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Procedia Engineering 51 (2013) 347 – 354

Procedia Engineering

www.elsevier.com/locate/procedia

Chemical, Civil and Mechanical Engineering Tracks of 3rd Nirma University International Conference (NUiCONE 2012)

Liquid-Liquid Extraction and Spectrophotometric Determination of Vanadium(*V*) with *p*-Carboxy-N-Phenyl-Calix[4]resorcinarene-hydroxamic Acid

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Abstract

The synthesized p-carboxy-N-phenyl-calix[4]resorcinarene-hydroxamic acid PCNPC4RAHA is reported for the extraction and preconcentration of V(V) from environmental samples in the presence of numerous ions. The extract has been subjected to the determination of V(V) by uv-vis spectrophotometry and inductively coupled plasma atomic emission spectrometry (ICP-AES). Various significant parameters like pH, concentration of V(V), concentration of reagent, and effect of solvents are optimized. The wavelength of maximum extraction (λmax), molar absorptivity (ε), linear concentration range obeying Beer's law, effect of diverse ions, limit of detection (LOD), limit of quantification (LOQ), and preconcentration factor has been determined. The two phase stability constant ($\log\beta_4$), and thermodynamic parameters viz. ΔG, ΔH, and ΔS have also been determined. The complexation of vanadium with PCNPC4RAHA is also characterized by favourable enthalpy change. The stoichiometry of metal-reagent complex has been established by modified Job's plot method. To check the validity of the proposed method, V(V) is also determined in environmental, biological samples, and some standard reference materials from NIST (National Institute of Standards and Technology) and BCS (British Chemical Standards).

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Keywords: Resorcinarenes, hydroxamic acid, liquid-liquid extraction, preconcentration.

1. Introduction

Calix[4]resorcinarenes deliver a flexible molecular platform for the elaboration of more complicated molecular host systems. Calix[4]resorcinarenes form an array of complexes with metal ions, organic molecules, neutral molecules and organometallics by changing the chelating groups on the eight hydroxyl groups present at extraannular position or on the upper rim . This capability makes them particularly attractive as multifunctional receptors which is to be used in molecular recognition studies[1-3].

Several methods have been reported for the determination of metal ions in diverse medium by calixarenes. Until now, few reports have appeared on the use of calix[4]resorcinarenes for extraction of metal ion. Several groups have studied the calix[4]resorcinarenes and their complexation with alkali metal ions especially potassium ions[4-5].

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1877-7058 © 2013 The Authors. Published by Elsevier Ltd.
Selection and peer-review under responsibility of Institute of Technology, Nirma University, Ahmedabad.
doi:10.1016/j.proeng.2013.01.048

Hydroxamic acids have emerged as a versatile chelating group for the separation and determination of the large number of metal ions[6-7]; especially for transition metal ions[8] and uranyl ion[9]. In recent years a few calixarene with hydroxamic acid as a functional group have been synthesized and used for the complexation[10] studies.

Vanadium is a trace element, and is highly essential for some living organisms[11]. In humans[12], it is mainly found in teeth, bone, hairs and nails. However, it becomes toxic when its concentration exceeds 0.5 ppm. Thus vanadium can play a vital role in biology as counter ions for protein, DNA, RNA, and in various biological organelles.[11-13] It has a great significance as a catalyst for petroleum refining, geochemical transportation etc. Hydroxamic acids are having remarkable versatility as complexing reagent for vanadium[8]. Several methods have been reported for the determination of vanadium mainly based on the liquid-liquid extraction technique followed by spectrophotometry[14-15]. These methods although sensitive, are not selective especially in food matrixes. The presence of cations such as molybdenum, iron, copper, zinc, etc shows significant interference.

In this paper, a eight armed p-carboxy-N-phenyl-calix[4]resorcinarene-hydroxamic acid (PCNPC4RAHA)[16] is reported for the extraction and preconcentration of **V**(*V*) from environmental samples in the presence of large number of ions by spectrophotometry. Further, the extract has also been subjected, to the determination of **V**(*V*), by inductively coupled plasma atomic emission spectrometry (ICP-AES).

