations of iron (III) were removed by adding 5–10 ml of saturated ammonium thiocyanate solution to the test solution, and the resulting Fe(III) and Fe(II) complexes with thiocyanate were extracted into methyl isobutyl ketone (MIBK) in an aqueous acidic medium prior to the determination of vanadium.

3. Result and discussion

3.1. Absorption spectra of color derivatives

The proposed methods involved the formation violet color derivative with λ_{max} of 550 nm or red color derivative with λ_{max} 495 nm and the measurement of the absorption spectra was shown in Fig. The reagent blanks had negligible absorption at these wavelengths.

Under the optimized conditions, although the color developed instantaneously, 1 min was allowed to obtain the maximum and constant absorbance in both colored derivatives. The violet color derivative was stable for 7 days and the red color derivative for 5 days. The absorbance varied by ±2% within 2 days for both violet and red color derivatives. The color development was independent of temperature in the range of 20–35 °C.

3.2. Effect of reagent and acid concentration

The effect of 4-BPH–NEDA mixture was studied in the range of 1–8 ml of a 1.5% (w/v) solution of 4-BPH–NEDA in doubly-distilled water. To achieve the maximum color intensity, a volume of 2–4 ml of this solution was necessary. Hence, 3 ml of 1.5% 4-BPH–NEDA in water were selected for further studies, under optimized conditions. The maximum intensity of the violet color was achieved in acidic medium (acetate buffer of pH 3).

The maximum intensity of the red color was achieved in the range of 2–6 ml of 2 M NaOH for 4-BPH–CA reagent mixture. Therefore, 4 ml of 2 M NaOH was used for best results. A range of 3–5 ml of 0.5% (w/v) solution of 4-BPH–CA in doubly-distilled water was necessary to achieve the maximum color intensity. Hence, 2 ml of 0.5% 4-BPH and 2 ml of 0.5% CA were employed for the experiments under optimized conditions.

3.3. Analytical data

Linear calibration graphs were obtained for 0.5–6.0 $\mu g\,ml^{-1}$ for 4-BPH–NEDA and 0.6–7.0 $\mu g\,ml^{-1}$ for 4-BPH–CA of vanadium in a final volume of 25 ml. The detection limit and limit of quantification of vanadium determination were found to be 0.359 and 2.897 $\mu g\,ml^{-1}$ for 4-BPH–NEDA and 0.793 and 3.363 $\mu g\,ml^{-1}$ for 4-BPH–CA, respectively. The calibration graph has correlation coefficient of 0.9989 for 4-BPH–NEDA and 0.9996 for 4-BPH–CA methods. Beer's law range, molar

Table 1
Optical characteristics, precision and accuracy of the spectrophotometric determination of vanadium (V) with 4-BPH–NEDA and 4-BPH–CA methods

Optical characteristics	4-BPH–NEDA method	4-BPH–CA method
Concentration range (μg ml^{-1})	0.5–6.0	0.6–7.0
Color	Violet	Red
λ_{max} (nm)	570	495
Stability (h)	7 days	5 days
Molar absorptivity (l mol^{-1} cm^{-1})	2.126×10^4	1.921×10^4
Sandell's sensitivity (μg cm^{-2})	0.00683	0.00525
Limit of detection (μg ml^{-1})	0.359	0.793
Limit of quantification (μg ml^{-1})	2.897	3.363
Regression[a] slope a	0.1625	0.1912
Intercept b	0.0526	0.0153
Correlation coefficient r	0.9989	0.9996
Relative standard deviation (%)[b]	0.676	0.579
Range of error (95% confidence level)	±0.732	±0.625

[a] Regression curve: $y = ax + b$, where x is the concentration of vanadium (μg ml^{-1}) and y is absorbance.
[b] Determination for $n = 5$.

absorptivity, Sandell's sensitivity, and other parameters of the oxidative-coupling mixtures are given in Table 1. The precision and accuracy of the method was studied by analyzing the coupling solution containing known amounts of the cited reagents within Beer's law limit. The low values of the relative standard deviation in (%) and the percentages of error indicated the high accuracy of the two methods.

