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Determination of vanadium(V) by direct automatic potentiometric titration with EDTA using a chemically modified electrode as a potentiometric sensor

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Abstract

A chemically modified electrode (CME) was prepared and studied as a potentiometric sensor for the end-point detection in the automatic titration of vanadium(V) with EDTA. The CME was constructed with a paste prepared by mixing spectral-grade graphite powder, Nujol oil and *N*-2-naphthoyl-*N*-*p*-tolylhydroxamic acid (NTHA). Buffer systems, pH effects and the concentration range were studied. Interference ions were separated by applying a liquid–liquid extraction procedure.

The CME did not require any special conditioning before using. The electrode was constructed with very inexpensive materials and was easily made. It could be continuously used, at least two months without removing the paste.

Automatic potentiometric titration curves were obtained for V(V) within 5×10^{-5} to 2×10^{-3} M with acceptable accuracy and precision. The developed method was applied to V(V) determination in alloys for hip prothesis.

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1. Introduction

Abundant references concerning the determination of vanadium with EDTA is available in literature.

As Schwarzenbach and Flaschka [1] and Pribil [2] stated, most of the published procedures are based on the use of V(IV) whether in direct or back titrations with end-point detection through metallochromic indicators. In all cases, the addition of some reductor reagents such as ascorbic acid or sulphite anion and the adjustment of pH previous to the determination are required.

Reilley et al. [3] developed a volumetric method with a potentiometric indication of the end point for V (IV).

Many efforts have been performed in order to develop direct procedures for the determination of vanadium(V) with EDTA.

Schwarzenbach, Flaschka and specially Pribil consider that the very significant difficulties found are due to the notable tendency of V(V) to form polymerized species strictly dependent on pH. As an example, these authors mentioned the determination proposed by Sajó, stated by Pribil, the titration being possible at a pH range between 6.7 and 6.9.

Pribil mentioned the studies performed by Ringbon concerning the complexation of vanadium(V) with EDTA. This researcher proposed the following reaction between V(V) and EDTA.

$$VO_3{}^- + H_2Y^{2-} \rightarrow VO_2Y^{3-} + H_2O$$

The complex VO_2Y^{3-} is very stable: $\log K = 18.1$. In spite of this favorable constant, titration becomes very difficult due

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to the narrow pH range in which the complex is stable, because of the formation of polymeric vanadium(V) species. According to Pribil, Sajó in his article suggested to carry out titration at pH 4.8–6.8 preventing the formation of polymeric species by adding glycerol or mannitol as auxiliary complexing agents. Pribil stated that none of these methods have been used in real practice.

As Bard et al. [4] stated, the polymeric species that are formed at the different pH ranges are still subject of disagreement.

The aim of this paper was to develop a new carbon paste electrode modified with *N*-2-naphthoyl-*N*-*p*-tolylhydroxamic acid (NTHA) to determine V(V) with EDTA in a direct procedure by a volumetric technique with automatic potentiometric end-point detection. The method has been applied to the determination of V(V) in several ferrous and non-ferrous alloys.

Concerning hydroxamic acids, these are organic reagents with a very weak acid character that form insoluble complexes in water with several metal ions but are soluble in hydroalcoholic medium and in organic solvents. Hydroxamic acid, particularly, *N*-benzoyl-*N*-phenylhydroxamic acid (BPHA) has been used in the gravimetric determination of Fe(III), Bi(III) and Mn(II) [5], but there are no references concerning this kind of determination for V(V). One of the authors of this paper determined V(V) [6] and Ti(IV) [7] with NTHA by a liquid–liquid extraction procedure and spectrophotometric determination of the extracted complexes. This previous paper permitted us to carry out the proposed work.

2. Experimental

2.1. Apparatus

All potentiometric titrations were made with an ORION Automatic Titrator (960 Model Autochemistry System, ORION Research Inc., Cambridge, MA), by using NTHA–graphite paste electrode in conjunction with a double junction Ag/AgCl electrode (Orion 90-02).

2.2. Reagents

All reagents were of analytical grade.

