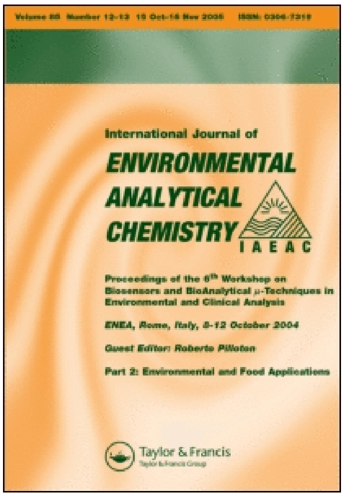

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# VOLTAMMETRIC DETERMINATION OF VANADIUM, BY USING 1,10-PHENANTHROLINE AS A COMPLEXING AGENT

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A new voltammetric method is described for the determination of vanadium. Vanadium forms a complex with 1,10-phenanthroline, giving one reduction peak in acetate buffer, pH=5.7, at –0.488 V. The response of the system was found to be linear in the range 4–250 μg/l. The limit of detection is 1.6 μg/l. The RSD at concentration level of 10 μg/l is 4.7 %. The effect of various potential interferences was also studied. Copper, lead, and cadmium interfere with the determination, which is overcome by addition of sodium sulphide.

The method was applied to the determination of vanadium in spiked seawater, as well as in spiked alloy sample.

*Keywords:* Voltammetric determination; vanadium (V); 1,10-phenanthroline; seawater; alloy

## INTRODUCTION

Vanadium is an essential trace element at low concentrations but is toxic at high concentrations and, therefore, a considerable interest exists in its determination in environmental sample, particularly in natural waters [1]. The concentration of vanadium in sea water is of the order of 2 μg/l but is about four times higher in the deep sea compared to the surface. Furthermore, a number of studies have shown that vanadium concentrations are ranging from 0.3 to about 200 μg/l in a variety of ground- and surface waters, including those used for drinking. It is also present in the earth's crust at a mean concentration of 150 mg/kg, and is therefore

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one of the most common metals. It is more abundant than copper and nickel, and of similar abundance to zinc [2,3].

In steels and alloys, vanadium concentrations may range from 1 to 40 mg/g.

Several analytical methods have been employed for the determination of vanadium but they all have certain drawbacks. Spectrophotometry has a wide applicability but offers low sensitivity and selectivity [4–7]. Inductively coupled plasma mass spectrometry (ICP-MS) is expensive and there are isobaric interferences, especially in seawater where $^{35}Cl^{16}O^+$ is formed [8]. Neutron activation analysis has also been used and despite its high sensitivity, it is not a convenient method and results are also affected by high salt matrices [9]. Vanadium can be also very sensitively determined by fluorimetry but Ti(IV) and Fe(III) interfere [10].

Electroanalytical methods [11–16] offer high sensitivity; among them is adsorptive stripping voltammetry (AdsV) which offers inexpensive and very sensitive methods for vanadium determination. In AdsV the analyte forms a complex with an added ligand which can be adsorbed onto the hanging mercury drop electrode. The adsorbed complex can then be stripped off using various voltammetric techniques. The various ligands used as well the achieved detection limits are summarized elsewhere [1].

In this work 1,10-phenanthroline is being used as ligand for the determination of vanadium. 1,10-phenantroline is a very common reagent in analytical laboratories and forms complexes with many common metals [17]. It has also been used as a ligand for the determination of copper [18, 19], cobalt [20] and molybdenum [21].

## EXPERIMENTAL

### Reagents

HCl, $CH_3COOH$, $CH_3COONa$, $N\alpha_2$-EDTA and 1,10-phenanthroline chloride monohydrate were obtained from Merck p.a. $NH_4VO_3$ from BDH analar, and $HNO_3$ from Merck s.p.

A $10^{-3}$ mol/l stock solution of 1,10-phenanthroline was prepared by dissolving an appropriate amount of 1,10-phenanthroline chloride monohydrate in 0.1 M HCl.

A 0.002 mol/l vanadium stock solution was prepared by dissolving 0.023 g of ammonium metavanadate ($NH_4VO_3$) in 10 ml of 1 M sulphuric acid and was diluted, with deionized water, up to a final volume of 100 ml.

## Apparatus

Voltammetric measurements were taken using a Metrohm Herisau E 506 Polarecord equipped with a Metrohm Herisau E 505 voltammetric stand. As working electrode an EA 290 Metrohm Hanging Mercury Drop Electrode (HMDE) with a surface area of 2.22 $mm^2$ was used; the counter electrode was platinum wire and the reference electrode was Ag/AgCl saturated with KCl. All measurements were taken in a thermostated 50 ml voltammetric cell. A thermostated water circulator Haake was used to maintain the temperature of the solution in the voltammetric cell at 25±0.05 °C.

