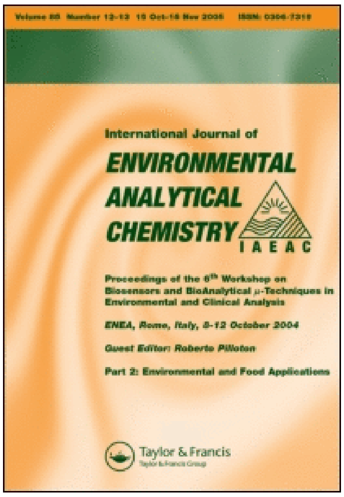

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HIGHLY SELECTIVE CATALYTIC DIFFERENTIAL PULSE POLAROGRAPHIC METHOD FOR DETERMINATION OF VANADIUM

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A differential pulse polarographic method is reported for the determination of trace amounts of vanadium, by its catalytic effect on the oxidation of Nile blue by bromate in acidic media. The oxidation product of Nile blue exhibits a polarographic wave at −0.17 V vs. Ag/AgCl reference electrode. The reaction rate was monitored by measuring the differential pulse polarographic current of the reaction product. A detection limit of 5 ng/ml and calibration graph from 10–500 ng/ml Vanadium(V) (V(V)) were obtained. The influence of potential interfering substances on the determination of vanadium was studied. The method was applied to the determination of vanadium in wastewater and river water, providing good results. Prior separation of some interfering elements is not necessary. The characteristics of the method, i.e. simplicity, and highly selectivity made it especially suitable for routine analysis.

Keywords: Vanadium; Nile blue; DPP

INTRODUCTION

Vanadium is an important element in environmental and biological studies. Vanadium's role in physiological system includes normalization of sugar levels, participation in various enzyme systems as an inhibitor and a co-factor [1] and catalysis of oxidation of various amines [2]. Although vanadium can exist in oxidation states from II to V in aqueous solution, most

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methods have concentrated on its determination in the states IV and V, as these are the most common forms encountered in inorganic and biological systems. The toxicity of vanadium is dependent on its oxidation state [3], Vanadium(V) (V(V)) as vanadate is more toxic than that V(IV) [4]. Due to its toxicity, the determination of vanadium is very important. Some types of samples such as water [5] and pure reagents [6], require ultra trace determination of vanadium.

Various methods have been used for determination of vanadium include atomic absorption spectrometry (AAS) [7], neutron activation analysis [5], inductively coupled plasma (ICP) [8], mass spectrometry [9] and catalytic-spectrophotometric methods [10–15]. However, many of these methods require laborious procedures for pre-concentration, or suffer from many interfering ions, and/or low detectibility. Disadvantage of ICP, Mass spectrometry, AAS, and neutral activation analysis include the high cost of the instrumentation. Among these, electrochemical methods have better selectivity. Several voltammetric methods have been reported for the determination of trace amounts of vanadium [16–19], but the above voltammetric methods for vanadium are not completely satisfactory, especially with respect to the sensitivity, selectivity and/or detection limit. Catalytic method with differential pulse polarographic (DPP) detection for vanadium is rare. According to our knowledge, there is not any report for vanadium determination based on its catalytic-differential pulse polarographic method. Vanadium catalyzed the bromate oxidation of Nile blue in acidic media, and the oxidized form of Nile blue exhibit on DPP a wave at −0.17 V vs. Ag/AgCl reference electrode. The peak current is related to vanadium concentration.

EXPERIMENTAL

Reagents

All chemicals used were of analytical reagents grade. Doubly distilled water was used throughout.

Stock V(V) solution (1000 μg/ml), were prepared from ammonium metavanadate by dissolving 0.2296 g NH_4VO_3 (Merck) in water in a 100-ml volumetric flask. The working solutions were prepared daily by diluting with water to appropriate concentration.

Nile blue stock solution (5.70×10^{-4} M) was prepared from Nile blue (Merck) by dissolving the reagent in water.

Potassium bromate solution (0.20 M) was prepared by dissolving 8.350 g $KBrO_3$ (Merck) in water and diluting to 250 ml in a 250-ml volumetric flask.

