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A highly sensitive and selective spectrophotometric method for the determination of vanadium at nanotrace levels in some environmental, biological, soil, food, and pharmaceutical samples using salicylaldehyde-benzoylhydrazone

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RESEARCH ARTICLE

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ABSTRACT

A very simple, non-extractive and new spectrophotometric method for the swift determination of trace amount of vanadium using salicylaldehyde-benzoylhydrazone (Sal-BH) has been developed. Sal-BH undergoes a reaction in a slightly acidic solution (0.0016-0.0032 M H_2S0_4) with vanadium to give a light greenish-yellow chelate, which has an absorption maximum at 392 nm. The reaction is instantaneous and absorbance remains stable for over 24 hrs. The average molar absorption co-efficient and Sandell's sensitivity were found to be 2.5039×10^5 L/mol.cm and 1.0 ng/cm^2 V, respectively. Beer's law was obeyed for 0.001-30 mg/L of V, providing a detection limit of 0.1 µg/L of V and RSD 0-2 %. The stoichiometric composition of the chelate is 1:1 (V:Sal-BH). Interference study shows that a large excess of over 60 cations, anions, and some common complexing agents (such as chloride, azide, tartrate, EDTA and SCN^-, etc.) satisfy the tolerance limit. The developed method was successfully used in the determination of vanadium in several standard reference materials as well as in some environmental waters, biological fluids, soil, food and pharmaceutical samples and solutions containing both vanadium (IV) and vanadium (V). The results of the proposed method for assessing biological, food and vegetable samples were comparable with ICP-OES and AAS were found to be in excellent agreement. The method has high precision and accuracy (s = ±0.01 for 0.5 mg/L).

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1. Introduction

Vanadium is widely distributed in the earth's crust in low abundance [1]. The major sources for the emission of vanadium in the environment are the combustion of fuel oils, dyeing, ceramics, inks, catalysts, and steel manufacturing [2]. Trace amount of vanadium is important industrially [3], as a biological nutrient [4], epidemiological preventive [5], toxicant [6], environmental pollutant [7], and occupational health hazard [8]. It is represented as an essential element for normal cell growth, but it can be toxic when present in higher concentrations [6]. However, vanadium plays an important role in physiological systems including normalization of blood sugar levels and participation in various enzyme systems as an inhibitor and co-factor of oxidation of amines [9]. Vanadium is more important in marine environment than terrestrial [10]. It can be highly toxic to human and animals and cause serious diseases [11]. Literature [12] reports that the toxicity of vanadium depends on its oxidation state, vanadium(V) valence is more toxic than other species.

Human body uptakes vanadium through foods. Vanadium can have a number of effects on human health, if the uptake is too high. When vanadium uptake occurs through air, it can cause bronchitis and pneumonia. The acute side effects of vanadium are irritation of the lungs, throat, eyes, and nasal cavities. The other side effects are cardiovascular disease, inflammation of the stomach and intestines, damage to the nervous system, liver and kidneys, skin rashes, headache, behavioral changes, etc. In the industry, workers exposed to vanadium peroxide dust were found to have severe eye, nose, and throat irritation [13]. All these findings cause great concern regarding public health, demanding accurate determination of this metal ion at trace levels.

Spectrophotometry is essentially a trace analysis technique and is one of the most powerful tools in chemical analysis. In this study, we developed a very simple method for the quantification of vanadium using a spectrophotometer. Salicylaldehyde-benzoylhydrazone (Sal-BH) has been reported as a spectrophotometric reagent for copper(II) [14] and molybdenum(VI) [15] but has not previously been used for vanadium.

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

1,5 Diphenyl carbazide (DPCH) [16]				
Solvent	Acetone	Beer's Law	0.1-30	Remarks
Medium	Aqueous	Molar absorption co-efficient	4.23×10^4	i) pH dependent.
pH	4.0-5.5	Detection limit	20	ii) Less sensitive.
λ_{max}	531	RSD %	1.5	iii) Less selective
Interference	Many			due to much interference.
2-(5-Chloro-2-pyridylazo)-5-dimethylaminophenol (5-Cl-DMPAP) [17]				
Solvent	Ethanol	Beer's Law	0.09-1.2	Remarks
Medium	Organic + aqueous	Molar absorption co-efficient	6.57×10^3	i) pH dependent.
pH	2.1	Detection limit	9	ii) Less sensitive.
λ_{max}	588	RSD %	1	iii) Less selective due to much interference.
Interference	Many			iv) Solvent extractive, hence, lengthy and time consuming.
				v) Limited application.
3,4-Dihydroxybenzaldehydeisonicotinoyl hydrazone (3,4-DHBINH) [18]				
Solvent	Alcohol	Beer's Law	0.5-5.3	Remarks
Medium	Aqueous	Molar absorption co-efficient	1.26×10^4	i) Less sensitive.
pH	5.5	Detection limit	16	ii) Less selective due to much interference.
λ_{max}	360	RSD %	0.5	iii) pH dependent.
Interference	Many			iv) Application in water only.
2,6-Dithiol-4-tert-butylphenol and aminophenol [19]				
Solvent	Chloroform	Beer's Law	0.02-18	Remarks
Medium	Organic + aqueous	Molar absorption co-efficient	3.5×10^4	i) Less sensitive.
pH	1.2-4.8	Detection limit	20	ii) Less selective due to much interference.
λ_{max}	590	RSD %	1.6	iii) Solvent extractive hence, lengthy and time consuming
Interference	Many e.g.: Cu^{2+}, Fe^{3+}, Mn^{7+}, etc.			iv) pH dependent.
				v) Limited application.
2-Hydroxy-5-bromothiophenol (HBTP) [20]				
Solvent	Chloroform	Beer's Law	0.05-15	Remarks
Medium	Organic + aqueous	Molar absorption co-efficient	2.7×10^4	i) Solvent extractive, hence, lengthy and time consuming.
pH	3.4-4.6	Detection limit	50	ii) Less sensitive.
λ_{max}	630	RSD %	3	iii) Less selective due to many interference
Interference	Many			iv) pH dependent.
				v) Limited application.
Salicylaldehyde-benzoylhydrazone (Sal-BH) - Proposed method				
Solvent	Absolute ethanol	Beer's Law	0.001-30	Remarks
Medium	Aqueous	Molar absorption co-efficient	2.5039×10^4	i) Highly selective.
pH	3.1-3.5	Detection limit	0.1	ii) Ultra sensitive.
λ_{max}	392	RSD %	0-2	iii) Aqueous reaction medium.
Interference	Using suitable masking agents, the reaction can be made highly selective			iv) Simple and rapid. v) Color stable for more than 24 h at room temp. vi) Non-extractive. vii) Application in various environmental, biological, soil, food, and pharmaceutical samples.

