DETERMINATION OF VANADIUM BY CATHODIC STRIPPING SQUARE-WAVE VOLTAMMETRY

Rubin Gulaboski, Valentin Mirčeski, Simka Petrovska-Jovanović,
Kornelija Stojanova and Valentina Trajkovska

*Institute of Chemistry, Faculty of Natural Sciences and Mathematics,
Skopje Republic of Macedonia*

Abstract. A cathodic stripping square-wave voltammetric method for determination of V(V) is developed. In 0.1 mol/L ammonia buffer with pH from 8.60 to 8.90, V(V) is involved in two redox processes. The first process corresponds to the reduction of V(V) to V(IV) at potential of about -0.55 V and the second one is the reduction of V(IV) to V(II) at potential of about -1.35 V vs. Ag/AgCl (saturated KCl). The reduction of V(V) to V(IV) appears to be a surface redox reaction in which both the reactant and the product of the redox reaction are strongly adsorbed at the surface of the hanging mercury drop electrode. Calibration curves in the concentration region from 10^{-8} to 10^{-5} mol/L were constructed. The effect of the interference ions is investigated. At accumulation time of 180 s, the detection limit of V(V) is 1.5×10^{-8} mol/L. The reproducibility of the method varied from 0.2 to 2.0 %.

Key words: Vanadium, cathodic stripping square-wave voltammetry, determination.

Introduction

Vanadium is an exceptionally important element in the industry of the specific types of steels. Also, it is usually present in large number of oil derivatives, such as petroleum, bitumen and as a trace element is presented in the sea, river and tape water [1-3]. Several voltammetric methods were reported for the determination of trace amounts of vanadium in different samples [1-3]. For lower concentrations of vanadium, the technique of adsorptive stripping voltammetry (AdSV) is suitable. Almost all voltammetric methods for quantitative determination of V(V) considered adsorption of vanadium complexes at a hanging mercury drop electrode (HMDE). As complexing reagents for V(V) some compounds are already known in literature, such as, solochrome violet RS [1], catechol [2], 2,5-dichloro-1,4-dihydroxy-3,6-benzoquinone (cholroanilic acid) [4], 2-(5-thiozalolylazo)-p-cresol [3], pyrogallol [5], 8-hydroxyquinoline [6], antipyrylazo III [7] and cupferron [8]. All voltammetric methods for the determination of V(V) mentioned above are characterized with complex matrix which produce a large number of interferences. Also, none of the complexing reagents an only specific for V, so, the determination of V(V) is additionally complicated. In this paper we demonstrated that with the careful selection of the supporting electrolyte, the same adsorption effects of V(V) complexes at a HMDE can be obtained, without additionally complexing ligands. This approach gets very few interferences, so a sensitive and simple adsorptive stripping square-wave voltammetric method for quantitative determination of V(V) is developed.

II. Experimental

The stock solution of V(V) was prepared by dissolving of an appropriate amount of NH_4VO_3 in twice distilled water. Working solutions were prepared daily from the stock solution of 1 mol/L ammonia buffer with pH = 8.60. All experiments were performed using a three-electrode configuration with a hanging mercury drop electrode (PAR 384B) at area of 0.0149 cm^2, Ag/AgCl (saturated KCl) as a reference and Pt wire as a counter electrode. The solutions were deoxigenyzed with pure nitrogen 8 minutes prior to each measurement. All experiments were achieved at room temperature.

Results and discussion

Several buffers with different pH values were tested as supporting electrolytes for V(V). The results for peak current i_p and peak potential E_p are listed in the Table 1. In aqueous solution of 0.1 mol/L ammonnia buffer with pH from 8.4 to 9.2 and in 0.1 mol/L sulfuric acid are mentioned usually two reduction steps which are assigned from V(V) to V(IV) and from V(IV) to V(II) . In ammonia buffer the first peak appears at potential of about −0.51 V and the second one at −1.45 V vs. Ag/AgCl (saturated KCl), respectively, which is in agreement with literature data [4]. It should be noted than in 0.1 mol/L ammonia buffer V(V) exists as a complex of $V(OH)_6^-$ [3]. The first redox process in ammonia buffer is more convenient for analytical purposes, so our attention was focused around this redox reaction.

Table 1. Supporting electrolytes for V(V). Frequency f = 120 Hz, amplitude E_{sw} = 20 mV, scan increment dE = 4 mV.

Supporting electrolyte	E_{p1}/V	i_{p1}/μA	E_{p2}/V	i_{p2}/μA
0.1 mol/L ammonia buffer with pH = 8.60	-0.54	0.59	-1.47	0.40
0.1 mol/L ammonia buffer with pH = 8.90	-0.52	0.50	-1.45	0.38
0.1 mol/L ammonia buffer with pH = 9.20	-0.50	0.44	-1.46	0.43
0.1 mol/L sulfuric acid	0.3	0.10	-1.152	0.50
0.05 mol/L sulfuric acid	/	/	-1.08	0.43

The reduction of V(V) hydroxy complex to V(IV) seems to be a surface redox reaction in which both the reactant and the product of the electrode reaction are immobilized at the electrode surface. The cyclic voltammetric response consists of a cathodic and an anodic peak. These are the narrowest with relatively closed peak potentials. With an increase of accumulation time both cathodic and anodic peaks of cyclic voltammogram were proportionally enhanced. The consequtive cyclization shows no changes in the height of both peaks which implicates no significant desorption of the electroactive material from the electrode surface during the experiment. Also, a phenomenon of splitting square-wave response was obtained. All these experiments confirm that the reduction of V(V) to V(IV)

hydroxy complexes at a HMD electrode is a surface redox reaction, when both the reactant and product are strongly adsorbed at the working electrode.