2.2.1. NTHA reagent

The reagent was synthesized and purified according to [8]. It was prepared by condensation of *N*-*p*-tolylhydroxylamine (0.15 mol) with 2-naphthoyl chloride (0.1 mol) at 0 °C in ethylether medium. Then ether was evaporated by vacuum and the dry residue was powdered in a mortar with a $NaHCO_3$-saturated solution for neutralization. The product was filtered, washed with water and recrystallized from ethanol; m.p. 143–144 °C, reported 145 °C.

2.2.2. Standard vanadium solution (ca. 0.001 M)

0.11699 g of NH_4VO_3 was dissolved in distilled water and diluted to the mark in a 1000 mL volumetric flask.

2.2.3. Standard EDTA solution (ca. 0.0025 M)

The EDTA disodium salt was dissolved in distilled water and standardized by potentiometric titration with a Ca(II) solution prepared from calcium carbonate salt.

2.2.4. Acetic acid–acetate buffers (ca. 0.2 M)

3.99 g of sodium acetate was dissolved in about 150 mL of distilled water. Acetic acid was added until the desired pH value was reached. The final pH adjustment was made after dilution to 250 mL.

2.2.5. KH_2PO_4–Na_2HPO_4 buffer (ca. 0.2 M)

6.8045 g of KH_2PO_4 and 8.9005 g of $Na_2HPO_4 \cdot 2H_2O$ were dissolved in distilled water and transferred to a 250 mL volumetric flask and diluted to mark with distilled water and the pH value was adjusted to 6.

2.2.6. NTHA solution 0.1%

0.1 g of NTHA was dissolved in 40 mL of alcohol-free Cl_3CH, transferred to a 100 mL volumetric flask and diluted to the mark with alcohol-free Cl_3CH.

2.2.7. $NaHCO_3$ solution (ca. 0.1 M)

2.075 g of $NaHCO_3$ was dissolved in 50 mL of distilled water, tranferred to a 250 mL volumetric flask and diluted to the mark with distilled water.

2.3. Preparation of the modified carbon paste electrode

The electrode was constructed as follows. The electrode body was built with a 140 mm long and 8 mm diameter borosilicate glass tubing. A tinned copper disk (about 7.5 mm diameter) was attached through an epoxy resin, inside the glass tubing and about 3 mm from one of its ends, forming a cavity. A copper wire (20 mm longer than the glass tube) was soldered to the copper disk to provide the electrical contact. Portions of 200 mg of a paste prepared with equal parts of spectral-grade graphite powder and Nujol oil and 7.5 mg of NTHA previously hand mixed in a mortar were packed into the cavity of the electrode and smoothed with a glass spatula as shown in Fig. 1. The first titration with this electrode prepared as described above gave erroneous results, so before titrating the samples the electrode must be activated by titrating an aliquot of standard V(V) solution.

The electrode durability was about two months, and when it was not in use, it was stored in a fresh and dry place.

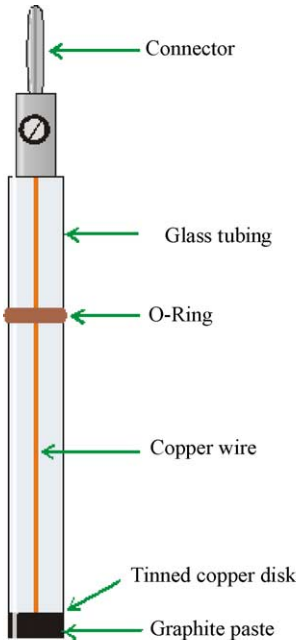


Fig. 1. Schematic representation of a longitudinal section of NTHA–graphite paste electrode.

3. Procedure

3.1. Vanadium(V) titrations

Twenty-five milliliters of a vanadium(V) 0.001 M standard solution was transferred into a cell and 3 mL of phosphate or acetate buffer solution (pH 6) was added to it. Both the working and reference electrodes were connected, the solution was stirred with a magnetic stirrer and then the titration was started with a EDTA 0.0025 M standard solution.

