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Potentiometric Titration of Vanadium (V) with Iron (II) in the Presence of NTA and DTPA Using Dry-Cell Graphite Electrode

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Abstract. *A sensitive potentiometric titration for vanadium (V) based effect of ligands such as nitrilotriacetic acid (NTA) and diethylenetriaminepenta-acetic acid (DTPA) are reviewed. The potential iron system decreased the presence of NTA and DTPA. In this case, iron (III) increased with respect to the vanadium (IV) volume. The production of iron (III)-ligand complex has increased. This result suggested that the formation of V(V)-NTA and V(V)-DTPA complexes were less favoured than that of V(IV)-NTA and V(IV)-DTPA complexes. The calculated correlation coefficients (r) conveyed the effectiveness of the graphite electrode as the indicator electrode for the potentiometric titrations.* ***On*** *comparing the potential jump values, the extent of potential caused by DTPA was found to be more than that of NTA. The utilization of graphite electrode has facilitated the potentiometric titration by significantly causing larger potential jump. This method was precise and accurate as no interference of foreign ions was observed. Hence, the approach could be applied to the vanadium (V) of any samples.*

Keywords: *Iron(III)/Iron(II); vanadium (IV)/vanadium (V); potentiometric titration; graphite electrode; ligands; pH; formal potential; potential jump*

1. Introduction

The chemical speciation and the determination of a metal ion have demand in several researches such that environmental pollution, industrial control etc. Among various metals, vanadium has important constitute of alloys as it could impart special properties to them. Natural water vanadium dependency is presented in [1]. Vanadium has been known to be valuable for the vascular diseases removal and also the safe dose of vanadium has the therapeutic potentials for diabetics [2]. Generally, vanadium can either be present as tetravalent state of water [3,4]. The vanadium has development of titrimetric methods for the determination of vanadium (IV) and vanadium (V) state results since they have different toxic and nutritional properties [5,6]. This could be due to the reason that the complexing agents could potentially modify the ions [7]. Vanadium shows the ease of interconversion between the +4 and +5 oxidation states and among which +5 is relatively more stable and toxic in selective forms. Hence, it is very important to determine vanadium (V) both quantitatively and qualitatively. It has been established that vanadium (V) Potentiometrically with iron (II) in the presence of diphosphate is presented in [8]. There have been comparatively several available methods [9] and Pribil [10] have reported the vanadium (IV). Volumetric method is discussed [11]. Nasir Ahmad [12] has reported the spectrophotometric of vanadium (IV) with nitrilotriacetic acid.

Mendez and Diez [13] have spectrophotometrically determined the vanadium (IV). Vanadium (IV) with DCTA titration at *p*H 4.0, 4.2 and 4.6 values [14]. Many spectrophotometric methods have been reported for the determination of vanadium based on the complex formation including rhodamine [15], indigo carmine [16], 1-naphthyl red [17,18] and o-phenylenediamine analysis is given in [19]. Flow injection analysis (FIA) has been extensively applied as a simple and convenient approach with high accuracy and less consumption of reagents for the rapid analyses of several metal species [20]. FIA instruments [21] and FIA methods have been reported in [22,23]. FIA has been used for the determinations of vanadium [24-26] especially for vanadium (IV). In 1976 Natarajan and Ramasubramanian [27] have reported the potentiometric use of graphite rod removed from a discharged dry cell. Subsequently, few more studies [28-42] have demonstrated that the dry cell graphite could be

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a completely acceptable and alternate substitute for the expensive platinum or special grade graphite in electroanalytical techniques. However few FIA methods were found to be insensitive and thus they could not be applied to any real samples [7].

Diethylenetriaminepenta-acetic acid (DTPA) were presented in more detail in the present work. DTPA (also known as pentetic acid) is an aminopolycarboxylic acid consisting of a diethylenetriamine backbone with five carboxymethyl groups. Both NTA and DTPA could be used as alternates for EDTA. However, unlike EDTA, they can be easily biodegradable. In order to compare the performance of graphite electrode, we have performed the potentiometric titration using platinum electrode also (for comparison purpose only) and confirmed the potential performance of graphite electrode. This proposed method was anticipated to be highly sensitive and rapid as the graphite electrode enhanced the ease of end point detection at high pH values. The performed interference study conveyed that there was no any interference due to foreign ions.

2.Materials and methods

Chemicals

All reagents used on purification with 0.01 M ammonium iron (II) sulphate solution was prepared by dissolving 3.92 g of iron (II) salt in 0.05 M sulphuric acid and standardized against potassium dichromate solution. 0.01 M vanadium(V) solution was prepared by dissolving 6.10 g of sodium metavanadate salt in 50.0 mL of (1:1) sulphuric acid, water and it was standardized against Iron (II) solution. 0.5 M Nitrilotriacetic acid (NTA) and 0.5 M diethylenetriaminepenta-acetic acid (DTPA) solutions were dissolved in sodium acetate and diluted with water. Various buffers for the desired *p*H were obtained by mixing suitable volumes of 1M hydrochloric acid and 1M sodium acetate in a total volume of 50 ml. Measurements of formal potentials were carried out with the solutions of ammonium ferric sulphate (0.01M) and vanadium (IV) solution (vanadyl sulphate).

Fabrication of the graphite electrode

Preparation of graphite electrode was carried out using low cost graphite rods. This is extracted from dry cell by abrasion followed by an overnight treatment. Mercury was poured on the polythene-tube and the electrical contact was made by inserting a thin copper wire enclosed in plastic sleeve.

V in NTA

Vanadium (V) titration vessel with 20 mL of acetate buffer and 20 mL of 0.1 M NTA are filled and then it is diluted to 100 mL with double distilled water. The potential measurements were followed by using (a) platinum electrode (V) vs. SCE and (b) dry cell graphite electrode (non-activated) vs. SCE from electrode placements. Six replicate titrations were performed for various amount of vanadium in order to establish the precision of the methods. Interference study was also performed in order to check the presence of any possible interference.

DTPA on Potentiometric titration of vanadium

To 100.0 mL titration cell, required amount of sodium meta vanadate was mixed with 20 mL of acetate buffer. The potential measurements were followed by using platinum electrode as an indicator electrode and saturated calomel electrode. Potentials were noted after each addition of the titrant. The titrations were repeated using dry cell graphite electrode as an indicator electrode and saturated calomel electrode as a reference electrode. The concentration of vanadium was varied and six replicate titrations at each concentration were performed using graphite electrode. Interference study was also performed in order to check the presence of any possible interference.

Alloy steels analysis

Steel sample was accurately analyzed and dissolved in 10 mL of 1:2 sulfuric acid and carefully covered with a watch glass. Then 5 mL of concentrated nitric acid was added and the solution was heated until all carbides were decomposed. An aliquot from this solution was taken, and then 50-60 mL of 0.10 M DTPA solution was added followed by the addition of 2.0 M sulphuric acid solution in order to maintain the solution *p*H at 5.0 and the resulting solution was titrated with appropriately diluted ferrous ammonium sulphate solution using dry-cell graphite electrode and saturated calomel electrode. The titrations is performed by titrating vanadium (V) with ferrous ammonium sulphate in a highly acidic medium. Both the methods were compared statistically.

