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Highly sensitive spectrophotometric method for the determination of vanadium in environmental, biological, food and soil samples using orthoaminophenol

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ABSTRACT

A simple, ultra-sensitive and highly selective non-extractive spectrophotometric method for the determination of trace amount of vanadium(V) using orthoamino phenol (OAP) has been developed. OAP reacts in highly acidic (0.005-0.015 mol/L H_2SO_4) and aqueous media with vanadium(V) to give a chocolate color chelate which has an absorption maximum at 405 nm. The reaction was instantaneous and absorbance remains stable for over 72 h. The average molar absorption co-efficient and Sandell's sensitivity were found to be 6.7×10^5 L/mol.cm and 10 ng/cm^2 of vanadium(V), respectively. Linear calibration graphs were obtained for 0.02-50.00 mg/L having detection limit 1 µg/L and quantification limit of the reaction were found to be 10 µg/L and RSD 0-2%. The stoichiometric composition of the chelate is 1:3 (Vanadium(V):OAP, *v:v*). Large excess of over 60 cations, anions and complexing agents (Like tartrate, EDTA, oxalate, chloride, phosphate, thiourea, SCN^- *etc.*) do not interfere in the vanadium determination. The method was successfully used in the determination of vanadium in several standard reference materials (Alloys and steels) as well as in some environmental waters(Potable and polluted), biological samples (Human blood and urine), food samples, soil samples, solution containing both vanadium(IV) and vanadium(V) and complex synthetic mixtures. The results of the proposed method for biological analyses were found to be in excellent agreement with those obtained by AAS. The method has high precision and accuracy (s = ±0.01 for 0.5 µg/mL).

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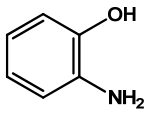
1. Introduction

Vanadium is the 22nd most abundant element in the earth's crust, occurring more than 65 minerals. Although it is an essential trace element for some creatures, a number of its compounds are toxic. Generally higher toxicity is associated with higher oxidation state [1].It is in trace amounts important industrially [2] as a biological nutrient [3], epidemiological preventive [4], toxicant [5], environmental pollutant [6] and occupational hazard [7]. Environmental scientists have declared vanadium as a potentially dangerous chemical pollutant that can play havoc with the productivity of plants, crops and the entire agricultural system. High amounts of vanadium are said to be present in fossil fuels such as crude petroleum, fuel oils, some coals and lignite. Burning these fuels releases vanadium into the air that then settles on the soil. There are cases of vanadium poisoning, the symptoms of which are nervous depression, irritation and respiratory damage, coughing, vomiting, gastrointestinal disturbance, diarrhea, anemia and an increased risk of lung cancer, that are sometimes fatal. Recently, vanadium has been noticed as the index element in urban environmental pollution, especially air pollution. Laboratory and epidemiological evidence suggest that vanadium may also play a beneficial role in the prevention of heart disease. Shamburger [8] has pointed out that human heart-disease death rates are lower in countries where more vanadium occurs in the environment. Therefore, its accurate determination at trace level using simple, rapid method is of paramount importance.

The aim of this study is to develop a simpler spectrophotometric method for trace determination of vanadium. In the search for a more sensitive reagent, in this work a new Schiff's base reagent orthoaminophenol (OAP) is found which gives a color reaction of OAP with vanadium(V). OAP has not previously been used for the spectrophotometric determination of vanadium (Scheme 1).



Orthoaminophenol (OAP)

Scheme 1

The method possess distinct advantages over existing methods [1,9-16] with respect to sensitivity, selectivity, range of determination, simplicity, speed, pH/ acidity range, thermal stability, accuracy, precision and ease of operation (Table 1).

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Table 1. Summary of the existing spectrophotometric methods for the determination of vanadium.

Reagent	λ_{max} (nm)	ε (L/mol. cm)	Beer's law (mg /L)	Interference	Remarks	Reference
Acetophenone 2,4-dihydroxy semicarbazone	380	3899	1-5	Many	i) Solvent extractive ii) Less sensitive iii) Less selective due to much interference	[1]
Napthaline-1,5 diamine	531	3.0×10^3	0.4-5.0	Many	i) pH- dependent ii) Less selective due to much interference iii) Less sensitive	[9]
1-(2-quinolylazo) 2,4,5-tryhydroxybenzene	590	2.5×10^4	0.32-2.00	Fe, Pd, Ag, Zn, CN^-	i) pH- dependent ii) Less selective due to much interference iii) Lengthy and time consuming	[10]
3-Hydroxybenzaldehyde-4-aminoantipyrine	435	4.0×10^3	0.5-7.0	Co(II), Zn, Mn, Cd, Pb *etc*.	i) Less selective due to much interference ii) Lengthy and time consuming due to pre- concentration iii) Less sensitive	[11]
Acetophenone- 2,4-dihydroxy thiosemicarbazone	378	3.4×10^3	1-10	Many	i) Solvent extractive ii) pH- dependent iii) Less sensitive Less selective iv)Limited application	[12]
Azure-B	636	4.3×10^4	0.02-9.00	Many	i) Time consuming ii) pH- dependent iii) Less selective due to much interference	[13]
Salicylaldehydeacetoacetic acid hydrazone (SAAH)	460	22.0×10^3	0.243-2.438	W(VI), Mn(II), Zn, Fe(II)	i)Less sensitive and ii) Less selective due to much interference iii) Toxic solvent is used. iv) pH- dependent	[14]
Ganus Green-Bromate	618	4.5×10^3	0.5-150	Many	i)Less sensitive ii) Less selective due to much interference ii)Limited application	[15]
1,5-diphenylcarbohydrazide	531	4.23×10^4	0.1-30.0	Ag, Al, Mo(VI)	i)Less sensitive ii) Less selective due to much interference iii) Toxic organic solvent was used.	[16]
Orthoaminophenol (Present method)	405	6.7×10^5	0.02-50.00	Using suitable masking agent, the reaction can be made highly selective	i)Non-extractive and very simple ii) Highly sensitive iii) Highly selective iv)Aqueous reaction media v) Simple and rapid method	Present Method

The method is based on the reaction of non-absorbent OAP in highly acidic solution with vanadium(V) to produce a highly absorbent chocolate color chelate product followed by direct measurement of the absorbance in aqueous solution. With suitable masking the reaction can be made highly selective and the reagent blank solution does not show any absorbance.