1000 μg/ml solutions of the studied interfering ions were prepared from appropriate salts.

Apparatus

All the polarographic measurements were performed on a Model 663 VA Stand (Methrom) using three-electrode system, dropping mercury electrode as a working, Ag/AgCl as a reference, and Pt as an auxiliary electrode. The measuring cell was thermostated at $20 + 0.1°C$, using a Heidolph circulation water bath.

Recommended procedure

All the solutions and distilled water were kept in thermostat water bath at 20°C for 30 min before initiation of the experiment. Into a 10-ml volumetric flask, 1.0 ml of potassium chloride (1.0 M), 1.5 ml 0.10 M H_2SO_4, 0.50 ml 5.7×10^{-4} M Nile blue and 1.0 ml of V(V) (containing 0.10–5.00 μg) were added. The solution was diluted to ca. 8 ml with water and 1.0 ml of 0.20 M bromate solution was added. The result solution was diluted to 10 ml with water. The result solution mixed and a portion of the solution transferred to the polarographic cell. Time was measured just after addition of the bromate solution. The initial scanning was set at +0.2 V (vs. Ag/AgCl reference electrode) and after 4.0 min from initiation of the reaction, the potential was scanned in the negative direction to -0.3 V with a 50 mV pulse amplitude height and mercury drop time of 1.0 sec. This signal was labeled as I_{ps}. The same procedure was repeated without addition of V(V) solution, and the peak current was labeled as I_{pb}. Then the calibration graph was constructed by plotting of ΔI_p ($\Delta I_p = I_{ps} - I_{pb}$) vs. V(V) concentration.

RESULTS AND DISCUSSION

Vanadium(V) acts as a catalyst on oxidation of organic materials when using bromate as an oxidizing agent in acidic media [13,14]. Nile blue (NB) is a metallochromic indicator. The oxidation rate of Nile blue by bromate in the absence of catalysis is very slow [20–22]. However, in the presence of trace amounts of V(V). Nile blue undergoes a rapid oxidation. The oxidation form of Nile blue (i.e to $(NB)_{ox}$) can reduce at the DME in about −0.17 V vs. Ag/AgCl reference electrode. The uncatalyzed reaction (without vanadium) produces only a very small DPP peak in the above potential range. The rate equation for the reaction can be expressed as:

$$\begin{aligned}\text{rate}_{ct} &= \{d[NB]_{ox}/dt\}\\ &= k_{ct}[H_2SO_4]^a[BrO_3^-]^b[NB]^c[V(V)] + k_{un}[H_2SO_4]^a[BrO_3^-]^b[NB]^c \quad (1)\end{aligned}$$

where k_{ct} and k_{un} are the rate constants for the catalyzed and uncatalyzed reaction, respectively, and a, b, and c are the reaction order for the reagents. Since under chosen conditions, the uncatalyzed reaction has very slow rate, therefore, equation 1 can be expressed as:

$$\text{rate} = k_{ct}[H_2SO_4]^a[BrO_3^-]^b[NB]^c[V(V)] \quad (2)$$

Under chosen conditions, Nile blue, bromate, and acid concentrations are greater than vanadium concentration, and their concentration held constant via the initial interval time of the reaction (< 4 min from initiation of the reaction), therefore, equation 2 can be written as:

$$\text{rate} = -d[NB]/dt = d[NB]_{ox}/dt = k[V(V)] \quad (3)$$

By integration of equation 3 gives:

$$\Delta[NB] = k'[V(V)]t \quad (4)$$

where $\Delta[NB]$ is the concentration change of NB in the catalytic reaction and it is equal to $[NB]_{ox}$. According to the fact that, $I_p = k''[NB]_{ox}$, therefore, for a fixed-time of initiation of the reaction, equation 4 can be written as:

$$I_p = (I_p)_{NB_{ox,cat}} - (I_p)_{NB_{ox,uncat}} = k''[V(V)] \quad (5)$$

where $(I_p)_{NB_{ox,cat}}$ is the current peak for the catalyzed reaction and $(I_p)_{NB_{ox,uncat}}$ is the current peak for the uncatalyzed reaction. Equation 5 shows that the ΔI_p term is proportional to the vanadium concentration where the other variables and reaction time is held constant for the given system.