* Units: λ_{max} (nm), Beer's Law (mg /L), Molar absorption co-efficient, ε (L/mol.cm), and Detection limit (ng/mL).

This paper reports its use in a very sensitive, highly specific spectrophotometric method for the trace determination of vanadium. The method possesses distinct advantages over existing methods [16-20] with respect to sensitivity, selectivity, range of determination, simplicity, speed, pH /acidity range, thermal stability, accuracy, precision and ease of operation (Table 1). The literature survey, it reveals that the existing methods are lengthy, time-consuming, pH dependent, and in most of the above-mentioned methods, the interference was high. It is needless to emphasize further that the direct spectrophotometric method in non-extractive way is more useful if it offers high sensitivity and selectivity. The search should be directed to a new simpler spectrophotometric method for non-extractive estimation of vanadium in very selective and sensitive ways. The method is based on the reaction of non-absorbent Sal-BH in a slightly acidic (0.0016-0.0032 M H_2SO_4) solution with vanadium to produce a highly absorbent light yellowish green chelate product followed by a direct measurement of the absorbance in an aqueous solution with suitable masking, the reaction can be made highly selective and the reagent blank solutions do not show any absorbance.

2. Experimental

2.1. Instrumentation

A Shimadzu (Kyoto, Japan) (Model-1800) double beam UV/VIS spectrophotometer and Jenway (England, U.K.) (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 spectrophotometer (AAS) equipped with microcomputer controlled air-acetylene flame and A Shimadzu (Japan) (Model: 9800) Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES), (λ = 418 nm, plasma gas flow rate (L/min) = 15, LOD: below 1 µg/L of vanadium, RF Power (W) = 1400, Nebulizer gas flow rate (L/min) = 1-10) were used for comparison of the results.

2.2. Synthesis and characterization of the reagent

The reagent was synthesized in our laboratory according to the method of Ahmed and Zannat [14]. The reagent salicyl aldehyde-benzoylhydrazone (Sal-BH) was synthesized by two steps. First, benzoylhydrazine (BH) was prepared by refluxing ethyl benzoate (0.7 mol) with hydrazine hydrate (0.7 mol) in a round-bottom flask equipped with a reflux condenser. It was refluxed at 140 °C for about 24 hours with continuous stirring. Then, it was kept standing overnight when white product separated out. The product was then filtered off, washed with ethanol, and dried in air and then in a desiccator over silica gel. The collected crystalline product was then re-crystallized twice in ethanol. The off-white crystalline product of benzoyl hydrazine was thus washed, dried in air, and finally in a desiccator under vacuum over silica gel. The product melting point was 114.5 °C (Lit. 112-114 °C) [14]. Finally, salicyl aldehyde-benzoylhydrazone (Sal-BH) was prepared by dissolving benzoylhydrazine (30 mmol) in 50 mL ethanol, and salicylaldehyde (30 mmol) was added dropwise in this solution with continuous stirring. The solution was refluxed for about

one hour. Then, it was cooled, allowed to stand for crystallization when a white crystalline product formed. A white crystalline product was obtained via filtration, washed with ethanol, and dried in desiccators over silica gel and calcium chloride. The yield of the product was 80% and the product melting point was 179-180 °C (Lit. 181 °C) [14,21].

2.3. Live subject statement

We were not aiming to carry out detailed human studies, but some samples from individuals were used in our study and as such we abided by all necessary procedures and regulations and our University gave consent. University of Chittagong, Bangladesh, is committed to the protection and safety of human subjects involved in research.

2.4. Reagents and solutions

Analytical grade reagents were used throughout the whole experiment. High-purity absolute ethanol and high-purity deionized water were used throughout. More rigorous contamination control was used when the vanadium levels in the specimens were low.

2.4.1. Sal-BH solution

Sal-BH solution (3.28×10^{-3} M) was prepared by dissolving the requisite amount of salicylaldehyde-benzoylhydrazone in a known volume solution of distilled absolute ethanol. More dilute solution of the reagent was prepared as required.

2.4.2. Vanadium (V) standard solution

A 100 mL amount of stock solution (1.96×10^{-2} M) of pentavalent vanadium was prepared by dissolving 229.6 mg of ammonium metavanadate (NH_4VO_3), (Merck proanalysis grade, purity 99%) in double distilled deionized water containing 1-2 mL of concentrated nitric acid (1:1) [22]. Aliquots of this solution were standardized with EDTA [22]. More dilute standard solutions were prepared by appropriate dilution of aliquots from the stock solution with deionized water as and when required. A freshly standardized solution was always used.

2.4.3. Vanadium (IV) standard solution

A 100 mL amount of stock solution (1.96×10^{-2} M) (1 mg/mL) of trivalent vanadium was prepared by dissolving 319.9 mg of vanadyl sulfate (Fisher Scientific, proanalysis grade, purity 97%) in distilled water containing 1-2 mL of (1:1) concentrated nitric acid and the solution was standardized with EDTA [22]. More dilute standard solutions were prepared by appropriate dilution of aliquots from the stock solution with distilled water as and when required. A freshly standardized solution was always used.

2.4.4. 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 (or oxides and carbonates in hydrochloric acid); those of niobium, tantalum, titanium, zirconium and hafnium were specially prepared from their corresponding oxides (Specpure, Johnson Matthey) according to the recommended procedures of Mukherji [23]. In the case of insoluble substances, special dissolution methods were adopted [24].

2.5. General procedure

A volume of 0.1-1.0 mL of neutral aqueous solution containing 0.01-300 µg of vanadium in a 10 mL volumetric flask was mixed with a 1:134 to 1:600 fold molar excess (preferably 1 mL of 3.28×10^{-3} M) of salicylaldehyde-benzoylhydrazone reagent solution followed by the addition of 0.8-1.6 mL (preferably 1 mL) of 0.002 M sulfuric acid. The solution was mixed well. After 1 minute, 1.5 mL of ethanol was added. The mixture was diluted up to the mark with deionized water. The absorbance was measured at 392 nm against a corresponding reagent blank. A concurrently prepared calibration graph was used for the determination of vanadium from any unknown solution.

2.6. Sample collection and preservation

2.6.1. Environmental samples

Polythene bottles were used for the collection of water samples from different places of Bangladesh and HNO_3 (1 mL/L) was added as a preservative.

2.6.2. Blood, urine, and milk samples

Polypropylene bottles were used to collect blood and urine samples from effected persons of Chittagong Medical College Hospital, Bangladesh. Milk sample was collected from a Bangladeshi lactating mother. After collection, they were stored at-20 °C.

