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A Simple Spectrophotometric Method For The Determination Of Vanadium In Real, Environmental, Biological And Soil Samples Using 2-Hydroxyacetophenobenzoylhydrazone

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ABSTRACT

A very simple, ultra-sensitive and highly selective non-extractive spectrophotometric method for the determination of trace amount of vanadium(V) using 2-Hydroxyacetophenobenzoylhydrazone(HAPBH) has been developed. 2-Hydroxyacetophenobenzoylhydrazine(HAPBH) reacts in slightly acidic (0.0005-0.025M H_2SO_4) 50% 1,4-dioxane media with vanadium(V) to give a yellow chelate which has an absorption maximum at 422 nm. The reaction was instantaneous and absorbance remains stable for over 48 hours. The average molar absorption co-efficient and Sandell's sensitivity were found to be 7.70×10^4 L mol^{-1} cm^{-1} and 10 ng cm^{-2} of V^V, respectively. Linear calibration graphs were obtained for 0.1-15 μg mL^{-1}. The stoichiometric composition of the chelate is 1:2 (V:HAPBH). Large excess of over 60 cations, anions and complexing agents (like tartrate, oxalate, chloride, phosphate, thio-urea, 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), soil samples and complex synthetic mixtures. The method has high precision and accuracy (s = ± 0.01 for 0.5 μg mL^{-1}).

KEYWORDS

Spectrophotometry;
Vanadium determination;
2-hydroxyacetophenobenzoylhydrazone;
Environmental;
Biological samples.

INTRODUCTION

Vanadium in trace amounts is important industrially[1]: as a biological nutrient[2], epidemiological preventive[3], toxicant[4], environmental pollutant[5] and occupational hazard[6]. 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 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 suggests that vanadium may also play a beneficial role in the prevention of heart disease. Shamberger[7] 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 using simple, rapid methods is of paramount importance. Various methods for the determination of vanadium have been suggested, several of which were spectrophotometry[8,9], FIA[10], polarography[11], and AAS[12]. Spectrophotometric methods, however, are the most attractive for the determination of trace-level elements owing to its simplicity, low cost of the instrument, easy handling and sensitivity. Most of the kinetic spectrophotometric methods based on solid and solvent phase extraction or catalytic effect of vanadium, when applied to real samples for the determination of vanadium in trace level lake of satisfactory, sensitivity and selectivity. Therefore, its accurate determination at trace levels using simple and rapid method is of paramount importance.

The aim of this study is to develop a simpler spectrophotometric method for trace determination of vanadium using newly synthesized unique reagent HAPBH. 2-Hydroxyacetophenobenzoylhydrazone (HAPBH) has been reported as a complexometric reagent but has not previously been used for the spectrophotmetric determination of metals. The method possess distinct advantages over existing methods[13-23] with respect to sensitivity, selectivity, range of determination, simplicity, speed, pH/acidity range, thermal stability, accuracy, precision and ease of operation. The method is based on the reaction of non-absorbent HAPBH in acidic solution with vanadium(V) to produce a highly absorbent yellow-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 do not show any absorbance.

EXPERIMENTAL

Apparatus

A Shimadzu (Kyoto, Japan) (Model-160) double-beam UV-VIS spectrophotometer and a Jenway (England, UK) (Model-3010) pH meter with combination electrodes were used for measurements of absorbance and pH, respectively. A polarized Zeeman (Model-Z5000) atomic absorption spectrometer equipped with a microcomputer controlled nitrous oxide-acetylene flame was used for comparing of the results.

Reagents and solutions

All chemicals used were of analytical-reagent grade of the highest purity available. Doubly distilled de-ionized water and HPLC-grade 1,4-dioxane, 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 vigorous contamination control was used when the vanadium levels in specimens were low.

2-Hydroxyacetophenonebenzoylhydrazone (HAPBH) (10^{-3} M): The reagent 2-Hydroxyaceto

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phenonebenzoylhydrazone(HAPBH) was synthesized according to the method of M.J.Ahmed et al.[24], was recrystallized from ethanol using 1,4-dioxanic solutions of HAPBH, no appreciable absorbance was observed with in seven days. In the present work freshly prepared 1,4-dioxanic solutions of the reagent (10^{-3} M) were used.