2.6 Characterization techniques

The potential and *p*H were carried out with a digital *p*H/mV meter (Elico, Model L1-120) at ambient temperature (25ºC) with a precision of ±1 mV. The conventional potentiometric assembly consisted of 100 mL titration cell, 10 mL burette and a mini magnetic stirrer. The pH meter was calibrated with 0.05 M phthalate (*p*H 4.02) and 0.05 M borax (*p*H 9) standard buffers prepared according to the specification.

Resuls and discussions

Redox reaction of V

Reduction potential of reactions are as follow;

$$Fe^{3+} + 1e^- \rightleftarrows Fe^{2+} \qquad E^0 = 0.77\,V \qquad (1)$$

$$VO_2^+ + 2H^+ + 1e^- \rightleftarrows VO^{2+} + H_2O \qquad E^0 = 1.00\,V \qquad (2)$$

From the above equations, it was found that the standard redox potential of the Fe(III)/Fe(II) system, E°_{Fe} (0.77 V) was lower than that of the standard redox potential of the Vanadium system, E°_{V} (1.00 V) [43].The redox potential of **V system, $E'_{V(H)}$,** is given by the following eqn.;

$$E'_{V(H)} = E^0_V - 0.118\,pH \qquad (3)$$

Influence of complexing agents

In order to assess the influence the potentiometric titrations of vanadium and presence of complexing agents (NTA and DTPA). Figure 1 shows the potentiometric titration with *p*H between 0.8-3.0 in the absence of complexing agents. The results indicated that as the *p*H increased, there was a continuous potential without any breaking (no potential jump). i.e., the breaking in the potential was gradually minimized. From Figure 1, it could be seen that a potential break of 129 mV was observed at the equivalence point at *p*H<1 and 21 mV were observed at *p*H 1.0 and 2.0 respectively. Unlike these cases, no potential jump was observed near the equivalence point when the titrations were carried out at *p*H 3.0. Thus, the results of the titration suggested that the reaction was not feasible at higher *p*H values and hence suitable chelating agents which could be able to form more stable complexes. The results are shown in Figure 2 and Figure 3 and the corresponding values are given in Table 1.

In order to check the suitability of these chelating agents (NTA and DTPA), we have also used the known ligand, EDTA [8]. This formation of V(IV)-EDTA is favoured [8]. Hence, the formation of V(V) EDTA complex, Tanaka *et al.*, [44] used. Unlike EDTA, the potential was increased with increase in the ligand concentration, when NTA and DTPA were used as ligands. This result suggested that the formation of V(IV)-NTA and V(IV)-DTPA complexes were more favoured than that of V(V)-NTA and V(V)-DTPA complexes. Hence NTA and DTPA were chosen as suitable chelating agents for the determination of vanadium in this study.

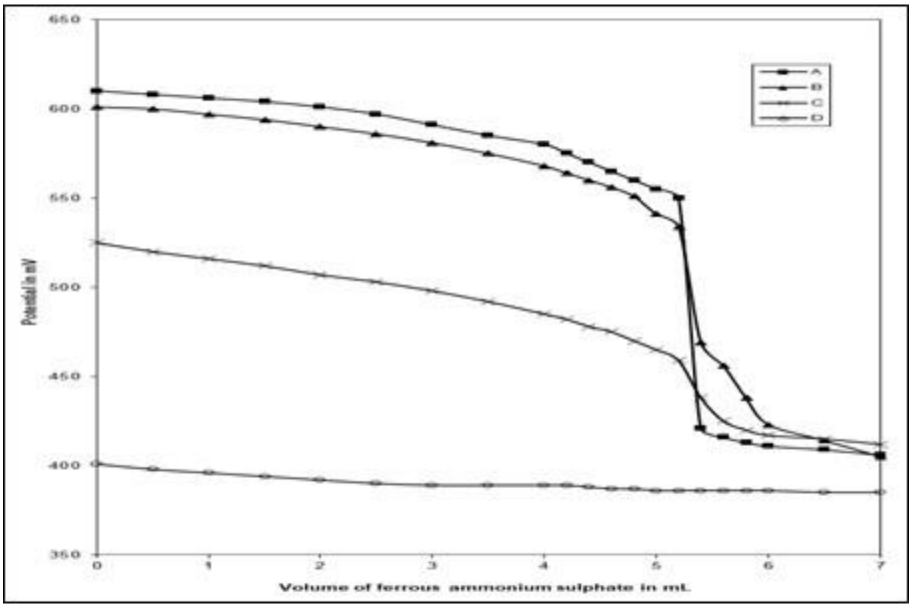

Figure 1. Potentiometric titration of 5.0 mL of 1.05 x 10^{-2} M vanadium (V) with 9.9 x 10^{-3} M iron (II) at various *p*H (Curve A *p*H 0.8; Curve B *p*H 1.0; Curve C *p*H 2.0; Curve D *p*H 3.0)