2.6.3. Soil samples

The soil samples were collected from different locations of Bangladesh. The samples were dried in air and homogenized with a mortar.

2.6.4. Food samples

Food samples (Rice, wheat, fruits, and vegetables) were collected from the local market of Chittagong. After collection, the samples (Fruits and vegetables) were stored in a refrigerator for preservation. Samples (Rice and wheat) were used as dry conditions and homogenized with a mortar.

2.6.5. Pharmaceutical samples

Pharmaceutical samples (Tablets and insulin) of different companies were collected from the local Pharmacy of Chittagong. Samples (tablets) were homogenized with a mortar.

3. Results and discussion

3.1. Factors affecting the absorbance

3.1.1. Absorption spectra

The absorption spectrum of a vanadium-Sal-BH system in aqueous medium in the presence of 1 mL 0.002 M sulfuric acid solution, was recorded using the spectrophotometer. The absorption spectrum of vanadium-Sal-BH is an asymmetric curve with maximum absorbance at 392 nm and an average molar absorptivity of 2.5039×10^5 L/mol.cm (Figure 1). Sal-BH without vanadium exhibited negligible absorbance despite having a wavelength at 392 nm. The reaction mechanism of the present method is as reported earlier [25].

3.1.2. Optimization of some parameters on the absorbance

3.1.2.1. Effect of solvent

As Sal-BH is partially soluble in water, an organic solvent was used for the system, considering the cost, availability, toxicity, and volatility of the solvents, such as acetone, benzene,

Table 2. Summary of selected analytical parameters obtained from optimization experiments.

Parameters	Studied value	Selected value
Wavelength, λ_{max} (nm)	200-800	392
Solvent (mL)	0-6	1-3 (preferably 1.5)
H_2SO_4 (M)	0.0004-0.004	0.0016-0.0032 (preferably 0.002)
pH	2.5-4.5	3.5-3.1 (preferably 3.3)
Time (h)	0-24	1 min - 24 h (preferably 5 min)
Temperature (°C)	10-80	25±5
Reagent (fold molar excess, M:R)	1:1-1:600	1:134-1:600 (preferably 1:168)
Linear range (mg/L)	0.0001-1000	0.001-30
Molar absorptivity (L/mol.cm)	1.528×10^5-4.064×10^4	2.5039×10^5
Limit of quantification (µg/L)	0.1-10	1.0
Detection limit (µg/L)	0-100	0.1
Sandell's sensitivity (ng/cm^2)	0-100	1.0
Reproducibility (% RSD)	0-10	0-2
Regression coefficient, R^2	0.9989-0.9999	0.9998

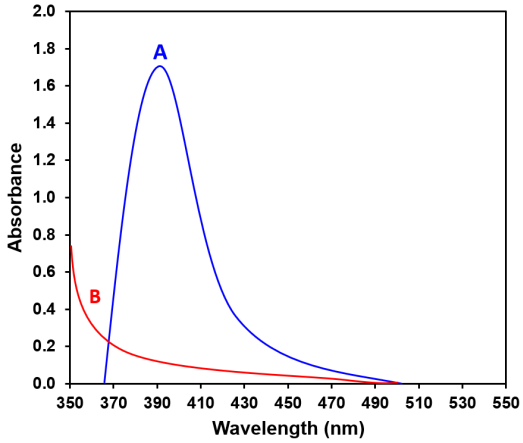


Figure 1. (A) Absorbance spectra of vanadium(V)-Sal-BH and (B) Blank (λ_{max} = 392 nm) in aqueous solutions.

carbon tetrachloride, chloroform, ethanol, 1-butanol, isobutyl methyl ketone, dimethylformamide, methanol and 1,4-dioxane. Ethanol was found to be the best solvent for the system. Different volumes (0-6 mL) of ethanol were added to a fixed metal ion concentration and the absorbance was measured according to the general procedure. Maximum absorbance was observed in 15±2% (*v*:*v*) ethanol:water medium, hence, a 15% ethanol solution was used in the determination procedure. It was observed that 10-70% (1-7 mL) ethanol produced a constant absorbance of vanadium-chelate. For all subsequent measurements, 15% (1.5 mL) of ethanol was added.

3.1.2.2. Effect of acidity

Among the various acids (Nitric, sulfuric, hydrochloric, and phosphoric acids) studied. Sulfuric acid was found to be the best acid for the system. The variation of the absorbance was noted after the addition of 0.1-2.5 mL of 0.002 M sulfuric acid to every 10 mL of the test solution. The maximum and constant absorbance was obtained in the presence of 0.8-1.6 mL of 0.002 M sulfuric acid at room temperature 25±5 °C. Outside this range (0.0016-0.0032 M H_2SO_4) of acidity, the absorbance decreased. For all subsequent measurements, 1.0 mL of 0.002 M sulfuric acid was added. This range of acidity (0.0016-0.0032 M H_2SO_4) also measured the corresponding pH was 3.51-3.31. This type conversion was also reported previously [26].

3.1.2.3. Effect of time

The reaction is very fast. A constant maximum absorbance was obtained just after dilution within a few seconds to volume and remained strictly constant for over 24 h; a longer period of time was not studied.

3.1.2.4. Effect of temperature

The influence of temperature was studied between 10-80 °C. From the temperature studies, it can be observed that the temperature effect is not pronounced between 20-80 °C and so room temperature (25±5 °C) is recommended for all subsequent measurements.

3.1.2.5. Effect of reagent concentration

Different molar excesses of Sal-BH were added to a fixed metal ion concentration and the absorbance was measured according to the general procedure. It was observed that vanadium metal, at the reagent molar ratio of 1:134 to 1:600, produced a constant and maximum absorbance of V-chelate. For different (0.5 and 1 mg/L) vanadium concentrations, an identical effect of varying the reagent concentration was noticed. Further concentration of the reagent was not studied. For all subsequent measurements, 1 mL of 3.28×10^{-3} M Sal-BH reagent was added.

3.1.3. Calibration graph (Beer's law and sensitivity)

The well-known equation for spectrophotometric analysis in a very dilute solution was derived from Beer's law. The effect of the metal concentration was studied over 0.001-100 mg/L distributed in four different sets (0.001-0.01, 0.01-0.1, 0.1-1.0, 1.0-10 and 10.0-100.0 mg/L) for the convenience of the measurement. The absorbance was linear for 0.001-30 mg/L at 392 nm. Of the five calibration graphs, one showing the limit of the linearity is given in Figure 2. The other four were straight-line graphs passing through the origin (r^2 = 0.9998). The molar absorption co-efficient and the Sandell's sensitivity [27] were found to be 2.5039×10^5 L/mol.cm and 1.0 ng/cm^2 of vanadium, respectively. The selected analytical parameters obtained from the optimization experiments are summarized in Table 2.