3.4. Reaction mechanism

Under the reaction condition, 4-BPH loses probably 2e$^-$ and a proton on oxidation with V^{5+} in acidic medium (acetate buffer of pH 3) to form an electrophilic intermediate (active coupling species), which couples with NEDA to give a violet derivative and the reaction mechanism was shown in Scheme 1.

Similarly, 4-BPH loses probably 4e$^-$ and proton on oxidation with V^{5+} in basic medium to form an electrophilic intermediate (active coupling species), which couples with chromotropic acid (CA) giving a red color product and the reaction mechanism was shown in Scheme 1.

3.5. Effect of non-target species

The effect of various species on the determination of vanadium was investigated. The tolerance limit was taken as the amount that caused ±2% absorbance error in determination of 2.5 μg ml^{-1} (4-BPH–NEDA method) and 3.0 μg ml^{-1} (4-BPH–CA method) of V(V) and the results were shown in Table 2.

The developed methods are based on the oxidation of 4-BPH–NEDA and 4-BPH–CA with vanadium. Therefore, strong oxidizing or reducing species are expected to interfere by oxidation of 4-BPH–NEDA and 4-BPH–CA. Chromium (VI), iron (III), cerium (IV) and tungsten (VI) at a 10 μg level caused low recovery of vanadium. Iron (III), copper (II), iodate, molybdenum (VI), and thiosulfate up to 350 μg level caused positive interferences. Masking agents like citrate, tartrate, EDTA and sodium fluoride are not interfering in the recovery of vanadium.

Therefore, these masking agents were used to obviate interferences such as iron (III), cerium (IV) and tungsten (VI) up to a 100 μg level in the determination of vanadium. Small concentrations of As(III) at temperature ≥45 °C can effectively reduce chromium (VI) and quantitatively eliminate its effects on the coloring reagents. Therefore, As(III) ion was adopted as an effective reducing agent for Cr(VI) in the presence of vanadium (V) [3]. If any precipitate was formed during the interference studies, it was removed by centrifugation.

3.6. Application and statistical comparison of proposed methods with reported methods

The proposed methods were applied for the determination of vanadium (V) in environmental and biological, pharmaceutical and alloy samples as shown in Table 3. The results were compared with the reported methods [9,16] and results were summarized in Table 3. The performances of the proposed

Table 2
Effect of non-target species in the determination of vanadium (V) 2.5 μg ml^{-1} for 4-BPH–NEDA and 3.0 μg ml^{-1} for 4-BPH–CA methods

Non-target species	Tolerance limit (μg ml^{-1})	Effect
4-BPH–NEDA method		
Na^+, Mg^{2+}, Cl^-, ClO_3^-, F^-, CH_3COO^-, CO_3^{2-}, K^+, Hg^{2+}, Ca^{2+}, BO_3^-, NO_3^-, SO_4^{2-}, PO_4^{3-}, citrate, oxalate, tartarate	3600	No interference
$P_2O_7^{4-}$, SeO_3^{2-}, SbO_7^{2-}	2500	No interference
Al^{3+}, Cd^{2+}, Ba^{2+}, Ni^{2+}, Co^{2+}, Te^{4+}, Zn^{2+}	600	No interference
Cu^{2+}, Ce^{4+}, Fe^{3+}, Cr^{3+}, Sn^{2+}, Pb^{2+}, W^{6+}, Mo^{6+}	65[a]	Positive interfere
4-BPH–CA method		
K^+, Hg^{2+}, Ca^{2+}, BO_3^-, NO_3^-, SO_4^{2-}, PO_4^{3-}, Na^+, Mg^{2+}, tartarate, citrate, oxalate, tartarate, oxalate, Mn^{2+}, NO^{2-}	3800	No interference
Ba^{2+}, SO_4^{2-}, CN^-, SCN^-, SeO_3^{2-}, SbO_7^{2-}	1500	No interference
$P_2O_7^{4-}$, SeO_3^{2-}, SbO_7^{2-}, SO_3^{2-}	800	No interference
Al^{3+}, Cd^{2+}, Ba^{2+}, Ni^{2+}, Co^{2+}, As^{5+}, Te^{4+}, Zn^{2+}	300	No interference
Cu^{2+}, Ce^{4+}, Fe^{3+}, Cr^{3+}, Sn^{2+}, Pb^{2+}, W^{6+}, Mo^{6+}	85[b]	Positive interfere

[a] Can be masked up to 65 μg ml^{-1} by the addition of 2 ml of 2% EDTA.
[b] Can be masked up to 85 μg ml^{-1} by the addition of 5 ml of 2% EDTA.

