

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 prosthesis.

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1. Introduction

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

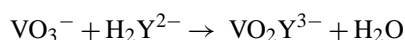
As Schwarzenbach and Flaschka [1] and Pribil [2] stated, most of the published procedures are based on the use of V(IV) whether in direct or back titrations with end-point detection through metallochromic indicators. In all cases, the addition of some reductor reagents such as ascorbic acid or sulphite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



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 NaHCO₃-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 NH₄VO₃ 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. KH₂PO₄–Na₂HPO₄ buffer (ca. 0.2 M)

6.8045 g of KH₂PO₄ and 8.9005 g of Na₂HPO₄·2H₂O 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 Cl₃CH, transferred to a 100 mL volumetric flask and diluted to the mark with alcohol-free Cl₃CH.

2.2.7. NaHCO₃ solution (ca. 0.1 M)

2.075 g of NaHCO₃ was dissolved in 50 mL of distilled water, transferred 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.

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