Table 3. Effect of interfering radicals.

Species x	Tolerance ratio x/V (*w*/*w*)	Species x	Tolerance ratio x/V (*w*/*w*)
Aluminum [a]	100	Lead(II)	100
Arsenic(III)	100	Magnesium	100
Arsenic (V)	100	Mercury(II)	100
Antimony	100	Molybdenum(VI)	100 [a]
Azide	100	Manganese(II), (VII)	100
Bismuth(III)	100	Nickel(II)	100 [c]
Bromide	100	Nitrate	100
Barium	100	Oxalate	100
Cadmium	100	Phosphate	100
Cobalt(II)	100 [b]	Potassium	100
Cobalt(III)	100 [b]	Selenium(IV)	50
Calcium	100	Selenium(VI)	100
Chloride	100	Strontium	100
Citrate	100	Sulphate	100
Chromium(VI)	100 [d]	Sodium	100
Chromium(III)	100	Tartrate	100
Cesium	100	Tin(II)	100
Copper(II)	100 [e]	Tin(IV)	100
Cerium(III)	100	Titanium(IV)	100
EDTA	100	Tellurium(IV)	100
Fluoride	100	Thallium	100
Iron(II)	100 [a]	Thiocyanate	100
Iron(III)	100 [a]	Tungsten(VI)	100
Iodide	100	Uranium	100 [a]
Lithium	100	Zinc	100

Tolerance limit was defined as a ratio that causes less than ±5 percent interference.
[a] with 10 mg/L EDTA.
[b] with 10 mg/L ethylenediamine.
[c] with 10 mg/L dimethylglyoxime.
[d] with 10 mg/L 1,5-diphenylcarbazide.
[e] with 10 mg/L SCN.

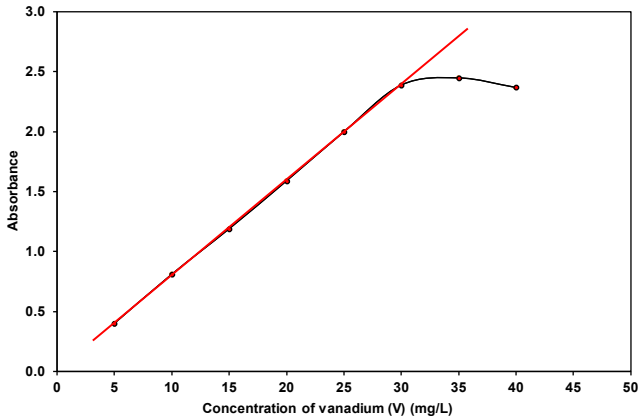


Figure 2. Calibration graph of A: 10-30 mg/L of vanadium(V).

3.1.4. Effect of foreign ions

The effect of over 60 anions, cations, and complexing agents on the determination of only 1 mg/L of vanadium was studied. The criterion for an interference was an absorbance value varying by more than 5% from the expected value for vanadium alone [16,28]. 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. The interference was from Cu^{2+} and Mo^{6+} ions. The interference from these ions is probably due to the complex formation with Sal-BH. The greater tolerance limits for these ions can be achieved by using several masking methods. To eliminate the interference of Mo^{6+} and Cu^{2+}, EDTA and SCN^- are used as masking agents, respectively. 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. However, for those ions whose tolerance limit has been studied, their tolerance ratios are mentioned in Table 3.

3.2. Composition of the absorbent complex

Job's method [29] of continuous variation method was applied to ascertain the stoichiometric composition of the complex under the optimum conditions (Table 2). A vanadium-Sal-BH (1:1) complex was indicated by this method. The molar ratio method [30] was also applied to ascertain the stoichiometric composition of the complex. A vanadium-Sal-BH complex was indicated by both methods and the stoichiometry was also found to be 1:1 (Metal: Ligand). The probable structure of the vanadium-Sal-BH complex is verified by Job's method [29] and the molar ratio method [30] shown in Scheme 1.

3.3. 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 0-2.0 % for 0.01-300 µg of vanadium in 10 mL, indicating that this method is highly precise and reproducible.

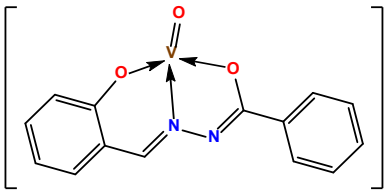
Table 4. Determination of vanadium(V) and vanadium(IV) speciation in mixtures.

V(V):V(IV)	Taken (mg/L)		Found (mg/L)		Error (mg/L)	
	V(V)	V(IV)	V(V)	V(IV)	V(V)	V(IV)
1:1	1.00	1.00	0.99	0.98	0.01	0.02
1:1	1.00	1.00	1.00	1.00	0.00	0.00
1:1	1.00	1.00	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						
1:5	1.00	5.00	0.99	4.98	0.01	0.02
1:5	1.00	5.00	0.98	4.98	0.02	0.02
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) = ±0.006						
1:10	1.00	10.00	0.98	9.99	0.02	0.01
1:10	1.00	10.00	0.99	9.98	0.01	0.02
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) = ±0.006						

Table 5. Determination of vanadium in some certified reference materials.

Certified reference materials (Composition, %)	Vanadium (%)		
	Certified value	Found (n=5)	RSD [b]
BCS-CRM-220/2 : High Speed steels : C=0.88, Si=0.19, Mn=0.30, Cr=5.12, Mo=4.92, V=1.94, Co=0.32, Cu=0.09, W=6.97	1.94	1.93	1.5
BCS-ECRM-577/1 : Ferro-Vanadium Alloy s: C=0.089, Si=1.79, Mn=0.158, Al=0.414, V=50.16, Cu=0.054	50.16	49.8	2.0
SS-CRM-486/1 : High Speed steel s: C=0.74, Si=0.27, Mn=0.21, Cr=4.54, Mo=5.20, V=1.82, W=5.80	1.82	1.83	1.8
GSBH-40101-96 $Cr_{12}MoV$: Dies steel : Cr=11.63, Mo=0.98, V=0.411, Ni=0.095, Cu=0.082, C=1.5, Si=0.235, Mn=0.155	0.411	0.4105	2.2
YSBC-11403-95 : High tensile steel: $W_7Mo_3Cr_5V_3Co_5$: C=1.17, Si=0.21, Mn=0.22, Cr=4.92, Ni=0.22, V=3.25, Mo=3.22	3.25	3.24	2.5
CRM-ASTMRCVD-74231 : Human Serum(Quest-Diagonistics, ISO-17025) [a]	0.83 [e]	0.81	1.2
CRM 029 : Sigma-Aldrich : Soil (ISO /17025)	71.0 [d]	70.0	1.9
CRM-MESS-3 : Sediments	234±10 [c]	232±3.0	2.5
NIST@SRM-1577c : Bovine liver	8.17±0.66 [d]	8.16±1.0	2.0
NIST-CRM-TMDW : Drinking water	30.0 [f]	29.5	1.5

[a] The CRMs were obtained from the National Research Council, Govt. of Canada.
[b] The measure of precision is the relative standard deviation (RSD).
[c] Values in µg/g.
[d] Values in mg/kg.
[e] Values in µg/kg.
[f] Values in µg/L.