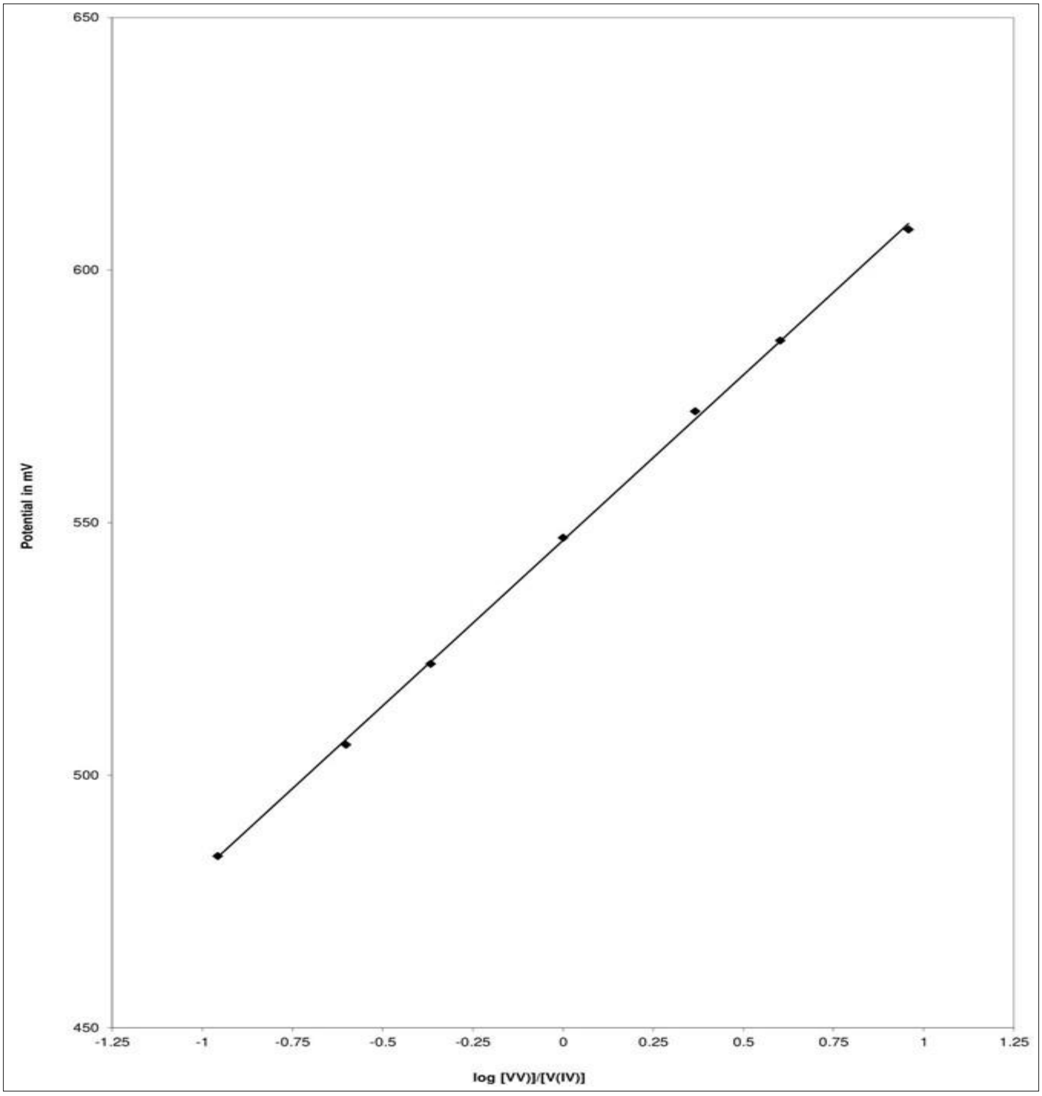

Figure 2. Sensitivity of graphite electrode towards V(V)-V(IV)-SCE

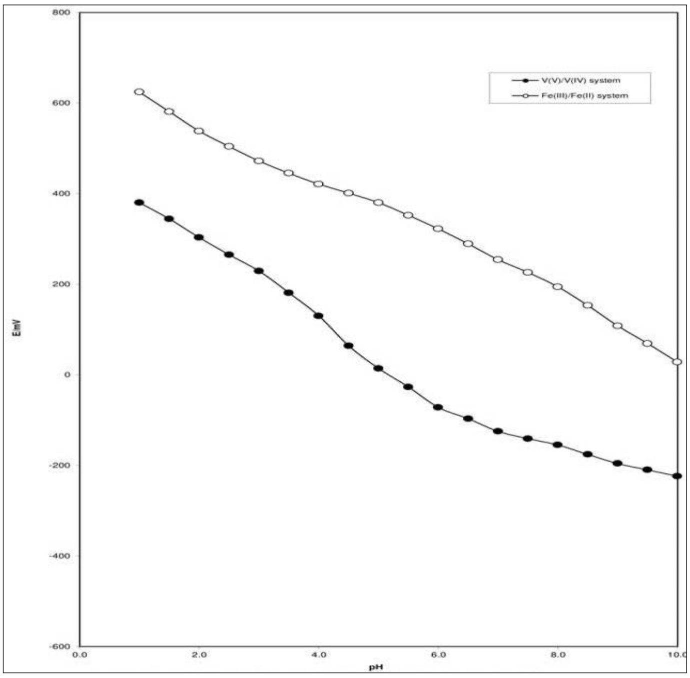

Figure 3. Effect of *p*H with equimolar mixtures of V and Fe with NTA

Table 1. Determination of formal potentials of V(V)/V(IV) system and Fe(III)/Fe(II) system in the presence of NTA and DTPA

pH	Potential (mV) in the presence of NTA		Potential (mV) in DTPA presence	
	V(V)/V(IV) system	Fe(III)/Fe(II) system	V(V)/V(IV) system	Fe(III)/Fe(II) system
1.0	380	624	280	670
1.5	344	581	243	594
2.0	303	538	201	542
2.5	265	504	172	510
3.0	229	472	145	485
3.5	181	445	106	450
4.0	130	421	24	432
4.5	64	401	-43	412
5.0	14	380	-94	390
5.5	-27	352	-136	367
6.0	-72	322	-182	332
6.5	-97	289	-208	294
7.0	-125	254	-237	261
7.5	-141	226	-254	233
8.0	-155	194	-269	210
8.5	-176	153	-291	153
9.0	-196	108	-312	10
9.5	-210	69	-327	-65
10.0	-224	28	-342	-120

3.3. Sensitivity of graphite electrode towards V(V)-V(IV) system

The redox sensitivity of dry-cell graphite electrodes was tested by observing the redox potential exhibited in a mixture of vanadyl sulphate and sodium metavanadate (in 1.0 M sulphuric acid) in different ratio as indicated in Table 2 and Figure 4. The potential vs log[V(V)]/[V(IV)] curves are represented in Figure 5. It could be seen that the response of the graphite electrode was linear over the range of log[V(V)]/[V(IV)] ratio from (-0.958 to +0.958), and this might be attributed to the relative response of the electrodes to the reducing and oxidizing species of the couple.

The response of the graphite electrode in the investigated redox system, calculated by the least square method is

$$E = 546 + 65\ \log[\mathrm{V(V)}]/[\mathrm{V(IV)}],\ \mathrm{mV}$$

The calculated correlation coefficients (r) showed the linearity of the obtained results, whereas the investigations performed using graphite electrode indicated the effectiveness of the graphite electrode as the indicator electrode for the potentiometric titrations. This characteristic response of the dry-cell graphite electrode to the changes in the rate of [Ox]/[Red] might be subjugated for the end point indication.