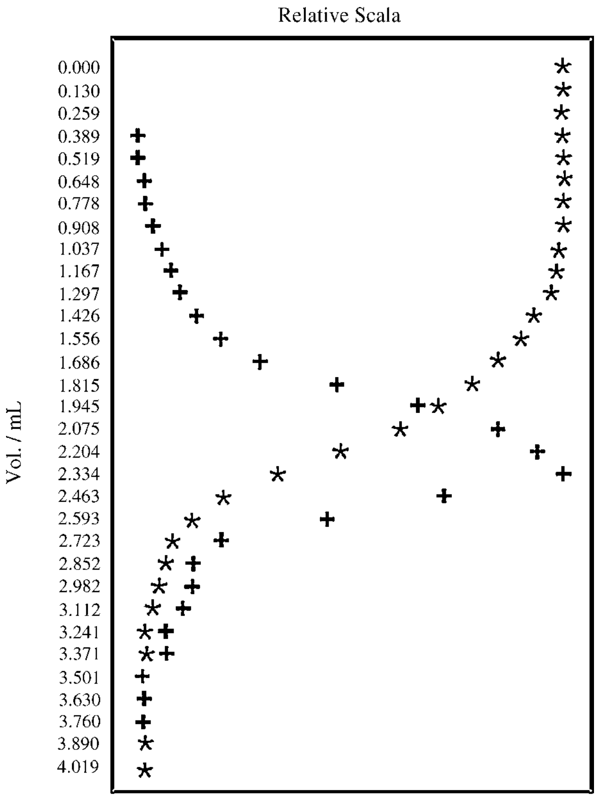
4. Results and discussion

4.1. Optimal experimental conditions

Buffer systems, pH and range of determinable concentrations were tested.

pH 2.5 and 3.9 (acetic acid–sodium acetate), pH 6 (potassium dihydrogen phosphate–disodium hydrogen phosphate and acetic acid–sodium acetate) and pH 9.5 (ammonia–ammonium chloride) buffer solutions were tested. The titration performed at pH 2.5 and 3.9 did not give any satisfactory results, observing that the solutions turned yellowish. Such results are in agreement with the formation of polymeric species that react very slowly with EDTA at these pH values as Sajó described.

Titrations at pH 9.5 were not possible to be performed. According to Bard et al. within the pH range 8.5–13 would prevail the $V_2O_7^{4-}$ species that obviously cannot react with EDTA.



* The curve of titration of 5 mL of V(V) solution 10^{-3} M at pH 6 with EDTA 2.5 x 10^{-3} M

+ Curve obtained by applying the first derivate method to the data for curve *

Fig. 2. The titration curve.

The titration carried out at pH 6 with either acetic acid–sodium acetate or potassium dihydrogen phosphate–disodium hydrogen phosphate buffers gave well-defined potentiometric titration and first derivative curves with a stoichiometry EDTA:V 1:1 as shown in Fig. 2.

The titration experiences carried out without doping the sensor electrode with NTHA (this is, with a pure carbon paste electrode) did not show titration curves, which reveals the main incidency of the reagent on the end-point indication. The absence of signal was also observed when the titration was performed with glassy carbon, platinum and gold electrodes.

With the electrode prepared as described above under the pH and buffer system-selected conditions, tests were performed in order to obtain the maximum and minimum limits of V(V) concentration. The results are shown in Table 1.

Table 1
Some typical results obtained in EDTA titrations of pure V(V) solutions using a NTHA–graphite paste electrode as potentiometric indicator of the end-point

Concentration V(V) added (M)	Found mean	Standard deviation
2×10^{-3}	2.05×10^{-3}	0.10
1×10^{-3}	1.04×10^{-3}	0.05
1×10^{-4}	1.006×10^{-3}	0.04
5×10^{-5}	4.98×10^{-5}	0.21

Six replicates in each case.

From these results we inferred that the optimal V(V) determinable concentration range was 5.00×10^{-5} to 2.00×10^{-3} M.