Scheme 1. Probable structure of [V(Sal-BH)] (1:1) complex according to Job's method.

The detection limit (3s/S of the blank) and Sandell's sensitivity (concentration for 0.001 absorbance unit) for vanadium were found to be 0.1 µg/L and 1.0 ng/cm², respectively. Speciation of vanadium(IV) and vanadium(V) in mixtures. The results obtained from speciation of vanadium(IV) and vanadium(V) in the mixtures were highly reproducible (Table 4). The method was also tested by analyzing several certified reference materials which were in good agreement with the certified values (Table 5). The reliability of our V-chelate procedure was tested by recovery studies. The average percentage recovery obtained with the addition of vanadium spikes to some environmental water samples was quantitative as shown in Table 6. The results of biological analysis by the spectrophotometric method were in excellent agreement with those obtained by AAS and ICP-OES (Table 7). The results of soil sample analysis by the spectrophotometric method were found to be in excellent agreement with those obtained by AAS (Table 8). The results of food and vegetable analysis by spectrophotometric method were also found to be in excellent agreement with those obtained by AAS and ICP-OES (Table 9). The results of pharmaceutical samples by the spectrophotometric method were in excellent agreement with those obtained by ICP-OES (Table 10). Hence, the precision and accuracy of the method were excellent, which is shown in Table 11. With suitable masking, the reaction can be made highly selective.

3.4. Application of the proposed method

To verify the validity, the proposed method was successfully applied to the determination of vanadium in a number of environmental, biological, soil, vegetable, and food and pharmaceutical samples, e.g., speciation vanadium(IV) and vanadium(V) in mixtures.

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

Suitable aliquots (1-2 mL) of vanadium(V+IV) mixtures (preferably 1:1, 1:5, 1:10) were taken in a 250 mL conical flask. 4 M H_2SO_4 (preferably 3-5 drops) and 2 % (*w*:*v*) freshly prepared ammonium persulphate (preferably 5-10 mL) were added for oxidation of tetravalent vanadium to pentavalent

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

Samples		Vanadium (µg /L)		Recovery ± s (%)	s_r (%) [b]
		Added	Found [a]		
Tap Water		0	6.80		
		100	106.0	99.25±0.5	0.31
		500	508.0	100.2±0.6	0.33
Well Water		0	5.50		
		100	106.0	100.4±0.5	0.16
		500	505.5	100.0±0.0	0.00
River Water	Karnaphuli (bank)	0	16.00		
		100	116.0	100.0±0.0	0.00
		500	518.0	100.3±0.8	0.22
	Karnaphuli (middle)	0	20.00		
		100	120.0	100.0±0.0	0.00
		500	522.0	100.3±0.6	0.25
	Halda (upper)	0	15.00		
		100	116.0	100.8±1.5	0.27
		500	520.0	100.9±1.8	0.42
	Halda (lower)	0	12.00		
		100	112.0	100.0±0.0	0.00
		500	515.0	100.5±1.0	0.25
Lake water	Kaptai (upper)	0	20.50		
		100	120.0	100.0±0.0	0.00
		500	525.0	100.9±0.8	0.39
	Kaptai (lower)	0	25.00		
		100	125.0	100.0±0.0	0.00
		500	530.0	100.9±1.5	0.32
Sea Water	Bay of Bengal (upper)	0	15.00		
		100	114.0	99.13±0.5	0.15
		500	518.0	100.5±0.8	0.28
	Bay of Bengal (lower)	0	18.00		
		100	118.0	100.0±0.0	0.00
		500	520.0	100.3±0.5	0.34
Drain Water	Eastern Cables [c]	0	65.00		
		100	168.0	101.8±1.0	0.52
		500	570.0	100.8±1.2	0.34
	Elite Paint [d]	0	85.00		
		100	182.0	98.3±1.8	0.46
		500	590.0	100.8±1.7	0.35
	BSRM steels [e]	0	155.0		
		100	153.0	106.0±1.5	0.26
		500	660.0	100.7±1.7	0.18

[a] Average of five replicate determinations of each sample.
[b] The measure precision is the relative standard deviation (s_r).
[c] Eastern Cables Ltd., North Patenga, Chittagong.
[d] Elite Paint and Chemical Industries Ltd., Byezid Bostami Road, Chittagong.
[e] BSRM steels, Byezid Industrial Area, Chittagong.

vanadium. After adding 10 mL water, the mixture was heated gently if necessary, for 5 minutes to drive off the excess persulphate and then cooled to room temperature (25±5°C). After cooling and neutralizing with dilute NH_4OH in the presence of 3-5 mL of 0.01 % (*w*:*v*) EDTA solution, the solution was transferred into a 25 mL volumetric flask and 2.5 mL of 3.28×10^{-3} M reagent (Sal-BH) solution was added followed by the addition of 2.5 mL of 0.002 M H_2SO_4. It was made up to the mark with de-ionized water. The absorbance was measured then being cooled at room temperature (25±5 °C), at 392 nm against a reagent blank. The total vanadium content was calculated with the help of a concurrently prepared calibration graph.

An equal aliquot (1-2 mL) of the vanadium(V+IV) mixture was taken into a 250 mL Pyrex conical flask. The solution was neutralized with dilute NH_4OH in the presence of 3-5 mL of 0.01 % (*w*:*v*) EDTA solution. After the content of the beaker was transferred quantitatively into a 25 mL volumetric flask, 2.5 mL of 3.28×10^{-3} M Sal-BH reagent solution was added, followed by the addition of 2.5 mL of 0.002 M H_2SO_4. It was made up to the mark with deionized water. After 5 min, the absorbance was measured following the general procedure at 392 nm against a reagent blank, as before. The vanadium concentration was calculated in µg/L or ng/L with the aid of a 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 determine the vanadium(IV) present in the mixture. The results of the assessment of speciation of vanadium(V) and vanadium(IV) were found to be highly reproducible. The occurrence of such reproducible results is also reported for different oxidation states of vanadium [31]. The results of a set of determination are given in Table 4.