Quantitative determination of V(V) was achieved using square-wave voltammetry. To obtain the best SWV response useful for quantitative determination of V(V), an optimization of the experimental as well as the instrumental parameters was carried out. The optimal conditions are: frequency $f = 120$ Hz, amplitude $E_{sw} = 20$ mV, scan increment $dE = 4$ mV and accumulation potential $E_{acc.} = -0.3$ V. The calibration plot ($R^2 = 0.99$) is shown in the Fig. 1.

The detection limit with an accumulation time of 180 s was 1×10^{-8} mol/L. The reproducibility of the method expressed in therms of the relative standard deviation varied from 0.2 to 2.0 %. The influence and limit of tolerance of different metal ions are listed in Table 2.
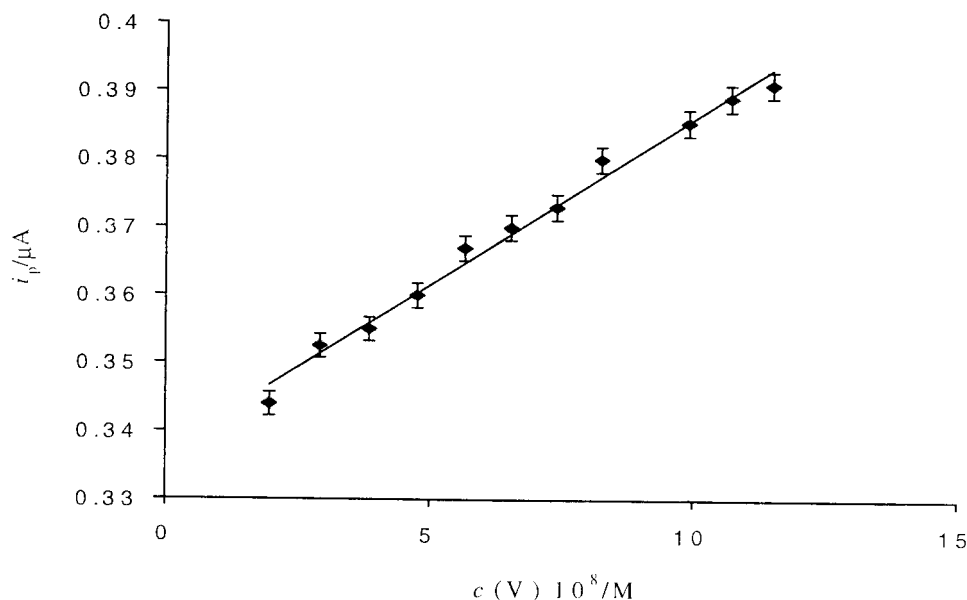

Figure 1. Calibration curve for V(V) in 0.1 mol/L ammonia buffer. The conditions are: frequency $f = 20$ Hz, amplitude $E_{sw} = 20$ mV, scan increment $dE = 4$ mV, accumulation potential $E_{acc.} = -0.3$ V and accumulation time $t_{acc.} = 180$ s.

Table 2. The tolerance limit of different metal ions to the SW voltammetric response of V(V)

Metal ion	Tolerance limit/$c(M^{x+})$/$c(V(V))$
Cd^{2+}	1000
Cu^{2+}	0.025
Pb^{2+}	0.040
Co^{2+}	1000
Ni^{2+}	1000
Cr^{2+}	400

References

[1] Farias, Percio A. M., Takase, Iracema, *Electroanalysis* **4** (8), 823, (1992).

[2] Van den Berg, Constant M. G., Huang Zi Quang, *Anal. Chem.*, **56** (13), 2383, (1984).

[3] Farias, A. M. Percio, A. K. Ohara, I. Takase, L. C. Sergio, J. S. Gold, *Anal. Chim. Acta*, **21** (2), 209 (1993).

[4] A. A. Ensafi, B. Naderi, *Fresenius J. Anal. Chem.*, **358**, 480, (1997).

[5] S. Sander, G. Henze, *Fresenius J. Anal. Chem.*, **356**, 259, (1996).

[6] M Vega, G. M. C. van der Berg, *Anal. Chim. Acta*, **293**, 19, (1994).

[7] S. B. O. Adeloju, F. Pablo, *Anal. Chim. Acta*, **288**, 157, (1994).

[8] G. Wilkinson, D. D. Gilard, *Comprehensive coordination chemistry*, Vol. 3 Pergamon Oxford.

Апстракт

Разработена е катодна стрипинг квадратно-бранова волтаметриска метода за определување на V(V). Во 0,1 mol/L амонијачен пуфер при pH вредности од 8,60 до 8,90, V(V) дава два сигнали на редукција и тоа од V(V) до V(IV) на потенцијал од околу -0,55 V и од V(IV) до V(II) на потенцијал од околу -1,35 V во однос на Ag/AgCl (заситен раствор од KCl). Реакцијата на редукција на V(V) до V(IV) спаѓа во редот на површински редокс реакции, при што и реактантот и продуктот на електрохемиската реакција се цврсто атсорбирани на површината од живината капка. Докажани се ефектите карактеристични за површински редокс процеси. Направени се калибрациони криви во концентрациските подрачја на V(V) од 10^{-8} до 10^{-5} mol/L. Испитано е влијанието на интерферентните јони. При време на акумулација од 180 s, границата на детекција изнесува $1,5 \times 10^{-8}$ mol/L. Репродуцибилноста на методата се движи во границите од 0,2 до 2,0 %.