4.2. Applications

The developed method was tested in the vanadium determination in two alloys:

(a) A certificated steel B.C.S. No. 241/1 percentual composition: W = 19.38; Mo = 0.52; Cr = 5.03; Co = 5.67; C = 0.85; Si = 0.33; P = 0.021; Mn = 0.30; Sn = 0.025 and V = 1.57.
(b) Non-ferrous alloy for hip implants percentual composition Ti–6Al–4V.

(1) In order to verify the effect of possible interferent, determinations were carried out in solutions that contained the same percentage of each separated component, as well as vanadium.

  (i) Tungsten.

  Two alternative procedures were tested in order to verify if W could interfere in vanadium determination.

  In the first one, the solution that contained tungsten as tungstate and vanadium as metavanadate in an approximate ratio 3W:1V was treated following the standard procedure acidifing the solution with HCl and precipitating it as tungstic acid. Then, the tungstic acid was separated by centrifugation and the supernatant solution was neutralized with NH_3 until pH 7. The required aliquot to perform titration was adjusted to pH 5.85–6 with 0.2 M sodium acetate buffer and V(V) was determined as previously described.

  A very low average (0.6×10^{-3} M) was found in four replicates, therefore this procedure was discarded to eliminate the tungsten interference.

  In the second one, the precipitation of Fe(III) was avoided by adding tartaric acid as in the case of the determination of Ni with dimethylglyoxime [9] meanwhile tungsten remained in solution as a complex. Then, from the available information, the complexation between NTHA and V(V) is not altered by the presence of high concentration of tartaric acid and therefore, 5 mL of tartaric acid 1.64 M was added to the vanadium–tungsten solution. After that, the vanadium titration was performed as previously described.

  The average value obtained for four replicates was 1.01×10^{-3} M with $s = 0.05$.

  (ii) Chromium.

  When a ferrous alloy containing chromium is dissolved in acidic medium, this one is found as Cr(III) since this is the most thermodynamically stable state.

  The interference of Cr(III) arises from the competition with V(V) for the auxiliary complexing agent (NTHA) and due to the fact that at optimal pH for the titration it would precipitate as $Cr(OH)_3$. Regarding the EDTA, its complex formation constant is not favorable compared with V(V), and its reaction with EDTA is slow.

  A solution was prepared from $Cr_2(SO_4)_3$ and NH_4VO_3 in an acid medium, and 5 mL of tartaric acid solution 1.64 M was added; the pH was adjusted and V(V) was determined.

  The average of four replicates was 1.03×10^{-3} M and $s = 0.06$.

  (iii) Molybdenum.

  The B.C.S. No. 241/1 is one of the few certified available steels in which vanadium is present in higher concentration than molybdenum. For the molar ratio 3V:1Mo, that corresponds to the percentage of both elements in the alloy, using a sodium acetate–acetic acid buffer, an average of 0.993×10^{-3} M with $s = 0.07$ was obtained for three replicates. It was possible to extend the determination of vanadium in presence of molybdenum for molar ratio up to 1:1.

  For ratios 2Mo:1V and above, a significant interference appears in the determination of vanadium possibly due to some competition of Mo with V(V) for NTHA since EDTA does not react directly with Mo.

  The addition of tartaric acid, that was effective for W, or oxalic acid, did not give any positive results.

  (iv) Cobalt.

  In the molar ratio 3Co:1V in which they are present in the studied alloy, it was not possible to determine V(V) in presence of Co(II), not even in molar relations 2:1 or 1:1 since the obtained data were very erratic. However, the alloys that contain these elements simultaneously are not very frequent. The bad electrode response can be attributed to Co that reacts with EDTA before than V(V) since its formation constant at the pH at which the titration is performed is much higher than the one for V(V) since at such pH the complex formation constant of EDTA–V(V) is between 7 and 8. Consequently, all the ions that can be titrated at those conditions will be first complexed with EDTA. This is precisely the case of Co(II). Besides, there can also be some competition between V(V) and Co(II) by NTHA.

  The remainder elements that take part of the alloy, except Fe (matrix) are at very low concentrations or else they are lost as gases during the acid attack (CO_2, SO_2); therefore the V(V) determination is not affected by them.

