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Study on solid phase extraction and spectrophotometric determination of vanadium with 2,3-dichloro-6-(2,7-dihydroxy-1-naphthylazo)quinoxaline

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ABSTRACT

A sensitive, selective and rapid method has been developed for the determination micrograms per liter level of vanadium ion based on the rapid reaction of vanadium(V) with 2,3-dichloro-6-(2,7-dihydroxy-1-naphthylazo)quinoxaline (DCDHNAQ) and the solid phase extraction of the colored complex with C18 cartridge. The DCDHNAQ reacts with V(V) in the presence of citric acid–sodium hydroxide buffer solution (pH 3.3) and benzyldimethyl tetradecylammonium chloride (zephiramine) medium to form a violet complex of a molar ratio 1:2 [V(V) to DCDHNAQ]. This complex was enriched by solid phase extraction with C18 cartridge and the enrichment factor of 100 was obtained by elution of the complex from the cartridge with acetonitrile. The molar absorptivity and Sandell sensitivity of the complex are 2.45×10^5 L mol^{-1} cm^{-1} and 0.0208 ng cm^{-2} at 573 nm in the measured solution. Beer's law is obeyed in the range of 0.01–0.45 μg mL^{-1}, whereas Ringbom optimum concentration ranges found to be 0.025–0.425 μg mL^{-1}. The detection and quantification limits are 3.2 and 9.9 μg L^{-1}, respectively in the original samples. This method was applied to the determination of vanadium(V) in steel, soil, water and biological samples with good results.

1. Introduction

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. The toxicity of vanadium is dependent on its oxidation state, with vanadium(V) being more toxic than vanadium(IV) [1]. Vanadium in trace amounts is an essential element for cell growth at micrograms per liter 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. The Threshold Limit Values (TLV) reported are 0.5 mg cm^{-3} of air and 0.1 mg cm^{-3} of fume [2]. The amount of vanadium in excess of the TLV value is reported to cause anemia, cough, emaciation, irritation of mucous membrane, gastrointestinal disturbances and bronchopneumonia [3]. Industrial applications of vanadium include dyeing, ceramics, ink and catalyst manufacture. Discharge from such sources can contribute to its presence in a water supply [4]. A substantial amount of vanadium is released burning crude petroleum, coal and lignite and it would then settle on the soil. Some plants accumulate vanadium up to 80 μg mL^{-1} by dry weight [5], and most of it will accumulate in leaves and roots [6]. Vanadium acts as a growth-promoting factor and participates in fixation and accumulation of nitrogen in plants [7], whereas high concentration of vanadium reduces the productivity of the plants. Therefore, the determination of vanadium in environmental, and biological samples is highly desirable. Commonly ETAAS [8,9] or ICP-MS [10,11] have been applied for vanadium analysis. However, in many cases, when the level of vanadium in natural samples is very low, an enrichment step is necessary to improve the precision and accuracy. Particularly the solid phase extraction (SPE) system has some advantages over the other techniques, yielding a higher enrichment factor, greater efficiency and handling simplicity [12,13].

Spectrophotometry is widely employed for conventional laboratory analysis because of its low cost, speed and easy automation. Therefore, a wide variety of spectrophotometric methods for the determination of vanadium have been reported [14–40]. Each chromogenic system has its advantages and disadvantages with respect to sensitivity, selectivity and rapidity. Some 2-quinolylazo reagents were reported for the determination of metal ions [41–51]. This type of reagent has higher sensitivity than pyridylazo reagents because of its larger conjugated system. In our previous work, Solid phase spectrophotometric determination of trace amounts of vanadium using 2,3-dichloro-6-(3-carboxy-2-hydroxynaphthylazo)quinoxaline was studied [46]. However, the utilization of 2,3-dichloro-6-(2,7-dihydroxy-1-naphthylazo) quinoxaline reagent for the determination of vanadium has not been reported yet.

