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SPECTROPHOTOMETRIC DETERMINATION OF VANADIUM (V) USING N-BENZYL CINNAMO HYDROXAMIC ACID AS CHELATING REAGENT

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ABSTRACT

The subject of this research is to study the possibility of determination of trace amount of hazardous element vanadium (V) in environmental samples by the simple, selective, rapid, highly sensitive and novel spectrophotometric method using N-benzyl cinnamo hydroxamic acid as analytical reagent. This method is based on the purple color complex reaction between N-benzyl cinnamo hydroxamic acid and vanadium (V). All variable were studied in order to optimize the reaction conditions. The Beer's law is obeyed for vanadium (V) in the concentration range 0.2-10.0 µg/ml at the maximum absorbance at 490nm. In this method molar absorptivity, sandell's sensitivity, detection limit and quantization limit were reported. The proposed method free from over a wide variety of interference species. The efficiency of the proposed method is shown by the successfully applied to the analysis of vanadium (V) in water and soil samples.

KEYWORDS: Spectrophotometric, Vanadium (V), Cinnamo Hydroxamic Acid, Reagent

Vanadium (V) is on the hazardous elements. Vanadium (V) is a gray or white, shiny powder or solid metal. High amount of vanadium (V) are said to be present in fossil fuels such as crude petroleum, fuel, oils, some, coals, and lignite, burning these fuels releases vanadium (V) in to the air that then seethes on the soil [Kadyan et. al., 2012]. There are cases of vanadium (V) poisoning [Viswanatha et. al., 2012]. The national institute for occupational safety and health [NIOSH] has reported that 35 mg/ml [Priya et. al., 2006] of vanadium (V) can be considered dangerous to human beings, animal and plants. Vanadium (V) amount of greater than this range causing many diseases like nervous depression, vomiting, diarrnoea, anemia lung cancer etc. Many techniques are developed for determination of vanadium (V) such as NAA, ICP, AES, AAS etc [Cherian T. and Narayana B., 2005]. This methods are disadvantageous costly of instruments and lacking sensitivity and simplicity [Keyvanfard M., 2007]. N-benzyl cinnamo hydroxamic acid is used as analytical reagent for the determination of trace amount of vanadium (V). N-benzyl cinnamo hydroxamic acid is derivative of hydroxamic acid reefer's to a class of chemical organic compound having formula $RCONHOHR^{'}$, R= C_6H_5-CH_2-, R'= C_6H_5-CH=CH-.and commonly synthesized by the coupling reaction between N- benzyl hydroxylamine and cinnamoyl chloride [Kakkar R. and Gupta S.P., 2013] (Figure 1).

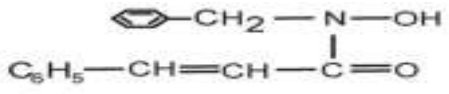

Figure 1: Structure of N-benzyl cinnamo hydroxamic acid

N-benzyl cinnamo hydroxamic acid having property to formed stable colored chelate complex with vanadium (V) due to their oxygen (O) and nitrogen (N) donor legands present structurally in N-benzyl cinnamo hydroxamix acid [Chen et. al., 2011, Lee et.al., 2007, Perkovic et.al., 2010, Reddy et.al., 2008]. In this reaction metal ion is attached with oxygen atom of N-benzyl cinnamo hydroxamic acid through metal-legand bond formation and purple stable chelate complex is formed in the presence of 3M HCl [Kumar et.al., 2008, Varghese and Khadar 2008, Mishra et.al., 2009, Rcheva et.al., 2010, Kadyan et.al., 2012] . The efficiency of the proposed method is shown by the successfully applied to the analysis of vanadium (V) in water and soil samples from Raipur area Siltara (Figure 2).