2. Experimental

2.1. Apparatus

A Shimadzu (Kyoto, Japan) (Model-1800) double beam UV/VIS the recording spectrophotometer and a Jenway (England UK) (Model-3010) pH-meter with a combination of electrodes were used for the measurements of absorbance and pH, respectively. A Shimadzu (Model: AA7000) atomic absorption spectrometer equipped with a microcomputer controlled air - acetylene flame was used for comparison of the results.

2.2. Reagents and solutions

All chemicals used were of analytical-reagent grade of the highest purity available. Doubly distilled de-ionized water and HPLC-grade ethyl alcohol, which is non-absorbent under ultraviolet radiation, were used throughout.

Glass vessels were cleaned by soaking in acidified solutions of $KMnO_4$ or $K_2Cr_2O_7$, followed by washing with concentrated HNO_3, and were rinsed several times with high-purity de-ionized water. Stock solutions and environmental water samples (1000 mL each) were kept in polypropylene bottle containing 1 mL of concentrated HNO_3. More rigorous contamination control was used when the vanadium levels in specimens were low.

2.2.1. Orthoaminophenol solution (9.17×10^{-3} M)

Orthoaminophenol solution was prepared by dissolving the requisite amount of orthoaminophenol (BDH Chemicals, purity > 99%) in a mixture of rectified spirit (30%) and doubly distilled deionized water. More dilute solutions of the reagent were prepared as and when required.

2.2.2 Vanadium(V) standard solution (1.96×10^{-2} M)

A 100 mL amount of stock solution (1 mg/L) of pentavalent vanadium was prepared by dissolving 226.9 mg of purified-grade (Merck proanalysis grade) ammonium metavanadate (Merck) in doubly distilled de-ionized water containing 1-2 mL of nitric acid (1+1). Aliquots of this solution were standardized with standard potassium iodated solution [17]. More dilute standard solutions were prepared by appropriate dilution of aliquots from the stock solution with de-ionized water as and when required.

2.2.3 Vanadium(IV) standard solution (1.96×10^{-2} M)

A 100 mL amount of stock solution (1 mg/L) of tetravalent vanadium was prepared by dissolving 390.7 mg of purified grade vanadyl sulfate (Fisher Scientific) in doubly distilled

deionized water. Aliquots of this solution were standardized with standard potassium iodated solution [17]. More dilute standard solutions were prepared from this stock solution as and when required.

2.2.4. Potassium permanganate solution

A potassium permanganate (1%)(Merck) solution was prepared by dissolving in de-ionized water. Aliquots of this solution were standardized with oxalic acid, sodium azide solution (2.5%,*w*:*v*) (Fluka purity > 99%) was also used.

2.2.5. Tartrate solution

A 100 mL stock solution tartrate (0.01%, *w*:*v*) was prepared by dissolving 10 mg of A.C.S.-Grade (99%) potassium sodium tartrate tetra hydrate in 100 mL de-ionized water.

2.2.6. EDTA

A 100 mL stock solution of EDTA (0.01%,*w*:*v*) was prepared by dissolving 10 mg A.C.S.-Grade (≥99%) ethylendiamine tetraacetic acid and dissolution salt dihydrate in 100 mL de-ionized water.

2.2.7. Aqueous ammonia solution

A 100 mL solution of an aqueous ammonia solution was prepared by diluting 10 mL concentrated NH_4OH (28-30% A.C.S.-Grade) to 100 mL with de-ionized water. The solution was stored in polypylene bottle.

2.2.8. Sodium azide solution

Sodium azide solution (2.5%, *w*:*v*) (Fluka purity >99%) was freshly prepared by dissolving 2.5 g in 100 mL of deionized water.

2.2.9. Other solutions

Solutions of a large number of inorganic ions and complexing agents were prepared from their Analar grade or equivalent grade water-soluble salts. In the case of insoluble substances, special dissolution methods were adopted [18].

2.3. Procedure

An aliquot containing not more than 0.2-500µg of vanadium(V) was transferred into 10 mL calibrated flask, 0.5-1.5 mL (preferably 1.0 mL) of 0.1 mol/L H_2SO_4, 40-140 fold molar excess of OAP reagent solution (1 mL of 9.17×10^{-3} M) and After one minute the mixture was diluted to the mark with deionized water. The absorbance was measured at 405 nm with a 1 cm glass cell against corresponding reagent blank solution. The reagent blank was prepared in a similar manner without vanadium. The vanadium content in an unknown sample was determined using a concurrently prepared calibration graph.

2.4. Sample collection and preservation

Water: Water samples were collected in polythene bottles from shallow tube-wells, tap-wells, river, sea and drain of different places of Bangladesh. All samples are collected in dry season. In case of Bay of Bangle, Karnafuly and Halda river samples are collected from both of upper (surface) and lower level (5 m depth). In case of Industrial effluent or drain water samples are collected from direct drainage systems which are located at 50-100 m distance from industry. After collection, HNO_3 (1 mL /L) was added as preservative.