3.4.2. Determination of vanadium in some certified reference materials

Following a method recommended by Mitra [32], a 50 mL Erlenmeyer flask was filled with accurately weighed 0.1 g amount of an alloy or steel sample containing 0.411-50.16% of vanadium in the presence of excess oxidizing agent to oxidize vanadium(IV) to vanadium(V). Then, 10 mL of 20 % (*w*:*v*) sulfuric acid was added and while carefully covered with a watch glass until the brisk reaction subsided. Followed by the addition of 10 mL of concentrated HNO_3, the solution was heated and simmered gently after until the decomposition of all residual carbides. After further addition of 2 mL of 1+1 H_2SO_4 and 2 mL 2% (*w*:*v*) freshly prepared ammonium persulphate, the solution was evaporated carefully to dense white fumes of sulphur trioxide, then cooled to room temperature (25±5 °C). To dissolve the soluble salts, the contents of the Erlenmeyer flask were warmed after suitable dilution with deionized water. After being cooled and neutralized with dilute NH_4OH solution in the presence of 1-2 mL of 0.01% (*v*:*v*) EDTA solution, the resulting solution was filtered through a Whatman No. 40 filter paper into a 100 mL calibrated flask. The residue (silica and tungstenic acid) was washed with a small volume of hot 1+99 H_2SO_4, followed by water; the volume was made up to mark with deionized water.

Table 7. Determination of vanadium in some human fluids.

Sample	Vanadium (µg /L)						Sample Source [a]
	AAS (n=5)		Proposed method (n=5)		ICP-OES (n=5)		
	Found [b]	RSD (%)	Found [b]	RSD (%)	Found [b]	RSD (%)	
Blood	10.0	1.0	11.0	1.2	10.5	1.3	Normal adult (M)
Urine	2.5	0.8	2.8	1.0	3.0	1.0	
Blood	15.0	1.5	16.8	1.5	14.8	1.5	Skin disease patient (F)
Urine	3.5	1.0	3.8	1.2	3.6	1.1	
Blood	375.0	2.0	380.5	2.0	385.0	2.5	Lung cancer patient (M)
Urine	76.0	1.5	80.8	1.8	78.0	1.8	
Blood	20.5	1.8	22.8	1.9	21.5	2.0	Manic patient (M)
Urine	4.8	1.0	5.0	1.3	4.9	1.5	
Blood	8.0	1.0	10.0	1.3	9.0	1.2	Diabetic patient (F)
Urine	2.0	0.8	2.5	1.0	2.8	0.8	
Blood	228.0	2.0	230.8	2.1	232.0	2.5	Liver cirrhosis patient (M)
Urine	58.0	1.5	60.2	1.8	61.5	1.8	
Blood	238.0	2.5	240.5	2.6	242.0	2.8	Kidney damage patient (F)
Urine	65.0	1.5	68.8	1.8	70.0	2.0	
Blood	12.0	1.0	13.0	1.0	13.8	1.3	Heart disease patient (F)
Urine	3.2	0.8	3.5	0.9	4.0	0.8	
Milk	5.5	1.0	6.5	1.2	6.8	1.5	Lactating mother

[a] Samples were collected from Chittagong Medical College Hospital, Chittagong.
[b] The measure of precision is the relative standard deviation.

Using EDTA or tartrate as the masking agent, a suitable aliquot (1-2 mL) of the above-mentioned solution was taken into a 10 mL calibrated flask and the vanadium(V) content was determined; as described under general procedure. The proposed procedure for the spectrophotometric determination of vanadium was applied to the analysis of single element CRM of V, estuarine sediment (CRM-MESS-3), soil (CRM 029), human serum (CRM-ASTMRCVD-74231), bovine liver (NIST@SRM - 1577c) and drinking water (NIST-CRM-TMDW), the CRMs obtained from the National Research Council, Govt. of Canada, using tartrate or EDTA as masking agents, following a method recommended by Melwanki *et al.* [33]. Based on five replicate analyses, the average vanadium concentration determined by the spectrophotometric method was in excellent agreement with the certified values. The results are given in Table 5.

3.4.3. Determination of vanadium in environmental water samples

Each filtered (with Whatman No. 40) environmental samples (25 mL) contained in a 50 mL Pyrex beaker were added to 1 mL of concentrated H_2SO_4 and 2 mL of concentrated HNO_3 in the presence of freshly prepared excess ammonium persulphate solution in a fume cupboard to oxidize vanadium(IV) to vanadium(V) and the mixture was heated on a hot plate until white fumes of sulfur trioxide, following a method recommended by Greenberg *et al.* [34]. The solution was cooled and neutralized with dilute NH_4OH solution in the presence of 1-2 mL of 0.01 % (*w*:*v*) EDTA solution. The resulting solution was then filtered through a Whatman No. 40 filter paper and quantitatively transferred into a 25 mL calibrated flask and made up to the mark with de-ionized water.

An aliquot (1-2 mL) of this water sample was pipetted into a 10 mL calibrated flask and the vanadium content was determined as described under the general procedure using tartrate or EDTA as the masking agent. To test the validity of our method, we have analyzed different types of portable and polluted waters in spike and unspike conditions. The reliability of our spectrophotometric method was tested by recovery studies. The average percentage recovery obtained for the addition of a vanadium(V) spike to some environmental water samples was quantitative. The results of analysis of environmental water samples from various sources for vanadium are shown in Table 6.

Most spectrophotometric methods for the determination of vanadium in natural and sea water require preconcentration or standard addition of vanadium [35]. The concentration of vanadium in natural and sea water is a few µg/L in Japan [36]. The mean concentration of vanadium found in US drinking waters is 6 µg/L [34].

3.4.4. Determination of vanadium in some biological samples

The biological samples were digested accordingly following a particular method [37]. The samples were initially dried in an oven at 120 °C for 24 h. The blood serum samples were further dried in an oven at 20 °C for an additional 24 h. Then, the biological samples were dry-ashed in a muffle furnace at 300 °C for 24 h, then at 450 °C for 4 h. After dry ashing, samples were wet-ashed with 5 mL of concentrated nitric acid and 2 mL of 30% hydrogen peroxide. The mixture was heated to just below boiling until complete oxidation of vanadium(IV) to vanadium(V). The samples were cooled and wet-ashed three more times in the same manner. At completion, the white residue was dissolved with 10 mL of 1 M HNO_3 by heating of an excess oxidizing agent according to the method recommended by Stahr [38] and diluted to 20.0 mL for analysis. After neutralizing pH by addition of dilute NH_4OH in the presence of 1-2 mL of a 0.01% (*w*:*v*) tartrate or EDTA solution. After being filtered, the resultant solution was transferred quantitatively into a 25 mL 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 using tartrate or EDTA as the masking agent. The results of biological analysis by the spectrophotometric method were found to be in excellent agreement with those obtained by AAS and ICP-OES. The results are shown in Table 7.