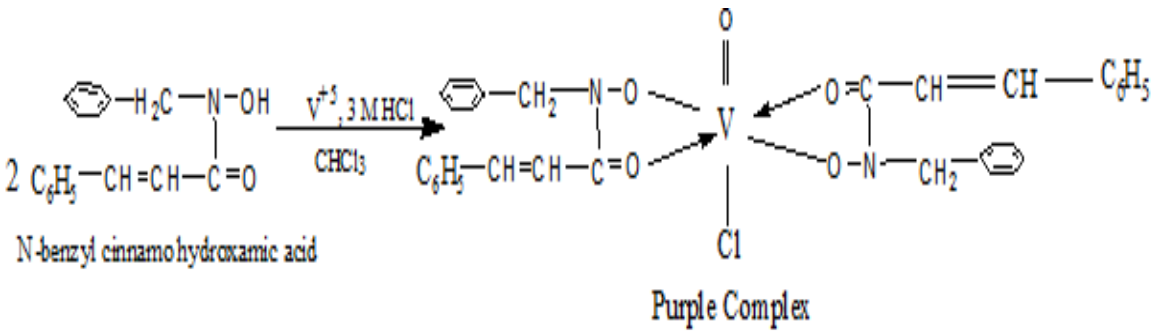

Figure 2: Complex formation between N-benzyl cinnamo hydroxamic acid and vanadium (V)

MATERIALS AND METHODS

Instrumentation

A Systronics UV-Vis 118 spectrophotometer with 1CM matched quartz cell was used for all analytical absorbance for study of complexation with vanadium (V). A digital pH meter (systronic model 331) was used for pH measurements to observe the effect of pH on metal complexation.

Reagents and Chemicals

All chemicals and solvents used were of analytical grade, and double distilled water was used to prepare all solutions in the experiments.

Stock Solution of Vanadium (V)

The stock solution of vanadium (V) 500ppm was prepared by dissolving 1.482gm of ammonium meta vanadate [BDH, AR] in double distilled water and dilute to 1 litre.

N–Benzyl Cinnamo Hydroxamic Acid

N–benzyl cinnamo hydroxamic acid was synthesized by standard method and its 0.09 M solution was used.

Hydrochloric Acid

3 M hydorchloric solutions was used for acidity maintained

Solution of Diverse Ion

Wets method was followed for preparing solution of diverse ions. To get approximately 5mg of metal ion per ml.

PROCEDURE

Standard stock solution containing (0.2-10.8µml) vanadium (V) was pipette out in to a 25ml standard cork calibrated flask,1 Each 0.5 ml of 3M hydrochloric acid (pH 2.4) 5ml of 1.4% (w/v) of N-benzyl cinnamo hydroxamic acid (6.5×10^{-2}M) was added to each solution. The purple color is developing instantaneously and make up to the final volume up to 25ml using double distilled water. Measured against reagent blank and the calibration graph were constructed for find the amount of vanadium (V) [Shekhawat, 2012].

Procedures for Determination of Vanadium (V) In Water Sample

Take 100 ml water sample, 1 ml of concentrated H_2SO_4 and 5 ml of concentrated HNO_3 in a fume cupboard. The solution was then cooled and neutralized with NH_4OH in the presence of 1-2 ml of 0.01% w/v titrate solution. The resulting solution was then transferred in to 25 ml standard flask and make up with distill water. 1ml of this solution was pipette out in to a 10 ml calibrated flask and the content of vanadium was determined contain of vanadium (V) was determined proposed method [Rajput, 2016]. The results are shown in (Table 9).

Procedure for Determination of Vanadium (V) In Soil Sample

An air-dried homogenized soil sample (1gm) was placed in a 100ml kjeldahl flask. The sample was digested with oxidizing agent by recommended method. The content of flask was filtered through Whatt man No. 40 filter paper, in to a 25 ml calibrated flask and neutralized with due dilute ammonia in the presence of 1-2 ml of 0.01% (w/v) titrate solution 1-2 ml of the solution was transferred in to a 25 ml calibrated flask and determination vanadium (V) according to the proposed method [Krishnan, 2012]. The results are shown in (Table 9).

RESULTS AND DISCUSSION

Absorption Spectra

The absorption spectra of the complex vanadium [V] with N-benzyl cinnamo hydroxamic acid, formed in aqueous solution against the reagent black, exhibited the wavelength of maximum absorbance around 490 nm [Table. 1, Figure. 3]. The proposed method involved the formation of purple colored complex with 490 nm absorption spectra against reagent blank. Since the reagent blank has the negligible absorbance at this wave length. The different concentration of metal composition (vanadium V) the effects on ʎ max position was no change (Table 1, Figure 3).

