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Spectrophotometric Determination of Vanadium (V) Using N–Methyl Cinnamo Hydroxamic Acid as Reagent

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Abstract
The subject of this research is to study the possibility of novel, rapid highly sensitive and selective spectrphotometric method was proposed for the determination of vanadium (V) using N- methyl cinnamo hydroxamic acid (N-MCHA) as a reagent. The method was based on the formation of purple coloured complex between N–methyl cinnamo hydroxamic acid and vanadium (V). The optimum conditions for the determination were established. The Beer's law is obeyed for vanadium (V) in the concentration range to 0.2-10.0µg/ml at the maximum absorbance at 480nm. In this method molar absorptivity, Sand ell's sensitivity, detection limit and quantization limit were reported. The proposed method free from over a wide variety of cations, anions, and complexion interference species. This method was successfully applied to the analysis of vanadium (V) in water, soil, urine, steel and pharmaceutical samples.
Keywords: Vanadium (V), N-methyl cinnamo hydroxamic acid, Absorptivity, Complexion.

1. Introduction

A series of hydroxamic acids are synthesized. Hydroxamic acid and their derivatives having many applications not only analytical chemistry but different fields. Hydroxamic acids are good reagent and having property to formed complex due to their oxygen (O) and Nitrogen (N) donor legends present structurally in N–methyl cinnamo hydroxamix acid is also made stable colored chelate complex with vanadium (V). 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 in to the air that then seethes on the soil [1]. There are cases of vanadium poisoning [2].

The national institute for occupational safety and health [NIOSH] has reported that 35 mg/m^3 [3] of vanadium be considered dangerous to human beings, animal and plants. Vanadium 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 such as NAA, ICP, AES, AAS etc [4]. This methods are disadvantageous costly of instruments and lacking sensitivity, simplicity [5-10]. The N–methyl cinnamo hydroxamic acid are of interest due to their ability to form stable transition metal complexes with vanadium through the formation of a five member chelate ring as shown in figure1

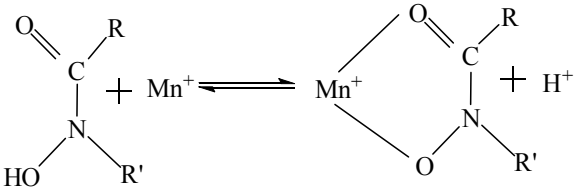

Figure 1. Formation of a five member chelate ring by the hydroxamic acids with matal ion

In this reaction metal ion is attached with oxygen atom of N–methyl cinnamo hydroxamic acid through metal–legend bond formed and chelate ring developed for simple, selective, sensitive spectrophotometric determination of vanadium (V) [11-15] using N–methyl cinnamo hydroxamic acid as chelating agent. Newly synthesized N–methyl cinnamo hydroxamic as analytical reagent by the standard method for determination trace amount of vanadium (V) and this method is, successfully applied for determination of vanadium (V) in water soil, urine, steel and pharmaceutical samples [16-19].

2. Experimental Section

2.1 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.

2.2 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.

2.3 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.

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

2.5 Hydrochloric acid
3 M Hydorchloric solutions was used for acidity maintained

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

3. Procedure
Standard stock solution containing (0.2-10.8 µml ml) vanadium (v) was pipette out in to a 25ml standard cork calibrated flask,1 Each 0.5 ml of 3M hydrochloric acid (pH 2.6) 5ml of 1.4% (w/v) of N-methyl cinnamo hydroxamic acid (7.5×10^{-2}M) was added to each solution. The purple color is develop 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) [20-23] (Table 5, Fig 6).

3.1 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 [24]. The results are shown in (Table 8).

3.2 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 Whatman No. 40 filter paper ,in to a 25ml 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 [25]. The results are shown in (Table 8).

3.3 Procedures For the determination of vanadium (V) in urine sample
50 ml. of urine sample was evaporated to 5ml.To this solution 5ml of HNO_3 and 5g of potassium sulfate added and heated to dryness then 1:3, 25ml, HNO_3 was added and digested or a water both for 30min the contents were again evaporated to dryness, cooled, and the residue was dissolve in water, filtered and neutralized with, dilute ammonia. .The mixture was diluted of a known volume with water and this solution were taken used to analyses contain of vanadium (V) by the proposed method [26]. The results are shown in (Table 8).