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In this paper, we firstly studied the color reaction of DCDHNAQ with vanadium(V) and the solid phase extraction of the colored complex with C18 cartridge. Based on this idea, a highly sensitive, selective and rapid method for the determination of vanadium in steel, soil, water and biological samples was developed.

2. Experimental

2.1. Apparatus

A PerkinElmer Lambda 12 UV–visible spectrophotometer with a 10 mm quartz cell was used for all spectral measurements. An Orion research model 601 A/digital ionalyzer pH meter was used for checking the pH of solutions. The extraction was performed on a Waters solid phase extraction device (that can prepare 20 samples simultaneously), and Zorbax C18 membrane disks [47 mm (diameter) × 0.5 mm (thickness), 8 μm, 50 mg] (Agilent Technologies, USA) were used. The samples were passed through the disks in a forward direction and the retained complex was eluted from the disks in a reverse direction.

2.2. Reagents

All chemicals used were of analytical grade unless otherwise stated. All of the solutions were prepared with ultra-pure water obtained from a Milli-Q50 SP Reagent Water System (Millipore Corporation, USA). Acetonitrile (Fisher Corporation, USA) was used. 2,3-Dichloro-6-(2,7-dihydroxy-1-naphthylazo)quinoxaline (DCDHNAQ) used in the present investigation was prepared according to the procedure described previously [47]. A stock 1×10^{-3} M solution of DCDHNAQ was prepared by dissolving an appropriate weight of the reagent in a minimum amount of pure ethanol and brought to 100 mL in measuring flask with ethanol.

Standard stock solution containing 100 mg L^{-1} of vanadium(V) was prepared by dissolving 0.2393 g of ammonium vanadate (E-Merck, India) in 1000 mL volumetric flask and diluted up to the mark with 0.01 M hydrochloric acid. The solution was standardized volumetrically using potassium permanganate [52]. Working solutions were prepared by appropriate dilution of the standard solution.

Citric acid–sodium hydroxide buffer solution (0.5 M, pH 3.3 (containing 0.1 M Na_2EDTA and 0.5 M NH_4F)) was prepared by dissolving 86 g of citric acid, 32.7 g of ethylenediamine tetraacetic acid disodium salt and 20.5 g ammonium fluoride in 600 mL of water, then the solution was neutralized to pH 3.3 with 20% sodium hydroxide, and diluted to the volume of 1000 mL. Benzyldimethyl tetradecylammonium chloride (zephiramine) (2.0% (w/v)) was prepared by dissolving zephiramine with 20% ethanol.

2.3. General procedure

To a standard or sample solution containing no more than 0.45 μg of V(V) in a 100 mL measuring flask, 5.0 mL of citric acid–sodium hydroxide buffer solution of pH 3.3 (containing 0.1 M Na_2EDTA and 0.5 M NH_4F), 2.5 mL of 1×10^{-3} M DCDHNAQ solution and 2.0 mL of 2.0% zephiramine solution were added. The mixture was diluted to volume of 100 mL and mixed well. After 5.0 min, the solution passed through the C18 cartridge at a flow rate of 20 mL min^{-1}. The colored complex would be retained on the cartridge. After the enrichment had finished, the retained complex was eluted from the cartridge with 1.0 mL of acetonitrile at a flow rate 5.0 mL min^{-1} in reverse direction, and the eluent was adjusted to the accurate volume of 1.0 mL in a 1.0 mL calibrated flask by adding microamount of acetonitrile with a 500 μL syringes. The absorbance of this solution was measured at 573 nm in a 10 mm cell against a reagent blank prepared in a similar way without vanadium.

2.4. Procedure for water samples

River water samples were filtered through 0.45 μm membrane filters after collecting them. The pH of filtrates was adjusted to approximately 2.0 by adding hydrochloric acid (6.0 M). For tap water, the sample was collected after discharging tap water about 30 min and bubbled with nitrogen gas for 30 min to remove chlorine. The bottled mineral water was used without pretreatment. To these samples known amounts of V(V) were added and analyzed by the proposed procedure for vanadium.