Table 1: Absorption spectra of vanadium (V), with N-benzyl cinnamo hydroxamic acid in aqueous medium

S. No.	Wavelength	0.4µg/ml (metal ion) Absorbance
1.	450	0.120
2.	460	0.131
3.	470	0.140
4.	480	0.162
5.	490	0.195
6.	500	0.185
7.	510	0.160

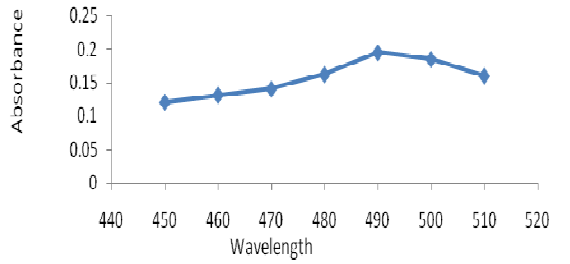

Figure 3: Absorption spectra of vanadium (V), with N-benzyl cinnamo hydroxamic acid in aqueous medium

ANALYTICAL DATA

Optimization of Procedure

In order to find the optimum conditions, the influence of the concentration of reagents (N-benzyl cinnamo hydroxamic acid), temperature, non-target species and pH on the determination of vanadium (V) compexation with N-benzyl cinnamo hydroxamic acid in aqueous medium were studies (Table 2, Figure 4).

Table 2: Effect of vanadium (V), on the position of λ_{max} of the complex in aqueous medium

S. No.	Wavelength	0.4µg/ml Absorbance	0.6µg/ml Absorbance	0.8µg/ml Absorbance	1.0µg/ml Absorbance
1.	450	0.120	0.170	0.200	0.230
2.	460	0.131	0.181	0.205	0.255
3.	470	0.140	0.197	0.233	0.266
4.	480	0.162	0.203	0.243	0.270
5.	490	0.195	0.210	0.260	0.295
6.	500	0.185	0.200	0.240	0.272
7.	510	0.160	0.178	0.225	0.240

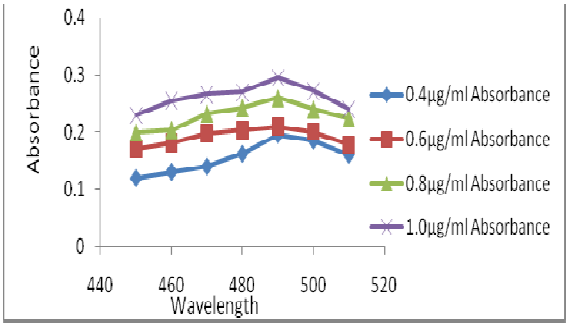

Figure 4: Effect of vanadium (V), on the position of λ_{max} of the complex in aqueous medium

Effect of pH

The influence of pH on the study of vanadium (v) N-benzyl cinnamon hydroxamic acid complex

optimum pH range detected was 1.5- 2.8 pH using hydrochloric acid according to the results the absorbance range of the complexes was decrease out of this pH range in this study it is found that sensitivity can be achieved at about pH 2.4, so this pH was selected as the optimum pH for determination of vanadium (V) [Table 3, Figure 5].

Table 3: Effect of pH on the formation and absorbance, of vanadium (v) N-MCHA complex in aqueous medium

S. No	pH	Absorbance
1.	0.2	0.265
2.	0.5	0.280
3.	1.0	0.310
4.	1.2	0.337
5.	1.5	0.377
6.	1.8	0.377
7.	2.0	0.377
8.	2.2	0.377
9.	2.5	0.377
10.	2.8	0.377
11.	3.0	0.372
12.	3.2	0.337
13.	3.5	0.305
14.	3.8	0.291