3.4 Procedure for determination of vanadium (V) in pharmaceutical samples
About 10ml concentration HNO_3 was heated to dryness in this solution added 5ml of H_2SO_4. The solution was diluted with distilled water and neutralized with dilute ammonia. It was then diluted to the mark with distilled water. The solution was used to analyze vanadium (V) by the proposed method [27]. The results are shown in (Table 8).

3.5 Procedure for determination of vanadium (V) in steels samples
An accurately weighed amount of vanadium steel (approximately 0.6g) of vanadium was dissolve in 40% nitric acid. This solution 0.5ml HCl was added and heated to dryness. Brown yellow precipitates of hydrated tungestic acid with other insoluble residue was filtered through a Whatman no 42. The filtrated again evaporate to dryness and this process is repeated 2-3 times by addition 100ml dilute HCl. Suitable aliquots of this solution were taken and the vanadium (V) was analyses by the proposed method [28]. The results are shown in (Table 8).

4. Result And Discussion

4.1 Absorption Spectra

The absorption spectra of the complex vanadium [V] with N-methyl cinnamo hydroxamic acid, formed in aqueous solution against the reagent black, exhibited the wavelength of maximum absorbance around 480 nm [Table. 1, Figure. 2]. The proposed method involved the formation of purple colored complex with 480 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. 2, Figure. 3].

5. Analytical Data

5.1 Optimization of procedure

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

5.2 Effect of pH

The influence of pH on the study of vanadium (v) N-methyl 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 2.0, so this pH was selected as the optimum pH for determination of vanadium (v) [Table.3, Figure. 4].

5.3 Effect of temperature

A study of the effect of the temperature on the complexion of vanadium (V) N–methyl cinnamo hydroxamic acid was performed in the temperature range $28 \pm 2°C$. beyond this range absorbance of the complex was decrease[Table. 4, Figure. 5].

5.4 Effect of reagents N–methyl cinnamo hydroxamic acid

A study of the influence of the N–methyl cinnamo hydroxamic acid on the complexion vanadium (V) and complete color development was performed in the N–methyl cinnamo hydroxamic acid range $5.9x10^{-2}$ further addition up to $11.2x10^{-2}M$ had no adverse effect on absorbance so $7.5x10^{-2}M$ N-methyl cinnamo hydroxamic acid was selected the optimum concentration for reaction [Table.5,Figure 6.]

5.5 Calibrations Graph

The calibration curve was obtained. from 0.2-10.0 ppm (µg/ml) of vanadium using 3M HCl (pH2.0) at ʎ max 480nm absorbance and quantization limit and detection limit are 0.78 µg ml^{-1} and 0.10µgml^{-1} the value of molar absorbivity and sandal's sensitivity were found 6.93×10^4 1 $mole^{-1}$ cm^{-1} and 0.0010 µg cm^{-2}.

5.6 Effect of concentration an N–methyl cinnamo hydroxamic acid

On the formation and absorbance of vanadium (V) N-methyl cinnamo hydroxamic acid complex in aqueous medium [Table.5, Figure 6.]

6. 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 0.390 and standard deviation value was ± 0.003 achieved giving a relative standard deviation (RSD) of ± 0.76% result shown in [Table.6].

6.1 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.7]

7. Analytical Application

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.

8. 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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Thanks to my supervisor Dr. S. K. Rajput co-supervisor Dr. K. N. Bapat, thanks to department of chemistry, govt. N. P .G. College of science, Raipur, and also thanks to deptt. of chemistry, Gujrat University Ahmedabad, Gujarat for IR analysis and SAIF Panjab University, Chandigarh for ^{1}HNMR analysis.