2. Experimental

2.1. Instrumentation and Measurements

Absorbance was measured by using Hitachi 3210 UV-visible spectrophotometer with matching 10 mm quartz cells. Plasma scan model 710 sequential inductively coupled plasma atomic emission spectrometer with plasma scan multitasking computer and peristaltic pump was used. The following operating conditions were set for ICP- AES. incident power, 2000 W; Rf 27.12 MHz; GMK nebulizer; sample concentration, 1ppm; RF power, 5W; observation height, 14 mm; peristaltic pump flow rate, 1 ml min^{-1}; argon coolant flow rate, 9.71 min^{-1}; argon carrier flow rate, 0.81 min^{-1}; Intergraph period, 10 s; resolution, 0.004 nm wavelength, 309.31 nm.

2.2. Chemicals and Reagents

All the chemicals used were of analytical reagent grade of E-Merck, Qualigens or BDH, unless otherwise specified. All aqueous solutions were prepared with Milli–Q water through out the entire studies. The standard stock solution of vanadium (1.00×10^{-2} M) was prepared by dissolving 0.585 g of ammonium metavanadate (NH_4VO_3) in 500 ml Milli–Q water. The concentration of the vanadium was determined spectrophotometrically. The stock solution of PCNPC4RAHA (3×10^{-4} M) were prepared in ethyl acetate. The experimental solution was subsequently prepared by appropriate dilution of the stock solution. For extraction studies, appropriate volumes of metal solutions and PCNPC4RAHA were mixed.

2.3. Sample Preparation of Reference Material, Soil, Plant and Blood Samples

The certified reference materials were analyzed to determine the accuracy of the proposed procedure in accordance with National Institute of Standards and Technology (NIST) and British Chemical Standard (BCS) guidelines[17].

The soil samples were prepared as, 1.5 g dried soil was digested with 50 ml concentrated hydrochloric acid and 10 ml concentrated nitric acid for 1 h on a sand-bath, then the solution was evaporated to dryness. The residue was moistened with 7 ml of HF in a Teflon beaker, digested on a water bath, and evaporated. The residue was boiled with 50 ml 0.1 M hydrochloric acid, filtered and the filtrate and washings were evaporated to dryness and the residue was taken up and diluted accurately to 100 ml with 0.1 M hydrochloric acid.

The plant samples were prepared as follows: 500 g of plant sample was ashed at 450 ºC for 2-3 h. 10 gm of this ash was transferred into a evaporating dish and digested on a sand-bath with 100 ml concentrated hydrochloric acid and 20 ml concentrated nitric acid for about 1 h. The solution was immediately centrifuged and the supernatant liquid was decanted from any siliceous plant matter. The residue obtained was boiled with 50 ml, 0.1 M hydrochloric acid and filtered. The filtrate was then evaporated to dryness, and the residue was taken up and diluted accurately to 100 ml with 0.1 M hydrochloric acid.

1-2 ml of blood sample was digested with 0.25 g of ammonium persulphate and 10-20 ml of concentrated hydrochloric acid for 1 h, and then the mixture was diluted and filtered. The filtrate was then evaporated to dryness and residue was taken up and diluted to volume in a 25 ml standard flask with 0.1 M hydrochloric acid.

2.4. Liquid-Liquid Extraction of Vanadium

The sample solution containing 1.37-93.6 µg of vanadium was transfer into a 25 ml colloquially sep funnel. The optimum acidity of 6 M was attuned with the conc. hydrochloric acid and water. The mixture was shaken with 3 ml of 3×10^{-4} M PCNPC4RAHA in ethyl acetate for 15 min. The organic extract was separated, dried and transferred to a 10 ml volumetric flask. To ensure the completion of the process, the extraction was repeated with addition ml of PCNPC4RAHA. The combined extracts and washings were diluted to the mark with ethyl acetate. Solutions thus prepared were examined for UV–visible absorptions at 495nm against the blank reagent. The concentration of the remaining vanadium ion present in the aqueous phase was measured by ICP-AES. The concentration of vanadium ion extracted into the organic phase $[VO_2^+{}_{org}]$ as complex was estimated by