Effect of variables on sensitivity

The influences of reagent concentrations and temperature on the reaction rate (peak current) were studied with drop time of 1.5 sec and pulse amplitude of 50 mV. Experimental results showed that the suitable peak current can be observed in strongly acidic media ($\text{pH} < 3$). Among various acids such as hydrochloric, phosphoric, nitric and sulfuric acids, sulfuric acid was the best due to its acidity strength relative to the other.

Figure 1 shows the influence of sulfuric acid concentration on the peak current in presence of 0.10 M KCl, 0.010 M bromate, 5.7×10^{-5} M Nile blue, and 0.10 µg/ml V(V) at 30°C. The results show that 0.015 M H_2SO_4 is the best. Greater amount of acid causes decrease in sensitivity. This effect is due to the fact that Nile blue is protonated in higher acid concentration, thus, the rate of oxidation reaction decreased. Therefore, 0.015 M sulfuric acid was selected.

The effect of Nile blue concentration on the reaction rate (peak current) was studied with 0.010 M bromate, 0.015 M sulfuric acid, 0.10 M potassium chloride, and V(V) concentration of 0.10 µg/ml with different Nile blue concentration in the range 1.4×10^{-5} to 2.0×10^{-4} M at 30°C (Fig. 2). The results show that the ΔI_p is proportional to Nile blue concentration at less than 2.8×10^{-5} M and decreases when its concentration is more than 2.8×10^{-5} M. Thus, 2.8×10^{-5} M Nile blue was selected.

Figure 3 shows the influence of bromate concentration on the peak current in the range 0.005–0.040 M for a solution containing 2.8×10^{-5} M Nile blue, 0.10 M KCl, 0.015 M H_2SO_4, and V(V) concentration of 0.10 µg/ml at 30°C. The results show that by increasing bromate concentration up to 0.020 M, there is a sharp increase in the DPP peak height. Beyond this, there is a slow decrease in the ΔI_p. This effect is due to the fact that at higher concentration of bromate, the uncatalyzed reaction rate is very fast. Thus 0.020 M bromate concentration was chosen for the study.

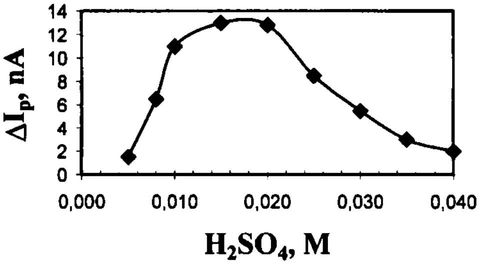

FIGURE 1 Influence of sulfuric acid concentration on the sensitivity.

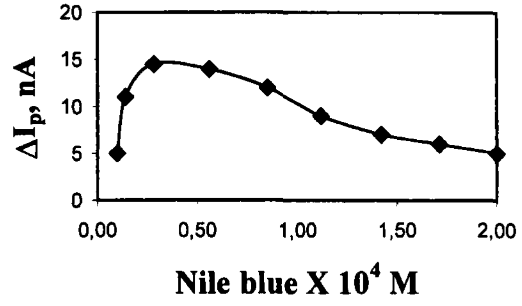

FIGURE 2 Effect of Nile blue concentration on the sensitivity.

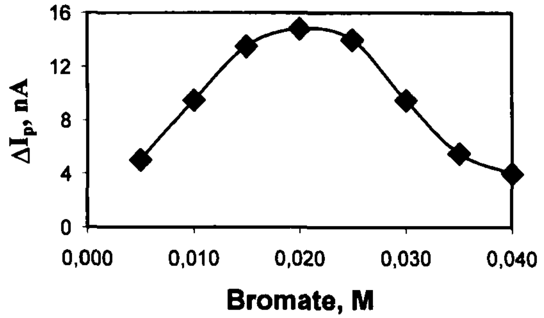

FIGURE 3 Influence of bromate concentration on peak current.