Vanadium(V) Standard Solution, (1.96×10^{-2} M): A 100 mL amount of stock solution (1 mg mL^{-1}) of pentavalent V was prepared by dissolving 0.2269 mg of purified-grade (Merck proanalysis grade) ammonium metavan-date (Merck) in doubly distilled de-ionized water containing 1-2 mL of nitric acid (1+1) to prevent hydrolysis. More dilute standard solutions were prepared by appropriate dilution of aliquots from the stock solution with de-ionized water as and when required.

Vanadium(IV) Standard Solution: A 100 mL amount of stock solution (1 mg mL^{-1}) of tetravalent vanadium was prepared by dissolving 390.7 mg of purified grade vanadyl sulfate (Fisher Scientific) in doubly distilled deionized water. More dilute standard solutions were prepared from this stock solution as and when required.

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[25].

Procedure

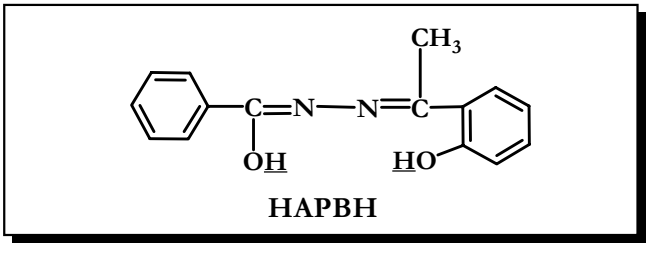
An aliquot containing not more than 1-150mg of V(V) was transferred into 10 mL calibrated flask, 0.5 - 2.0 mL (preferably 1.0 ml) of 2.5×10^{-3} M H_2SO_4, 3-5 mL 1,4-dioxane solution and 100-200 fold molar excess of HAPBH reagent solution (1 ml of 1.96×10^{-2} M)were added successively and the mixture diluted to volume with water. The absorbance was measured at 422 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.

RESULTS AND DISCUSSION

Factors affecting the absorbance

Absorption spectra

The absorption spectra of vanadium-HAPBH system in 1.0 mL 2.5×10^{-3} M H_2SO_4 sulfuric acid medium was recorded using the spectrophotometer. The absorption spectra of the vanadium(V)-HAPBH system is a symmetric curve absorbance at 422 nm with maximum and the average molar absorption coefficient was found to be 7.70×10^4 L mol^{-1} cm^{-1}(Figure 1), where as the reagent HAPBH did not show any absorbance. In order to obtain high sensitivity, a wavelength of 422 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[24].



HAPBH

Effect of a solvent

Because HAPBH is partially soluble in water, an organic solvent was used for the system. of the various solvents (benzene, chloroform, acetone, carbon tetrachloride, nitrobenzene, isobutyl alcohol, 1- butanol, isobutyl methyl ketone , ethanol and 1,4- dioxane) studied, 1,4-dioxane was found to be the best solvent for the system. No absorbance was observed in the organic phase with the exception of 1- butanol. In 50 ± 2% (v/v) 1,4- dioxane medium, however, the maximum absorbance was observed; hence, a 50% 1,4- dioxane solution was used in the determination procedure.

Effect of acidity

Among the various acids (nitric, hydrochloric , sulfuric and phosphoric acid) sulfuric acid was found to be the best acid for the system. The absorbance was at a maximum and constant when the 10ml of solution(1 mg mL^{-1}) contained 0.5 - 2.0 mL (preferably 1.0 mL) of 2.5 X 10^{-3} M H_2SO_4 at room tem-

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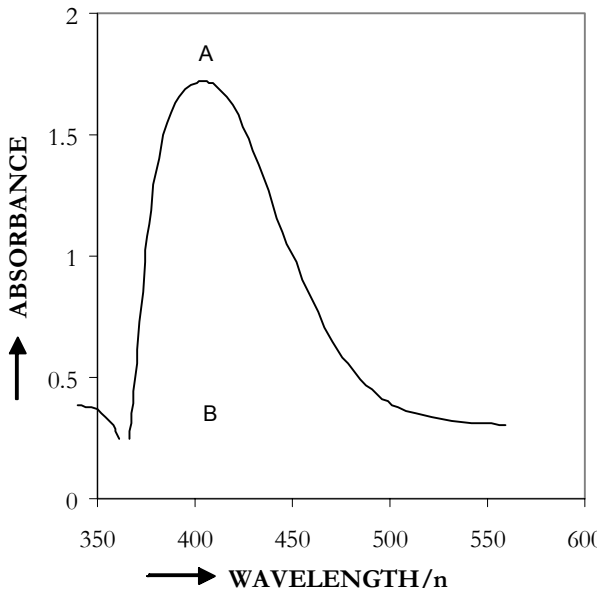