  The assays carried out have revealed that ferrous alloys that contain cobalt at any molar relation with respect to vanadium do not allow the application of the proposed method to determine vanadium. For the case of molybdenum, the tolerance is a bit larger even though limited. Indeed, ferrous alloys that contain molybdenum and vanadium instead of cobalt and vanadium are more frequent as it occurs in high-speed steels, but for these, the percentage of molybdenum is higher than vanadium.

In spite of these difficulties, the determination of V(V) with EDTA can be applied after a liquid–liquid extraction step of vanadium as it will be described in the determination of vanadium in hip implants alloys.

(2) Determination of V(V) in alloys for hip prothesis.

The alloy for hip prothesis is a special material that must have very severe resistance requirements to corrosion and to high loads that in general result from a combination of static and cyclic loads that create a very complex stress. Amongst the most used biocompatible alloys in osseous surgery, there are some special stainless steels, unalloyed titanium and titanium alloyed with Al and V likes the Ti–6Al–4V one.

The latter contains a percentage of vanadium that can be determined under optimal conditions for the developed method.

It was not possible to obtain a certified sample of this material so a simulated solution containing the percentage of the components was prepared from the reagents.

It was not possible to apply direct titration because at the pH at which the titration is performed, titanium and aluminium interfere with precipitates formation. So, previously titration was performed, and a liquid–liquid extraction step was introduced using NTHA dissolved in Cl_3CH as extractant in 4 M hydrochloric acid in order to extract V(V) to the organic phase as V(V)–NTHA complex while aluminium and titanium remain the aqueous phase since they are not complexed by NTHA at high-acidity conditions. Then, the V(V)–NTHA complex was retroextracted with a $NaHCO_3$ solution. After that, V(V) determination was performed following the recommended procedure.

The extraction–retroextraction procedure is explained as follows.

Ten milliliters of solution containing the percentual quantities of V(V), Al(III) and Ti(IV) in 4 M HCl was added in a separatory funnel. Then, 5 mL 0.1% NTHA chloroformic solution was also added. The separatory funnel was then shaken vigorously for about 2 min. After the phases separated, Al(III) and Ti(IV) remained behind in the aqueous phase while V(V) was transferred to the organic phase as V(V)–NTHA complex.

This process was repeated six times with fresh NTHA solution. The organic extracts, after being dried with anhydrous Na_2SO_4, were collected into a 50 mL volumetric flask and diluted to the mark with chloroform. The chloroformic extracts were transferred to another separatory funnel into which 10 mL of 0.1 M $NaHCO_3$ solution was added. The separatory funnel was mechanically shaken for 30 min. This retroextraction was repeated once again with a fresh $NaHCO_3$ solution.

The aqueous phases were collected into a beaker and heated on a sand bath to evaporate the chloroform, otherwise, the remaining chloroform would dissolve the carbon paste.

Six replicated extractions–retroextractions were performed.

The obtained results are shown in Table 2.

Table 2
Results obtained in six replicates in the determination of V(V) in alloys for hip prothesis

V(V) added (%)	V(V) found (%)
4.00	3.95
4.00	3.97
4.00	4.01
4.00	3.95
4.00	4.02
4.00	3.98

Mean = 3.98; standard deviation = 0.03.

5. Conclusions

The developed method allows the determination of V(V) in several ferrous and non-ferrous alloys within a concentration interval of 5×10^{-5} to 2×10^{-3} M that covers the majority of the alloys that contain vanadium. In most frequent cases, it is necessary to include a separative step (liquid–liquid extraction) in order to separate the vanadium(V) from their alloy concomitants to avoid interferences.

According to the reported results, it is almost impossible to determinate V(V) in a direct way with EDTA; however, we have proved in this work that it is possible to overcome the limitations of the narrow range of pH in which V(V) quickly reacts with EDTA. Also, the final point of the titration is much more reliable than the one obtained with any metallochromic indicator. Besides, we have to point out the known advantages of the automatic potentiometric indication.

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