Blood and Urine: Blood and urine samples were collected in polypropylene bottles from effected persons of Chittagong Medical College Hospital, Bangladesh. Immediately after collection they were stored in a salt-ice mixture and latter, at the laboratory, were kept at -20 °C.

Soil: Soil (surface) samples were collected from different locations in Bangladesh. Samples were dried in air and homogenized with a mortar.

Food: Food samples were collected from local market of Chittagong in Bangladesh.

3. Results and discussions

3.1. Factors affecting the absorbance

3.1.1. Absorption spectra

The absorption spectra of vanadium(V)-OAP system in 1.0 mL of 0.1 M H_2SO_4 sulfuric acid medium was recorded using the spectrophotometer. The absorption spectra of the vanadium(V)-OAP system is a symmetric curve which absorbance at 405 nm with maximum and the average molar absorption co-efficient was found to be 6.7×10^5 L/mol.cm (Figure 1), where as the reagent OAP did not show any absorbance. In order to obtain high sensitivity, a wavelength of 405 nm was chosen for the spectrophotometric measurement of the vanadium complex against a reagent blank. The reaction mechanism of the present method is as reported earlier [19].

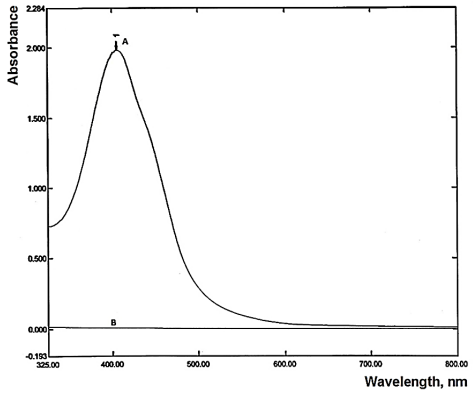


Figure 1. A and B Absorbance spectra of vanadium(V)-OAP system and the reagent blank (λ_{max} = 405 nm) in aqueous solutions, respectively.

3.1.2. Effect of acidity

Of the various acids (nitric, hydrochloric, sulfuric and phosphoric acid) studied, sulfuric acid was found to be the best acid for the system. The absorbance was at a maximum and constant when the 10 mL of solution (1 mg/L) contained 0.5-1.5 mL (preferably 1.0 mL) of 0.1 M H_2SO_4 at room temperature (25±5 °C). Outside this range of acidity, the absorbance was decreased (Figure 2). For all subsequent measurements, 1.0 mL of 0.1 M sulfuric acid was added.

3.1.3. Effect of time

The reaction was very fast. Constant maximum absorbance was obtained within few seconds after the dilution to volume and remained strictly unaltered for over 24 h. A longer period of time was not studied.

3.1.4. Effect of temperature

Effect of various temperatures (10-90 °C) on vanadium(V)-OAP system was studied.

Table 2. Selected analytical parameters obtained with the optimization experiments.

Parameters	Studied range	Selected value
Wavelength, λ_{max} (nm)	200-800	405
Acidity (M H_2SO_4)	0.001-0.050	0.005 - 0.015 (Preferably 0.01)
Time (h)	0-72	1 min - 24 h (Preferably 1 min)
Temperature (°C)	10-90	25±5
Reagent (fold molar excess, M:R)	1:4-1:140	1:40 - 1:140 (Preferably 1:50)
Linear range (mg/L)	0.01-100	0.02-50
Molar Absorption Co-efficient (L/mol.cm)	5.1×10^5- 8.4×10^5	6.7×10^5
Sandell's sensitivity (ng /cm^2)	1-100	10
Detection limit (µg/L)	0.01-100	1
Reproducibility (% RSD)	0-5	0-2
Regression co-efficient (r^2)	0.9996-0.9999	0.9998

The vanadium(V)-OAP system attained maximum and constant absorbance at room temperature (25±5 °C).

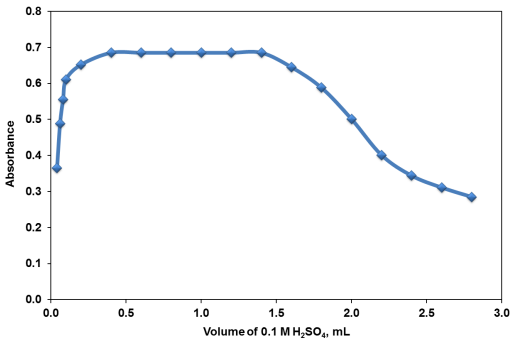


Figure 2. Effect of acidity on the absorbance of vanadium(V)-OAP system.

3.1.5. Effect of reagent concentration

Different molar excesses of OAP were added to fixed metal ion concentration and absorbances were measured according to the standard procedure. It was observed that at 1 mg/L vanadium(V)metal, the reagent molar ratios of 1:40-1:140 produced a constant absorbance of the vanadium(V)-chelate (Figure 3). For all subsequent measurements, 1 mL of 9.17×10^{-3} M OAP reagent was added.

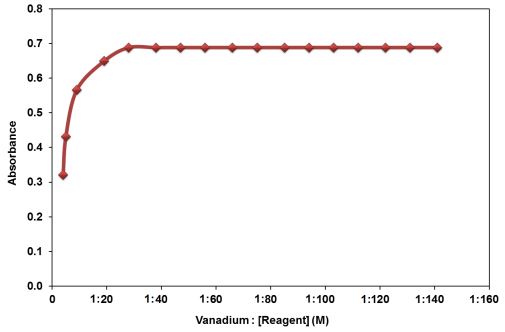


Figure 3. Effect of reagent (vanadium(V)-OAP molar concentration ratio) on the absorbance of vanadium(V)-OAP system.