Figure 1: A and B absorption spectra of vanadium (V)-HAPBH and the reagent blank (λ_{max} = 422 nm) in aqueous solutions

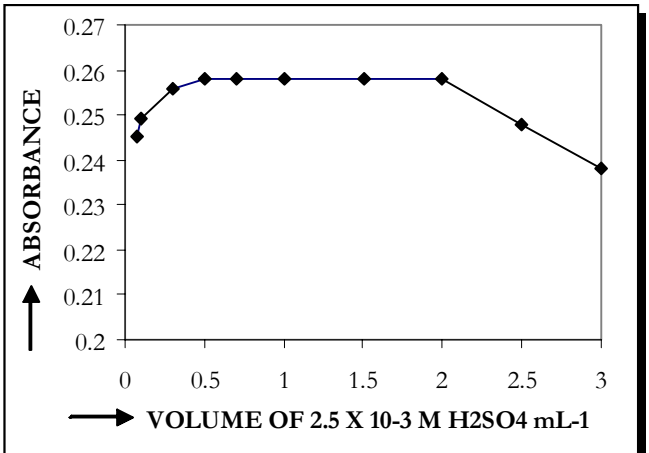

Figure 2: Effect of the acidity on the absorbance of vanadium(V)-HAPBH system

perature(25 ± 5°C). Outside this range of acidity, the absorbance decreased (Figure 2). For all subsequent measurements, 1.0 mL of 0.0025 M sulfuric acid was added.

Effect of time and temperature

The reaction is instantaneous, Vanadium(V)-HAPBH system attained maximum and constant absorbance just after the dilution to volume at room temperature (25 ± 5°C) and remained strictly unaltered for 48 h.(Figure 3)

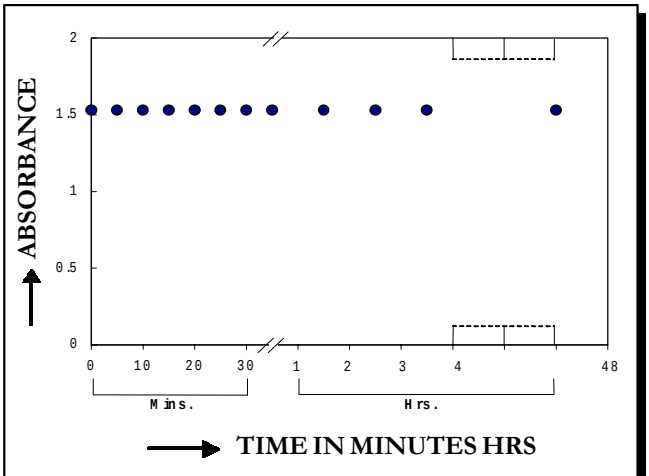

Figure 3: Effect of the time on the absorbance of vanadium(V)-HAPBH system

Effect of reagent concentration

Different molar excesses of HAPBH were added to fixed metal ion concentration and absorbences were measured according to the standard procedure. It was observed that at 1 μg mL^{-1} V^{V} metal, the reagent molar ratios of 1:100-1:200 produced a constant absorbance of the V-chelate (Figure 4). Greater excesses of reagent were not studied. For all subsequent measurements, 1 mL of 1.97 × 10^{-3} M HAPBH reagent was added.

Calibration Graph (Beer's Law and Sensitivity): The effect of metal concentration was studied over