Table 2. Sensitivity of graphite electrode towards V(V)-V(IV) ratio

Range (Log [V(V)]/[V(IV)])	(-0.958 to +0.958)
Slope	65.48
Intercept	546.43
Correlation coefficient (r)	0.9998

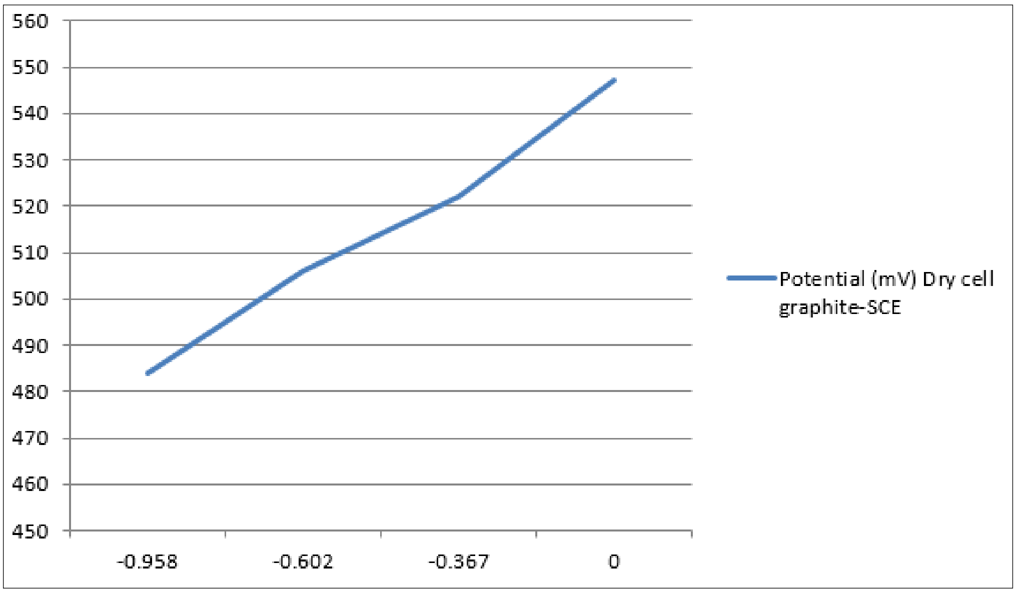

Figure 4. Sensitivity of graphite electrode versus SCE

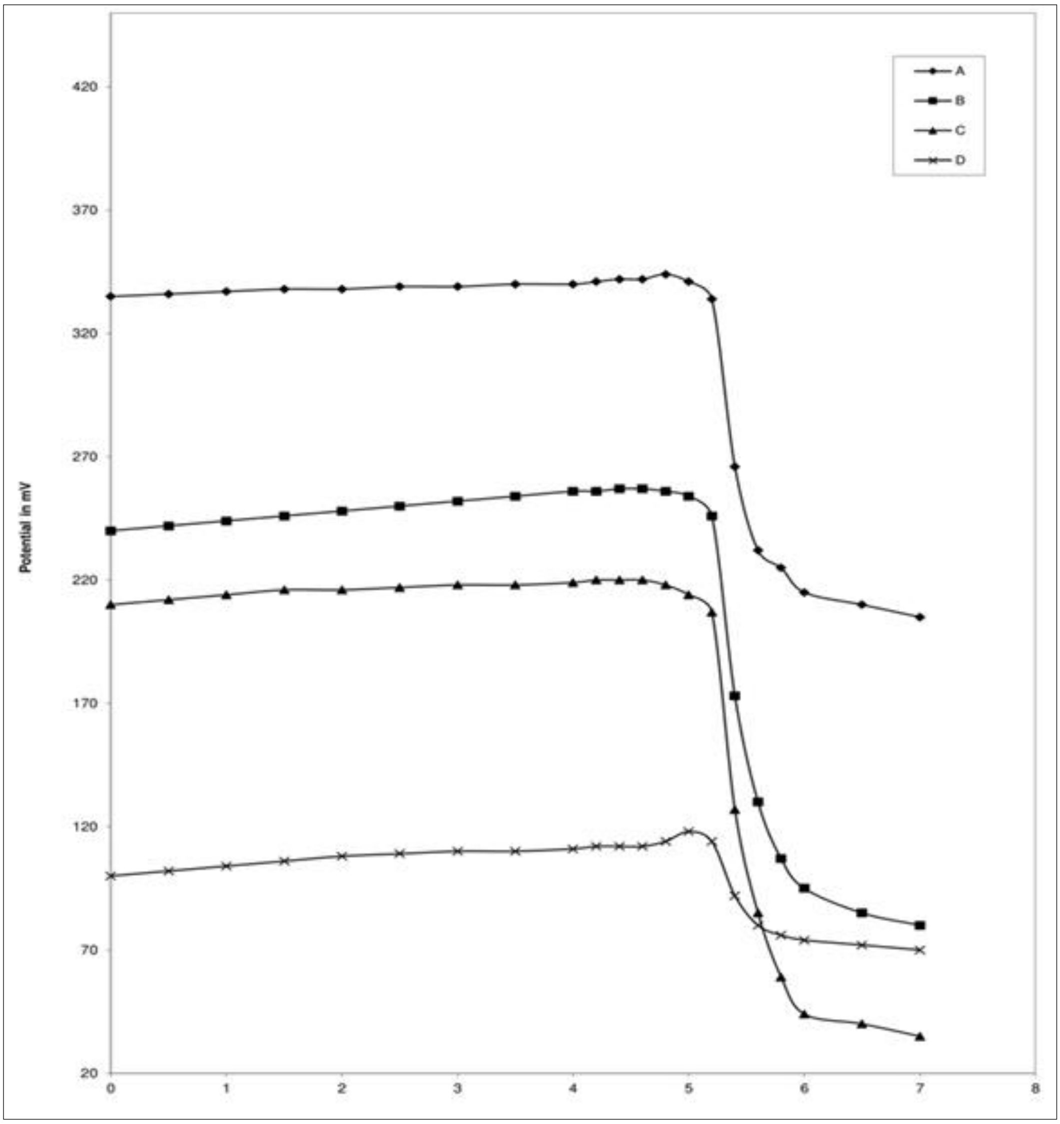

Figure 5. Effect of *p*H study towards Vanadium system

Titration of vanadium with nitrilotriacetic acid (NTA) and diethylenetriaminepenta-acetic acid (DTPA)

The effects of NTA and DTPA on of metal ions are discussed in [45-48]. NTA can form a 1:1 complex with the vanadium ions and the complex ion $VO(NTA)^-$ formed was indefinitely stable. The five-membered ring chelate formed by vanadium (IV) along with NTA caused for the formation of more stable complex with high stability constant value (logK=11.6) [49,50]. The value of vanadium (IV) with DTPA (log K=20.8) [50] could facilitate the feasible titration and the completion of the reaction. The titrations were quantitative and satisfactory enough when they were carried out even at room temperatures (25-30^o C).

Influence of *p*H

In order to get the *p*H, the NTA and DTPA was observed that in the case of NTA, the potential jump near the equivalence point increased linearly from *p*H 3-5 [1], and a maximum potential jump of 80 mV was observed at *p*H 5 after which the potential jump decreased on further increase with the *p*H of the solution. At *p*H 6 and above, a blue precipitate, probably $VO(OH)_2$ was formed immediately, which could be re-dissolved on lowering the *p*H values. The *p*H of the resulting solution was adjusted and the results are shown in Figure 6.

In the case of DTPA, at *p*H above 6, the reduction of vanadium with iron is considerably the potential jump observed at the equivalence point was also very low. The potential jump of 175 mV was observed at *p*H 4.5 in the presence of 0.05 M DTPA. This result suggested that the chelating agent DTPA has facilitated more the potentiometric titration than that of NTA by causing a significant potential jump. This could be attributed to the reason that the presence of five carboxymethyl groups in DTPA could ease the formation of more stable complexes and the results are shown in Figure 7.