2.5. Determination of vanadium in alloy steel

A 0.1 g amount of a steel 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 5.0 mL of concentrated HNO_3 until all carbides were decomposed. Then, 2.0 mL of a 1:1 (v/v) H_2SO_4 solution was added and the mixture was evaporated carefully until the dense white fumes derived off the oxides of nitrogen, and then cooled to room temperature. After appropriate dilution with 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 2.0 mL of 0.01% (w/v) tartrate as masking agent. The resulting solution was filtered, if necessary, through a Whatman No. 40 filter paper into a 50 mL calibrated flask. The residue (silica) was washed with a small volume of hot 1.0% H_2SO_4 followed by water and the volume was made up to the mark with water.

A suitable aliquot of the above solution was taken into a 10-mL calibrated flask and the vanadium content was determined using the above general procedure using 2.0 mL of saturated thiocyanate or fluoride solution as masking agent. Higher concentrations of iron(III) were removed by adding 5.0–10 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.

2.6. Determination of vanadium in soil

An air-dried homogenized soil sample (2.0 g) was weighed accurately and placed in a 100-mL Kjeldahl flask. The sample was digested in the presence of an oxidizing agent following the method recommended by Jackson [48]. The content of flask was filtered through a Whatman No. 40 filter paper, into a 25 mL calibrated flask and neutralized with dilute ammonia in the presence of 2.0 mL of 0.01% (w/v) tartrate solution. It was then diluted to the mark with water. Appropriate aliquots of 1.0–2.0 mL of the solution was transferred into a 10-mL calibrated flask and analyzed for vanadium content according to the above general procedure, after adding 2.0 mL of 0.01% (w/v) thiocyanate or fluoride solution as masking agent [49].

2.7. Determination of vanadium in urine

50 mL of the urine sample was concentrated to 5.0 mL, by evaporation. To this solution was spiked a known amount of vanadium and mixed with 5.0 mL of concentrated HNO_3 and 5.0 g of potassium sulfate, and heated to dryness. The process was repeated 2–3 times. Then HNO_3 (1:3, 25 mL) was added to the residue and digested on a water bath for 30 min [49]. The contents were again evaporated

to dryness, cooled, and the residue was dissolved in water, filtered, and neutralized with dilute ammonia. The mixture was diluted to a known volume with water. Appropriate aliquots of this solution were taken and the above general procedure was followed for the vanadium determination.

2.8. 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. They were carefully wiped with filter paper before taking their wet weight. The samples were then dried, ashed and brought into solution by acid treatment as per standard procedures [27,50], 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 above general procedure for vanadium. Synthetic samples were prepared by the addition of known amounts of vanadium to each sample prior to digestion.

3. Results and discussion

3.1. Absorption spectra

The absorption spectra of DCDHNAQ and its V(V) complex under the optimum conditions are shown in Fig. 1. The absorption peaks of DCDHNAQ and its complex at pH 3.3 are located at 451 and 573 nm.

3.2. Effect of acidity

Results showed that the optimal pH for the reaction of V(V) with DCDHNAQ is 2.8–3.7 (Fig. 2). A citric acid–sodium hydroxide buffer solution of pH 3.3 was recommended to control pH. As the use of 4.0–7.0 mL of the buffer solution (pH 3.3) per 100 mL of final solution was found to give a maximum and constant absorbance value. The use of 5.0 mL buffer solution was recommended.

3.3. Effect of surfactants

The V(V)–DCDHNAQ complex has a poor solubility in water solution. It is need to add a suitable amount of surfactants to enhance the solubility of the complex. Experiments showed that all