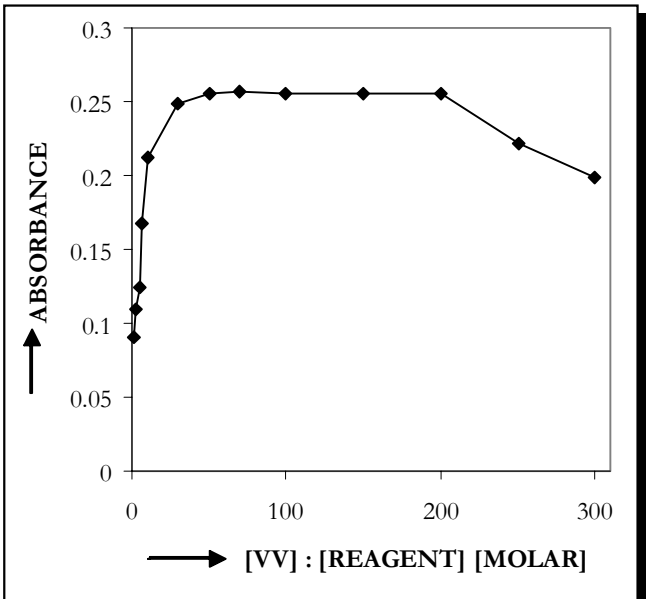

Figure 4: Effect of reagent on the absorbance of vanadium(V)-HAPBH system

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0.1-50 μg mL^{-1} distributed in three sets (1.0, 1.0-10.0, 1.0-50.0) for convenience of measurement. The absorbance was linear for 0.1-15 mg mL^{-1} of vanadium at 422 nm. Of the three calibration graphs(Figure 5-7), the one showing the limit of the linearity range is given in figure 5, the next two were straight-line graphs passing through the origin. The average molar absorption co-efficient and Sandell's sensitivity[26] were found to be 7.70×10^4 L mol^{-1} cm^{-1} and 10 ng cm^{-2} of V^V, respectively.

Precision and accuracy

The relative standard deviation (n=5) was 0-2% for 1-600 μg of V(V) in 10.0 mL, indicating that this method is highly precise and reproducible. The average molar absorption co-efficient and Sandell's sensitivity (concentration for 0.001-absorbance unit) were found to be 7.70×10^4 L mol^{-1} cm^{-1} and 10 ng cm^{-2} of V^V, respectively. The detection limit (3s of the blank) for V(V) was found to be 5 ng mL^{-1}. Regression analyses of Beer's law plots at 422nm revealed a good correlation(R^2= 0.998). The results for total V were in good agreement with certified values (TABLE 4). The reliability of our V-chelate procedure was tested by recovery studies. The average percentage recovery obtained for addition of V(V) spike to some environmental water samples was quantitative as shown in TABLE 5. The method was also tested by analyzing several synthetic mixtures containingV(V) and diverse ions (TABLE 3). The results of biological analyses by the spectrophotometric method were in excellent agreement with those obtained by AAS (TABLE 6). The results of speciation of V(IV) and V(V) in mixtures were highly reproducible (TABLE 8). Hence, the precision and accuracy of the method were excellent.

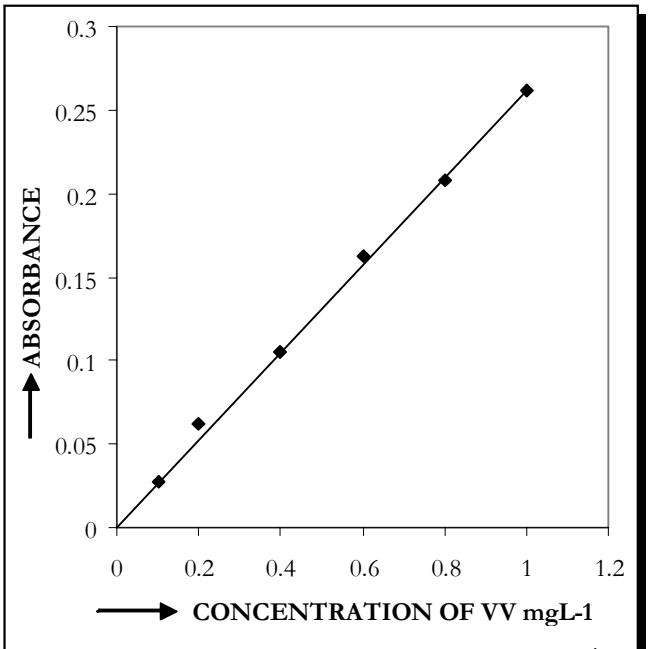

Figure 5: Calibration graph- A: 0.1 – 1.0 mgL^{-1} of Vanadium(V)