Table 3
Determination of vanadium (V) in various environmental, biological, pharmaceutical and alloy samples

Sample	Vanadium added (ppm)	Proposed methods								Reference method [9]	ICP-OES [16]
		4-BPH–NEDA method				4-BPH–CA method					
		Found[a]	Recovery	*t*- and *F*-tests[b]	*t*- and *F*-tests[b]	Found[a]	Recovery	*t*- and *F*-tests[b]	*t*- and *F*-tests[b]		
Soil[c]	5.0	4.96 ± 0.05	99.20	*t* = 0.56 *F* = 1.38	*t* = 0.72 *F* = 1.32	4.97 ± 0.06	99.40	*t* = 0.65 *F* = 1.04	*t* = 0.68 *F* = 1.09	4.98 ± 0.04	4.99 ± 0.02
	10.0	9.97 ± 0.05	99.70	*t* = 0.67 *F* = 1.06	*t* = 0.31 *F* = 1.21	9.9[illegible]	99.80	*t* = *F* = 0.	*t* = 0.83 *F* = 1.51	9.99 ± 0.03	9.99 ± 0.01
Natural water[c]	6.0	5.98 ± 0.03	99.66	*t* = 0.95 *F* = 1.22	*t* = 0.55 *F* = 0.59	.96 ± 0.03	99.33	*t* = 0.63 *F* = 1.14	*t* = 0.52 *F* = 1.24	5.97 ± 0.05	5.99 ± 0.02
	10.0	9.97 ± 0.03	99.70	*t* = 0.73 *F* = 1.02	*t* = 0.45 *F* = 1.05	[illegible]96 ± 0.05	99.80	*t* = 0.51 *F* = 1.09	*t* = 0.71 *F* = 1.24	9.99 ± 0.03	10.0 ± 0.01
Urine[c]	7.0	6.989 ± 0.03	99.85	*t* = 0.28 *F* = 1.24		6.98[illegible]0		*t* = 0.72 *F* = 1.32	–	6.97 ± 0.06	–
	10.0	9.99 ± 0.02	99.90	*t* = 0.95 *F* = 1.22		[illegible] 0.03	99.80	*t* = 0.51 *F* = 1.12	–	9.97 ± 0.04	–
Plant material[c] (raddish)	12.0	11.97 ± 0.03	99.75	[illegible].63 *F* = [illegible]	–	11.98 ± 0.02	99.83	*t* = 0.31 *F* = 1.09	–	11.95 ± 0.03	–
Human hair	–	1.97 ± 0.05	98[illegible]	*t* = 0 *F* = [illegible]3	–	1.94 ± 0.06	94.00	*t* = 0.51 *F* = 1.09	–	1.81 ± 0.04	–
Pig liver[c]	9.0	8.97 ± 0.03	99[illegible]	[illegible]0.91 *F* = 1.54		8.96 ± 0.04	99.55	*t* = 0.52 *F* = 1.06	–	8.96 ± 0.02	–
Pharmaceutical preparation[d]	–	7.95[illegible].02	99.90	[illegible]=0.65 [illegible]1.07	–	7.90 ± 0.04	99.95	*t* = 0.21 *F* = 1.01	–	7.86 ± 0.06	–
	5.0	[illegible].95 ± 0.0[illegible]	99.90	*t* = [illegible].39 *F* = 0.81	–	12.90 ± 0.05	99.80	*t* = 0.32 *F* = 1.31	–	12.85 ± 0.04	–
Steel[e]	–	3.91 ± 0.02	9[illegible]	*t* = 0.45 *F* = 1.21	–	3.97 ± 0.03	99.25	*t* = 0.41 *F* = 1.32	–	3.87 ± 0.05	–