The solutions were stirred by a magnetic stirrer at 55 Rps a polyethylene covered magnetic bar of 1.5 cm length, 3 mm width. Highly purified nitrogen gas was used to deoxygenate all solutions for 5 min before recording the voltammograms and its flow was maintained over the solution to prevent oxygen interference. pH-measurements were taken with an ORION Research Model 701 A digital ionanalyzer at 25±0.05 °C. Eppendorf micropipettes were used to pipette μl volumes of solutions.

## Sample preparation

### *Seawater*

Seawater samples were collected into polyethylene bottles with teflon screw caps. Each sample was filtered through a 0.45 μm filter (Millipore) and was subsequently acidified at pH 2 after addition of 1 ml supra pure nitric acid in 1l of seawater. All the samples were stored at 4°C.

### *Alloy sample*

Two different alloy samples were analyzed: Alloy I) HERAUS (Ni 59,3%, Cr 24,0%, Mo 10,0%, Fe, Mn, Ta, Si, Nb <2%); and Alloy II) VITALIUM (Co 60,6%, Cr 31,5%, Mo, 6,0%, Mn, Si, C <1%),

An alloy sample weighing 0.1 g (VITALIUM) was transferred into a beaker and was subsequently decomposed and evaporated to dryness with 25 ml of concentrated HCl on a hot plate. The residue was taken up with 10 ml of concentrated HCI and diluted, with deionized water, up to a final volume of 250 ml.

The second alloy sample (HERAUS) was treated in the same way as the first one but aqua regia was used instead of concentrated HCl.

### Voltammetric procedure

#### *Seawater*

10.0 ml of the seawater sample and 10.0 ml of the acetate buffer were pipetted into the polarographic cell; 200 μl of 1,10-phenanthroline $10^{-3}$mol/l were added (final concentration, in the voltammetric cell, 10 μM). The solution was deaerated by purging with $N_2$ gas for 5 min. The nitrogen flow was stopped and after 15 s equilibration time the potential was set to –0.2 V and a new mercury drop was extruded. The voltammogram was recorded using the differential pulse modulation (DP) with a scan rate of 10 mV/s, and a pulse amplitude of –50 mV

#### *Alloy sample*

200 μl of the final solution of the alloy (I) and 200 μl of the final solution of the alloy (II), respectively, were placed in a 50 ml volumetric flask and diluted with the acetate buffer up to the mark. 20 ml of the solution were placed in the voltammetric cell. 200 μl of 1,10-phenanthroline $10^{-3}$ mol/l were added (final concentration, in the voltammetric cell, 10 μM) as well as sodium sulphide to a final concentration of 0.032 mol/l and the same previous procedure for the voltammetric determination, was followed.

## RESULTS AND DISCUSSION

### Optimization of studied parameters

#### *Electrochemical behavior*

The electrochemical behavior of vanadium(V) in the form of $VO_3^-$ has been studied elsewhere [22]. According to this study at concentration of $10^{-5}$ M and even higher, $VO_3^-$ shows the multi-layer formation phenomena. At pH 4, 5 and 6, $VO_3^-$ gives a two-peak pattern, one peak at –0.03 V and the other at –0.1 V. The peaks are independent of pH in the range of 4–6. The effect of plating time on the $VO_3^-$ signal was studied. Only the first peak shows a proportional increase with plating time. This increase suggests that there is an outer multi-layer formed by $HgVO_3$ and $Hg(VO_3)_2$ around the mercury drop. The monolayer is strongly bound to the mercury drop and is being stripped at more negative potentials. At lower concentrations only one peak is observed for the DPCSV (Differential pulse cathodic stripping voltammetry) of $VO_3^-$.

Also, the peak potential (*Ep*) varies with concentration. As the concentration increases, the peak potential moves towards more negative potentials.

In our study V(V) in the form of $VO_3^-$ forms a complex with 1,10-phenanthroline, in acetate buffer, which is being reduced at –0.488 V. A voltammogram is shown in Figure 1.