3.1.6. Effect of metal concentration (Beer's law)

The effect of metal concentration was studied over 0.01-80.00 mg/L distributed in four sets (0.01-0.10, 0.1-1.0, 1.0-10.0, 10-100) for convenience of measurement. The absorbance was linear for 0.02-50.00 mg/L of vanadium at 405 nm. Of the four calibration graphs, the first three straight line graphs were passing through the origin (r^2 = 0.9998). The next one showing the limit of the linearity is given in Figure 4. The average molar absorption co-efficient and Sandell's sensitivity [20] were found to be 6.7×10^5 L/ mol.cm and 10 ng/cm^2 of vanadium(V), respectively. The selected analytical parameters obtained with the optimization experiments are summarized in Table 2.

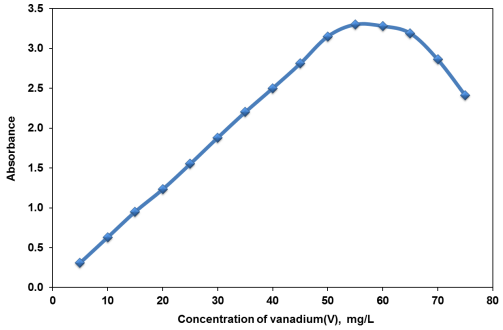


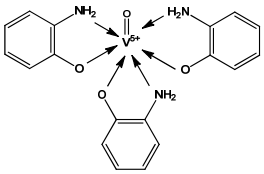
Figure 4. Calibration graph, 10-50 mg/L of vanadium (V).

3.1.7. Effect of foreign ions

The effect of over 60 cations, anions and complexing agents on the determination of only 1 mg/L of vanadium(V) was studied. The criterion for an interference [21] was an absorbance value varying by more than ±5% from the expected value for vanadium(V) alone. The results are summarized in Table 3. As can be seen, a large number of ions have no significant effect on the determination of vanadium(V). The most serious interference were from Fe(III) ion which can be easily masked with EDTA [18]. Interference from these Fe(III) is probably due to complex formation with OAP. During the interference studies, if a precipitate was formed, it was removed by centrifugation. The amount mentioned is not the tolerance limit but the actual amount studied. The effect was also studied for 10 µg/L of vanadium(V) and it was found that this was also similar as 1 mg/L of vanadium(V). However, for those ions whose tolerance limit has been studied, their tolerance ratios are given in Table 3.

3.1.8. Composition of the absorbance

Job's method [22] of continuous variation and the molar ratio [23] method were applied to ascertain the stoichiometric composition of the complex. A vanadium(V)-OAP (1:3, *v*:*v*) complex was indicated by both methods (Scheme 2).



Probable structure of vanadium(V)-OAP [1:3] complex

Scheme 2

Table 3. Tolerance limits [a] of foreign ions, tolerance ratio/[Species (x) /V (*w*:*w*)].

Species, x	Tolerance ratio [Species (x) /V (*w*:*w*)]	*Species, x*	Tolerance ratio [Species (x) / V (*w*:*w*)]
Acetate	1000	Iodide	1000
Aluminum	500	Lithium	100
Ammonium	1000	Nitrite	1000
Arsenic(III)	1000	Lead(II)	100
Arsenic(V)	1000	Magnesium	100
Ascorbic acid	500	Manganese(II)	1000
Antimony	50	Manganese(VII)	100
Azide	100	Mercury(II)	100
Barium	50	Molybdenum(VI)	50
Beryllium(II)	100	Nickel(II)	500
Bromide	1000	Nitrate	1000
Biphosphate	1000	Oxalate	20
Cadmium	100	Phosphate	1000
Calcium	1000	Potassium	1000
Cesium	1000	Selenium(IV)	25
Chloride	1000	Selenium(VI)	1000
Chromium(III)	100	Silver	100
Chromium(VI)	100	Sodium	50
Citric acid	1000	Strontium	100
Copper(II)	100	Tartrate	100
Cyanide	1000	Tellurium	500
Cobalt	50	Thiocyanate	10
Carbonate	1000	Tin(II)	50
Cerium(III)	100	Tin(IV)	100
EDTA	10,000	Titanium(IIII)	100
Fluoride	1000	Tungsten(VI)	100
Iron(II+III)	10 [b]	Zinc	100

[a] Tolerance limit was defined as ratio that causes less than ±5 percent interference.
[b] With 10,000 EDTA.

Table 4. Determination of vanadium in some synthetic mixtures.

Sample	Composition of mixtures (mg/L)	Vanadium (V) (mg/L)		
		Added	Found [a]	Recovery ± s [b] (%)
A	V^{5+}	0.50	0.49	98±1.0
		1.00	1.00	100±0.0
B	As in A + Se^{6+} (50) + Ca (50) + Cu^{2+} (25)	0.50	0.50	100±0.0
		1.00	0.99	99±1.0
C	As in B + Mg^{2+} (25) + Ni^{2+} (25)	0.50	0.50	100±1.0
		1.00	1.02	102±1.0
D	As in C + Cd (25) + Mn^{2+} (25) + Hg^{2+} (25)	0.50	0.51	102±1.3
		1.00	1.03	103±1.0
E	As in D + Sr (25) + Pb^{2+}(25) + Cr^{3+} (25)	0.50	0.54	108±1.0
		1.00	1.05	105±1.2
F	As in E +Na (25) +As^{3+}(25) + Sr (25)	0.50	0.55	110±1.8
		1.00	1.10	110±1.5

[a] Average of five analysis of each sample.
[b] The measure of precision is the standard deviation(s).