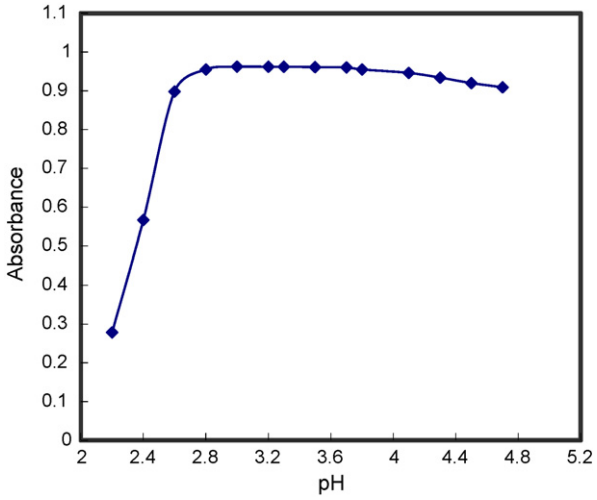

Fig. 2. Effect of pH on complexation of 0.2 μg mL^{-1} V(V), under the optimum reaction conditions.

the nonionic and cationic surfactants have good effect to enhance the solubility, whereas the anionic surfactants has no effect on the solubility of the formed complex. In addition to enhance the solubility, in the nonionic and cationic surfactants medium, the sensitivity of the V(V)–DCDHNAQ complex was increased markedly too. The effect of the four nonionic (Triton X-100, Tween-80, Tween-20 and Emulsified–OP) and five cationic (benzyldimethyl tetradecyl-ammonium chloride (zephiramine), cetyl trimethylammonium bromide (CTAMB), cetylpyridinium bromide (CPB), tetradecyl trimethylammonium bromide (TDTAB) and cetylpyridinium chloride (CPC) were studied to choose the most favorable one which gave higher solubility and sensitivity. Zephiramine and CTAMB surfactants improving the solubility and sensitivity. The results showed that, zephiramine was the best and most a probable additive, whereas CTAMB harms the retention on C18 cartridge. The use of 1.5–3.0 mL of 2.0% zephiramine gives a constant and maximum absorbance value for the studied complex (Fig. 3), in addition to harmless the complex retention on C18 cartridge. Accordingly, 2.0 mL zephiramine solution was recommended.

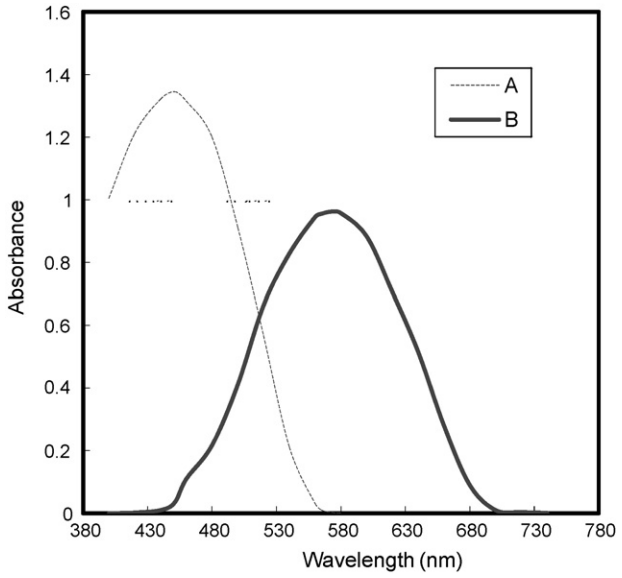

Fig. 1. Absorption spectra of (A) 2.5×10^{-3} M DCDHNAQ, and (B) its complex with 0.2 μg mL^{-1} V(V) under the optimum conditions.