The low value for the heart disease patient is probably due to a low vanadium concentration in the environment. On the other hand, the abnormally high values for the human lung cancer patients are probably due to the involvement of high vanadium concentrations with As and Zn. The occurrence of such high vanadium contents is also reported in lung cancer patients from some developed countries [39].

3.4.5. Determination of vanadium in some surface soil samples

An air-dried homogenized soil sample (10 g) was accurately weighed and placed in a 100 mL micro-Kjeldahl flask. The sample was digested in the presence of an excess oxidizing agent (2 mL of 2% freshly prepared ammonium persulfate solution) to oxidize vanadium(IV) to vanadium(V) following the method recommended by Jackson [40].

Table 8. Determination of vanadium in some Bangladesh surface soil samples.

Serial no	Vanadium (µg/g)				Sample source [c]
	Proposed method (n=5)		AAS (n=5)		
	Found (n=5) [a]	RSD (%) [b]	Found (n=5) [a]	RSD (%) [b]	
S_1	80.5	1.0	83.0	1.3	Road side soil (Dhaka-Chittagong)
S_2	75.0	1.0	78.5	1.5	Agricultural soil (Chittagong University Campus)
S_3	90.5	1.5	93.8	1.8	Industrial soil (Eastern cables)
S_4	115.5	1.6	120.0	2.0	Industrial soil (Eastern refinery)
S_5	135.8	1.8	140.0	2.0	Industrial soil (BSRM, Byezid, Chittagong)
S_6	92.5	1.5	95.8	1.8	Madina tannery soil (Jalalabad, Chittagong)
S_7	105.0	1.8	108.0	2.0	Paint soil (Berger paint, Chittagong)
S_8	70.5	1.5	72.0	1.8	Beach soil (Bay of Bengal)
S_9	88.5	1.8	90.5	2.0	Triple super phosphate complex soil (Patenga, Chittagong)
S_{10}	125.8	2.0	128.0	2.5	Esturine soil (Karnaphuli river)

[a] Average of five analyses of each sample.
[b] The measure of precision is the relative standard deviation (RSD).
[c] Composition of the soil samples: C, N, P, K, Na, Ca, Mg, Ce, Cu, Mo, Fe, Pb, V, Zn, Mn, Co, NO_3^- and SO_4^- etc.

Table 9. Determination of vanadium in some food, fruit, and vegetable samples collected from the local market of Chittagong.

Sample	Vanadium (mg/kg)					
	Proposed method (n=5)		AAS (n=5)		ICP-OES (n=5)	
	Found [a]	RSD (%) [b]	Found [a]	RSD (%) [b]	Found [a]	RSD (%) [b]
Chicken meat (*Gallus cibum*)	2.61	1.0	2.53	1.0	2.65	1.2
Chicken liver (*Gallus jecur*)	2.98	1.2	2.95	1.0	3.01	1.5
Egg white (*Albumen*)	1.88	0.8	1.85	0.8	1.92	0.9
Egg yolk (*Vitellus*)	2.38	1.2	2.35	1.0	2.42	1.0
Carrot (*Daucus carota*)	0.82	0.5	0.79	0.5	0.85	0.8
Tomato (*Lycopersicon esculentum*)	1.21	0.8	1.15	0.5	1.22	1.0
Parsley (*Petroselinum crispum*)	1.91	0.9	1.85	0.8	1.95	1.0
Rice (*Oryza sativa)*	1.52	0.8	1.48	0.8	1.55	1.0
Spinach (*Spinacia oleracea*)	0.85	0.5	0.84	0.5	0.845	0.6
Black pepper (*Piper nigrum*)	1.05	0.8	0.998	0.5	1.08	1.0
Cashew nut (*Anacardium occidentale*)	2.85	1.0.	2.55	1.0	2.75	1.0
Milk	0.42	0.1	0.35	0.1	0.40	0.1
Mushrooms (*Agaricus bisporus*)	2.08	0.9	2.05	0.8	2.10	1.0
Shellfish	108	1.5	105	1.5	106	1.6
Dill seed (*Anethum graveolens*)	0.535	0.5	0.531	0.1	0.333	0.8

[a] Average of five replicate analyses of each sample.
[b] The measure of precision is the relative standard deviation (RSD).

As the heating process continued 1-mL of H_2SO_4 is added and heated for about 5 minutes to dense white fumes of sulphur trioxide. The solution was then cooled at room temperature and neutralized with dilute NH_4OH solution in presence of 1-2 mL of 0.01 % (*w*:*v*) EDTA solution. The content of the flask was then filtered through a Whatman No. 40 filter paper and quantitatively transferred into a 25 mL calibrated flask and made up to the mark with deionized water.

A suitable aliquot (1-2 mL) of the final solution was pipetted out into a 10 mL calibrated flask and the vanadium content was determined as described under the general procedure using tartrate or EDTA as the masking agent. The vanadium content was then determined by the above procedure and quantified from a calibration graph prepared concurrently. The results of soil analysis by spectrophotometric method were also found to be in excellent agreement with those obtained by AAS. The average value of vanadium in the Chittagong region surface soil was found to be 53.27 µg/kg. The results are shown in Table 8.

3.4.6. Determination of vanadium in vegetable, food, and fruit samples

The vegetable and fruit samples collected prior to determination were pretreated in the following way: Edible portion of the samples was first washed clean with tap water followed by rewashing with deionized water. After removing deionized water from the surface of vegetables and fruits, the samples were cut into small pieces and dried at 65 °C in oven. An air dried vegetables and fruits samples (10 g) were ground in a mortar and taken in a 100 mL micro-Kjeldahl flask in the presence of excess oxidizing agent and digested following a method recommended by Stahr [38] 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 at room temperature. 1 mL volume of concentrated sulfuric acid was added carefully, followed by the addition of 2 mL of concentrated HF, and the heating was continued for at least ½ hr and then cooled. In the resulting solution, 2 mL of 2% (*w*:*v*) of freshly prepared ammonium persulfate is added. The mixture of each foodstuff was heated below the boiling point for 5-10 min to oxidize vanadium(IV) to vanadium(V). The solutions were then cooled and neutralized with dilute NH_4OH in the presence of 1-2 mL of 0.01 % (*w*:*v*) EDTA solution. The resulting solution was filtered through a Whatman No. 40 filter paper and quantitatively transferred into a 25 mL calibrated flask and mixed well and made up to the mark with deionized water.