Table 5. Determination of vanadium in certified reference materials.

Certified reference materials [a]	Vanadium (%)		
	Certified value	Found [b] (n=5)	R.S.D [c] (%)
GSBH 40101-96, Cr_{12}MoV-Dies steel (Cr=11.63, Ni=0.095, Mo=0.986,V=0.411, Cu=0.082, Co=0.02)	0.411	0.402±0.02	1.3
BH-1013-1-95*, $9Cr_{17}$MoVCo High tensile steel (C = 90, Si = 0.44, Mn = 0.81, Cr = 16.3, Mo = 0.52, V = 0.24, Co = 1.45)	0.24	0.224±0.04	1.8
BAS-CRM 64b, high-speed steel (Cr=4.55, Mo=4.95,V=1.99, Te=0.52)	1.99	1.973±0.03	1.5
NBS SRM1577a Bovine Liver	0.099±0.008	0.098±0.009	1.6

[a] These CRMs were obtained from Beijing NCS Analytical Instruments Co. Ltd, China.
[b] Average of five replicate determinations of each sample.
[c] The measure of precision is the relative standard deviation (RSD).

3.1.9. Precision and accuracy

The precision of the present method was evaluated by determining different concentrations of vanadium (each analyzed at least five times). The relative standard deviation (n = 5) was 0-2% for 0.2-500 µg of vanadium in 10mL, indicates that this method is highly precise and reproducible. The detection limit (3s of the blank) and Sandell's sensitivity (concentration for 0.001 absorbance unit) for vanadium (V) were found to be 1 µg /L and 10ng/cm^2, respectively. The method was also tested by analyzing several synthetic mixtures containing vanadium(V) and diverse ions (Table 4). The results for total vanadium were in good agreement with certified values (Table 5). The reliability of our vanadium(V)-OAP chelate procedure was tested by recovery studies. The average percentage recovery obtained for addition of vanadium(V) spike to some environmental water samples was quantitative as shown in Table 6. The results of biological analyses by the spectrophotometric method were in excellent agreement with those obtained by AAS (Table 7). The results of soil and food samples were also shown in Table 8 and Table 9, respectively, which were highly precise. The results of speciation of vanadium(IV) and vanadium(V) in mixtures were highly reproducible (Table 10). Hence, the precision and accuracy of the method were excellent.

3.1.10. Applications

The proposed method was successfully applied to the determination of vanadium(V) in a series of synthetic mixtures

Table 6. Determination of vanadium in some environmental water samples.

Sample		Vanadium (µg/L)		Recovery ± s (%)	s_r (%) [b]
		Added	Found [a]		
Tap water		0	2.0	-	-
		100	103.0	100.9±0.2	0.22
		500	503.0	100.2±0.5	0.31
Well water		0	9.5	-	-
		100	108.0	99±0.4	0.15
		500	510.0	100± 0.5	0.29
Rain water		0	0.00	-	-
		100	101.1	101±0.5	0.13
		500	502.3	100.5±0.5	0.25
River water	Karnaphuly (upper)	0	12.0	-	-
		100	112.0	100±0.00	0.17
		500	515.0	100.6±0.5	0.35
	Karnaphuly (lower)	0	18.0	-	-
		100	120.5	101.7±0.2	0.21
		500	518.0	100±0.0	0.00
	Halda (upper)	0	4.0	-	-
		100	106.0	101.9±0.3	0.00
		500	508.0	100.8±0.2	0.18
	Halda (lower)	0	6.0	-	-
		100	107.0	100.9±0.6	0.25
		500	509.0	100.6±0.5	0.19
Sea water	Bay of Bengal (upper)	0	7.6	-	-
		100	109.0	101.3±0.3	0.35
		500	511.5	100.8±0.1	0.15
	Bay of Bengal (lower)	0	8.2	-	-
		100	110.5	102.1±0.5	0.22
		500	510.0	100.2±0.4	0.31
Drain water	KSRM [c]	0	12.00	-	-
		100	114.0	101.8±0.8	0.35
		500	515.0	100.6±0.5	0.45
	TSP Complex [d]	0	29.5	-	-
		100	131.0	101.1±0.7	0.15
		500	532.0	100.5±0.6	0.00
	KDS Texile [e]	0	40.0	-	-
		100	243.0	102.1±0.3	0.16
		500	645.0	100.9±0.7	0.28
	Karnaphuly paper Mill [f]	0	45.0	-	-
		100	145.0	100±0.0	0.0
		500	548.0	100.5±0.6	0.55
	Elite Paint [g]	0	35.6	-	-
		100	138.0	102.2±0.4	0.21
		500	540.0	100.90.1	0.18
	Eastern Refinery [h]	0	150.0	-	-
		100	255.0	102±0.7	0.49
		500	645.0	99.2±0.6	0.45

[a] Average of the five replicate determination of each sample.
[b] The measure precision is the relative standard deviation (s_r).
[c] Kabir Steel Re-Rolling Mills, Chittagong.
[d] TSPcomplex Ltd., Patenga, Chittagong.
[e] KDS Textile Ltd., Oxygen,Chittagong.
[f] Karnaphuly Paper Mill, Chandraghona, Chittagong.
[g] Elite Paint, Nasirabad, Chittagong.
[h] Eastern Refinery, Chittagong.