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

S.No.	Wavelength	0.4µg/ml (metal ion) Absorbance
1.	450	0.130
2.	460	0.142
3.	470	0.157
4.	480	0.160
5.	490	0.152
6.	500	0.139
7.	510	0.125

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	0.130	0.159	0.220	0.307
2.	460	0.142	0.170	0.235	0.312
3.	470	0.157	0.187	0.260	0.322
4.	480	0.160	0.199	0.280	0.333
5.	490	0.152	0.180	0.250	0.315
6.	500	0.139	0.165	0.225	0.302
7.	510	0.125	0.133	0.215	0.298

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

S.No	pH	Absorbance
1	0.5	0.317
2	0.5	0.315
3	1.0	0.349
4	1.2	0.362
5	1.5	0.365
6	1.8	0.365
7	2.0	0.365
8	2.2	0.365
9	2.5	0.365
10	2.8	0.365
11	3.0	0.36
12	3.2	0.325
13	3.5	0.31
14	3.8	0.28

N- MCHA =7.5×10^{-2} M, HCl= 3M

Table.4 Effect of temperature on formation and absorbance of vanadium [V] N–methyl cinnamo hydroxamic acid complex in aqueous medium.
N-methyl cinnamo hydroxamic acid =$7.5x10^{-2}$M, HCl=3M, pH =2.0

S.No	Tem.	Absorbance
1.	5	0.331
2.	10	0.365
3.	15	0.365
4.	20	0.365
5.	25	0.365
6.	30	0.365
7.	35	0.365
8.	40	0.365
9.	45	0.342
10.	50	0.327

Table.5 Adherence to Beer's law for the determination of vanadium using N-methyl cinnamo hydroxamic acid as chelating reagents.
N–MCHA =$7.5x10^{-2}$ M, HCl=3M, pH= 2.0

S.No.	Vanadium /ml	Absorbance
1.	0.2	0.103
2.	0.6	0.110
3.	1.0	0.128
4.	1.4	0.155
5.	1.8	0.200
6.	2.4	0.238
7.	3.0	0.298
8.	3.8	0.343
9.	4.6	0.428
10.	5.4	0.469
11.	6.2	0.545
12.	7.0	0.588
13.	7.8	0.738
14.	8.4	0.788
15.	9.2	0.875
16.	10.0	0.878
17.	10.8	0.879

Table. 6 Statistical data of the method:-

S.No	Absorbance	Mean	S.D.	RSD[%]
1.	0.391			
2.	0.385			
3.	0.392	0.390	±0.003	± 0.76%
4.	0.393			
5.	0.389			
6.	0.386			
7.	0.395			

Table. 7 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+}	1400
2.	Cu^{2+}	1000
3.	Cd^{2+}	650
4.	Al^{3+}	1650
5.	Pb^{2+}	1600
6.	Ni^{2+}	800
7.	Cr^{3+}	1800
8.	CH_3COO^-	1000
9.	SO_4^{2-}	450
10.	NO_3^-	600
11.	Sn^{2+}	100*
12.	PO_4^{3-}	250*
13.	Mo^{6+}	300*
14.	Co^{3+}	400*
15.	Bi^{3+}	100*
16.	Ba^{2+}	150*
17.	Fe^{3+}	200*
18.	BO_3^{3-}	500*

Table 8 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	4.80	2.0	4.76±0.03	0.2	98.00
	5.06	4.0	5.10±0.03	0.2	99.0
Polluted Soil	-	2.0	1.88±0.04	0.3	94.00
	-	4.0	3.84±0.02	0.4	96.00
Urine Sample	-	2.0	1.91±0.01	0.3	95.5%
	-	4.0	3.93±0.03	0.2	98.25%
Steel Sample	-	0.04	0.036±0.04	0.06	95.00
Pharmaceutical Sample	-	9.0	8.55±0.002	0.6	95.00
	-	8.00	7.65±0.03	0.5	95.62

Mean ± Standard deviation [n=5]