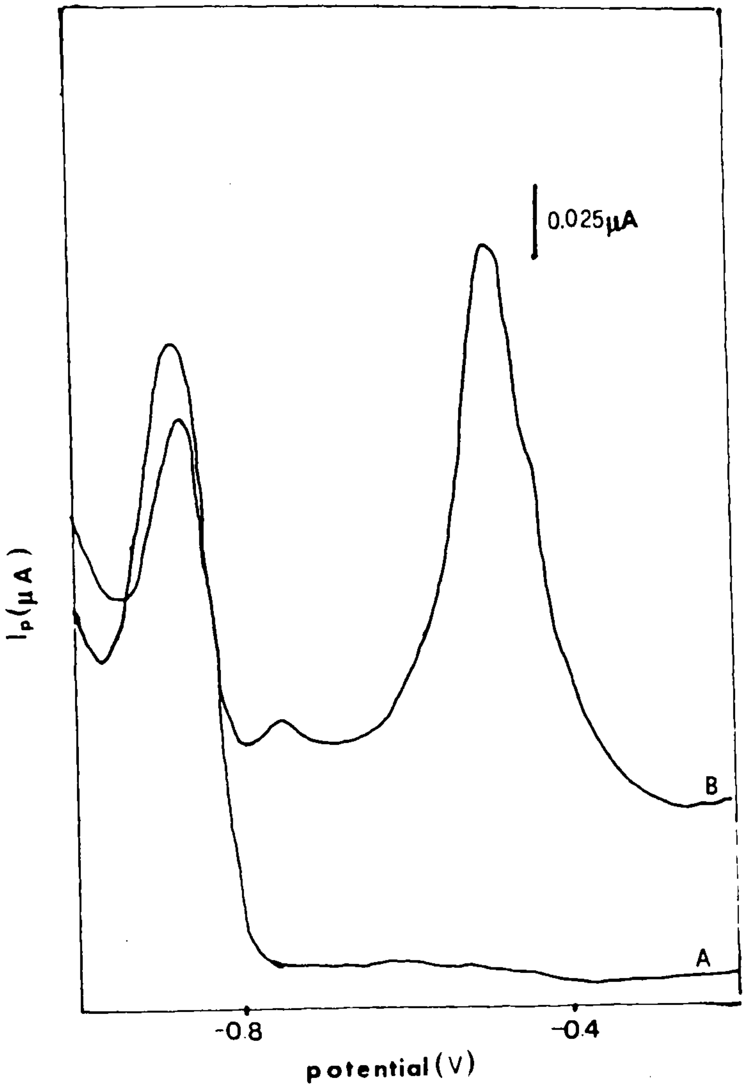

FIGURE 1 Voltammogram in acetate buffer pH 5.7 after addition of : A) 1,10-phenanthroline (3.2 μmol/l) and B) vanadium (0.8 μmol/l). see the experimental section for instrumental parameters

The effect of other parameters affecting the voltammetric determination were studied and the results are being discussed in the following paragraphs.

### *Effect of pH variation and ligand concentration*

The dependence of the stripping peak height on pH variation was studied over the range 4.0–6.5. Optimum pH was observed in the range 5.5–6.0. The results are shown in Figure 2.

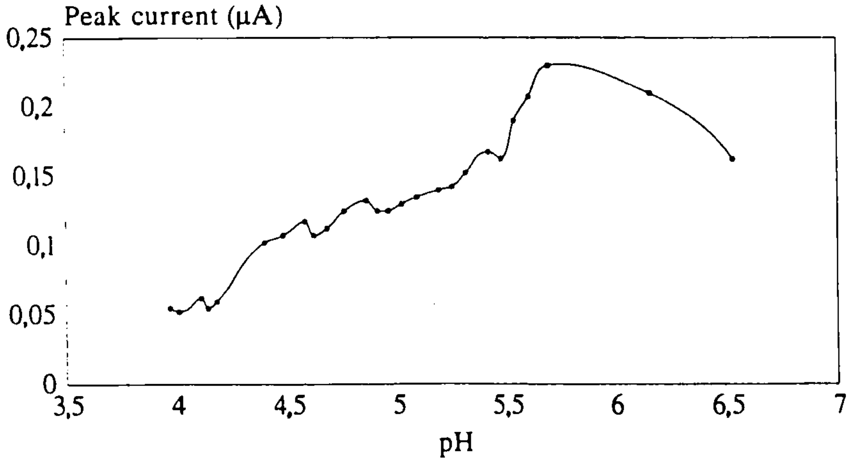

FIGURE 2 Effect of variation of pH on the differential pulse peak height of vanadium (0.8 μmol/l). See the experimental section for instrumental parameters

1,10-phenanthroline concentration was varied in the concentration range 0.8–44 μmol/l, optimum ligand concentration being observed at the ratio $C_M/C_L=1:4$. The results are shown in Figure 3.

### *Effect of the preconcentration potential and time variation*

The dependence of the reduction peak height on the preconcentration potential was studied over the range –0,1– (–0,6) V. The higher peak current was observed at –0.1 V.