Table 7. Concentration of vanadium in blood and urine samples

Serial no	Sample	Vanadium (µg/L)				Sample source[a]
		AAS (n = 5)		Proposed method (n = 5)		
		Found	RSD [b],%	Found	RSD [b],%	
1	Blood	360.0	1.0	365	1.0	Lung cancer (Male)
	Urine	67.2	1.2	70.2	1.3	
2	Blood	8.5	1.5	9.2	1.5	Diabetis (Female)
	Urine	2.0	1.7	3.2	1.8	
3	Blood	30	1.3	32.3	1.3	Neurological disorder (Female)
	Urine	12.5	1.5	13.4	1.6	
4	Blood	12.2	1.5	13.5	1.2	Cardiovascular patient (Male)
	Urine	3.5	1.3	4.2	1.5	
5	Blood	11.2	1.2	12.1	1.7	Normal (Male)
	Urine	4.3	1.4	4.8	1.3	

[a] The samples were from Chittagong Medical College Hospital, Chittagong.
[b] The measure of precision is the relative standard deviation (RSD).

Table 8. Determination of vanadium in some surface soil.

Serial no	Vanadium (mg/kg) [a]	Sample source
S_1[c]	0.027±0.010 [b]	Agriculture soil (Chittagong University Campus)
S_2[c]	0.032±0.005	Marine soil (Bay of Bengal)
S_3[c]	0.063±0.010	Estuarine soil (Karnaphuli)
S_4[c]	0.035±0.005	Road side soil (Dhaka-Chittagong High way)
S_5[c]	0.075±0.015	Industrial soil (T. S. P. Complex, Chittagong)

[a] Average of five analyses of each sample.
[b] Measure of precision is the standard deviation.
[c] Composition of the soil samples: C, N, P, K, Na, Ca, Mg, Cu, Fe, Pb, NO_3, NO_2, Zn, SO_4, Mn, Mo, Co, *etc*.

Table 9. Determination of vanadium in some food samples.

Serial no	Sample	Vanadium (mg/kg or mg/L)	Sample source
		Found ± s [a]	
1	Fanagreek *(Trigonellafoenum-graecum)*	9.4±1.5	Chittagong Market
2	Potato *(Solanumtuberosum)*	6.2±1.2	Chittagong Market
3	Tomato *(Licopersiconesculentum)*	1.0±1.3	Chittagong Market
4	Olive oil *(OleaEuropeus)* [b]	11.2±1.5	Chittagong Market
5	Wheat *(Triticumaestivum)*	3.2±1.4	Chittagong Market
6	Cabbage *(Brassica oleracea)*	4.8±1.4	Chittagong Market
7	Black pepper *(Peeper Nigrum)*	13.4±2.0	Chittagong Market
8	Rice *(Oryza sativa)*	1.08±1.6	Chittagong Market

[a] Average of the five replicate determinations of each sample
[b] Values in mg /L.

Table 10. Determination of vanadium(IV) and vanadium(V) in mixtures.

Serial no	V(IV) : V(V)	V, taken (mg/L)		V, found (mg/L)		Error (mg/L)	
		V(IV)	V(V)	V(IV)	V(V)	V(IV)	V(V)
1	1:3	1.00	3.00	0.98	0.99	0.02	0.01
1	1:3	1.00	3.00	1.00	1.00	0.00	0.00
1	1:3	1.00	3.00	0.99	0.98	0.01	0.02
Mean error: V(V) = 0.0067; V(IV) = ±0.013, Standard deviation: V(V) = ±0.0058; V(IV) = ±0.011							
1	1:5	1.00	5.00	0.99	4.98	0.01	0.02
1	1:5	1.00	5.00	0.98	4.98	0.02	0.02
1	1:5	1.00	5.00	0.99	4.99	0.01	0.01
Mean error: V(V) = 0.013; V(IV) = ±0.016, Standard deviation: V(V) = ±0.0058; V(IV) = ±0.0058							
1	1:10	1.00	10.00	0.98	9.99	0.02	0.01
1	1:10	1.00	10.00	0.99	9.98	0.01	0.02
1	1:10	1.00	10.00	0.98	9.98	0.02	0.02
Mean error: V(V) = 0.016; V(IV) = ±0.016, Standard deviation: V(V) = ±0.0058; V(IV) = ±0.0058							

of various compositions (Table 4) and also in a number of real samples e.g. several Certified Reference Materials (CRMs) (Table 5). The method was also extended to the determination of vanadium in a number of environmental, biological, soil and food samples. In view of the unknown composition of environmental water samples, the same equivalent portions of each such samples were analyzed for vanadium content; the recoveries in both the "*spiked*" (Added to the samples before the mineralization or dissolution) and the "*unspiked*" samples are in good agreement (Table 6). The results of biological analyses by spectrophotometric method were found to be in excellent agreement with those obtained by AAS (Table 7). The results of soil analyses by the spectrophotometric method are shown in (Table 8). The results of food sample analyses by the spectrophotometric method are shown in Table 9. The results of speciation of vanadium(IV) and vanadium(V) in mixtures are shown in Table 10.

3.1.10.1. Determination of vanadium in synthetic mixtures

Several synthetic mixtures of varying compositions containing iron and diverse ions of known concentrations were determined by the present method and the results were found to be highly reproducible. The results are shown in Table 4. Accurate recoveries were achieved in all solutions.