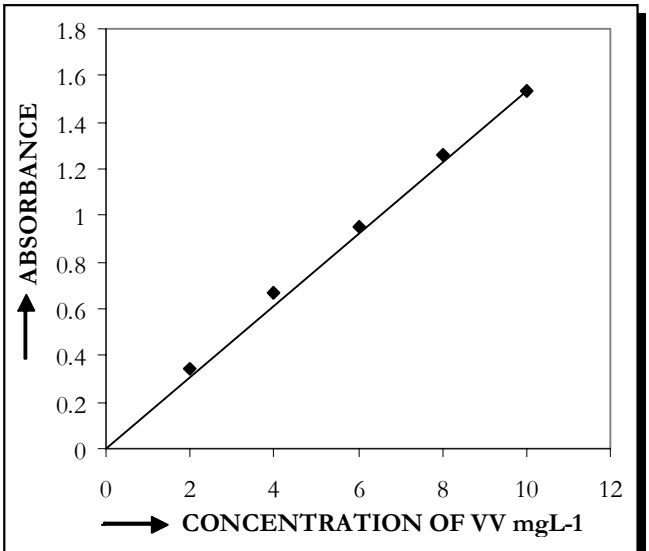

Figure 6: Calibration graph- B, 1 – 10 mgL^{-1} of vanadium(V)

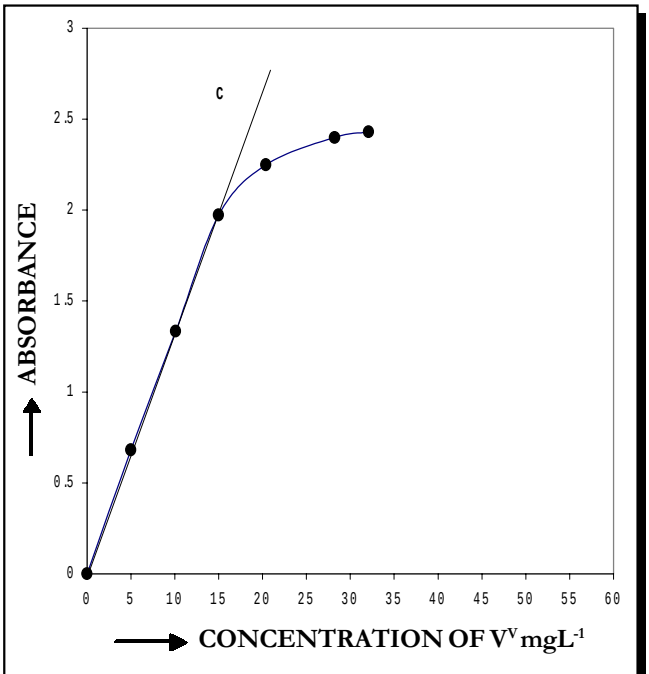

Figure 7: Calibration graph- C, 0 – 15 mgL^{-1} of vanadium(V)

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Effect of foreign icons

The effect of over 50 ions and complexing agents on the determination of only 1 gmL^{-1} of V^{V} was studied. The criterion for an interference[27] was an absorbance value varying by more than 5% from the expected value for vanadium alone. There was no interference from the following: 1000-fold amount of sulfate, sulfite, nitrate, perchloride, bromide, chloride, iodide, thiocynade, No, Mg, Ba, K, Mn^{II}, Zn, NH_4^+, Ca or Cd; 100-fold amounts of tartrate, fluoride, Co^{III}, Ni^{II}, or Hg^{II}; 10-fold amounts of EDTA, oxalate, citrate, Cr^{III}, Pb^{II} azide, persulphate, phosphate, W^{VI}, As^{III}, As^{V}, Cs, Mn^{VII}, Cr^{VI}, Fe^{II}, Fe^{III}, CN^-, or U^{VI}. EDTA prevented the interference of a 10-fold amounts of Ag, Al, Cu^{II} or $Mo^{VI.}$ The quantities of these diverse ions mentioned were the acutal amounts added and not the tolerance limits. A 50-fold excess of iron Fe^{II} and Fe^{III} or Cu^{II} could be masked with ammonium thiocyanide or fluoride. During the interference studies, if a precipitate was formed, it was removed by centrifugation.

Composition of the absorbance

Job's method[28] of continuous variation and the molar ratio[29] method were applied to ascertain the stoichiometric composition of the complex. A V-HAPBH (1:2) complex was indicated by both methods.