The dependence of the stripping peak current on the preconcentration time was subsequently studied. The preconcentration time was varied in the range 30–480 s at a deposition potential of –0.1 V. The peak height increased linearly until 360 s of deposition and after further deposition a plateau was reached.

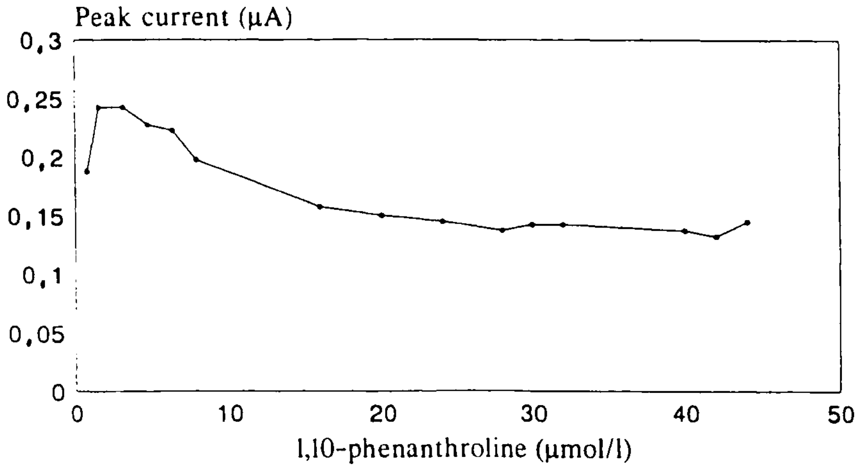

FIGURE 3 Effect of variation of 1,10-phenanthroline concentration on the differential pulse peak height of vanadium (0.8 μmol/l). See the experimental section for instrumental parameters

### *Linearity*

Under the optimal experimental conditions acceptable linearity is being observed in the concentration range 0.004 to 0.250 mg/l and is being described by the least-square equation $y=(0.022\pm0.065)+(0.002\pm8*10^{-5})x$, (confidence level 95%, n=21) with a correlation coefficient of 0.994. The standard deviation of the slope is 0.031, and the standard deviation of the intercept is $3.82*10^{-5}$.

The limit of detection ($C_L$) according to the IUPAC definition [23] is calculated by measuring 9 low level samples and using as criterion the equations: A) $X_L=X_b+3S_b$ and B) $C_L=(X_L-X_B)/S$, where $X_L$ is the smallest measurement of response, $X_b$ is the mean of the low level measurements and $S_b$ is the standard deviation of the low level measurement.

The limit of detection was found to be 1.6 μg/l. In Table I the results of 5 replicate determinations of vanadium at 2 different concentration levels are shown.

TABLE I Replicate determinations of vanadium in aqueous solutions (n= 7)

| *Added (μg/l)* | *Found (μg/l)* | *Recovery (%)* | *RSD (%)* |
|---|---|---|---|
| 10.0 | 10.3 | 103 | 4.7 |
| 200 | 199 | 99.5 | 2.8 |

### *Interferences*

Other metals can interfere either by forming complexes with 1,10-phenanthroline which would be adsorbed on the surface of the mercury drop electrode or because they are reducible near the potential where the vanadium-phenanthroline complex is being reduced. From the common heavy metals, Cu, Pb and Cd interfere with the determination even at equimolar concentrations of vanadium. They form complexes with the ligand which are being reduced at –0.51, –0,54 and –0.68, respectively. The interference was overcome by addition of sodium sulphide.

## Applications

The method is applied in the determination of vanadium in spiked sea water and spiked alloy sample. The analyzed samples were spiked with V(V) in the form of $VO_3^-$ prior to the sample preparation procedure. The results are shown in Table II.

TABLE II Recovery of vanadium in spiked seawater and spiked alloy sample (n=7)

| *Sample* | *Added µg/l (µg/g)** | *Found µg/l (µg/g)** | *Recovery (%)* | *RSD (%)* | *D.L µg/l (µg/g)** |
|---|---|---|---|---|---|
| Sea water | 15.0 | 15.7 | 105 | 6.90 | 10.0 |
| Alloy* | 3,500 | 3,600 | 103 | 3.70 | 3,000 |

## CONCLUSIONS

A very common reagent, 1,10-phenanthroline, is being used as a complexing agent, for the voltammetric determination of vanadium.

Vanadium forms a complex with 1,10-phenanthroline which is being reduced at –0.488 V. The method is applied to the determination of vanadium in spiked sea water and spiked alloy sample by using simple sample preparation procedures.

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