$$[VO_2^+{}_{org}] = [VO_2^+{}_{aq}]_{(initial)} - [VO_2^+{}_{aq}]_{(final)}$$

where $[VO_2^+{}_{aq}]_{(initial)}$ is the initial concentration of vanadium and $[VO_2^+{}_{aq}]_{(final)}$ is the final concentration of the vanadium ion in the aqueous phase.

The percent extraction (%E) of metal ion, was calculated by

$$\%E = [VO_2^+{}_{org}] / [VO_2^+{}_{aq}]_{(initial)} \times 100$$

The extraction of vanadium complex in the ethyl acetate after suitable dilution was also determined by ICP-AES.

3. Experimental

3.1. Spectrophotometric Determination of V(V)

The liquid-liquid extraction and followed by spectrophotometric determination of vanadium [17] was carried out with the newly synthesized p-carboxy-N-phenyl-calix[4]resorcinarene-hydroxamic acid. The maximum absorption of the pinkish violet colored complex was measured at 495 nm and showed a bathochromic shift of 172 nm from that of the reagent blank (Fig. 1). The molar absorptivity (L mol^{-1} cm^{-1}) was found to be 5540. The system obeys Beer's law in the range of 0.137–9.36 µg ml^{-1} of vanadium (V).

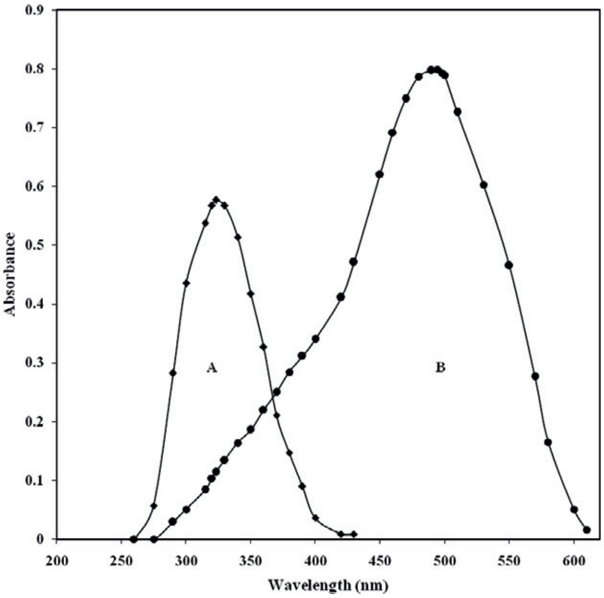

Fig. 1. Comparative spectra of reagent PCNPC4RAHA (3×10^{-4} M) (A) and its vanadium complex (B) in ethyl acetate

The regression analysis equation obtained from the calibrated standard solution can be represented as Abs = 0.1218 × Conc. - 0.00032 with the correlation coefficient, r = 0.997. Under the optimum conditions of the extraction process, the limit of detection (LOD), limit of quantification (LOQ) and precision as RSD (relative standard deviation) was 8.89 ppb, 30.5 ppb and 1.9% respectively. For ICP-AES measurements, the vanadium calix[4]resorcinarene-hydroxamate ethyl acetate extract was inserted into plasma by means of peristaltic pump after appropriate dilution with ethyl acetate. For the ICP-AES measurements, a linear calibration graph was obtained from 11 to 200 ppb of vanadium (V) in the aqueous phase.

3.2. Effect of Variables on the extraction

- Acidity

  Maximum color intensity of vanadium- PCNPC4RAHA complex was obtained with 6.0-6.5 M HCl, but as the concentration of acid solution decreases, the percentage extraction of vanadium also decreased (Fig. 3), hence all the extraction were carried out at 6.0 M HCl.