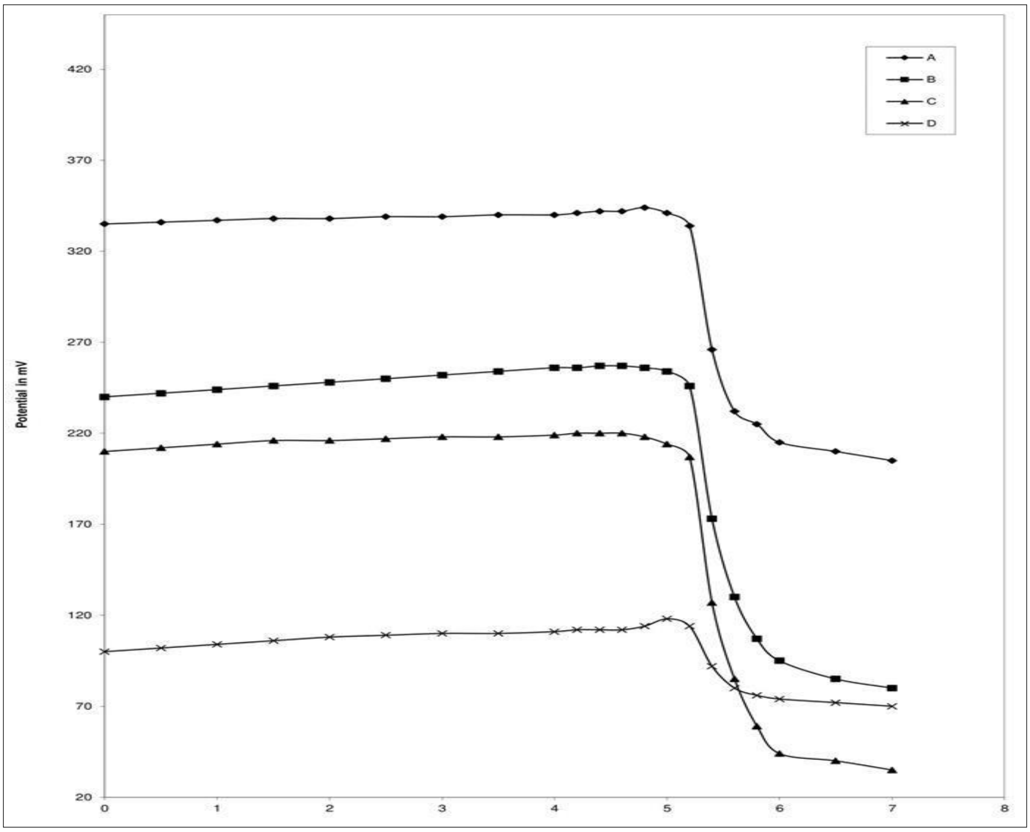

Figure 6. Potentiometric titration of 5.0 mL of 1.02 x 10^{-2} M vanadium (V) with 9.3 x 10^{-3} M iron (II) at various *p*H in the presence of 0.05 M NTA using platinum as an indicator electrode (Curve A *p*H 3.0; Curve B *p*H 4.0; Curve C *p*H 5.0; Curve D *p*H 6.0)

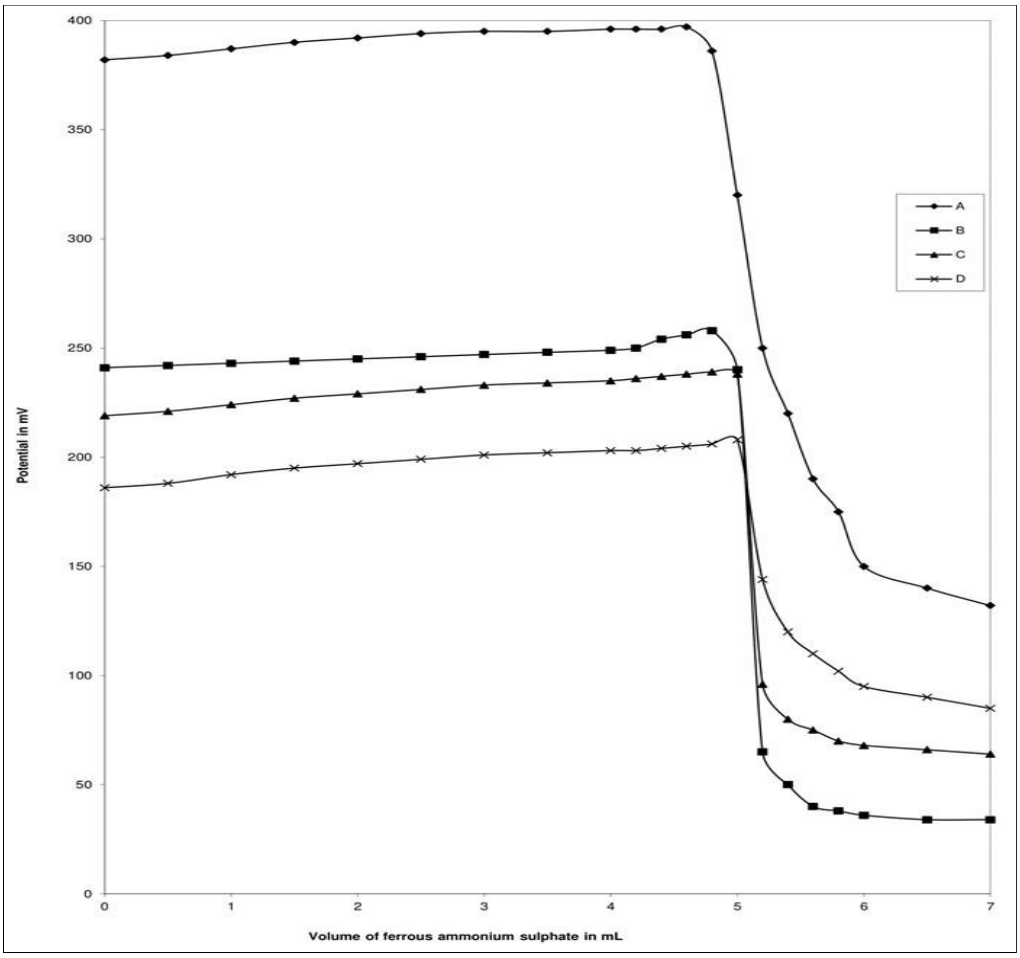

Figure 7. Potentiometric titration of 5.0 mL of 1.06 x 10^{-2} M vanadium (V) with 9.64 x 10^{-3} M iron (II) at various *p*H in the presence of 0.05 M DTPA using platinum as an indicator electrode (Curve A *p*H 3.5; Curve B *p*H 4.5; Curve *p*H 5.5; Curve D *p*H 6.5)

Influence of concentration of NTA and DTPA

In order to study the influence of concentration of chelating agents, the titration was also carried out in the absence of NTA and DTPA and found that there was no potential jump near the equivalence point. The influence of concentration of NTA as shown in Figure 8. From Figure 8, it was observed that a maximum potential jump of 148 mV was observed for 0.3 M NTA at *p*H 5.0. This study suggested that as the concentration of NTA increased, with respect to the concentration of vanadium present in the solution, the potential jump also increased.