TABLE 1: Selected analytical parameters obtained with the optimization experiments

Parameters	Studied Value	Selected valuefor V^{V}
Wavelength/λ_{max}(nm)	200 - 600	422
Acidity/ M H_2SO_4	0.0003-0.01	0.0013-0.005 (preferably 0.0025)
Time/h	0 – 48	48
Temperature/ ^{O}C	25 ± 5	25 ± 5
Reagent (fold molar excess, M:R)	1:1- 1:300	1:100 - 1:200
Linear range/mg L^{-1}	0.01 – 100	0.1 - 15
Average Molar Absorption Co-efficient / L mol^{-1} cm^{-1}	4.79 X 10^4	4.79 X 10^4
Detection limit / μg L^{-1}	10	10
Reproducibility (% RSD)	0 – 2	0 – 2

TABLE 2: Table of tolerance limits of foreign ions

Species x	Tolerance ratio x/V (w/w)	Species x	Tolerance ratio x/V (w/w)
Aluminium	50 [b]	Iron(II)	50
Ammonium(I)	200	Iron(III)	50 [c]
Arsenic(III)	100	Indium(III)	50 [a]
Arsenic(V)	100	Mercury(II)	50 [a]
Ascorbic acid	50	Magnesium	100
Azide	100	Manganese(II)	100
Barium	100	Manganese(VII)	10[b]
Beryllium	50 [b]	Molybdenum(VI)	20[a]
Bromide	100	Nickel	50[b]
Chloride	200	Phosphate	100
Citrate	1000	Potassium	100
Tartrate	1000	Sodium	100
EDTA	200	Silver(I)	50
Fluoride	200	Strontium	100
Iodide	100	Selenium(IV)	50[a]
Calcium	100	Selenium(VI)	50
Cadmium	100	Thallium(I)	100
Cobalt(II)	50	Tungsten(VI)	50[b]
Cobalt(III)	100	Vanadium(IV)	50 [a]
Chromium(III)	100	Zinc	50 [a]
Chromium(VI)	50[a]	Bismuth(III)	50 [a]
Cesium	50[a]	oxalate	1000
Copper(II)	100	Thiocyanide	100
Cerium(III)	100	Nitrate	1000

Tolerance limit was defined as ratio that causes less than 5 percent interference
[a]with 10 mgL^{-1} tartrate. [b]with 10 mgL^{-1} EDTA. [c]with 10 mgL^{-1} chloride.

Applications

The present method was successfully applied to the determination of vanadium(V) in a series of synthetic mixtures of various compositions, in a number of real samples e.g. several Certified Reference Materials (CRM), in a number of environmental, biological and soil 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 5). The results of biological analyses by the spectrophotometric method were found to be in excellent agreement

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with those obtained by AAS. The results are shown in TABLE 6

A) Determination of vanadium in synthetic mixtures

Several synthetic mixtures of varying compositions containing V and diverse ions of known concentrations were determined by the present method using tartrate as masking agent and the results were found to be highly reproducible. The results are shown in TABLE 3.

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

A 0.1-g amount of alloy or steel sample containing 0.52- 2.09% of venadium was weighed accurately and placed in a 50-mL Erlenmeyer flask[30]. To it, 10 mL of 20%(v/v) H_2SO_4 was added, carefully covering the flask with a watch glass until the brisk reaction subsided. The solution was heated and simmered gently after the addition of 5 ml of concentrated HNO_3 until all carbides were decomposed. The solution was evaporated carefully to dense white fumes to drive off the oxides of nitrogen and then cooled to room temperature (25+5°C). After suitable dilution with de-ionized 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 in the presence of 1-2 mL of 0.01% (w/v) tartrate or EDTA solution. The resulting solution was filtered, if necessary, through a Whatman No. 40 filter paper into a 50-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 de-ionized water.

A suitable aliquot (1 -2 mL) of the above solution was taken into a 10-mL calibrated flask and the vanadium content was determined as described under procedure, using fluoride or thiocyanide as masking agent. Results are shown in TABLE 4.