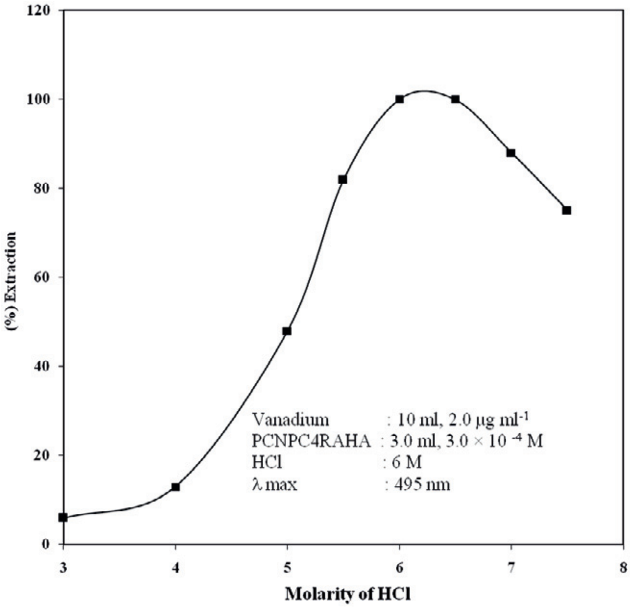

Fig.2 Effect of molarity of acid on the extraction of vanadium- PCNPC4RAHA complex

- Reagent Concentration

  Extraction with various concentration of reagent (PCNPC4RAHA) showed that 3 ml of 0.05 % was sufficient for the quantitative extraction of vanadium, whereas the extraction was incomplete at the lower concentration of PCNPC4RAHA (table 1).

Table.1. Effect of Reagent (PCNPC4RAHA) Concentration for the Extraction of V(*V*)

Vanadium: 10 ml, 2.0 µg ml^{-1}
HCl : 6 M
Solvent : Ethyl acetate
λ_{max} : 495 nm

PCNPC4RAHA (0.05 %) (ml)	Colour of the Complex	Molar absoptivity (l mol^{-1} cm^{-1})
1.0	Pinkish violet	0.95×10^3
1.5	Pinkish violet	2.40×10^3
2.0	Pinkish violet	3.74×10^3
2.5	Pinkish violet	4.86×10^3
3.0	Pinkish violet	5.54×10^3
3.5	Pinkish violet	5.54×10^3
4.0	Pinkish violet	5.54×10^3
4.5	Pinkish violet	5.54×10^3

- Solvents

  The vanadium- PCNPC4RAHA complex was extracted with various solvents like ethyl acetate, chloroform, toluene, and benzene (table 2). For extraction of vanadium under the optimum conditions, ethyl acetate was found to be best solvent in comparison to the others.

Table.2 Effect of Solvents on the Extraction of V(*V*)-PCNPC4RAHA Complex

Vanadium : 10 ml, 2.0 μg ml-1
HCl : 6 M
PCNPC4RAHA: Ethyl acetate
λ max : 495 nm

Solvent	Dielectric Constant	Extraction (%)	Molar absoptivity ($l\ mol^{-1}\ cm^{-1}$)
Benzene	2.28	12	0.61×10^3
Toluene	2.30	38	2.28×10^3
Chloroform	4.80	86	4.83×10^3
Ethyl acetate	6.40	100	5.54×10^3

- Shaking Time

  The optimum shaking time was found to be 14-15 min, which was sufficient for quantitative extraction of vanadium. The extraction was not affected by further shaking, indicating the equilibrium state for complexation.

3.3. Stoichiometry of the Complex

The stoichiometric ratio of the vanadium- PCNPC4RAHA complex was determined by the modified Job's method of continuous variation. The absorbance of complex 'A_{comp}' of a series of solution containing vanadyl ion (VO_2^+) 'm' and PCNPC4RAHA 'n' at a constant total concentration 'm+n', but different concentration ratios were measured at 495 nm. The absorbance of 'n' was subtracted from the observed absorbance 'Acomp' to obtain the difference absorbance 'ΔA'.

$$\mathbf{\Delta A = A_{comp} - A_n}$$

ΔA values were plotted against the molar ratio of dioxovanadium (V) ion m / (m+n) (Fig. 3). The maximum value for ΔA was clearly obtained at m / (m+n) = 0.82, indicating 4 : 1 stoichiometric ratio of VO_2^+ and PCNPC4RAHA. The accuracy of this result is possible if only a single complex is formed. To verify this, measurement were taken at different selected wavelength, which gave same value for m / (m+n) ratio.