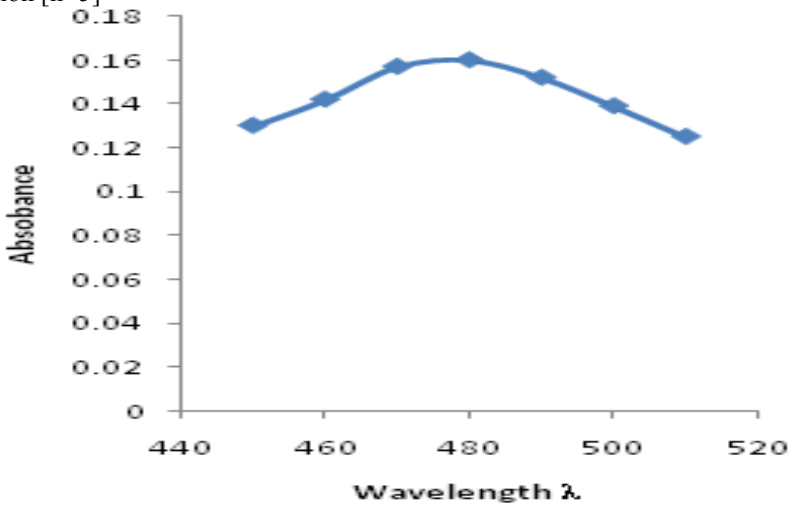

Figure : 2 Absorption spectra of vanadium (V) , with N-methly cinnamo hydroxamic acid in aqueous medium.

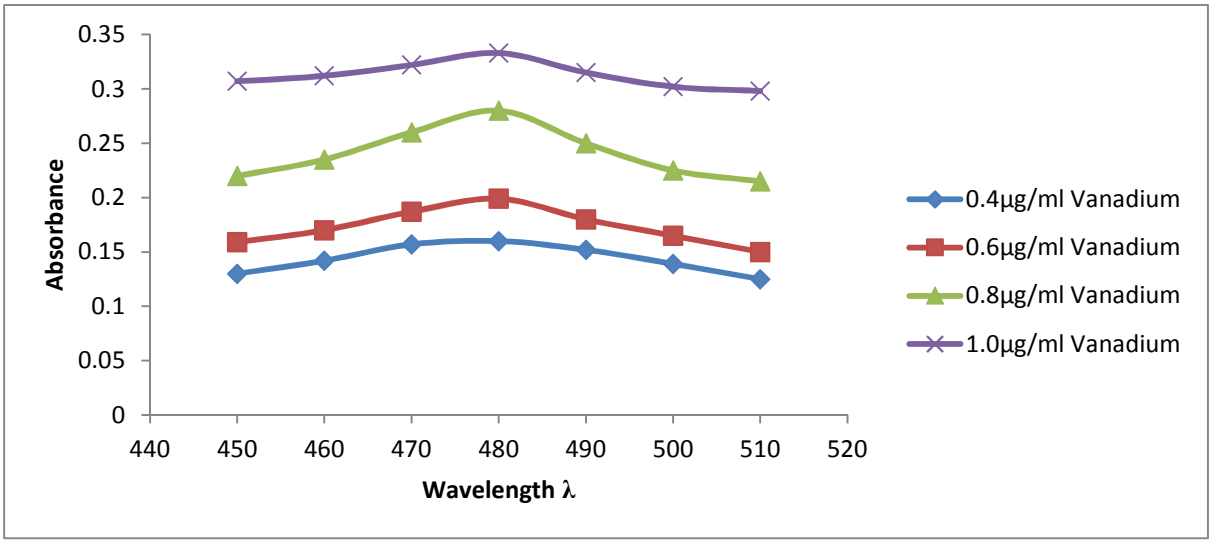

Figure. 3 Effect of vanadium (V), on the position of λ_{max} of the complex in aqueous medium.

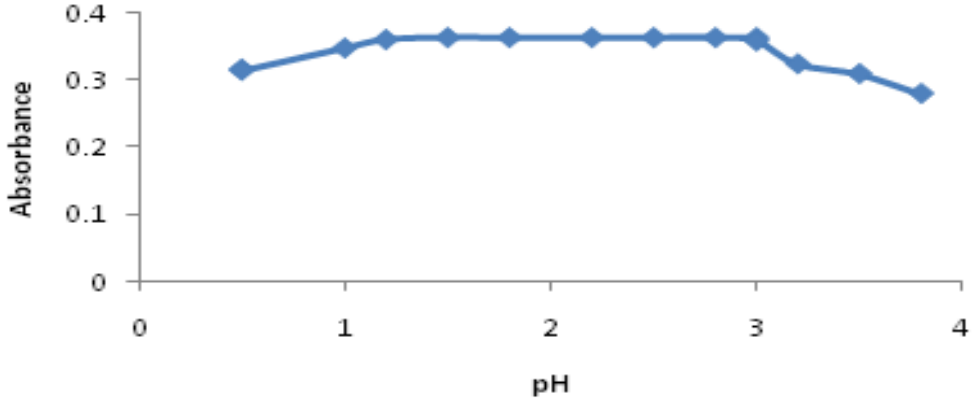

Figure.4 Effect of pH on the formation and absorbance, of vanadium (V) N-methyl cinnamo hydroxamic acid complex in aqueous medium.