The effect of concentration of DTPA on the redox titration of 2.7 mg of vanadium (V) with ferrous ammonium sulphate was examined in the range (0.1-0.005 M) of DTPA at *p*H 4.5 as shown in Figure 9. From the results, it was evident that, with the concentration of 0.01 M DTPA solution, the course of the reaction was entirely quantitative and the potential jump observed at the equivalence point was still disproportionately higher and also the stabilization of the potential was considerably faster. With the increase in the concentration of DTPA solutions, more than ten times of the vanadium concentration was expected, which could favorably influence the size of the potential jump.

The titrations were repeated for different concentrations of vanadium (V). Vanadium (V) could be quantitatively determined with ferrous ammonium sulphate in the presence of 0.05 M concentration of DTPA at *p*H 4.5. The *p*H of the solution was maintained using acetic acid-sodium acetate buffer solution. In the presence of DTPA, the potentials were stabilized instantaneously except near the end point, where the potential stabilization required about 2-3 min.

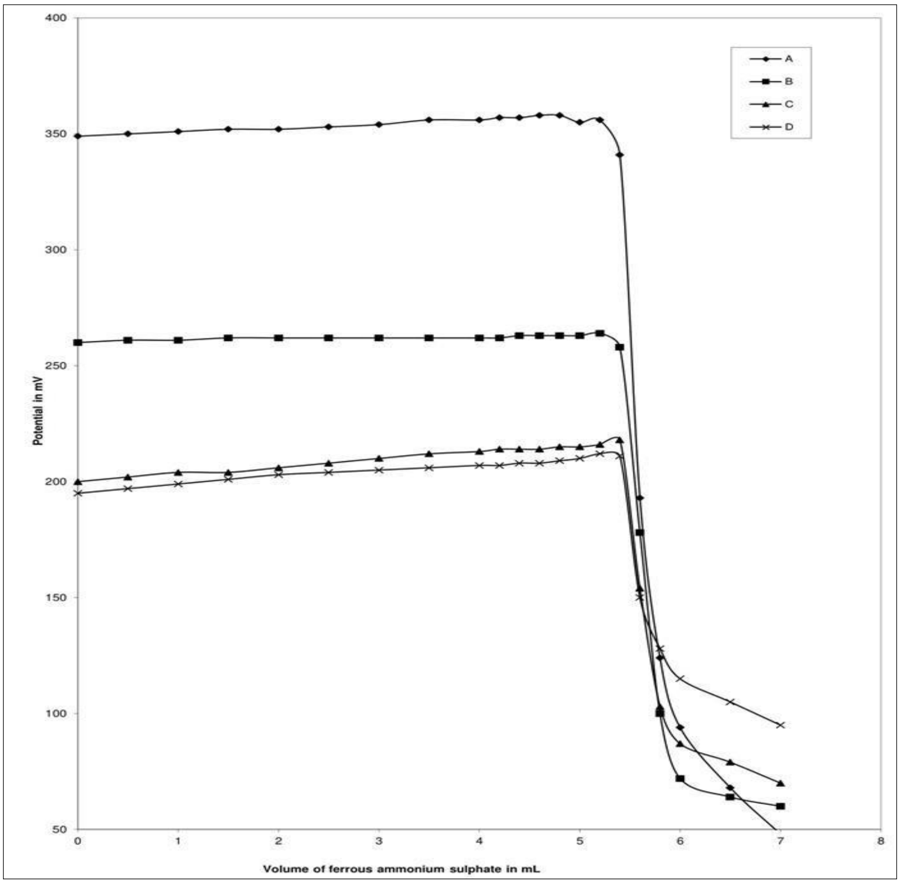

Figure 8. Effect of NTA concentration on the titration curves of 2.60 mg of vanadium (V) with 9.30×10^{-3} M iron (II) at *p*H 4.5 using platinum as an indicator electrode (Curve A 0.30 M; Curve B 0.20 M; Curve C 0.10 M; Curve D 0.01 M)

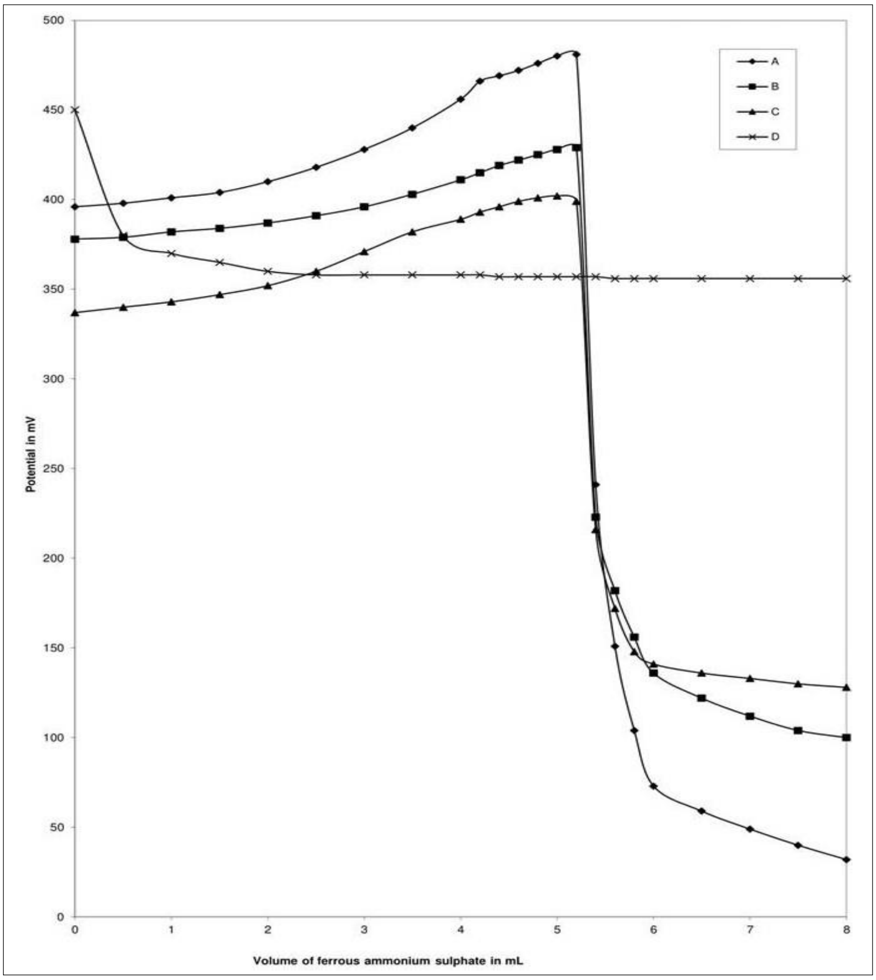

Figure 9. Effect of DTPA titration with 2.70 mg of vanadium (V) with 9.64×10^{-3} M iron (II) at pH 5.0 using platinum as an indicator electrode (Curve A 0.1 M; Curve B 0.05 M; Curve C 0.01 M; Curve D Absence of DTPA)