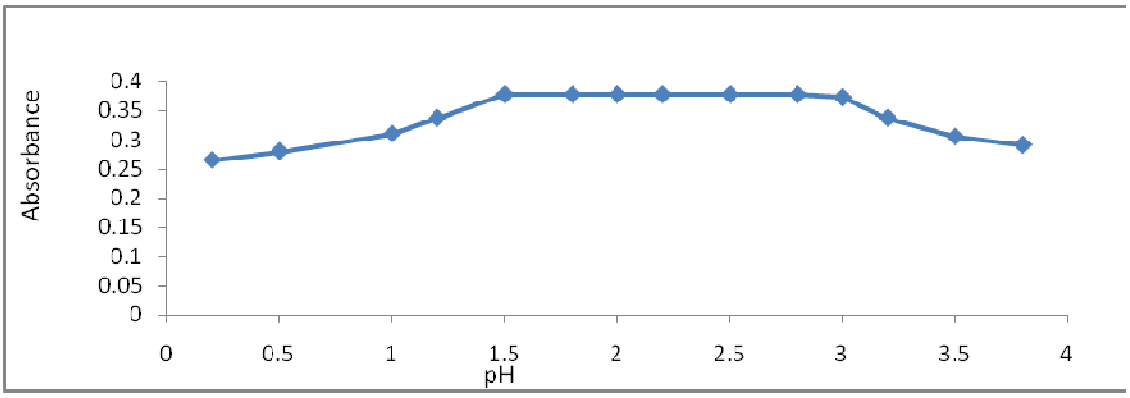

Figure 5: Effect of pH on the formation and absorbance, of vanadium (V) N-benzyl cinnamo hydroxamic acid complex in aqueous medium

Effect of Temperature

A study of the effect of the temperature on the complexion of vanadium (V) N–benzyl cinnamo hydroxamic acid was performed in the temperature range 28±2°C beyond this range absorbance of the complex was decrease (Table 4, Figure 6).

Table 4: Effect of temperature on formation and absorbance of vanadium [V] N–benzyl cinnamo hydroxamic acid complex in aqueous medium

S. No	Tem.	Absorbance
1.	5	0.330
2.	10	0.377
3.	15	0.377
4.	20	0.377
5.	25	0.377
6.	30	0.377
7.	35	0.377
8.	40	0.350
9.	45	0.321
10.	50	0.315

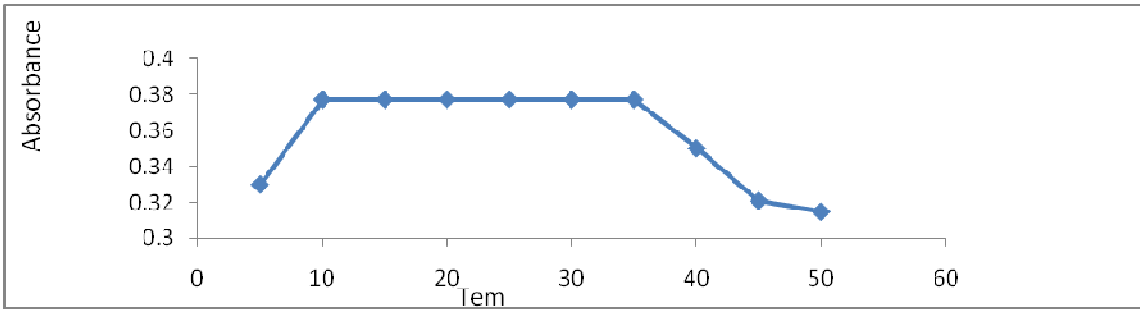

Figure 6: Effect of temperature on formation and absorbance of vanadium [V] N–benzyl cinnamo hydroxamic acid complex in aqueous medium

Effect of Reagents N–benzyl Cinnamo Hydroxamic Acid

A study of the influence of the N–benzyl cinnamo hydroxamic acid on the complexion vanadium (V) and complete color development was performed in the N–benzyl cinnamo hydroxamic acid range 5.5 x10^{-2} further addition up to 11.5 x10^{-2}M had no adverse effect on absorbance so 6.5x10^{-2}M N-benzyl cinnamo hydroxamic acid was selected the optimum concentration for reaction (Table 5,Figure 7).