The food samples used were rice, wheat, and corn and these were used under dry conditions. Each sample was first ground in a mortar. Corn and fruit samples (2 g) or rice and wheat samples (1 g) were weighed accurately and placed in a porcelain crucible and charred in an electric furnace; the sample was ashen at 555 °C in a muffle furnace in the presence of excess oxidizing agent following a method recommended by Mitra [32]. To it, 2.0 mL of HCl and 10 mL of water were added to the ash. The mixture of each foodstuff was heated with 2 mL of 2 % (*w*:*v*) and freshly prepared ammonium persulphate was added below the boiling point for 5-10 min to complete the oxidation from vanadium(IV) to vanadium(V). The solutions were cooled and neutralized with dilute NH_4OH in the presence of 1-2 mL of 0.01 % (*w*:*v*) EDTA solution and filtered. The resulting solution was quantitatively transferred into a 25 mL calibrated flask and mixed well and made up to the mark with deionized water.

A suitable aliquot (1-2 mL) of the final digested solution was pipetted into a 10 mL calibrated flask and the vanadium content was determined as described under the general procedure using tartrate as the masking agent.

Table 10. Determination of vanadium in some pharmaceutical samples.

Sample Type [a]	Brand name	Trade name	Vanadium (mg/kg or m/dL)				
			Reported / Claimed value	Proposed method (n=5)		ICP-OES (n=5)	
				Found (n = 5)	RSD (%) [b]	Found (n = 5)	RSD (%) [b]
Tablet	Renata	Bigmet	500	505.0	1.5	508.0	1.5
Tablet	Incepta	Nobesit	500	498.0	1.8	499.0	1.8
Tablet	ACI	Metform	500	495.0	1.8	497.0	2.0
Tablet	Unimed Unihealth MFG Ltd.	Meglu	500	499.0	2.0	503.0	2.0
Tablet	Drug International Ltd.	Oramet	500	496.0	1.8	498.0	2.1
Tablet	United Chemicals and Pharmaceuticals	Alaxen	0.5	0.498	0.1	0.495	0.15
Insulin	Square	Ansulin	15 [c]	14.8 [c]	1.0	14.5 [c]	1.0
Insulin	ESKAYEF	Mixtard	20 [c]	19.5 [c]	1.5	19.8 [c]	1.8

[a] Samples were collected from local market, Chittagong.

[b] The measure of precision is the relative standard deviation.

Table 11. Statistical comparison of the proposed method with ICP-OES and AAS (conventional) methods *.

Sample	F-test results		
	AAS method (n=5)	Proposed method (n=5)	ICP-OES method (n=5)
	(s_1^2/s_2^2)	(s_1^2)	(s_1^2/s_3^2)
Water	0.29	0.31	0.35
Water	0.00	0.00	0.00
Water	0.25	0.23	0.26
Blood	0.98	0.83	0.78
Blood	1.00	1.00	1.00
Blood	0.95	0.97	1.00
Urine	0.80	0.83	0.85
Urine	0.81	0.92	1.00
Urine	1.00	0.84	0.90
Rice	0.81	0.85	0.88
Chicken meat	1.00	1.00	0.84
Egg (yolk)	0.85	1.00	1.00

* Tabulated F-value for (5, 5) degrees of freedom at $P(0.98)$ is 5.72. s_1 = Standard deviation of the proposed method, s_2 = Standard deviation of AAS method, s_3 = Standard deviation of ICP-OES method.

The results of food and vegetable analysis by spectrophotometric method were also found to be in excellent agreement with those obtained by AAS and ICP-OES. The results are shown in Table 9.

3.4.7. Determination of vanadium in pharmaceutical samples

The finished pharmaceutical samples (each V containing tablets or 10 mL insulin or required weight) were quantitatively taken in a beaker and digested following a method recommended by Ahmed *et al.* [41]. 10 mL of concentrated nitric acid was added and heated to dryness and then added to 10 mL of 20% (*v*:*v*) of H_2SO_4. For complete oxidation from vanadium(IV) to vanadium(V), the mixture was heated with 2 mL of 2 % (*w*:*v*) freshly prepared ammonium persulphate was added below the boiling point for 5-10 min.The volume was reduced to 2.5 mL and then cooled to room temperature. The solution was then neutralized with dilute NH_4OH in the presence of a 1-2 mL of 0.01% (*w*:*v*) EDTA or tartrate solution. The resulting solution was then filtrated and quantitatively transferred to a 25 mL calibrated flask and made up to the mark with deionized water.

An aliquot (1-2 mL) of this digested sample was pipetted into a 10 mL calibrated flask and then the vanadium content was determined as described under the general procedure using tartrate as a masking agent. The results of some pharmaceutical analyses by the spectrophotometric method were found to be in excellent agreement with those obtained by reported values and ICP-OES. The analyses of pharmaceutical samples from several Pharmaceutical Companies for vanadium are given in Table 10.

Precision and accuracy of the results have been supported statistically by F-test and confidence interval (95%) to compare the proposed method with ICP-OES and AAS results. It has been sufficient to give the statistical results in the explanation of the statements. Hence, the precision and accuracy of the method were excellent, which are shown in Table 11.

4. Conclusions

A new simple, sensitive, and inexpensive method based on vanadium-Sal-BH complex was developed for the determination of vanadium in some environmental, biological, soil, food, and pharmaceutical samples. Compared with other methods [16-20,41,42] in the literature Table 1, the proposed method has several remarkable analytical characteristics:

i) The proposed method is highly sensitive with molar absorptivity of the complex of 2.5039×10^5 L/mol.cm. Thus, the amount of ng/g of vanadium can be determined.
ii) The proposed method is very simple, rapid, and stable. The reaction of vanadium(V) with Sal-BH is completed rapidly in 1 min at room temperature, so it does not involve any stringent reaction conditions and offers the advantage of high complex stability (24 h).
iii) The method has added an advantage of determining individual amounts of vanadium(IV) and vanadium(V). With suitable masking agents, the reaction can be made highly selective.

The proposed method using Sal-BH in aqueous solutions is not only highly sensitive, but also highly selective and simple. Therefore, this method will be successfully applied to the routine monitoring of trace amounts of vanadium in environmental, biological, soil, food, and pharmaceutical samples.

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Disclosure statement

Conflict of interest: The authors declare that they have no conflict of interest.
Author contributions: All authors contributed equally to this work.
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