Titration of vanadium against ferrous ammonium sulphate

In the presence of NTA and DTPA were carried out using platinum and dry-cell graphite electrodes vs saturated calomel electrode (SCE). Graphical representation of the potential against the volume of titrant added, gave an inverted S-shaped curves as shown in Figure 10. The results indicated the gradual increase of potential before the end point and a large potential break at the end point. In the case of NTA, a potential difference of 80 mV for platinum electrode and 53 mV for graphite electrode was observed for 2.6 mg of vanadium (V) in this study.

In the case of DTPA, the concentration of vanadium (V) was varied from 0.51 mg to 71.32 mg in 50 mL of solution using dry-cell graphite. Figure 11 shows the electrode response during the titration of vanadium (V) with iron (II) using platinum and dry-cell graphite electrode vs SCE respectively. A potential difference of 220 mV for platinum electrode and 180 mV for graphite electrode was observed for 2.7 mg of V(V). In the case of both NTA and DTPA, after the end point, the potential values decreased and then they remained almost constant for both type of indicator electrodes on the addition of Fe(II) solutions. Stable potentials and reproducible end points were obtained using both the type of electrodes combination in both NTA and DTPA.

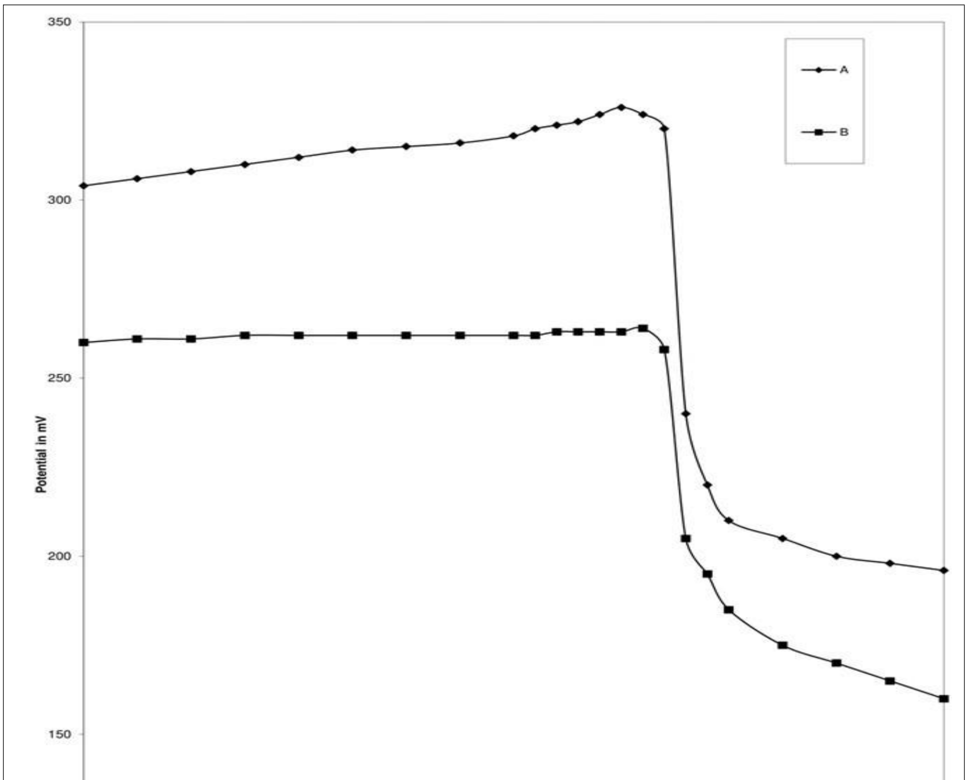

Figure 10. Potentiometric titration of 2.60 mg of vanadium (V) NTA using both platinumand graphite as indicator electrode Vs SCE (Curve A platinum; Curve B graphite)