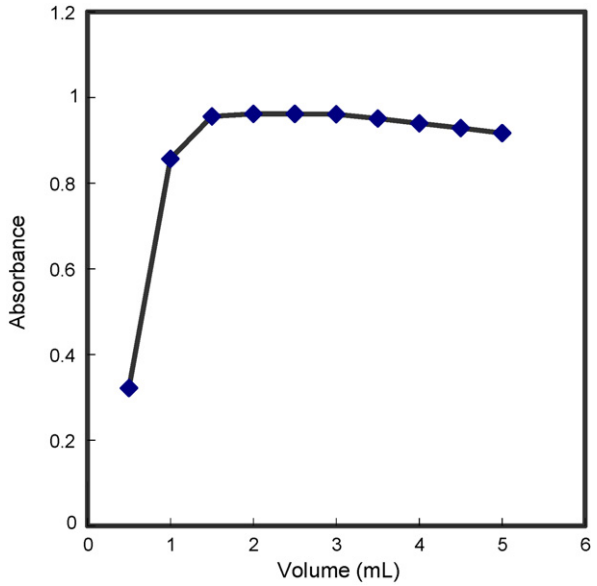

Fig. 3. Effect of 2.0% zephiramine on complexation of 0.2 μg mL^{-1} at the optimum conditions.

Table 1
Comparison of the sensitivity for different solvents on the complexation of V(V) at the optimum conditions.

Solvent	Acetone	Tetrahydrofuran	Dioxane	Acetonitrile	Ethanol	Methanol
λ_{max} (nm)	570	569	571	573	570	568
$\varepsilon \times 10^{-4}$ L mol^{-1} cm^{-1}	13.3	9.8	15.1	24.5	11.7	8.7

3.4. Effect of DCDHNAQ concentration

For up to 0.45 μg of V(V), the use of about 2.0–3.0 mL of 1×10^{-3} M of DCDHNAQ solution has been found to be sufficient for a complete reaction. Accordingly, 2.5 mL of 10^{-3} M solution was added in all further measurement.

3.5. Nature of the complex

The nature of the complex was established at the optimum conditions described above using the molar ratio and continuous variation methods. The plot of absorbance versus the molar ratio of V(V) to DCDHNAQ, obtained by varying the DCDHNAQ concentration, showed inflection at molar ratio 2.0, indicating presence of two DCDHNAQ molecules in the formed complex. Moreover, the Job method showed a ratio of 2.0. Consequently, the results indicated that the stoichiometric ratio was (1:2) [V(V):DCDHNAQ]. The conditional formation constant, calculated using Harvey and Manning equation applying the data obtained from the above two methods, was found to be 5.43, whereas the true constant was 5.50.

3.6. Stability of the chromogenic system

After mixing the components, the absorbance reaches its maximum within 5.0 min at room temperature and remains stable for at least 24 h. When extracted into the acetonitrile medium, the complex can keep stable at least 15 h.

3.7. Solid phase extraction

Both the enrichment and the elution were carried out on a Waters SPE device (it is able to prepare twenty samples simultaneously), using variable flow rate to select the optimum rate for different elution. The flow rate was set to 20 mL min^{-1} for enrichment and 5.0 mL min^{-1}, for elution for highly concordant results.

Some experiments were carried out in order to investigate the retention of the complex on the cartridge. It was found that the DCDHNAQ and its V(V) complex could be retained on cartridge quantitatively when they pass the cartridge as aqueous solution. The capacity of the cartridge for DCDHNAQ was 17 mg and for its V(V) complex was 5.9 mg in a 100 mL of solution. In this experiments, the cartridge has adequate capacity to enrich the V(V)–DCDHNAQ complex and the excess DCDHNAQ.

To investigate the optimum sample volume, different volumes (25–500 mL) were examined. 100 mL was selected as the optimum volume due to highly sensitivity and stability of the formed complex, in addition to highly concordant results.

In order to choose a proper eluent for the retained DCDHNAQ and its V(V) complex, various of organic solvents were studied. It was found that the acetone, tetrahydrofuran, dioxane, acetonitrile, ethanol and methanol could elute the DCDHNAQ and its V(V) complex from cartridge quantitatively. The acetonitrile has a higher absorbance value of the formed complex in addition to rapidity for elution, so acetonitrile was selected as eluent (Table 1) for its high sensitivity and more environmental friendly solvent, in addition to a single extraction step was required. Experiment showed that, it was easier to elute the retained DCDHNAQ and its V(V) complex in reverse direction than in forward direction, so it is necessary to upturned cartridge during elution. 1.0 mL of acetonitrile was sufficient to elute the DCDHNAQ and its V(V) complex from cartridge at a flow rate of 5.0 mL min^{-1}. The volume of 1.0 mL eluent was used in this study.