[a] Mean ± standard deviation (*n*[illegible]
[b] Tabulated *t*-value for 8 degrees[illegible]eedom a[illegible].95) is 2.65 and tabulated *F*-value for (4,4) degrees of freedom at *P*(0.95) is 5.72.
[c] Gave no test for vanadium.
[d] Neogadine Elixir®, R[illegible]s Brett &[illegible]d., India (each[illegible]l contains Iodised peptone 29 mg, magnesium chloride 20 mg, magnesium sulfate 4 mg, sodium metavanadate 0.66 mg, zinc sulfate 6 mg, pyridomine HCl 0.75 mg, cyanoc[illegible]µg, nicoti[illegible]de 10 m[illegible]ohol (95%) 0.95 ml, Total alcohol 6% (v/v)), vanadium taken 7.89 ppm.
[e] GKW Steel Lt[illegible]ndia (C, 0[illegible]%; Mn, 0.8[illegible]%; P, 0.034%; Si, 0.33%; Cr, 1.02%; V, 0.13%), vanadium taken 3.9 ppm.

Table 4
Comparison of proposed methods with reported methods for the determination of vanadium (V) in various environmental matrices

Reagent	Range of determination	Remarks	Reference
Varamine blue	0.1–2.0	Less sensitive and less stable	[11]
Eriochrom cyanine R	0.01–5.0	Require solvents for the extraction, large number of metal ions are interfere	[12]
2-Benzoylacetate	0.05–4.0	Poor selectivity and interfering large number of metal ions	[13]
Pyrogallol	0.01–0.6	Less sensitivity	[14]
2-Hydroxyacetophenone oxime	0.05–4.0	Less sensitive and less detection limit	[15]
2-(5-Chloro-2-pyridylazo)-5-dimethylaminophenol	0.02–5.0	30 min is needed for color development and require solvent extraction of color derivatives	[16]
N,N′-bis(-2-Hydroxyl-3-sulfopropyl)-tolidine	0.01–3.0	Require tiron activator	[19]
4-BPH–NEDA	0.5–6.0	Facile, sensitive, rapid, non-extractive, stable color derivatives and less interference	Present work
4-BPH–CA	0.6–7.0		

methods were compared statistically in terms of Students *t*-test and the Variance ratio *F*-test. At 95% confidence level, the calculated *t*-values and *F*-values do not exceed the theoretical values for the two methods. The theoretical *t*-value was 2.65 ($n = 5$) and *F*-values was 5.72 ($n = 5$). It is found that from Table 3, that there is no significant difference between the proposed methods and reported methods [9,16] indicating that the proposed methods are as accurate and precise as the reported methods.

It is evident from the above data that the proposed methods are simple, highly sensitive and rapid than the reported methods in literature as shown in Table 4.

4. Conclusion

The rapidity of color development with 4-BPH–NEDA and 4-BPH–CA by V(V) is an advantage in analyzing various samples, in which vanadium can vary over a wide range. The coupling reagents employed in the present methods, i.e., 4-BPH–NEDA and 4-BPH–CA are sensitive, economical and rapid spectrophotometric reagents for the determination of vanadium (V). In these methods, non-target species do not interfere with the determination when masked with EDTA, citrate, tartarate and sodium fluoride. The detection limit 0.059 μg ml^{-1} for 4-BPH–NEDA and 0.793 μg ml^{-1} for 4-BPH–CA in original samples and μg l^{-1} level vanadium in water and biological samples can be determined with good results. When compared to other existing methods [9,16], the developed method retains the specific interaction of vanadium (V) with 4-BPH–NEDA and 4-BPH–CA to form colored derivatives and a good sensitivity is achieved at room temperature without the need for extraction. It indicates that the present methods are non-toxic and safer than those methods using other organic solvents. The proposed oxidative coupling methods have significant advantages over other existing methods [9,16] in terms of its simplicity and free from most interfering substances. Statistical analysis of the results reveals that the proposed methods yield accurate and reproducible values in the determination of vanadium (V) in various environmental matrices.

Hence, the proposed methods were successfully applied for the determination of vanadium (V) in environmental, biological, pharmaceutical and alloy samples.

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