3.1.10.2. Determination of vanadium in brass, alloys and steels (Certified reference materials)

A 0.1 g amount of a brass or alloy or steel sample containing 0.24-1.99% of vanadium was weighed accurately and placed in a 50 mL Erlenmeyer flask following a method recommended by Parker [24] to it, 10 mL of concentrated HNO_3, 2 mL of concentrated H_2SO_4 and 1-2 mL of 1% $KMnO_4$ were added to oxidize vanadium (IV) to vanadium (V), excess of $KMnO_4$ was removed by addition of 1-2 mL of freshly prepared 2.5% sodium azide solution and carefully covering the flask with a watch glass until the brisk reaction subsided. The solution was heated to drive off excess azide solution and simmered gently after the addition of 5 mL of concentrated HNO_3 until all carbides were decomposed. The solution was carefully evaporated to dense white fumes to drive off the oxides of nitrogen and then cooled to room temperature (25±5 °C). After suitable dilution with deionized water, the contents of the Erlenmeyer flask were warmed to dissolve the soluble salts. The solution was then cooled and neutralized with a dilute NH_4OH solution in the presence of 1-2mL of 0.01% (*w*:*v*) tartrate solution. The resulting solution was filtered, if necessary, through a Whatman No. 40 filter paper into a 25 mL calibrated flask. The residue was washed with a small volume of hot (1 + 99) H_2SO_4, followed by water and the volume was made up to the mark with deionized water.

A suitable aliquot (1-2 mL) of the above solution was taken into a 10mL calibrated flask and the vanadium content was determined as described under general procedure using EDTA as a masking agent. The proposed procedure for the spectrophotometric determination of vanadium was applied to the analysis of Bovine liver (NBS SRM1577a) CRM obtained from the National Research Council of Canada using EDTA as a masking agent, following a method recommended by Sun *et al.* [25]. Based on five replicate analyses, average vanadium concentration determined by spectrophotometric method was in close agreement with the certified values (Table 5). The results are shown in Table 5.

3.1.10.3. Determination of vanadium in environmental waters

Each filtered with Whatman No. 40 environmental water sample (1000 mL) evaporated nearly to dryness with a

mixture of 5 mL concentrated H_2SO_4 and 10 mL of concentrated HNO_3 in a fume cupboard and 1-2 mL of $KMnO_4$, following a method recommended by Greenberg *et al.* [26]. Excess of 1% $KMnO_4$ was removed by 2.5% freshly prepared sodium azide solution and was heated with 10 mL of deionized water in order to remove excess azide solution and dissolves the salts. The solution was then cooled and neutralized with dilute NH_4OH solution in the presence of 1-2 mL of 0.01% (*w*:*v*) tartrate solution. The resulting solution was then filtered (if necessary) and quantitatively transferred into a 25 mL calibrated flask and made up to the mark with deionized water.

An aliquot (1-2 mL) of this pre-concentrated water sample was pipetted into a 10 mL calibrated flask and the vanadium content was determined as described under the general procedure. The analyses of environmental water samples for vanadium from various sources are shown in Table 6.

Most spectrophotometric methods for determination of vanadium in natural and seawater require pre-concentration of vanadium [26]. The concentration of vanadium in natural and seawater is a few mg/L in Japan [27]. The mean concentration of vanadium found in US drinking waters is 6 µg/L [28].

3.1.10.4. Determination of vanadium in biological samples

Human blood (2-5 mL) or urine (20-50 mL) was taken into a 100 mL micro-Kjeldahl flask. A glass bead and 10 mL of concentrated nitric acid were added and the flask was placed on the digester under gentle heating. When the initial brisk reaction was over, the solution was removed and cooled following a method recommended by Stahr [29]. A 2 mL volume of concentrated sulfuric acid was added carefully, followed by the addition of 1.0 mL of 70% $HClO_4$, and heating was continued to dense white fumes, while repeating HNO_3 addition if necessary. Heating was continued for at least ½ hr and then cooled. The content of the flask was filtered and neutralized with dilute NH_4OH in the presence of 1-2 mL of a 0.01 % (*w*:*v*) tartrate solution, transferred quantitatively into a 10mL calibrated flask and made up to the mark with de-ionized water.

A suitable aliquot (1-2 mL) of the final solution was pipetted into a 10 mL calibrated flask and the vanadium content was determined as described under general procedure using EDTA as a masking agent. The results of biological analyses by the spectrophotometric method were found to be in excellent agreement with those obtained by AAS. The results are shown in Table 7.

The abnormally high value for the lung cancer patient is probably due to the involvement of a high vanadium concentration with Zn and As. The occurrence of such high vanadium contents are also reported in cancer patients from some developed countries [5]. The low value for the heart-disease patient is probably due to low vanadium concentrations in the environment. There is an inverse correlation between human heart-disease and vanadium concentration in the environment [26].

3.1.10.5. Determination of vanadium in some soil samples

An air-dried homogenized soil sample (100 g) was weighed accurately and placed in a 100 mL micro-Kjeldahl flask. The sample was digested in the presence of excess oxidizing agent, following the method recommended by Hesse [30]. The content of the flask was filtered through a Whatman No.40 filter paper into a 25 mL calibrated flask and neutralized with dilute NH_4OH solution in the presence of 1-2 mL of a 0.01 % (*w*:*v*) tartrate or EDTA solution. It was then diluted up to the mark with de-ionized water.

Suitable aliquots (1-2 mL) were transferred into a 10 mL calibrated flask and a calculated amount of 0.1 mol/L H_2SO_4 needed to give a final acidity of 0.005-0.015 mol/L H_2SO_4 was added, followed by 1-2 mL of 0.1% (*w*:*v*) EDTA solution as masking agent. The vanadium content was then determined by the above procedure and quantified from a calibration graph prepared concurrently. The results are shown in Table 8.