3.8. Analytical parameters

The calibration curve shown that Beer's law is obeyed in the concentration range of 0.01–0.45 μg V(V) per mL in the measured solution, whereas Ringbom optimum concentration

Table 2
Comparison of the sensitivity for spectrophotometric determination of V(V).

Reagent	λ_{max} (nm)	$\varepsilon \times 10^{-4}$ L mol^{-1} cm^{-1}	Medium	Ref.
Butaperazine dimaleate.	513	10.50	Aqueous	[18]
4-(2-Pyridylazo)-resorcino + iodo-nitro-tetrazolium chloride	560	2.40	Aqueous	[21]
8-HydroxyQuinoline	550	0.318	pH 3.5–4.5	[23]
Sulfochlorophenol-N-benzoyl-N-phenylhydroxylamine	530	0.465	pH 5.0–9.0	[24]
Benzohydroxamic acid	450	0.365	pH 1.2–5.5	[25]
N-benzoyl-2-naphthohydroxamic acid	430	1.82	0.05 M H_2SO_4	[26]
N-P-methoxyphenyl 2-furylacrolo-hydroxamic acid + 3-(ocarboxy-phenyl)-1-phenyltriazine-N-oxide	450	1.40	pH 1.0–2.0	[27]
N-hydroxy-N-m-tolyl-N′-phenyl benzamidine + TX-100	570	0.474	1.0–10 M acetic acid	[28]
N-benzoyl-N-phenylhydroxylamine	440	0.38	Aqueous	[29]
2-(5-Nitro-2-pyridylazo)-5-(N-propyl-N-sulfopropylamino)phenol	592	8.00	Aqueous	[30]
4-(2-Pyridylazo)-resorcinol + H_2O_2	542	1.85	Aqueous	[31]
4-(2-Pyridylazo)resorcinol +N-phenyl benzohydroxamic acid	560	3.60	DMF	[32]
6-Chloro-3-hydroxy-7-methyl-2(2-thienyl)-4H-chromen-4-one	420	8.26	Aqueous	[33]
2-(5-chloro-2-pyridylazo)-5-dimethyl-aminophenol + H_2O_2	588	6.57	Aqueous	[34]
5,7-Dichlorooxime + Rhodamine 6G	515	2.65	Aqueous	[35]
2-(2-Quinolylazo)-5-diethylamino-phenol	590	12.8	SPE ethanol	[36]
Variamine Blue	570	1.65	Aqueous	[37]
N-Phenylbenzohydroxamic acid and crystal violet	535	0.72	$CHCl_3$	[38]
2-(2-Thiazolylazo)-p-cresol + ascorbic acid	525	2.11	pH 4.0–6.0	[39]
4-(2-Thazolylazo)resorcinol, + Thiazolyl blue	550	2.60	$CHCl_3$	[40]
1,5-Diphenyl carbohydrazide	531	4.23	Aqueous	[49]
2,3-Dichloro-6-(2,7-dihydroxy-1-naphthylazo)quinoxaline	573	24.5	Acetonitrile	This work

range (obtained as a result of drawing the logarithmic value of concentration in micrograms per liter against the transmittance) was found to be 0.025–0.425 μg mL^{-1}. The linear regression equation obtained was: $A = 4.808\,C$ (μg mL^{-1}) − 0.012 ($r = 0.9996$). The molar absorptivity and Sandell sensitivity were calculated to be 2.45×10^5 L mol^{-1} cm^{-1} and 0.0208 ng cm^{-2} at 573 nm. The relative standard deviation at a concentration level of 0.20 μg of V(V) per mL (11 repeat determination) was 1.34%.

The standard deviations of the absorbance measurements were calculated from a series of 13 blank solution. The limits of detection ($K = 3$) and of quantification ($K = 10$) of the method were established [51] according to the IUPAC definitions ($C_1 = KS_o/s$ where C_1 is the limit of detection, S_o is the standard error of blank, s is the slope of the standard curve and K is the constant related to the confidence interval and found to be 3.2 and 9.9 μg in the final assay solution.