Table 5: Effect of N-BCHA×10^{-2} on formation and absorbance of vanadium [V] N–benzyl cinnamo hydroxamic acid complex in aqueous medium

S. No	N-BCHA×10^{-2}	Absorbance
1.	2.5	0.287
2.	3.5	0.347
3.	4.5	0.364
4.	5.5	0.377
5.	6.5	0.377
6.	7.5	0.377
7.	8.5	0.377
8.	9.5	0.377
9.	10.5	0.377
10.	11.5	0.355
11.	12.5	0.351
12.	13.5	0.327
13.	14.5	0.298

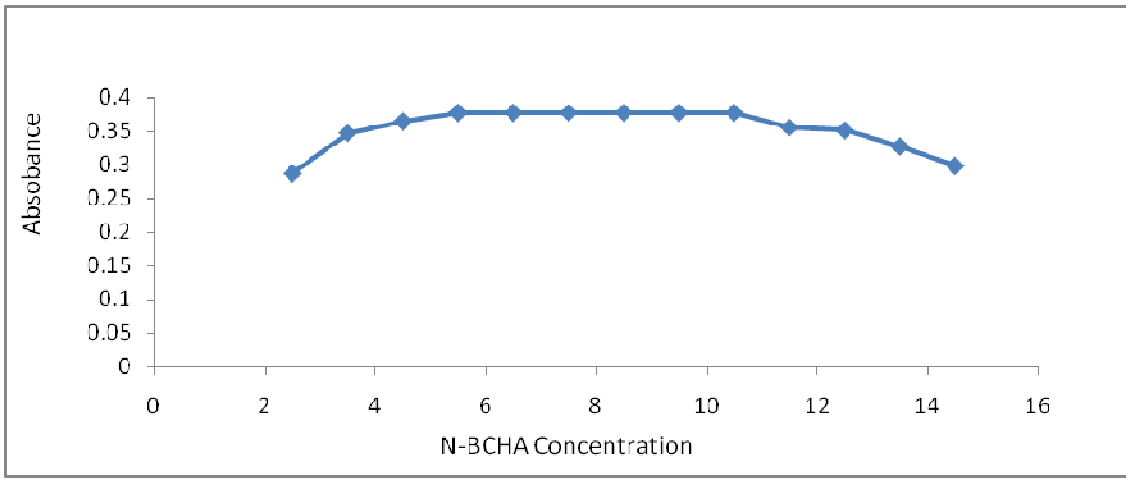

Figure 7: Effect of N-BCHA×10^{-2} on formation and absorbance of vanadium [V] N–benzyl cinnamo hydroxamic acid complex in aqueous medium

Calibrations Graph

The calibration curve was obtained. from 0.2-10.0 ppm (µg/ml) of vanadium using 3M HCl (pH2.4) at ʎ max 490nm absorbance and quantization limit and detection limit are 0.46 µg ml^{-1} and 0.13µgml^{-1} the value of molar absorptivity and sendel's sensitivity were found 8.92×10^{4} $mole^{-1}$ cm^{-1} and 0.0011 µg cm^{2} [(Table 6, Figure 8).

Table 6: Adherence to Beer's law for the determination of vanadium using N-benzyl cinnamo hydroxamic acid as chelating reagents

S. No.	Vanadium /ml	Absorbance
1.	0.2	0.108
2.	0.6	0.115
3.	1.0	0.133
4.	1.4	0.160
5.	1.8	0.205
6.	2.4	0.243
7.	3.0	0.303
8.	3.8	0.348
9.	4.6	0.433
10.	5.4	0.474
11.	6.2	0.550
12.	7.0	0.593
13.	7.8	0.743
14.	8.4	0.793
15.	9.2	0.880
16.	10.0	0.883
17.	10.8	0.884