C) Determination of vanadium in environmental waters

TABLE 3: Determination of vanadium in some synthetic mixtures

Sample No.	Composition of mixture / mgL^{-1}	Vanadium (V)/mgL^{-1}		Recovery ± s (%)
		Added	Found*	
A	V^V	0.50	0.49	98 ± 0.5
		1.00	1.00	100 ± 0.0
B	As in A + Cd(25) + Mg^{2+}(25) + Hg^{2+}(25) + Tartrate (50)	0.50	0.50	100 ± 0.0
		1.00	1.02	102 ± 0.6
C	As in B + NH_4^+(25) + Zn(25) + NO_3^-(25) + EDTA (20)	0.50	0.49	98 ± 0.5
		1.00	0.99	99 ± 0.4
D	As in C + Ca(25) + Ba(25) + Cr^{3+}(25)	0.50	0.53	106 ± 1.0
		1.00	1.05	105 ± 0.8
E	As in D + Bi^{3+}(25) + Mn^{2+}(25)	0.50	0.54	108 ± 2.0
		1.00	1.08	108 ± 1.8

[a] Average of five analyses of each sample, [b] The measure of precision is the SD.

TABLE 4: Determination of vanadium in certified reference materials

Certified Reference Materials	Vanadium(%)		
	Certified value	Found[a](n=5)	R.S.D(%)
BAS - CRM 64b high-speed steel(Cr, Mo,V and Te)	1.99	1.985	1.35
BCS - CRM 220/1 high - speed steel (C, Si, S, P, Mn, Mo, V, Ni, Co, Cr, W and Cu)	2.09	2.095	1.45
BCS - CRM 200/2 high - speed tool steel (C, Si, S, P, Mn, Mo, V, Cr, W and Ni)	0.54	0.58	1.20

[a]Average of five determinations

Each filtered environmental water sample (1000 mL) evaporated nearly to dryness with a mixture of 1 ml concentrated H_2SO_4 and 5 ml of concentrated HNO_3 in a fume cupboard, following a method recommended by Greenberg et al.[22] and was heated with a 10 mL of de-ionized water in order to dissolves the salts. The solution was then cooled and neutralized with dilute NH_4OH solution in the presence of a 1-2 mL of 0.01 % (w/v) tartrate solution. The resulting solution was then filtered and quantitatively transferred into a 25-ml calibrated flask and made up to the mark with de-ionized water.

An aliquot (1mL) of this preconcentrated water sample was pipetted into a 10-mL calibrated flask and the vanadium content was determined as described under the Procedure, using thiocynide or fluoride as masking agent. The analyses of environmental water samples from various sources for vanadium is shown in TABLE 5.

Most spectrophotometric methods for determination of vanadium in natural and seawater require preconcentration of vanadium[23]. The concentration of vanadium in natural and seawater is a few μgmL^{-1} in Japan[17]. The mean concentration of vanadium found in US drinking water is 6 ng mL^{-1}[23].

D) Determination of vanadium in biological samples

Human blood (10-20 mL) or urine (30-50 mL) was taken into a 100-mL micro-Kjeldahl flask. A glass bead and 50 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[31]. A 1 mL volume of concentrated sulfuric acid was added carefully, followed by the addition of 1.0 mL of 70% $HCIO_4$, and heating was continued to dense white fumes, while repeating HNO_3 addition if nec-

TABLE 5: Determination of vanadium in some environmental water samples

Sample		Vanadium/µg L^{-1}		Recovery ± s (%)	s_r[b] (%)
		Added	Found [a]		
Tap water		0	1.8		
		100	102.0	99.8 ± 0.3	0.32
		500	503.0	99.7 ± 0.2	0.35
Well water		0	9.5		
		100	108.0	101± 0.4	0.19
		500	510.0	99.7 ± 0.5	0.29
River water	Karnaphuly (upper)	0	12.5		
		100	112.0	100.4 ± 0.1	0.18
		500	515.0	99.5 ± 0.5	0.30
	Karnaphuly (lower)	0	15.0		
		100	115.5	99.6 ± 0.2	0.21
		500	515.0	100 ± 0.0	0.00
Sea water	Bay of Bengal (upper)	0	6.5		
		100	106.0	100.5 ± 0.3	0.35
		500	507.5	99.8 ± 0.1	0.15
	Bay of Bengal (lower)	0	7.5		
		100	107.5	100 ± 0.0	0.00
		500	509.0	99.7 ± 0.4	0.30
Drain water	Karnaphuly paper Mill[c]	0	35.0		
		100	135.0	100.3 ± 0.5	0.45
		500	540.0	99.2 ± 0.6	0.55
	Elite Paint	0	40.5		
		100	140.0	100 ± 0.0	0.00
		500	545.0	99 ± 0.1	0.18
	Eastern Refinery [e]	0	150.0		
		100	255.0	98 ± 0.7	0.49
		500	645.0	100.4 ± 0.6	0.45

[a] average of the five replicate determination, [b] The measure precision is the relative standard deviation(s_r) , [c] Karnaphuly Paper Mill, Chandraghona, Chittagong, [d]Elite Paint, Nasirabad, Chittagong, [e] Eastern Refinery, Chittagong.