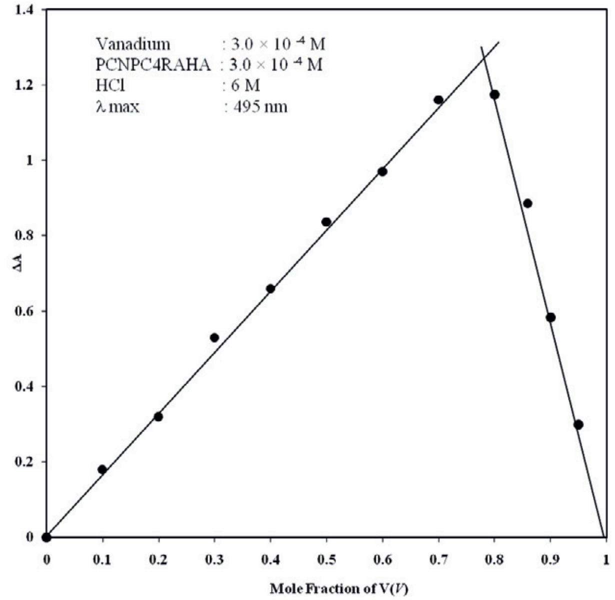

Fig 3. Stoichiometry of V(v)- PCNPC4RAHA complex

3.4. Effect of Temperature and Thermodynamic Parameters

The equilibrium constant (k_{ex}) and two-phase stability constant (log $\beta_4.P_{V\text{-}H8A}$) of vanadium (V) extraction from aqueous solution were also studied at different temperatures between 298 K and 318 K and the results show that the extraction equilibrium constant and two-phase stability constant increases with increase in temperature. The change in extraction equilibrium constant (ln k_{ex}) with temperature can be expressed by Van't Hoff equation

$$d(\ln k_{ex})/dT = \Delta H°/RT^2$$

In order to utilize this equation for calculation, it must be integrated assuming the heat of reaction ΔH remains constant over a small range of temperature.

$$\ln(k_{ex}) = -\Delta H°/RT + \text{constant (intercept)}$$

The plot of (log $\beta_4.P_{V\text{-}H8A}$) against 1/T yields a straight line equation 9401.8 x + 45.694 with slope(x) = -ΔH°/2.303 R Fig.4(a). The mean enthalpy change accompany the complexation is found to be -177.56 kJ mol^{-1} for vanadium in the given range of temperature. The inspection of Fig. 4(b) (ΔH°, -TΔS°, ΔG° → T) reveals that the complexation is driven by favorable enthalpy changes. The negative values of free energy suggest that the reaction is exothermic and favorable for complexation.