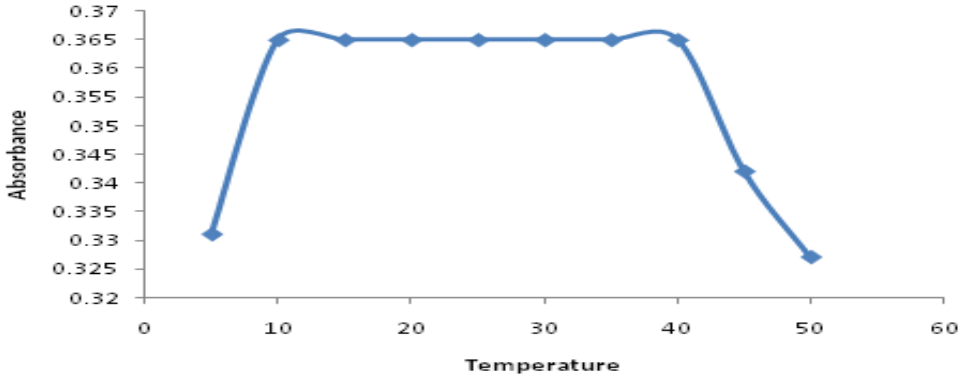

Figure.5 Effect of temperature on formation and absorbance of vanadium [V] N–methyl cinnamo hydroxamic acid complex in aqueous medium.

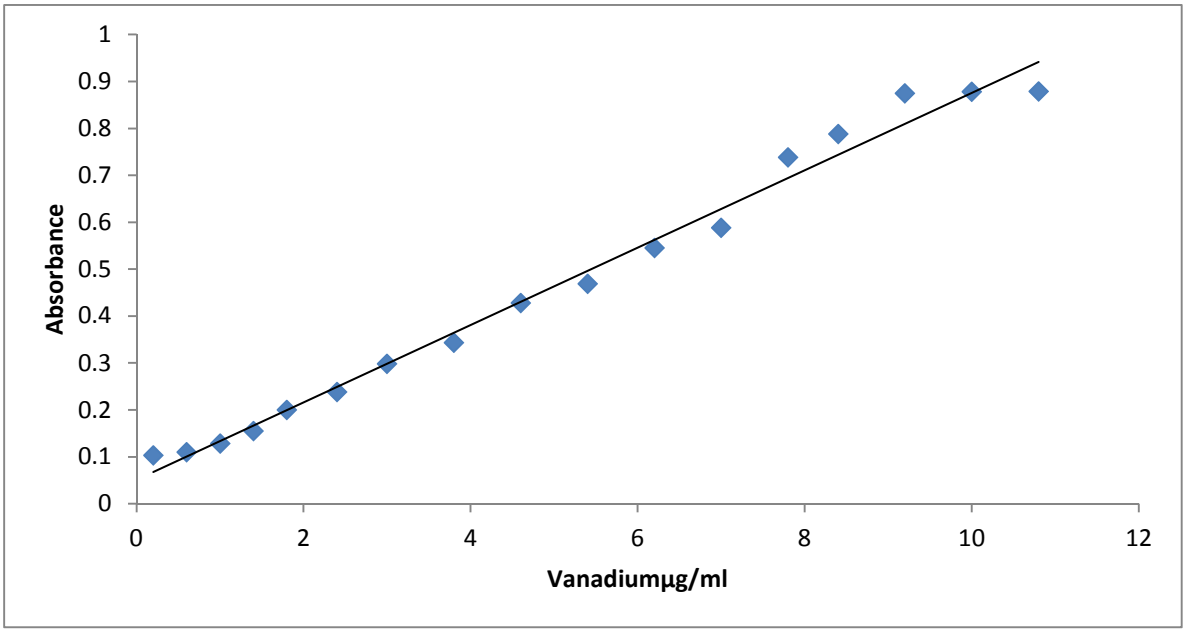

Figure.6 Adherence to Beer's law for the determination of vanadium using N–methyl cinnamo hydroxamic acid as chelating reagents.