The sensitivity expressed as molar absorptivity of the proposed method is compared with those of published spectrophotometric methods [Table 2]. The higher sensitivity of the proposed method is notable, greater even than that of the SPE [36] that used 2-(2-quinolylazo)-5-diethylaminophenol. Also, the proposed method is more sensitive than other method [18–40] that based on spectrophotometry (Table 2).

3.9. Interference

A systematic study of the effect of potentially interfering species on the vanadium determination was undertaken. This study was carried out by adding a known amount of foreign species to a vanadium solution of 0.2 μg mL^{-1}. The tolerance limit was taken as ±5.0% change in absorbance. The buffer solution containing 0.08–0.15 M of Na_2EDTA and 0.4–0.6 M of NH_4F could markedly increase the selectivity of this system. Without Na_2EDTA and NH_4F in the buffer solution, the tolerance limits of foreign ions were 0.01 mg for Cu(II), Co(II), Ni(II), and Fe(III); 0.005 mg for Zn(II), Pd(II)). However, the tolerance limits of foreign ions reached 4.0 mg for Fe(III); 0.8 mg for Cu(II), Zn(II); 0.6 mg for Co(II), and Ni(II); 0.25 mg for Pd(II) when Na_2EDTA and NH_4F existed in the buffer solution. Therefore, 0.1 M of Na_2EDTA and 0.5 M of NH_4F in the buffer were recommended. The results are listed in Table 3, showing that most common ions do not interfere with the determination suggesting the highly selectivity of the proposed method. Results showed that Pt(IV) gives a serious interfere. The interfere due to Pt(IV) can be eliminated by mask with NH_4SCN. This method is highly selective.

Table 3
Tolerance limits in the determination of 0.2 μg of V(V) with DCDHNAQ (relative error ± 5.0%).

Foreign ions	Tolerance limit, μg
Na^+, K^+, Li^+, CH_3COO^-, cetrate	30,000
Cl^-, ClO_4^-, PO_4^{3-}, SO_4^{2-}, thiourea	25,000
Ca^{2+}, Mg^{2+}, Sr^{2+}, Ba^{2+}, NO_3^-, SiO_3^{2-}	20,000
Mn^{2+}, Ce^{4+}, SnO_3^{2-}, tartrate	17,500
WO_4^{2-}, MoO_4^{2-}, CrO_4^{2-}	15,000
Ti^{4+}, Bi^{3+}, F^-	12,500
Cr^{3+}, Al^{3+}, Ru^{3+}, Ag^+, Br^-	10,000
Ir^{4+}, Rh^{3+}, Pd^{2+}, I^-	8,000
OsO_5^{2-}, SeO_3^{2-}, TeO_3^{2-}	5,500
Hg^{2+}, Sb^{3+},CN^-, SCN^-	4,000
Th^{4+}, UO_4^{2-}	2,500
Pb^{2+}, Ru^{3+}, Bi^{3+}	1,750
La^{3+}, Sm^{3+}, Gd^{3+}, Sc^{3+}	1,200
Be^{2+}, Fe^{2+}, Cd^{2+}	850
Fe^{3+}, Pt^{4+} [a]	400
Cu^{2+}, Zn^{2+}	80
Co^{2+}, Ni^{2+}	60
Pd^{2+}	25

[a] Masked with NH_4SCN.

Table 4
Determination of vanadium in various samples.