3.1.10.6.Determination of vanadium in food samples

An air dried food sample fenugreek seed (5 g), potato (5g), tomato (5 g), olive oil (50 mL), wheat (5 g), cabbage (10 g) and black pepper (5 g) were weight accurately and placed in a porcelain crucible and charred in an electric furnace. The sample was ashed at 555 °C in a muffle furnace in presence of excess oxidizing agent following a method recommended by Stahr [29]. Concentrated hydrochloric acid (2 mL) and water (10 mL) were added to the ash. The mixture of each food stuff was heated in presence of 1-2 mL of 1% $KMnO_4$ and excess of $KMnO_4$ was removed by 2.5% freshly prepared sodium azide solution followed by the addition of 0.5 mL of 70% $HClO_4$ and heating was continued for at least ½ hr to remove excess azide solution and then cooled. The resultant solution was neutralized with NH_4OH in presence of 1-2 mL of 0.01% (*w*:*v*) tartrate solution and then transferred quantitatively into a 25mL calibrated flask and made up to the mark with deionized water.

A suitable aliquot (1-2 mL) of the final solution was pipetted into a 10 mL calibrated flask and the vanadium content was determined as described under the procedure. High value of vanadium for black peeper is probably due to the involvement of high vanadium concentration in the soil. The results are shown in Table 9.

3.1.10.7. Determination of vanadium(IV) and vanadium(V) speciation in mixtures

Suitable aliquots (1-2 mL) of vanadium (IV+V) mixtures (preferably 1:1, 1:5, 1:10) were taken in a 25 mL conical flask. A few drops of 0.1mol/L sulfuric acid and 1-3 mL of 1% (*w*:*v*) potassium permanganate solution were added to oxidize the tetratavalent vanadium to pentavalent vanadium. A 5 mL volume of water was added to the mixtures, which were then heated on a steam bath for 10-15 min, with occasional gentle shaking, and then cooled to room temperature (25±5 °C). Then, 3-4 drops of a freshly prepared sodium azide solution (2.5%, *w*:*v*) was added and heated gently with the further addition of 2-3 mL of water, if necessary, for 5 min to drive off the azide cooled to room temperature. The reaction mixture was transferred quantitatively into a 10 mL volumetric flask, 1 mL of 9.17×10^{-3} mol/L OAP reagent solution was added followed by addition of 1 mL of 0.1 mol/L H_2SO_4 and up to the mark with de-ionized water. The absorbance was measured after 1 min at 405 nm against a reagent blank. The total vanadium content was calculated with help of the calibration graph.

An equal aliquot of the above vanadium (IV + V) mixture was taken into a 25 mL beaker. One mL of 0.01% (*w*:*v*) tatrate was added to mask vanadium(IV) and neutralize with dilute NH_4OH. The concentration of the beaker was transferred into a 10-mL volumetric flask, then 1 mL of 0.1 mol/L H_2SO_4 solution was added followed by addition of 1 mL of 9.17×10^{-3} mol/L OAP and up to the mark with de-ionized water. After 1 min the absorbance was measured against a reagent blank, as before. The vanadium concentration was calculated in mg/L or µg/L with the aid of calibration graph. This gives a measure of vanadium(V) originally present in the mixture. This value was subtracted from that of the total vanadium to get vanadium(IV) present in the mixture. The results were found to be highly reproducible. Occurrences of such reproducible results are also reported for different oxidation states of vanadium [27]. The results of a set of determination are given in Table 10.

Table 11. Statistical comparison of proposed method with reference methods.

Samples	F-test results [a]				
	(s_1^2/ s_2^2) [16]	(s_1^2/ s_3^2) [31]	(s_1^2/ s_4^2) [11]	(s_1^2/ s_5^2) [13]	(s_1^2/ s_6^2) [14]
Water	0.132	0.04	0.69	0.16	0.0023
Water	0.0416	0.002	0.043	0.017	0.0018
Water	0.2	0.003	0.095	0.265	
Water	0.127	0.002			
Blood	0.86				
Blood	0.87				
Blood	0.59				
Soil	0.25		0.0001	0.00002	
Soil	1		0.0001	0.0002	
Soil	1		0.0003	0.0003	
Alloy	0.081	0.00015			0.0036
Alloy	0.14	0.00018			0.074
Synthetic mixture	0.59	0.094			
Synthetic mixture	0.75	0.14			
Synthetic mixture	0.83	0.28			
Food				0.42	0.192
Food				3.26	0.074
Urine	1			1.2	
Urine	0.75			2.51	

[a] Tabulated F-value for (5,5) degrees of freedom at P(0.98) is 5.72. s_1= Standard deviation of proposed method, s_2= Standard deviation of reference method [16], s_3= Standard deviation of reference method [30], s_4= Standard deviation of reference method [11], s_5= Standard deviation of reference method [13], s_6= Standard deviation of reference method [14].

The present method was compared with some reported methods [11,13,14,16,30] statistically. It was found that present method is much superior those of the reported methods. The results are shown in Table 11.

4. Conclusions

In this manuscript, a new sensitive, selective and inexpensive method in completely aqueous media was developed for the determination of vanadium in industrial, environmental, biological, food and soil samples, for continuous monitoring to establish the trace levels of vanadium in difficult samples matrices. Although many sophisticated techniques such as pulse polarography, AAS, NAA, FIA, ICP-MS and ICP-OES are available for the determination of vanadium at trace levels in numerous complex materials, factors such as the low cost of the instrument, easy handling, lack of requirement for consumables, and almost no maintenance have caused spectrophotometry to remain a popular technique, particularly in laboratories of developing countries with limited budgets. The sensitivity in terms of molar absorption coefficient and precision in terms of relative standard deviation of the present method are very reliable for the determination of vanadium in real samples down to ng/g levels in aqueous medium at room temperature (25±5 °C).

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