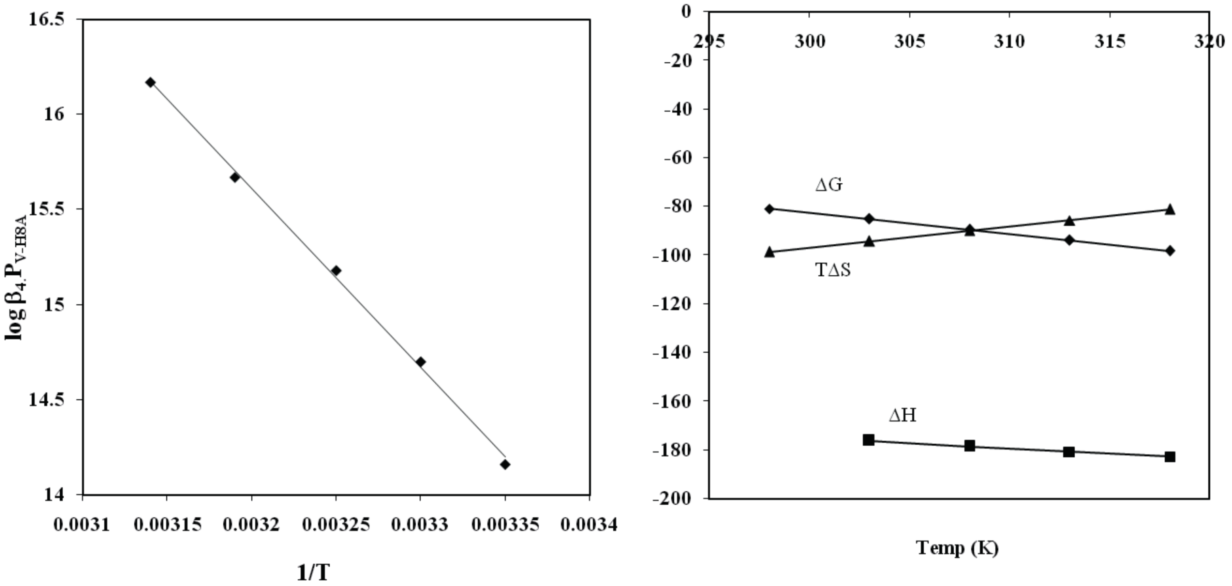

Fig. 4(a). Variation of two phase stability constant with temperature and Fig. 4(b).Variation of thermodynamic parameters with temperature

3.5. Effect of Diverse Ions

The potential sensitivity of the proposed method is indicated by the extraction of the metal ion under the specific extraction conditions. On the other hand, the selectivity of a reagent can be more practically determined under the extraction condition, carried out from the solution which contains numerous metal ions. In order to check the sensitivity and selectivity by the present method, the effect of various ions in the separation and determination of vanadium was studied. The Interference studies were performed by measuring the absorbance of the extracted organic phase and also by carrying out the measurements by ICP-AES of both the extract as well as aqueous phase. Under optimum conditions, tolerance limit of the proposed method was set as the amount of diverse ions which causes a change in the absorbance by ± 0.025 or 2.2 % error in the recovery of the vanadium.

Vanadium was extracted in the presence of large number of metal ions at 6 M HCl and none of them affected the absorbance of vanadium complex. But, niobium, tantalum, titanium, and molybdenum did interfere in the determination of vanadium, which resulted in the increase in the absorbance. The interference due to niobium and tantalum was tolerated by masking them with 0.1 % tartaric acid while the interference of titanium and molybdenum was masked by using 0.25 M oxalic acid as masking agent (table 3).

3.6. Preconcentration of Vanadium

In natural water, the concentration of vanadium is very low for its direct determination. Hence preconcentration or enrichment of vanadium in the sample is essential for detection. The preconcentration of vanadium was measured in terms of its preconcentration factors. The preconcentration study was carried out by extracting 20 μg of vanadium in 1000 ml aqueous phase with 7.5 ml of 0.015% PCNPC4RAHA in ethyl acetate. To evaluate the efficiency of preconcentration, expressed as recovery, the concentration of vanadium in organic phase and the aqueous phase was determined by ICP-AES. Quantitative determination was possible with recovery up to 98% with a conc. factor of 133.