The effect of temperature on the sensitivity was studied in the range of 10–45°C with a solution containing optimum reagent concentration in the presence of 0.10 μg/ml V(V) (for the catalyzed reaction). The results showed that by increasing temperature up to 20°C the sensitivity increased, whereas higher temperature decreased the sensitivity. This means that the rate of uncatalyzed reaction increases with temperature to a greater extent than the catalyzed reaction and thus, the difference between the rate of the catalyzed and uncatalyzed reaction (equal to ΔI_p) diminished at higher temperature. Therefore, 20°C was selected in this study.

Differential pulse polarogram for the system reported at various drop times and with various pulse amplitude. The results illustrate that the peak current increases as the drop time increases up to 1.0 sec. On the other hand, the sensitivity increased as the pulse amplitude increases up to 50 mV. Thus 1.0 sec for the drop time and 50 mV for the pulse amplitude were selected for this study.

Calibration, precision, and detection limit

The peak current at about −0.17 V vs. Ag/AgCl reference electrode was found to increase linearly for the V(V) concentration range of 0.010–0.500 µg/ml under the optimum conditions with a fixed time method of 4.0 min from initiation of the reaction. Four minutes was selected due to comparison between reproducibility, sensitivity and reaction time. The regression equation for the dependence of peak current with concentration of the vanadium is: $\Delta I_p = 0.054 + 3.96C$ ($r = 0.9987$, $n = 10$), where C is the concentration of vanadium as ng/ml, and ΔI_p in nA.

Interference study

In order to validate the possible analytical applications of the method, the effects of different cations and anions on the determination of 0.100 µg/ml V(V) were investigated. The results are given in Table I. The tolerance limit was defined as the concentration of added species causing less than 3% relative error for vanadium determination. The results show that many ions do not affect the determination of vanadium at trace levels.

Determination of vanadium in wastewater and in river water samples

In order to test the reliability of the method, the proposed method was applied to the determination of vanadium in wastewater, and in river water. Because of unknown organic compounds and their functional group activity at the working potential, it is better to destroy organic compound (if there is) with acid leaching. For this proposes, into 10 ml of the

TABLE I Interference of foreign ions on the determination of 0.100 µg/ml vanadium(V) under the optimum conditions

Foreign ion	*Tolerance limit* ($W_{ion}/W_{V(V)}$)
Ca^{2+}, Ba^{2+}, K^+, MnO_4^-, Cl^-, Li^+, Br^-, NO_3^-, Sn(II), Ni(II), Cu(II), I^-, SCN^-, ClO_3^-, IO_3^-, Bi(III), Sr^{2+}, Ge(IV), CrO_4^{2-}, Zn(II), Fe(II), Pb(II), CO_3^{2-}, Al(III), Cd(II), NH_4^+, Ag(I), Co(II), Mn(II), $H_2PO_4^-$, Na^+	10000*
Hg(II)	500

*Maximum amount of the ions tested.

TABLE II Determination of vanadium in wastewater and river water

Sample	*V(V) added* (ng/ml)	*Total V(V) found* ($n = 5$) (ng/ml)	*Recovery* %
Wastewater(I)	–	125 ± 7	–
Wastewater(I)	50	173 ± 8	99.0
Wastewater(I)	100	227 ± 12	101.0
Wastewater(II)	–	108 ± 8	–
Wastewater(II)	50	162 ± 9	102.0
Wastewater(II)	100	204 ± 11	98.0
River Water	–	20.0 ± 1.0	–
River Water	20.0	39.0 ± 3.0	97.5
River Water	35.0	56.5 ± 3.2	102.7
River Water	40.0	58.8 ± 3.4	98.0

water sample, 3 ml conc. HNO_3 was added and the solution was heated to dryness. After that, the residue was dissolved in 10 ml distilled water followed analysis by the recommended procedure. The determinations were made by standard addition procedure. The results are shown in Table II. The values showed good agreement and good recoveries of added vanadium.

CONCLUSION

With the proposed method it is possible to determine vanadium in real samples by using a simple, sensitive and highly selective procedure. Apart from the high selectivity of the method, use of a suitable and simple apparatus permit the determination of vanadium in river water and wastewater samples.

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