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essary. Heating was continued for at least ½ hr and then cooled. The content of the flask was filtered and neutralized with dilute ammonia in the presence of 1-2 mL of a 0.01 % (w/v) tartrate solution, transferred quantitatively into a 10-mL 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 the procedure using fluoride or thiocyanide as 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 6.

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 is also reported in cancer patients from some developed countries[4]. 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[23].

TABLE 6: Determination results for human fluids

Serial No.	Sample	Vanadium / μg L^{-1}		
		AAS (n=5)	Proposed method (n = 5)	RSD,%
1	Blood 1	9.5	10.0	1.2
	Urine 1	2.5	2.8	1.0
2	Blood 2	375.0	382.0	1.5
	Urine 2	75.0	84.0	1.3
3	Blood 3	10.0	12.0	1.2
	Urine 3	3.0	3.1	1.0

***Samples were from Chittagong Medical College Hospital: 1. Heart-disease patient; 2. Lung cancer patient (M), and 3. Normal adult (M)**

E) Determination of vanadium in 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 an oxidizing agent, following the method recommended by Jakson[32]. 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 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 0.05 M H_2SO_4 needed to give a final acidity of 0.01-0.06 M H_2SO_4 was added, followed by 1-2 mL of 0.01% (w/v) fluride or thiocyanide 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 7.

TABLE 7: Determination of vanadium in some surface soil

Serial No.	Vanadium [a] / μg g^{-1}	Sample Source
S_1[c]	0.0225 ± 0.01[b]	Agriculture soil (Chittagong University Campus)
S_2[c]	0.029 ± 0.005	Marine soil (Bay of Bengal)
S_3[c]	0.065 ± 0.01	Estuarine Soil (Karnaphuli)
S_4[c]	0.028 ± 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.

F) Determination of vanadium (V) and vanadium (IV) in mixtures

Suitable aliquots (1-2 mL) of molybdenum (VI +V) mixtures (preferably 1:1, 1:5, 1:10) were taken in a 25 mL conical flask. A few drops of 0.001M sulfuric acid and 1-3 mL of 1% (w/v) potassium permanganate solution were added to oxidize the tetratavalent 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. 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 1.96×10^{-2} M HAPBH reagent solution was added followed by addition of 0.5 mo of .001 M H_2SO_4., it was made up to the mark with de-ionized water. The absorbance was measured after 1 min at 422 nm

TABLE 8: Determination of vanadium(IV) and vanadium (V) in mixtures

Sl No.	V(IV) : V(V)	V taken/mgL^{-1}		V, found/ mgL^{-1}		Error/ mgL^{-1}	
		V(IV)	V(V)	V(IV)	V(V)	V(IV)	V(V)
1	1:1	1.00	1.00	0.99	0.98	0.01	0.02
1	1:1	1.00	1.00	1.00	1.00	0.00	0.00
1	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	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; Mo V(IV)= ± 0.0058							

against a reagent bland. The total vanadium content was calculated with help of the calibration graph.

An equal aliquot of the above vanadium (VI + 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 0.5 mL of 0.001 M H_2SO_4 solution was added followed by addition of 1 mL of 1.96×10^{-2} M HAPBH and made up to a volume with de-ionized water. After 1 min the absorbance was measured against a reagent blank, as before. The vanadium concentration was calculated in μgL^{-1} or μgmL^{-1} 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. Occurrence of such reproducible results are also reported for different oxidation states of vanadium[33]. The results of a set of determination are given in TABLE 6.

CONCLUSION

In this paper, a new simple, sensitive, selective and inexpensive method with V-HAPBH complex was developed for the determination of vanadium in industrial, environmental, biological and soil samples, for continuous monitoring to establish the trace levels of vanadium in different samples matrices. Although many sophisticated techniques such as pulse polarography, HPLC, AAS, ICP-AES, and ICP-MS, are available for the determination of rare metals 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 rare metals in real samples down to ng g^{-1} levels in aqueous medium at room temperature (25 ± 5)°C.

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Full Paper

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