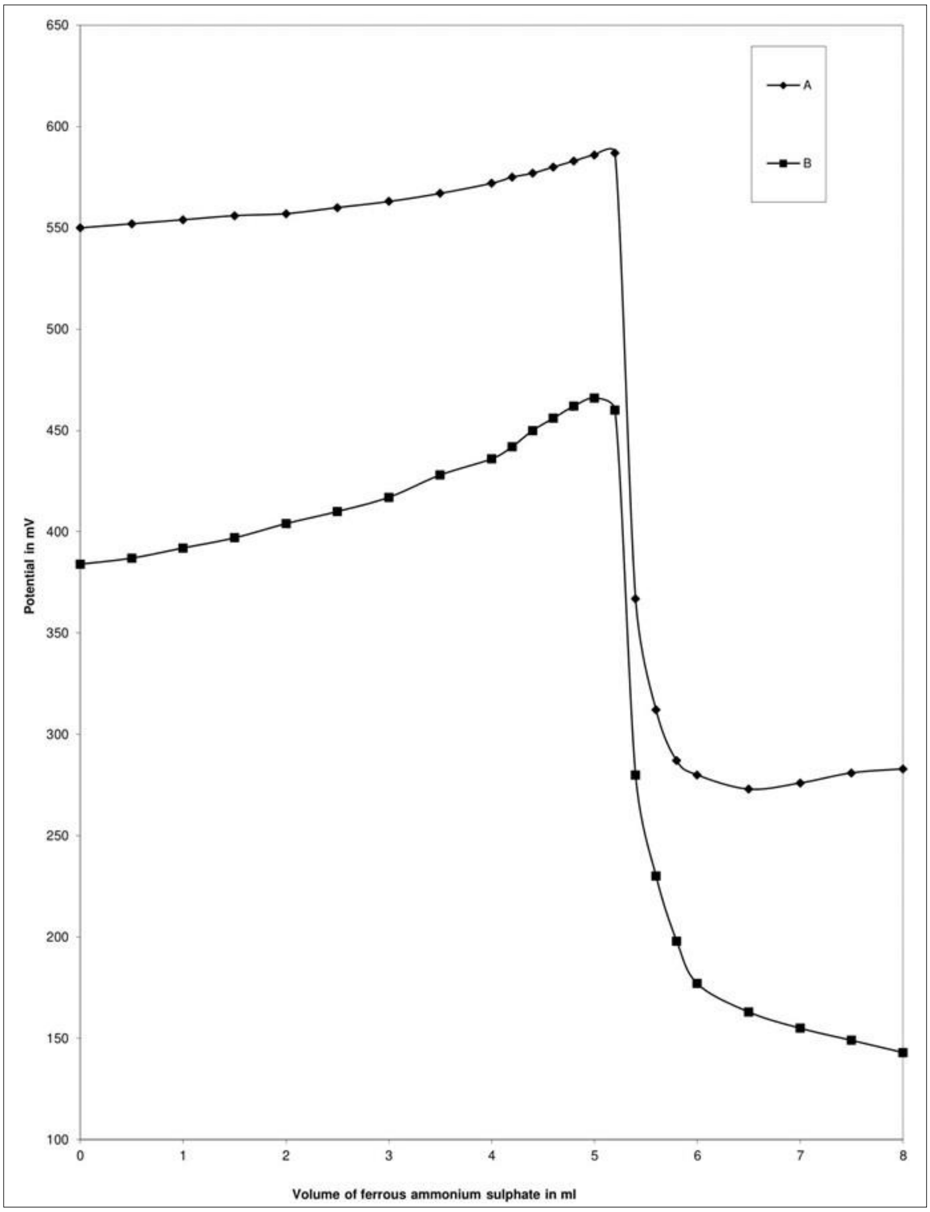

Figure 11. Potentiometric titration of 5.12 mg of vanadium (V) DTPA using both platinum and graphite as indicator electrode Vs SCE (Curve A platinum; Curve B graphite)

Performance metrics

Eight concentrations of vanadium (V) solutions (containing 0.25 mg to 50.88 mg for NTA and 0.51 mg to 71.32 mg for DTPA) were performed using graphite electrodes in the presence of 0.01-0.3 M of NTA and DTPA at *p*H 5.0. The results are presented in Table 3 Table 4. The mean recovery for NTA was 100.24% and the mean standard analytical error was found to be 0.0062.

Table 3. Result of potentiometric titration of V with F

Amt.Taken (mg)	**Amt. Found (mg)**	**Mean $(\overline{x})$ ± SD**	**Mean Recovery (%)**	**Standard Analytical Error**	**Student's 't'**
0.25	0.25, 0.25, 0.26, 0.25, 0.25, 0.26	0.253±0.005	101.33	0.0021	1.58
0.51	0.51, 0.51, 0.50, 0.52, 0.52, 0.50	0.510±0.009	100.24	0.0036	0.34
1.53	1.53, 1.52, 1.53, 1.52, 1.55, 1.53	1.530±0.011	100.24	0.0045	0.83
2.54	2.54, 2.55, 2.54, 2.51, 2.55, 2.54	2.538±0.015	99.78	0.0060	0.91
5.09	5.09, 5.11, 5.09, 5.12, 5.09, 5.08	5.097±0.015	100.18	0.0061	1.47
15.26	15.27, 15.26, 15.27, 15.29, 15.30, 15.25	15.273±0.019	100.07	0.0076	1.37
25.44	25.44, 25.44, 25.43, 25.48, 25.46, 25.4.3	25.447±0.020	100.03	0.0080	1.08
50.88	50.89, 50.88, 50.87, 50.92,50.91, 50.87	50.890±0.028	100.02	0.0114	0.93
Mean:			100.24	0.0062	1.06

Table 4. Potentiometric titration of V with Fe of DTPA

Amount Taken (mg)	**Amount Found (mg)**	**Mean ($\overline{x}$) ± SD**	**Mean Recovery (%)**	**Standard Analytical Error**	**Student's 't'**
0.51	0.51, 0.52, 0.50, 0.52, 0.51, 0.51	0.512 ±0.008	100.33	0.0031	0.54
1.01	1.03, 1.03, 1.00, 1.02, 1.03, 1.02	1.021±0.012	100.96	0.0048	2.02
3.06	3.08, 3.04, 3.02, 3.08, 3.06, 3.04	3.053±0.024	99.78	0.0099	0.67
5.09	5.12, 5.07, 5.08, 5.13, 5.06, 5.09	5.092±0.028	100.03	0.0113	0.15
10.19	10.22, 10.16, 10.20, 10.22, 10.18, 10.14	10.187±0.033	99.97	0.0133	0.25
20.38	20.32, 20.36, 20.42, 20.38, 20.30, 20.42	20.367±0.050	99.93	0.0204	0.65
50.94	50.98, 50.92, 50.90, 50.98, 51.02, 50.90	50.950± 0.051	100.01	0.0205	0.39
71.32	71.24, 71.34, 71.36, 71.26, 71.36, 71.34	71.317± 0.053	99..99	0.0215	0.15
		Mean:	100.12	0.0131	0.60

Table 5. Determination of vanadium in steel samples

Sample composition	Amount of (V) present in samples (%)	Amount of vanadium found by proposed method	Amount of vanadium found by reference method	*t*	*F*
C,0.56; Si,0.24; Mn,0.90; Ni,0.23; Cr,1.03; Mo,0.03; V,0.12; Cu,0.17; P,0.021; S,0.016;	0.12	0.10, 0.06, 0.08, 0.07, 0.11, 0.08, 0.10 Mean = 0.08 ± SD = 0.02	0.12,0.07,0.06,0.10, 0.08,0.11,0.08 Mean = 0.09 ± SD = 0.02	0.26	1.46
C,0.17; Si,0.13; Mn,0.53; Cr,1.03; Mo,0.85; V,0.28; Cu,0.10; P,0.015; S,0.025;	0.28	0.24, 0.26, 0.22, 0.20 0.21, 0.26, 0.24 Mean = 0.23 ± SD = 0.02	0.24, 0.28, 0.26, 0.22, 0.20, 0.24, 0.26 Mean = 0.24 ± SD = 0.03	0.74	1.30

Potentiometric with iron for the determination of vanadium in alloy steel samples of two different percentage composition of vanadium. Vanadium in these steel samples were also determined by potentiometrically titrating vanadium (V) with iron (II) at highly acidic medium *p*H = 1 and seven replicate titrations were performed. The results are given in Table 5. *F*-test of comparing variances was calculated and F-ratio (1.46 and 1.30) did not exceed the critical value of 5.82 at 5% level of significance and 6, 6 degrees of freedom indicating that no significant difference in the precision.

4.Conclusions

Thus the experiment of potentiometric titration model is done and it is used for analyzing the vanadium (V) based effect of NTA and DTPA with conditional redox potentials. This could be titrated with potentiometrically Vanadium and Fe. Especially the use of complexing agents could provide sharp end point for detection and the satisfactory reproducibility of the end points with a very large potential jump using graphite electrodes. Here the comparative study carried out between NTA and DTPA indicated that the extent of potential jump caused by DTPA was found to be higher than that of NTA. On the other hand, the response of the graphite electrode was satisfactory, reproducible and in good agreement with the various studies. The results suggested that the graphite electrode showed better performance when compared to the platinum electrode (for comparison purpose only) and hence it was suggested that the above method could be used for the vanadium in steel and pharmaceutical samples evaluation.

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