Sample	V(V) added, μg mL^{-1}	Proposed method			Reference method [14]			*F*-test[b]	*t*-test[c]
		Found, [a] μg mL^{-1}	RSD (%)	Recovery (%)	Found, [a] μg mL^{-1}	RSD (%)	Recovery (%)		
Steel[d] (0.1 g/100 mL^{-1})	–	4.07 ± 0.04	1.00	101.75	3.97 ± 0.05	1.35	99.25	2.63	1.19
	6.0	10.10 ± 0.03	0.37	101.00	9.85 ± 0.04	0.77	99.8	2.81	1.36
Soil[e] (1 g)	5.0	5.03 ± 0.03	0.94	100.60	4.98 ± 0.04	0.95	99.60	2.70	1.22
	8.0	8.05 ± 0.02	0.44	100.63	7.97 ± 0.03	1.25	99.63	2.95	1.41
River water[e]	6.0	6.05 ± 0.04	0.56	100.83	5.97 ± 0.05	1.35	99.50	2.48	1.09
	9.0	8.99 ± 0.02	0.87	99.89	8.98 ± 0.03	0.88	99.78	2.90	1.44
Tap water[e]	3.0	2.99 ± 0.04	0.88	99.67	3.01 ± 0.06	1.17	100.33	3.43	1.76
	6.0	6.01 ± 0.02	0.54	100.17	5.98 ± 0.06	0.97	99.67	2.68	1.22
Mineral water[e]	4.0	4.01 ± 0.03	0.63	100.25	3.98 ± 0.04	1.21	99.50	2.87	1.39
	8.0	7.98 ± 0.05	0.46	99.75	7.97 ± 0.05	1.42	99.63	3.04	1.50
Urine[e]	7.0	6.96 ± 0.05	0.60	99.43	6.95 ± 0.06	0.75	99.29	2.56	1.13
	10	9.95 ± 0.04	0.40	99.50	9.92 ± 0.04	0.95	99.20	2.77	1.32
Plant material[e] (cabbage 5 g)	8.0	7.95 ± 0.04	0.55	99.38	7.93 ± 0.05	1.15	99.13	2.46	1.08
	12	11.98 ± 0.02	0.95	99.82	11.91 ± 0.03	1.10	99.25	2.12	0.99
Goat liver[e] (3 g)	7.0	6.98 ± 0.04	0.80	99.71	6.94 ± 0.05	1.00	99.14	2.35	1.06
	9.0	9.05 ± 0.03	0.85	100.56	8.95 ± 0.02	1.20	99.44	2.87	1.41
Human hair[e]	3.0	3.05 ± 0.02	1.00	101.67	2.97 ± 0.04	1.35	99.00	2.67	1.30
	12	11.95 ± 0.03	0.75	99.58	12.10 ± 0.05	0.95	100.83	2.49	1.11
Tea leaf[e]	6.5	6.47 ± 0.03	1.00	99.54	6.55 ± 0.04	1.25	100.77	2.66	1.28
	13	13.07 ± 0.02	0.95	100.54	12.85 ± 0.06	1.30	98.85	2.37	1.05

[a] Mean ± standard deviation ($n = 5$).
[b] Tabulated *F*-value for 5 degrees of freedom at P (0.95) is 5.05.
[c] Tabulated *t*-value for 5 degrees of freedom at P (0.95) is 2.57.
[d] GKW Steel Ltd., India [C, 0.54%; Mn, 0.89%; S, 0.018%; P, 0.034%; Si, 0.33%; Cr, 1.02%; V, 0.13%], vanadium taken 5.00 μg mL^{-1}.
[e] Gave no test for vanadium.

3.10. Analytical application

The proposed method was successfully applied to determine the vanadium contents of alloy steel, soil, water, human hair, urine, plant material and animal tissue samples by the proposed method, and the results are summarized in Table 4. In all cases, the results were compared with the 2-pyridylazo resorcinol (PAR) method [53]. The performance of the proposed method was assessed by calculation of the *t*-value (for accuracy) and *F*-test (for precision) compared with PAR method [53]. The mean values were obtained in a Student's *t*- and *F*-tests at 95% confidence limits for five degrees of freedom [54]. The results showed that the calculated values (Table 4) did not exceed the theoretical values. Therefore, there is no significant difference between the proposed and the reference method, indicating that the developed method is as accurate and precise as the reference method [53] and the certified values of the samples.

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