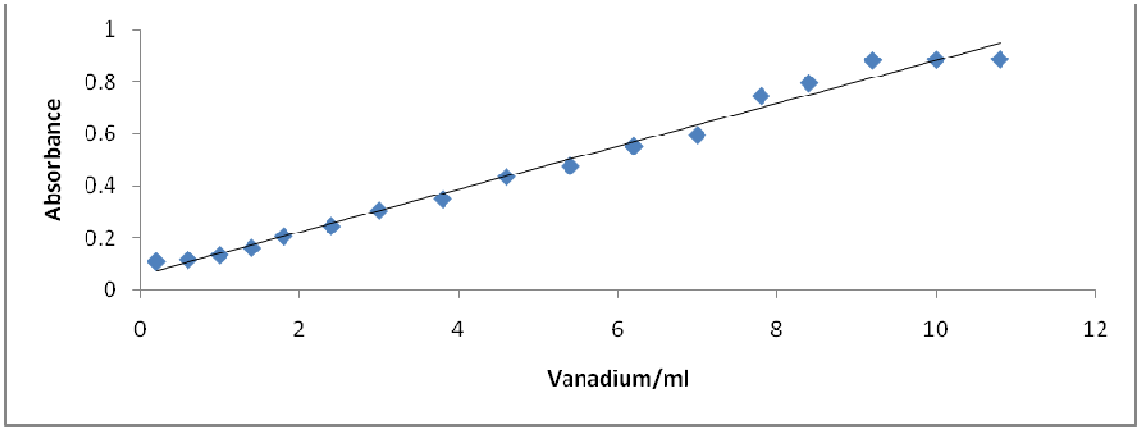

Figure 8: Adherence to Beer's law for the determination of vanadium using N–benzyl cinnamo hydroxamic acid as chelating reagents

STATISTICAL DATA AND PRECISION

The precision of method was determined by taking 7 replicate's measurements each containing 9.9µg/ml of aqueous solution The mean absorbance value found to be 0.377 and standard deviation value was ± 0.002 achieved giving a relative standard deviation (RSD) of ± 0.53% result shown in (Table 7).

Table 7: Statistical data of the method

S. No	Absorbance	Mean	S.D.	RSD[%]
1.	0.376	0.377	±0.002	± 0.53%
2.	0.374			
3.	0.378			
4.	0.380			
5.	0.379			
6.	0.378			
7.	0.374			

Effect of Diver's Ions

The influence of various species on the determination of vanadium (V) was investigated. The tolerance limit was taken as the amount that 1% relative error in determination of vanadium (V) 9.9 µg/ml. The results shows that Sn^{2+}, PO_4^{3-}, Mo^{6+} ,Co^{3+}, Bi^{3+}, Ba^{2+}, Fe^{3+}, BO_3^{3-} gives a serious interfere. These interferes can be removed by NH_4SCN as masking agent (Table.8).

Table 8: Effect of non-Target species in the determination of vanadium (V) N–methyl cinnamo hydroxamic acid complex in aqueous medium

S. No.	Ions or species added	Tolerance limit
1.	Mn^{2+}	2300
2.	Cu^{2+}	1900
3.	Cd^{2+}	1350
4.	Al^{3+}	2550
5.	Pb^{2+}	2500
6.	Ni^{2+}	1700
7.	Cr^{3+}	2700
8.	CH_3COO^-	1900
9.	SO_4^{2-}	1100
10.	NO_3^-	1300
11.	Sn^{2+}	1000*
12.	PO_4^{3-}	900*
13.	Mo^{6+}	850*
14.	Co^{3+}	400*
15.	Bi^{3+}	700*
16.	Ba^{2+}	750*
17.	Fe^{3+}	250*
18.	BO_3^{3-}	300*

ANALYTICAL APPLICATION

The proposed method under the already established optimum condition was applied for the determination of vanadium (v) in water and soil samples [Table 9].

Table 9: The proposed method under the already established optimum condition was applied for the determination of vanadium (v) in water, soil, urine, pharmaceutical and steels samples

Samples	Vanadium originally found in µg/ml	Vanadium added found in µg/ml	Vanadium found in µg/ml ±SD	Relative error	Recovery%
Polluted Water	4.20	2.0	4.18±0.02	0.2	99.00
	4.47	4.0	4.5±0.02	0.2	99.25
Polluted Soil	-	2.0	1.85±0.03	0.3	92.50
	-	4.0	3.87±0.02	0.4	96.75

Mean ± Standard deviation [n=5]

CONCLUSION

A simple, rapid, highly sensitive selective method is reported for the determination of vanadium (V) using N-methyl cinnamo hydroxamic acid as reagent. This newly synthesized chelating reagent can be successfully used for the determination of vanadium (V) in water, soil, urine, pharmaceutical and steel sample and proposed of good accuracy and precision for determination of vanadium.

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