Table.3 Effect of Diverse Ions on the Extraction of V(V)-PCNPC4RAHA Complex

Vanadium : 10 ml, 1.5 μg ml-1
HCl : 6 M
PCNPC4RAHA: 3 ml, 3×10^{-4} M in Ethyl acetate
λ max : 495 nm

Ions	Added as	Amount added (mg)	Recovery of Vanadium (ppm)	
			Spectrophotometry	ICP-AES
Mg^{2+}	$Mg(NO_3)_2$	100	1.48	1.49
Ca^{2+}	$CaCl_2$	100	1.51	1.49
Sr^{2+}	$Sr(NO_3)_2$	100	1.48	1.50
Cu^{2+}	$CuSO_4$	80	1.48	1.50
Cd^{2+}	$CdSO_4$	80	1.48	1.50
Zn^{2+}	$ZnCl_2$	80	1.51	1.50
Hg^{2+}	$HgCl_2$	100	1.51	1.50
Pb^{2+}	$Pb(NO_3)_2$	100	1.48	1.50
Co^{2+}	$CoCl_2$	80	1.49	1.51
Ni^{2+}	$NiCl_2$	80	1.46	1.47
Ga^{3+}	$GaCl_3$	100	1.47	1.50
La^{3+}	$La(NO_3)_3$	100	1.46	1.48
Fe^{3+}	$FeCl_3$	70	1.50	1.51
Cr^{3+}	Cr_2O_3	70	1.49	1.48
Sb^{3+}	$SbCl_3$	80	1.48	1.49
Ti^{4+}[a]	$TiCl_4$	100	1.49	1.52
Nb^{5+}[b]	Nb_2O_5	100	1.51	1.50
Ta^{5+}[b]	Ta_2O_5	100	1.48	1.51
Mo^{6+}[b]	$(NH_4)_6Mo_7O_{24}.4H_2O$	100	1.47	1.50

[a] masked with oxalic acid , [b] masked with tartaric acid

3.7. Sample Analysis

In order to test the accuracy and applicability of the proposed method to the analysis of real samples, some standard reference materials of steel and natural samples of plant and rocks from the industrial area of Naroda and Vatva, Ahmedabad, Gujarat were analyzed. The results for the analysis of standard samples of vanadium are given in Table 4 and for rock, soil, blood samples etc in table 5.

Table.4 Determination of Vanadium in NIST and BCS Standard Samples

No.	Sample	Certified Vanadium (%)	Vanadium Found With Present Method[a] (%)
30	Cr- V steel (NIST)	0.18- 0.21	0.201 ±0.01
153	Cr-V-Co-Mo-W steel (NIST)	1.63- 1.86	1.80 ±0.02
224	Cr-V steel (BCS)	0.240	0.241 ±0.12
242/1	High speed steel (BCS)	1.570	1.569 ±0.02

[a] Average ± standard deviation (10 determinations)

4. Conclusion

The results obtained from the analysis of standard geological samples, standard reference steel samples and natural samples of plants and rocks prove the reliability of the proposed methods for real samples. The limit of detection (8.89 ppb), limit of quantification (30.5 ppb) and the molar absorptivity (5540 L mol^{-1} cm^{-1}) achieved in the present method suggests that the proposed method is simple, specific, and sensitive for extraction and preconcentration of **V**(*V*).

Table.5 Vanadium Found in Natural Sources

Sample	Vanadium Found [a] (ppm)	No. of Determinations	ICP-AES
Rice	1.07± 0.03	10	0.989
Peas	0.75± 0.02	8	0.740
Cabbage	5.90± 0.07	8	6.015
Carrots	3.56± 0.03	9	3.595
Spinach	6.30± 0.06	8	6.290
Potato sample	5.64± 0.09	10	5.623
Onion sample	7.83± 0.08	10	7.750
Tomato	1.61± 0.03	8	1.650
Ripe mango skin	1.81± 0.04	8	1.850
Unripe mango skin	3.45± 0.03	8	3.450
Tobacco	2.29± 0.04	12	2.320
Sea water	0.79± 0.05	12	0.833
Effluent #	1.70± 0.05	12	1.735
Effluent ^	1.86± 0.08	12	1.810
Lake water	1.11± 0.05	10	1.079
Blood sample [c]	0.02± 0.02	12	0.021
Soil [b]	0.08± 0.02	8	0.084

[a] Mean ± standard deviation (spectrophotometrically) from 5 determination
[b] Samples from industrial area of #Naroda and ^Vatva, Ahmedabad, India
[c] Whole blood samples from adult male

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